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Synthesis of di- and trisilanes with potentially chelating substituents

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Abstract

Silylenes **2** or **4**, generated by thermolysis of cyclotrisilanes **1** and **3**, were inserted into the Si–Cl or Si–H bonds of monosilanes to yield a variety of disilanes, which can be further functionalized subsequently. In a few cases, trisilanes are accessible by the reaction of **1** with disilanes. The reaction of a metalated silane with a chlorosilane is an alternative method for the formation of Si–Si bonds, which turned out to be especially useful for the synthesis of bulkily substituted disilanes. Some of the new dichlorodi- and trisilanes themselves serve as thermal precursors of silylenes **2** or **4**, the extrusion of which can be catalyzed by **1** or **3** in certain cases. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Silylenes; Oligosilanes; Halosilanes; Silicon–silicon bond formation

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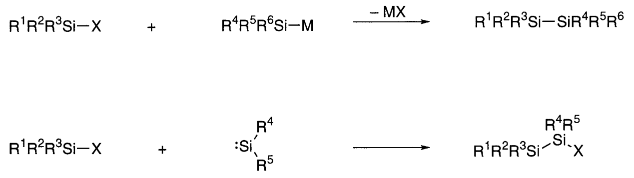
1. Introduction

Two principal reaction pathways are available for the formation of Si–Si bonds (Scheme 1). The nucleophilic attack of a metalated silane on a silicon center, which bears a leaving group, or, alternatively, the insertion of a silylene into a Si–X bond (X=H or Hal). The first method in particular, a Wurtz-type coupling reaction, was used repeatedly for the synthesis of disilanes.

Reacting a monohalogenated silane with metals such as Li, Na, or Mg gives rise—via a metalated silane as crucial intermediate—to the formation of symmetrically substituted disilanes [1]. In contrast, geminally dihalogenated silanes do not serve as synthetically useful starting material for disilanes. When treated with metals, they are transformed to either polysilanes [2] or, in the case of dihalosiloles, to silole dianions [3]; 1,2-dihalodisilanes could be isolated from the reaction mixture only in a few cases [4]. Unsymmetrically substituted disilanes are in general synthesized by reaction of a preformed metalated silane with a halosilane [5], although it was reported that treatment of a mixture of two different halosilanes with lithium may result in the formation of unsymmetrical disilanes in good yield [6]. The alternative, aforementioned method to create a Si–Si bond, the insertion of a silylene into a Si–H bond, proceeds extremely fast [7] and thus silanes serve frequently as trapping agents for short-lived silylenes [8]. Contrasting the wealth of silylene insertion reactions into Si–H bonds, only few examples of a insertion into Si–Hal bonds are known [9]. We have used both methods, i.e. silylene insertion and nucleophilic displacement, for the synthesis of di- and trisilanes, which bear the potentially chelating 2-(dimethylaminomethyl)phenyl substituent [9c,10], and want to report here the results of these studies.



Scheme 1. Formation of Si–Si bond; M = Li, Na, MgHal; X = H, Hal.

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Table 1
Synthesis of disilanes by silylene insertion; Ar = 2-(Me_2NCH_2)C_6H_4; Mes = 2,4,6-$Me_3C_6H_2$

Entry	Silylene precursor	Silane	Disilane(s)	Yield (%)
1	**1**	Me_3SiCl (**5**)	$ClAr_2Si–SiMe_3$ (**6a**)	54
2	**1**	Me_2SiCl_2 (**7a**)	$ClAr_2Si–SiMe_2Cl$ (**8a**)	95
3	**1**	Me_2SiHCl (**7b**)	$Har_2Si–SiMe_2Cl$ (**8b**)	78
			$ClAr_2Si–SiMe_2H$ (**8c**) [a]	
4	**1**	Ph_2SiH_2 (**9a**)	$HAr_2Si–SiPh_2H$ (**10a**)	78
5	**1**	Ph_2SiCl_2 (**9b**)	$ClAr_2Si–SiPh_2Cl$ (**10b**)	78
6	**1**	Ph_2SiHCl (**9c**)	$HAr_2Si–SiPh_2Cl$ (**10c**)	83
			$ClAr_2Si–SiPh_2H$ (**10d**) [b]	
7	**1**	$(4\text{-}MeC_6H_4)_2SiCl_2$ (**11**)	$ClAr_2Si–Si(4\text{-}MeC_6H_4)_2Cl$ (**12a**)	44
8	**1**	$(4\text{-}ClC_6H_4)_2SiCl_2$ (**13**)	$ClAr_2Si–Si(4\text{-}ClC_6H_4)_2Cl$ (**14a**)	40
9	**1**	$(2\text{-}EtC_6H_4)_2SiCl_2$ (**15**)	$ClAr_2Si–Si(2\text{-}EtC_6H_4)_2Cl$ (**16**)	88
10	**1**	Ar_2SiH_2 (**17a**)	$HAr_2Si–SiAr_2H$ [12] (**18a**)	96
11	**1**	Ar_2SiCl_2 (**17b**)	$ClAr_2Si–SiAr_2Cl$ (**18b**)	68
12	**1**	Ar_2SiHCl (**17c**)	$HAr_2Si–SiAr_2Cl$ (**18c**)	97
13	**1**	**19**	**20**	75
14	**1**	**21**	**22**	98
15	**1**	$PhSiCl_3$ (**23**)	$ClAr_2Si–SiPhCl_2$ (**24a**)	85
16	**3**	Ph_2SiCl_2 (**9b**)	$ClAr(Mes)Si–SiPh_2Cl$ (**26b**)	80
17	**3**	$Ar(Mes)SiCl_2$ (**27b**)	$ClAr(Mes)Si–SiAr(Mes)Cl$ (**28b**)	38
18	**3**	**21**	**29**	35
19	**3**	$MesSiCl_3$ (**30**)	$ClAr(Mes)Si–SiMesCl_2$ (**31**)	82
20	**1**	Mes_2SiH_2 (**32a**)	$HAr_2Si–SiMes_2H$ (**33a**)	traces

[a] **8b**:**8c** = 3:1.

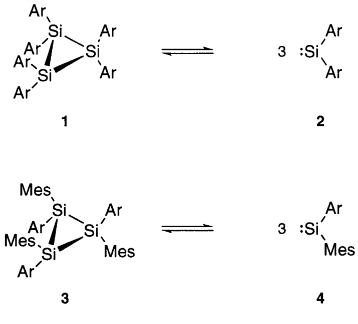
[b] **10c**:**10d** = 2:1.

2. Results and Discussion

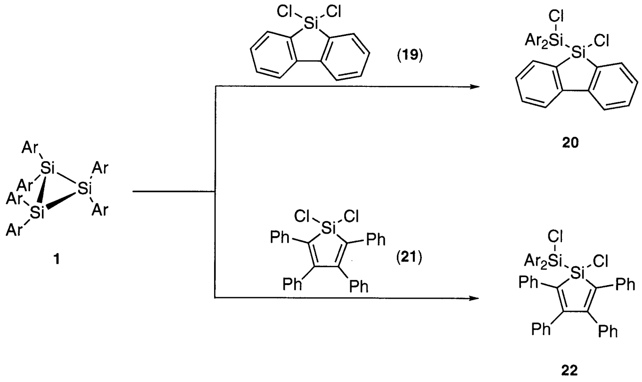
2.1. Formation of disilanes by silylene insertion

The insertion reactions of silylenes into Si–H and Si–Cl bonds of a variety of silanes were investigated (Table 1) making extensive use of cyclotrisilanes **1** and **3** as thermal precursors of silylenes **2** and **4** (Scheme 2) [9c,11]. When **1** was heated at 50 °C with trimethylchlorosilane (**5**) in benzene, chlorodisilane **6a** was formed quantitatively and could be isolated in 54% yield (entry 1). Using dimethyldichlorosilane (**7a**) as starting material, the vicinally dihalogenated disilane **8a** was obtained as sole product; no formation of a trisilane was observed, i.e. no subsequent insertion of silylene **2** into a Si–Cl bond of initially formed **8a** did occur under the reaction conditions employed (entry 2). With dimethylmonochlorosilane (**7b**) as trapping agent, a 3:1 mixture of regioisomeres **8b** and **8c** was formed indicating that silylene **2** inserts preferentially into the Si–H bond of the chlorosilane (entry 3). The reaction of cyclotrisilane **1** with diphenylsubstituted silanes **9a**–**c** proceeded analogously (Table 1, entries 4, 5, 6), again the insertion of silylene **2** in the Si–H bond of Ph_2SiHCl (**9c**) being preferred to that into the Si–Cl bond. When treating **1** with diarylsilanes **11**, **13**, **15**, and **17a**–**c**, in which the aromatic rings bear a *para*- or *ortho*-substituent, the corresponding disilanes **12a**, **14a**, **16**, **18a** [12], **18b**, and **18c** were obtained in reasonable to good yields (entries 7–12). Similarly, 1,2-dichlorodisilanes **20** and **22** could be synthesized by insertion of silylene **2** into a Si–Cl bond of dichlorosiloles **19** or **21** (entries 13 and 14; Scheme 3). Using trichlorosilane **23** as substrate clean formation of trichlorodisilane **24a** was observed (entry 15). However, reaction of **1** with highly coordinated trichlorosilane $ArSiCl_3$ (Ar = 2-(Me_2NCH_2)C_6H_4; **25**) did not give the corresponding trichlorodisilane. Instead, dichlorosilane **17b** was obtained quantitatively besides a solid, which is insoluble in all common solvents.

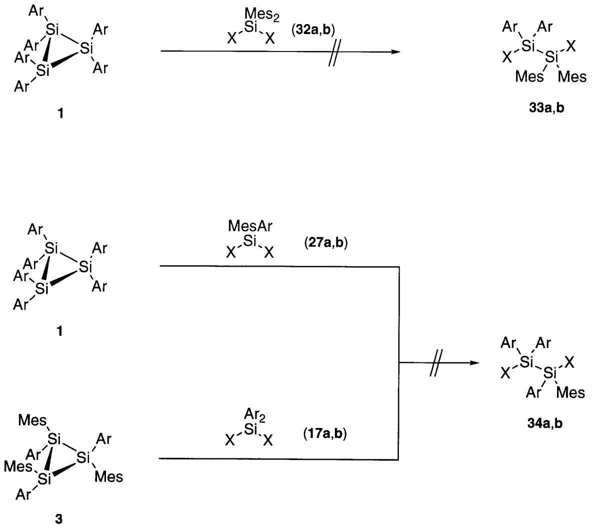
The reactions of thermally more stable cyclotrisilane **3** with silanes are less well investigated. However, treatment of **3** with three equivalents of dichlorosilanes **9b**, **27b**, or **21** at temperatures between 80 and 90 °C allowed the synthesis of the corresponding 1,2-dichlorodisilanes **26b**, **28b** [9c], or **29** (entries 16–18). With



Scheme 2. Cyclotrisilanes as silylene precursors; Ar = 2-(Me_2NCH_2)C_6H_4; Mes = 2,4,6-$Me_3C_6H_2$.



Scheme 3. Reaction of **1** with dichlorosiloles; Ar = 2-(Me_2NCH_2)-C_6H_4.



Scheme 4. Failed syntheses of disilanes; **17a**, **27a**, **32a**, **33a**, **34a**: X = H; **17b**, **27b**, **32b**, **33b**, **34b**: X = Cl; Ar = 2-(Me_2NCH_2)C_6H_4; Mes = 2,4,6-$Me_3C_6H_2$.

trichlorosilane **30** as starting material, the insertion product **31** was obtained in good yield (entry 19).

Albeit the reaction of cyclotrisilanes **1** and **3** with monosilanes has proven to be a quite generally applicable procedure for the synthesis of disilanes, some attempts to obtain disilanes by this method were without success: Thus, e.g., reaction of **1** with bulkily substituted dimesityldichlorosilane (**32b**) did not yield the corresponding 1,2-dichlorodisilane **33b** (Scheme 4, top). Instead, a complex product mixture was formed which contained, besides a variety of unidentified compounds, some starting material **32b** as well as minor amounts of dichlorosilane **17b** and dichlorodisilane **18b**. Using sterically less demanding dimesitylsilane (**32a**) as substrate was not successful either, only traces of the expected insertion product **33a** could be identified by means of ^{1}H-NMR spectroscopy in the reaction mixture. Attempts to synthesize 1,2-dichlorodisilane **34b**, either by treatment of **1** with three equivalents of **27b** or alternatively by treatment of **3** with three equivalents of **17b**, failed (Scheme 4, bottom). In both cases, the respective cyclotrisilane was totally consumed under formation of a complex product mixture consisting of 1,2-dichlorodisilane **18b** as major product besides minor amounts of dichlorosilanes **27b** and **17b** as well as various unidentified compounds. Similarly, reaction of cyclotrisilane **1** with silane **27a** or, alternatively, of **3** with silane **17a** did not yield disilane **34a**.

2.2. Formation of trisilanes by silylene insertion

It was shown (vide supra) that reaction of cyclotrisilanes **1** or **3** with different monosilanes gives exclusively disilanes. Competing formation of trisilanes, which in principle could arise from insertion of the silylene into a Si–H or Si–Cl bond of the newly formed disilane, was never observed under the reaction conditions employed. This selectivity implies that the reaction of the silylenes **2** and **4** with monosilanes is appreciably faster than that with disilanes. However, the synthesis of trisilanes from disilanes and cyclotrisilanes **1** or **3** as silylene precursors proved to be possible using the appropriate stoichiometry of starting materials and, in most cases, performing the reaction at higher temperatures (Table 2). Thus, e.g. treatment of cyclotrisilane **1** with three equivalents of disilane **35** yielded trisilane **36** (entry 1). With an excess of **1** no further insertion of a silylene under formation of a tetrasilane occurred, even under forcing reaction conditions. Reaction of **1** with three equivalents of unsymmetrical disilane **10a** delivered trisilane **37a** in good yield (entry 2). Interestingly, the silylene inserts regioselectively into the Si–H bond of the phenyl substituted silicon center of **10b**. The reaction of **1** with three equivalents of 1,2-dichlorodisilane **10b** proceeds analogously, giving exclusively the symmetrical 1,3-dichlorotrisilane **37b**, which also may be obtained directly from monosilane **9b** and **1** employing a 3:2 ratio of the reactants (entry 3). The observed regioselectivity

Table 2
Synthesis of trisilanes by silylene insertion; Ar = 2-(Me_2NCH_2)C_6H_4; Mes = 2,4,6-$Me_3C_6H_2$

Entry	Silylene precursor	Disilane	Trisilane	Yield (%)
1	**1**	$ClPh_2Si$–$SiPh_2Cl$ (**35**)	$ClPh_2Si$–$SiPh_2$–$SiAr_2Cl$ (**36**)	35
2	**1**	HAr_2Si–$SiPh_2H$ (**10a**)	HAr_2Si–$SiPh_2$–$SiAr_2H$ (**37a**)	89
3	**1**	$ClAr_2Si$–$SiPh_2Cl$ (**10b**)	$ClAr_2Si$–$SiPh_2$–$SiAr_2Cl$ (**37b**)	78

Table 3
Synthesis of di- and trisilanes by nucleophilic substitution; Ar = 2-(Me_2NCH_2)C_6H_4; Mes = 2,4,6-$Me_3C_6H_2$

Entry	Precursor of metallated silane	Metal	Halosilane	Product	Yield (%)
1	Ar_2SiHCl (**17c**)	K	Ar_2SiHCl (**17c**)	$HAr_2Si–SiAr_2H$ (**18a**)	91
2	**17c**	K	Me_3SiCl (**5**)	$HAr_2Si–SiMe_3$ (**6b**)	49
3	$HAr_2SiSiAr_2H$ (**18a**)	Li	Me_3SiCl (**5**)	**6b**	63
4	**18a**	Li	Mes_2SiCl_2 (**32b**)	$HAr_2Si–SiMes_2Cl$ (**33c**)	75
5	**18a**	Li	Me_2SiCl_2 (**7a**)	$HAr_2Si–SiMe_2–SiAr_2H$ (**38**)	43
6	Mes_2SiHCl (**32c**)	Li	$ArMesSiCl_2$ (**27b**)	$HMes_2Si–SiAr(Mes)Cl$ (**39a**)	13

Table 4
Transformation of disilanes; Ar = 2-(Me_2NCH_2)C_6H_4; Mes = 2,4,6-$Me_3C_6H_2$

Entry	Disilane(s)	Reagent	Product	Yield (%)
1	$ClAr_2Si–SiMe_3$ (**6a**)	$LiAlH_4$	$HAr_2Si–SiMe_3$ (**6b**)	51
2	$HAr_2Si–SiMe_2Cl$ (**8b**) $ClAr_2Si–SiMe_2H$ (**8c**)	$LiAlH_4$	$HAr_2Si–SiMe_2H$ (**8d**)	47
3	$HAr_2Si–SiPh_2Cl$ (**10c**) $ClAr_2Si–SiPh_2H$ (**10d**)	$LiAlH_4$	$HAr_2Si–SiPh_2H$ (**10a**)	96
4	$ClAr_2Si–Si(4-MeC_6H_4)_2Cl$ (**12a**)	$LiAlH_4$	$HAr_2Si–Si(4-MeC_6H_4)_2H$ (**12b**)	91
5	$ClAr_2Si–Si(4-ClC_6H_4)_2Cl$ (**14a**)	$LiAlH_4$	$HAr_2Si–Si(4-ClC_6H_4)_2H$ (**14b**)	65
6	$ClAr_2Si–SiPhCl_2$ (**24a**)	$LiAlH_4$	$HAr_2Si–SiPhH_2$ (**24b**)	41
7	$HAr_2Si–SiMes_2Cl$ (**33c**)	$LiAlH_4$	$HAr_2Si–SiMes_2H$ (**33a**)	65
8	$HMes_2Si–SiAr(Mes)Cl$ (**39a**)	$LiAlH_4$	$HMes_2Si–SiArMesH$ (**39b**)	47
9	$HAr_2Si–SiAr_2H$ (**18a**)	NCS [a]	$ClAr_2Si–SiAr_2Cl$ (**18b**)	72
10	$HAr_2Si–SiAr_2H$ (**18a**)	NCS [b]	$HAr_2Si–SiAr_2Cl$ (**18c**)	59
11	$HAr_2Si–SiMes_2Cl$ (**33c**)	NCS	$ClAr_2Si–SiMes_2Cl$ (**33b**)	77

[a] Two equivalents NCS, solvent: CCl_4.
[b] One equivalent NCS, solvent: hexane.

indicates that insertion of silylene **2** at a silicon center, which bears *ortho*-substituted aryl groups, is sterically hindered. In accordance with this conclusion, **1** reacts neither with **16** nor with **18b** or $ClMes_2Si–SiAr_2Cl$ (**33b**) under formation of trisilanes.

2.3. Formation of disilanes by nucleophilic substitution

Nucleophilic coupling of a halosilane with a metalated silane, which is easily prepared by reaction of a halosilane or a disilane with alkali metals, is an alternative procedure for the synthesis of disilanes [13]. Thus, disilane **18a** is not only available by insertion of silylene **2** into the Si–H bond of silane **17a** (vide supra), but also can be obtained in good yield by reaction of chlorosilane **17c** with potassium in toluene via a potassio silane Ar_2SiHK as intermediate (Table 3, entry 1). This reaction could not be performed using more easily manageable lithium in THF or toluene as under these conditions cleavage of the Si–C bond of the starting material occurred. Interestingly, treatment of a mixture of chlorosilanes **17c** and **5** with potassium resulted in the formation of the unsymmetrical cross-coupling product **6b** (entry 2). A better yield of this disilane was obtained when employing lithium in order to transform disilane **18a** into Ar_2SiHLi, which subsequently was reacted with **5** (entry 3). Similarly, disilane **33c** was obtained from Ar_2SiHLi and dichlorosilane **32b** (entry 4). Using sterically less hindered **7a** as electrophile the reaction could not be stopped after the first substitution step and therefore only trisilane **38** was isolated from the reaction mixture (entry 5). Finally, bulkily substituted disilane **39a** was synthesized by treatment of preformed Mes_2SiHLi with dichlorosilane **27b** (entry 6).

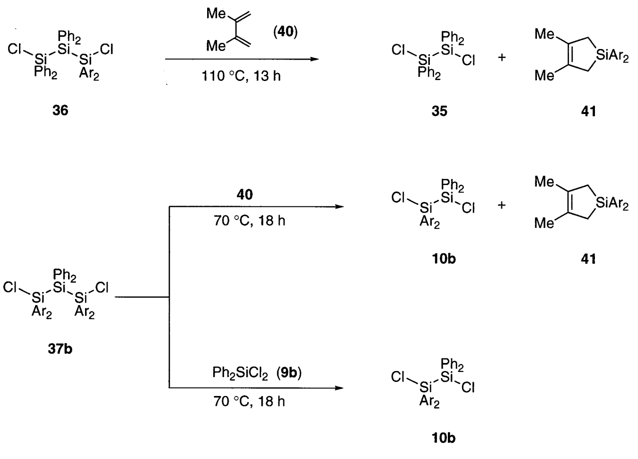
2.4. Transformations of disilanes

Various halogen substituted disilanes (Table 4) can easily be reduced to the corresponding hydrido disilanes using $LiAlH_4$ in Et_2O. However, silole based dichlorodisilanes **20** and **22** undergo cleavage of the Si–Si bond under these reaction conditions.

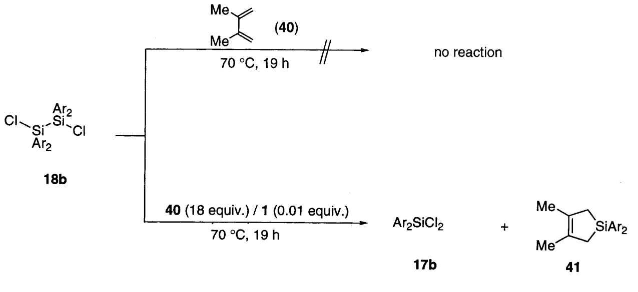
N-Chlorosuccinimide (NCS) has proven in several cases to be a superior reagent for chlorination of disilanes [1a,5b]. Thus, **18a** could be chlorinated at both silicon centers by means of two equivalents of NCS in CCl_4. When performing the reaction in hexane as solvent, the monochlorinated product **18c** could be isolated as main product. Dichlorodisilane **33b**, which could not be obtained by insertion of silylene **2** into the Si–Cl bond of dichlorosilane **32b** (vide supra) and which might be a useful precursor for a chelated disilene, was synthesized by treatment of **33c** with NCS in CCl_4.

2.5. Thermal stability of tri- and disilanes

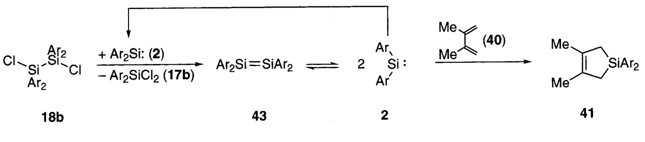
When 1,3-dichlorotrisilane **36** was heated in benzene in the presence of excess 2,3-dimethylbuta-1,3-diene (**40**) to 110 °C for 13 h quantitative conversion into a 1:1 mixture of **35** and silylene trapping product **41** occurred (Scheme 5, top). 1,3-Dichlorotrisilane **37b** underwent an analogous silylene extrusion under similar conditions (Scheme 5, bottom): With 1,3-diene **40** as trapping agent equimolar amounts of silacyclopentene **41** and dichlorodisilane **10b** were formed, whereas thermal silylene extrusion in the presence of one equivalent of dichlorosilane **9b** resulted in the clean formation of two equivalents of dichlorodisilane **10b**. It is worth noting that in all these reactions exclusively the chelated and therefore thermodynamically more stable silylene **2** and not diphenylsilylene was generated. A similar reactivity, i.e. extrusion of a coordinated silylene, was reported for the thermal and/or metal-catalyzed decomposition of disilanes bearing the 8-dimethylamino-naphth-l-yl substituent [14].



Scheme 5. Thermal silylene extrusion from trisilanes; Ar = 2-$(Me_2NCH_2)C_6H_4$.



Scheme 6. Silylene extrusion from **18b**; Ar = 2-$(Me_2NCH_2)C_6H_4$.



Scheme 7. Mechanism of the silylene-catalyzed reaction of **18b** with **40**; Ar = 2-$(Me_2NCH_2)C_6H_4$.

1,2-Dichlorodisilanes are thermally more stable: **35** or 1,2-dichloro-1,1,2,2-tetramesityldisilane (**42**), which bear no potentially chelating 2-(dimethylaminomethyl)phenyl substituent, do not extrude silylenes when heated to 110 °C for 15 h in the presence of a silylene trap. In contrast, highly coordinated dichlorodisilane **10b** transfers silylene **2** to **40** under these conditions; however, due to the relatively high temperatures, minor amounts of by-products with unknown structure are formed in this case. 1,2-Dichlorodisilane **18b** remains unchanged when treated with diene **40** at 70 °C for 19 h (Scheme 6, top). However, when **18b** was treated under almost identical conditions, the only variation being the presence of a catalytic amount of cyclotrisilane **1**, the 1,2-dichlorodisilane was totally consumed and a 1:1 mixture of **17b** and **41** was formed (Scheme 6, bottom). **28b** (used as a mixture of the *d,l*- and *meso*-diastereomers) shows a similar behavior. Neither silylene transfer to **40** nor change of the diastereomeric ratio, which might result from extrusion and re-insertion of silylene **2**, were observed after 24 h at 90 °C in the presence of excess **40**. But **28b** underwent in the presence of **40** and a trace of **3** clean conversion into a roughly equimolar mixture of **27b** and the corresponding silacyclopentene [15], which results from the transfer of silylene **4** to the diene. From these observations it can be concluded that cyclotrisilanes **1** and **3**, i.e. the silylenes in equilibrium with these cyclotrisilanes, catalyze the extrusion of silylene **2** or **4** from the respective 1,2-dichlorodisilane. Scheme 7 shows a possible mechanism for this reaction. The first step is a dehalogenation of **18b** by **2** under formation of **17b** and disilene **43**. Such kind of reduction of a 1,2-dichlorodisilane by a silylene yielding a disilene is, to the best of our knowledge, not known [16]. Jutzi, however, has shown that silicocene reduces 1,2-dibromocyclohexane to cyclohexene, thereby being transformed itself into the corresponding dibromosilane [17], and we have found that **2** reacts analogously with 1,2-dihaloethanes under formation of a olefin and **17b** [18]. Disilene **43** is assumed to be in equilibrium with silylenes **2** [11,19], which can either be trapped irreversibly by diene **40** or can re-enter into the catalytic cycle and reduce a further molecule of **18b**. The efficiency of the mechanism presented here depends crucially on a delicate balance of the different steps involved in the overall reaction. Thus, e.g. the dehalogenation of **18b** by **2** needs to be faster than the reaction of the silylene with **40** or its insertion into a Si–Cl bond of **18b**. When, as in the case of **10b**, silylene **2** inserts faster into the Si–Cl bond under formation of

Table 5
^{29}Si-NMR data of chlorinated disilanes Ar = 2-(Me_2NCH_2)C_6H_4; Mes = 2,4,6-$Me_3C_6H_2$

Disilane	δ (Si 1)	δ (Si 2)
$ClPh_2Si–SiPh_2Cl$ (**35**) [31b]	−6.1	−6.1
$ClMes_2Si–SiMes_2Cl$ (**42**) [1a]	+0.2	+0.2
$ClAr_2Si–SiPh_2Cl$ (**10b**)	−21.7	−2.3
$ClAr_2Si–Si(4\text{-}MeC_6H_4)_2Cl$ (**12a**)	−19.6	−1.8
$ClAr_2Si–Si(4\text{-}ClC_6H_4)_2Cl$ (**14a**)	−24.3	−3.4
$ClAr_2Si–Si(2\text{-}EtC_6H_4)_2Cl$ (**16**)	−4.5	+0.4
$ClAr_2Si–SiAr_2Cl$ (**18b**)	−2.9	−2.9
ClAr(Mes)Si–$SiPh_2Cl$ (**26b**)	−15.0	−2.1
ClAr(Mes)Si–SiAr(Mes)Cl (**28b**)	−2.6	−2.6
ClAr(Mes)Si–$SiMesCl_2$ (**31**)	−9.0	9.4
ClAr(Mes)Si–$SiMes_2H$ (**39a**)	+1.5	−51.4
$ClAr_2Si–SiMes_2Cl$ (**33b**)	−4.8 [a]	+0.2 [a]

[a] The assignment is ambiguous.

37b (vide supra) as it reduces **10b** to the corresponding disilene, an auto-catalyzed extrusion of silylenes **2** is impossible.

2.6. Structures in the solid state and in solution

Several 1,2-dichlorotetraaryldisilanes were investigated in regard to the ability of the 2-(dimethylaminomethyl)phenyl substituent to coordinate intramolecularly to the silicon center (Table 5). If coordination occurs in solution, the chelated silicon center is expected to resonate at higher field in comparison to the silicon nucleus of an appropriate reference compound, in which the silicon center is non-coordinated [20]. The ^{29}Si-NMR signal of dichlorodisilane **10b**, e.g. is shifted significantly to higher field in comparison to $ClPh_2Si–SiPh_2Cl$ (**35**) indicating that there is a coordinative interaction between the amino group of the 2-(dimethylaminomethyl)phenyl substituent and the silicon center. This coordination is hardly affected by introducing substituents into the *para*-position of the phenyl rings of the adjacent $SiPh_2Cl$ group. Dichlorodisilanes **12a** and **14a** absorb at similar frequencies as **10b**. However, when the neighboring silicon center bears *ortho*-substituted aryl groups as in **16** or **18b**, the coordination breaks down, presumably due to steric hindrance. Accordingly, the silicon center of the ClAr(Mes)Si group of **26b** appears to be chelated, because it is significantly highfield shifted as compared with **35** or $ClMes_2Si–SiMes_2Cl$ (**42**). In contrast, the 2-(dimethylaminomethyl)phenyl substituted silicon center of chlorinated disilanes **28b**, **31** and **39a**, in all of which the neighboring silicon center bears substituents, which are sterically more demanding in comparison to the phenyl groups of **26b**, is not coordinated by the amino group as is evident from the small shift differences in regard to the reference compounds **35** or **42**. Not only the chemical shifts of the silicon centers, but also the different sensitivity of their resonance frequencies towards temperature changes allow a discrimination of chelated and non-chelated silicon. The position of the ^{29}Si-NMR signal of the phenyl substituted silicon center of **10b** remains virtually constant upon temperature changes, whereas the resonance frequency of the coordinated silicon moves from $\delta = -29.7$ at 280 K to $\delta = -20.6$ at 320 K (Fig. 1a). This shift indicates that chelated and non-chelated **10b** is in equilibrium, the non chelated form being favored at higher temperature [21]. In contrast, the chemical shift of both silicon centers of **33b** remains essentially unchanged over a temperature interval of 40 K (Fig. 1b) and thus supports the conclusion that the 2-(dimethylaminomethyl)phenyl substituted center of **33b** is not chelated by the amino group.

Chlorosilane **39a** adopts in the solid state a staggered conformation (Fig. 2), which already was reported for other tetraaryl disilanes [5b,22]. The Si(1)–N(1) distance (3.312(2) Å) is shorter than the sum of the van der

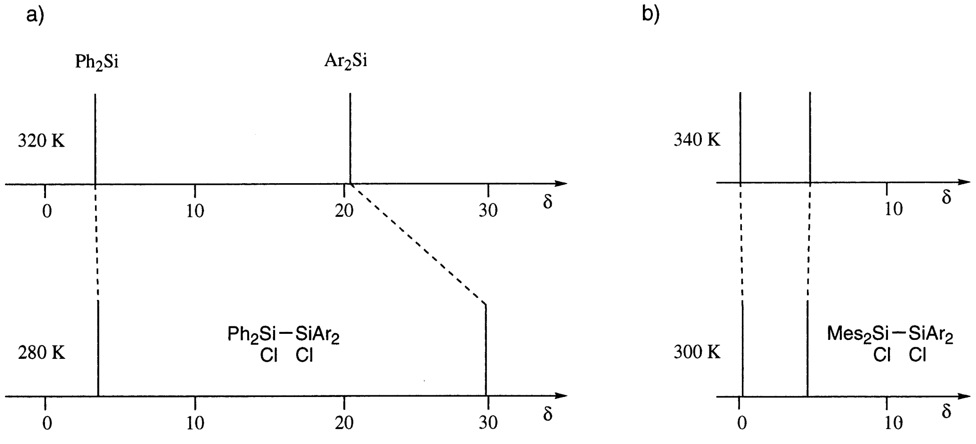


Fig. 1. ^{29}Si-NMR spectra of **10b** and **33b** at variable temperature; Ar = 2(Me_2NCH_2)C_6H_4;(a) Spectra of **10b** at 320 K (top) and 280 K (bottom); (b) Spectra of **33b** at 340 K (top) and 300 K (bottom).

Waals-radii of both elements (3.6 Å) [23], but appreciably longer than that of dative Si → N bonds (ca. 1.8–3.0 Å) [24]. Thus, there is apparently no significant coordinative interaction between Si(1) and N(1) in the solid state as it was found for the structure of **39a** in solution. This conclusion is corroborated by the fact that the lone pair of the amino nitrogen is not directed exactly towards the silicon center. Instead, the vector [25] of the lone pair forms an angle of 31.8° with the line which joins Si(1) and N(1).

3. Experimental

^{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), a Bruker AMX 300 (^{1}H-NMR: 300 MHz, ^{13}C-NMR: 75.5 MHz) and a Varian VXR 500 (^{1}H-NMR, 500 MHz,^{13}C-NMR, 125.7 MHz). 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) or a Varian XL 500 (99.3 MHz) using a refocused INEPT pulse sequence or performing a direct acquisition. Chemical shifts refer to $\delta_{\mathrm{TMS}} = 0.0$. IR spectra were recorded on a Bruker IFS 66 (film or KBr). Mass spectra were recorded on a Varian MAT 311 A. High resolution mass spectra were determined with a Varian MAT 311 A, using preselected ion peak matching at $R \sim 10\,000$ to be within ± 2 ppm of the exact mass. FAB mass spectra were obtained by using an *ortho*-nitrophenyl octyl ether (NOE) or *meta*-nitrobenzylalcohol (3-NBA) matrix. Elemental analyses were performed at Mikroanalytisches Labor der Georg-August-Universität Göttingen [26].

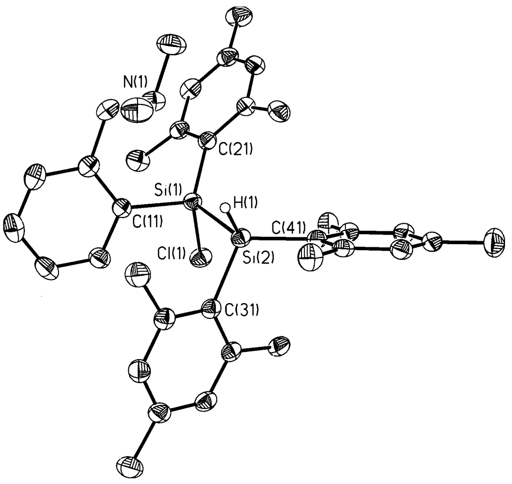


Fig. 2. X-ray structure of **39a**; selected distances [Å], bond angles and torsion angles [°]: Si(1)–N(1) 3.312(2), Si(1)–Si(2) 2.3692(10), Si(1)–Cl(1) 2.1066(9), Si(1)–C(11) 1.887(2), Si(1)–C(21) 1.891(2), Si(2)–H(1) 1.39, Si(2)–C(31) 1.908(2), Si(2)–C(41) 1.894(2); Cl(1)–Si(1)–C(11) 103.13(7), Cl(1)–Si(1)–Si(2) 102.56(3), Cl(1)–Si(1)–C(21) 104.63(7), C(11)–Si(1)–Si(2) 104.19(6), C(11)–Si(1)–C(21) 113.82(9), C(21)–Si(1)–Si(2) 125.78(7); C(21)–Si(1)–Si(2)–C(31) 172.24(10), Cl(1)–Si(1)–Si(2)–H(1) 163.8, C(11)–Si(1)–Si(2)–C(41) 176.64(10).

All manipulations of air and moisture sensitive compounds were carried out under an inert argon atmosphere using carefully dried glassware. Ethereal solvents, hexane, pentane, toluene and C_6D_6 used were dried by refluxing over sodium benzophenone ketyl and distilled immediately before use; $CDCl_3$, CCl_4 was dried using molecular sieve (4 Å). Mes_2SiHLi [27], **19** [28], **21** [3a], **32b** [29], **32c** [30], and **35** [31] were obtained by published procedures.

3.1. Formation of disilanes by silylene insertion

3.1.1. 1-Chloro-1,1-bis[2-(dimethylaminomethyl)-phenyl]-2,2,2-trimethyldisilane (*6a*)

A solution of 120 mg (0.14 mmol) of **1** and 51 μl (0.40 mmol) of **5** in 0.5 ml of C_6D_6 was heated at 50 °C. After 4 h only **6a** and surplus **5** could be detected in the reaction mixture by means of ^{1}H-NMR spectroscopy. The solvent was removed in vacuo, 5 ml of hexane were added and the resulting suspension was filtered leaving behind 87 mg (54%) of **6a** as a white solid (melting point (m.p.) 92–93 °C). ^{1}H-NMR (C_6D_6): $\delta = 0.36$ (s, 9H, $SiMe_3$), 1.78 (s, 12H, NMe_2), 2.99, 3.42 (AB system, $^{2}J_{AB} = 13$ Hz, 4H, CH_2N), 7.13–7.24 (m, 4H, ar H), 7.38 (dd, $^{3}J = 8$ Hz, $^{4}J = 2$ Hz, 2H, ar H), 8.07 (dd, $^{3}J = 6$ Hz,$^{4}J = 2$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = -0.3$ ($SiMe_3$), 45.3 (NMe_2), 64.2 (CH_2N), 126.6 (ar CH), 128.7 (ar CH), 129.9 (ar CH), 135.6 (ar C_q), 136.6 (ar CH), 146.0 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -1.2$ (SiCl)), -13.3 ($SiMe_3$).

3.1.2. 1,2-Dichloro-1,1-bis[2-(dimethylaminomethyl)-phenyl]-2,2-dimethyldisilane (*8a*)

A solution of 118 mg (0.13 mmol) of **1** and 48 μl (0.40 mmol) of **7a** in 0.5 ml of C_6D_6 was heated for 2.5 h at 55 °C. After removal of the solvent and excess silane in vacuo 161 mg (95%) of **8a** were obtained as a ^{1}H-NMR spectroscopically pure, colorless oil. ^{1}H-NMR (C_6D_6): $\delta = 0.75$ (s, 6H, $SiMe_2$), 1.86 (s, 12H, NMe_2), 3.00, 3.46 (AB system, $^{2}J_{AB} = 13$ Hz, 4H, CH_2N), 7.11–7.27 (m, 6H, ar H), 8.22–8.26 (m, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 4.5$ ($SiMe_2$), 45.5 (NMe_2), 64.3 (CH_2N), 126.9 (ar CH), 128.2 (ar CH), 130.1 (ar CH), 135.3 (ar C_q), 136.9 (ar CH), 145.9 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = 16.2$ ($SiMe_2Cl$), -29.6 ($SiAr_2Cl$). MS (EI), *m/z* (%): 424 (8) $[M]^+$, 290 (92) $[M^+{-}Ar]$, 134 (36) $[Ar]^+$, 91 (75) $[C_7H_7]^+$, 58 (45) $[CH_2NMe_2]^+$.

*3.1.3. 2-Chloro-1,1-bis[2-(dimethylaminomethyl)phenyl]-2,2-dimethyldisilane (**8b**) and 1-chloro-1,1-bis[2-(dimethylaminomethyl)phenyl]-2,2-dimethyldisilane (**8c**)*

A solution of 140 mg (0.16 mmol) of **1** and 51 µl (0.47 mmol) of **7b** in 0.5 ml of C_6D_6 was heated for 2 h at 70 °C. After removal of the solvent and surplus silane in vacuo 154 mg (78%) of a 3:1 mixture of **8b** and **c** were obtained as a viscous oil. **8b**: ^{1}H-NMR (C_6D_6): $\delta = 0.55$ (s, 6H, SiMe$_2$), 1.82 (s, 12H, NMe$_2$), 3.27 (s, 4H, CH$_2$N), 5.22 (s (d, $^1J_{SiH} = 202$ Hz), 1H, SiH), 7.06–7.21 (m, 6H, ar H), 7.84 (d, $^3J = 6$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 4.4$ (SiMe$_2$), 45.7 (NMe$_2$), 65.0 (CH$_2$N), 126.5 (ar CH), 129.1 (ar CH), 129.4 (ar CH), 134.2 (ar C$_q$), 137.5 (ar CH), 145.7 (ar C$_q$). ^{29}Si-NMR (C_6D_6): $\delta = 22.8$ (SiMe$_2$Cl), -41.1 (d, $^1J_{SiH} = 202$ Hz, SiAr$_2$H). IR (film): $\tilde{\nu} = 2114$ cm^{-1}. **8c**: ^{1}H-NMR (C_6D_6): $\delta = 0.36$ (d, $^3J = 4$ Hz, 6H, SiMe$_2$), 1.79 (s, 12H, NMe$_2$), 3.05, 3.39 (AB System, $^2J_{AB} = 14$ Hz, 4H, CH$_2$N), 4.26 (sep, $^3J = 4$ Hz (d, $^1J_{SiH} = 182$ Hz), 1H, SiH), 7.06–7.21 (m, 4H, ar H), 7.28 (d, $^3J = 7$ Hz, 2H, ar H), 8.10 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = -5.0$ (SiMe$_2$), 45.2 (NMe$_2$), 64.1 (CH$_2$N), 126.7 (ar CH), 128.1 (ar CH), 129.7 (ar CH), 135.7 (ar C$_q$), 136.8 (ar CH), 145.5 (ar C$_q$). ^{29}Si-NMR (C_6D_6): $\delta = -16.8$ (SiAr$_2$Cl) $\delta = -35.0$ (dsep, $^1J_{SiH} = 182$, $^2J_{SiH} = 7$ Hz, SiMe$_2$H). IR (film): $\tilde{\nu} = 2114$ cm^{-1}.

*3.1.4. 1,1-Bis[2-(dimethylaminomethyl)phenyl]-2,2-diphenyldisilane (**10a**)*

A solution of 148 mg (0.17 mmol) of **1** and 93 µl (0.50 mmol) of **9a** in 2 ml of toluene was heated for 2 h at 90 °C. After removal of the solvent in vacuo 188 mg (78%) of **10a** were obtained as a viscous oil. ^{1}H-NMR (C_6D_6): $\delta = 1.83$ (s, 12H, NMe$_2$), 3.31 (s, 4H, CH$_2$N), 5.45 (d, $^3J = 3$ Hz (d, $^1J_{SiH} = 189$ Hz), 1H, SiH), 5.61 (d, $^3J = 3$ Hz (d, $^1J_{SiH} = 200$ Hz), 1H, SiH), 6.99 (ddd, $^3J = 7$ Hz, $^3J = 7$ Hz, $^3J = 7$ Hz, $^4J = 1$ Hz, 2H, ar H) 7.08–7.22 (m, 10H, ar H), 7.64–7.68 (m, 4H, ar H), 7.77 (d, $^3J = 7$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 44.7$ (NMe$_2$), 65.0 (CH$_2$N), 126.5 (ar CH), 128.2 (ar CH), 129.1 (ar CH), 129.1 (ar CH), 129.1 (ar CH), 135.1 (ar C$_q$), 135.5 (ar C$_q$), 136.5 (ar CH), 138.1 (ar CH), 146.0 (at C$_q$). ^{29}Si-NMR (C_6D_6): $\delta = -30.8$ (ddqin, $^1J_{SiH} = 189$ Hz, $^2J_{SiH} = 5$ Hz, $^3J_{SiH} = 4$ Hz, SiPh$_2$H), -42.3 (ddt, $^1J_{SiH} = 200$ Hz, $^2J_{SiH} = 5$ Hz, $^3J_{SiH} = 6$ Hz, SiAr$_2$H). IR (film): $\tilde{\nu} = 2128$ cm^{-1}. MS (EI, 70 eV), *m/z* (%): 479 (1) [M$^+$–H], 435 (8) [M$^+$–NMe$_2$–H], 420 (12) [M$^+$–NMe$_2$–Me–H], 346 (11) [M$^+$–Ar], 297 (100) [M$^+$–Ph$_2$SiH], 252 (10) [M$^+$–Ph$_2$SiH–NMe$_2$–H], 238 (13) [M$^+$–Ph$_2$SiH–NMe$_2$–Me], 209 (8) [M$^+$–Ph$_2$SiH–2NMe$_2$], 182 (8) [Ph$_2$Si]$^+$, 134 (2) [Ar]$^+$, 105 (13) [PhSi]$^+$, 91 (3) [C$_7$H$_7$]$^+$, 58 (10) [CH$_2$NMe$_2$]$^+$. $C_{30}H_{36}N_2Si_2$ (480.2417): correct HRMS. Anal. Calc. for $C_{30}H_{36}N_2Si_2$ (480.80): C, 74.94; H 7.55. Found: C, 75.40; H, 8.01%.

*3.1.5. 1,2-Dichloro-1,1-bis[2-(dimethylaminomethyl)phenyl]-2,2-diphenyldisilane (**10b**)*

A solution of 5.00 g (5.62 mmol) of **1** and 3.25 ml (16.9 mmol) of **9b** in 50 ml of toluene was stirred for 2 days at 55 °C. The solvent was removed in vacuo and 150 ml of pentane were added to the solid residue. The resulting suspension was filtered and the filtrate was reduced in vacuo to a volume of 40 ml. After cooling at −20 °C for 15 h 7.77 g (78%) of **10b** were obtained as a colorless solid (m.p. 114–115 °C). ^{1}H-NMR (C_6D_6): $\delta = 1.82$ (s, 12H, NMe$_2$), 3.04, 3.42 (AB system, $^2J_{AB} = 14$ Hz, 4H, CH$_2$N), 7.04–7.20 (m, 10H, ar H), 7.29 (d, $^3J = 8$ Hz, 2H, ar H), 7.90–7.94 (m, 4H, ar H), 8.39 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 45.4$ (NMe$_2$), 64.0 (CH$_2$N), 126.5 (ar CH), 127.9 (ar CH), 128.3 (ar CH), 130.2 (ar CH), 130.3 (ar CH), 134.0 (ar C$_q$), 134.8 (ar C$_q$), 135.8 (ar CH), 137.5 (ar CH), 146.0 (ar C$_q$). ^{29}Si-NMR (C_6D_6): $\delta = -2.3$ (Si 2), -21.7 (Si 1). MS (EI, 70 eV), *m/z* (%): 552/550/548 (1/3/4) [M]$^+$, 418/416/414 (11/41/55) [M$^+$–Ar], 333/331 (18/44) [M$^+$–Ph$_2$SiCl], 288/286 (20/35) [M$^+$–Ph$_2$SiCl–HNMe$_2$], 274/272 (18/47) [M$^+$–Ph$_2$SiCl–NMe$_2$–Me], 200/198 (14/39) [M$^+$–Ph$_2$SiCl–Ar + H], 134 (18) [Ar]$^+$, 91 (19) [C$_7$H$_7$]$^+$, 77 (21) [C$_6$H$_5$]$^+$, 58 (49) [CH$_2$NMe$_2$]$^+$. $C_{30}H_{34}N_2Si_2Cl_2$ (548.1637): correct HRMS. Anal. Calc. for $C_{30}H_{34}N_2Si_2Cl_2$ (549.69): C, 65.55; H, 6.23. Found: C, 66.01; H, 6.66%.

*3.1.6. 2-Chloro-1,1-bis[2-(dimethylaminomethyl)phenyl]-2,2-diphenyldisilane (**10c**) and 1-chloro1,1-bis[2-(dimethylaminomethyl)phenyl]-2,2-diphenyldisilane (**10d**)*

A solution of 123 mg (0.14 mmol) of **1** and 81 µl (0.42 mmol) of **9c** in 0.5 ml of C_6D_6 was stirred for 20 min at 90 °C. After removal of the solvent in vacuo 178 mg (83%) of a 2:1 mixture of **10c** and **10d** were obtained as a viscous oil. **10c**: ^{1}H-NMR (C_6D_6): $\delta = 1.77$ (s, 12H, NMe$_2$), 3.18, 3.38 (AB system, $^2J_{AB} = 13$ Hz, 4H, CH$_2$N), 5.72 (s (d, $^1J_{SiH} = 209$ Hz), 1H, SiH), 6.93–7.28 (m, 12H, ar H), 7.68–7.71 (m, 4H, ar H), 7.82 (d, $^3J = 7$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 44.8$ (NMe$_2$), 64.8 (CH$_2$N), 126.4 (ar CH), 128.2 (ar CH), 128.9 (ar CH), 129.5 (ar CH), 130.0 (ar CH), 132.9 (ar C$_q$), 135.2 (ar CH), 136.7 (ar C$_q$), 138.2 (ar CH), 146.1 (ar C$_q$). ^{29}Si-NMR (C_6D_6): $\delta = 3.5$ (Ph$_2$SiCl), -31.9 (dt, $^1J_{SiH} = 209$ Hz, $^3J_{SiH} = 6$ Hz, Ar$_2$SiH). **10d**: ^{1}H-NMR (C_6D_6): $\delta = 1.80$ (s, 12H, NMe$_2$), 3.13, 3.34 (AB system, $^2J_{AB} = 13$ Hz, 4H, CH$_2$N), 5.46 (s (d, $^1J_{SiH} = 190$ Hz), 1H, SiH), 6.93–7.28 (m, 12H, ar H), 7.84–7.87 (m, 4H, ar H), 8.22 (d, $^3J = 7$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 45.4$ (NMe$_2$), 64.1 (CH$_2$N), 126.6 (ar CH), 128.1 (ar CH), 128.9 (ar CH), 129.6 (ar CH), 133.9 (ar C$_q$), 134.8 (ar CH), 135.3

(ar C_q), 136.9 (ar CH), 137.5 (ar CH), 145.9 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -18.2$ (Ar_2SiCl), -45.2 (dqin, $^1J_{SiH} = 189$ Hz, $^3J_{SiH} = 5$ Hz, Ph_2SiH).

*3.1.7. 1,2-dichloro-1,1-bis[2-(dimethylaminomethyl)-phenyl]-2,2-bis(4-methylphenyl)disilane **(12a)***

A solution of 247 mg (0.28 mmol) of **1** and 234 mg (0.83 mmol) of **11** in 8 ml of toluene was heated for 17 h at 50 °C. The solvent was removed in vacuo and 14 ml of Et_2O were added to the solid residue. The resulting suspension was filtered, the filtrate was evaporated in vacuo and the residue was dissolved in 10 ml of pentane. The solution was cooled at −20 °C for 3 days and 214 mg (44%) of **12a** were obtained as a colorless solid (m.p. 105–107 °C). ^{1}H-NMR (C_6D_6): $\delta = 1.85$ (s, 12H, NMe_2), 1.95 (s, 6H, CH_3), 3.04, 3.43 (AB system, $^2J_{AB} = 14$ Hz, 4H, CH_2N), 6.93 (d, $^3J = 8$ Hz, 4H, ar H), 7.12–7.20 (m, 4H, ar H), 7.28–7.32 (m, 2H, ar H), 7.89 (d, $^3J = 8$ Hz, 4H, ar H), 8.44–8.48 (m, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 21.4$ (CH_3), 45.5 (NMe_2), 64.1 (CH_2N), 126.6 (ar CH), 128.4 (ar CH), 129.0 (ar CH), 130.4 (ar CH), 131.6 (ar C_q), 134.4 (ar C_q), 136.0 (ar CH), 137.7 (ar CH), 140.2 (ar C_q), 146.2 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -1.8$ (Si 2), -19.6 (Si 1). MS (EI, 70 eV), *m*/*z* (%): 578/576 (2/3) $[M]^+$, 508/506 (3/5) $[M^+–NMe_2–Me–H]$, 446/444/442 (8/33/48) $[M^+–Ar]$, 333/331 (19/57) $[Ar_2SiCl]^+$, 274/272 (35/100) $[M^+–(MeC_6H_4)SiCl–NMe_2–Me]$, 200/198 (31/100) $[ArSiClH]^+$, 178 (82) $[C_{12}H_6Si]^+$, 91 (43) $[C_7H_7]^+$, 58 (56) $[CH_2NMe_2]^+$. $C_{32}H_{38}Cl_2N_2Si_2$ (576.1950): correct HRMS. Anal. Calc. for $C_{32}H_{38}Cl_2N_2Si_2$ (577.74): C, 66.53; H, 6.63. Found: C, 67.26; H, 6.71%.

*3.1.8. 1,2-Dichloro-1,1-bis[2-(dimethylaminomethyl)-phenyl]-2,2-bis(4-chlorophenyl)disilane **(14a)***

A solution of 300 mg (0.34 mmol) of **1** and 326 mg (1.01 mmol) of **13** in 8 ml of toluene was heated for 17 h at 50 °C. The solvent was removed in vacuo and 20 ml of Et_2O were added to the solid residue. The resulting suspension was filtered and the solvent was evaporated from the filtrate in vacuo. The residue was solved in 10 ml of pentane and the solution was cooled to −20 °C. After 3 days, 249 mg (40%) of **14a** were obtained as a colorless solid (m.p. 115–116 °C). ^{1}H-NMR (C_6D_6): $\delta = 1.81$ (s, 12H, NMe_2), 3.03, 3.40 (AB system, $^2J_{AB} = 14$ Hz, 4H, CH_2N), 7.04 (d, $^3J = 8$ Hz, 4H, ar H), 7.09–7.31 (m, 6H, ar H), 7.65 (d, $^3J = 8$ Hz, 4H, ar H), 8.28 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 45.5$ (NMe_2), 64.1 (CH_2N), 126.8 (ar CH), 128.4 (ar CH), 130.5 (ar CH), 133.2 (ar C_q), 134.0 (ar C_q), 135.6 (ar CH), 137.0 (ar C_q), 137.3 (ar CH), 137.4 (ar CH), 145.9 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -3.4$ (Si 2), -24.3 (Si 1). MS (El, 70 eV), *m*/*z* (%): 620/618/616 (5/8/6) $[M]^+$, 585/583/581 (5/13/12) $[M^+–Cl]$, 488/486/484/482 (17/50/82/57) $[M^+–Ar]$, 333/331 (38/100) $[Ar_2SiCl]^+$, 288/286 (33/61) $[M^+–(ClC_6H_4)_2SiCl–NMe_2–H]$, 178 (58) $[C_{12}H_6Si]^+$, 134 (45) $[Ar]^+$, 58 (53) $[CH_2NMe_2]^+$. $C_{30}H_{32}Cl_4N_2Si_2$ (616.0858): correct HRMS. Anal. Calc. for $C_{30}H_{32}Cl_4N_2Si_2$ (618.58): C, 58.25; H, 5.21. Found: C, 59.19; H, 5.42%.

*3.1.9. 1,2-Dichloro-2,2-bis(2-ethylphenyl)-1,1-bis[2-(dimethylaminomethyl)phenyl]disilane **(16)***

A solution of 1.00 g (1.12 mmol) of **1** and 1.04 g (0.37 mmol) of **15** in 20 ml of toluene was heated for 8 h at 50 °C. The solvent was removed in vacuo, 50 ml of pentane was added to the solid residue and the resulting suspension was filtered. The solvent was evaporated in vacuo from the filtrate leaving behind 1.79 g (88%) of **16** as ^{1}H-NMR spectroscopically pure, yellowish oil. ^{1}H-NMR (C_6D_6): $\delta = 0.94$ (t, $^3J = 7$ Hz, 6H, $CH_2C\underline{H}_3$), 1.87 (s, 12H, NMe_2), 2.64 (q, $^3J = 7$ Hz, 4H, $C\underline{H}_2CH_3$), 3.19, 3.57 (AB System, $^2J_{AB} = 14$ Hz, 4H, CH_2N), 6.92 (dd, $^3J{=}^3J = 7$ Hz, 2H, ar H), 6.95 (dd, $^3J{=}^3J = 7$ Hz, 2H, ar H), 7.05 (d, $^3J = 7$ Hz, 2H, ar H), 7.05–7.30 (m, 4H, ar H), 7.50 (d, $^3J = 8$ Hz, 2H, ar H), 7.98–8.15 (m, 4H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 15.3$ ($CH_2\underline{C}H_3$), 29.9 ($\underline{C}H_2CH_3$), 45.3 (NMe_2), 64.0 (CH_2N), 125.4 (ar CH), 126.4 (ar CH), 128.8 (ar CH), 128.9 (ar CH), 130.6 (ar CH), 131.0 (ar CH), 133.0 (ar C_q), 133.1 (ar C_q), 137.0 (ar CH), 137.6 (ar CH), 146.6 (ar C_q), 151.0 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = +0.4$ (Si 2), -4.5 (Si 1). MS (FAB, NOE), *m*/*z* (%): 603 (100) $[M^+ - 1]$.

*3.1.10. 1,1,2,2-Tetrakis[2-(dimethylaminomethyl)-phenyl]disilane [12] **(18a)***

110 mg (0.12 mmol) of **1** and 112 mg (0.38 mmol) of **17a** were dissolved in 0.5 ml of C_6D_6 and heated for 3 days at 70 °C and additional 2 days at 90 °C. The cloudy solution was filtered. Removing of the solvent from the filtrate in vacuo left behind 223 mg (96%) of **18a** as a colorless solid (m.p. 90–92 °C). ^{1}H-NMR (C_6D_6): $\delta = 1.91$ (s, 24H, NMe_2), 3.35, 3.57 (AB System, $^2J_{AB} = 14$ Hz, 8H, CH_2N), 5.51 (s (dd, $^1J_{SiH} = 200$ Hz, $^3J_{HH} = 2$ Hz), 2H, SiH), 6.99 (ddd, $^3J{=}^3J = 7$ Hz, $^4J = 1$ Hz, 4H, ar H), 7.16 (ddd, $^3J{=}^3J = 7$ Hz, $^4J = 1$ Hz, 4H, ar H), 7.28 (d, $^3J = 7$ Hz, 4H, ar H), 7.68 (dd, $^3J = 7$ Hz, $^4J = 1$ Hz, 4H, ar H). ^{13}C-NMR ($CDCl_3$): $\delta = 44.9$ (NMe_2), 64.5 (CH_2N), 125.8 (ar CH), 128.3 (ar CH), 128.4 (ar CH), 136.1 (ar C_q), 137.6 (ar CH), 145.2 (ar C_9). ^{13}C-NMR (C_6D_6): $\delta = 45.0$ (NMe_2), 65.3 (CH_2N), 126.3 (ar CH), 128.6 (ar CH), 128.9 (ar CH), 137.6 (ar C_q), 138.2 (ar CH), 145.7 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -41.5$. IR (KBr): $\tilde{\nu} = 2140$ cm^{-1}. MS (FAB, 3-NBA), *m*/*z* (%): 593 (1) $[M^+–H]$, 297 (100) $[(M/2)]^+$. Anal. Calc. for $C_{36}H_{50}N_4Si_2$ (595.0): C, 72.67; H, 8.47; N, 9.42. Found: C, 72.58; H, 8.53; N, 9.37%.

*3.1.11. 1,2-Dichloro-1,1,2,2-tetrakis[2-(dimethylamino-methyl)phenyl]disilane **(18b)***

A solution of 50 mg (56 μmol) of **1** and 62 mg (0.17 mmol) of **17b** in 0.5 ml of C_6D_6 was heated for 4.5 h at

50 °C. The solvent was removed in vacuo leaving behind 102 mg (91%) of crude **18b**, which was solved in 2 ml of hexane. On cooling the solution to −20 °C for 4 days, 77 mg (68%) of **18b** were obtained as a white solid ^{1}H-NMR (C_6D_6): $\delta = 1.80$ (s, 24H, NMe_2), 3.20, 3.46 (AB system, $^2J_{AB} = 14$ Hz, 8H, CH_2N), 6.83 (dd, $^3J = 7$ Hz, $^3J = 7$ Hz, 4H, ar H), 7.07 (ddd, $^3J = 7$ Hz, $^3J = 7$ Hz, $^4J = 1$ Hz, 4H, ar H), 7.52 (d, $^3J = 7$ Hz, 4H, ar H), 8.00 (d, $^3J = 7$ Hz, 4H, ar H). ^{13}C-NMR (C_6D_6): $\delta =$ 45.4 (NMe_2), 63.9 (CH_2N), 126.4 (ar CH), 128.9 (ar CH), 130.7 (ar CH), 133.2 (ar C_q), 137.5 (ar CH), 146.8 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -2.9$. MS (EI, 70 eV), *m/z* (%): 662 (< 1)) [M]$^+$, 627 (10) [M$^+$–Cl], 331 (85) [(M/2)]$^+$, 178 (100) [$C_{12}H_6Si$]$^+$. Anal. Calc. for $C_{36}H_{48}Cl_2N_4Si_2$ (663.9): C, 65.13; H, 7.29; N, 8.44. Found: C, 65.08; H, 7.61; N, 8.35%.

*3.1.12. 1-Chloro-1,1,2,2-tetrakis[2-(dimethylaminomethyl)phenyl]disilane (**18c**)*

A solution of 85 mg (96 μmol) of **1** and 95 mg (0.29 mmol) of **17c** in 0.8 ml of C_6D_6 was heated for 6 h at 50 °C. The solvent was removed in vacuo leaving behind 175 mg (97%) of **18c** as a colorless solid (m.p. 80–82 °C). ^{1}H-NMR (C_6D_6): $\delta = 1.83$ (s, 12H, NMe_2), 1.96 (s, 12H, NMe_2), 3.31, 3.37 (AB system, $^2J_{AB} = 13$ Hz, 4H, CH_2N), 3.39, 3.60 (AB system, $^2J_{AB} = 14$ Hz, 4H, CH_2N), 5.90 (s, (d, $^1J_{SiH} = 201$ Hz), 1H, SiH), 6.98 (dd, $^3J = 7$ Hz, $^3J = 7$ Hz, 2H, ar H), 7.05–7.23 (m, 6H, ar H), 7.40 (d, $^3J = 7$ Hz. 2H, ar H), 7.44 (d, $^3J = 7$ Hz, 2H, ar H), 8.04 (d, $^3J = 8$ Hz, 2H, ar H), 8.28 (d, $^3J = 8$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 45.0$ (NMe_2), 45.1 (NMe_2), 64.1 (CH_2N), 64.8 (CH_2N), 126.2 (ar CH), 126.4 (ar CH), 128.3 (ar CH), 128.8 (ar CH), 129.4 (ar CH), 129.9 (ar CH), 133.9 (ar C_q), 137.0 (ar C_q), 137.7 (ar CH), 138.8 (ar CH), 145.7 (ar C_q), 146.3 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -44.8$ (Si 2), -8.6 (Si 1). Anal. Calc. for $C_{36}H_{49}ClN_4Si_2$ (629.4): C, 68.70; H, 7.85; N, 8.90. Found: C, 68.57; H, 7.90; N, 8.82%.

*3.1.13. 1-{Bis[2′-(dimethylaminomethyl)phenyl]chlorosilyl}-1-chlorodibenzo[b,d]silole (**20**)*

A solution of 2.21 g (2.49 mmol) of **1** and 1.88 g (7.47 mmol) of **19** in 40 ml of toluene was stirred for 17 h at 55 °C. The solvent was removed in vacuo and the remaining yellow–orange solid was washed with 20 ml of dry hexane to give 3.05 g (75%) of **20** as yellow crystals (m.p. 85–86 °C), which are, according to ^{1}H-NMR spectrum, contaminated with traces of an unidentified compound. ^{1}H-NMR (C_6D_6): $\delta = 1.66$ (s, 12H, NMe_2), 2.90, 3.40 (AB system, 4H, CH_2N, $^2J_{AB} = 13$ Hz), 7.03 (ddd, $^3J = {}^3J = 7$ Hz, $^4J = 1$ Hz, ar H, 2H), 7.12–7.18 (m, 8H, ar H), 7.49 (d, $^3J = 8$ Hz, 2H, ar H), 7.90 (dd, $^3J = 6$ Hz, $^4J = 1$ Hz, 2H, ar H), 8.38 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 45.1$ (NMe_2), 64.3 (CH_2N), 121.6 (ar CH), 126.9 (ar CH), 128.2 (ar CH), 128.5 (ar CH), 130.4 (ar CH), 131.6 (ar CH), 134.0 (ar C_q), 134.3 (ar CH), 136.4 (ar C_q), 137.4 (ar CH), 145.9 (ar C_q), 148.0 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -1.0$, -19.0.

*3.1.14. 1-Chloro-1-{bis[2′-(dimethylaminomethyl)phenyl]chlorosilyl}-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**22**)*

A solution of 610 mg (1.34 mmol) of **21** and 400 mg (0.45 mmol) of **1** in 10 ml of toluene was stirred for 4 h at 65 °C. The solvent was removed in vacuo leaving behind 1.00 g (98%) of **22** as yellow crystals (m.p. 94–96 °C). ^{1}H-NMR (C_6D_6): $\delta = 1.78$ (s, 12H, NMe_2), 2.92, 3.41 (AB System, $^2J_{AB} = 13$ Hz, CH_2N, 4H), 6.72–6.87 (m, ar H, 12H), 6.95 (ddd, $^3J = {}^3J = 7$ Hz, $^4J = 1$ Hz, 2H, ar H), 7.02–7.15 (m, 8H, ar H), 7.28 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, ar H, 4H), 8.23 (d, $^3J = 8$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 45.5$ (NMe_2), 64.1 (CH_2N), 126.1 (ar CH), 126.6 (ar CH), 126.8 (ar CH), 128.3 (ar CH), 128.5 (ar CH), 129.3 (ar CH), 130.1 (ar CH), 130.2 (ar CH), 130.3 (ar CH), 134.2 (ar C_q), 138.0 (ar CH), 138.5 (ar C_q), 138.8 (ar C_q) 140.6 (ar C_q), 145.7 (ar C_q), 156.7 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = 0.6$, -26.4. MS (FAB (NOE), pos. mode), *m/z* (%): 753/751 (1/2) [M + 1]$^+$, 715 (2) [M$^+$–Cl, correct isotope pattern].

*3.1.15. 1,1-Bis[2-(dimethylaminomethyl)phenyl]-2-phenyl-1,2,2-trichlorodisilane (**24a**)*

A solution of 527 mg (0.60 mmol) of **1** and 284 μl (1.78 mmol) in 10 ml of toluene was stirred for 7 days at room temperature (r.t.). After removing the solvent in vacuo 10 ml of hexane were added to the residue and the resulting suspension was filtered. The solvent was removed from the filtrate in vacuo leaving behind 768 mg (85%) of **24a** as a viscous oil. ^{1}H-NMR (C_6D_6): $\delta = 1.78$ (s, 12H, NMe_2), 2.90, 3.43 (AB system, $^2J_{AB} = 13$ Hz, 4H, CH_2N), 6.97–7.16 (m, 9H, ar H), 7.89–7.97 (m, 2H, ar H), 8.29–8.33 (m, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 45.5$ (NMe_2), 64.3 (CH_2N), 127.0 (ar CH), 128.1 (ar CH), 128.7 (ar CH), 130.6 (ar CH), 131.0 (ar CH), 132.9 (ar C_q), 134.6 (ar CH), 135.2 (ar C_q), 137.2 (ar CH), 146.0 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = 9.5$ ($PhSiCl_2$), -23.6 (Ar_2SiCl).

*3.1.16. Reaction of **1** with **25***

A solution of 258 mg (0.29 mmol) of **1** and 215 mg (0.80 mmol) of **25** in 5 ml toluene was stirred for 5 days at r.t. The suspension was filtered. After removal of the solvent from the filtrate in vacuo 293 mg (99%) of **17b** were obtained as a colorless solid. The white solid, which was filtered off, was insoluble in hydrocarbons, etheral solvent and halogenated solvents. Anal. for the precipitate found: C, 51.65; H, 6.59; N, 6.09%.

3.1.17. 1,2-Dichloro-1-[2-(dimethylaminomethyl)-phenyl]-2,2-diphenyl-1-(2,4,6-trimethylphenyl)disilane ***(26b)***

A solution of 432 mg (0.51 mmol) of **3** and 315 μl (1.50 mmol) of **9b** in 20 ml of toluene was stirred for 3 days at 80 °C. The solvent was removed in vacuo and 20 ml of pentane were added to the residue. The resulting suspension was filtered leaving behind 642 mg (80%) of **26b** as colorless crystals (m.p. 130–132 °C). ^{1}H-NMR (C_6D_6): $\delta = 1.82$ (s, *o*-Me, 6H), 2.04 (s, *p*-Me, 3 H), 2.47 (s, NMe_2, 6H), 2.43, 3.37 (AB system, $^2J_{AB} = 13$ Hz, 2H, CH_2N), 6.64 (s, ar H, 2H), 6.90–7.13 (m, ar H, 10H), 7.69 (dd, $^3J = 6$ Hz, 2H, ar H), 8.14 (dd, $^3J = 8$ Hz, $^4J = 3$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 21.0$ (Me), 25.3 (Me), 45.8 (CH_3N), 64.9 (CH_2N), 127.2 (ar CH), 128.2 (ar CH), 129.6 (ar CH), 130.0 (ar CH), 130.2 (ar CH), 130.5 (ar CH), 134.0 (ar C_q), 134.5 (ar C_q), 134.9 (ar C_q), 136.5 (ar CH), 136.7 (ar CH), 138.5 (ar CH), 139.4 (ar C_q), 144.6 (ar C_q), 145.5 (ar C_q), 146.0 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -2.1$ ($SiPh_2Cl$), -15.0 (SiArMesCl).

3.1.18. 1-Chloro-1-{[2′-(dimethylaminomethyl)-phenyl][(2,4,6-trimethylphenyl]chlorosilyl}-2,3,4,5-tetraphenyl-1-silacyclopentadiene ***(29)***

A solution of 799 mg (1.75 mmol) of **21** and 511 mg (0.61 mmol) of **3** in 20 ml of toluene was heated for 24 h at 90 °C. The solvent was removed in vacuo and the residue was suspended in 20 ml of pentane. After filtration of the suspension 453 mg (35%) of **29** remained as a white solid (m.p. 73–75 °C). ^{1}H-NMR (C_6D_6): $\delta = 1.76$ (s, 6H, *o*-Me), 2.00 (s, 3H, *p*-Me), 2.31 (s, 6H, NMe_2), 2.65 3.10 (AB system, $^2J_{AB} = 13$ Hz, 2H, CH_2N), 6.53 (s, ar H, 2H), 6.66–7.23 (br.m, 19H, ar H), 7.40 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 2H, ar H), 7.49 (d, $^3J = 7$ Hz, 2H, ar H), 8.31 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 1H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 21.4$ (Me), 25.2 (Me), 45.6 (NMe_2), 64.7 (CH_2N), 125.6 (ar CH), 126.2 (ar CH), 126.3 (ar CH), 126.7 (ar CH), 126.8 (ar CH), 127.6 (ar CH), 127.8 (ar CH), 128.1 (ar CH), 128.5 (ar CH), 128.8 (ar CH), 128.9 (ar CH), 129.3 (ar CH), 129.5 (ar CH), 129.7 (ar CH), 129.8 (ar CH), 129.9 (ar CH), 129.9 (ar CH), 130.0 (ar CH), 130.1 (ar CH), 134.3 (ar CH), 135.9 (ar C_q), 137.1 (ar C_q), 138.2 (ar CH), 138.5 (ar C_q), 138.6 (ar C_q), 138.8 (ar C_q), 139.5 (ar C_q), 139.6 (ar C_q), 141.1 (ar C_q), 144.0 (ar C_q), 145.4 (ar C_q), 155.3 (ar C_q), 156.9 (ar C_q), 157.3 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = 0.6$, -21.3. MS (FAB, 3-NBA), *m*/*z* (%): 736/38/40 (70/54/14) [$M^+ + H$], 700/02/04 (50/24/ < 1) [(M^+–Cl], 316/318 (30/10) [ArMesClSi]$^+$.

3.1.19. 1,2,2-Trichloro-1-[2-(dimethylaminomethyl)-phenyl]-1,2-bis-(2,4,6-trimethylphenyl)disilane ***(31)***

A solution of 1.49 g (1.80 mmol) of **3** and 1.34 g (5.30 mmol) of **30** in 35 ml of toluene was stirred for 17 h at 85 °C. The solvent was removed in vacuo and 30 ml of hexane were added to the remaining solid. The resulting suspension was filtered to yield 2.30 g (82%) of **31** as colorless crystals (m.p. 116–119 °C). ^{1}H-NMR (C_6D_6): $\delta = 1.74$ (s, 6H, CH_3), 2.00 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.47 (s, 6H, CH_3), 2.50 (s, 6H, CH_3), 2.81 3.42 (AB system, $^2J_{AB} = 13$ Hz, 2H, CH_2), 6.59 (s, 4H, ar H), 6.99–7.22 (m, 3H, ar H), 8.32 (d, $^3J = 7$ Hz, 1H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 20.9$ (*p*-Me), 25.4 (*o*-Me), 26.0 (*o*-Me), 45.3 (NMe_2), 64.5 (CH_2N), 127.5 (ar CH), 128.8 (ar CH), 129.8 (ar CH), 130.5 (ar CH), 130.8 (ar CH), 133.8 (ar C_q), 137.6 (ar CH), 140.2 (ar C_q), 141.2 (ar C_q), 144.7 (ar C_q), 145.5 (ar CH), 145.7 (ar C_q), 146.3 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = 9.4$ ($SiMesCl_2$), -9.0 (SiArMesCl). MS (EI, 70 eV), *m*/*z* (%): 533 (16) [M^+, correct isotope pattern], 380/82/84 (100/76/18) [$M^+ + H$–Mes–Cl], 350/52/54 (28/24/8) [380–2 Me], 316/318 (64/22) [MesArClSi]$^+$, 306/308 (12/8) [$MesArCl_2Si^+$–H–NMe_2], 217/19 (44/20) [$MesCl_2Si$]$^+$, 120 (100) [MesH]$^+$, 105 (68) [$MesH^+$–Me].

3.1.20. Reaction of ***1*** *with* ***32b***

A solution of 100 mg (296 μmol) of **32b** and 88 mg (99 μmol) of **1** in 0.4 ml of C_6D_6 was heated for 60 h at 90 °C. The ^{1}H-NMR and ^{29}Si-NMR spectra of the product mixture showed that, besides a small amount of **32b**, dichlorosilane **17b** and dichlorodisilane **18b** were formed as major products in a 4:1 ratio.

3.1.21. Reaction of ***1*** *with* ***32a***

A solution of 72 mg (0.27 mmol) of **32a** and 80 mg (0.09 mmol) of **1** in 0.4 ml of C_6D_6 was heated for 84 h at 90 °C. In the product mixture small amounts of **33a** were identified by comparing the ^{1}H-NMR spectrum with that of an authentic sample besides the starting materials and unknown compounds.

3.1.22. Reaction of ***1*** *with* ***27b***

A solution of 47 mg (0.14 mmol) of **27b** and 40 mg (45 μmol) of **1** in 0.5 ml of C_6D_6 was heated for 2 h at 45 °C. ^{1}H-NMR spectroscopic analysis showed **18b** to be the major product besides minor amounts of **17b** and **27b**.

3.1.23. Reaction of ***3*** *with* ***17b***

A solution of 52 mg (0.14 mmol) of **17b** and 40 mg (47 μmol) of **3** in 0.5 ml of C_6D_6 was heated for 2 h at 85 °C. ^{1}H-NMR spectroscopic analysis showed **18b** to be the major product besides minor amounts of **27b** and **17b**.

3.1.24. 2-(Dimethylaminomethyl)phenyl-(2,4,6-trimethylphenyl)silane ***(27a)***

A solution of 460 mg (1.31 mmol) **27b** in 5 ml of a 1:1 mixture of THF–Et_2O (1:1) was added to a stirred suspension of 105 mg (2.76 mmol) of $LiAlH_4$ in 5 ml of Et_2O at 0 °C. The suspension was warmed to r.t., the solvent was removed in vacuo and 15 ml of Et_2O were added to the residue. After filtration of the resulting suspension 0.5 ml of H_2O was added to the filtrate at − 78 °C. The resulting suspension was warmed to r.t. and filtered. The solvent was removed in vacuo from the filtrate leaving behind 279 mg (75%) of **27a** as a colorless oil. ^{1}H-NMR (C_6D_6): $\delta = 1.96$ (s, 6H, NMe_2), 2.18 (s, 3H, *p*-Me), 2.45 (s, 6H, *o*-Me), 3.29 (s, 2H, CH_2N), 5.28 (s(d, $^2J_{SiH} = 209$ Hz), 2H, SiH), 6.83 (s, 2H, ar H), 6.98 (dd, $2\cdot{}^3J = 7$ Hz, 1H, ar H), 7.08 (d, $^3J = 7$ Hz, 1H, ar H), 7.10 (d, $^3J = 7$ Hz, 1H, ar H), 7.56 (d, $^3J = 7$ Hz, 1H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 21.3$ (Me), 23.7 (Me), 43.9 (NMe_2), 64.5 (CH_2N), 127.2 (ar CH), 127.9 (ar CH), 128.7 (ar CH), 129.7 (ar CH), 130.7 (ar C_q), 133.2 (ar C_q), 137.5 (ar CH), 138.7 (ar C_q), 144.7 (ar C_q), 146.5 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -55.6$ (dt, $^1J_{SiH} = 209$ Hz, $^4J_{SiH} = 6$ Hz). MS (EI, 70 eV), *m/z* (%): 282 (4) $[M^+ - 1]$, 237 (5) $[M^+\text{–H–HNMe}_2]$, 223 (12) $[M^+\text{–CH}_2\text{NMe}_2\text{–Me–H}]$, 164 (100) $[M^+\text{–Mes}]$, 148 (30) $[M^+\text{–H–Ar}]$, 135 (8) $[ArH]^+$, 119 (20) $[Mes]^+$, 91 (12) $[C_7H_7]^+$, 58 (18) $[CH_2NMe_2]^+$. Anal. Calc. for $C_{18}H_{25}NSi$ (283.49): C 76.26; H, 8.89, Found: C 76.56; H, 9.12%.

3.1.25. Reaction of **1** with **27a**

A solution of 50 mg (0.18 mmol) of **27a** and 52 mg (59 µmol) of **1** in 0.5 ml of C_6D_6 was heated for 2 h at 60 °C and additional 15 h at 80 °C. The ^{1}H-NMR spectrum of the product mixture showed the signals of **17a** besides that of starting material **27a**; no signals of **1** could be detected.

3.1.26. Reaction of **3** with **17a**

A solution of 45 mg (0.15 mmol) of **17a** and 42 mg (50 µmol) of **3** in 0.5 ml of C_6D_6 was heated for 18 h at 90 °C. The ^{1}H-NMR spectrum of the product mixture showed the signals of **27a** besides that of starting material **17a**; no signals of **1** could be detected.

3.2. Formation of trisilanes by silylene insertion

3.2.1. 1,3-Dichloro-1,1-bis[2-(dimethylaminomethyl)-phenyl]-2,2,3,3-tetraphenyltrisilane (**36**)

A solution of 100 mg (0.11 mmol) of **1** and 147 mg (0.34 mmol) of **35** in 0.5 ml of C_6D_6 was heated for 16 h at 45 °C. ^{1}H-NMR spectroscopic analysis of the reaction mixture at this point showed that still some **35** was present, although all **1** was consumed. Addition of further 15 mg (0.02 mmol) of **1** and heating for additional 3 h at 60 °C did not lead to further conversion. The solvent was removed in vacuo and the residue was suspended in 5 ml of pentane. After filtration of the suspension, the filtrate was reduced in vacuo to half of its volume and stored overnight at 3 °C leading to 85 mg (35%) of **36** as colorless crystals (m.p. 106–108 °C), which were still contaminated with traces of **35**. ^{1}H-NMR (C_6D_6): $\delta = 1.71$ (s; 12H, NMe_2), 3.17, 3.23 (AB system, $^2J_{AB} = 14$ Hz, 4H, CH_2N), 6.95–7.15 (m, 14H, ar H), 7.18 (ddd, $^3J = {}^3J = 8$ Hz, $^4J = 1$ Hz, 2H, ar H), 7.55 (d, $^3J = 8$ Hz, 2H, ar H), 7.60 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 4H, ar H), 7.87 (dd, $^3J = 8$ Hz, $^4J = 1$ Hz, 4H, ar H), 8.02 (d, $^3J = 7$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 45.0$ (NMe_2), 63.8 (CH_2N), 126.4 (ar CH), 128.1 (ar CH), 128.3 (ar CH), 128.9 (ar CH), 129.8 (ar CH), 130.3 (ar CH), 130.6 (ar CH), 132.9 (ar C_q), 134.0 (ar C_q), 135.1 (ar C_q), 135.8 (ar CH), 137.6 (ar CH), 138.0 (ar CH), 146.6 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = +3.3$ (SiCl), + 1.2 (SiCl), − 38.3 ($SiPh_2$). MS (EI, 70 eV), *m/z* (%): 730 (1) $[M]^+$, 695 (1) $[M^+\text{–Cl}]$, 598/596 (4/5) $[M^+\text{–Ar}]$, 333/331 (3/9) $[Ar_2SiCl]^+$, 297 (18) $[Ar_2SiH]^+$, 259 (100), 217 (52) $[Ph_2SiCl]^+$, 182 (23) $[Ph_2Si]^+$. $C_{42}H_{44}N_2Si_3Cl_2$ (730.2189): correct HRMS.

3.2.2. 1,1,3,3-Tetrakis[2-(dimethylaminomethyl)-phenyl]-2,2-diphenyltrisilane (**37a**)

(a) A solution of 201 mg (0.23 mmol) of **1** and 326 mg (0.68 mmol) of **10a** in 10 ml of toluene was heated for 6 days at 90 °C. The cloudy solution was filtered and the solvent was removed in vacuo from the filtrate leaving behind 467 mg (89%) of **37a** as a colorless oil. (b) Heating of a solution of 33 µl (0.18 mmol) of **9a** and 106 mg (0.12 mmol) of **1** in 0.5 ml of C_6D_6 for 6 days at 90 °C gave after removal of the solvent 125 mg (90%) of **37a**. ^{1}H-NMR (C_6D_6): $\delta = 1.89$ (s, 24H, NMe_2), 3.31, 3.43 (AB system, $^2J_{AB} = 14$ Hz, 8H, CH_2N), 5.85 (s (d, $^1J_{SiH} = 197$ Hz), 2H, SiH), 6.91 (dd, $^3J = 7$ Hz, $^3J = 7$ Hz, 4H, ar H), 7.03–7.16 (m, 10H, ar H), 7.45 (d, $^3J = 8$ Hz, 4H, ar H), 7.57 (d, $^3J = 7$ Hz, 4H, ar H), 7.63 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 45.1$ (NMe_2), 64.5 (CH_2N), 126.1 (ar CH), 128.1 (ar CH), 128.9 (ar CH), 129.3 (ar CH), 134.4 (ar C_q), 135.9 (ar C_q), 136.5 (ar CH), 137.5 (ar CH), 138.4 (ar CH), 146.1 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -40.8$ (dt, $^1J_{SiH} = 198$ Hz, $^3J_{SiH} = 6$ Hz, $SiAr_2H$), − 41.4 ($SiPh_2$).

3.2.3. 1,3-Dichloro-1,1,3,3-tetrakis[2-(dimethyl-aminomethyl)phenyl]-2,2-diphenyltrisilane (**37b**)

(a) A solution of 0.90 g (1.01 mmol) of **1** and 1.67 g (3.03 mmol) of **10b** in 8 ml of toluene was heated for 2 h at 70 °C. The solvent was removed in vacuo, the resulting residue was suspended in 10 ml of pentane and the suspension was filtered. The remaining solid was dissolved in a mixture of ca. 1 ml of THF and 2 ml of hexane. Storing the solution at + 3 °C for 16 h yielded 2.10 g (78%) of **37b** as colorless crystals. (b) A solution of 21.4 g (24 mmol) of **1** and 7.5 ml (36 mmol) of **9b** in 100 ml of toluene was heated for 2 h at 70 °C. The solvent was removed in vacuo, 6.18 g of the resulting residue (total: 30 g) were suspended in 100 ml of pentane and the suspension was filtered. The remaining solid was dissolved in a mixture of ca. 10 ml of

THF and 20 ml of hexane. The solution was kept at +3 °C overnight and 4.70 g (76%) of **37b** was isolated as colorless crystals (m.p. 161–162 °C). ^{1}H-NMR (C_6D_6): $\delta = 1.77$ (s; 24H, NMe_2), 3.16, 3.24 (AB system, $^2J_{AB} = 14$ Hz, 8H, CH_2N), 6.95–7.10 (m, 10H, ar H), 7.20 (ddd, $^3J = 8$ Hz, $^3J = 7$ Hz, $^4J = 1$ Hz, 4H, ar H), 7.70 (d, $^3J = 8$ Hz, 4H, ar H), 8.00–8.15 (m, 8H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 44.1$ (NMe_2), 63.4 (CH_2N), 126.1 (ar CH), 128.4 (ar CH), 128.9 (ar CH), 129.7 (ar CH), 130.8 (ar CH), 133.7 (ar C_q), 134.1 (ar C_q), 137.6 (ar CH), 138.5 (ar CH), 146.8 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = +5.5$ ($SiAr_2Cl$), -36.7 ($SiPh_2$). MS (FAB, NOE, pos. mode), *m/z* (%): 846 (3) [$M^+ + H$], 807 (100); (EI, 70 eV), *m/z* (%): 550/548 (8/12) [M^+–Ar_2Si], 416/414 (79/100) [M^+–Ar_2Si–Ar]. Anal. Calc. for $C_{48}H_{58}N_4Si_3Cl_2$ (846.17): C, 68.13; H, 6.91, Found: C 68.05; H, 6.83%.

3.3. Formation of disilanes by nucleophilic substitution

*3.3.1. 1,1,2,2-Tetrakis[2-(dimethylaminomethyl)phenyl]disilane (**18a**)*

A suspension of 13.63 g (40.9 mmol) of **17c** in 200 ml of toluene and 1.92 g (49.1 mmol) of finely cut potassium was stirred for 48 h at r.t. The suspension was filtered and the solvent was removed from the filtrate in vacuo leaving behind 11.02 g (91%) of **18a** as an analytically pure, crystalline solid (m.p. 91–92 °C).

*3.3.2. 1,1-Bis[2-(dimethylaminomethyl)phenyl]-2,2,2-trimethyldisilane (**6b**)*

(a) A suspension of 2.50 g (7.60 mmol) **18a**, 626 mg (16.00 mmol) finely cut potassium and 1.26 ml (9.97 mmol) of Me_3SiCl (**5**) in 20 ml of toluene was stirred for 4 days at r.t. The suspension was filtered and the solvent was removed from the filtrate in vacuo leaving behind the crude product as an oil. Distillation at 200 °C/10^{-3} torr gave 1.34 g (49%) of **6b** as colorless oil. (b) 13 mg (1.9 mmol) of finely cut lithium were added to a solution of 560 mg (0.94 mmol) of **18a** in 10 ml of THF and the resulting suspension was stirred for 16 h at r.t. After filtration of the suspension 0.27 ml (2.1 mmol) of **5** were added to the filtrate at −78 °C and the solution was allowed to warm up to r.t. The solvent was removed in vacuo and the residue was suspended in 15 ml of Et_2O. The suspension was filtered and the solvent was removed in vacuo from the filtrate. Kugelrohr distillation of the remaining oil yielded to 439 mg (63%) of **6b** as a colorless oil (boiling point (b.p.) 180 °C/0.001 torr). ^{1}H-NMR (C_6D_6): $\delta = 0.30$ (s; 9H, $SiMe_3$), 1.94 (s; 12H, NMe_2), 3.35, 3.42 (AB system, $^2J = 13$ Hz, 4H, CH_2N), 5.27 (s (d, $^1J_{SiH} = 186$ Hz); 1H, SiH), 7.08–7.22 (m, 4H, ar H), 7.34 (d, $^3J = 7$ Hz, 2H, ar H), 7.74 (dd, $^3J = 7$ Hz, $^4J = 2$ Hz, 2H; ar H). ^{13}C-NMR (C_6D_6): $\delta = -0.1$ ($SiMe_3$), 45.0 (NMe_2), 64.4 (CH_2N), 126.4 (ar CH), 128.9 (ar CH), 129.5 (ar CH), 136.1 (ar C_q), 137.4 (ar CH), 146.0 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -17.6$ ($SiMe_3$), -39.6 (d, $^1J_{SiH} = 186$ Hz, $SiAr_2H$). IR (film): $\tilde{\nu} = 2125$ cm^{-1} (SiH). MS (EI, 70 eV) *m/z* (%): 369 (8) [M^+–H], 355 (4) [M^+–Me], 326 (10) [M^+–NMe_2], 297 (100) [M^+–$SiMe_3$], 236 (55) [M^+–Ar], 134 (7) $[Ar]^+$, 73 (14) $[SiMe_3]^+$, 58 (12) $[CH_2NMe_2]^+$. Anal. Calc. for $C_{21}H_{34}N_2Si$ (370.68): C 68.23; H, 9.00; N, 7.58; Found: C 68.16; H, 8.93; N, 7.37%.

*3.3.3. 1-Chloro-2,2-bis[2-(dimethylaminomethyl)phenyl]-1,1-bis(2,4,6-trimethylphenyl)disilane (**33c**)*

A suspension of 2.60 g (4.38 mmol) of **18a** and 100 mg (14.4 mmol) of finely cut lithium in 42 ml of THF was vigorously stirred for 19 h at r.t. The liquid phase was transferred through a Teflon cannula by means of a positive argon pressure to a solution of 2.57 g (7.60 mmol) of **32b** in 20 ml of THF at 0 °C during 10 min. The reaction mixture was allowed to warm up to r.t. and was stirred for additional 20 h. The solvent was removed in vacuo and the residue suspended in 50 ml of hexane. After filtration of the suspension the remaining residue was washed several times by recondensation of the solvent. The filtrate was concentrated in vacuo to a volume of ca. 7 ml. At −20 °C 3.41 g (75%) of **33c** precipitated from the solution as colorless crystals (m.p. 155 °C). ^{1}H-NMR (C_6D_6): $\delta = 1.95$ (s; 12H, NMe_2), 2.04 (s; 6H, Me), 2.36 (s; 12H, Me), 2.95, 3.36 (AB system, $^2J = 14$ Hz, 4H, CH_2N), 5.93 (s (d, $^1J_{SiH} = 204$ Hz); 1H, SiH), 6.61 (s, 4H, ar H), 7.01 (ddd, $^3J = ^3J = 7$ Hz, $^4J = 1$ Hz, 2H, ar H), 7.19 (ddd, $^3J = ^3J = 7$ Hz, $^4J = 1$ Hz, 2H, ar H), 7.47 (d, $^3J = 7$ Hz, 2H, ar H), 8.22 (dd, $^3J = 7$ Hz, $^4J = 1$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 20.9$ (Me), 24.4 (Me), 45.2 (NMe_2), 63.9 (CH_2N), 126.3 (ar CH), 128.8 (ar CH), 129.7 (ar CH), 130.0 (ar CH), 132.9 (ar C_q), 133.0 (ar C_q), 138.5 (ar CH), 139.5 (ar C_q), 144.2 (ar C_q), 146.4 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = +1.8$ ($SiMes_2Cl$), -44.8 (d, $^1J_{SiH} = 204$ Hz, $SiAr_2H$). MS (EI, 70 eV), *m/z* (%): 598 (< 1) $[M]^+$, 562 (1) [$Ar_2Si{=}SiMes_2^+$], 553 (1) [M^+–NMe_2–H], 538 (3) [M^+–CH_2NMe_2–2H], 464 (11) [M^+–Ar], 331 (6) [M^+–Ar_2Si], 297 (100) $[Ar_2SiH]^+$, 120 (22) $[MesH]^+$, 58 (8) $[CH_2NMe_2]^+$. $C_{36}H_{47}N_2Si_2Cl$ (548.1637): correct HRMS. Anal. Calc. for $C_{36}H_{47}N_2Si_2Cl$ (599.41): C 72.14; H, 7.90; Found: C 72.88; H, 8.27%.

*3.3.4. 1,1,3,3-Tetrakis[2-(dimethylaminomethyl)phenyl]-2,2-dimethyltrisilane (**38**)*

A suspension of 317 mg (0.53 mmol) of **18a** and 8 mg (1.2 mmol) of finely cut lithium in 5 ml of THF was stirred at r.t. for 3.5 h. After 1.5 h of supersonic irradiation it was stirred for additional 1 h at r.t. The suspension was filtered and the filtrate was transferred through a Teflon cannula by means of a positive argon pressure to solution of 0.2 ml (1.6 mmol) of **7a** in 5 ml of THF at 0 °C. The resulting suspension was stirred for 12 h at r.t. and filtered. The solvent was removed from the filtrate and the residue was suspended in 10 ml of hexane. After filtration the solvent was removed from the filtrate in vacuo leaving behind 334 mg (97%) of crude **38** as a viscous oil. Distillation at 300 °C/10^{-4} torr gave 151 mg (43%) of ^{1}H-NMR spectroscopically pure **38**. ^{1}H-NMR (C_6D_6): $\delta = 0.50$ (s, 6H, $SiMe_2$), 1.95 (s, 24H, NMe_2), 3.39 (s, 8H, CH_2N), 5.43 (s (d, $^{1}J_{SiH} = 191$ Hz); 2H, Ar_2SiH), 7.01 (dd, $^{3}J=^{3}J = 7$ Hz, 4H, ar H), 7.14 (ddd, $^{3}J = 7$ Hz, $^{3}J = 7$ Hz, $^{4}J = 1$ Hz, 4H, ar H), 7.35 (d, $^{3}J = 7$ Hz, 4H, ar H), 7.67 (d, $^{3}J = 7$ Hz, 4H, ar H). ^{13}C-NMR (C_6D_6): $\delta = -2.7$ ($SiMe_2$), 44.9 (NMe_2), 64.8 (CH_2N), 126.3 (ar CH), 128.9 (ar CH), 129.4 (ar CH), 135.9 (ar C_q), 137.8 (ar CH), 145.6 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -36.1$ (d, $^{1}J_{siH} = 191$ Hz, Ar_2SiH), -44.2 (Me_2Si). IR (film): $\tilde{\nu} = 2124$ cm^{-1}. MS (EI, 70 eV), *m/z* (%): 650 (1) [M^{+}–2H], 608 (1) [M^{+}–NMe_2], 564 (1) [M^{+}–2NMe_2], 355 (4) [M^{+}–Ar_2SiH], 297 (100) [Ar_2SiH]$^{+}$, 281 (4) [Ar_2SiH^{+}–Me–H], 238 (5) [Ar_2SiH^{+}–NMe_2–Me], 209 (6) [Ar_2SiH^{+}–2NMe_2], 134 (2) [Ar]$^{+}$, 58 (4) [CH_2NMe_2]$^{+}$.

3.3.5. 1-Chloro-1-[2-(dimethylaminomethyl)-phenyl]-1,2,2-tris(2,4,6-trimethylphenyl)disilane (39a)

A solution of 1.45 g (3.20 mmol) Mes_2SiHLi in 20 ml of toluene was added dropwise over 10–15 min to a solution of 1.12 g (3.20 mmol) of **27b** in 20 ml of toluene at 0 °C. The resulting suspension was stirred 2 h at 0 °C and for additional 2 h at r.t. The solvent was evaporated in vacuo and 40 ml of pentane were added to the residue. The resulting suspension was filtered and the filtrate was concentrated in vacuo to 5 ml. After 1 week at r.t. 225 mg (13%) of **39a** were obtained as colorless crystals (m.p. 153–155 °C). ^{1}H-NMR ($CDCl_3$): $\delta = 1.84$ (s, 6H, NMe_2), 1.92 (s, 6H, Me), 2.23 (s, 3H, Me), 2.25 (s, 3H, Me), 2.26 (s, 3H, Me), 2.30 (s, 3H, Me), 2.34 (s, 3H, Me), 2.79, 3.37 (AB system,$^{2}J_{AB} = 13$ Hz, 2H, CH_2N), 5.36 (d, $^{1}J_{SiH} = 188$ Hz, 1H, SiH), 6.66 (s, 2H, ar H), 6.80 (s, 4H, ar H), 6.92–6.98 (m, 1H, ar H), 7.22–7.30 (m, 3H, ar H). ^{13}C-NMR ($CDCl_3$): $\delta = 21.1$ (Me), 24.0 (Me), 24.5 (Me), 24.7 (Me), 45.1 (NMe_2), 63.8 (CH_2N), 126.4 (ar CH), 128.1 (ar C_q), 128.5 (ar CH), 128.7 (ar CH), 129.3 (ar CH), 129.6 (ar CH), 130.6 (ar C_q), 130.6 (ar C_q), 134.8 (ar C_q), 136.8 (ar CH), 138.7 (ar C_q), 139.8 (ar C_q), 145.0 (ar C_q), 145.6 (ar C_q). ^{29}Si-NMR ($CDCl_3$): $\delta = 1.5$ ($SiAr_2Cl$), -51.4 ($SiMes_2H$). MS (EI, 70 eV), *m/z* (%): 583 (3) [M]$^{+}$, 463 (2) [M^{+}–Mes–H], 448 (8) [M^{+}–Ar], 418 (4) [M^{+}–Ar–2Me–H], 316 (100) [MesArClSi]$^{+}$, 147 (9) [MesSi]$^{+}$, 133 (4) [$C_9H_{11}N$]$^{+}$, 91 (2) [C_7H_7]$^{+}$, 58 (2) [CH_2NMe_2]$^{+}$.

3.4. Transformations of disilanes

3.4.1. 1,1-Bis[2-(dimethylaminomethyl)phenyl]-2,2,2-trimethyldisilane (6b)

A suspension of 62 mg (0.15 mmol) of **6a** and 10.0 mg (0.53 mmol) of $LiAlH_4$ in 2 ml of Et_2O was stirred for 15 min at r.t. The solvent was removed in vacuo and the residue was suspended in 5 ml of wet hexane. The resulting suspension was filtrated and the solvent was removed from the filtrate in vacuo leaving behind 28 mg (51%) of **6b** as a colorless, ^{1}H-NMR spectroscopically pure oil.

3.4.2. 1,1-Bis[2-(dimethylaminomethyl)phenyl]-2,2-dimethyldisilane (8d)

436 mg (1.1 mmol) of a 3:1 mixture of **8b** and **8c** were suspended in 10 ml of Et_2O. This suspension was added dropwise at 0 °C to a suspension of 73 mg (1.9 mmol) of $LiAlH_4$ in 10 ml of Et_2O. After stirring for 1 h at r.t. the solvent was removed in vacuo and the residue was suspended in 10 ml of hexane. After filtration the solvent was removed from the filtrate leaving behind 342 mg as a viscous oil. It was stirred with wet Et_2O, the solvent was removed in vacuo and distillation of the remaining oil at 200 °C/10^{-3} torr gave 184 mg (47%) of **8d** at 200 °C/10^{-3} torr. ^{1}H-NMR (C_6D_6): $\delta = 0.28$ (d, $^{3}J = 4$ Hz, 6H, $SiMe_2$), 1.90 (s, 12H, NMe_2), 3.29, 3.39 (AB system, $^{2}J_{AB} = 13$ Hz, 4H, CH_2N), 4.35 (dsep, $^{3}J = 4$ Hz, $^{3}J = 2$ Hz, 1H, $SiMe_2H$), 5.23 (d, $^{3}J = 2$ Hz (d, $^{1}J_{SiH} = 193$ Hz); 1H, $SiAr_2H$), 7.07–7.24 (m, 6H, ar H), 7.77 (dd, $^{3}J = 7$ Hz, $^{4}J = 2$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = -4.6$ ($SiMe_2$), 44.7 (NMe_2), 65.1 (CH_2N), 126.5 (ar CH), 128.8 (ar CH), 129.2 (ar CH), 136.1 (ar C_q), 137.5 (ar CH), 145.9 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -37.1$ (dsep, $^{1}J_{SiH} = 179$, $^{2}J_{SiH} = 7$ Hz, $SiMe_2H$), -35.0 (d, $^{1}J_{SiH} = 193$ Hz, $SiAr_2H$). IR (film): $\tilde{\nu} = 2108$ cm^{-1}. MS (EI, 70 eV), *m/z* (%): 355 (1) [M^{+}–H], 311 (8) [M^{+}–NMe_2–H], 297 (100) [M^{+}–$SiMe_2H$], 252 (18) [M^{+}–$SiMe_2H$–NMe_2–H], 222 (19) [M^{+}–Ar], 162 (4) [ArSi]$^{+}$, 134 (3) [Ar]$^{+}$, 58 (5) [CH_2NMe_2]$^{+}$. $C_{20}H_{32}N_2Si_2$ (356.2104): correct HRMS.

3.4.3. 1,1-Bis[2-(dimethylaminomethyl)phenyl]-2,2-diphenyldisilane (10a)

A suspension of 56 mg (1.50 mmol) of $LiAlH_4$ and 187 mg (0.63 mmol) of a 2:1 mixture of **10c** and **10d** in 3 ml of Et_2O was stirred for 20 min at r.t. The solvent was removed in vacuo and 5 ml of hexane were added to the residue. After filtration of the resulting suspension the solvent was removed from the filtrate leaving behind 167 mg (96%) of **10a**.

3.4.4. 1,1-Bis[2-(dimethylaminomethyl)phenyl]-2,2-bis-(4-methylphenyl)disilane (12b)

65 mg (1.71 mmol) of $LiAlH_4$were added at 0 °C to a suspension of 534 mg (0.98 mmol) of **12a** in 15 ml of

Et_2O, and the suspension was stirred for 1 h at r.t. 31 µl of H_2O were added to the reaction mixture at −78 °C, the solvent was removed in vacuo and 10 ml of hexane were added to the remaining solid. The suspension was filtered and the solvent was removed from the filtrate leaving behind 452 mg (91%) of **12b** as a colorless waxy solid. ^{1}H-NMR (C_6D_6): $\delta = 1.87$ (s, 12H, NMe_2), 2.03 (s, 6H, CH_3), 3.32, 3.34 (AB system, $^2J_{AB} = 7$ Hz, 4H, CH_2N), 5.51 (d, $^3J = 3$ Hz (d, $^1J_{SiH} =$ 188 Hz); 1H, SiH), 5.65 (d, $^3J = 3$ Hz (d, $^1J_{SiH} = 198$ Hz), 1H, SiH), 6.96 (d, $^3J = 7$ Hz, 4H, ar H), 7.02–7.25 (m, 6H, ar H), 7.64 (d, $^3J = 8$ Hz, 4H, ar H), 7.84 (dd, $^3J = 7$ Hz, $^4J = 1$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 21.4$ (CH_3), 44.8 (NMe_2), 65.1 (CH_2N), 126.4 (ar CH), 128.9 (ar CH), 129.0 (ar CH), 129.1 (ar CH), 131.8 (ar C_q), 135.3 (ar C_q), 136.6 (ar CH), 138.2 (ar CH), 138.5 (ar C_q), 146.0 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -31.5$ (d, $^1J_{SiH} = 190$ Hz, $SiPh_2H$), −42.2 (d, $^1J_{SiH} = 194$ Hz, $SiAr_2H$). MS (EI, 70 eV), *m*/*z* (%): 507 (1) [M^+–H], 463 (8) [M^+–NMe_2–H], 448 (8) [M^+–NMe_2–Me–H], 374 (10) [M^+–Ar], 297 (100) [M^+–$(MeC_6H_4)_2SiH$], 253 (4) [M^+–$(MeC_6H_4)_2SiH$–NMe_2–H], 238 (8) [M^+–$(MeC_6H_4)_2SiH$–NMe_2–Me].

3.4.5. *2,2-Bis(4-chlorophenyl)-1,1-bis[2-(dimethylaminomethyl)phenyl]disilane* (***14b***)

80 mg (2.12 mmol) of $LiAlH_4$ were added at 0 °C to a suspension of 653 mg (1.06 mmol) of **14a** in 15 ml of Et_2O, and the suspension was stirred for 1 h at r.t. 38 µl of H_2O were added to the reaction mixture at −78 °C, the solvent was removed in vacuo and the residue was suspended with 10 ml of hexane. The suspension was filtered and the solvent was removed from the filtrate leaving behind 380 mg (65%) of **14b** as a colorless waxy solid. ^{1}H-NMR (C_6D_6): $\delta = 1.78$ (s, 12H, NMe_2), 3.25 (s, 4H, CH_2N), 5.22 (d, $^3J = 3$ Hz (d, $^1J_{SiH} = 190$ Hz), 1H, SiH), 5.47 (d, $^3J = 3$ Hz (d, $^1J_{SiH} = 201$ Hz), 1H, SiH), 6.98 (ddd, $^3J = {^3J} = 7$ Hz, $^4J = 2$ Hz, 2H, ar H), 7.06–7.12 (m, 8H, ar H), 7.32 (d, $^3J = 8$ Hz, 4H, ar H), 7.65 (dd, $^3J = 7$ Hz, $^4J = 4$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 44.6$ (NMe_2), 65.0 (CH_2N), 126.5 (ar CH), 128.5 (ar CH), 129.3 (ar CH), 133.7 (ar C_q), 134.6 (ar C_q), 135.8 (ar C_q), 137.7 (ar CH), 137.7 (ar CH), 137.9 (ar CH), 145.9 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -43.0$ (d, $^1J_{SiH} = 203$ Hz), −31.0 (d, $^1J_{SiH} = 192$ Hz). MS (EI, 70 eV), *m*/*z* (%): 547 (1) [M^+–H], 503 (2) [M^+–NMe_2–H], 488 (6) [M^+–NMe_2–Me–H], 414 (7) [M^+–Ar], 297 (100) [M^+–$(ClC_6H_4)_2SiH$], 253 (100) [M^+–$(ClC_6H_4)_2SiH$–NMe_2–H].

3.4.6. *1,1-Bis[2-(dimethylaminomethyl)phenyl]-2-phenyldisilane* (***24b***)

To a suspension of 656 mg (1.29 mmol) of **24a** in 10 ml of Et_2O 70 mg (1.80 mmol) of $LiAlH_4$ were added at 0 °C and the suspension was stirred for 45 min at r.t. The solvent was removed in vacuo and the residue was suspended in 10 ml of wet hexane. The resulting suspension was filtered and the solvent was removed from the filtrate leaving behind 210 mg (41%) of **24b** as a colorless oil. ^{1}H-NMR (C_6D_6): $\delta = 1.82$ (s, 12H, NMe_2), 3.24, 3.32 (AB system, $^2J_{AB} = 13$ Hz, 4H, CH_2N), 4.68 (d, $^3J = 2$ Hz (d, $^1J_{SiH} = 186$ Hz), 2H, SiH_2), 5.37 (t, $^3J = 2$ Hz (d, $^1J_{SiH} = 206$ Hz), 1H, SiH), 6.99–7.17 (m, 9H, ar H), 7.59–7.64 (m, 2H, ar H), 7.88 (dd, $^3J = 7$ Hz, $^4J = 1$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 44.6$ (NMe_2), 65.2 (CH_2N), 126.6 (ar CH), 128.0 (ar CH), 128.9 (ar CH), 128.9 (ar CH), 128.9 (ar CH), 133.4 (ar C_q), 135.6 (ar C_q) 136.5 (ar CH), 137.6 (ar CH), 146.7 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -42.1$ (dtt, $^1J_{SiH} = 205$ Hz, $^2J_{SiH} = 6$ Hz, $^3J_{SiH} = 5$ Hz, Ar_2SiH), −56.3 (dtt, $^1J_{SiH} = 186$ Hz, $^2J_{SiH} = 6$ Hz, $^3J_{SiH} = 5$ Hz, $PhSiH_2$). IR (film): $\tilde{\nu} = 2134$ cm^{-1}. MS (EI, 70 eV), *m*/*z* (%): 403 (1) [M^+–H], 359 (3) [M^+–NMe_2–H], 344 (4) [M^+–NMe_2–Me–H], 297 (34) [M^+–$PhSiH_2$], 281 (8) [M^+–$PhSiH_2$–Me–H], 270 (6) [M^+–Ar], 253 (57) [M^+–$PhSiH_2$–NMe_2], 238 (100) [M^+–$PhSiH_2$–CH_2-NMe_2–H], 208 (23) [M^+–$PhSiH_2$–$2NMe_2$–H], 164 (62) [M^+–$PhSiH_2$–Ar + H], 148 (7) [M^+–$PhSiH_2$–Ar–Me], 134 (4) [Ar]$^+$, 119 (16) [Ar^+–Me], 105 (8) [Ar^+–2Me + H], 91 (6) [C_7H_7]$^+$, 58 (16) [CH_2NMe_2]$^+$, 44 (4) [NMe_2]$^+$. $C_{24}H_{32}N_2Si_2$ (404.2104): correct HRMS.

3.4.7. *1,1-Bis(2,4,6-trimethylphenyl)-2,2-bis(2-(dimethylaminomethyl)phenyl]disilane* (***33a***)

A suspension of 500 mg (0.83 mmol) of **33c** and 134 mg (3.53 mmol) of $LiAlH_4$ in 10 ml of Et_2O was stirred for 2 h at r.t. and refluxed for additional 13 h. After addition of 240 µl (13 mmol) of H_2O at −78 °C the mixture was allowed to warm to r.t. and was stirred for 30 min. The solvent was removed in vacuo and the residue was extracted once with 30 ml and twice with 5 ml of hexane. The solvent was removed in vacuo from the collected filtrates leaving behind 310 mg (65%) of **33a** as an NMR spectroscopically pure, white solid (m.p. 45–48 °C). ^{1}H-NMR (C_6D_6): $\delta = 1.90$ (s, 12H, NMe_2), 2.07 (s, 6H, Me), 2.31 (s, 12H, Me), 3.04, 3.41 (AB system, $^2J_{AB} = 13$ Hz, 4H, CH_2N), 5.75, 5.86 (AB system, $^3J_{AB} = 8$ Hz, 2H, Si_2H_2), 6.65 (s, 4H, ar H), 6.93 (ddd, $^3J = {^3J} = 7$ Hz, $^4J = 1$ Hz, 2H, ar H), 7.13 (ddd, $^3J = {^3J} = 7$ Hz, $^4J = 1$ Hz, 2H, ar H), 7.37 (d, $^3J = 7$ Hz, 2H, ar H), 7.77 (dd, $^3J = 7$ Hz, $^4J = 1$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 21.0$ (Me), 24.2 (Me), 45.0 (NMe_2), 64.3 (CH_2N), 126.5 (ar CH), 128.8 (ar CH), 129.0 (ar CH), 129.3 (ar CH), 130.7 (ar C_q), 135.4 (ar C_q), 137.2 (ar CH), 138.6 (ar C_q), 145.1 (ar C_q), 146.0 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -41.8$ (d, $^1J_{SiH} =$ 205 Hz, $SiAr_2H$), −55.7 (dd, $^1J_{SiH} = 178$ Hz, $^2J_{SiH} = 9$ Hz, $SiMes_2H$). MS (EI, 70 eV), *m*/*z* (%): 563 (30) [M^+–H], 297 (37) [Ar_2SiH]$^+$, 91 (100) [C_7H_7]$^+$.

*3.4.8. 1-[2-(Dimethylaminomethyl)phenyl]-1,2,2-tris-(2,4,6-trimethylphenyl)disilane (**39b**)*

A suspension of 445 mg (0.76 mmol) of **39a** and 280 mg (11.73 mmol) of $LiAlH_4$ in 20 ml of Et_2O was refluxed for 19 h. The suspension was filtered and the solvent was removed from the filtrate in vacuo. Distillation of the crude product (170 °C/10^{-4} torr) gave 197 mg (47%) of **39b** as a colorless oil. ^{1}H-NMR (C_6D_6): $\delta = 1.85$ (s, 6H, NMe_2), 2.06 (s, 6H, Me), 2.10 (s, 3H, Me), 2.32 (s, 6H, Me), 2.35 (s, 6H, Me), 2.43 (s, 6H, Me), 2.98, 3.30 (AB system, $^2J_{AB} = 13$ Hz, 2H, CH_2N), 5.89, 5.94 (AB system, $^3J_{AB} = 7$ Hz, 2H, SiH), 6.65 (s, 4H, ar H), 6.72 (s, 2H, ar H), 6.92 (dd, $^3J = ^3J = 8$ Hz, 1H, ar H), 7.12 (dd, $^3J = ^3J = 8$ Hz, 1H, ar H), 7.28 (d, $^3J = 8$ Hz, 1H, ar H), 7.98 (d, $^3J = 8$ Hz, 1H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 21.1$ (Me), 24.1 (Me), 24.3 (Me), 24.8 (Me), 30.2 (*o*-Me), 44.6 (NMe_2), 64.3 (CH_2N), 127.0 (ar CH), 128.7 (ar CH), 128.8 (ar CH), 128.9 (ar CH), 129.1 (ar CH), 129.2 (ar CH), 129.7 (ar CH), 130.5 (ar CH), 130.6 (ar CH), 130.9 (ar CH), 135.8 (ar C_q), 138.3 (ar CH), 138.5 (ar CH), 138.5 (ar CH), 138.9 (ar CH), 144.6 (2·ar C_q), 145.1 (2·ar C_q), 145.3 (ar C_q), 145.5 (2·ar C_q), 146.8 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -44.9$ (d, $^1J_{SiH} = 199$ Hz, SiArMesH), -55.9 (dd, $^1J_{SiH} = 179$ Hz, $^4J_{SiH} = 7$ Hz, $SiMes_2H$). MS (EI, 70 eV), *m/z* (%)*:* 548 (8) [M^+–H], 430 (12) [M^+–Mes], 414 (20) [M^+–Ar], 400 (4) [M^+–Mes–2Me], 282 (100) [ArMesSiH]$^+$, 267 (4) [Mes_2SiH]$^+$.

*3.4.9. 1,2-Dichloro-1,1,2,2-tetrakis[2-(dimethylaminomethyl)phenyl]disilane (**18b**)*

A suspension of 2.50 g (4.20 mmol) of **18a** and 1.18 g (8.83 mmol) of *N*-chlorosuccinimide in 50 ml of CCl_4 was stirred for 5 h at 20 °C. The solvent was removed in vacuo, 50 ml of hexane were added to the residue and the resulting suspension was filtered. The filtrate was reduced in vacuo to half of its volume and on cooling for several days at −15 °C 2.01 g (72%) of **18b** were obtained as a colorless solid.

*3.4.10. 1-Chloro-1,1,2,2-tetrakis[2-(dimethylaminomethyl)phenyl]disilane (**18c**)*

A suspension of 2.27 g (3.81 mmol) of **18a** and 1.07 g (8.00 mmol) of *N*-chlorosuccinimide in 40 ml of hexane was stirred for 6 h at 20 °C. The suspension was filtered and the filtrate was reduced to half of its volume in vacuo. On cooling to −6 °C 1.43 g (59%) of **18c** were obtained as colorless crystals (m.p. 80–82 °C). The mother liquor contained further **18c** as main component besides traces of **18b**.

*3.4.11. 1,2-Dichloro-2,2-bis[2-(dimethylaminomethyl)-phenyl]-1,1-bis(2,4,6-trimethylphenyl)disilane (**33b**)*

A solution of 1.00 g (1.67 mmol) of **33c** in 10 ml of CCl_4 was added dropwise to a stirred suspension of 245 mg (1.84 mmol) of *N*-chlorosuccinimide in 10 ml of CCl_4. After stirring for 2 h at r.t. the suspension was filtered and the remaining solid was washed several times by recondensation of the solvent. The solvent was removed from the filtrate in vacuo leaving behind the crude product. It was suspended in 35 ml of hexane and the resulting suspension was filtered. The solvent was removed from the filtrate in vacuo leaving behind 819 mg (77%) of **33b** as NMR spectroscopically pure, colorless solid (m.p. 63–65 °C). ^{1}H-NMR (C_6D_6): $\delta = 2.00$ (s, 12H, NMe_2), 2.04 (s, 6H, Me), 2.41 (s, 12H, Me), 3.22, 3.65 (AB system, $^2J_{AB} = 15$ Hz, 4H, CH_2N), 6.63 (s, 4H, ar H), 6.92 (dd, $^3J = ^3J = 7$ Hz, 2H, ar H), 7.24 (dd, $^3J = 7$ Hz, $^3J = 8$ Hz, 2H, ar H), 7.86 (d, $^3J = 8$ Hz, 2H, ar H), 8.06 (d, $^3J = 7$ Hz, 2H, ar H). ^{13}C-NMR (C_6D_6): $\delta = 20.9$ (Me), 25.0 (Me), 45.3 (NMe_2), 63.2 (CH_2N), 126.0 (ar CH), 129.3 (ar CH), 130.2 (ar CH), 131.0 (ar CH), 132.5 (ar C_q), 137.9 (ar CH), 140.0 (ar C_q), 144.5 (ar C_q), 147.6 (ar C_q). ^{29}Si-NMR (C_6D_6): $\delta = -0.2$ ($SiMes_2Cl$), -4.8 ($SiAr_2Cl$). MS (FAB, NOE), *m/z* (%)*:* 631 (100) [M^+–H].

3.5. Thermal stability of di- and trisilanes

*3.5.1. Silylene extrusion from **36***

A solution of 20 mg (27 µmol) of **36** and 13 µl (118 µmol) of **40** was heated in an NMR tube at 110 °C. After 13 h the ^{1}H-NMR spectrum of the mixture showed signals of a 1:1 mixture of **35** and **41** [11] besides that of left over **40**.

*3.5.2. Silylene extrusion from **37b***

(a) A solution of 20 mg (24 µmol) of **37b** and 13 µl (118 µmol) of **40** in 0.4 ml of C_6D_6 was heated in an NMR tube at 70 °C. After 18 h, the ^{1}H-NMR spectrum showed signals of a 1:1 mixture of **10b** and **41** besides that of left over **40**. (b) A solution of 47 mg (56 µmol) of **37b** and 12 µl (56 µmol) of **9b** in 0.4 ml of C_6D_6 was heated in an NMR tube at 70 °C for 18 h. The ^{1}H-NMR spectrum showed only the signals of **10b** besides traces of left over **9b**.

*3.5.3. Attempted silylene extrusion from **35***

A solution of 20 mg (46 µmol) of **35** and 26 µl (229 µmol) of **40** in 0.4 ml of C_6D_6 was heated in an NMR tube at 110 °C for 10 h. According to the ^{1}H-NMR spectrum, the composition of the reaction mixture was unchanged.

*3.5.4. Attempted silylene extrusion from **42***

A solution of 20 mg (33 µmol) **7** and 19 µl (166 µmol) of **42** in 0.4 ml of C_6D_6 was heated in an NMR tube at 90 °C for 15 h. According to the ^{1}H-NMR spectroscopic analysis the composition of the reaction mixture was unchanged.

3.5.5. Silylene extrusion from **10b**

A solution of 20 mg (36 μmol) of **10b** and 20 μl (182 μmol) of **40** in 0.4 ml of C_6D_6 was heated in an NMR tube at 110 °C. After 12 h ^{1}H-NMR spectroscopic analysis showed the signals of **9b** and **41** besides those of starting material; the grade of conversion was 20%. Further heating did not result in increased amounts of **9b** and **41**, but favors the formation of decomposition products of unknown structure.

3.5.6. Silylene extrusion from **18b**

A solution of 60 mg (90 μmol) of **18b** and 0.10 ml (0.91 mmol) of **40** in 0.4 ml of C_6D_6 was heated for 19 h at 70 °C. The ^{1}H-NMR spectrum showed the signals of starting materials and traces of an unidentified decomposition product. To this solution 5 mg (6 μmol) of **1** were added and the mixture was heated at 65 °C for 19 h. ^{1}H-NMR spectroscopic analysis showed besides signals of excess **40** only the signals of a 1:1 mixture of **17b** and **41**.

3.5.7. Silylene extrusion from **28b**

A solution of 30 mg (0.05 mmol) of **28b** and 27 μl (0.24 mmol) of **40** in 0.4 ml of C_6D_6 in an NMR tube was heated at 90 °C. ^{1}H-NMR spectroscopy showed the mixture to be unchanged after 24 h. About 1 mg of **3** was added to this mixture and heating at 90 °C was resumed for additional 15 h. The ^{1}H-NMR spectrum showed besides signals of excess **40** only the signals of a equimolar mixture of **27b** and 1-[2′-(dimethylaminomethyl)-phenyl]-1-mesityl-3,4-dimethylsilacyclopent-3-ene.

3.5.8. Single crystal X-ray diffraction analysis of **39a**

Monoclinic, space group $P2_1/n$, $a = 8.572(2)$, $b = 37.4218(17)$, $c = 10.322(2)$ pm, $\beta = 96.10(3)°$; $V = 3292.9(11)$ Å^3, $\rho_{calc} = 1.179$ g cm^{-3}, 2Θ range from 4 to 51°, ($-10 = h = 10$, $0 = k = 45$, $0 = l = 12$), Mo–K$_\alpha$, $\lambda = 71.073$ pm, $T = 133$ K, crystal dimensions $0.5 \times 0.4 \times 0.4$ mm, 33 615 reflections, 6039 independent ($R_{int} = 0.0361$) reflections were used for the structure refinement; final R values: $R_1 = 0.0412$ $[I > 2\sigma(I)]$, $wR_2 = 0.1014$ (all data), residual electron density: 0.298 and -0.253 e Å^{-3}. The structure was solved by direct methods using SHELXS [32] and refined against F^2 using a full matrix least squares target (SHELXL-97) [33]. The R-values were defined as $R_1 = [\Sigma||F_o| - F_c||^2/\Sigma|F_o|^2$ and $wR_2 = \Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2}$. The Si-bound hydrogen atom was localized in the difference Fourier map and refined with the help of 1,3-distance restraints. The other hydrogen atoms were set at geometrically calculated positions and refined using a riding model.

4. Supplementary material

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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