Monatshefte für Chemie 114, 1271—1280 (1983)

Monatshefte für Chemie
Chemical Monthly

Novel Inorganic Ring Systems. XL: A Dimeric Cycloalumadisiladiazane[1,2]

Thomas Blumenthal[a], **Ulrich Wannagat**[a,*], **David J. Brauer**[b], and **Hans Bürger**[b]

[a] Institut für Anorganische and Analytische Chemie, Technische Universität Braunschweig, D-3300 Braunschweig, Federal Republic of Germany

[b] Anorganische Chemie, Fachbereich 9, Universität-Gesamthochschule Wuppertal, D-5600 Wuppertal, Federal Republic of Germany

(Received 16 May 1983. Accepted 30 May 1983)

The first cycloalumadisiladiazane (**F1**) has been prepared by reacting dilithiated 1,2-bis(methylamino)tetramethyldisilane with $AlCl_3$ at —80 °C. The compound has been characterized by elemental analysis, ^1H NMR, mass spectroscopy and single crystal X-ray diffraction. Crystals belong to the orthorhombic space group Pbca with $a = 8.3506$ (4), $b = 16.1056$ (8), $c = 19.1186$ (6) Å, $Z = 4$ and $d_{calc} = 1.22$ g/cm³. The structure was refined to a conventional R value of 0.030 using 1 810 counter-measured, observed reflections. The crystal contains discrete nitrogen bridged dimeric molecules possessing crystallographic $\bar{1}$ symmetry. Both NMR and mass spectral data indicate that this structure persists in solution and in the gas phase.

(Keywords: Aluminum compounds; Silicon-nitrogen chemistry; X-ray diffraction structure analysis)

Neue anorganische Ringsysteme. XL: Ein dimeres Cycloalumadisiladiazan

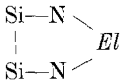
Das erste Cycloalumadisiladiazan (**F1**) wurde durch Reaktion von dilithiiertem 1,2-Bis(methylamino)tetramethyldisilan mit $AlCl_3$ bei —80 °C erhalten und durch Elementaranalyse, ^1H-NMR, Massenspektroskopie und eine Einkristall-Röntgenstrukturanalyse charakterisiert. **F1** kristallisiert in der orthorhombischen Raumgruppe Pbca mit $a = 8{,}3506$ (4), $b = 16{,}1056$ (8), $c = 19{,}1186$ (6) Å, $Z = 4$ und d_{ber} 1,22 g/cm³. Die Struktur wurde für 1 810 mit Zählrohr-Technik gemessene Reflexe mit einem konventionellen R-Wert von 0,030 verfeinert. Im Kristall liegen isolierte, stickstoffverbrückte dimere Moleküle vor, die kristallographische $\bar{1}$-Symmetrie aufweisen.

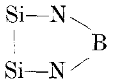
Sowohl NMR- als auch Massenspektren weisen nach, daß diese Struktur auch in Lösung und in der Gasphase erhalten bleibt.

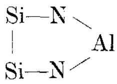
0026-9247/83/0114/1271/$ 02.00

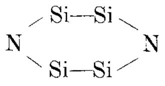
Introduction

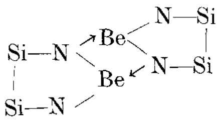
Previously we have prepared fivemembered heterocyclosilazanes (**A**) with such heteroatoms *El* as Be[3], B, C, Si, Ge, Sn, P, As, Sb and S[4]. The present study is concerned with the synthesis of the corresponding cycloalumadisiladiazane **C**. In contrast to the monomeric boron derivative **B**[5] but in analogy to the dimeric Be system **E**, **C** would be expected to dimerize to **F**. Such aggregates would be similar to **G** which contains the sixmembered cycloalumadisilatriazane ring[1].

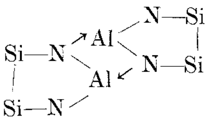

A

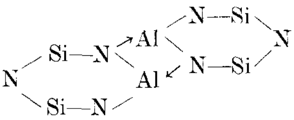

B


C


D


E


F


G

Experimental

Preparation of F 1

A solution of 10 g (57 mmol) bis(methylamino)tetramethyldisilane[6] in 100 ml petroleum ether (50-70°) was metallated at —60 °C with 48.4 g (113 mmol) of a 15% solution of butyllithium in hexane. The mixture was brought briefly to room temperature in order to complete the reaction and then cooled to —80 °C. A solution of 7.6 g (57 mmol) $AlCl_3$ in 50 ml benzene/triethylamine (1/1) was added dropwise to the suspension. The brown, turbid mixture was held at —80 °C for an additional 2 h and then slowly brought to room temperature over a 12 h period. The precipitate was filtered off, and a red-brown residue was obtained upon concentrating the clear solution under vacuum at room temperature. Repeated recrystallization from benzene/petroleum ether (1/1) and finally from benzene lead to 6.0 g (45%) **F 1**.

Analysis

Found: C 30.0, H 7.8, Cl 14.8, N 11.6, Si 23.3; Al strong, positive reaction with aurintricarbonic acid. *M*, mass-spectrometrically, 472. $C_{12}H_{36}Al_2Cl_2N_4Si_4$ requires C 30.43, H 7.66, Cl 14.97, N 11.83, Si 23.72. *M* 472.

Table 1. *Mass spectrum of* $[\mathrm{ClAl}(\mathrm{N}Me\mathrm{Si}Me_2)_2]_2$ *at 70 eV and 80 °C*[a,b]

m/e		Fragment Ion	*m*/e		Fragment Ion
472/474	(50)[c]	M^+	235/237	(34)	$[M/2\text{-H}]^+$
457/459	(100)	$[M\text{-}Me]^+$	221/223	(47)	$[M/2\text{-}Me]^+$
413/415	(87)	$[M\text{-}(\mathrm{Si}Me_2+\mathrm{H})]^+$	201	(56)	$[M/2\text{-Cl}]^+$
399/401	(39)	$[M\text{-}(\mathrm{Si}Me_2+Me)]^+$	186	(62)	$[M/2\text{-}(Me+\mathrm{Cl})]^+$
379/381	(30)	$[M\text{-}(\mathrm{Si}Me_2+\mathrm{Cl})]^+$	159	(68)	$[\mathrm{Si}_2Me_5\mathrm{N}_2]^+$
365/367	(26)	$[399\text{-}(\mathrm{Cl}+\mathrm{H})]^+$	144	(42)	$[\mathrm{Si}_2Me_4\mathrm{N}_2]^+$
345	(77)	$[379\text{-}(\mathrm{Cl}+\mathrm{H})]^+$	132	(48)	$[\mathrm{Si}_2Me_4\mathrm{H}_2\mathrm{N}]^+$
326/328	(34)	$[M\text{-}2(\mathrm{Si}Me_2+Me)]^+$			or $[159\text{-HCN}]^+$
298/300	(72)	$[M\text{-}(\mathrm{Si}Me_2\mathrm{N}Me)]^+$?			

[a] Further ions at *m*/e = 130, 116, 100, 86, 73, 59 and 45 are all typical for cyclosilazanes with Si*Me*$_2$ and N*Me* units[13].

[b] Ions derived from thermally formed **D 1** are 231 (44) $[M\text{-}(\mathrm{Si}Me_2+\mathrm{H})]^+$ and 217 (44) $[M\text{-}(\mathrm{Si}Me_2+Me)]^+$.

[c] Relative intensities.

Table 2. *Mass spectrum of thermal decomposition products of* $[\mathrm{ClAl}(\mathrm{N}Me\mathrm{Si}Me_2)_2]_2$[a]

m/e		Fragment Ion	*m*/e		Fragment Ion
290	(66)[b]	M^+[c]	188	(73)	$[203\text{-}Me]^+$
275	(83)	$[M\text{-}Me]^+$	174	(56)	$[\mathrm{Si}_2Me_6\mathrm{N}_2]^+$
231	(96)	$[M\text{-}(\mathrm{Si}Me_2+\mathrm{H})]^+$	160	(56)	$[\mathrm{Si}_2Me_6\mathrm{N}]^+$
216	(100)	$[M\text{-}(\mathrm{Si}Me_2+Me)]^+$	144	(47)	$[\mathrm{Si}_2Me_4\mathrm{N}_2]^+$
203	(48)	$[M\text{-}(\mathrm{Si}Me_2+\mathrm{N}Me)]^+$	93/95	(54)	$[\mathrm{Si}Me_2\mathrm{Cl}]^+$

[a] Ions typical of cyclosilazanes with Si*Me*$_2$ and N*Me* units (Table 1) were also observed.

[b] Relative intensity.

[c] M is $Me\mathrm{N}(\mathrm{Si}Me_2\mathrm{Si}Me_2)_2\mathrm{N}Me$.

^{1}H *NMR Spectrum*

Employing a Bruker WM 250, a solution of **F 1** in C_6D_6 was shown to give two resonances in the NCH_3 region ($\delta = 2.680$ and 2.635 ppm) and four in the $SiCH_3$ region ($\delta = 0.576$, 0.487, 0.302 and 0.275 ppm), the internal standard being C_6D_5H ($\delta = 7.270$ ppm).

Mass Spectra

The fragmentation patterns obtained from pure **F 1** and from thermal decomposition products of **F 1**, which were formed at 120 °C over a 48 h period, are listed in Tables 1 and 2, respectively. Both spectra were registered with a Varian MAT CH-7 spectrometer.

X-Ray Examination

A crystal of **F 1** was mounted in a thin-walled glass capillary under argon. The orthorhombic unit cell was found by a search procedure on a CAD-4 diffractometer. Intensity data were collected by the variable-speed ω-2 Θ scan technique employing Ni filtered Cu-Kα radiation. Negligible fluctuations were noted for the three periodically monitored standard reflections during the measurement. The intensities were corrected numerically for absorption and converted to $|F_0|$'s. Crystal data and details of the data collection and reduction procedure are included in Table 3.

Table 3. *Crystal data for* $[ClAl(NMeSiMe_2)_2]_2$

Crystal system	orthorhombic
a	8.3506 (4) Å
b	16.1056 (8) Å
c	19.1186 (6) Å
Z	4
d_{calc}	1.22 g/cm^3
t	20 °C
Systematic absences	h k 0, h = 2 n + 1 h 0 l, l = 2 n + 1 0 k l, k = 2 n + 1
Space group	P_{bca}
λ (CuK$\bar{\alpha}$)	1.54178 Å
Filter	Ni
Scan range (ω)	0.70° + 0.14° tan Θ
Scan speed (2 Θ)	0.53-5°/min
Octant measured	h k l
Θ limits	$1° \leq \Theta \leq 70°$
Unique reflections	2 427
with $\lvert F_0\rvert \geq 4\,\sigma(\lvert F_0\rvert)$	1 810
Crystal size	0.72 × 0.19 × 0.16 mm^3
μ (CuKα)	48.6 cm^{-1}
Transmission Factors	0.236-0.521

The structure was solved by direct methods and refined by fullmatrix least-squares techniques. The function minimized was $\Sigma w \Delta^2$, where $w = [\sigma^2(|F_0|) + 0.0004\,|F_0|^2]^{-1}$ and $\Delta = ||F_0| - |F_c||$, the sum including only those reflections with $|F_0| \geq 4\,\sigma(|F_0|)$. Dispersion corrected relativistic *Hartree-Fock* scattering factors were used for all atoms except H (SDS)[7]. After an initial anisotropic refinement, the H coordinates were taken from a difference *Fourier* map (0.26-0.52 e/Å^3), idealized [C—H 0.95 Å, H—C—H 109,5°, staggered except at C (6)] and constrained to ride on the respective C atoms. Refinement including an extinction correction of the form $F_c = F'_c(1 - \varkappa F'^2_c/\sin\Theta)$ converged with $\varkappa = 4.8(2)\cdot 10^{-7}$. The final residuals are $R = \Sigma\Delta/\Sigma|F_0| = 0.030$ and

Table 4. *Positional parameters*[a] *for the nonhydrogen atoms of* $[\mathrm{ClAl}(\mathrm{N}Me\mathrm{Si}Me_2)_2]_2$

Atom	x	y	z
Cl	.23314 (9)	.41363 (4)	.39846 (4)
Si (1)	.15288 (9)	.46295 (4)	.63193 (3)
Si (2)	.00193 (9)	.34051 (4)	.61985 (4)
Al	.06348 (9)	.42623 (4)	.48096 (4)
N (1)	.1265 (2)	.5115 (1)	.54692 (9)
N (2)	.0150 (2)	.3347 (1)	.5298 (1)
C (1)	.2762 (3)	.5607 (2)	.5288 (1)
C (2)	.3662 (4)	.4285 (2)	.6382 (1)
C (3)	.1154 (4)	.5382 (2)	.7040 (1)
C (4)	.1015 (4)	.2499 (2)	.6633 (1)
C (5)	−.2078 (4)	.3424 (2)	.6545 (2)
C (6)	−.0369 (4)	.2581 (2)	.4936 (1)

[a] Thermal parameters may be obtained from the authors.

Table 5. *Hydrogen parameters*[a, b] *for* $[\mathrm{ClAl}(\mathrm{N}Me\mathrm{Si}Me_2)_2]_2$

Atom	x	y	z	Atom	x	y	z
H (1 A)	.3011	.5962	.5670	H (4 A)	.0921	.2552	.7126
H (1 B)	.3616	.5227	.5217	H (4 B)	.2115	.2488	.6507
H (1 C)	.2614	.5931	.4877	H (4 C)	.0516	.1998	.6486
H (2 A)	.3779	.3921	.6770	H (5 A)	−.2636	.3876	.6338
H (2 B)	.4337	.4754	.6443	H (5 B)	−.2061	.3492	.7039
H (2 C)	.3952	.4003	.5965	H (5 C)	−.2603	.2919	.6431
H (3 A)	.0076	.5568	.7018	H (6 A)	.0135	.2116	.5147
H (3 B)	.1855	.5843	.6994	H (6 B)	−.1498	.2528	.4977
H (3 C)	.1339	.5118	.7477	H (6 C)	−.0084	.2606	.4455

[a] Errors derived for the fractional coordinates are those of the bonded carbon atom.

[b] The isotropic thermal parameters have the form $\exp[-8\pi^2 U \sin^2\Theta/\lambda^2]$ and are 0.062 (5), 0.092 (7), 0.129 (9), 0.079 (6), 0.125 (9) and 0.115 (8) Å^2 for the H atoms of C(1) to C(6), respectively.

$Rw = [\Sigma w\Delta^2/\Sigma w|F_0|^2]^{1/2} = 0.041$ for those reflections included in the refinement; the respective value of these residuals are 0.051 and 0.047 for all reflections[8]. A tabulation of the parameters is given in Tables 4 and 5. The numbering scheme is defined in Fig. 1, H atoms being numbered after the C atoms to which they are attached. Computer programs were described previously[9].

Results and Discussion

Preparation and Properties

In analogy to the preparation of $(Me_2SiNEt)_2BCl$[10] from BCl_3 and $EtN(SiMe_2SiMe_2)_2NEt$[11], an attempt was made to combine $AlCl_3$ with $MeN(SiMe_2SiMe_2)_2NMe$ (**D 1**) (Scheme **1**, eq. 1) since Si—N bonds are known to be cleaved by AlCl bonds[12] (eq. 1).

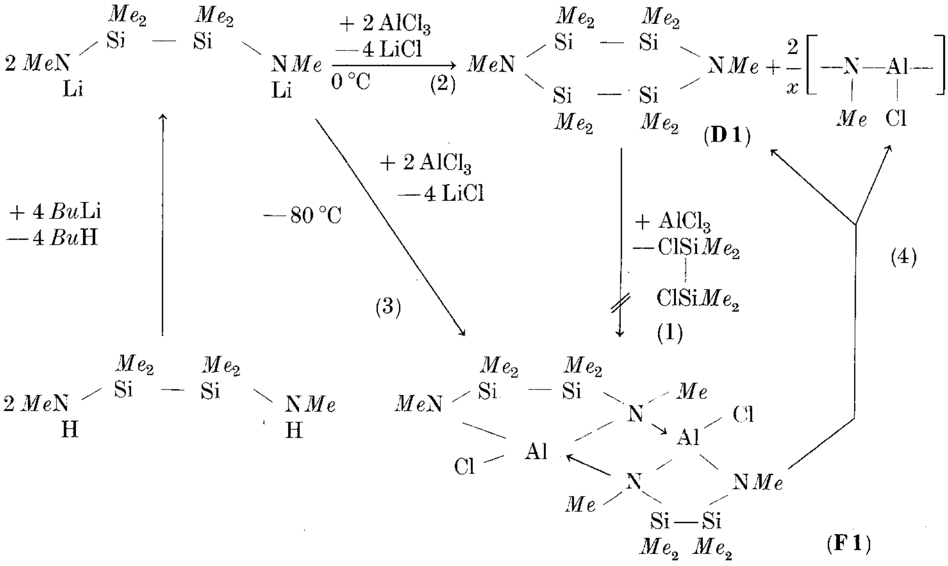
$$\text{Si—N} + \text{Al—Cl} \rightarrow \text{Si—Cl} + \text{Al—N} \qquad (1)$$

Nevertheless, $AlCl_3$ did not attack the Si_4N_2 rings of **D 1** in petroleum ether at temperatures between 0 and 40 °C.

Thus the method used to prepare **G** (Scheme 1, eq. 3)[1] was applied. While combining $(Me_2SiNMeLi)_2$ with $AlCl_3$ in C_6H_6/NEt_3 solution at 0 °C only lead to formation of **D 1** and polymeric material (Scheme 1, eq. 2), working at —80 °C allowed the isolation of **C 1**, which dimerizes to **F 1**, in yields as high as 45%. The principal impurity **D 1**, which is invariably formed, may be removed by recrystallization from benzene/petroleum ether.

The large, colorless needles of **F 1** are slightly soluble in benzene, chloroform, petroleum ether or cyclohexane. The crystals are very moisture sensitive, quickly becoming opaque and then decaying to a white, amorphous mass upon exposure to air. They decompose upon melting at 125 °C.

Scheme 1. Preparation and decomposition of **F 1**



The six sharp singletts of essentially equal intensity found in the ^{1}H NMR spectrum of **F 1** indicate that the molecule contains six stereochemically distinct methyl groups in solution. This requirement is fulfilled by **F 1**, which is the structure found in the solid state, but not by **C 1** or chlorine-bridged dimers.

Both the parent ion and the fragmentation pattern (Table 1) found in the mass spectrum of **F 1** confirm the dimeric formulation. Additional ions apparently stem from **D 1**, which is formed by thermal decomposition of **F 1** (Scheme 1, eq. 4). This reaction must be slow since the ratio **F 1**/**D 1** is fairly independent of the temperature of the inlet. Incidently, thermal decomposition of **G 1** commences at a higher temperature and proceeds at a greater rate. After a sample of **F 1** is held at 120 °C for 48 h, the mass spectrum (Table 2) is essentially the same as that of **D 1**. Interestingly, the fragment with $m/e = 93/95$, which apparently may be assigned to Me_2SiCl^+, suggests that the above-mentioned cleavage reaction (1) is occuring as a secondary process.

The intensity of the $[M/2—H]^+$ ion is also nearly independent of the inlet temperature. This ion is more likely to result from decay of M^+ in the mass spectrometer than from decay of the monomer **C 1** formed from **F 1**.

Crystal Structure

As in the cycloalumadisilatriazane derivative $[ClAl(NMeSiMe_2)_2NMe]_2$ **G 1**[1], crystals of **F 1** contain well separated, nitrogen bridged dimers possessing $\bar{1}$ crystallographic symmetry. Intermolecular distances are normal, the shortest being H(2A)—H(5B) $(0.5 + x, y, 1.5—z)$, 2.482 (4) Å. Bond distances and angles are listed in Table 4.

In general, the structure of **F 1** confirms conclusions drawn from the structure of **G 1** on the dependence of nitrogen coordination number on N—Al, N—Si and N—C distances[1]. Whenever possible, structural features of **F 1** and **G 1** will be compared in the following (Fig. 1).

The conformation of the cycloalumadisiladiazane ring is not planar but rather twisted about the Si(1)—Si(2) midpoint, Al vector. Replacement of the Si—N*Me*—Si fragment in **G 1** by the Si—Si moiety in **F 1** mainly leads to a closing of endocyclic bond angles by ca. 7° at Al and N(2). Interestingly, both the Si(1)—N(1) and Si(2)—N(2) bonds, 1.817 (2) and 1.727 (2) Å respectively, are significantly longer than the corresponding bonds in **G 1**, 1.798 (2) and 1.717 (2) Å. The lengthening may reflect a reduction in polarity of the Si—N bonds, but in light of the smaller angles in the five-membered ring, steric effects can not be convincingly eliminated. The small value of the Si(1)—Si(2)—N(2) angle, 96.28 (7)°, compared to Si(2)—Si(1)—N(1), 102.00 (7)°, deserves

Table 6. *Selected bond distances (Å) and angles (°) in* $[ClAl(NMeSiMe_2)_2]_2$

Al—Cl	2.130(1)	Si(1)—C(2)	1.869(3)
Al—N(1)	1.937(2)	Si(1)—C(3)	1.862(3)
Al—N(1)'[a]	1.952(2)	Si(2)—C(4)	1.874(3)
Al—N(2)	1.792(2)	Si(2)—C(5)	1.873(3)
Si(1)—N(1)	1.817(2)	N(1)—C(1)	1.521(3)
Si(2)—N(2)	1.727(2)	N(2)—C(6)	1.480(3)
Si(1)—Si(2)	2.352(1)		
Cl—Al—N(1)	111.64(7)	Si(2)—Si(1)—C(2)	105.6(1)
Cl—Al—N(1)'	112.80(6)	Si(2)—Si(1)—C(3)	121.9(1)
Cl—Al—N(2)	117.26(7)	Si(1)—Si(2)—C(4)	111.8(1)
N(1)—Al—N(1)'	92.0(1)	Si(1)—Si(2)—C(5)	116.9(1)
N(1)—Al—N(2)	107.77(9)	N(1)—Si(1)—C(2)	107.5(1)
N(1)'—Al—N(2)	112.45(9)	N(1)—Si(1)—C(3)	111.2(1)
Al—N(1)—Al'	88.0(1)	N(2)—Si(2)—C(4)	111.8(1)
Al—N(1)—Si(1)	108.09(9)	N(2)—Si(2)—C(5)	114.4(1)
Al'—N(1)—Si(1)	124.3(1)	C(2)—Si(1)—C(3)	107.8(1)
Al—N(1)—C(1)	116.4(1)	C(4)—Si(2)—C(5)	105.7(1)
Al'—N(1)—C(1)	109.7(1)	Al—N(2)—Si(2)	119.3(1)
Si(1)—N(1)—C(1)	109.2(1)	Al—N(2)—C(6)	120.5(2)
Si(2)—Si(1)—N(1)	102.00(7)	Si(2)—N(2)—C(6)	119.6(2)
Si(1)—Si(2)—N(2)	96.28(7)		

[a] Primed atoms are related to those of the asymmetric unit by x', y', $z' = -x$, $1-y$, $1-z$.

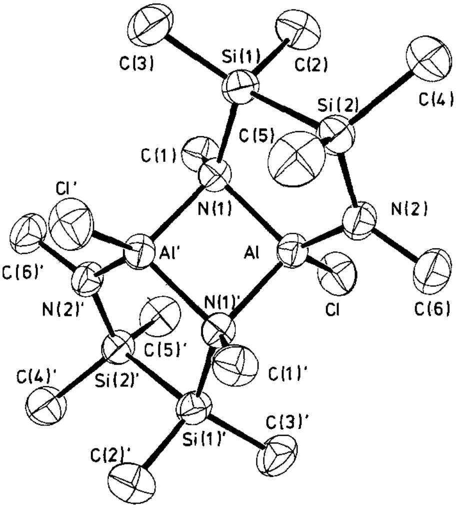


Fig. 1. A perspective drawing of $[ClAl(NMeSiMe_2)_2]_2$ (**F 1**) with hydrogen atoms omitted

particular notice since N(2) should be more negatively charged than N(1). Assuming that both Si atoms carry a positive charge, then the electrostatic attraction along Si(1)...N(2) should be greater than that along Si(2)...N(1).

In the central, planar $(Al—N)_2$ ring, the N(1)—Al bond, 1.937 (2) Å, is slightly but significantly shorter than N(1)—Al′, 1.952 (2) Å. Equality of these valencies is not required since their conformations differ; e.g., the N(1)—Si(1) bond is partially eclipsed with Al—N(2) and Al′—Cl′ along N(1)—Al and N(1)—Al′ respectively. In **G1** these bonds have the same conformation as in **F1** and their respective distances, 1.941 (2) and 1.952 (2) Å, compare excellently with those found in this study. Despite this good agreement, the central ring in **F1** is decidedly less rectangular than that in **G1**, the N(1)—Al—N(1)′ angles being 92.0 (1) and 89.4 (1)° respectively.

The Al—N(2) and Al—Cl bonds are 0.011 (3) and 0.010 (1) Å shorter than the analogous bonds in **G1** and the Cl—Al—N(2) angle is opened 6.03 (9)° further in **F1**. In both structures the Si atom bonded to the quaternary N atom forms Si—C bonds which are probably shorter and possesses a C—Si—C angle which is significantly larger than those of the other Si atom.

Acknowledgements

Thanks is due to Prof. Dr. *C. Krüger* of the Max-Planck-Institut für Kohlenforschung for use of the diffractometer and Dr. *H. M. Schiebel* and Dipl.-Chem. *H. Kluge* (Techn. Univ. Braunschweig) for help in mass and NMR spectrometry. Support by Fonds der Chemischen Industrie, Frankfurt am Main, and Bayer AG, Leverkusen, is gratefully acknowledged.

References

[1] For part XXXIX see *Wannagat, U., Blumenthal, Th., Brauer, D. J., Bürger, H.*, J. Organometal. Chem., in press.

[2] Also: Contributions to the Chemistry of SiN compounds. CLXI. For part CLX see Ref.[1].

[3] *Brauer D. J., Bürger H., Moretto H. H., Wannagat U., Wiegel K.*, J. Organometal. Chem. **170**, 161 (1979).

[4] Survey: *Wannagat U., Schlingmann M., Autzen H.*, Z. Naturforsch. **31 b**, 621 (1976).

[5] *Wannagat U., Eisele G., Schlingmann M.*, Z. Anorg. Allg. Chem. **429**, 83 (1977).

[6] *Wannagat U., Autzen H., Schlingmann M.*, Z. Anorg. Allg. Chem. **419**, 41 (1976).

[7] *Ibers J. A., Hamilton W. C.*, eds., International Tables for X-Ray Crystallography, Vol. IV, Table 2.3.1 and Table 2.2 B. Birmingham: The Kynoch Press. 1974.

[8] An $|F_0|$, $\sigma(|F_0|)$ list may be obtained from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen, by quoting the deposit number CSD 50441, the authors and the literature reference.

[9] *Brauer D. J.*, *Bürger H.*, *Pawelke G.*, Inorg. Chem. **16**, 2305 (1977).

[10] *Me* = Methyl, *Et* = Ethyl, *Bu* = *n*-Butyl.

[11] *Wannagat U.*, *Eisele G.*, unpublished results; *Eisele G.*, Thesis, Techn. Univ. Braunschweig 1978.

[12] *Wannagat U.*, *Bogusch E.*, *Geymayer P.*, Monatsh. Chem. **95**, 801 (1964).

[13] *König A.*, *Wannagat U.*, unpublished results; *König A.*, Thesis, Techn. Univ. Braunschweig 1978.