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SYNTHESIS AND HYDROLYSIS OF A FLUOROSILYL-t-BUTYLAMINODICHLOROALANE. CRYSTAL STRUCTURES OF THE CYCLIC COMPOUNDS $[(Me_3SiNMe)_2SiNCMe_3]_2$ AND $(Me_3CNHAlCl_2)_2$

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Summary

The lithium salt of t-butylaminofluorobis(methyltrimethylsilylamino)silane, $(Me_3SiNMe)_2SiFNLiCMe_3$, reacts with aluminium trichloride to form a dimeric silylaminodichloroalane, $[(Me_2SiNMe)_2SiFNCMe_3AlCl_2]_2$ (I); the cyclodisilazane $[(Me_3SiNMe)_2SiNCMe_3]_2$ (II) is formed as a by-product. Hydrolysis of I cleaves the Si–N bonds to produce the four-membered ring compound $(Me_3CNHAlCl_2)_2$ (III). II forms monoclinic crystals, space group $P2_1/n$, with a 10.721(2), b 10.099(2), c 17.166(3) Å, β 93.46(2)°, $Z = 2$. III also crystallises in $P2_1/n$, with a 6.500(2), b 11.957(2), c 10.802(2) Å, β 96.31(2)°, $Z = 2$. The structures were determined from 2655 and 1382 diffractometer-measured intensities, and refined to $R = 0.046$ and 0.032, respectively. Molecules of both compounds have crystallographic inversion centres, requiring planar four-membered rings (Si_2N_2 and Al_2N_2, respectively), and additionally a *trans* arrangement of the nitrogen substituents in III.

Introduction

We have recently demonstrated that halides of some main-group elements give substitution reactions with lithiated aminofluorosilanes, eliminating lithium halides [1,2]. Acyclic products thus obtained undergo thermal ring closure with loss of dihalosilane [1]. Lithium salts of t-butylamino-diorganofluorosilanes react with Al_2Cl_6 in a 2/1 molar ratio to give $AlCl_3$ adducts of silicenium ylids $(R_2SiNCMe_3)AlCl_3$ [2].

Dimeric silylaminoalanes have been obtained previously from reactions of aluminium halides with bis(trimethylsilyl)amine [3–5]. The chlorination of *N*-alkyliminoalanes with HCl, $HgCl_2$ or $TiCl_4$ provides a preparative method for aluminium-nitrogen ring compounds with chlorine substituents [6,7].

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We report here the synthesis of a silyl substituted Al_2N_2 ring, hydrolysis of which leads to a dimeric alkylaminodichloroalane $(Me_3CHNAlCl_2)_2$.

Experimental

Mass spectrometry: Varian CH5; NMR spectroscopy: Bruker 60E and FT80 instruments.

Preparation of I and II

Solvents were dried before use, and the reaction was carried out in a dry nitrogen atmosphere. A solution of 0.05 mol Al_2Cl_6 in 100 ml Et_2O was added dropwise at room temperature to a stirred solution of the freshly lithiated aminofluorosilane, $(Me_3SiNMe)_2SiFNLiCMe_3$ (0.1 mol), in 100 ml petrol ether (b.p. 40–60°C). The mixture was heated under reflux for 1 h and the solvent removed. Compound I was obtained pure by fractional distillation. The by-product II was separated by sublimation, and recrystallised from n-hexane.

I: $C_{24}H_{66}Al_2Cl_4F_2N_6Si_6$, yield 32 g (78%), m.p. 48°C, b.p. 110°C/0.01 Torr. Mol.wt. 841.2 calcd., 809 obs. (cryoscopy in C_6H_{12}). Analysis: Found: C, 34.35; H, 7.97; calcd.: C, 34.27, H, 7.91%. Mass spectrum (70 eV): $m/e = 419$ (relative intensity 1) $[M/2]^+$, 404(100) $[M/2 - CH_3]^+$. ^1H NMR (30% soln. in CH_2Cl_2, TMS internal standard): δ 0.20 ($SiMe_3$, J(H–F) 1.8 Hz), 0.45 ($SiMe_3$, J(H–F) 1.7 Hz), 1.28 (CMe_3), 2.64 (NMe, J(H–F) 1.7 Hz), 2.73 (NMe, J(H–F) 1.0 Hz) ppm. ^{19}F NMR (30% soln. in CH_2Cl_2, C_6F_6 internal standard): δ 42.7 ppm. ^{27}Al NMR (30% soln. in C_6H_6/C_6D_6, $AlCl_3/H_2O$ external standard): δ 107 ppm. ^{29}Si NMR (30% soln. in CH_2Cl_2/C_6F_6, TMS internal standard): δ -44.5 (SiF, J(Si–F) 272.9 Hz), 11.75 ($SiMe_3$), 25.53 ($SiMe_3$, ^3J(Si–F) 2.6 Hz) ppm.

II: $C_{24}H_{66}N_6Si_6$, yield 2 g (7%), m.p. 242°C. Analysis: Found: C, 47.35; H, 11.06; calcd.: C, 47.46; H, 10.95%. Mass spectrum (70 eV): $m/e = 606(9)$ $[M]^+$, 591(100) $[M - CH_3]^+$. ^1H NMR (30% soln. in CH_2Cl_2/C_6H_6, TMS): δ 0.23 ($SiMe_3$), 1.25 (CMe_3), 2.73 (NMe) ppm.

Hydrolysis of I

A solution of 0.05 mol I in 100 ml Et_2O was stirred for 3 h at room temperature with 0.05 mol H_2O. The solid product was filtered off under vacuum, sublimed, and recrystallised from n-hexane.

III: $C_8H_{20}Al_2Cl_4N_2$, yield 6 g (35%), m.p. 82°C. Analysis: Found: C, 28.03; H, 6.14; calcd.: C, 28.26; H, 5.93%. Mass spectrum (70 eV): $m/e = 338(1)$ $[M]^+$, 323(100) $[M - CH_3]^+$.

Crystal data

II: $C_{24}H_{66}N_6Si_6$, $M_r = 607.3$, monoclinic, space group $P2_1/n$ ($P2_1/c$ with a different choice of c axis), a 10.721(2), b 10.099(2), c 17.166(3) Å, β 93.46(2)°, U 1855.2 Å^3, $Z = 2$, D_c 1.087 g cm^{-3}, $F(000) = 672$, λ(Mo-K_α) 0.71069 Å, μ 2.41 cm^{-1}.

III: $C_8H_{20}Al_2Cl_4N_2$, $M_r = 340.0$, monoclinic, space group $P2_1/n$, a 6.500(2), b 11.957(2), c 10.802(2) Å, β 96.31(2)°, U 834.5 Å^3, $Z = 2$, D_c 1.353 g cm^{-3}, $F(000) = 352$, λ(Mo-K_α) 0.71069 Å, μ 7.97 cm^{-1}.

Data collection

Crystals were sealed in glass capillaries and examined on a Stoe-Siemens AED

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($Å^2 \times 10^4$) FOR II

Atom	x	y	z	U
Si(1)	700(1)	4287(1)	5456(1)	291(2)
N(2)	2247(2)	3922(2)	5309(1)	376(6)
C(2)	2847(3)	4864(3)	4784(2)	628(11)
Si(2)	3281(1)	2661(1)	5594(1)	440(2)
C(21)	4534(3)	3344(4)	6281(2)	705(12)
C(22)	4050(4)	1995(4)	4728(2)	846(15)
C(23)	2549(3)	1213(3)	6059(2)	674(12)
N(3)	398(2)	3567(2)	6343(1)	378(6)
C(3)	1362(3)	3902(3)	6982(1)	524(10)
Si(3)	−837(1)	2738(1)	6754(1)	530(3)
C(31)	−1958(3)	1885(3)	6056(2)	716(12)
C(32)	−188(3)	1411(4)	7430(2)	830(14)
C(33)	−1753(4)	3874(4)	7355(2)	869(16)
N(1)	336(2)	5980(2)	5343(1)	313(6)
C(1)	421(3)	7105(2)	5902(1)	456(8)
C(11)	1781(3)	7339(3)	6182(2)	680(11)
C(12)	−92(3)	8361(3)	5506(2)	609(11)
C(13)	−369(3)	6833(3)	6599(2)	708(13)

diffractometer at room temperature. Unit cell parameters were obtained from 2θ values of reflections centered at $\pm\omega$. Intensities were measured by a real-time profile-fitting procedure [8]. No absorption corrections were applied.

II: crystal size 0.2 × 0.3 × 0.6 mm, $2\theta_{max}$ 50°, 2655 reflections with $F > 4\sigma(F)$.

III: crystal size 0.8 × 0.7 × 0.6 mm, $2\theta_{max}$ 50°, 1382 reflections with $F > 4\sigma(F)$.

Structure solution and refinement

Both structures were solved by automatic direct methods and refined to a minimum value of $\Sigma w\Delta^2$ [$\Delta = |F_0| - |F_c|$; $w^{-1} = \sigma^2(F) + gF^2$, with $g = 0.00099$ for II, 0.0001 for III). The hydrogen atom attached to nitrogen in III was refined freely; all others were constrained to give C–H = 0.96 Å, H–C–H 109.5°, U(H) $1.2U_{eq}$(C),

TABLE 2

ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($Å^2 \times 10^4$) FOR III

Atom	x	y	z	U
Al	4123(1)	3936(1)	4922(1)	359(2)
Cl(1)	993(1)	3600(1)	4282(1)	607(2)
Cl(2)	5736(1)	2460(1)	5449(1)	659(3)
N	5699(3)	4852(1)	3905(1)	353(5)
H	6775(37)	4571(21)	4061(20)	426(64)
C(1)	5389(3)	4952(2)	2488(2)	437(7)
C(2)	5694(5)	3793(2)	1955(2)	660(10)
C(3)	7013(4)	5757(3)	2101(2)	684(10)
C(4)	3249(4)	5384(3)	2080(2)	649(9)

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) FOR II (A prime denotes a symmetry-related atom)

Si(1)-N(2)	1.733(2)	Si(1)-N(3)	1.735(2)
Si(1)-N(1)	1.761(2)	N(2)-C(2)	1.484(4)
N(2)-Si(2)	1.738(2)	Si(2)-C(21)	1.866(3)
Si(2)-C(22)	1.868(4)	Si(2)-C(23)	1.862(3)
N(3)-C(3)	1.500(3)	N(3)-Si(3)	1.751(2)
Si(3)-C(31)	1.857(3)	Si(3)-C(32)	1.878(4)
Si(3)-C(33)	1.862(4)	N(1)-C(1)	1.487(3)
C(1)-C(11)	1.525(4)	C(1)-C(12)	1.526(4)
C(1)-C(13)	1.533(4)	Si(1)-N(1′)	1.733(2)
N(2)-Si(1)-N(3)	105.6(1)	N(2)-Si(1)-N(1)	113.4(1)
N(3)-Si(1)-N(1)	116.9(1)	N(2)-Si(1)-N(1′)	115.2(1)
N(3)-Si(1)-N(1′)	119.0(1)	N(1)-Si(1)-N(1′)	86.4(1)
Si(1)-N(2)-C(2)	114.0(2)	Si(1)-N(2)-Si(2)	135.6(1)
C(2)-N(2)-Si(2)	110.4(2)	N(2)-Si(2)-C(21)	109.2(1)
N(2)-Si(2)-C(22)	110.2(1)	C(21)-Si(2)-C(22)	107.5(2)
N(2)-Si(2)-C(23)	114.7(1)	C(21)-Si(2)-C(23)	109.0(2)
C(22)-Si(2)-C(23)	106.0(2)	Si(1)-N(3)-C(3)	113.0(2)
Si(1)-N(3)-Si(3)	137.7(1)	C(3)-N(3)-Si(3)	108.5(2)
N(3)-Si(3)-C(31)	115.9(1)	N(3)-Si(3)-C(32)	109.2(1)
C(31)-Si(3)-C(32)	105.6(2)	N(3)-Si(3)-C(33)	111.4(1)
C(31)-Si(3)-C(33)	107.5(2)	C(32)-Si(3)-C(33)	106.6(2)
Si(1)-N(1)-C(1)	131.8(1)	Si(1)-N(1)-Si(1′)	93.6(1)
C(1)-N(1)-Si(1′)	129.9(2)	N(1)-C(1)-C(11)	110.0(2)
N(1)-C(1)-C(12)	110.0(2)	C(11)-C(1)-C(12)	108.9(2)
N(1)-C(1)-C(13)	110.6(2)	C(11)-C(1)-C(13)	110.2(2)
C(12)-C(1)-C(13)	107.2(2)		

where U_{eq} is the equivalent isotropic thermal parameter for the corresponding C atom, defined as one-third of the trace of the orthogonalised U_{ij} matrix. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Complex scattering factors were used [9]. Final difference syntheses contained no significant features.

TABLE 4

BOND LENGTHS (Å) AND ANGLES (°) FOR III

Al-Cl(1)	2.114(1)	Al-Cl(2)	2.099(1)
Al-N	1.924(2)	N-H	0.778(24)
N-C(1)	1.526(3)	C(1)-C(2)	1.522(4)
C(1)-C(3)	1.521(4)	C(1)-C(4)	1.503(3)
Al-N′	1.920(2)		
Cl(1)-Al-Cl(2)	111.3(1)	Cl(1)-Al-N	118.4(1)
Cl(2)-Al-N	110.6(1)	Cl(1)-Al-N′	110.2(1)
Cl(2)-Al-N′	117.6(1)	N-Al-N′	87.1(1)
Al-N-H	98.7(18)	Al-N-C(1)	126.6(1)
H-N-C(1)	105.6(17)	Al-N-Al′	92.9(1)
H-N-Al′	101.3(17)	C(1)-N-Al′	126.5(1)
N-C(1)-C(2)	107.4(2)	N-C(1)-C(3)	107.9(2)
C(2)-C(1)-C(3)	110.4(2)	N-C(1)-C(4)	109.7(2)
C(2)-C(1)-C(4)	110.9(2)	C(3)-C(1)-C(4)	110.5(2)

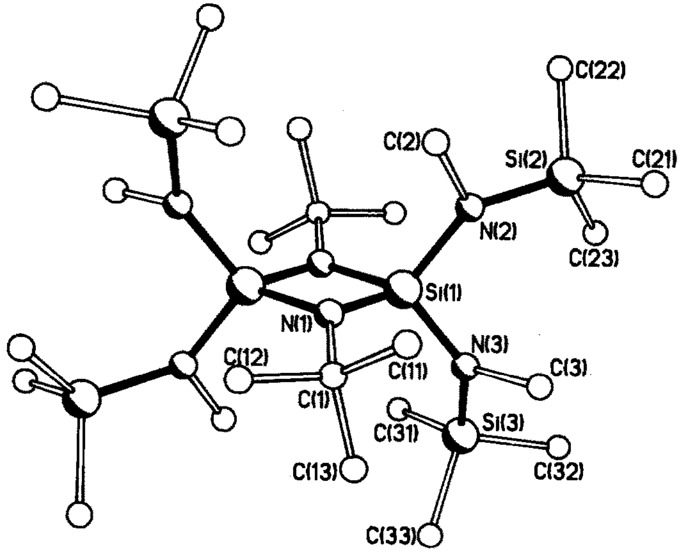


Fig. 1. Molecular structure of II showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

II: 196 parameters, $R = 0.046$, R' $[= (\Sigma w\Delta^2/\Sigma wF_0^2)^{1/2}] = 0.062$, mean shift/e.s.d. = 0.10, max. = 0.62; slope of normal probability plot = 1.27 [10].

III: 86 parameters, $R = 0.032$, $R' = 0.053$, mean shift/e.s.d. = 0.001, max. = 0.002; slope of normal probability plot = 2.61.

Final atomic coordinates, bond lengths and angles are given in Tables 1-4. Tables of structure factors, hydrogen atom parameters and anisotropic thermal parameters may be obtained from the authors. Figs. 1 and 2 show the molecular structures.

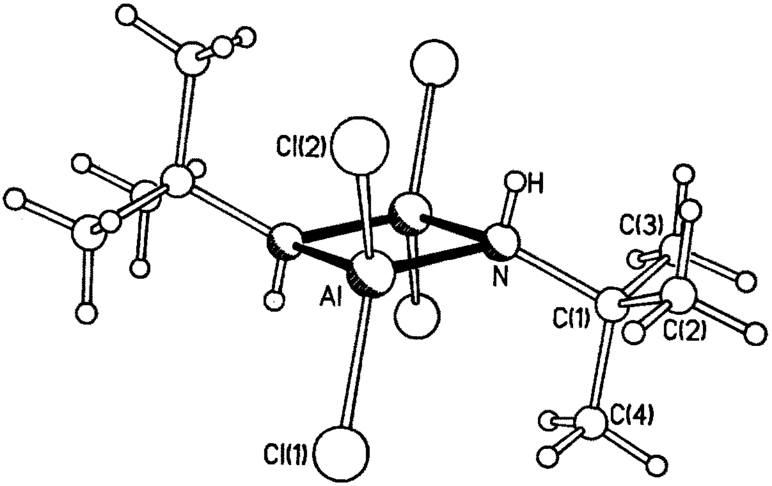
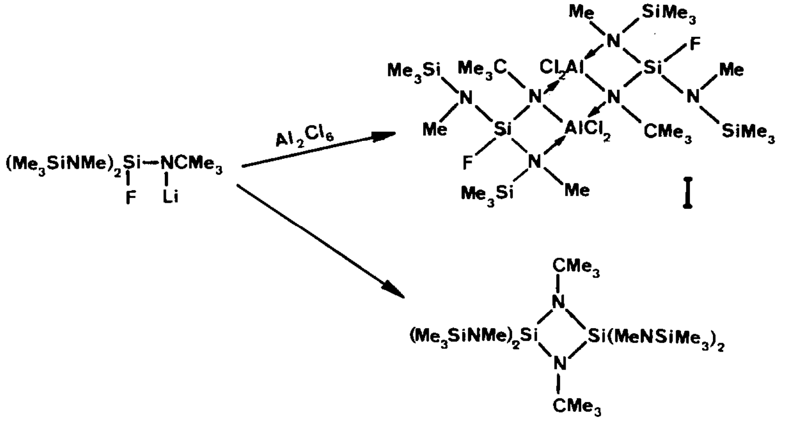


Fig. 2. Molecular structure of III showing the atom numbering scheme.

Results and discussion

Freshly lithiated t-butylaminofluorobis(methyltrimethylsilylamino)silane, $(Me_3SiNMe)_2SiFNLiCMe_3$ [11] reacts with Al_2Cl_6 in a 2/1 molar ratio, eliminating LiCl and forming compound I (reaction 1). The cyclodisilazane II is obtained as a by-product in this reaction. It is formed quantitatively when the initial lithium compound is heated alone at about 100°C.

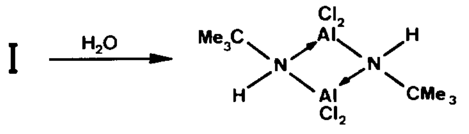


I

II

(1)

A dimeric structure is suggested for I for the following reasons: (i) a cryoscopic measurement indicates the dimer formula in C_6H_{12} solution; (ii) the product of hydrolysis of I contains the Al_2N_2 ring, as indicated by its crystal structure determination. The rather low boiling point and the mass spectrum, however, indicate that it may be monomeric in the gas phase. NMR spectra demonstrate the equivalence of the two fluorine-substituted silicon atoms, but there are two non-equivalent pairs of Me_3SiNMe groups, as indicated by chemical shifts and coupling constants in both the ^1H and ^{29}Si NMR spectra. For this reason, it can not be a simple Al_2N_2 ring with terminal substituents on the nitrogen atoms and chlorine atoms attached to Al. It is necessary to postulate additional bonding between nitrogen and aluminium atoms. The formula suggested is consistent with the spectra and with the product of hydrolysis of I, but other structures can not be ruled out. Additional bonding to aluminium to form four-membered rings containing both Si and Al has been observed in other related compounds [2]. The low melting point and ready hydrolysis of I (reaction 2) have prevented a single-crystal structure determination.



III

(2)

The structure of II is comparable to those of other cyclodisilazanes previously investigated [12], with a planar Si_2N_2 ring and with exocyclic Si–N shorter than ring Si–N bonds.

III exists in the solid state as the *trans* isomer, in contrast to $(Me_2AlNHCHMe_2)_2$, for which a 2/1 *cis/trans* mixture has been found, both in solution and in the crystal structure [13]. The Al–N bonds in III are shorter than those in this dimethylalane dimer and in related dimethyl-substituted compounds [14], and very similar to those in $(Cl_2AlNMe_2)_2$ [15].

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