

**Generation and Investigation of Various (Alkylamino)phenylsilyllithium Species – Behaviour in Coupling Reactions with Chlorosilanes**

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Received November 25th, 1997, respectively May 7th, 1998

*Dedicated to Professor G. Marx on the Occasion of his 60th Birthday*

**Abstract.** The partially diethylamino substituted phenylchloromono- and -disilanes  $\text{Cl}_2\text{Ph}(\text{NEt}_2)\text{Si}$  (**2**),  $\text{ClPh}(\text{NEt}_2)_2\text{Si}$  (**3**),  $[\text{ClPh}(\text{NEt}_2)\text{Si}]_2$  (**7**) and  $\text{Cl}(\text{NEt}_2)\text{PhSi-SiPh}(\text{NEt}_2)_2$  (**8**) were synthesized. **3** and **8** are able to react with lithium powder to form the corresponding silyllithium compounds. The resulting species were characterized in solution by  $^{13}\text{C}$  and  $^{29}\text{Si}$

NMR spectroscopy. To prove the expected substitution patterns of the silyllithium compounds some coupling reactions with chlorosilanes were carried out and the resulting new oligosilanes were characterized by means of NMR spectroscopy and MS.

(Dialkylamino)phenyl substituted chlorosilanes are able to form silyllithium compounds, first mentioned by Tamao *et al.* for the monosilyl functions  $(\text{NEt}_2)\text{Ph}_2\text{Si-}$  and  $(\text{NEt}_2)_2\text{PhSi-}$  [1]. Because the generated lithium species have an unusually high stability, compared with other known silyllithium compounds, they are useful synthons for the synthesis of oligosilane structures. The resulting oligomers can be converted into the chlorophenyl analogues by treatment with dry HCl and used for further reactions [2].

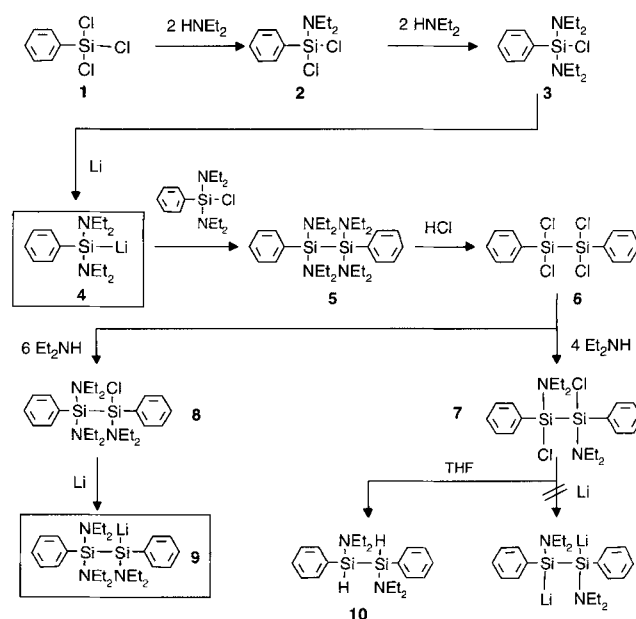
Our aim was to create new silane molecules containing diethylamino, phenyl and chloro substituents and to investigate their reaction with lithium metal.

**Results and Discussion**

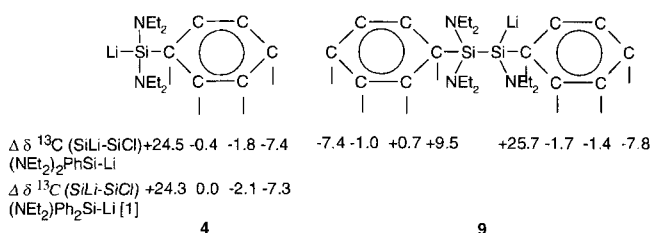
A stepwise substitution of chloro functions for diethylamino can easily be obtained by the reaction of chlorosilanes with  $\text{HNEt}_2$  [4]. Using this procedure the (dialkylamino)-chlorophenylmono- and -disilanes were synthesized from trichlorophenylsilane (**1**) or tetrachloro-1,2-diphenyldisilane (**6**), respectively.

The tetrachloro-1,2-diphenyldisilane (**6**) was generated by coupling of  $(\text{NEt}_2)_2\text{PhSiLi}$  (**4**) with  $\text{ClPh}(\text{NEt}_2)_2\text{Si}$  (**3**) and following treatment with HCl [2] (Scheme 1).

Species actually formed during reacting between lithium metal and chloro(dialkylamino)silanes in solution were investigated by means of  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopy. The reaction of lithium with chloro-bis(diethylamino)phenylsilane (**3**) starts at  $-5 - 0^\circ\text{C}$  after

**Scheme 1** Preparation of Aminophenylsilyldisilanes

15–20 min, indicated by a light green colour of the solution. A change of the colour to dark red occurs and after 4 h the conversion into the lithium compound is complete. At this time one  $^{29}\text{Si}$  resonance at +27.8 ppm ( $T = -5^\circ\text{C}$ ) is observed. In table 2 the  $^{13}\text{C}$  NMR shifts of the phenyl groups are given. The differences between the corresponding carbon atoms in the chloro- and lithium silanes ( $\Delta\delta[\text{SiLi}-\text{SiCl}]$ ) are in accordance with the values found by Tamao *et al.* for  $\text{Ph}_2(\text{NEt}_2)\text{SiLi}$  [3], Scheme 2.

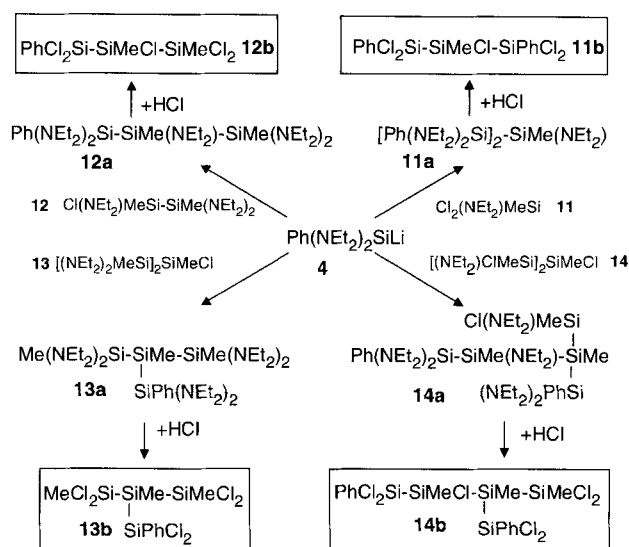


**Scheme 2** Comparison of  $^{13}\text{C}$  NMR shifts of phenyl carbon atoms in chloro- and lithium amino(phenyl)silanes

Coupling reactions of bis(diethylamino)phenylsilyllithium succeeded with 1-chloro-1,2,2-tris-(diethylamino)dimethyldisilane as well as dichloro(diethylamino)methylsilane to form trisilanes. With 2-chlorotetrakis(diethylamino)-1,2,3-trimethyltrisilane and 1,2,3-trichloro-1,3-bis(diethylamino)trimethyltrisilane [5] we got branched structures (Scheme 3). In the last case only two chloro functions were exchanged for bis(diethylamino)phenylsilyl groups. Because of the high boiling points and high solubility the synthesized pentasilane, which occurs in several diastereomers, could not be isolated from the remaining educts. But the conversion of the crude product into the chloro compounds by treatment with HCl yielded after removing of the volatile products *in vacuo* the pure branched chloromethylphenylpentasilane. The found  $^{29}\text{Si}$  NMR shifts of all obtained products are summarized in tables 1–3.

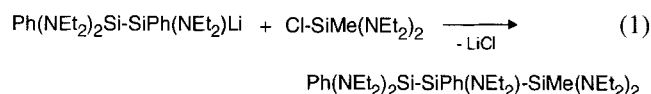
We were not able to synthesize pentakis(diethylamino)-1,2,3-triphenyltrisilane neither from  $\text{Ph}(\text{NEt}_2)_2\text{SiLi}$  and  $\text{Cl}_2\text{Ph}(\text{NEt}_2)\text{Si}$  (the monosubstituted product resulted) nor from  $\text{Ph}(\text{NEt}_2)_2\text{SiLi}$  and  $\text{Cl}(\text{NEt}_2)\text{PhSi}-\text{SiPh}(\text{NEt}_2)_2$  probably due to sterical overcrowding of the desired molecule (Scheme 3).

It takes 1 h at  $-5^\circ\text{C}$  before the reaction of 1-chloro-1,2,2-tris(diethylamino)-1,2-diphenyldisilane with lithium starts. After 4 h at  $0^\circ\text{C}$  the  $^{29}\text{Si}$  NMR spectrum indicates the presence of  $(\text{NEt}_2)_2\text{PhSi}-\text{SiPh}(\text{NEt}_2)\text{Li}$  (80%) and  $(\text{NEt}_2)_2\text{PhSi}-\text{SiPh}(\text{NEt}_2)\text{Cl}$  (20%). The  $^{13}\text{C}$  resonances of both phenyl groups of the disilane are influenced by the exchange of the chlorine substituent for lithium. The  $^{13}\text{C}$  signals which exhibit the largest shift differences compared with the chloro analogues are assigned to the silyllithium unit. The silyllithium forma-



**Scheme 3** Coupling products of  $\text{Ph}(\text{NEt}_2)_2\text{SiLi}$  with chlorosilanes

tion causes a strong downfield shift for the *ipso* carbons (+25.7/+9.46 ppm) and an upfield shift for the *para* carbons (−7.4/−7.8 ppm). The influence on the ortho and meta carbons is very small (about 1 ppm) (Scheme 2). Probably these facts reflect a transfer of the partially negative charge from the silicon atom into both phenyl rings. The coupling reaction with bis(diethylamino)chloromethylsilane resulted in the pentakis(diethylamino)-1,2-diphenyl-3-methyltrisilane (eq. 1).



The coupling with  $\text{ClPh}(\text{NEt}_2)_2\text{Si}$  (3) failed, as already mentioned above.

The reaction of the dichloro compounds  $\text{Cl}_2\text{Ph}(\text{NEt}_2)_2\text{Si}$  as well as  $[\text{Cl}(\text{NEt}_2)\text{PhSi}]_2$  with Li powder starts immediately at  $0^\circ\text{C}$  but it takes about 20–30 min to start at  $-65^\circ\text{C}$ . The process was monitored by means of  $^{29}\text{Si}$  NMR at  $-5^\circ\text{C}$ . In the case of the reaction between lithium and disilane 7 over a period of about 2.5 h the signal at  $-8.3$  ppm, assigned to one diastereomer of 7 decreased and a new resonance at  $-19.2$  ppm appeared. The other diastereomer ( $-10.8$  ppm) which was unchanged, disappeared after warming up to room temperature. Because of this specific reaction progress we assume, that one diastereomer is more reactive than the other one which did not react with lithium at temperatures below  $0^\circ\text{C}$ . The  $^{29}\text{Si}$  NMR spectrum at  $20^\circ\text{C}$  indicated only one Si-species at  $-19.2$  ppm but this new signal did not belong to the expected twofold lithiated disilane. Instead, the hydrodisilane (10) was formed by H abstraction from the solvent. This can be deduced

from the  $^1\text{H}$  coupled  $^{29}\text{Si}$  NMR spectrum which exhibits a doublet due to  $^1J_{\text{SiH}}$  as well as from the  $^{13}\text{C}$  NMR spectrum which shows no characteristic resonance for  $\text{PhSiLi}$  species above 135 ppm.

Reaction of  $\text{Cl}_2\text{Ph}(\text{NET}_2)\text{Si}$  with lithium in THF leads to a complex mixture of several Si containing species. In this case the primarily formed Si–Li species seemed to be very unstable and we were not able to give an unambiguous assignment of the found  $^{29}\text{Si}$  NMR shifts.

## Experimental

All  $^{29}\text{Si}$  NMR spectra were recorded on a Bruker DPX 400 using the IGATED pulse sequence with TMS as internal standard.

**Table 1** NMR spectroscopic data of amino(phenyl)mono- and -disilanes

compound	$\delta_{\text{Si}}^{\text{A}}$ (ppm)	$\delta_{\text{Si}}^{\text{B}}$ (ppm)
$[\text{Ph}(\text{NET}_2)_2\text{Si}]_2$ ( <b>5</b> )	–16,4	
$\text{Ph}(\text{NET}_2)_2\text{Si}^{\text{A}}\text{–Si}^{\text{B}}\text{Ph}(\text{NET}_2)\text{Cl}$ ( <b>8</b> )	–18,9 ( $^1J_{\text{Si–Si}} = 150,3\text{Hz}$ )	–5,0
$[\text{Ph}(\text{NET}_2)\text{ClSi}]_2$ ( <b>7</b> )	–8,38/–10,62 <sup>a)</sup>	
$[\text{PhCl}_2\text{Si}]_2$ ( <b>6</b> )	1,98	
$\text{Ph}(\text{NET}_2)_2\text{SiLi}$ ( <b>4</b> )	27,9	
$\text{Ph}(\text{NET}_2)_2\text{Si}^{\text{A}}\text{–Si}^{\text{B}}\text{Ph}(\text{NET}_2)\text{Li}$ ( <b>9</b> )	–5,0	4,0

<sup>a)</sup> means two diastereomers

MS spectra were recorded on a HEWLETT PACKARD 5971 (ionization energy: 70 eV, column: 30 m × 0.25 mm × 0.25  $\mu\text{m}$ , phenylmethylpolysiloxane). The HR MS spectra were recorded on a Finnigan MAT 212.

Because of the undesired formation of  $\text{SiC}$  and  $\text{Si}_3\text{N}_4$  elemental analysis of silanes did not give reproducible results using the available technical equipment. For this reason information about compound composition is based on MS and NMR spectra mainly.

**Table 2**  $^{13}\text{C}$  NMR data of the phenyl substituents in chloro- and lithiumsilanes ( $\delta/\text{ppm}$ )

compound	$C_{\text{ipso}}$	$C_{\text{ortho}}$	$C_{\text{meta}}$	$C_{\text{para}}$
$\text{ClPh}(\text{NET}_2)_2\text{Si}$ ( <b>3</b> )	134.8	134.8	127.8	130.0
$\text{Ph}(\text{NET}_2)\text{ClSi–Si}(\text{NET}_2)_2\text{Ph}$ ( <b>8</b> )	136.7/138.2	135.0/135.3	127.5/127.6	129.1/129.5
$[\text{Ph}(\text{NET}_2)\text{ClSi}]_2$ ( <b>7</b> )	133.8/133.76	135.02/134.97	127.9	130.3/130.4
$\text{Ph}(\text{NET}_2)_2\text{SiLi}$ ( <b>4</b> )	159.3	134.4	126.0	122.6
$\text{Ph}(\text{NET}_2)_2\text{Si–SiPh}(\text{NET}_2)\text{Li}$ ( <b>9</b> )	147.7/162.4	133.3/136.0	126.1/126.6	121.7

**Table 3**  $^{29}\text{Si}$  NMR shifts of coupling products (shifts in ppm, coupling constants in Hz)

X compound	$\text{NET}_2$					Cl $\delta_{\text{Si}}^{\text{A}}$	$\delta_{\text{Si}}^{\text{B}}$	$\delta_{\text{Si}}^{\text{C}}$	$\delta_{\text{Si}}^{\text{D}}$	$\delta_{\text{Si}}^{\text{E}}$
	$\delta_{\text{Si}}^{\text{A}}$	$\delta_{\text{Si}}^{\text{B}}$	$\delta_{\text{Si}}^{\text{C}}$	$\delta_{\text{Si}}^{\text{D}}$	$\delta_{\text{Si}}^{\text{E}}$					
$\text{PhX}_2\text{Si}^{\text{A}}\text{–Si}^{\text{B}}\text{MeX–Si}^{\text{C}}\text{MeX}_2$ ( <b>12a/b</b> )	–10.4	–19.4	–7.8	$^1J_{\text{AB}}: 106$	$^1J_{\text{BC}}: 108$	8.7	–5.0	23.7		
$[\text{PhX}_2\text{Si}^{\text{A}}]_2\text{Si}^{\text{B}}\text{MeX}$ ( <b>11a/b</b> )	–11.2	–18.6				8.7	–4.9			
$\text{PhX}_2\text{Si}^{\text{A}}\text{–Si}^{\text{B}}\text{PhX–Si}^{\text{C}}\text{MeX}_2$ ( <b>16a</b> )	–12.3	–21.5	–6.5							
$[\text{MeX}_2\text{Si}^{\text{A}}]_2\text{Si}^{\text{B}}\text{Me–Si}^{\text{C}}\text{PhX}_2$ ( <b>13a/b</b> )	3.8	–90.4	0.2			30.6	–63.2	16.5		
$\text{PhX}_2\text{Si}^{\text{A}}\text{–Si}^{\text{B}}\text{MeX–Si}^{\text{C}}\text{Me}(\text{Si}^{\text{D}}\text{MeClX})\text{–Si}^{\text{E}}\text{PhX}_2$ ( <b>14a/b</b> )	–7.6 <sup>a)</sup>	–11.8 <sup>a)</sup>	–79.8 <sup>a)</sup>	17.6 <sup>a)</sup>	–4.0 <sup>a)</sup>	9.4	4.6		31.6	17.3
	–6.9 <sup>a)</sup>	–11.5 <sup>a)</sup>	–77.7 <sup>a)</sup>	17.8 <sup>a)</sup>	–3.5 <sup>a)</sup>			–62.7		
	–6.7 <sup>a)</sup>	–10.7 <sup>a)</sup>	–76.8 <sup>a)</sup>	19.6 <sup>a)</sup>	–3.3 <sup>a)</sup>					
	–6.1 <sup>a)</sup>	–10.3 <sup>a)</sup>	–76.6 <sup>a)</sup>	20.6 <sup>a)</sup>	–2.6 <sup>a)</sup>					

<sup>a)</sup> several diastereomers caused by 3 asymmetric Si atoms

## Monosilanes

The same procedure was used for all monosilanes:  $\text{HNET}_2$  was added to a solution of the chlorosilane in *n*-hexane under stirring. After 48 h the precipitated  $\text{HNET}_2\text{–HCl}$  was filtered off and the solvent evaporated *in vacuo*. The residue was distilled under reduced pressure.

### (Diethylamino)dichloromethylsilane (**11**)

62 g (0.85 mol) of  $\text{HNET}_2$  were added to 63 g (0.42 mol) of trichloro(methyl)silane and yielded 31 g, 40% of  $(\text{NET}_2)\text{MeSiCl}_2$ . *Kp*: 27 °C/0.2 kPa. –  $^{29}\text{Si}$  NMR:  $\delta/\text{ppm} = -2.4$ . –  $^1\text{H}$  NMR:  $\delta/\text{ppm} = 0.77$  (Si–CH<sub>3</sub>), 1.08 T (CH<sub>3</sub>~N), 2.98Q (CH<sub>2</sub>~N). –  $^{13}\text{C}$  NMR:  $\delta/\text{ppm} = 4.2$  (Si–CH<sub>3</sub>), 14.8 (CH<sub>3</sub>~N), 39.4 (CH<sub>2</sub>~N).

### Bis(diethylamino)chloromethylsilane (**16**)

181 g (2.5 mol)  $\text{HNET}_2$  were added to 132 g (0.62 mol) trichloromethylsilane and yielded 85.5 g, 48%  $\text{Cl}(\text{NET}_2)_2\text{MeSi}$ . –  $^{29}\text{Si}$  NMR:  $\delta/\text{ppm} = -10.4$ . –  $^1\text{H}$  NMR:  $\delta/\text{ppm} = 0.40$  (Si–CH<sub>3</sub>), 1.03 T (CH<sub>3</sub>~N), 2.90 Q (CH<sub>2</sub>~N). –  $^{13}\text{C}$  NMR:  $\delta/\text{ppm} = 1.39$  (Si–CH<sub>3</sub>), 14.96 (CH<sub>3</sub>~N), 38.9 (CH<sub>2</sub>~N).

### Diethylaminodichlorophenylsilane (**2**)

42 g (0.58 mol)  $\text{HNET}_2$  were added to 59 g (0.28 mol) trichlorophenylsilane **1** and yielded 44.5 g, 64%  $\text{Cl}_2(\text{NET}_2)\text{PhSi}$ . *Kp* 130 °C/0.3 kPa. –  $^1\text{H}$  NMR:  $\delta/\text{ppm} = 1.05$  t (CH<sub>3</sub>~N), 3.00 q (CH<sub>2</sub>~N), 7.4–7.49, 7.77–7.79 M (Ph). –  $^{13}\text{C}$  NMR:  $\delta/\text{ppm} = 14.7$  (CH<sub>3</sub>~N), 39.4 (CH<sub>2</sub>~N), 128.2, 131.49, 134.26 (Ph).

### Bis(diethylamino)chlorophenylsilane (**3**)

83 g (1.14 mol)  $\text{HNET}_2$  were added to 59 g (0.28 mol) trichlorophenylsilane (**1**) and yielded 48 g, 60%  $\text{Cl}(\text{NET}_2)_2\text{PhSi}$ . *Kp* 130 °C/0.3 kPa. –  $^1\text{H}$  NMR:  $\delta/\text{ppm} = 1.01$  T (CH<sub>3</sub>~N), 2.92 q (CH<sub>2</sub>~N), 7.36–7.41, 7.69–7.70 (Ph). –  $^{13}\text{C}$  NMR:  $\delta/\text{ppm} = 14.5$  (CH<sub>3</sub>~N), 38.7 (CH<sub>2</sub>~N), 127.8, 130.0, 134.83 (Ph).

### Aminodisilanes

#### *Tetrakis(diethylamino)-1,2-diphenyldisilane (5)*

7 g (0.0246 mol)  $\text{Cl}(\text{NEt}_2)_2\text{PhSi}$  (**3**) were added to a suspension of 0.85 g (0.123 mol) lithium in 30 ml THF at 0 °C. After 4 h the dark red solution was filtered and the silyllithium solution added to 7 g (0.0246 mol) **3** in THF. The mixture was stirred over night, and the THF was exchanged by the same volume of *n*-hexane. The LiCl was separated and the solvent removed *in vacuo* until at -18 °C the crystallisation of **5** started. The crystal fractions yielded 7.5 g, 61% of the pure compound. -  $^1\text{H}$  NMR:  $\delta/\text{ppm}$  = 0.92 ( $\text{CH}_3\sim\text{N}$ ); 2.99 ( $\text{CH}_2\sim\text{N}$ ); 7.18–7.25, 7.47/7.49 (Ph). -  $^{13}\text{C}$  NMR:  $\delta/\text{ppm}$  = 14.0 ( $\text{CH}_3\sim\text{N}$ ) 39.3 ( $\text{CH}_2\sim\text{N}$ ); 127.0, 128.2, 135.4, 141.5 (Ph). - MS:  $\text{C}_{28}\text{H}_{50}\text{N}_4\text{Si}_2$  found (calcd.): 497.9 (498.3)

#### *1,2-Bis(diethylamino)-1,2-dichlorodiphenyldisilane (7)*

5 g (0.068 mol)  $\text{HNEt}_2$  were added to a solution of 4.9 g (0.014 mol)  $[\text{Cl}_2\text{PhSi}]_2$  (**6**) in *n*-hexane. After stirring for 24 h the precipitated  $\text{HNEt}_2\cdot\text{HCl}$  was filtered off and the solvent was evaporated. Yield 4.1 g, 68.9%. -  $^1\text{H}$  NMR:  $\delta/\text{ppm}$  = 0.90–0.95 ( $\text{CH}_3\sim\text{N}$ ); 2.84–2.90, 2.96–3.0 ( $\text{CH}_2\sim\text{N}$ ); 7.40–7.47, 7.72–7.78 (Ph). -  $^{13}\text{C}$  NMR:  $\delta/\text{ppm}$  = 14.1/14.3 ( $\text{CH}_3\sim\text{N}$ ), 40.2 ( $\text{CH}_2\sim\text{N}$ ), 127.9 sh, 130.3/130.4, 133.81/133.76, 134.97/135.02(Ph).

#### *1-Chloro-1,2,2-tris(diethylamino)diphenyldisilane (8)*

The procedure was the same as described for **7** but the molar ratio silane: $\text{HNEt}_2$  was changed to 1:6. yield 65%. -  $^1\text{H}$  NMR:  $\delta/\text{ppm}$  = 0.88–0.96, 2.91–3.0, 7.27–7.30, 7.63–7.67 (Ph). -  $^{13}\text{C}$  NMR: 13.8/14.2/14.27 ( $\text{CH}_3\sim\text{N}$ ); 39.0/39.5/39.8 ( $\text{CH}_2\sim\text{N}$ ); 127.5/127.6, 129.1/129.5, 135.0/135.3, 136.7/138.2 (Ph). - MS:  $\text{C}_{24}\text{H}_{40}\text{ClN}_3\text{Si}_2$  (calcd.) found: (461.2) 461.2 ( $\text{M}^+$ ), 249 ( $\text{Ph}(\text{NEt}_2)_2\text{Si}$ ).

### Silyllithium Derivatives

#### *Bis(diethylamino)phenylsilyllithium (4)*

To a mixture of 0.24 g (0.035 mol) lithium in 25 ml THF were added 1 g (3.5 mmol)  $\text{Cl}(\text{NEt}_2)_2\text{PhSi}$  (**3**) at 0 °C. After 5 min the start of the reaction was indicated by a greenish coloured solution. After stirring for 4 h the lithiation was completed and the dark red solution could be separated from the lithium for using in further reactions.

#### *1,1,2-Tris(diethylamino)-1,2-diphenyldisilyllithium (9)*

0.46 g (1 mmol) **8** were added to a mixture of 0.42 g (0.06 mol) lithium in 10 ml THF. The reaction start was observed after stirring for 20–30 min at 0 °C by the change of the colour. The  $^{29}\text{Si}$  NMR investigation of the silyllithium solution after a reaction time of 6 h resulted in 80% lithium compound and 20% starting compound.

#### *$^{29}\text{Si}$ -NMR Investigations of the reaction of 1,2-bis(diethylamino)-1,2-dichlorodiphenyldisilane (7) with lithium*

The NMR tube was filled with 0.5 g (1.17 mmol) **7** and 0.07 g (0.01 mol) lithium in 5 ml THF. After 30 min the first  $^{29}\text{Si}$  NMR measurement was started (at -5 °C) during the period

of 30 min. Then a new experiment was performed for another 30 min period. This procedure was repeated three times. The last spectrum was registered after warming up at room temperature.

### Oligosilanes

The oligosilanes were synthesized by salt elimination of a silyllithium species with chlorosilanes as already described for the preparation of **5**.

### Coupling reactions

#### *Pentakis(diethylamino)-1-phenyl-2,3-dimethyltrisilane (12a)*

4.6 g (16 mmol) **3** were converted into the silyllithium species **4** as described and added to 5 g (14.8 mmol)  $\text{ClNEt}_2\text{MeSi-SiMe}(\text{NEt}_2)_2$  (**12**) [4]. The crude product was warmed up to 110 °C/0.1 kPa to remove the volatiles. -  $^1\text{H}$  NMR:  $\delta/\text{ppm}$  = 0.51, 0.04 (Si-Me), 0.8–1.3 ( $\text{N}\sim\text{CH}_3$ ), 2.85–2.89 ( $\text{N}\sim\text{CH}_2$ ), 7.2–7.6 (Ph). - MS:  $\text{C}_{28}\text{H}_{61}\text{N}_5\text{Si}_3$  (calcd.) found: (551.4) 551.3 ( $\text{M}^+$ ), 364 ( $\text{Si}_2(\text{NEt}_2)_3\text{PhMe}$ ), 249 ( $\text{Si}(\text{NEt}_2)_2\text{Ph}$ ), 187 ( $\text{Si}(\text{NEt}_2)_2\text{Me}$ ).

#### *Pentakis(diethylamino)-1,3-diphenyl-2-methyltrisilane (11a)*

A silyllithium solution made from 7 g (24.6 mmol) **3** was added to 7.4 mmol **11** in THF. The remaining educt was distilled off *in vacuo* (up to 0.1 kPa/110 °C). Yield 45%. -  $^1\text{H}$  NMR:  $\delta/\text{ppm}$  = 0.37 (Si-Me), 0.94–1.05 ( $\text{N}\sim\text{CH}_3$ ), 2.84–2.98 ( $\text{N}\sim\text{CH}_2$ ), 7.24–7.27, 7.56–7.59 (Ph). -  $^{13}\text{C}$  NMR:  $\delta/\text{ppm}$  = 1.2 (Si-Me), 13.9, 14.1 ( $\text{N}\sim\text{CH}_3$ ), 39.3, 39.5 ( $\text{N}\sim\text{CH}_2$ ), 127.1, 128.2, 135.8, 140.4 (Ph). - HRMS:  $\text{C}_{33}\text{H}_{63}\text{N}_5\text{Si}_3$  (calc.) found: (613.4391) 613.432

#### *Pentakis(diethylamino)-1,2-diphenyl-3-methyltrisilane (16a)*

A silyllithium solution in THF made from 0.46 g (1 mmol) **8** in THF was added to 0.18 g (0.8 mmol) **16**. - HRMS:  $\text{C}_{33}\text{H}_{63}\text{N}_5\text{Si}_3$  (calcd.) found: (613.4391) 613.438

#### *Bis[bis(diethylamino)methylsilyl][bis(diethylamino)phenylsilyl]methylsilane (13a)*

A solution of **4** in THF (prepared from 20 mmol **3** and 0.17 mol Li) was dropped into a solution of 5.3 mmol  $\text{SiClMe}(\text{Si}(\text{NEt}_2)_2\text{Me})_2$  (**13**) [5] and yielded 70% pure product. -  $^1\text{H}$  NMR:  $\delta/\text{ppm}$  = 0.24, 0.44 (Si-Me), 1.0–1.2 ( $\text{N}\sim\text{CH}_3$ ), 3.0–3.2 ( $\text{N}\sim\text{CH}_2$ ), 7.2–7.8 (Ph). - MS:  $\text{C}_{33}\text{H}_{74}\text{N}_6\text{Si}_4$  (calcd.) found: (666.5) 666.4 ( $\text{M}^+$ ), 593 ( $\text{M}^+\text{-NEt}_2$ ), 249 ( $\text{Si}(\text{NEt}_2)_2\text{Ph}$ ), 187 ( $\text{Si}(\text{NEt}_2)_2\text{Me}$ ), 178 ( $\text{Si}(\text{NEt}_2)\text{Ph}$ ), 116 ( $\text{Si}(\text{NEt}_2)\text{Me}$ ).

#### *1-Chloro-1,3,4,4-tetrakis(diethylamino)-2-[bis(diethylamino)phenylsilyl]-1,2,3-trimethyl-4-phenyltetrasilane (14a)*

A silyllithium solution was prepared from 0.4 g (0.057 mol) Li and 1.68 g (5.9 mmol) **3** in THF at -70 °C. After stirring for 4 h the resulting solution was separated from the lithium and dropped into a solution of 0.5 g (1.32 mmol) 1,3-bis(diethylamino)-1,2,3-trichlorotrimethyltrisilane (**14**) in THF at -70 °C. The solution was stirred and warmed up over night. The solvent THF was exchanged by *n*-hexane, and the precipitated LiCl was filtered off. The residue (1.3 g, 96% yield) was characterized by means of  $^{29}\text{Si}$  NMR. Because of the great number of resonances 1 g of the product was converted

into the chlorine derivative  $\text{Cl}_2\text{MeSi-SiMe}(\text{SiPhCl}_2)\text{-SiMeCl-SiCl}_2\text{Ph}$  (**14b**) by treatment with dry HCl to prove the constitution as a branched pentasilane.

### Chlorination of Some Oligosilanes

The same procedure as described for **6** was used for all chlorination reactions. The colourless products were obtained in 70–80% yield.

#### *Tetrachloro-1,2-diphenyldisilane (6)*

Dry HCl was bubbled through a solution of 7.5 g (0.015 mol) **5** in 50 ml  $\text{CCl}_4$ . The solution grew warm and became cloudy. The reaction was completed when the precipitate was dissolved, and two phases were obtained. After evaporation of the solvent of the lower phase a white solid remained which could be purified by treatment with *n*-hexane and crystallisation of the clear solution at  $-18^\circ\text{C}$ . yield 4.3 g, 81%. –  $^1\text{H NMR}$ :  $\delta/\text{ppm} = 7.24/7.27, 7.46/7.54, 7.72/7.78$  (Ph). –  $^{13}\text{C NMR}$ :  $\delta/\text{ppm} = 128.6, 132.3, 134.0$  (Ph).

#### *Pentachloro-1-phenyl-2,3-dimethyltrisilane (12b)*

was prepared by chlorination of **12a**.  $\delta/\text{ppm} = ^1\text{H NMR}$ :  $\delta/\text{ppm} = 0.92$  (Si–Me), 7.3, 7.6 (Ph). –  $^{13}\text{C NMR}$ :  $\delta/\text{ppm} = -2.2, 6.6$  (Si–Me), 128.6, 132.4, 133.7 (Ph).

#### *Pentachloro-1,3-diphenyl-2-methyltrisilane (11b)*

was prepared by chlorination of **11a**. –  $^1\text{H NMR}$ :  $\delta/\text{ppm} = 0.86$  (Si–Me), 7.31–7.47, 7.61, 7.71 (Ph). –  $^{13}\text{C NMR}$ :  $\delta/\text{ppm} = -1.8$  (Si–Me), 128.5, 128.6, 132.0, 132.3, 133.5, 133.8 (Ph).

#### *Bis(dichloromethylsilyl)(dichlorophenylsilyl)methylsilane (13b)*

was prepared by chlorination of **13a**. –  $^1\text{H NMR}$ :  $\delta/\text{ppm} = 0.55, 0.85$  (Si–Me), 7.2–7.8 (Ph).

#### *Pentachloro-2-(dichlorophenylsilyl)-1,2,3-trimethyl-4-phenyltetrasilane (14b)*

was prepared by chlorination of **14a**. –  $^1\text{H NMR}$ :  $\delta/\text{ppm} = 0.53, 0.86, 0.86$  (Si–Me), 7.40–7.53, 7.67–7.78 (Ph). –  $^{13}\text{C NMR}$ :  $\delta/\text{ppm} = -11.9, 1.0, 9.4$  (Si–Me), 128.3–128.5, 131.6–133.86 (Ph).

### References

- [1] K. Tamao, A. Kawachi, Y. Nakagawa, Y. Ito, *J. Organomet. Chem.* **1994**, *473*, 29
- [2] K. Trommer, U. Herzog, G. Roewer, *J. Organomet. Chem.* **1997**, *540*, 119
- [3] K. Tamao, A. Kawachi, Y. Ito, "Progress in Organosilicon Chemistry", Gordon and Beach 1995, p.209
- [4] K. Trommer, G. Roewer, E. Brendler, *J. Prakt. Chem.* **1997**, *339*, 82
- [5] U. Herzog, K. Trommer, G. Roewer, *J. Organomet. Chem.*, in press

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