Synthesis of Spirocyclic Aminosilanes with Electron Withdrawing Substituents at Nitrogen

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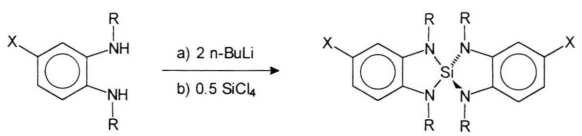
The first synthesis of spirocyclic tetrasulfonamidosilanes is described. According to the X-Ray structure analysis of the most stable tetratosylamidosilane obtained the Silicon is bonded to four Nitrogen atoms in a spirocycle and surrounded by four Oxygen atoms which are located above the planes of the SiN_4 tetrahedron.

1. Introduction

Cyclic and spirocyclic aminosilanes have been prepared for theoretical, structural and reactivity reasons and for specific applications [1 - 4]. Despite the chelating effect [5], substituents at both amino groups of ethylene diamine are necessary for the formation of spirocyclic aminosilanes. A survey of the known spirocyclic aminosilanes shows, that hitherto bulky and σ-donating substituents are used for enhancing the stability of these compounds. In the course of our interest in bridged spiro aminosilanes we investigated the formation of spiro aminosilanes from *o*-phenylene diamine with the amino groups bearing electron withdrawing substituents. In view of the propensity of silanes with electronegative substituents to form penta- and hexacoordinate complexes and to undergo substitution reactions readily [6], the isolation of such spiro aminosilanes is remarkable.

2. Results and Discussion

In a first attempt we treated 1,2-phenylenediamine with $SiCl_4$ in the presence of base. Since a stable product could not be isolated, we used the 1,2-phenylene sulfonamides **1** - **3** [7 - 9] rather than N,N'-dialkyl phenylene amines as bidentate ligands. The silaspiranes **4** - **6** were prepared by deprotonation of the sulfonamides using *n*-BuLi and reaction with $SiCl_4$. Due to the poor solubility of the starting material in methylene chloride, the Cl-substituted compound **5** was separated by solid/liquid extraction of the concentrated reaction mixture while **4** could hitherto not be obtained as a pure compound. The Si-compound **5** was highly sensitive to moisture but was sufficiently stable in $CDCl_3$ solutions for NMR measurements.



	1	2	3
X	H	Cl	H
R	Mes	Mes	Tos

Mes = SO_2CH_3

Tos = SO_2

	4	5	6
X	H	Cl	H
R	Mes	Mes	Tos

Information about the geometry of the central SiN_4 substructure in **5** was obtained by NMR studies in $CDCl_3$. The ^1H and ^{13}C NMR spectra showed only 2 signals of the same intensity for the CH_3 groups of the mesyl substituents, indicative of a tetrahedral coordination of the Si atom. In the case of a planar arrangement, **5** would exist as a mixture of two diastereomers leading to 3 NMR signals for the methyl groups.

In contrast to **4** and **5**, the spiro compound **6** with the bulky tosyl groups was sufficiently stable to be purified by chromatography on silica gel and was isolated in 29% yield. In the IR spectrum, a new, intensive band was observed at 970 cm^{-1}, which is not present in **3**. This band is most likely

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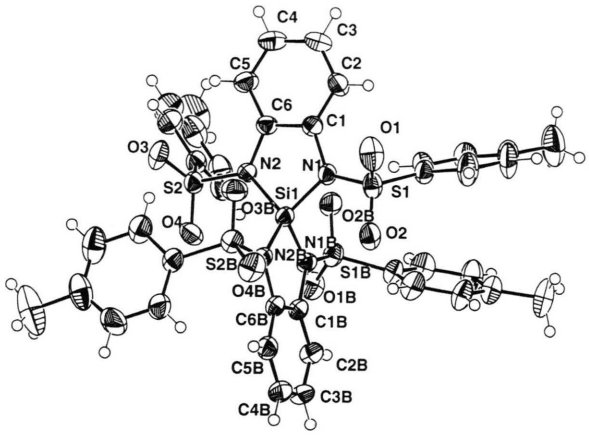

Fig. 1. Structure of 2,2'-spirobi[2-silabenzimidazoline-1,3-bis-*p*-toluenesulfonamide] (**6**) with 50% thermal ellipsoids. Selected bond lengths (Å), bond and torsional angles (°) N(1)-C(1) 1.446(4), N(1)-S(1) 1.653(2), N(1)-Si(1) 1.728(3); N(2)-Si(1)-N(1B) 119.93(13), N(1)-Si(1)-N(2) 91.34(12), Si(1)-N(2)-C(6) 112.1(2), N(2)-C(6)-C(1) 112.5(3), C(6)-C(1)-N(1) 11.6(3), C(1)-N(1)-Si(1) 112.4(2); Si(1)-N(1)-C(1)-C(2) –176.70(27), Si(1)-N(2)-C(6)-C(5) –178.51(28), S(1B)-N(1B)-C(1B)-C(2B) 1.48(44).

caused by a Si-N vibration [10]. The ^{29}Si NMR spectrum showed a broad signal at –95.3 ppm relative to TMS. This value is closer to the signal of $Si(OCH_3)_4$ at –79.0 ppm [11]) than to that of $Si[N(CH_3)_2]_4$ (–28.1 ppm [12]) and indicates, that the Si nucleus is strongly shielded.

3. X-Ray Structure Analysis

The structure analysis of **6** revealed two essentially planar silabenzimidazoline ring systems almost orthogonal to one another (Fig. 1). The angle between the two planes defined by the silicon atom and the two N atoms, N(1)-Si(1)-N(2) and N(1B)-Si(1)-N(2B), respectively, was found to be 88.4(1)°. The Si atom shows a tetrahedral coordination with smaller endocyclic (*ca.* 91.3(1)°) and larger exocyclic angles (*ca.* 119.2(1)°) [13]. The average value of the N-Si bond (1.733(2) Å) is within the normal range [13].The torsion angle C(2)-C(1)-N(1)-S(1) is 15.5(4)° indicating a slight pyramidalization of N(1) while the other N atoms are essentially trigonal planar. Strikingly, four sulfonamide oxygens cap the $(N)_4Si$ tetrahedron each bisecting one of the four tetrahedron faces, somewhat reminiscent of nucleophilic additions to silicon (torsion angles:

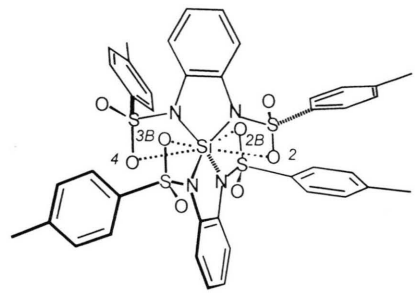

Fig. 2. Drawing of **6** illustrating the octahedral coordination. Selected nonbonded distances (Å) and angles (°): O(4)···Si(1) 2.953(2), O(2B)···Si(1) 2.982(2), O(3B)···Si(1) 2.912(3); O(2)-Si(1)-O(2B) 101.5(1), O(2)-Si(1)-O(3B) 86.3(1), O(2)-Si(1)-O(4) 158.7(1), O(2B) -Si(1)-O(3B) 158.4(1), O(2B)-Si(1)-O(4) 88.3(1), O(3B)-Si(1)-O(4) 91.5(1).

Si-N-S-O ±5°). This geometry can be described as a distorted dodecahedral arrangement for a [4+4] octacoordinated Si [14, 15] (Fig. 2). It is unclear, whether the average value of the short O···Si distances of 2.95(1) Å indicates a bonding interaction or whether this structural feature is a result of crystal packing.

4. Concluding Remarks

In contrast to $Si[N(CH_3)_2]_4$ [17] and the compounds **4** and **5** the spirocyclic tetrasulfonylamidosilane **6** containing the bidentate ligand **3** is rather stable to moisture. According to its spectrum the Si nucleus is highly shielded in compound **6**. An X-ray analysis reveals that one Oxygen atom of each sulfonyl group is located above a plane of the tetrahedron, defined by the central SiN_4 unit of the spirocycle in **6**. The tetrahedral arrangement of the central SiN_4 substructure in **6** corroborates the earlier observations of the 1,2-dihydroxyphenylene esters of $Si(OH)_4$ which show tetrahedral coordination for the Si in the central SiO_4 substructures [18 - 20]. Whether further spirocyclic amidosilanes can be prepared from chelating diamines bearing electron withdrawing substituents will be investigated.

Experimental

General remarks. All chemicals were obtained from Fluka, Buchs, and used as purchased. The silica gel (C 560, 60 - 200 mesh) for column chromatography was purchased from CU Chemie Uetikon AG. TLC plates (Alugram SIL G/UV_{254}) were obtained from

Macherey-Nagel, Düren. Melting points (uncorrected) were determined on a Büchi 510 apparatus. Infrared spectra were recorded on a Perkin Elmer 1600 series FTIR. ^{1}H-NMR (300 MHz) and ^{13}C NMR (75 MHz) and ^{29}Si NMR (99.3 MHz) spectra were determined on Bruker 300 MHz and 400 MHz Spectrospin AC 300 and AC 400 instruments, δ in ppm using TMS as internal standard. Mass spectra were obtained on a Varian MAT CH 7A spectrometer (70 eV, EI), high resolution MS were performed on a VG ZAB 2F instrument. All reactions were run under Ar. Elemental analyses were performed by the Lab. de Chimie Pharmaceutique, Université de Genève. For further details see [21].

To a soln. of 1,2-phenylenediamine (14.00 g, 129.5 mmol) in CH_2Cl_2 (200 ml) and pyridine (42 ml) was added a soln. of MsCl (20.1 ml, 259 mmol) in CH_2Cl_2 (200 ml) at 0°C. After stirring at r. t. for 20 h H_2O (300 ml) and 300 ml 1N HCl were added and **1** precipitated. More **1** was obtained by evaporation of the CH_2Cl_2 soln.. Crude **1** was washed with 1N HCl, acetic acid and dried in vacuo to afford orange crystals 30.56 g (89%).

M. p. 206 - 208°C (214° corr. [8]); IR (KBr): 3275, 3020, 2932, 1332, 1152; ^{1}H NMR (DMSO-d_6): 8.93 (s, 2 H), 7.45 (m, 2 H), 7.25 (m, 2 H), 3.06 (s, 6 H); ^{13}C NMR (DMSO-d_6): 130.8 (s, 2 C), 126.6 (d, 2 C), 124.9 (d, 2 C), 40.1 (q, 2 C); MS: 264 (M^+,19), 185(100), 107 (70).

*4-Chloro-N,N'-1,2-phenylenebismethanesulfonamide (**2**)*

Similarly to **1**, **2** was obtained from 4-chloro-1,2-phenylenediamine (7.00 g, 49.1 mmol), 15.8 ml pyridine and MsCl (7.63 ml, 98.2 mmol) in 200 mL CH_2Cl_2 at 0 °C and stirring for 20 h at r. t. The precipitated **2** was recrystallized from acetic acid (*ca.* 300 ml) to give reddish crystals of **2** (9.12 g, 62%).

M. p. 194°C; R_f (ethyl acetate) 0.54; IR (KBr): 3264, 3014, 2936, 1330, 1148; ^{1}H NMR (DMSO-d_6): 9.15 (s, 1 H), 9.07 (s, 1 H), 7.50 - 7.45 (m, 2 H), 7.30 (dd, J = 15.0, 2.3 Hz, 1 H), 3.19 (s, 3 H), 3.08 (s, 3 H); ^{13}C NMR (DMSO-d_6): 132.5, 130.4, 129.1, 126.7, 126.0, 123.5, 40.4, 40.1; MS: 300 (M^+ +1, 7), 298 (19), 219(100), 141 (85).

Analysis for $C_8H_{11}ClN_2O_4S_2$ (298.77)
Calcd C 32.16 H 3.71 Cl 11.87 N 9.38 S 21.46%,
Found C 32.35 H 3.74 Cl 11.99 N 9.16 S 21.11%.

*N,N'-1,2-Phenylenebistoluenesulfonamide (**3**) [9]*

As described above, 1,2-phenylenediamine (7.00 g, 64.7 mmol), 20.8 ml pyridine and *p*-TsCl (24.67 g, 129.4 mmol) gave after stirring in 200 ml CH_2Cl_2 at r. t. for 3 h, addition of water (200 mL) and extraction with 1N HCl (300 ml) crude **3** which was washed with 1N HCl. Recrystallization from acetic acid provided orange crystals (26.49 g, 98%).

M. p. 199°C (203° corr. [9]); IR (KBr): 3220, 1596, 1498, 1326, 1148; ^{1}H NMR ($CDCl_3$): 7.57 (d, J = 8 Hz, 4 H), 7.22 (d, 4 H), 7.05 - 7.01 (m,2 H), 6.97 - 6.93 (m, 2 H), 6.93 (s, 2 H), 2.39 (s, 6H); ^{13}C NMR ($CDCl_3$): 144.2 (s, 2 C), 135.4 (s, 2 C), 130.8 (s, 2 C), 129.6 (d, 4 C), 127.6 (d, 4 C), 127.4 (d, 2 C), 126.2 (d, 2 C), 21.6 (q, 2 C); MS: 416 (M^+, 22), 261(100), 182 (31), 91 (64).

*2,2'-Spirobi(1,3-bismethylsulfonyl)-2-silabenzimidazoline (**4**)*

To a suspension of **1** (2.00 g, 7.57 mmol) in THF (60 ml) was added 9.46 ml *n*-BuLi (1.6M solution in hexane, 15.14 mmol) at 0°C. After stirring at 0°C for 15 min a soln. of $SiCl_4$ (3.79 ml, 3.79 mmol) in THF was added at 0°C. After reflux for 20 h the suspension was concentrated to dryness, the residue taken up in CH_2Cl_2 (60 ml), stirred at room temperature for 45 min and filtered through celite. Crystallization from CH_2Cl_2 at –20 °C provided a mixture (370 mg) of **4** (11%) and **1** (7%) in the ratio of 4:3 according to ^{1}H NMR.

^{1}H NMR ($CDCl_3$): δ 7.55 (4 H), 7.21 (4 H), 3.37 (s,12 H); MS: 552 (M^+ -1, 1), 342 (14), 263 (71), 185(100), 107 (80); HR-MS: calc. for $C_{16}H_{20}N_4O_8S_4Si$: 551.9933, found 551.9933.

*2,2'-Spirobi(6-chloro-1,3-bismethylsulfonyl)-2-silabenzimidazoline (**5**)*

Similarly to **4**, **5** was prepared from **2** (2.00 g, 6.69 mmol) in THF (80 ml), 8.36 ml *n*-BuLi (1.6 M soln. in hexane, 13.38 mmol) and a soln. of $SiCl_4$ (3.35 ml, 3.35 mmol) in THF first by stirring at 0°C then refluxing for 20 h. The solvent was evaporated and the residue taken up in CH_2Cl_2 (60 ml), stirred at r. t. for 45 min and filtered through celite (sublimation at 170 °C/0.1 Torr or GC failed). Crystallization from CH_2Cl_2 at –20 °C gave **5** as colorless crystals (672 mg, 32%).

M. p. 260°C (dec.); IR (KBr): 3030, 2936, 1356, 1156; ^{1}H NMR ($CDCl_3$): 7.55 (d, J = 2.2Hz, 2 H), 7.47 (d, J = 8.8 Hz, 2 H), 7.19 (dd, J = 8.8, 2.2 Hz, 2 H), 3.38 (s,6 H), 3.35 (s, 6 H); ^{13}C NMR ($CDCl_3$): 130.1, 129.0, 126.8, 124.5, 115.0, 114.7, 40.6, 40.5; MS: 622 (M^+, 89), 620(100), 543 (34), 541 (39), 341 (12), 141 (28); HR-MS: calc. for $C_{16}H_{18}Cl_2N_4O_8S_4Si$: 619.9154, found 619.9158.

*2,2'-Spirobi(1,3-bistoluenesulfonyl)-2-silabenzimidazoline (**6**)*

As described for **4** and **5**, **6** was prepared from **3** (2.00 g, 4.80 mmol) 6.00 ml *n*-BuLi (1.6 M in hexane, 9.60 mmol) and $SiCl_4$ (2.40 ml, 2.40 mmol) in dry THF at 0 °C. The soln. was refluxed for 20 h and concentrated to dryness. The residue was twice chromatographed on silica gel

(cyclohexane / ethylacetate 1:1 + 1% triethylamine, R_f (**3**) = 0.42, R_f (**6**) = 0.63]) providing **6** after recrystallization from acetonitrile as colorless crystals (595 mg, 29%).

M. p. 230°C; IR (KBr): 2924, 1598, 1482, 1348, 1170, 970; ^{1}H NMR ($CDCl_3$): 8.18 (d, J = 8 Hz, 8 H), 7.32 - 7.23 (m,12 H), 6.94 (m, 4 H), 2.37 (s,12 H); ^{13}C NMR ($CDCl_3$): 145.0 (4 s), 135.1 (4 s), 129.7 (8 d), 128.8 (4 d), 128.5 (4 s), 123.5 (8 d), 114.5 (4 d), 21.6 (4 q); ^{29}Si NMR ($CDCl_3$): -95.3 (br. s); MS (EI, 70 eV): 857 (M^{+}, 100) 702 (23), 547 (5), 483 (30), 419 (15), 91 (13); HR-MS: calc for C_{40} H_{36} N_4 O_8 S_4 Si: 856.1185; found 856.1193.

Analysis calc. for $C_{40}H_{36}N_4O_8S_4Si$ (857.07)
Calcd C 56.06 H 4.23 N 6.54 S 14.96%,
Found C 56.01 H 4.27 N 6.66 S 14.88%.

X-Ray analysis of **6**

Single crystals of **6** were grown by slow evaporation of acetonitrile solutions at room temperature. Intensity data were measured on a Stoe AED2 four-circle diffractometer at room temperature, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures of **6** was solved by direct methods using the program SHELXS-90 [22]. The program SHELXL-93 [23] was used for refinement. Hydrogen atoms were included in calculated positions. Weighted full-matrix least-squares refinement on F^2 was used in all cases. Fig. 1 was prepared using the program XTAL_GX [24]. Further details are available from the Cambridge Crystallographic Data Centre, on quoting the full journal citation, and from H. St.-E.

6: $C_{40}H_{36}N_4O_8S_4Si$, FW = 857.07, triclinic, space group $P\bar{1}$ (No. 2), a = 12.887(3), b = 12.987(4), c = 14.020(5) Å, α = 98.40(1), β = 95.92(2), γ = 119.47(1)°, V = 1978.8 (10) Å^3, Z = 2, $\rho_{calc.}$ = 1.438 gcm^{-3}, F(000) = 892, crystal size: 0.38 × 0.38 × 0.34 mm, reflections collected 6942, independent reflections 6942, final R indices [I > 2σ(I)]: $R1$ = 0.0454, $wR2$ = 0.0974.

Acknowledgements

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