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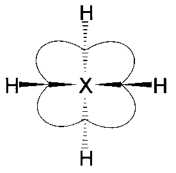
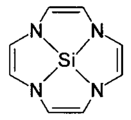
First Synthesis and Structure of a Tetraazasilafenestrane[**]

Bangwei Ding, Reinhart Keese,[*] and
Helen Stoeckli-Evans

According to quantum-chemical calculations planar tetracoordination should inherently be easier to achieve in silicon compounds than in the corresponding carbon compounds. These conclusions are based on results by Hoffmann, Alder, and Wilcox, who discussed the structural features of fenestranes of type **1** with X = C,[1] as well as our computational results for silafenestranes of type **1** with X = Si.[2] Despite considerable computional efforts no structures with a planar-tetracoordinate C(C)$_4$ substructure have been found.[3] Schleyer et al. have computationally explored the prerequisites for enhanced planarization in compounds such as **1** (X = Si), and proposed that planar-tetrasubstituted silicon should be favored by electronegative, π-donor substituents.[4] In 1992 Boldyrev, Schleyer, and Keese reported computational results according to which **2** is planar and has a minimum energy at the ab initio HF/3-21G* level.[5]



1 X = C, Si



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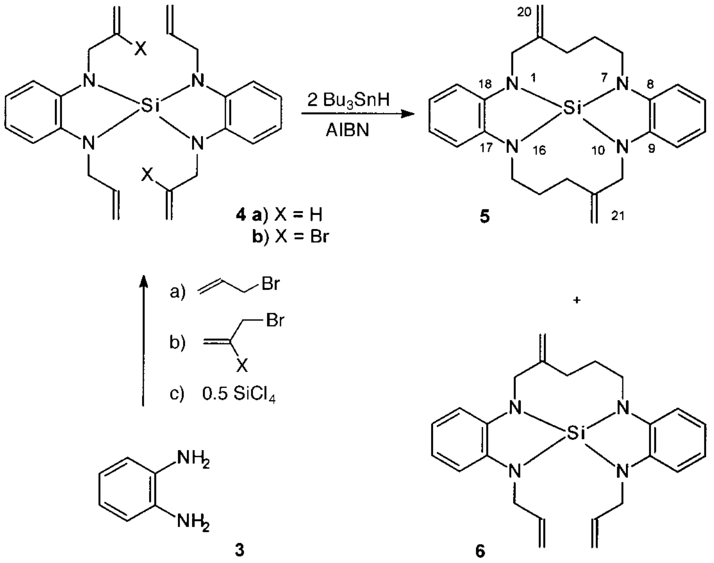
Whereas fenestranes have been prepared by a variety of methods,[7] neither silafenestranes nor tetraazasilafenestranes have hitherto been reported. In the course of our investigations of these structurally unusual molecules, we examined ring-closure reactions of appropriately functionalized spirotetraazasilanes. Although Si–N bonds are kinetically labile and sensitive to moisture, spirotetraazasilanes such as **4a** and **4b** could readily be prepared from *o*-phenylenediamine (**3**). Since ring-closure metathesis reactions of **4a** with Grubbs' catalyst[8] remained unsuccessful and radical-induced reactions with a dialkylborane led only to hydroboration of a double bond, we considered cyclization reactions of **4b**. Whereas Pd^0- and Pd^{II}-induced cyclizations remained unsuccessful as well, ring-forming radical reactions were observed when **4b** was treated with Bu$_3$SnH and azibisisobutyronitrile (AIBN) under carefully controlled conditions (Scheme 1).[9]



Scheme 1. Synthesis of **5** and **6**.

The tetraazasilafenestrane **5**, formed by a double 8-*endo* radical cyclization, was separated from the tricyclic compound **6** by chromatography and showed the expected number of NMR signals.[10] In comparison with **4a**, **b** and **6** the ^{29}Si NMR signal of **5** is shifted downfield, indicating a different environment for the silicon atom. Definite proof of the tetracyclic structure was established by an X-ray structure analysis (Figure 1).[11] A salient feature of the SiN$_4$ core structure of **5** is the 84.7° angle between the planes of the diazasilacyclopentene rings. Since the planes of the two five-membered rings in tetraazasilaspiro[4.4]nonanes are almost perpendicular to each other, the distortion must be due to the alkylene chains bridging the spiro rings.[12] Three of the four nitrogen atoms are in a pyramidal environment, leading to a pseudo-envelope conformation for both diazasilacyclopentene rings.[13]

To realize planarization in the central SiN$_4$ core of tetraazasilafenestranes, smaller rings are required. Our efforts to

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[*] Prof. Dr. R. Keese, Dipl.-Chem. B. Ding
Departement für Chemie und Biochemie der Universität
Freiestrasse 3, CH-3012 Bern (Switzerland)
Fax: (+41)31-631-3423
E-mail: reinhart.keese@ioc.unibe.ch
Prof. H. Stoeckli-Evans
Institut de Chimie, Université de Neuchâtel
Avenue de Bellevaux 51, CH-2000 Neuchâtel (Switzerland)

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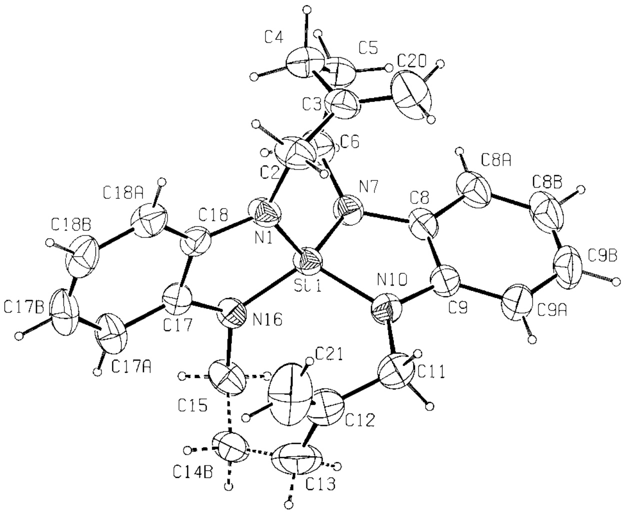

Figure 1. Structure of **5** in the crystalline state (thermal ellipsoids at the 50% probability level). Selected bond lengths [Å] and bond and torsional angles [°]: N–Si 1.7132(15) – 1.7182(13); N1-Si-N16 91.81(7), N1-Si-N7 115.46(7), N1-Si-N10 121.96(7), N7-Si-N10 92.08(7); N16-Si-N1-C2 179.68(15), N16-Si-N1-C18 7.26(11), N1-Si-N16-C15 −171.47(13), N1-Si-N16-C17 −6.97, N10-Si-N7-C6 −173.26(14), N10-Si-N7-C8 −5.92(12), N7-Si-N10-C11 −175.09(15), N7-Si-N10-C9 5.92(12).

prepare such tetraazasilafenestranes by silylation of tetraazacycloalkanes have so far not led to pure compounds.[14]

Experimental Section

A solution of Bu$_3$SnH (64 mg, 0.22 mmol) and AIBN (10 mg) in degased benzene (10 mL) was added to **4b** (61 mg, 0.11 mmol) in degased benzene (50 mL) under reflux. After 5 h another portion (10 mL) of the Bu$_3$SnH solution was added, and the reaction mixture heated under reflux overnight. After removal of the solvent and column chromatography, the mixture of **5** and **6** (34 mg) was separated by preparative thin-layer chromatography (TLC) to give 10 mg (22.7%) of **5** and 20 mg (45.4%) of **6**.

5: M.p. 180 – 182 °C; R_f (hexane/diethyl ether 40/1) = 0.60; ^{1}H NMR (300 MHz, CDCl$_3$, TMS; see Scheme 1 for atom numbering): δ = 6.76 – 6.82 (m, 4H), 6.64 – 6.71 (m, 4H), 4.66 (s, C20-H$_b$ + C21-H$_b$, 2H), 4.46 (s, C20-H$_a$ + C21-H$_a$, 2H), 3.95 (d, J = 12.2 Hz, C2-H$_a$ + C11-H$_a$, 2H), 3.71 (dt, J = 14.3, 3.7 Hz, C6-H$_b$ + C15-H$_b$, 2H), 3.64 (d, J = 12.5 Hz, C2-H$_b$ + C11-H$_b$, 2H), 3.31 (ddd, J = 14.5, 12.7, 2.6 Hz, C6-H$_b$ + C15-H$_b$, 2H), 2.40 (dd, J = 14.34, 5.56 Hz, C4-H$_b$ + C13-H$_b$, 2H), 2.16 (approx. dtt, J = 13.97, 11.40, 2.57 Hz, C5-H$_b$ + C14-H$_b$, 2H), 1.82 (m, C4-H$_a$ + C13-H$_a$, 2H), 1.60 (m, C5-H$_a$ + C14-H$_a$, 2H); ^{13}C NMR: δ = 145.29, 136.51, 135.64, 117.56, 117.49, 112.58, 108.03, 106.91, 50.19, 43.07, 32.47, 26.61; ^{29}Si NMR: δ = −21.39; MS (EI): m/z (%): 400 (100) [M^+], 385 (9), 371 (8), 200 (12), 149 (9), 137 (8), 109 (9), 97 (10), 81 (9), 69 (8), 56 (10); IR (CHCl$_3$): $\tilde{\nu}$ = 1480 (s), 1262 (s), 1228 (vs), 1100 cm^{-1} (vs); elemental analysis calcd for C$_{24}$H$_{28}$N$_4$Si: C 71.96, H 7.05, N 13.99; found: C 71.70, H 7.12, N 13.84.

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[11] Crystal structure analysis of **5**: Single crystals of **5** were obtained from CH$_2$Cl$_2$ by slow evaporation at 500 mbar for 6 – 8 h at 19 – 21 °C. C$_{24}$H$_{28}$N$_4$Si, M_r = 400.59, colorless blocks, crystal dimensions 0.6 × 0.4 × 0.25 mm^3, monoclinic, space group $P2_1/c$, a = 10.1412(9), b = 9.8408(6), c = 21.5219(19) Å, β = 97.513(11)°, V = 2129.4(3) × 10^6 pm^3, Z = 4, ρ_{calcd} = 1.250 g cm^{-3}, F(000) = 856, μ = 0.128 mm^{-1}. Imaging plate diffraction system (STOE); of 16247 reflections measured, 4046 were independent. The structure was solved with SHELXS-97[15] and refined for F^2 with SHELXL-97.[16] $R1$ $[=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|]$ = 0.0579 and $wR2$ $\{=[\Sigma(w(F_o^2-F_c^2)^2)/\Sigma wF_o^4)]^{1/2}\}$ = 0.0931 for all data, GOF = 0.922, max./min. residual electron density 0.210/−0.276 e Å^{-3}. Atom C15 of one of the SiN$_2$C$_5$ rings is disordered (ratio A:B = 0.556:0.444). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102562. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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