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cis-2,4-Diamino-2,4-dichloro-1,3-bis(di-*tert*-butylmethylsilyl)-cyclodisilazane—synthesis and crystal structure

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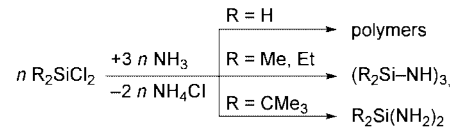
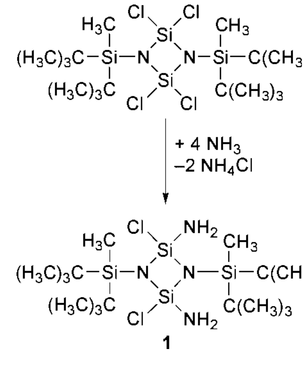
The reaction between the cyclodisilazane [Cl_2Si–$NSiMe(CMe_3)_2]_2$ and NH_3 afforded the first *cis*-2,4-diamino-2,4-dichloro-1,3-bis(di-*tert*-butylmethylsilyl)cyclodisilazane [$Cl(H_2N)Si$–$NSiMe(CMe_3)_2]_2$ 1; the nitrogen of the NH_2 group has a planar environment and the shortest Si–NH_2 bond length found so far in an aminosilane (167.1 pm).

Three pathways are known in the reaction of dichlorosilanes Cl_2SiR_2 with ammonia, *e.g.*



Depending on the bulk of the substituents, dichlorodiorganosilanes react with ammonia to give polymers, three- and four-membered SiN-rings or stable diaminosilanes.[1–4] In every case both chlorine atoms are substituted by nitrogen groups. In the present paper we report the synthesis and X-ray structure of the first cyclodisilazane where both the chlorine atoms and the amino groups at the silicon are in a *cis*-arrangement.

The ammonolysis of the tetrachlorocyclodisilazane [Cl_2Si–$NSiMe(CMe_3)_2]_2$[2] leads selectively—even with an excess of NH_3—to the substitution of only two chlorine atoms by NH_2 groups. The *cis*-2,4-diamino-2,4-dichloro-1,3-bis(di-*tert*-butylmethylsilyl)cyclodisilazane [$Cl(H_2N)Si$–$NSiMe(CMe_3)_2]_2$ **1** is formed.† No other isomer could be found.



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Crystals of **1** with space group *Pnma* were obtained as colourless plates from a saturated solution of diethyl ether. The asymmetric unit consists of half a molecule of **1** and half a molecule of diethyl ether (Fig. 1), the second half of each generated by a crystallographic mirror plane passing through the silicon atoms of the four membered ring, the attached chlorine and nitrogen atoms, the amino hydrogens and the central oxygen of the solvent molecule (latter not shown).‡

Unlike in most other cyclodisilazanes[2–6] the four membered ring is not entirely planar, but folded by 7.1(1)° across the mirror plane. The angle Si(3)–N(1)–Si(2) is 89.9(1)°, the angles across Si(2) and Si(3) [89.7(1)° and 90.1(1)°] inside the ring show typical values, too. The endocyclic bonds N(1)–Si(2) and N(1)–Si(3) are slightly shorter than usual [173.5(2) and 172.9(2) pm, respectively], probably a consequence of the negative inductive effect of the adjacent chlorine atom.

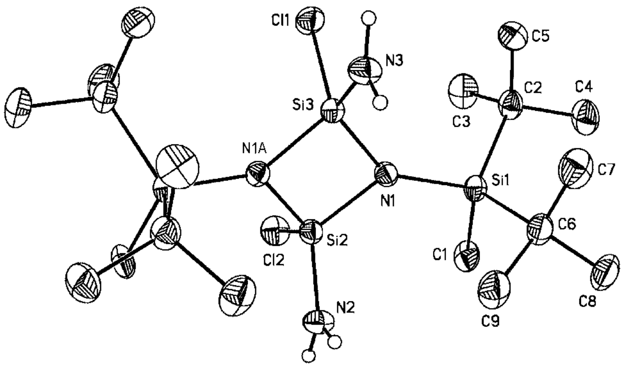

Fig. 1 Molecular structure of **1** (50% anisotropic probability ellipsoids); selected bond lengths [pm] and angles [°]: Si(1)–N(1) 175.1(2), Si(2)–N(2) 167.1(3), Si(2)–N(1) 173.5(2), Si(2)–Cl(2) 207.6(1), Si(3)–N(1) 172.9(2), Si(3)–Cl(1) 207.8(1), Si(3)–N(3) 167.1(3); N(1)–Si(2)–N(1A) 89.7(1), N(1A)–Si(3)–N(1) 90.1(1), Si(3)–N(1)–Si(2) 89.9(1), Si(3)–N(1)–Si(1) 140.5(1), Si(2)–N(1)–Si(1) 129.3(1).

Whereas the exocyclic bond Si(1)–N(1) is slightly longer [175.1(2) pm] than the endocyclic bonds, the bonds Si(2)–N(2) and Si(3)–N(3) are both significantly shorter [167.1(3) pm] and represent the shortest Si–NH_2-bonds observed so far, the usual value is 174.0 pm.[2–8] This bond shortening could to some extent be explained by the overlap of a free p-orbital on the nitrogen atom with an empty d-orbital on silicon. However, *ab initio* calculations do not support this proposition.[7] A further bond shortening is caused by the −I-effect of the chlorine mentioned above.

The bonds Si(2)–Cl(2) and Si(3)–Cl(1) [207.6(1) and 207.8(1) pm, respectively] are both about 5 pm longer than a standard Si–Cl-bond.[8] The relatively high binding orders of the adjacent Si–N-bonds and intermolecular interactions (see below) at the chlorine atoms are supposed to be responsible for this elongation.

The sum of angles at the amino nitrogens are both exactly 360°. Yet this planarity is caused by the special position of the involved atoms on the crystallographic mirror plane, so that a slight deviation is not traceable. However, *ab initio* calculations carried out on the molecule H_3Si–NH_2 also predict a planar geometry at the nitrogen,[7] although often nitrogen atoms of $SiNH_2$ groups are found to be pyramidal.[9,10] The coordination of the endocyclic N(1) is planar (359.7°) as expected.

The transannular distance Si(2)···Si(3), at 244.6(1) pm, is about 10 pm longer than a Si–Si single bond.[8]

The molecules of **1** are connected *via* hydrogen bonds between the amino hydrogens HN(1) and HN(4), respectively, and the oxygen atom of the solvent diethyl ether O(1E), forming quasi-endless chains in the crystal (Fig. 2). The found dis-

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Table 1 Full lengths [pm] and angles [°] of hydrogen bonds for **1** and the bridging diethyl ether

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(2)–HN(1)···O(1E)	85(2)	225(2)	306.5(3)	162(3)
N(3)–HN(4)···O(1E)	86(2)	226(2)	310.7(3)	171(3)
N(3)–HN(3)···Cl(2)	86(2)	286(2)	358.6(3)	144(3)

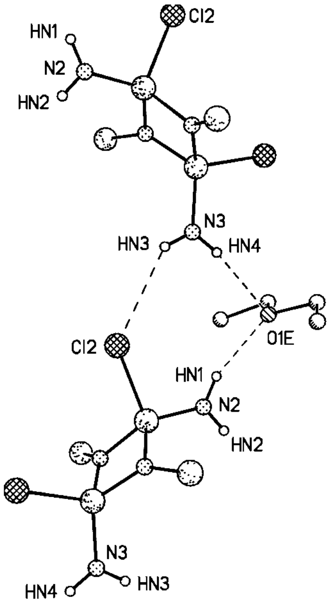

Fig. 2 Hydrogen bonds in the crystal of **1**, carbon atoms not shown.

tances between hydrogen donor and acceptor atom of 306.5(3) and 310.7(3) pm, respectively, show characteristic values (see Table 1).

The interaction between the chlorine atom Cl(2) and HN(3) shows a donor–acceptor-distance of 358.6(3) pm and therefore can only be regarded as a very weak hydrogen bond.

Acknowledgements

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Notes and references

† Preparative details. Compound **1**: 1,3-Bis(di-*tert*-butylmethylsilyl)-2,2,4,4-tetrachlorocyclodisilazane (0.02 mol, 10.8 g) in diethyl ether (100 ml) was cooled to −40 °C and mixed with 4 equivalents ammonia (0.08 mol, 1.4 g). The mixture was warmed to room temperature and heated to reflux for 1 h. Ammonium chloride was filtered off and **1** was crystallised in diethyl ether. No other compound could be isolated. Yield 40%, mp 212 °C; MS (EI) *m*/*z* (%): = 500(2) [M^+], 443 (100) [$M - C(CH_3)_3]^+$; IR: $\nu = 3491.7$, 3409.4 cm^{-1} (NH). Compound **1** is analytically pure, air stable, but moisture sensitive. ^1H NMR ($CDCl_3$, 0.03% TMS), **1**: δ 0.23 (s, CH_3, 6 H), 1.05 (s, $C(CH_3)_3$, 36 H), 1.62 (s, NH_2, 4H); ^{13}C NMR ($CDCl_3$, 0.03% TMS), δ −6.04 (s, CH_3), 20.68 (s, $\mathit{C}(CH_3)_3$), 28.60 (s, $C(\mathit{C}H_3)_3$; ^{29}Si NMR ($CDCl_3$, 0.03% TMS), δ −41.07 (s, $SiCH_3$), 6.94 (s, SiCl).

‡ X-Ray structure determination of **1**: the structure was solved by direct methods[11] and refined using a full matrix least squares algorithm against F^2.[12] Crystal data for **1**: $C_{18}H_{46}Cl_2N_4Si_4 \cdot C_4H_{10}O$, $M_r = 575.97$, orthorhombic, space group *Pnma*, $a = 1673.3(3)$, $b = 2268.7(2)$, $c = 871.9(1)$ pm, $U = 3.3099(8)$ nm^3, $Z = 4$, ρ(calc.) = 1.156 Mg m^{-3}, μ(Mo-Kα) = 0.362 mm^{-1}, 37478 reflections collected of which 2999 were unique ($R_{int} = 0.0481$), $T = -140$ °C, $R1 = 0.0369$ for $I > 2\sigma(I)$, $wR2 = 0.0886$ for all data. CCDC reference number 186/1978. See http://www.rsc.org/suppdata/dt/b0/b002634o/ for crystallographic files in .cif format.

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