Synthesis and Structure of a Manxane-Cage Silazane Molecule

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Dedicated to Professor Dr. Dr. h. c. mult. E. O. Fischer on the occasion of his 75. birthday

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Silazanes, Cage-Type, Silicon-Nitrogen Compounds

The reaction of tris(chlorodimethylsilyl)methane HC(SiMe2Cl)3 (1) with dry ammonia in hexane leads to the tris(disilazane) molecule HC(Me2SiNHMe2)3CH (3) in satisfactory yields. According to its 1H, 13C, and 29Si NMR spectra this bicyclic cage-molecule exhibits virtual (time-averaged) D3h symmetry. In the crystal (rhombohedral, space group R3) the manxane-type structure has a crystallographic three-fold axis, but the structure obeys only D3d symmetry to a good approximation, owing to a disrotatory twist of the two Si3 triangles against each other. The crystals of compound 3 are isomorphous with those of the analogous tris(disiloxane) 2.

Tris(chlorodimethylsilyl)methane CH(SiMe2Cl)3 (1) is an important trifunctional synthon for the preparation e.g. of silicon-based tripod ligands or capping units. It is readily available through standard transformation reactions starting from tris(trimethylsilyl)methane HC(SiMe3)3 or tris(dimethylsilyl)methane HC(SiMe2H)3 [1]. Halogen exchange in 1 or halogenation of HC(SiMe2H)3 gives the corresponding fluoride, bromide and iodide HC(SiMe2X)3 [2]. Hydrolysis of compound 1 leads to a trisilamole HC(SiMe2OH)3, which reacts with chlorotrimeethylsilane to afford the branched trisiloxane HC(SiMe2OSiMe3)3 [2]. Alkylation of HC(SiMe2H)3 or 1 leads to trialkoxy derivatives HC(SiMe2OR)3, and aminolysis with primary amines affords trifunctional silylamines HC(SiMe2NRH)3 [3]. These triamines are readily N-lithiated on treatment with organolithium reagents [4]. Upon thermal condensation at 150 °C the trisilanol yields an interesting cage-type trisiloxane HC(SiMe2OSiMe2)3CH (2) [2]. A study of the aminolysis with 1 with dry ammonia has not been published. Investigation of this simple reaction appeared quite promising in that both the simple triamine and its condensation products could be expected to be useful building blocks in silazane and heterosilazane chemistry.

Results

Compound 1 reacts instantaneously in hexane solution at room temperature with dry ammonia gas to form a voluminous precipitate of ammonium chloride. Work-up of the reaction mixture gives high yields of a bicyclic trisilazane:

\[ 2 \text{HC(SiMe}_2\text{Cl)}_3 + 9 \text{NH}_3 \rightarrow 6 \text{NH}_4^+\text{Cl}^- + \text{HC(SiMe}_2\text{NHMe}_2)_3\text{CH} \]

Compound 3 crystallizes from hexane upon cooling as colorless plates, which are soluble in most common organic solvents including di- and trichloromethane, benzene, diethyl ether and tetrahydrofuran. The composition has been confirmed by complete elemental analysis. In the mass spectrum (electron impact) the ion M – Me+ is observed as the base peak at m/e = 404 (100%). The infrared spectrum (NaCl) closely resembles that of other simple methylsilazane prototypes, and tentative assignments have been made accordingly (Experimental).

The 1H and 13C NMR spectra (in C6D6) show two signals each, which indicate chemically equivalent methyl and methyne groups, respectively. The 29Si NMR spectrum features only one resonance, which suggests the equivalence of all six SiMe2 groups in the molecule. These data are evidence for a highly symmetrical structure, probably with three-fold symmetry (point groups D3h or D3d). This conclusion has been confirmed by a single crystal X-ray analysis at −45 °C.

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Compound 3 crystallizes (from hexane) in the rhombohedral space group R \^3 [Nr. 148 Internat. Tables] with six formula units in the unit cell. These molecules have crystallographic three-fold symmetry. The positions of the atoms closely approach point group C_{3h} (Fig. 1).

Selected bond distances and angles are given in the caption to Fig. 1. There are no unusual features regarding these data. As might be expected from values of other strain-free silazane molecules, the Si–N–Si angles in compound 3 are relatively large at 135.79(7)°. With Si–N–H angles of 114.0(11) and 109.6(11)° (for Si1 and Si2, respectively) the sum of the angles at nitrogen is 359.4° indicating a planar configuration.

The dihedral angles H1–C1–Si1–N = -156.4° and H2–C2–Si2–N = 159.1° are a measure of the twist of the tridentate capping units HC(SiMe2)3 out of the ideal geometry with D_{3h} symmetry. The difference of the two angles is the origin of the violation of point group D_{3d} symmetry, leaving the molecule in the crystal with point group C_{3}. Another way of representing this twist is the dihedral angle C1–Si1···Si2–C2 = -2.91°. Finally, if Z, Z1 and Z2 are taken as the centers of the triangles formed by the three nitrogen or the three silicon atoms Si1 and Si2, respectively, the twist angles are -17.96° for Si1–Z1–Z–N and +15.73° for Si2–Z2–Z–N.

Compound 3 thus has a “manxane”-type structure ([3.3.3]bicyclobutadiene). The bicyclic tris(disiloxane) analogue 2 is isomorphous with the tris(disilazane) 3 and has very similar structural characteristics [2]. The only major difference is the much larger Si–O–Si angle of 145.2(1)°. The dihedral angles H1–C1–Si1–O1, H2–Si2–Si1–O1 and C1–Si1···Si2–C2 are -164.6, 159.3 and 5.60°, respectively. The element triangles (three oxygen atoms, three silicon atoms Si1 and Si2) are rotated against each other by -12.17° for Si1–Z1–Z–O and +16.39° for Si2–Z2–Z–O.

Compound 3 is an interesting precursor for N-metalated species. Work with lithiated derivatives in particular is in progress. This work is complementary with respect to our previous study of simple trisilylmethane and its precursors [5–8] and of analogous, or even isoelectronic tris-(dimethylphosphanyl)methane and its borane adducts or metal complexes [9–11].

### Experimental

All experiments were carried out in an atmosphere of pure dry nitrogen. Solvents were dried and distilled prior to use. Glassware was oven-dried and filled with nitrogen. NMR: Jeol GX 270 and GX 400 spectrometers. MS: MAT 311A spectrometer (EI). GC/IR: HP 5890 A, detector IR 5905 A.

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Fig. 1. Molecular structure of HC(Me2SiNHSiMe2)_3 CH, 3 (SCHAKAL). The molecule has a three-fold axis passing through both CH groups (H1, C1 and C2, H2). Selected bond distances [Å] and angles [°]: Si1–N 1.735(1), Si2–N 1.734(1), Si1–C1 1.882(1), Si2–C2 1.885(1), Si1–C11 1.874(1), Si1–C12 1.868(1), Si2–C21 1.874(1), Si2–C22 1.867(1), C1–Si1–N 111.0(1), C2–Si2–N 111.3(1), Si1–N–Si2 135.8(1), Si1–C1–Si1' 113.3(1), Si2–C2–Si2' 113.7(1).
**Compound 3**

Tris(chlorodimethylsilyl)methane (1.00 g, 3.40 mmol) is dissolved in hexane (140 ml) and a stream of dry ammonia admitted through a glass tube from a cylinder. A white precipitate appears immediately. After 20 min the reaction mixture is allowed to settle and is then filtered. The filtrate is concentrated in vacuo. Large colorless crystals separate, which can be recrystallized from hexane. Yield 0.44 g (62%), m.p. 85 °C, soluble in benzene, dichloromethane, diethyl ether, and tetrahydrofuran.

$^1{H}$ NMR (C$_6$D$_6$): $\delta = -0.73$ [s, 2H, CH]; 0.21 [s, 36H, CH$_3$]; 0.28 [br. s, 3H, NH].

$^13{C}$ NMR (C$_6$D$_6$): $\delta = 7.06$ [s, CH$_3$]; 13.66 [s, CH].

$^29$Si NMR (C$_6$D$_6$): $\delta = 0.52$ [s].

$^29$Si MS (El): m/z = 404 (100%) [M+- CH$_3$].

IR (gas): 2989, w, vasCH; 2955, m, vasCH$_3$; 2906, w, CH$_3$; 1262, s, δ(NH); 1001, s; 955, vs, δCH$_3$; 833, m, $\delta$CH$_3$.

C$_{14}$H$_{41}$N$_3$Si$_6$ (420.025)

Calcd C 40.03 H 9.94 N 9.96 Si 40.12%

Found C 39.75 H 9.89 N 9.96 Si 39.93%

**Crystal structure determination**

A singly crystal of compound 3 (from hexane) was mounted on the diffractometer (Enraf Nonius CAD4) in a sealed glass capillary at dry ice temperature under an argon atmosphere. Reduced cell calculations gave no indication of higher symmetry. The crystals are rhombohedral, space group R$^3$ (Nr. 148, Internat. Tables) with six formula units in the unit cell. C$_{14}$H$_{41}$N$_3$Si$_6$, Mr = 420.019, a = 45.369(1), c = 17.569(1) Å (hexagonal setting), V = 3593.8 Å$^3$, $\rho_{calc} = 1.164$ gcm$^{-3}$; $\mu_{MoK\alpha} = 3.4$ cm$^{-1}$, $\lambda = 0.71069$ Å, T = −45 °C; sin(θ/λ)$_{max}$ = 0.637. Of 5216 measured reflections 1742 were unique ($R_{int} = 0.014$). 1670 were considered observed with $F_0 \geq 2\sigma(F_0)$ and used for solution and refinement of the structure. Solution was by direct methods (SHELXS 86). Positions of the heavy atoms were refined with anisotropic temperature factors (SHELX 76). The positions of all hydrogen atoms were localized in difference Fourier syntheses and refined isotropically. For 126 refined parameters the structure converged with an $R(R_w)$ factor of 0.026 (0.040) [w = 6.1752/F$^2$ + 0.000183 F$^2$] and residual electron density +0.34/−0.28 eÅ$^{-3}$.

Further details may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, by quoting the Registry-No. CSD 57441, the names of the authors and the journal citation.

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