

Preparation and ^{29}Si NMR Spectroscopical Investigations of (Diethylamino)-methylchlorotetra- and Pentasilanes**Kristin Trommer, Uwe Herzog and Gerhard Roewer**

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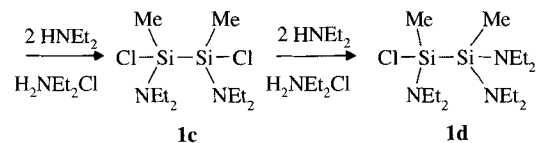
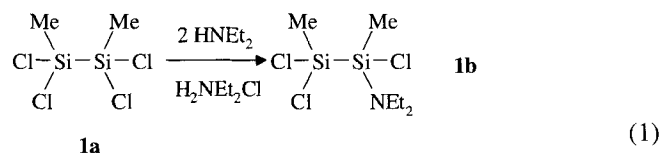
Received May 14th, 1997 respectively July 28th, 1997

Abstract. The treatment of several branched methylchlorooligosilanes (Si_4 , Si_5) with diethylamine leads to a partial or complete substitution of the chloro substituents for diethylamino groups under formation of the first known (diethylamino)-methylchlorooligosilanes containing more than two Si atoms. The condensation of $(\text{Et}_2\text{N})_2\text{MeSi-SiMeCl}(\text{NEt}_2)$ (**1d**)

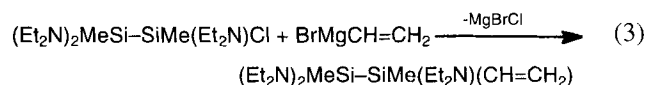
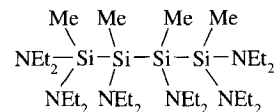
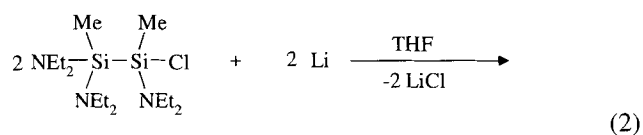
with Li in THF yields the linear tetrasilane $(\text{Et}_2\text{N})_2\text{MeSi-SiMe}(\text{NEt}_2)-\text{SiMe}(\text{NEt}_2)-\text{SiMe}(\text{Et}_2\text{N})_2$ (**2a**).

The NMR investigations provided information of the general shift ranges of several Si units in (diethylamino)-methylchlorooligosilane systems as well as the number of stereoisomers of the prepared products.

Any oligosilanes containing simultaneously chlorine, diethylamino and methyl substituents are not known until now. The stepwise reaction of diethylamine with methylchlorooligosilanes offers the possibility to obtain (diethylamino)-methylchlorooligosilanes. We have already reported this route for the substitution of $\text{SiCl}_2\text{Me-SiCl}_2\text{Me}$ [1]:



Because the diethylaminogroup can act as protecting group, the aminochlorosilanes are interesting synthons for the preparation of higher oligomers, for instance *via* reductive cross coupling with lithium [1–3] as well as *via* salt elimination reactions [4]:



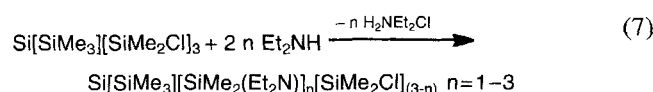
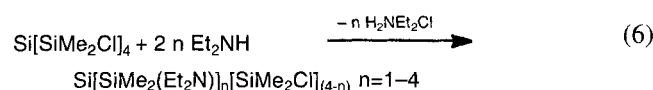
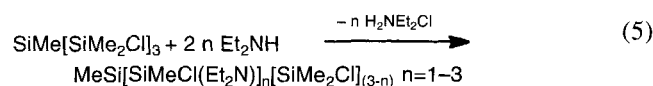
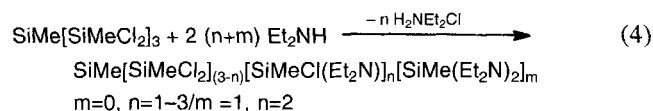
A reconversion of the remaining dialkylaminogroups at the formed aminosilanes into chloro substituents is easily possible by treatment with HCl [4].

Some examples of mixed substituted tetra- and pentasilanes will be reported in this paper.

Because only few mono- and disilanes bearing Et_2N and chloro functions are known, this work should also give a new insight in ^{29}Si NMR shift ranges of diethylaminosubstituted oligosilanes. The found results could be helpful for the assignment of Si-sites in polymers and Si–C–N ceramics.

Results and Discussion

The new branched diethylaminochloromethyltetra- and pentasilanes were synthesized by the reaction of the corresponding chlorosilanes with diethylamine (equations 4–7, scheme 1):

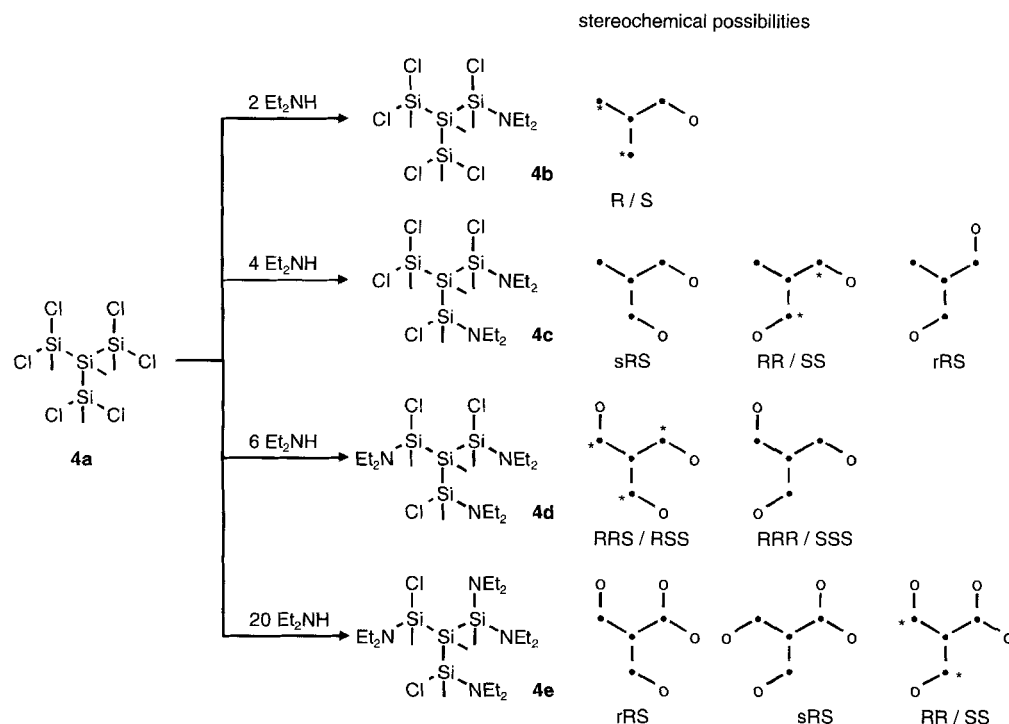


The tetrasilane **2a** which contains the silicon atoms bonded in a chain results by condensation of $\text{Me}(\text{Et}_2\text{N})_2\text{Si}-\text{Si}(\text{Et}_2\text{N})\text{MeCl}$ with lithium. In contrast to the observations by K. Tamao *et al.* [2] this reaction yields the desired tetrasilane in high yields (scheme 2).

The treatment of the aminosubstituted tetrasilane **2a** with HCl in dried CCl_4 leads to the chlorosubstituted tetrasilane **2b**. The hydrogenation of **2b** with excess Me_3SnH according to [6] gives the previously described hydrogen substituted derivative [7] **2g** (see scheme 2). As found from the hydrogenation of $\text{SiMeCl}(\text{SiMe}_2\text{Cl})_2$ and $\text{SiMeCl}(\text{SiMeCl}_2)_2$ [6] chlorine substituents bonded to the central silicon atoms are favoured in hydrogenation by stannanes. The tetrasilanes, containing diethylamino and chloro substituents simultaneously, are obtained by equilibration of $[(\text{Et}_2\text{N})_2\text{MeSi}-\text{SiMe}(\text{NEt}_2)]_2$ with trichloromethylsilane in various molar ratios (scheme 2).

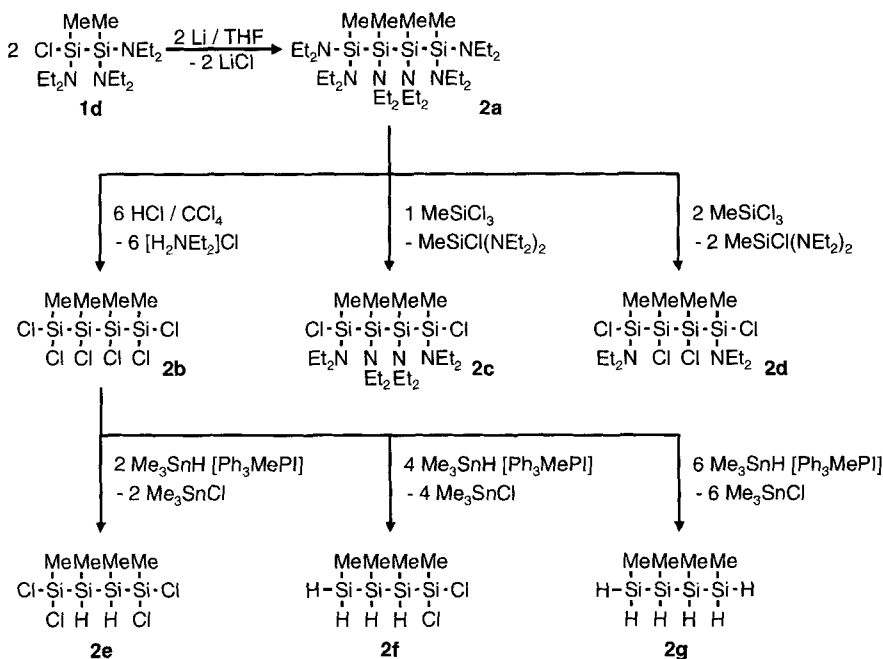
The interpretation of the ^{29}Si NMR data, given in tables 1–2, demonstrates that an exchange of chlorine for diethylamino substituents causes a downfield shift for silyl groups involving at least one electron withdrawing substituent ($-\text{SiMeCl}_2$, $-\text{SiMe}_2\text{Cl}$, $-\text{SiMe}(\text{NEt}_2)_2$, $-\text{SiMeCl}(\text{NEt}_2)$) and an upfield shift for $-\text{SiMe}_3$, $\equiv\text{SiMe}$ as well as quaternary silicon atoms.

Isotetrasilanes $\text{SiMe}(\text{SiMeCl}_2)_{3-x-m}(\text{SiMeCl}(\text{Et}_2\text{N})_2)_x(\text{SiMe}(\text{Et}_2\text{N})_2)_m$ form either diastereomers or diastereotopic silyl groups or may have both ones. The possible stereochemical arrangements of the isotetrasilanes are illustrated in scheme 1. Every expected splitting of signals due to diastereomers and diastereotopic silyl groups has been observed in the ^{29}Si NMR spectra except in the case of the tertiary unit of the threefold ami-



Scheme 1

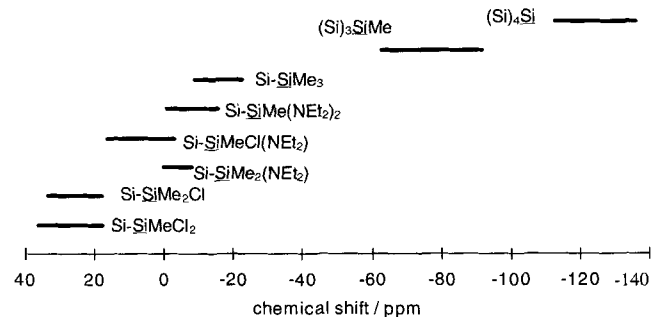
• silicon atom, o nitrogen atom, * diastereotopic silicon atoms



Scheme 2

nosubstituted isotetrasilane. The differences between the ^{29}Si NMR signals vary from 0.1 up to 1.2 ppm. The differences between the ^{29}Si NMR shifts of the diastereotopic branched silicon structures are lower in comparison with disilanes. The stereoisomers of 1,2-dichloro-1,2-bis-(diethylamino)-dimethyldisilane for instance distinguish from each other by 2.05 ppm [1]. If the diethylamino groups in this disilane are exchanged for diisopropylamine the difference increases even up to 2.5 ppm.

The general shift ranges of the investigated silicon units are summarized in scheme 3.



Scheme 3

Experimental

All ^{29}Si NMR spectra were recorded on a Bruker MSL 300 using the IGATED pulse sequence with TMS or Si_2Me_6 (δ_{Si}

–19.68 ppm, used if signals near 0 ppm were expected) as internal standard.

MS spectra were recorded on a HEWLETT PACKARD 5971 (ionization energy: 70 eV, column: 30 m \times 0.25 mm \times 0.25 μm , phenylmethylpolysiloxane). All isotopic patterns are in agreement with the expected number of chlorine atoms in the fragments.

Preparation of Methylchlorooligosilanes

Tris-(chlorodimethylsilyl)-methylsilane (3a)

To a solution of 11 g (0.04 mol) $\text{SiMe}(\text{SiMe}_3)_3$ in 30 ml hexane 21.5 g (0.16 mol AlCl_3) and 12.5 g (0.16 mol) acetyl chloride were added under stirring. After reacting for three hours at room temperature the upper layer was isolated. The fractionated distillation gave 8 g (62% yield) pure $\text{SiMe}(\text{SiClMe}_2)_3$ (*b.p.* 110–120 $^\circ\text{C}/0.7$ kPa, solidifies at ambient temperature). GC/MS (*m/e*, rel. Int.): 324 (M^+ , 0.5), 309 ($\text{Si}_4\text{Me}_6\text{Cl}_3$, 2), 287 ($\text{Si}_4\text{Me}_7\text{Cl}_2$, 6), 229 ($\text{Si}_3\text{Me}_5\text{Cl}_2$, 78), 209 ($\text{Si}_3\text{Me}_6\text{Cl}$, 12), 194 ($\text{Si}_3\text{Me}_5\text{Cl}$, 39), 151 ($\text{Si}_2\text{Me}_4\text{Cl}$, 26), 131 (Si_2Me_5 , 58), 116 (Si_2Me_4 , 26), 93 (SiMe_2Cl , 26), 73 (SiMe_3 , 100). –NMR: $^1J_{\text{SiSi}}$ 71 Hz; ^1H NMR: δ/ppm = 0.24 (3 H), 0.55 (18 H), δ_{Si} : see table 1

Tris-(dichloromethylsilyl)-methylsilane (4a)

900 g (4 mol) $\text{SiCl}_2\text{Me}-\text{SiCl}_2\text{Me}$ were Lewis base catalyzed disproportionated with a fixed catalyst as described in [8]. The formed mixture of oligomers could be fractionated to give beside other oligomers 45 g (0.12 mol) $\text{SiMe}(\text{SiCl}_2\text{Me})_3$, *b.p.* 120 $^\circ\text{C}/0.8$ kPa (solidifies at room temperatures), 9% yield. –GC/MS (*m/e*, rel. Int.): 384 (M^+ , 0.4), 369 ($\text{Si}_4\text{Me}_3\text{Cl}_6$, 1), 349 ($\text{Si}_4\text{Me}_4\text{Cl}_5$, 5), 271 ($\text{Si}_3\text{Me}_3\text{Cl}_4$, 100), 251 ($\text{Si}_3\text{Me}_4\text{Cl}_3$, 2), 236 ($\text{Si}_3\text{Me}_3\text{Cl}_3$, 11), 193 ($\text{Si}_2\text{Me}_2\text{Cl}_3$, 2), 171 ($\text{Si}_2\text{Me}_3\text{Cl}_2$,

Tab. 1 ^{29}Si NMR data of the investigated tetrasilanes, δ/ppm

compound	Si ^A	Si ^B	Si ^C	Si ^D
Si ^A Me(Si ^B Me ₂ Cl) ₃ (3a)	-76.3	27.0		
Si ^A Me(Si ^B Me ₂ Cl) ₂ (Si ^C Me ₂ (NEt ₂)) (3b)	-82.4	28.6	1.0	
Si ^A Me(Si ^B Me ₂ Cl)(Si ^C Me ₂ (NEt ₂)) ₂ (3c)	-87.0	30.7	2.1	
Si ^A Me(Si ^C Me ₂ (NEt ₂)) ₃ (3d)	-91.1		3.3	
Si ^A Me(Si ^B MeCl ₂) ₃ (4a) [5]	-63.4	31.0		
Si ^A Me(Si ^B MeCl ₂) ₂ (Si ^C MeCl(NEt ₂)) (4b)	-66.35	33.73/33.63	7.35	
Si ^A Me(Si ^B MeCl ₂)(Si ^C MeCl(NEt ₂)) ₂ (4c) ^{a)}	-70.52/ -70.77/-70.93	36.56/36.40/ 36.20	10.42/10.33/ 10.02/9.84	
Si ^A Me(Si ^C MeCl(NEt ₂)) ₃ (4d) ^{a)}	-76.46		13.38/13.24/13.04	
Si ^A Me(Si ^B Me(NEt ₂)) ₂ (Si ^C MeCl(NEt ₂)) ₂ (4e) ^{a)}	-80.45/-81.23/ -81.62	-1.80/-1.98/ -2.24	16.06/15.87/15.77/ 15.15	
[Me(NEt ₂) ₂ Si ^B -Si ^C Me(NEt ₂)] ₂ (2a) ^{a)}		-16.0/-15.7	-7.3/-6.4	
[Me(NEt ₂)ClSi ^B -Si ^C Me(NEt ₂)] ₂ (2c) ^{a)}		3.5/4.2	-8.1/-7.7	
[Me(NEt ₂)ClSi ^B -Si ^C MeCl] ₂ (2d)		2.4	0.2	
[MeCl ₂ Si ^A -Si ^B MeCl] ₂ (2b)	24.8	-0.5		
[MeCl ₂ Si ^A -Si ^B MeH] ₂ (2e) ^{a)}	34.7	-64.3/-65.4		
MeH ₂ Si ^A -Si ^B MeH-Si ^C MeH-Si ^D MeCl ₂ (2f) ^{a)}	-64.3/-64.5	-73.9/-74.6	-63.0/-63.7	36.0
[MeH ₂ Si ^A -Si ^B MeH] ₂ (2g) ^{a)}	-64.6	-72.6/-73.1		

^{a)} diastereomers

57), 156 (Si₂Me₂Cl₂, 12), 151 (Si₂Me₄Cl, 5), 136 (Si₂Me₃Cl, 15), 113 (SiMeCl₂, 28), 93 (SiMe₂Cl, 55), 78 (SiMeCl, 5), 73 (SiMe₃, 66). - NMR: $^1J_{\text{SiSi}}$ 86 Hz; ^1H NMR: δ/ppm = 0.46 (3 H), 0.90 (9 H), δ_{Si} : see table 1.

Tetrakis-(chlorodimethylsilyl)-silan (5a) and Tris-(chlorodimethylsilyl)-trimethylsilylsilane (6a)

In the same way as described for SiMe(SiClMe₂)₃, the reaction of 3.7 g (0.014 mol) Si(SiMe₃)₄ with 7.7 g (0.058 mol) AlCl₃ and 4.5 g (0.057 mol) acetyl chloride gave 3.6 g of a crystalline residue of 75% Si(SiClMe₂)₄ (**5a**) and 25% Si(SiClMe₂)₃(SiMe₃) (**6a**) after removal of hexane under reduced pressure. **5a**: GC/MS (*m/e*, rel. Int.): 402 (M⁺, 0.3), 387 (Si₅Me₇Cl₄, 5), 367 (Si₅Me₈Cl₃, 7), 309 (Si₄Me₆Cl₃, 31), 272 (Si₄Me₆Cl₂, 100), 229 (Si₃Me₅Cl₂, 14), 209 (Si₃Me₆Cl, 55), 174 (Si₃Me₆, 54), 131 (Si₂Me₅, 35), 116 (Si₂Me₄, 27), 93 (SiMe₂Cl, 38), 73 (SiMe₃, 74). - NMR: $^1J_{\text{SiSi}}$ 63 Hz; ^1H NMR: δ/ppm = 0.62, δ_{Si} : see table 2.

6a: GC/MS (*m/e*, rel. Int.): 382 (M⁺, 0.1), 367 (Si₅Me₈Cl₃, 9), 345 (Si₅Me₉Cl₂, 5), 287 (Si₄Me₇Cl₂, 5), 272 (Si₂Me₆Cl₂, 100),

267 (Si₄Me₈Cl, 3), 252 (Si₄Me₇Cl, 3), 209 (Si₃Me₆Cl, 28), 194 (Si₃Me₅Cl, 11), 174 (Si₃Me₆, 54), 159 (Si₃Me₅, 9), 131 (Si₂Me₅, 23), 93 (SiMe₂Cl, 14), 73 (SiMe₃, 100). - ^1H NMR: δ/ppm = 0.30 (9 H), 0.59 (18 H), δ_{Si} : see table 2.

1,1,2,3,4,4-Hexachlorotetramethyltetrasilane (2b)

Through a solution of 2 g (3.3 mmole) **2a** in 50 ml CCl₄ dry HCl was bubbled. The solution became cloudy and warmed up. At the end of the reaction the formed precipitate dissolved and two phases were obtained. The solvent of the lower phase containing the product was evaporated to yield a residue of pure **2b**. Attempts to distillate **2b** under reduced pressure resulted in a rearrangement of **2b** into **4a**. - GC/MS (*m/e*, rel. Int.): 384 (M⁺, 0.5), 369 (Si₄Me₃Cl₆, 1), 349 (Si₄Me₄Cl₅, 4), 271 (Si₃Me₃Cl₄, 100), 251 (Si₃Me₄Cl₃, 3), 236 (Si₃Me₃Cl₃, 6), 193 (Si₂Me₂Cl₃, 3), 171 (Si₂Me₃Cl₂, 67), 156 (Si₂Me₂Cl₂, 15), 151 (Si₂Me₄Cl, 3), 136 (Si₂Me₃Cl, 19), 113 (SiMeCl₂, 27), 93 (SiMe₂Cl, 66), 73 (SiMe₃, 78). - ^1H NMR: δ/ppm = 0.76 (6 H), 0.86 (6 H); $^1J_{\text{SiSi}}$ 111 Hz, δ_{Si} : see table 1.

Tab. 2 ^{29}Si NMR data of the neopentasilanes Si(SiMe₂Y)₄ and Me₃SiSi(SiMe₂Y)₃ (Y = Cl, NEt₂), δ/ppm

compound	Si ^A	Si ^B	Si ^C	Si ^D
Si ^A (Si ^B Me ₂ Cl) ₄ (5a)	-113.9	27.5		
Si ^A (Si ^B Me ₂ Cl) ₃ (Si ^C Me ₂ (NEt ₂)) (5b)	-120.7	29.6	3.3	
Si ^A (Si ^B Me ₂ Cl) ₂ (Si ^C Me ₂ (NEt ₂)) ₂ (5c)	-126.2	31.6	4.3	
Si ^A (Si ^B Me ₂ Cl)(Si ^C Me ₂ (NEt ₂)) ₃ (5d)	-130.6	33.7	5.3	
Si ^A (Si ^C Me ₂ (NEt ₂)) ₄ (5e)	-134.5		6.3	
Si ^A (Si ^D Me ₃)(Si ^B Me ₂ Cl) ₃ (6a)	-118.4	28.9		-9.3
Si ^A (Si ^D Me ₃)(Si ^B Me ₂ Cl) ₂ (Si ^C Me ₂ (NEt ₂)) (6b)	-123.5	31.4	3.9	-10.1
Si ^A (Si ^D Me ₃)(Si ^B Me ₂ Cl)(Si ^C Me ₂ (NEt ₂)) ₂ (6c)	-130.6	33.5	5.0	-10.8
Si ^A (Si ^D Me ₃)(Si ^C Me ₂ (NEt ₂)) ₃ (6d)	-135.5		6.2	-11.5

Preparation of Aminomethyloligosilanes

1,1,2,3,4,4-Hexakis-(diethylamino)-tetramethyltetrasilane [(Et₂N)₂MeSi^A-Si^BMe(Et₂N)]₂ (**2a**)

To a mixture of 1.0 g (0.14 mol) lithium in 50 ml THF dropwise 8 g (0.023 mol) (Et₂N)₂MeSi-SiMe(Et₂N)Cl (**1d**) [1] diluted in 5 ml THF were added. The mixture was stirred overnight, filtered and the THF was exchanged for the same volume of *n*-hexane. After stirring for 10 h and filtration the solvent was evaporated to give 6.2 g (86% yield) of **2a**.

C₂₈H₇₂N₆Si₄ calcd.: 55.56 H 11.99 N 13.88 (605.26) found: 55.45 H 12.17 N 13.06.

GC/MS (*m/e*, rel. Int.): 604 (M⁺, 1), 460 (Si₄Me₄(NEt₂)₄, 1), 187 (SiMe(NEt₂)₂, 58), 115 (SiMe(NEt₂), 26). – ¹H NMR: β/ppm = 0.394 (Si^ACH₃), 0.594/0.670 (Si^BCH₃), 1.166 (N~CH₃, ³J_{HH}: 6.4 Hz), 3.064 (N~CH₂); ¹³C NMR: δ/ppm = 0.2/0.5 (Si^BCH₃, splitting due to the two diastereomers), 1.3 (Si^ACH₃), 15.0/15.3/15.7 (Si^AN~CH₃, Si^BN~CH₃, NEt₂ groups at Si^A are diastereotopic), 39.8/40.2 (Si^ANCH₂, NEt₂ groups are diastereotopic), 42.8/42.9 (Si^BNCH₂, splitting due to the two diastereomers), δ_{Si}: see table 1. The two diastereomers occur in a 1:2 molar ratio.

1,4-Dichloro-1,2,3,4-tetrakis(diethylamino)-tetramethyltetrasilane (**2c**)

A solution of 0.3 g (0.5 mmol) **2a** and 0.074 g (0.5 mmol) MeSiCl₃ in 1.5 ml CDCl₃ was stirred overnight and investigated by ²⁹Si NMR spectroscopy. The by-product MeSiCl(NEt₂)₂ showed a ²⁹Si NMR shift of -10.3 ppm.

1,2,3,4-Tetrachloro-1,4-bis-(diethylamino)-tetramethyltetrasilane (**2d**)

The procedure was the same as mentioned for **2c** but the molar ratio was changed from 1:1 to 1:2.

SiMe(SiMe₂Cl)_(3-n)(SiMe₂(Et₂N))_n (**3b-d**) *n* = 1 (diethylaminodimethylsilyl-bis-(chlorodimethylsilyl)-methylsilane, **3b**), *n* = 2 (bis-(diethylaminodimethylsilyl)-chlorodimethylsilyl-methylsilane, **3c**), *n* = 3 (tris-(diethylaminodimethylsilyl)-methylsilane, **3d**) and SiMe(SiMeCl₂)_(3-n)(SiMeCl(Et₂N))_n (SiMe(Et₂N)₂)_m *m* = 0, *n* = 1 (diethylaminochloromethylsilyl)-bis-(dichloromethylsilyl)-methylsilane, **4b**), *m* = 0; *n* = 2 (bis-(diethylaminochloromethylsilyl)-dichloromethylsilyl-methylsilane, **4c**), *m* = 0; *n* = 3 (tris-(diethylaminochloromethylsilyl)-methylsilane, **4d**), *m* = 1; *n* = 2 (bis-(diethylamino)-methylsilyl)-bis-(diethylaminochloromethylsilyl)-methylsilane, **4e**)

The reaction was carried out in the same manner as described for **2a**. In every batch 0.3 g (0.927 mmol) **3a** or 0.4 g (1 mmol) **4a** were used. The molar ratios of tetrasilane to diethylamine 1:2, 1:4, 1:6 and 1:20 were chosen.

Si(SiMe₂Cl)_(4-n)(SiMe₂(Et₂N))_n *n* = 1 (diethylaminodimethylsilyl-tris-(chlorodimethylsilyl)-silane, **5b**), *n* = 2 (bis-(diethylaminodimethylsilyl)-bis-(chlorodimethylsilyl)-silane, **5c**), *n* = 3 (tris-(diethylaminodimethylsilyl)-chlorodimethylsilylsilane, **5d**), *n* = 4 (tetrakis-(diethylaminodimethylsilyl)-silane, **5e**)

Mixtures of 0.3 g (0.75 mol) Si(SiMe₂Cl)₄ and diethylamine

(molar ratios 1:2, 1:4, 1:6, 1:8) in 2 ml CDCl₃ were stirred for 12 h.

Si(SiMe₃)(SiMe₂Cl)_(3-n)(SiMe₂(Et₂N))_n *n* = 1 (diethylaminodimethylsilyl-bis-(chlorodimethylsilyl)-trimethylsilylsilane, **6b**), *n* = 2 (bis-(diethylaminodimethylsilyl)- (chlorodimethylsilyl)-trimethylsilylsilane, **6c**), *n* = 3 (tris-(diethylaminodimethylsilyl)-trimethylsilylsilane, **6d**)

These compounds were identified as by-products during the preparation of Si(SiMe₂Cl)_(4-n)(SiMe₂(Et₂N))_n 1 ≤ *n* ≤ 4 because the starting **5a** contained 25% of **6a**.

Hydrogenations with stannanes

The hydrogenations were carried out with Me₃SnH in toluene as solvent and Ph₃MePI as catalyst (molar ratios **2b** : Me₃SnH: 1:2, 1:4 and 1:6, molar ratio Me₃SnH : Ph₃MePI > 100:1). After reacting for 6 hours toluene and the formed trimethylchlorostannane were removed from the oligosilane mixture *in vacuo* at room temperature.

2e as well as **2g** could be obtained in pure state by hydrogenation with two and six equivalents of Me₃SnH, respectively. The hydrogenation with four equivalents of Me₃SnH yields **2f** in 60% amount beside **2e** and **2g**. **2e-2f** could be identified by ²⁹Si NMR spectroscopy. **2g** was already known from [7]. The found NMR chemical shifts are almost identical.

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