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# Hexa(amino)disilanes with Saturated Cyclic Amino Ligands

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**Summary.** *Hexakis*-(N-aziridino)-, -(N-azetidino)-, -(N-pyrrolidino)-, and -(N-piperidino)-disilane ($Si_2(N(CH_2)_n)_6$, $n = 2$, 3, 4, and 5) have been prepared from $Si_2Cl_6$ and an excess of the corresponding cyclic secondary amine in diethyl ether. For the synthesis of the piperidino compound, N-lithio-piperidine was required as a stronger nucleophile to overcome the increasing steric hindrance with this largest of the four amines. The volatile small ring compounds ($n = 2$: **1**; $n = 3$: **2**) are thermally labile and undergo decomposition upon storage at ambient temperature (mainly through oligomerization *via* opening of the strained small rings). Compounds **3** ($n = 4$) and **4** ($n = 5$) are stable if kept in an inert atmosphere.

**Keywords.** Disilane; Aminodisilane; Hexa(amino)disilane; Aziridino-disilane; Azetidino-disilane; Pyrrolidino-disilane; Piperidino-disilane.

#### Hexa(amino)disilane mit gesättigten cyclischen Aminliganden

**Zusammenfassung.** *Hexakis*-(N-aziridino)-, -(N-azetidino)-, -(N-pyrrolidino)- und -(N-piperidino)-disilan ($Si_2(N(CH_2)_n)_6$, $n = 2$, 3, 4 und 5) wurden ausgehend von $Si_2Cl_6$ und einem Überschuß des entsprechenden sekundären cyclischen Amins in Diethylether dargestellt. Wegen des hohen sterischen Anspruchs der Piperidinliganden mußte zur Synthese der mit diesem größten Amin substituierten Verbindung zusätzlich N-Lithio-piperidin als stärkeres Nucleophil eingesetzt werden. Die beiden Verbindungen mit den kleinen Heterocyclen ($n = 2$: **1**, $n = 3$: **2**) sind flüchtig, thermisch labil und zersetzen sich allmählich bei Raumtemperatur (hauptsächlich durch Öffnung der kleinen gespannten Ringe und anschließende Oligomerisierung). Die Verbindungen **3** ($n = 4$) und **4** ($n = 5$) sind unter Inertgasatmosphäre stabil.

## Introduction

Disilane ($Si_2H_6$) is known to be sensitive towards base-catalyzed degradation which leads to monosilane ($SiH_4$) and higher silanes. A similar reaction pattern has been observed for several substituted disilanes which also undergo rearrangement with cleavage of the Si–Si bond upon treatment with *e.g.* tertiary amines. A related process initiated by (amine) base is employed for the conversion of polychlorinated di- or polysilanes into the corresponding monosilanes [1–5].

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It is therefore no surprise that very few amino substituted disilanes have been prepared in which the presence of an internal basic function is likely to promote decomposition. We have recently developed reliable synthetic pathways to a variety of amino-polysilanes which could be shown or are expected to be a new family of volatile precursors for the deposition of silicon nitride from the vapour phase [6, 7].

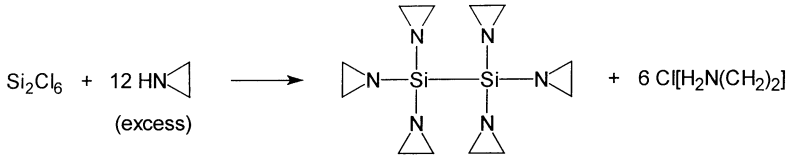
As part of this current program we became interested in the properties of disilanes fully substituted with small cyclic amino groups. These groups should enhance the volatility of the compounds and facilitate thermal elimination of fragments of the substituents.

Per(amino)disilanes are few in number in the literature [8–10]. A prominent example is *hexakis*(dimethylamino)disilane, first described by *Wiberg et al.* in 1965, but obtained in pure form and structurally characterized much later by *Verkade et al.* (in 1993). The dodeca-ethyl homologue was also included in this recent work [10].

We recently revisited the preparation, properties, and structure of several *tetrakis*(amino)monosilanes with cyclic amino substituents ($(CH_2)_nN$-, $n = 2$, 3, 4, and 5) [11, 12]. This work has provided useful reference data for the *disilane* investigations reported in this communication.

## Results and Discussion

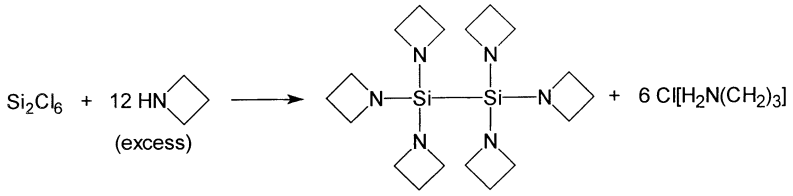
*Hexakis*(N-aziridino)dissilane (**1**) can be prepared from hexachlorodisilane and excess aziridine in diethyl ether in the temperature range from $-60$ to $+25$°C. A precipitate of aziridinium hydrochloride is formed, and from the mother liquor the product can be isolated in low yield (14%) through sublimation in a vacuum and recrystallization from pentane. Compound **1** is a colourless crystalline material, m.p. = 42°C, which is very sensitive to moisture and readily decomposes when stored at room temperature. Even freshly sublimed or crystallized samples show oligomerization products in their mass spectra, indicating oligomerization through aziridine ring opening.




**1**

**Scheme 1**

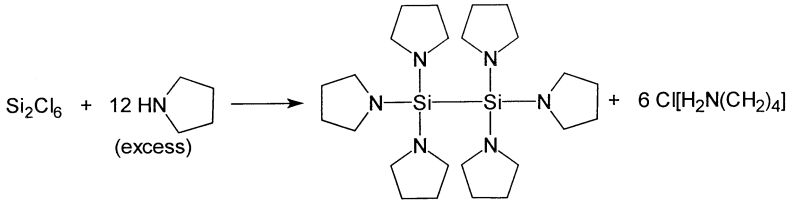
*Hexakis*(N-*azetidino*)disilane (**2**) is obtained similarly with excess azetidine as the reagent for $Si_2Cl_6$. It is isolated as a colourless oil by vacuum distillation (b.p. = 120°C/0.01 mbar with decomposition, yield: 13%). Compound **2** is also sensitive to moisture, but thermally more stable. Its mass spectrum shows oligomerization products, although in lower intensity than observed for **1**.




**2**

**Scheme 2**

*Hexakis*(N-*pyrrolidino*)disilane (**3**) is synthesized by an analogous procedure as described for **1** and **2**, but can be isolated as a crystalline solid (from pentane) in much higher yield (50%); it is less sensitive to temperature, air, and moisture. In the mass spectrum there are no peaks for ions with masses greater than the parent ion [$\mathbf{3}^+$]. Even after prolonged storage at room temperature no decomposition and oligomerization is observed.

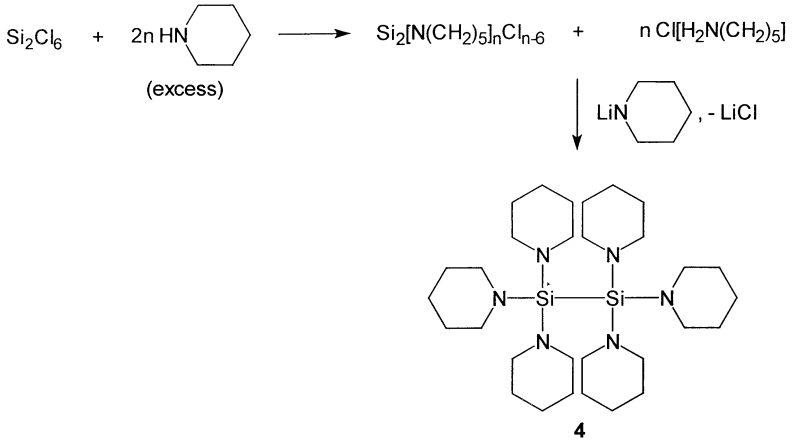



**3**

**Scheme 3**

*Hexakis*(N-*piperidino*)disilane (**4**) cannot be prepared directly from $Si_2Cl_6$ and excess piperidine; this reaction leads only to mixed chloro(N-piperidino)disilanes. Owing to steric hindrance, substitution of the chlorine atoms is becoming increasingly difficult as the number of piperidino groups is growing. The last two chlorine atoms therefore can only be replaced by the use of N-lithio-piperidine as a more powerful nucleophile. The overall yield of the fully substituted product is low (37%) even after long reaction times. As for compound **3**, purification of **4** is easily accomplished by crystallization from pentane. Both compounds have melting points beyond 200°C. Attempted vacuum sublimation/distillation is accompanied by decomposition. The mass spectrum shows the parent ion of the compound; no ions of higher mass were detected.

The NMR data of compounds **1**–**4** are in agreement with the proposed structures. The $^{29}Si$ resonances are difficult to detect owing to the adverse relaxation properties of the silicon nuclei in an asymmetrical environment of nitrogen quadrupolar nuclei. All nitrogen heterocycles undergo rapid inversion at the ring atoms, including the nitrogen atoms, rendering the $CH_2$ hydrogen atoms equivalent at all carbon atoms at room temperature (virtual $C_{2v}$ symmetry for each ligand). This behaviour resembles that of the corresponding mononuclear tetra(amino)-silanes $Si(N(CH_2)_n)_4$, $n = 2-5$. The number of $^{13}C$ resonances is in agreement with




**Scheme 4**

at least local $C_s$ symmetry at each ligand, or even virtual $C_{2v}$ symmetry (on the NMR time scale). Attempts to grow single crystals of high quality were not successful.

## Experimental

All experiments were carried out under an atmosphere of dry, pure nitrogen. Solvents and glassware were treated accordingly. Standard equipment was used throughout. Aziridine [13] and azetidine [14] were prepared following literature procedures. Due to the method of preparation, the sample of azetidine contained benzene which was quantified by $^1$H NMR. *Tetrakis*(N-aziridino)silane was prepared as described earlier [12]. All other starting materials were commercially available. NMR: Jeol GX 400 and Jeol GX 270, solutions in $C_6D_6$ at 23°C unless otherwise stated; *TMS* as internal standard; MS: MAT 311 A (EI 70 eV).

*Hexakis(N-aziridino)disilane* (**1**)

A solution of aziridine (3.58 ml, 70 mmol) in 20 ml of diethyl ether was added within 15 min to a solution of hexa(chloro)disilane (0.86 ml, 5.0 mmol) in 50 ml of diethyl ether at −60°C. The reaction mixture was allowed to warm to room temperature. After stirring for 2 h at this temperature, the precipitate was separated and the solvent was removed from the filtrate under reduced pressure. The remaining colourless oil was purified by sublimation (100°C/0.01 mbar) and recrystallized from pentane.

Colourless crystals; yield: 0.21 g (14%); m.p.: 42°C; $^1$H NMR: $\delta = 1.94$ (s, 24H, $CH_2$) ppm; $^{13}$C{$^1$H} NMR: $\delta = 20.9$ ($CH_2$) ppm; $^{29}$Si{$^1$H} NMR: $\delta = -12.1$ ppm; $^{29}$Si NMR: $\delta = -12.1$ (m, $^3J_{Si,H} = 5$ Hz) ppm; MS (EI, 70 eV): $m/z = 576$ (4.8%), 502 (20.1%), 429 (15.0%), 355 (100%), 308 ($M^+$, 1.5%), 266 ($M^+$-$N(CH_2)_2$, 2.6%).

*Hexakis(N-azetidino)disilane* (**2**)

A solution of hexa(chloro)disilane (0.17 ml, 1.0 mmol) in 10 ml of diethyl ether was added dropwise to a solution of azetidine (21.9 mmol, 3 ml of a solution of azetidine containing 42% benzene) in 50 ml of diethyl ether at −60°C. The reaction mixture was allowed to warm to room temperature and

stirring was continued at this temperature for 12 h. After filtration the solvent was removed under reduced pressure, and the residue was purified by distillation (120°C/0.01 mbar) to give a colourless oil.

Yield: 0.05 g (13%); $^1$H NMR: $\delta = 1.54$ (quin, 12H, $^3J_{H,H} = 7$ Hz, $CCH_2$), 3.58 (t, 24H, $^3J_{H,H} = 7$ Hz, $NCH_2$) ppm; $^{13}C\{^1H\}$ NMR; $\delta = 16.3$ ($CCH_2$), 50.2 ($NCH_2$) ppm; $^{29}Si\{^1H\}$ NMR: not detected; MS (EI, 70 eV): $m/z = 430$ (2.2%), 410 (24.3%), 394 ($M^+$+2, 92.6%), 393 ($M^+$+1, 3.1%), 392 ($M^+$, 3.1%), 336 ($M^+$-$N(CH_2)_3$, 31.3%), 280 (336-$N(CH_2)_3$, 3.2%), 224 (280-$N(CH_2)_3$, 6.8%), 196 ($Si(N(CH_2)_3)_3$, 30.5%), 140 (196-$N(CH_2)_3$, 8.2%).

*Hexakis(N-pyrrolidino)disilane* (**3**)

Hexa(chloro)disilane (1.72 ml, 10 mmol) was added dropwise to a solution of pyrrolidine (16.52 ml, 200 mmol) in 250 ml of diethyl ether at 0°C. After stirring at room temperature for 72 h, the precipitate was separated, the solvent and excess pyrrolidine were removed from the filtrate *in vacuo*, and the residue was extracted with pentane. **3** crystallized from this solution at −30°C.

Colourless crystals; yield: 2.37 g (50%); m.p.: > 200°C; $^1$H NMR: $\delta = 1.68$ (m, 24 H, $CCH_2$), 3.13 (m, 24 H, $NCH_2$) ppm; $^{13}C\{^1H\}$ NMR: $\delta = 27.1$ ($CCH_2$), 46.6 ($NCH_2$) ppm; $^{29}Si\{^1H\}$ NMR: $\delta = -34.5$ ppm; MS (EI, 70 eV): $m/z = 476$ ($M^+$), 406 ($M^+$-$N(CH_2)_4$), 336 (406-$N(CH_2)_4$), 266 (336-$N(CH_2)_4$), 238 ($Si(N(CH_2)_4)_3$), 168 (238-$N(CH_2)_4$); $C_{24}H_{48}N_6Si_2$ (476.86); calcd: C 60.5, H 10.2, N 17.6; found: C 58.8, H 10.0, N 17.0.

*Hexakis(N-piperidino)disilane* (**4**)

Piperidine (8.26 ml, 83 mmol) was added dropwise to a solution of hexa(chloro)disilane (1.72 ml, 10 mmol) in 200 ml of diethyl ether at room temperature. After the reaction mixture had been stirred for 12 h, another 10 ml of piperidine (100 mmol) was added, and stirring continued for another 2 h at room temperature. The precipitate was then separated, and the filtrate was treated with a suspension of N-lithio piperidine in 50 ml of hexane/diethyl ether (30 mmol, from 5.00 ml (51 mmol) of piperidine and 17.65 ml (30 mmol) of a 1.7 *M* solution of *n*-butyllithium in hexane: *n*-butyllithium was added dropwise to a solution of the amine in diethyl ether (27 ml) at room temperature; the reaction mixture was stirred for 0.5 h and then used immediately). The reaction mixture was stirred for 72 h at room temperature, the solvent was removed *in vacuo*, and the residue was extracted with pentane. **4** crystallized from this solution at −30°C.

Colourless crystals; 2.09 g (37%); m.p.: > 200°C; $^1$H NMR: $\delta = 1.47$ (pseudo-quint, 24H, $^3J_{H,H} = 5$ Hz , $NCH_2CH_2$), 1.61 (pseudo-quint, 12 H, $^3J_{H,H} = 5$ Hz, $NCH_2CH_2CH_2$), 2.90 (pseudo-t, 24 H, $^3J_{H,H} = 5$ Hz $NCH_2$) ppm; $^{13}C\{^1H\}$ NMR: $\delta = 26.4$ ($NCH_2CH_2CH_2$), 29.2 ($NCH_2CH_2$), 50.2 ($NCH_2$)ppm; $^{29}Si\{^1H\}$ NMR: $\delta = -29.7$ ppm; MS (EI, 70 eV): $m/z = 561$ ($M^+$), 281 ($Si(N(CH_2)_5)_3$); $C_{30}H_{60}N_6Si_2$ (561.02); calcd.: C 64.2, H 10.8, N 15.0; found: C 61.6, H 10.9, N 14.2

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