

DIMERISATION OF A SILICENIUM YLID BY METHANIDE AND SILYLAMINE MIGRATION

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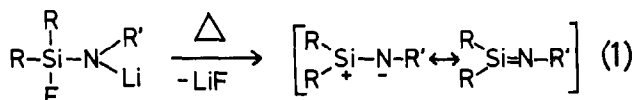
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Summary

The thermal elimination of LiF from lithium aminofluorosilanes provides a simple synthetic route to four-membered silicon-nitrogen rings. In attempts to inhibit sterically the otherwise ready dimerisation of such lithium salts, *t*-butyl, mesityl and silylamine substituents were introduced. The lithiation of the fluorotris(silylamino)silane $(\text{Me}_3\text{SiNMe})_2\text{SiF-NHSiMe}_2\text{CMe}_3$ and the thermal elimination of LiF led to the formation of a cyclodisilazane, involving migration of a methanide and a silylmethylamine in one of the monomer precursors. The crystal structure of this product has been determined from 3375 unique diffractometer-measured intensities, and refined to $R = 0.070$. The space group is $P2_1/n$, with a 12.458(2), b 22.589(3), c 16.376(4) Å, β 102.33(1)° and $Z = 4$.

Introduction

Numerous attempts have been made in recent years to produce silicenum ylids (silimines) by elimination of silylazide or of lithium fluoride from suitable precursors [1–7].



Although these attempts have been unsuccessful, the results actually obtained are of considerable interest in their own right. Elimination of LiF from lithiated aminofluorosilanes has been established as a simple route to Si_2N_2 ring compounds. Depending on the type and particularly the bulkiness of the substituents on Si and N, different cyclodisilazanes are produced by the following reaction mechanisms:

(a) (2 + 2)cycloaddition, when R and R' are organic groups other than CMe₃ or small organosilylamino [4];

(b) methanide ion migration and ring closure, when R = t-butylsilylamino, R' = organo [5];

(c) 1,3-silyl group migration and cycloaddition, when R = bis(trimethylsilyl)amino, R' = organo [6];

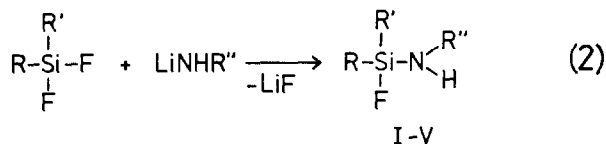
(d) cross-dimerisation of two ylids, one of which has undergone a 1,3-methanide ion migration, when R = bis(trimethylsilylamino), R' = trimethylsilylamino [7].

(Me₃C)₂SiF-NLiCMe₃ undergoes no thermal LiF elimination; it can be sublimed unchanged at reduced pressure. Reaction with aluminium trihalides is necessary, in order to displace LiF and stabilise the resultant silicenium ylid by adduct formation [3].

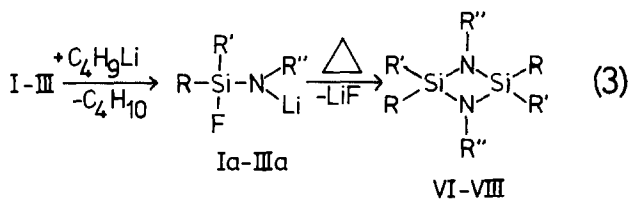
The aim of the research reported here was to prevent the dimerisation of silicenium ylids formed by reaction 1. To this end, aminofluorosilanes were prepared, containing bulky substituents which also avoid high polarity in the ylid.

Results and discussion

Some substituents fulfilling the above criteria are mesityl (2,4,6-trimethylphenyl), isopropyl, t-butyl and trimethylsilylamino groups. Aminofluorosilanes I-V were obtained by reaction of difluorosilanes containing these substituents with lithiated t-butylamine and t-butyltrimethylsilylamine.

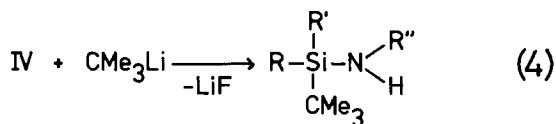


When treated with n-butyllithium at room temperature, I-III form stable lithium salts Ia-IIIa, which eliminate LiF on heating in n-heptane, to give the (2 + 2) cycloadducts VI-VIII.



A surprising result was obtained in the case where all substituents are mesityl. The initial aminofluorosilane IV reacts with organolithium compounds, even with t-butyllithium, to introduce an organo-substituent in place of fluorine.

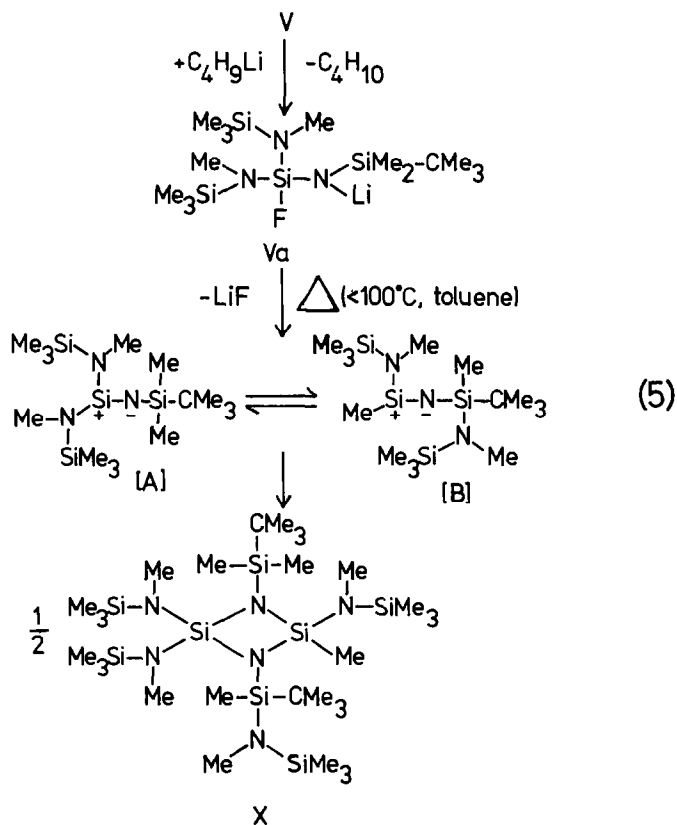
The lithium salt of V (Va) was easily formed, and was less reactive than Ia-IIIa. Only after several days' refluxing in toluene did the ¹⁹F NMR spectrum of the solution indicate that Va had completely disappeared. Colourless crystals were obtained from the reaction mixture after suitable work-up. The molecular mass, as determined by mass spectrometry, is that of a dimer of the silicenium ylid obtained by LiF elimination, but it was not possible to assign the NMR spectra unambiguously. Crystal structure determination revealed an unsymmetrically substituted



	R	R'	R''
I, VI	CHMe ₂	CMe ₃	CMe ₃
II, VII	2, 4, 6-C ₆ H ₂ Me ₃	2, 4, 6-C ₆ H ₂ Me ₃	CMe ₃
III, VIII	F	NCMe ₃ SiMe ₃	CMe ₃
IV, IX	2, 4, 6-C ₆ H ₂ Me ₃	2, 4, 6-C ₆ H ₂ Me ₃	2, 4, 6-C ₆ H ₂ Me ₃
V	NMeSiMe ₃	NMeSiMe ₃	SiMe ₂ CMe ₃

cyclodisilazane. One half of the molecule corresponds directly to the silicenium ylid precursor initially obtained (A), but the other half (B) is somewhat rearranged. Its formation can reasonably be explained only by a nucleophilic 1,3-methanide ion migration from the SiMe₂CMe₃ group to the central silicon atom and a previously unknown 1,3-methyl(trimethylsilyl)amino-group migration in the reverse direction.

The bulk of the substituents in A prevents its direct dimerisation and so introduces the possibility of rearrangement to a form which permits a cross-dimeri-



sation. The ylid **B** also appears to undergo no self-dimerisation under the conditions of the reaction.

Experimental

Compounds were handled under dry nitrogen. Mass spectroscopy: Varian CH5; NMR spectroscopy: Bruker 60E and FT 80 instruments.

Aminofluorosilanes RR'SiFNHR'' (I-V)

A solution of 0.05 mol LiNHR' in 100 ml petroleum ether/tetrahydrofuran (PE/THF) was added dropwise at room temperature to a stirred solution of 0.05 mol F₂SiRR' in 100 ml PE/THF. After heating for 2 h, the solvents and LiF were removed and the pure product isolated by distillation. IV was recrystallised from n-hexane.

I: R = CHMe₂, R' = R'' = CMe₃. C₁₁H₂₆FNSi, yield 8 g (73%), b.p. 41°C/1.5 Torr. Mol.wt. 219.4 calcd., mass spectrum: 219 (field ion measurement). Analysis: Found: C, 60.05; H, 11.83; calcd.: C, 60.21, H, 11.94%. ¹H NMR (30% soln. in CH₂Cl₂, TMS int.): δ 1.02 [SiCMe₃, J(HF) 0.9 Hz]; 1.2 [CHMe₂]; 1.25 [NCMe₃, J(HF) 0.6 Hz], ¹⁹F NMR (C₆F₆ int.): δ 5.58 ppm.

II: R = R' = 2,4,6-C₆H₂Me₃, R'' = CMe₃. C₂₂H₃₂FNSi yield 14 g (78%), b.p. 155°C/0.01 Torr. Mol.wt. 357.6 calcd.: mass spectrum (70 eV): m/e = 357 (49%) M⁺. Analysis: Found: C, 74.10, H, 9.24; calcd.: C, 73.90; H 9.02%. ¹H NMR (30% soln. in CH₂Cl₂, TMS int.): δ 1.21 [CMe₃], 2.21 [4-C₆H₂Me], 2.43 [2,6-C₆H₂Me₂, J(HF) 2.5 Hz], 6.8 [C₆H₂] ppm; ¹⁹F NMR (C₆F₆ int.): δ 40.6 ppm.

III: R = F, R' = NCMe₃SiMe₃, R'' = CMe₃. C₁₁H₂₈F₂N₂Si₂, yield 8 g (57%), b.p. 40°C/0.01 Torr. Mol wt. 282 calcd., mass spectrum (70 eV) m/e = 282 (3%) M⁺. Analysis: Found: C, 46.56, H, 9.61; calcd.: C, 46.76, H, 9.99%. ¹H NMR (30% soln. in CH₂Cl₂, TMS int.): δ 0.26 [SiMe₃, J(HF) 1 Hz], 1.22 [CMe₃, J(HF) 0.5 Hz], 1.38 [CMe₃, J(HF) = 0.7 Hz]; ¹⁹F NMR (C₆F₆ int.): 41.4 ppm.

IV: R, R', R'' = 2,4,6-C₆H₂Me₃. C₂₇H₃₄FNSi, yield 16 g (80%), m.p. 162°C. Mol. wt. calcd. 419.7; mass spectrum (70 eV) m/e = 419 (100%) M⁺. Analysis: Found: C, 77.01; H, 7.99; calcd.: C, 77.28, H, 8.17%. ¹H NMR (30% soln. in C₆H₆, TMS int.): δ 2.08 [4-C₆H₂Me], 2.12 [2,6-C₆H₂Me₂], 2.37 [N-4-C₆H₂Me], 2.41 [N-2,6-C₆H₂Me₂], 3.33 [NH] ppm; ¹⁹F NMR (C₆F₆ int.) δ 46.1 ppm.

V: R, R' = NMeSiMe₃, R'' = SiMe₂CMe₃. C₁₄H₄₀FN₃Si₄, yield 15 g (78%), b.p. 87°C/0.01 Torr. Mol.wt. calcd. 381.8, mass spectrum (70 eV) m/e = 381 (2%) M⁺. Analysis: Found: C, 43.76; H, 10.24; calcd.: C, 44.04, H, 10.56%. ¹H NMR (30% solv. in CH₂Cl₂, TMS int.): δ 0.07 [SiMe₂, J(HF) 0.7 Hz], 0.12 [SiMe₃, J(HF) 0.9 Hz], 0.91 [CMe₃], 2.47 [NMe, J(HF) 0.9 Hz], 0.91 [CMe₃], 2.47 [NMe, J(HF) = 1.5 Hz] ppm; ¹⁹F NMR (C₆F₆, int.) δ 38.6 ppm.

Cyclodisilazanes (RR'Si-NR'')₂ (VI-VIII)

A solution of 0.05 mol n-C₄H₉Li (15% in n-hexane) was added at room temperature to a stirred solution of 0.05 mol I-III in 100 ml n-hexane. After removal of butane, the lithium salt solutions were boiled for 24 h. The solvent and LiF were removed and the crude products recrystallised from n-hexane (VIII from acetone), to

give pure VI–VIII. The NMR spectra showed VI and VIII to be mixtures of *cis* and *trans* isomers, and these were not separated by recrystallisation.

VI: R = CHMe₂; R', R'' = CMe₃. C₂₂H₅₀N₂Si₂, yield 14 g (70 %), m.p. 237°C. Mol wt. calcd. 398.8; mass spectrum (70 eV) *m/e* = 341 (19%) [*M* – CMe₃]⁺. Analysis: Found: C, 66.01, H, 12.43; calcd.: C, 66.25, H, 12.65%.

VII: R, R' = 2,4,6-C₆H₂Me₃; R'' = CMe₃. C₄₄H₆₂N₂Si₂, yield 22 g (66%), m.p. 64°C. Mol. wt. calcd. 675.2, mass spectrum 674 (field-ion measurement). Analysis: Found: C, 77.97, H, 8.98. calcd.: C, 78.28, H, 9.26; ¹H NMR (30% solv. in CH₂Cl₂, TMS int.): δ 1.07 [CMe₃], 2.18 [4-C₆H₂Me], 2.30 [2,6-C₆H₂Me₂], 6.8 [C₆H₂] ppm.

VIII: R = F; R' = NCMe₃SiMe₃; R'' = CMe₃. C₂₂H₅₄F₂N₄Si₄, yield 19 g (73%), m.p. 220–226°C. Mol. wt. calcd. 525.0; mass spectrum 524 (1%) *M*⁺. Analysis: Found: C, 50.02, H, 10.06; calcd.: C, 50.33, H, 10.37%.

Aminosilane (RR'CM₃Si–NHR'') (IX)

A solution of 0.05 mol CMe₃Li (15% in n-pentane) was added at 0°C to a stirred solution of 0.05 mol IV in 100 ml n-hexane. After heating for 2 h, the solvents and LiF were removed and pure XI obtained by recrystallisation from n-hexane.

R, R', R'' = 2,4,6-C₆H₂Me₃, C₂₃H₁₉NSi yield 19 g (85%), m.p. 116°C. Mol. wt. calcd. 457.8, mass spectrum (70 eV) *m/e* = 457.8, mass spectrum (70 eV) *m/e* = 457 (1%) *M*⁺. Analysis: Found: C, 81.03, H, 9.17; calcd.: C, 81.34, H, 9.47%. ¹H NMR (30% soln. in CH₂Cl₂, TMS int.): δ 1.22 [CMe₃], 2.08 [N-2,6-C₆H₂Me₂], 2.17 [N-4-C₆H₂Me], 2.25 [Si-2,4-C₆H₂Me₂], 2.28 [Si-4-C₆H₂Me], 6.8 [C₆H₂] ppm.

Cyclodisilazane X. C₂₈H₇₈N₆Si₈

Yield 21 g (58%), b.p. 205°C/0.01 Torr; m.p. 132°C. Mol. wt. calcd. 723.7, mass spectrum (70 eV) *m/e* = 722 (5%) *M*⁺. Analysis: Found: C, 46.22, H, 10.61; calcd.: C, 46.47, H, 10.86%. ¹H NMR (30% soln. in CH₂Cl₂, TMS int.): δ 0.08, 0.11, 0.20, 0.22 [SiMe₃]; 0.13 [SiMe]; 0.54 [SiMe₂]; 0.93, 0.98 [CMe₃]; 2.62, 2.67, 2.68, 2.71 [NMe] ppm. ²⁹Si NMR (20% soln. in C₆D₆/CDCl₃, TMS int.) δ –44.31, –24.71 [Si-ring]; –7.33, 2.07 [SiCMe₃]; 5.34, 5.43, 5.60, 5.95 [SiMe₃] ppm.

Crystal data

X: monoclinic, space group *P*2₁/*n*, *a* 12.458(2), *b* 22.589(3), *c* 16.376(4) Å, β 102.33(1)°, *U* 4502.1 Å³, *Z* = 4, *D*_c 1.067 g cm^{–3}, *F*(000) = 1600, λ(Mo-K_α) 0.71069 Å, μ 2.57 cm^{–1}. Crystal size 0.3 × 0.3 × 0.4 mm, sealed in capillary, Stoe-Siemens AED diffractometer, unit cell parameters from 2θ values of 44 reflections centred at ±ω (20 < 2θ < 25°). 5859 reflections with 2θ < 45° measured by profile analysis [8], 3377 with *F* > 4σ(*F*); no absorption corrections.

Structure determination

Atoms were located by direct methods and difference synthesis, and were refined with anisotropic thermal parameters, to a minimum value of ΣwΔ² [Δ = |*F*_o| – |*F*_c|; w^{–1} = σ²(*F*)]. Hydrogen atoms were constrained in rigid methyl groups, with C–H 0.96 Å, H–C–H 109.5°, *U*(H) = 1.2 *U*_{eq}(C) where *U*_{eq} is the equivalent isotropic thermal parameter for a C atom, defined as one-third of the trace of the orthogonalised *U*_{*ij*} matrix. Complex scattering factors were used [9]. A final difference synthesis showed no significant features. 457 parameters; *R* = 0.070, *R*' [=

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U
Si(1)	3952(1)	1846(1)	7327(1)	33(1)
Si(2)	4486(1)	2872(1)	7010(1)	37(1)
Si(3)	3716(1)	926(1)	8753(1)	46(1)
Si(4)	2135(1)	1287(1)	5808(1)	46(1)
Si(5)	2482(1)	2829(1)	7931(1)	43(1)
Si(6)	6200(1)	1919(1)	6620(1)	41(1)
Si(7)	6955(2)	579(1)	6441(1)	71(1)
Si(8)	4389(2)	3898(1)	5622(1)	57(1)
N(1)	3368(3)	2548(2)	7325(2)	27(2)
N(2)	5089(3)	2168(2)	7022(2)	30(2)
N(3)	4260(3)	1527(2)	8309(2)	34(2)
N(4)	3274(3)	1323(2)	6653(2)	32(2)
N(6)	6584(3)	1208(2)	6938(3)	43(2)
N(8)	4152(3)	3219(2)	6043(3)	38(2)
C(2)	5244(5)	3393(2)	7809(3)	52(3)
C(3)	5125(4)	1840(3)	8932(3)	49(3)
C(31)	3493(5)	1134(3)	9810(3)	68(3)
C(32)	4714(5)	293(2)	8891(4)	62(3)
C(33)	2356(4)	661(3)	8163(4)	56(3)
C(4)	3948(4)	775(2)	6641(3)	48(3)
C(41)	2596(5)	1293(3)	4800(3)	69(3)
C(42)	1151(5)	1901(3)	5810(4)	77(3)
C(43)	1380(5)	573(3)	5836(4)	74(3)
C(51)	3243(5)	3051(3)	9001(3)	66(3)
C(52)	1487(5)	2244(3)	8090(4)	65(3)
C(53)	1703(4)	3513(2)	7462(3)	48(3)
C(54)	1142(5)	3424(3)	6543(4)	73(3)
C(55)	2455(5)	4060(3)	7497(4)	78(3)
C(56)	798(6)	3665(3)	7939(4)	93(4)
C(6)	6897(5)	1143(3)	7876(3)	70(3)
C(61)	5798(5)	1940(3)	5451(3)	59(3)
C(62)	7446(4)	2426(3)	6928(4)	51(3)
C(63)	8439(5)	2132(3)	6673(4)	84(4)
C(64)	7248(5)	3025(3)	6455(4)	86(4)
C(65)	7766(5)	2559(3)	7872(4)	83(3)
C(71)	6399(9)	559(4)	5291(4)	148(6)
C(72)	8477(6)	496(4)	6606(7)	157(6)
C(73)	6441(7)	-94(3)	6880(5)	100(4)
C(8)	3463(5)	2838(2)	5395(3)	53(3)
C(81)	3044(5)	4273(3)	5190(4)	75(3)
C(82)	5102(6)	3800(3)	4735(4)	90(4)
C(83)	5211(6)	4429(3)	6375(4)	93(4)

$(\Sigma w\Delta^2/\Sigma wF_0^2)^{1/2} = 0.043$, mean shift/e.s.d. = 0.03; max. = 0.19; slope of normal probability plot [10] = 1.41.

Final atomic coordinates, bond lengths and angles are given in Tables 1 and 2. Structure factor tables may be obtained from the authors. Figure 1 shows the molecular structure.

TABLE 2
BOND LENGTHS (Å) AND ANGLES (°)

Si(1)–N(1)	1.744(4)	Si(1)–N(2)	1.756(4)
Si(1)–N(3)	1.730(4)	Si(1)–N(4)	1.712(4)
Si(2)–N(1)	1.746(4)	Si(2)–N(2)	1.756(4)
Si(2)–N(8)	1.736(4)	Si(2)–C(2)	1.861(5)
Si(3)–N(3)	1.741(4)	Si(3)–C(31)	1.871(6)
Si(3)–C(32)	1.877(6)	Si(3)–C(33)	1.861(5)
Si(4)–N(4)	1.760(4)	Si(4)–C(41)	1.859(6)
Si(4)–C(42)	1.850(7)	Si(4)–C(43)	1.874(7)
Si(5)–N(1)	1.752(5)	Si(5)–C(51)	1.873(5)
Si(5)–C(52)	1.868(6)	Si(5)–C(53)	1.898(6)
Si(6)–N(2)	1.748(5)	Si(6)–N(6)	1.726(5)
Si(6)–C(61)	1.872(5)	Si(6)–C(62)	1.909(6)
Si(7)–N(6)	1.748(5)	Si(7)–C(71)	1.862(7)
Si(7)–C(72)	1.867(7)	Si(7)–C(73)	1.853(7)
Si(8)–N(8)	1.732(5)	Si(8)–C(81)	1.877(6)
Si(8)–C(82)	1.869(8)	Si(8)–C(83)	1.863(7)
N(3)–C(3)	1.495(6)	N(4)–C(4)	1.497(7)
N(6)–C(6)	1.508(7)	N(8)–C(8)	1.487(6)
C(53)–C(54)	1.531(8)	C(53)–C(55)	1.543(8)
C(53)–C(56)	1.540(10)	C(62)–C(63)	1.538(9)
C(62)–C(64)	1.552(8)	C(62)–C(65)	1.540(8)
N(3)–Si(1)–N(4)	106.9(2)	N(3)–Si(1)–N(1)	113.0(2)
N(4)–Si(1)–N(1)	118.6(2)	N(3)–Si(1)–N(2)	113.9(2)
N(4)–Si(1)–N(2)	114.8(2)	N(1)–Si(1)–N(2)	89.2(2)
C(2)–Si(2)–N(8)	110.0(2)	C(2)–Si(2)–N(1)	112.0(2)
N(8)–Si(2)–N(1)	114.0(2)	C(2)–Si(2)–N(2)	114.4(2)
N(8)–Si(2)–N(2)	116.0(2)	N(1)–Si(2)–N(2)	89.1(2)
N(3)–Si(3)–C(31)	109.8(3)	N(3)–Si(3)–C(32)	109.7(3)
C(31)–Si(3)–C(32)	107.8(3)	N(3)–Si(3)–C(33)	115.2(2)
C(31)–Si(3)–C(33)	105.1(3)	C(32)–Si(3)–C(33)	108.9(3)
N(4)–Si(4)–C(41)	110.3(2)	N(4)–Si(4)–C(42)	112.9(2)
C(41)–Si(4)–C(42)	109.1(3)	N(4)–Si(4)–C(43)	110.2(2)
C(41)–Si(4)–C(43)	106.2(3)	C(42)–Si(4)–C(43)	107.9(3)
N(1)–Si(5)–C(51)	111.8(2)	N(1)–Si(5)–C(52)	109.9(3)
C(51)–Si(5)–C(52)	106.1(3)	N(1)–Si(5)–C(53)	113.3(2)
C(51)–Si(5)–C(53)	105.9(3)	C(52)–Si(5)–C(53)	109.5(3)
N(2)–Si(6)–C(61)	108.4(2)	N(2)–Si(6)–C(62)	111.9(2)
C(61)–Si(6)–C(62)	106.3(3)	N(2)–Si(6)–N(6)	112.2(2)
C(61)–Si(6)–N(6)	109.1(3)	C(62)–Si(6)–N(6)	108.7(2)
N(6)–Si(7)–C(71)	114.3(3)	N(6)–Si(7)–C(72)	112.0(3)
C(71)–Si(7)–C(72)	106.9(5)	N(6)–Si(7)–C(73)	109.8(3)
C(71)–Si(7)–C(73)	106.7(4)	C(72)–Si(7)–C(73)	106.7(4)
N(8)–Si(8)–C(81)	109.5(3)	N(8)–Si(8)–C(82)	110.7(3)
C(81)–Si(8)–C(82)	107.2(3)	N(8)–Si(8)–C(83)	115.1(3)
C(81)–Si(8)–C(83)	106.2(3)	C(82)–Si(8)–C(83)	107.8(3)
Si(1)–N(1)–Si(2)	91.2(2)	Si(1)–N(1)–Si(5)	129.9(2)
Si(2)–N(1)–Si(5)	130.9(2)	Si(1)–N(2)–Si(2)	90.5(2)
Si(1)–N(2)–Si(6)	136.5(2)	Si(2)–N(2)–Si(6)	131.1(3)
Si(1)–N(3)–C(3)	114.9(3)	Si(1)–N(3)–Si(3)	133.2(2)
C(3)–N(3)–Si(3)	111.9(3)	Si(1)–N(4)–C(4)	112.2(3)
Si(1)–N(4)–Si(4)	137.9(2)	C(4)–N(4)–Si(4)	108.2(3)
Si(6)–N(6)–C(6)	113.1(4)	Si(6)–N(6)–Si(7)	134.5(3)
C(6)–N(6)–Si(7)	111.0(4)	Si(2)–N(8)–C(8)	112.2(3)

(continued)

TABLE 2 (continued)

Si(2)–N(8)–Si(8)	137.3(2)	C(8)–N(8)–Si(8)	110.5(3)
Si(5)–C(53)–C(54)	112.1(4)	Si(5)–C(53)–C(55)	112.5(4)
C(54)–C(53)–C(55)	106.7(5)	Si(5)–C(53)–C(56)	110.1(4)
C(54)–C(53)–C(56)	107.3(5)	C(55)–C(53)–C(56)	107.9(5)
Si(6)–C(62)–C(63)	109.0(4)	Si(6)–C(62)–C(64)	110.9(4)
C(63)–C(62)–C(64)	107.0(5)	Si(6)–C(62)–C(65)	113.8(4)
C(63)–C(62)–C(65)	107.8(5)	C(64)–C(62)–C(65)	108.0(5)

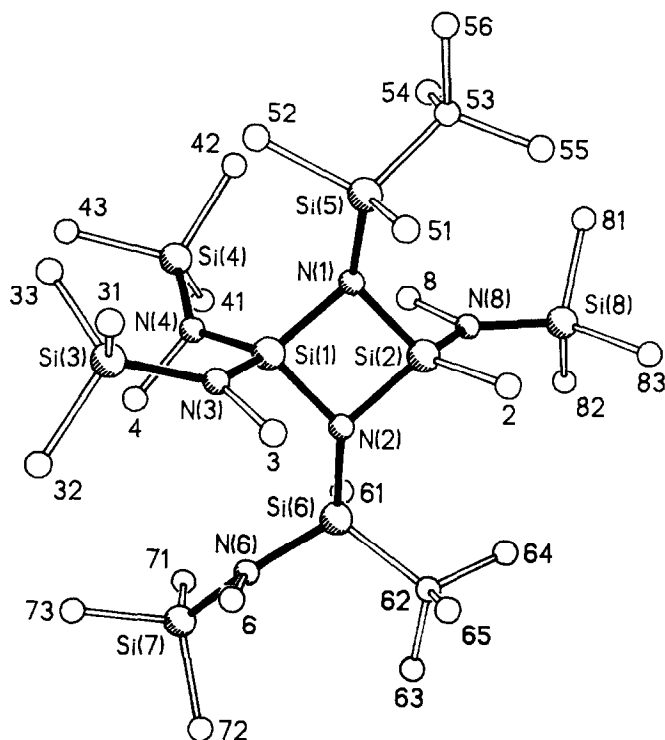


Fig. 1. Molecular structure of X. Carbon atoms are labelled by number only. Hydrogen atoms are omitted. Si–N bonds filled, others open.

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