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Reactions of a cyclotrisilane with Lewis acids—formation of new cyclotrisilanes and siliconium ions

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Abstract

Treatment of cyclotrisilane **1** with pyridinium bromide yields siliconium bromide **8a**. In contrast, **1** reacts with six equivalents of $AlMe_3$ as Lewis acid via an initial complex **13** to silane **10**. Reaction of **1** with only three equivalents of $AlMe_3$ forms **12**, which is also obtained upon treatment of **10** with quinuclidine or **1**. No analogous insertion reaction occurs with BH_3, in which case the stable complexed cyclotrisilane **15** is formed.

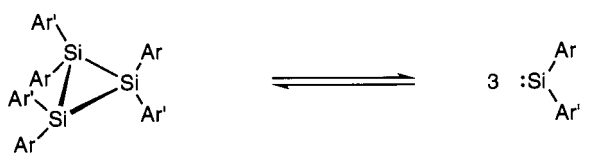
Keywords: Cyclotrisilane; Lewis acid; Donor-acceptor complex; X-ray diffraction

1. Introduction

Sterically congested cyclotrisilanes are known to undergo simultaneous cleavage of two Si–Si bonds under photolytic conditions, and the formed silylene and disilene can be trapped by a variety of substrates [1]. In contrast, cyclotrisilanes **1**, **2** and **3**, which bear the 2-(dimethylaminomethyl)phenyl substituent, were reported by us to react thermally under cleavage of not only two, but all three Si–Si bonds [2]. Thus, these compounds can be used as convenient thermal precursors of the corresponding silylenes. We assume that this unprecedented reactivity goes back to an equilibrium between the cyclotrisilanes and their ring-forming silylene subunits (Scheme 1). Moreover, we assume that the thermal dissociation of these cyclotrisilanes is facilitated by the thermodynamic stabilization of the formed silylenes by intramolecular coordination of the silicon center by one or two NMe_2 substituents [3]. Due to this chelation, which reduces the electron deficiency at the silicon center, silylene **4** shows nucleophilic reactivity [4], which is in contrast to the electrophilic character of the rate-determining step of the addition of Me_2Si or H_2Si: with C–C double and triple bonds [5].

Against this background we were interested in the reactions of **1** with Lewis acids. A priori two alternative pathways appear feasible.

The dimethylamino groups, which are not coordinated to the silicon centers in **1** [6], may be quaternized by the Lewis acid under preservation of the three-membered silicon ring. A cyclotrisilane functionalized in this



1–3 **4–6**

Scheme 1. Ar = Ar′ = 2-$(Me_2NCH_2)C_6H_4$: **1**, **4**; Ar = Ar′ = 2-(Me_2NCH_2)-4-Me-C_6H_3: **2**, **5**; Ar = 2-$(Me_2NCH_2)C_6H_4$, Ar′ = Mes: **3**, **6**.

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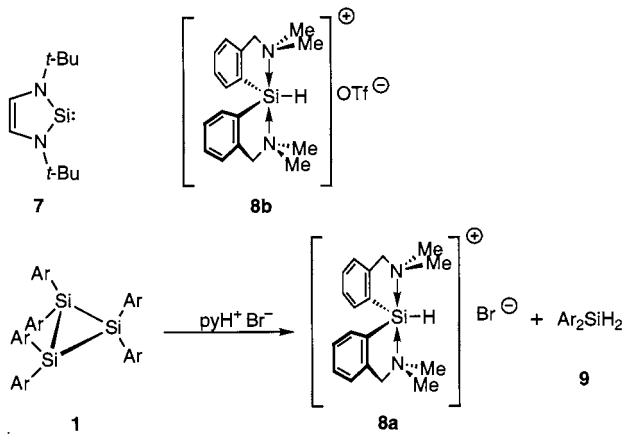


Scheme 2. Reaction of cyclotrisilane **1** with pyridinium bromide; Ar = 2-(Me_2NCH_2)C_6H_4.

way may be the appropriate compound to prove the hypothesis that the equilibrium between **1** and **3** goes back to the coordinating property of the dimethylamino group towards silicon.

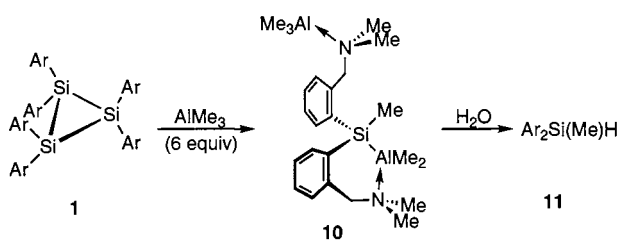
Alternatively, the Lewis acid may trap the nucleophilic silylene **4** out of the equilibrium by reacting with the lone pair at silicon. A similar complex formation was reported for the reaction of the stable silylene **7** with $B(C_6F_5)_3$ [7].

Here we report that, depending on the Lewis acid used, cyclotrisilane **1** undergoes both possible reactions.

2. Results and discussion

When **1** was treated with three equivalents of pyridinium bromide as proton source in THF, the siliconium ion **8a** was obtained in a 51% yield. In addition, silane **9** (47%) was formed (Scheme 2). Compound **6** was identified by its ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra, which are very similar to that of siliconium ion **8b** [8]. Whereas the formation of silane **9** remains puzzling, a reasonable mechanistic pathway to **8a** may be the protonation of silylene **3** by hydrogen bromide, which is in equilibrium with pyridinium bromide. In this respect, the reactivity of **4** resembles that of nucleophilic carbenes which are known to be protonated by Brønsted acids [9]. It is worth mentioning that the silicon center of silylene **4** appears to be more basic than the nitrogen center of the benzyldimethylamino units of **1**; on the other side, the observed reactivity may just reflect the fact that both dimethylaminogroups are coordinating to the silicon center of **4** and thus are not available for protonation.

The reaction of cyclotrisilane **1** with trimethylaluminum took another course (Scheme 3). When **1** was treated with six equivalents of trimethylaluminum in toluene, an extremely moisture sensitive solid **10** was isolated. The ^{1}H-NMR spectrum (Fig. 1, top) indicated the formation of a 1:2 product between the silylene **4** and trimethylaluminum, in which the aryl substituents are chemically inequivalent. Moreover, the benzylic protons as well as the N–Me groups of each aryl substituent are anisochronous, as is evidenced by two AB systems in the benzylic region as well as four different N–Me signals around $\delta = 2$. One of the $AlMe_3$ units incorporated into the product **10** obviously stayed intact during the reaction and was observed as a singlet at $\delta = -0.36$, whereas the methyl groups of the second equivalent of $AlMe_3$ became chemically inequivalent during product formation. Two of them absorb in the region which is typical for aluminum-bound alkyl groups ($\delta = -0.63$ and -0.56). In contrast, the signal of the third methyl group was shifted significantly to a lower field ($\delta = 0.79$) indicating that this substituent was no longer bound to aluminum. This assumption was confirmed by the hydrolysis of **10** which yielded methyl substituted silane **11** [10] as main product thus indicating that a silicon-bound methyl group is also present in **10**. Final elucidation of the structure comes from the X-ray diffraction analysis, which shows that silylene **4** formally has undergone insertion into an Al–C bond (Fig. 2). The length of the Al–Si bond (247.5 pm) is in between those found for [$Al(SiMe_3)_3 \cdot Et_2O$] (246.4–248.0 pm) [11]. One of the dimethylamino groups chelates the $AlMe_2$ substituent at silicon whereas the second dimethylamino group coordinates intermolecularly to a trimethylaluminum unit. Both Al···N distances (205.5 and 205.7 pm) are slightly shorter than those reported for $H_3Al \cdot N,N$-dimethylbenzylamine (208.8 pm) in the solid [12a] and $Me_3Al \cdot NMe_3$ (209.9 pm), which was determined by electron diffraction in the gas phase [12b]. The coordinative interactions can be broken up in solution: upon heating to 75°C the benzylic AB systems as well as the four NMe signals begin to coalescence, whereas the signals of the $AlMe_2$ unit remain essentially unchanged (Fig. 1, bottom). Furthermore, the coordinated $AlMe_3$ unit can be removed under formation of **12** by addition of one equivalent of quinuclidine as competing Lewis base (Scheme 4). More efficiently, i.e. without any by-product, **12** is obtained upon treatment of **10** with one third equivalent of **1**, i.e. one equivalent of silylene



Scheme 3. Synthesis and hydrolysis of **10**; Ar = 2-(Me_2NCH_2)C_6H_4.

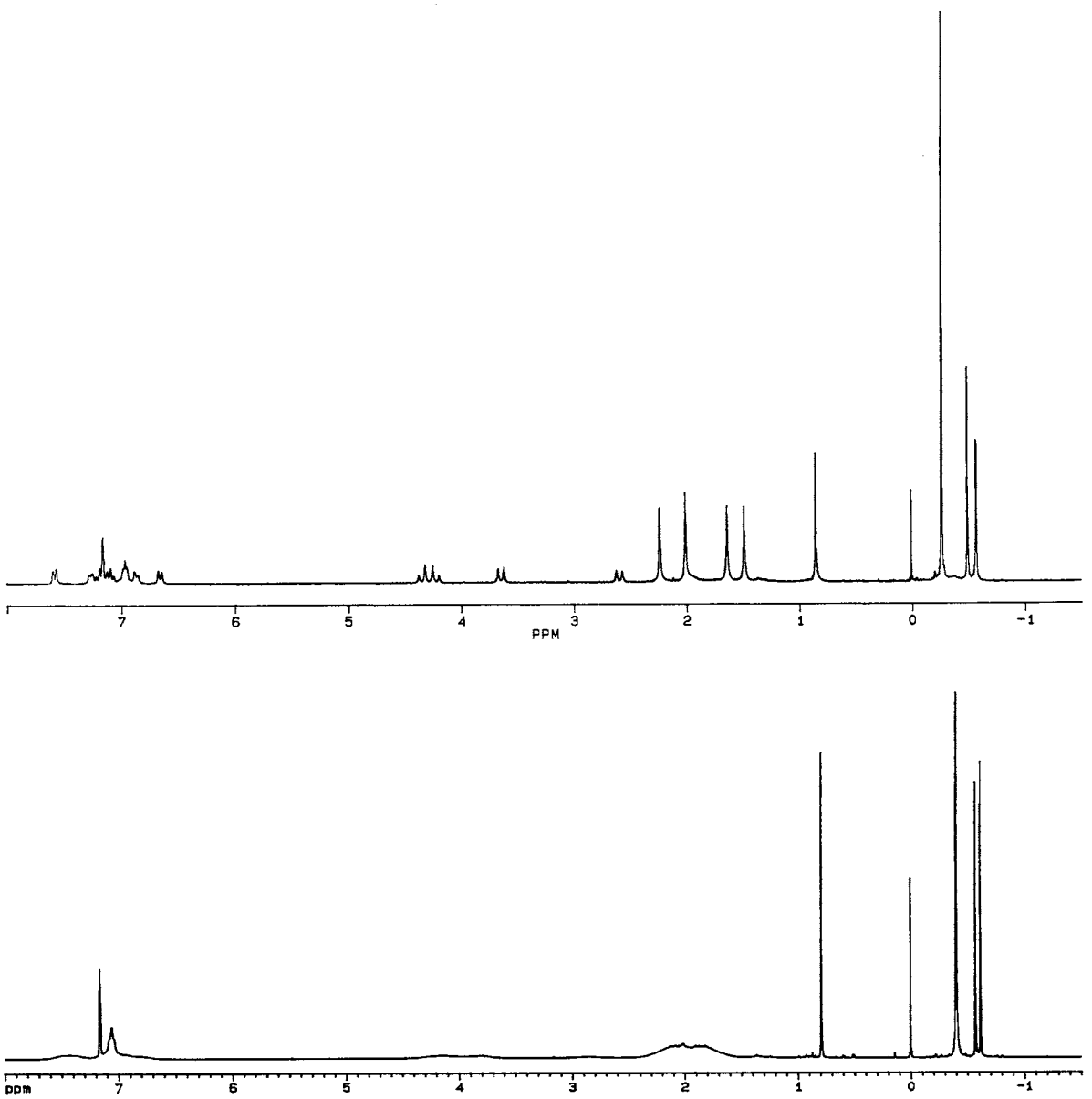


Fig. 1. ^{1}H-NMR spectra of **10** in C_6D_6 at 294 K (top) and 346 K (bottom).

3 as Lewis base, thereby forming a second equivalent of **12**. In agreement with these results, 1:1 product **12** can also be prepared directly by reaction of only three equivalents of $AlMe_3$ with **1** (Scheme 4). The ^{1}H-NMR spectrum of the **12** shows that the 2-(dimethylaminomethyl)phenyl substituents are chemically equivalent at room temperature (r.t.), whereas the $AlMe_2$ group gives rise to two singlets. From these spectroscopic results it is concluded that the aluminum center is chelated by one dimethylamino group and that at r.t. this ligand is rapidly displaced by the dimethylamino group of the second aryl substituent. In order to maintain the chemical inequivalence of the aluminum-bound methyl groups throughout this mutual exchange reaction, the coordination-recoordination-process must be fast in comparison to the rotation around the Si–Al bond.

When the reaction of six equivalents of $AlMe_3$ in toluene with **1** was stopped, immediately after addition of the Lewis acid, by removing the solvent in vacuo and adding pentane, a solid was obtained. Neither a ^{13}C- nor a ^{29}Si-NMR spectrum could be obtained because the compound was rapidly converted to **10** in solution. However, the ^{1}H-NMR spectrum showed, besides the aromatic signals, three extremely broad signals for the benzylic as well as the NMe_2 protons and the $AlMe_3$ groups in the ratio 2:6:9. It was observed that the resonance of the $AlMe_3$ group is shifted to high field in comparison with that of uncomplexed $AlMe_3$. Taking into regard that a comparable highfield shift of the

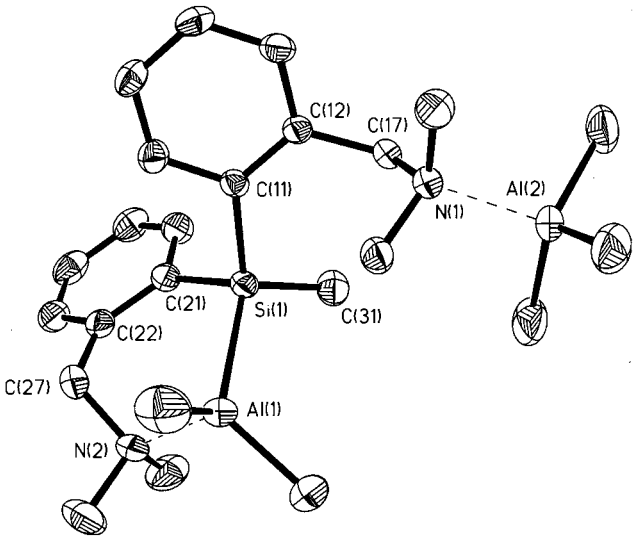
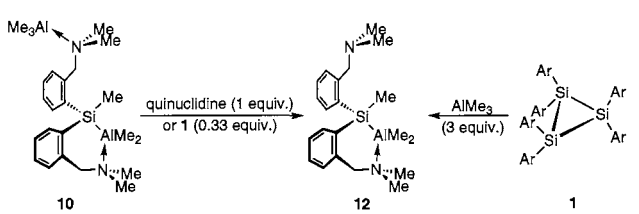
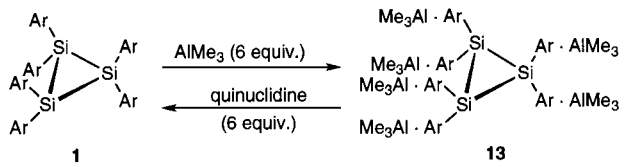


Fig. 2. Crystal structure of **10**. Hydrogen atoms are omitted for clarity, displacement ellipsoids are at the 50% probability level. Selected bond lengths (pm) and bond angles (°): Si(1)–Al(1) 247.5(1), Si(1)–C(11) 191.5(2), Si(1)–C(21) 191.1(2), Si(1)–C(31) 189.8(3), Al(1)···N(2) 205.5(2), Al(2)···N(1) 205.7(2); Al(1)–Si(1)–C(11) 118.23(7), Al(1)–Si(1)–C(21) 106.99(7), Al(1)–Si(1)–C(31) 113.13(8), C(11)–Si(1)–C(21) 102.42(9), C(11)–Si(1)–C(31) 112.2(1), C(21)–Si(1)–C(31) 101.6(1).

signals of the α-CH protons has been reported to occur upon complexation of various trialkylalanes by piperidine [13] we assume that the ^{1}H-NMR spectroscopically characterized intermediate may be cyclotrisilane **13**, in which each dimethylamino group coordinates to an $AlMe_3$ unit (Scheme 5). In agreement with this hypothesis the coordinated Lewis acid could be transferred to quinuclidine under regeneration of the uncomplexed cyclotrisilane **1**. Further confirmation for the initial formation of a cyclotrisilane–Lewis acid adduct comes from the reaction of **1** with six equivalents of $Al(i\text{-}Bu)_3$. Using this bulkier Lewis acid, again a significant highfield shift of the protons in α-position to aluminum is observed upon addition of **1**. Moreover, the initial product **14** is stable enough [14] to allow the determination of its ^{29}Si-NMR shift. The value of $\delta = -55.3$ is shifted to lower field in comparison to that of free **1**, but is still in the typical range of cyclotrisilanes [1,15]. By treatment of **14** with quinuclidine the starting cyclotrisilane **1** was re-formed, thus resembling the reactivity of **13**. Taken together, it appears reasonable

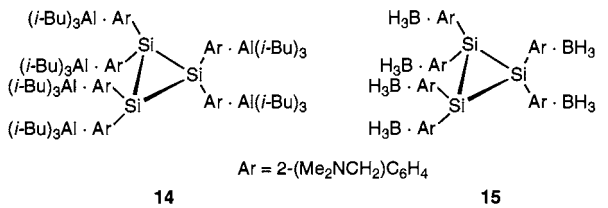


Scheme 4. Synthesis of **12**; Ar = 2-$(Me_2NCH_2)C_6H_4$.



Scheme 5. Complexation and decomplexation of **1**; Ar = 2-$(Me_2NCH_2)C_6H_4$.

to assume that upon treatment of **1** with $AlMe_3$ or $Al(i\text{-}Bu)_3$ the Lewis acid initially coordinates to the Lewis basic dimethylamino groups under conservation of the cyclotrisilane structure; the Si–Si bond cleavage occurs at a later stage of the reaction.



When **1** was treated with six equivalents of $BH_3 \cdot THF$, the cyclotrisilane **15**, in which each dimethylamino group is coordinated to a borane unit, was obtained. In contrast to the aluminum-coordinated cyclotrisilanes **13** and **14** the BH_3 units cannot be removed by quinuclidine. The ^{29}Si-NMR shift of $\delta = -59.4$ indicates that the three-membered silicon ring remained intact. In the solid state **15** forms an isosceles triangle (Fig. 3) as it is known for other cyclotrisilanes

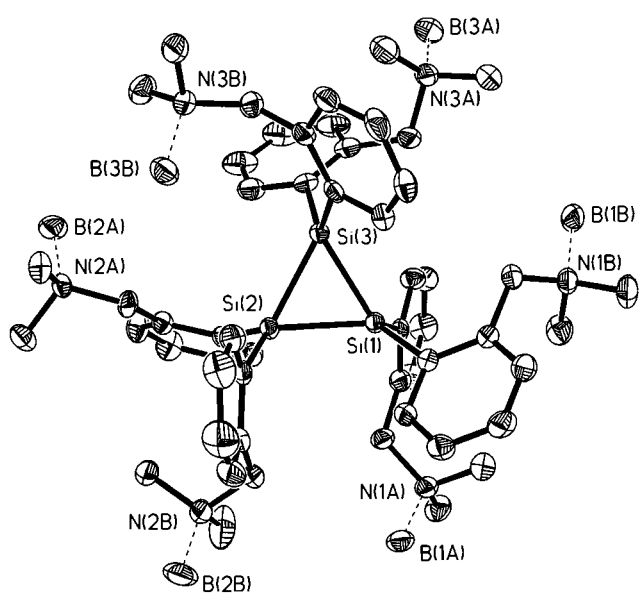


Fig. 3. Crystal structure of **15**. Hydrogen atoms and two THF molecules are omitted for clarity, displacement ellipsoids are at the 50% probability level. Selected bond lengths (pm) and bond angles (°): Si(1)–Si(2) 237.8(1), Si(2)–Si(3) 237.3(1), Si(3)–Si(1) 240.2(1), B···N (average) 163.0; Si(1)–Si(2)–Si(3) 60.74(4), Si(2)–Si(3)–Si(1) 59.72(4), Si(3)–Si(1)–Si(2) 59.54(3).

[1]. In comparison to the solid state structure of **1** [6] the Si–Si bond lengths are only slightly elongated (average: 238.4 vs. 236.1 pm). The lengths of the six dative B···N vary between 161.9 and 163.9 pm. This is above the value of 158.7 pm which was reported as average B···N bond lengths in acyclic amine–borane complexes [16], but is still smaller than the dative bond length of 166.1 pm in the $BH_3 \cdot$ urotropine complex [17].

Ongoing experiments are addressing the question whether complexation of the nucleophilic dimethylamino groups in **1**, as realized in cyclotrisilane **15**, surpresses the silylene activity, which is typical for cyclotrisilanes **1**–**3**.

3. Experimental

3.1. General

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AM 250 (^{1}H-NMR: 250 MHz; ^{13}C-NMR: 62.9 MHz) or a Bruker AMX 300 (^{1}H-NMR: 300 MHz; ^{13}C-NMR: 75.5 MHz) spectrometer. C_q, CH, CH_2 and CH_3 were determined using the DEPT or APT pulse sequence. ^{29}Si-NMR spectra were recorded on a Bruker AMX 300 (59.6 MHz) using a refocused INEPT pulse sequence or direct acquisition. Chemical shifts refer to $\delta_{TMS} = 0.0$. All manipulations were carried out under inert argon atmosphere using carefully dried glassware. Halogen-free solvents used were dried by refluxing over sodium/benzophenone ketyl and distilled immediately before use. $CDCl_3$ was distilled from CaH_2.

3.2. Bis[2-(dimethylaminomethyl)phenyl]siliconium bromide (**8a**)

A solution of **1** (202 mg, 0.23 mmol) and pyridinium bromide (109 mg, 0.68 mmol) in THF (50 ml) was stirred for 4 days at r.t. The solvent was removed in vacuo and the residue was washed with hexane (2×10 ml) leaving behind **8a** (132 mg, 51%) as a white solid. The solvent was removed from the hexane phase in vacuo and the remaining oil was distilled at 160°C/10^{-3} Torr to yield **9** (95 mg, 47%). **8a**: m.p.: 212°C.—^{1}H-NMR ($CDCl_3$): $\delta = 2.72$ (s; 6H, NMe), 2.93 (s; 6H, NMe), 4.41, 4.42 (AB-system, $^2J_{HH} = 15$ Hz; 4H, CH_2N), 4.66 (s (d, $^1J_{SiH} = 273$ Hz); 1H, SiH), 7.3–7.5 (m; 6H, ar H), 7.79 (d, $^3J_{HH} = 7$ Hz; 2H, ar H).—^{13}C-NMR ($CDCl_3$): $\delta = 45.3$ (NMe), 47.5 (NMe), 64.7 (CH_2N), 127.2 (ar CH), 128.0 (ar C_q), 128.3 (ar CH), 132.0 (ar CH), 135.4 (ar CH), 144.4 (ar C_q).—^{29}Si-NMR ($CDCl_3$): $\delta = -51.5$ ($^1J_{SiH} = 269$ Hz).—IR (nujol): $\nu = 2164$ cm^{-1}.

3.3. Bis[2-(dimethylaminomethyl)phenyl](dimethylaluminum)methylsilane · $AlMe_3$ (**10**)

A 2 M solution of $AlMe_3$ in toluene (1.69 ml, 3.39 mmol) was added to a solution of **1** (503 mg, 0.57 mmol) in toluene (7 ml) and stirred for 15 h at r.t. The solvent was removed in vacuo and pentane (7 ml) was added. The resulting suspension was stirred for further 15 h and filtered. The remaining solid was washed with pentane to yield **10** as white solid (470 mg, 63%). Crystals suitable for X-ray diffraction analysis were obtained by crystallization from toluene/pentane.—Dec.: 87°C.—^{1}H-NMR (C_6D_6): $\delta = -0.63$ (s; 3H, AlMe), -0.56 (s; 3H, AlMe), -0.36 (s; 9H, $AlMe_3$), 0.79 (s; 3H, SiMe), 1.55 (s; 3H, NMe), 1.71 (s; 3H, NMe), 2.02 (s; 3H, NMe), 2.23 (s; 3H, NMe), 2.67, 3.66 (AB system, $^2J = 13$ Hz; 2H, CH_2N), 4.20, 4.33 (AB system, $^2J = 13$ Hz; 2H, CH_2N), 6.68 (d, $^3J = 7$ Hz; 2H, ar H), 6.9–7.2 (m; 6H, ar H), 7.54 (d, $^3J = 7$ Hz; 2H, ar H).—^{13}C-NMR (C_6D_6): $\delta = -9.9$ (AlMe), -9.1 (AlMe), -8.75 ($AlMe_3$), 0.8 (SiMe), 42.2 (NMe_2), 43.4 (NMe_2), 45.0 (NMe_2), 47.9 (NMe_2), 60.6 (CH_2N), 66.2 (CH_2N), 127.1 (ar C), 127.6 (ar C), 128.4 (ar C), 129.1 (ar C), 131.5 (ar C), 132.6 (ar C), 136.6 (ar C), 136.7 (ar C_q), 137.3 (ar C), 139.6 (ar C_q), 145.4 (ar C_q), 146.6 (ar C_q).—^{29}Si-NMR (C_6D_6): $\delta = -31.4$.

3.4. Hydrolysis of **10**

To a solution of **10** in C_6D_6 in an NMR tube was added a drop of water. After ceasing of the gas evolution the ^{1}H-NMR spectrum of the slurry showed mainly the signals of bis[2-(dimethylaminomethyl)-phenyl]methylsilane (**11**) [10].

3.5. Bis[2-(dimethylaminomethyl)phenyl](dimethylaluminum)methylsilane (**12**)

(a) A crystal of quinuclidine was added to a solution of **10** (20 mg, 45 μmol) in C_6D_6 (0.4 ml) in an NMR tube. After dissolution of the amine the signals of **12** were observed besides that of left over quinuclidine and the quinuclidine $AlMe_3 \cdot$ complex. (b) To a solution of **10** (120 mg, 0.27 mmol) in C_6D_6 (0.6 ml) in an NMR tube was added **1** (80 mg, 0.09 mmol). A ^{1}H-NMR spectrum taken after 15 h at r.t. showed exclusively the signals of **12**. (c) A 2 M solution of $AlMe_3$ in toluene (84 μl, 0.17 mmol) was added to a solution of **1** (50 mg, 0.06 mmol) in toluene (0.5 ml) and stirred for 3 h at r.t. The solvent was removed in vacuo and the remaining yellow oil was dissolved in 0.4 ml C_6D_6. The ^{1}H-NMR spectrum showed, besides traces of **1**, only signals of **12**.—^{1}H-NMR (C_6D_6): $\delta = -0.58$ (s; 3H, AlMe), -0.52 (s; 3H, AlMe), 0.73 (s; 3H, SiMe), 1.97 (s; 12H, NMe_2), 3.33, 3.81 (AB system, $^2J = 13$ Hz; 4H, CH_2N), 7.01–7.15 (m; 6H, ar H), 7.49–7.51 (m; 2H, ar H).

Table 1
Summary of crystal data, details of intensity collection, and least-squares refinement parameters for **10** and **15 · 2 THF**

	10	**15 · 2 THF**
Empirical formula	$C_{24}H_{42}Al_2N_2Si$	$C_{62}H_{106}B_6N_6O_2Si_3$
Formula weight	440.65	1116.66
Temperature (K)	193(2)	153(2)
Crystal size (mm)	$0.8 \times 0.4 \times 0.3$	$0.8 \times 0.6 \times 0.5$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	Cc
Unit cell dimensions		
a (pm)	858.4(1)	2446.9(5)
b (pm)	2865.2(9)	1573.7(3)
c (pm)	1121.7(2)	1898.1(4)
β (°)	100.18(1)	108.76(3)
V (nm^3)	2.715(1)	6.92(1)
Z	4	4
$D_{calc.}$ (g cm^{-3})	1.078	1.072
μ (mm^{-1})	0.163	0.112
$F(000)$	960	2432
2θ range (°)	$7 \leq 2\theta \leq 53$	$7 \leq 2\theta \leq 50$
Range of h, k, l	$-10 \leq h \leq 10$, $-19 \leq k \leq 35$, $-14 \leq l \leq 14$	$-29 \leq h \leq 28$, $-18 \leq k \leq 18$, $-3 \leq l \leq 22$
Reflections collected	8626	7142
Independent reflections	5591	7134
R_{int}	0.1135	0.0106
Data/restraints/parameters	5591/0/272	7134/339/805
Absolute structure parameter	–	0.4(1)
R_1 [$I > 2\sigma(I)$]	0.0541	0.0378
wR_2 (all data)	0.1542	0.0899
Largest difference peak (e nm^{-3})	514	227
Largest difference hole (e nm^{-3})	−409	−190

3.6. Hexakis[2-(dimethylaminomethyl)phenyl]-cyclotrisilane · 6 $AlMe_3$ (13)

A solution of $AlMe_3$ in toluene (2 M, 1.41 ml, 2.82 mmol) was added at 0°C to a solution of **1** (416 mg, 0.47 mmol) in toluene (15 ml). Immediately after the addition was completed the solvent was removed at this temperature in vacuo and pentane (10 ml) was added to the semi-solid residue. After 15 h the pentane was decanted leaving behind **13** (617 mg, 99%) as a white solid.—^{1}H-NMR (C_6D_6): $\delta = -0.61$ (br. s; 54H, $AlMe_3$), 2.05 (br. s; 36H, NMe_2), 3.46, 4.14 (br. AB system; 12H, CH_2N), 6.60 (br. s; 6H, ar H), 7.02 (br. s; 18H, ar H).

3.7. Reaction of 13 with quinuclidine

A crystal of quinuclidine was added to a solution of **10** (20 mg, 15 μmol) in C_6D_6 (0.4 ml) in an NMR tube. After dissolution of the amine the signals of **1** were observed besides that of left over quinuclidine and the quinuclidine · $AlMe_3$ complex [18].

3.8. Reaction of 1 with Al(i-Bu)$_3$

A solution of Al(i-Bu)$_3$ in toluene (1 M, 2.52 ml, 2.52 mmol) was added at −78°C to a solution of **1** (372 mg, 0.42 mmol) in toluene (7 ml). The solution was warmed to r.t. during 45 min and the solvent was removed in vacuo leaving behind **14** (571 mg, 99%) as a colorless oil.—^{1}H-NMR (C_6D_6): $\delta = 0.11$ (d, $^3J = 7$ Hz; 36H, $AlCH_2$), 1.24 (d, $^3J = 6$ Hz; 108H, CMe_2), 1.98–2.20 (m; 18H, $CMe_2\underline{H}$), 2.09 (s; 36H, NMe_2), 3.67, 4.01 (AB system, $^2J = 13$ Hz; 12H, CH_2N), 6.74 (dd, $^3J = {}^3J = 7$ Hz; 6H, ar H), 6.66–7.24 (m; 12H, ar H), 7.53 (d, $^3J = 7$ Hz; 6H, ar H).—^{29}Si-NMR (C_6D_6): $\delta = -55.3$.

3.9. Reaction of 14 with quinuclidine

A crystal of quinuclidine was added to a solution of **14** (35 mg, 17 μmol) in C_6D_6 (0.4 ml) in an NMR tube. After dissolution of the amine the signals of **1** were observed besides that of left over quinuclidine and the quinuclidine · Al(i-Bu)$_3$ complex.

3.10. Hexakis[2-(dimethylaminomethyl)phenyl]-cyclotrisilane · 6 BH_3 (15)

A solution of BH_3 in THF (1 M, 2.52 ml, 2.52 mmol) was added at r.t. to a solution of **1** (855 mg, 96 mmol) in toluene (20 ml) and stirred for 15 min. The solvent was removed in vacuo, the remaining white solid was washed with toluene (20 ml) and raw **15** was dissolved in THF (20 ml). After addition of Et_2O (10 ml) and

standing at 4°C **15** (822 mg, 77%) was obtained as colorless crystals, which contained two equivalents of THF.—^{1}H-NMR ($CDCl_3$): $\delta = 1.72$ (br. s; 18H, BH_3), 1.83 (s; 8H, THF, 3-H, 4-H), 2.36 (br. s; 36H, NMe_2), 3.72 (s; 8H, THF, 1-H, 5-H), 4.25 (br. s; 12H, CH_2N), 6.88 (s; 6H, ar CH), 7.17 (s; 6H, ar CH), 7.38 (dd, $^3J = {}^3J = 7$ Hz; 6H, ar CH), 7.87 (s; 6H, ar CH).—^{29}Si-NMR ($CDCl_3$): $\delta = -59.4$.

3.11. Single crystal X-ray diffraction analysis of **10** and **15 · 2 THF**

Crystal data, data collection, and least square parameters are summarized in Table 1. Data were collected on a Stoe-Siemens-Huber (for **10**) and on a Stoe-Siemens-AED2 diffractometer (for **15 · 2 THF**), both with monochromated Mo–K_α radiation ($\lambda =$ 71.703 pm). Both structures were solved by direct methods [19] and refined versus F^2 (SHELXL-97) [20]. All non-hydrogen atoms were refined anisotropically. A riding model starting from calculated positions was employed for the hydrogen atoms. In structure **15 · 2 THF** the THF molecules are disordered over two positions. They were refined with distance restraints and restraints for the anisotropic parameters. The structure was refined as a racemic twin [21]. The R-values were defined as $R_1 = \Sigma||F_o| - |F_c||^2/\Sigma|F_o|^2$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. Further details of the crystal structure determinations may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ.

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