

# The Synthesis of Stable Intramolecularly Dialkylamino-Coordinated Silenes and Their Methyl Iodide Induced Isomerization into Cyclic Aminosilanes<sup>[‡]</sup>

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**Keywords:** Rearrangement / Silaethenes / Silanes / Silenes / Silicon

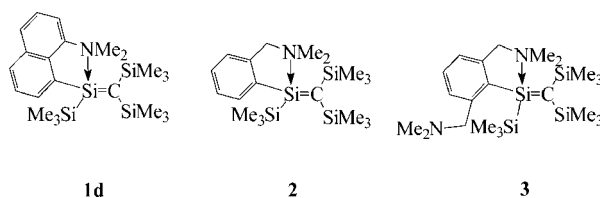
The reaction of the (dichloromethyl)oligosilanes  $R(\text{Me}_3\text{Si})_2\text{-SiCHCl}_2$  **4a–d** (**4a**:  $R = \text{Me}$ ; **4b**:  $R = t\text{Bu}$ ; **4c**:  $R = \text{Ph}$ ; **4d**:  $R = \text{SiMe}_3$ ) with 8-(dimethylamino)-1-naphthyllithium leads to the intramolecularly donor-stabilized silenes **1a–d**. Whereas **1a,b**, and **d** were isolated as thermally stable yellow crystalline compounds, **1c** could not be separated in a pure form but was characterized by NMR spectroscopy and mass spectroscopy as well as by its chemical reactivity with a variety of substrates. Dynamic  $^1\text{H}$  NMR spectroscopic studies of **1a** and **1d** revealed coalescence of the signals of the two  $\text{CSiMe}_3$  groups. In agreement with theoretical calculations, this effect was interpreted as the result of internal rotations about the silene double bond. These findings and the known relatively

long  $\text{Si}=\text{C}$  distances for **1d**, **2** and **3** help establish the ylide-like nature of the silenes prepared. Treatment of **1a–d** with water produced the silanols **9a–d**. Treatment of **1a,b**, and **d** with methyl iodide caused a rearrangement of the silenes, one methyl substituent formally migrating from the coordinated dimethylamino group to the silene carbon atom producing the respective cyclic aminosilanes **11a,b**, and **d**. As the outcome of the reaction of **1d** with benzaldehyde, 2,2-bis(trimethylsilyl)vinylbenzene (**14**) and a mixture of the two isomers of the cyclodisiloxane **13** were obtained.

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## Introduction

Silenes, silicon derivatives with a  $\text{Si}=\text{C}$  double bond, are known as extremely reactive compounds, which in absence of scavenger reagents rapidly undergo dimerization or polymerization. Only very few kinetically stabilized silenes have been isolated and structurally characterized.<sup>[1]</sup> Coordination of amines, THF or fluoride ions to the electrophilic silene silicon atom leads to an effective stabilization of the compounds;<sup>[2a]</sup> Wiberg et al. have succeeded in the isolation of an amine adduct of a silene, which is unstable in the absence of a donor molecule.<sup>[2b]</sup> Recently we presented the synthesis, by a new pathway, isolation and structural characterization of the first intramolecularly donor-stabilized silenes **1d**, **2**, and **3**.<sup>[3]</sup> The compounds proved to be thermally stable up to 140 °C and, compared with uncomplexed silenes, their reactivity was also dramatically reduced.



In this paper we report on the general applicability of the newly developed synthetic route, describe some further stable silenes, and discuss the results of recent studies characterizing their chemical behavior. Dynamic NMR studies in combination with quantum mechanical calculations give an insight into rotational processes about the  $\text{Si}=\text{C}$  bonds of these compounds. Furthermore, we describe an unexpected methyl iodide induced isomerization of intramolecularly amine-coordinated silenes into cyclic aminosilanes.

## Results and Discussion

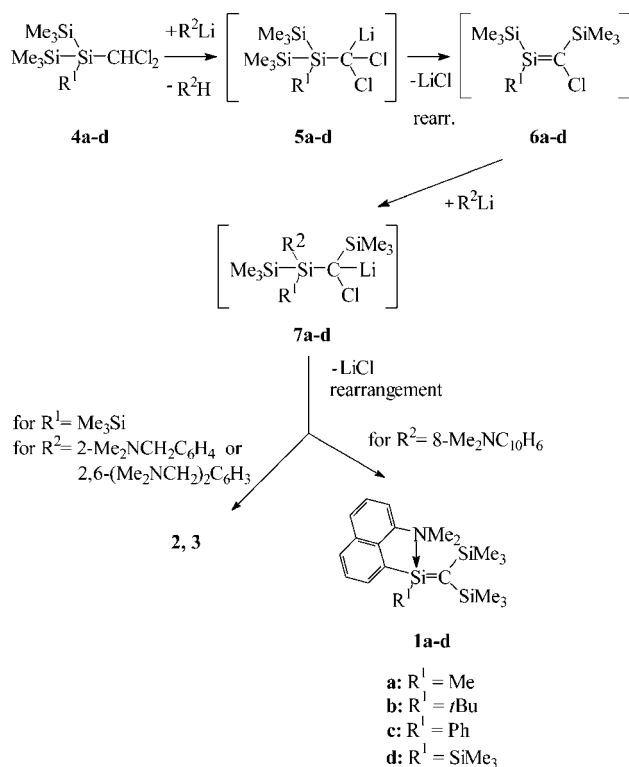
### Synthesis of Intramolecularly Donor-Stabilized Silenes

As described previously, the silenes **1d**, **2**, and **3** are easily accessible in a one-pot reaction by treatment of (dichloromethyl)tris(trimethylsilyl)silane (**4d**,  $R^1 = \text{SiMe}_3$ ) with two equivalents of 8-(dimethylamino)-1-naphthyllithium, 2-(dimethylaminomethyl)phenyllithium or 2,6-bis(dimethylami-

[‡] Intramolecularly Donor-Stabilized Silenes, 4. Part 3: Ref.<sup>[3c]</sup>

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Scheme 1. The formation of the intramolecularly donor-stabilized silenes **1a–d**, **2**, and **3** by the reaction of the (dichloromethyl)oligosilanes **4a–d** with 8-(dimethylamino)-1-naphthyllithium, 2-(dimethylaminomethyl)phenyllithium and 2,6-bis(dimethylaminomethyl)phenyllithium, respectively (molar ratio 1:2)

nomethyl)phenyllithium, respectively, following the route outlined in Scheme 1.<sup>[3]</sup> The reaction path, which we have already discussed in detail,<sup>[3,4]</sup> involves the deprotonation of **4d**, lithium chloride elimination from **5d** and migration of one trimethylsilyl group from the central silicon atom to the neighboring carbon atom producing the transient silene **6d**. Subsequent addition of a second equivalent of the organolithium derivative across the Si=C double bond of **6d**, repeated elimination of LiCl, and a second trimethylsilyl migration leads to the formation of the silenes **1d**, **2**, and **3**. Whereas uncomplexed silenes, generated according to the same pattern by the reaction of **4d** with ordinary organolithium compounds ( $R^2\text{Li} = \text{MeLi}$ ,  $\text{PhLi}$ ,  $n\text{BuLi}$ ,  $\text{MeSLi}$ ) immediately add excess  $R^2\text{Li}$  finally producing after hydrolysis the silanes  $R^1R^2\text{Si}-\text{CH}(\text{SiMe}_3)_2$ ,<sup>[4]</sup> **1d**, **2**, and **3** proved to be stable with respect to the attack of an excess of the aryllithium compounds applied, could be isolated and structurally characterized. X-ray structural analyses were also performed. The high stability of these compounds can no doubt be attributed to the strong interaction between the amino groups and the silene silicon atoms, which dramatically reduces the electrophilic properties of the Si=C moieties of **1d**, **2**, and **3**.

The reaction path outlined involves the migration of two trimethylsilyl groups from the central silicon atom in **4d** ( $R^1 = \text{SiMe}_3$ ) to the neighboring carbon atom replacing the two chlorine substituents and forming the  $\text{C}(\text{SiMe}_3)_2$  unit in **1d**, **2**, and **3**. Consequently, one trimethylsilyl group of

the original (dichloromethyl)tris(trimethylsilyl)silane (**4d**) can be replaced by any alkyl or aryl group, and treatment of these related (dichloromethyl)oligosilanes with dialkylaminoaryllithium compounds should produce stabilized silenes with a further carbon substituent at the silene silicon atom. We chose (dichloromethyl)methylbis(trimethylsilyl)silane (**4a**), *tert*-butyl(dichloromethyl)bis(trimethylsilyl)silane (**4b**), and (dichloromethyl)phenylbis(trimethylsilyl)silane (**4c**) and studied their reactions with 8-(dimethylamino)-1-naphthyllithium (molar ratio 1:2). The first experiments were unsuccessful, the main problem being the complete separation of the 1-(dimethylamino)naphthalene formed in the first step of the reaction by protonation of the aryllithium compound through the dichloromethylsilanes **4a–c**. As subsequently discovered, however, the high thermal stability of the products allowed the application of more aggressive purification methods. Thus, silene **1a** was generated by the reaction of **4a** with 8-(dimethylamino)-1-naphthyllithium (1:2) following the general procedure described for the synthesis of **1d**, **2**, and **3**,<sup>[3]</sup> to our surprise, this compound could be purified by distillation in vacuo (150 °C/0.0005 mbar) to give a yellow solid. Similarly, **1b** was obtained from **4b** and 8-(dimethylamino)-1-naphthyllithium (1:2). 1-(Dimethylamino)naphthalene was distilled from the product mixture (100 °C/0.01 mbar) and **1b** was obtained as an orange-yellow oil, which gradually solidified. Unfortunately, the crystal quality of **1a** was insufficient for an X-ray structural analysis, but extended NMR, IR, and MS spectroscopic studies as well as chemical reactions of **1a** and **1b** unambiguously confirmed the proposed structures. Particularly the  $^{29}\text{Si}$  and  $^{13}\text{C}$  chemical shifts of the silicon and carbon atoms of the Si=C groups in **1a** and **1b**, which are in good agreement with those of **1d**, **2**, and **3**,<sup>[3]</sup> characterize the compounds as intramolecularly donor-stabilized silenes (see Exp. Sect.).

Silene **1c**, the expected product of the reaction of **4c** with 8-(dimethylamino)-1-naphthyllithium (1:2) could not be obtained in a pure form. Aqueous workup of the reaction mixture, however, gave the silanol **9c** in a yield of approximately 80%. Similarly, treatment of the reaction mixture with methanol produced (8-dimethylamino-1-naphthyl)(methoxy)phenyl[bis(trimethylsilyl)methyl]silane **10** (78%). Both results indicate that silene **1c** was indeed formed and is indefinitely stable.

As expected for the magnetically non-equivalent  $\text{CSiMe}_3$  groups of **1a–d**, two separate signals were observed in the  $^1\text{H}$  NMR spectra at room temperature. For **1a** and **1d** dynamic  $^1\text{H}$  NMR studies were performed, which revealed that at elevated temperatures coalescence of the signals of the two trimethylsilyl groups at the silene carbon atoms occurred. The data obtained were used for calculations of the rotational barriers about the Si=C bond in **1a** and **1d** (Table 1).

The assignment of the above-mentioned coalescence phenomena to rotation about the Si=C double bond is supported by theoretical calculations performed on **2** and a related silene bearing a methyl group at the silene Si instead of a  $\text{Me}_3\text{Si}$  group. These computations led to calculated

Table 1. Coalescence temperatures ( $T_c$ ) and signal separations ( $\Delta\nu_c$ ) of the  $\text{CSiMe}_3$  groups and rotational barriers ( $\Delta G_c^\ddagger$ ) about the  $\text{Si}=\text{C}$  bond in **1a** and **1d**

|           | $T_c$ (K) | $\Delta\nu_c$ (Hz) | $\Delta G_c^\ddagger$ [a] ( $\text{kJ}\cdot\text{mol}^{-1}$ ) |
|-----------|-----------|--------------------|---------------------------------------------------------------|
| <b>1a</b> | 317       | 95                 | 63.3                                                          |
| <b>1d</b> | 353       | 98                 | 71.0                                                          |

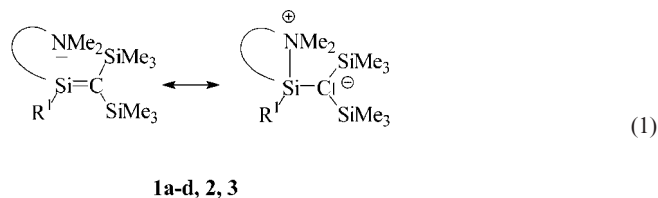
[a] The free energies of activation  $\Delta G_c^\ddagger$  at the coalescence temperature were calculated from the Eyring equation.<sup>[5]</sup> The error limits were estimated to be  $T_c = \pm 2$  K,  $\Delta\nu_c = \pm 5\%$ , and  $\Delta G_c^\ddagger = \pm 1.0$   $\text{kJ}\cdot\text{mol}^{-1}$ .

values of the rotational barriers of the same order of magnitude as those found experimentally for **1a** and **1d**. These results will be communicated separately.<sup>[6]</sup>

The magnitude of the rotational barrier to isomer interconversion in uncomplexed silenes was found to be about  $160$   $\text{kJ}\cdot\text{mol}^{-1}$ .<sup>[1a]</sup> As expected, this figure is considerably lower than the height of the barrier to *cis/trans* isomerization in alkenes, which amounts to approximately  $250$   $\text{kJ}\cdot\text{mol}^{-1}$ .<sup>[7]</sup> The reported rotational barriers for the silene donor adducts  $\text{THF}\cdot\text{Me}_2\text{Si}=\text{C}(\text{SiMe}_3)\text{SiMe}_t\text{Bu}_2$  and  $\text{Me}_3\text{N}\cdot\text{Me}_2\text{Si}=\text{C}(\text{SiMe}_3)\text{SiMe}_t\text{Bu}_2$  of  $50$   $\text{kJ}\cdot\text{mol}^{-1}$  and  $65$   $\text{kJ}\cdot\text{mol}^{-1}$ , respectively,<sup>[8]</sup> are very close to those found for **1a** and **1d**. That means that the interaction of silenes with donor molecules leads to a weakening of the  $\text{Si}-\text{C}$   $\pi$ -interaction, and **1a-d** as well as **2** and **3** may equally be described as ylidic compounds [Equation (1)].

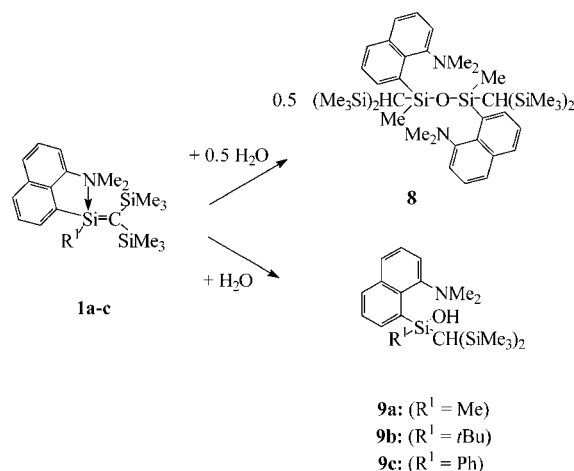
### The Reactions of the Silenes **1a**, **1b**, and **1d** with Water, Methyl Iodide and Benzaldehyde

The established pyramidalization at the silene silicon atoms of **1a**, **2**, and **3** in the solid state<sup>[3]</sup> and the relatively low rotational barriers of the  $\text{Si}=\text{C}$  bonds in **1a** and **1d** point to a pronounced ylid-like character of the compounds [Equation (1)]. Consequently, compared with uncomplexed silenes, enhanced nucleophilic properties of the silene carbon atoms of the intramolecularly donor-stabilized silenes would be expected. This was confirmed by studies of the behavior of **1a**, **1b**, and **1d** towards methyl iodide. The reactions of the newly synthesized silenes with water and benzaldehyde were also investigated as a further method of characterization.



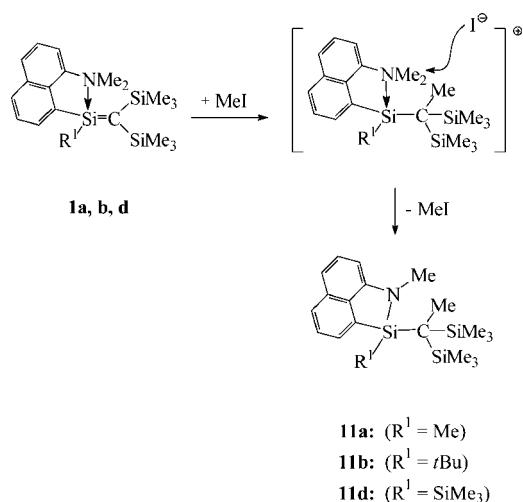
The addition of water or alcohols across the  $\text{Si}=\text{C}$  double bonds with formation of silanols or alkoxysilanes, respectively, is typical of silenes and is frequently used for their chemical characterization.<sup>[1]</sup> Compounds **1a-c**, after treat-

ment with water or methanol, also gave the expected products. **1a** proved to be extraordinarily moisture sensitive. Wet solvents immediately decolorize the yellow solutions of the silene to give a mixture of the two diastereomeric forms of the disiloxane **8** (Scheme 2). Compounds **1b** and **1c** are less reactive, but with excess water **1b,c** as well as **1a** are converted into the silanols **9b**, **9c**, and **9a**, respectively. The conversion of **1d** into the silanol **9d** has been previously described.<sup>[3b]</sup> The formation of **8** can be understood as the result of the addition of silanol **9a** to the  $\text{Si}=\text{C}$  unit of **1a**. As expected, thermolysis of **9a** (heating to  $120$   $^\circ\text{C}$ ) also formed the disiloxane **8**. As mentioned above, methoxysilane **10** was prepared by addition of methanol to the impure silene for the characterization of **1c**.



Scheme 2. The reaction of the intramolecularly donor-stabilized silenes **1a-c** with water.

The reaction of the stable amine-coordinated silenes with methyl iodide was expected to lead, after methylation of the nucleophilic  $\text{C}(\text{SiMe}_3)_2$  group with  $\text{H}_3\text{Cl}$ , to the intramolecularly donor-stabilized silylium iodides  $[(\text{Me}_2\text{NC}_{10}\text{H}_6)\text{R}^1\text{Si}-\text{CMe}(\text{SiMe}_3)_2]^+ \text{I}^-$  or, alternatively, to the respective iodosilanes  $(\text{Me}_2\text{NC}_{10}\text{H}_6)\text{R}^1\text{SiI}-\text{CMe}(\text{SiMe}_3)_2$ . Hydrolysis of both products should then give the silanols  $(\text{Me}_2\text{NC}_{10}\text{H}_6)\text{R}^1\text{Si}(\text{OH})-\text{CMe}(\text{SiMe}_3)_2$ . In fact, studies of the reaction of **1a**, **1b**, and **1d** with methyl iodide revealed an unforeseen rearrangement of the silenes finally producing the azasilaacenaphthenes **11a**, **11b**, and **11d**, respectively (Scheme 3). Formally, one methyl substituent migrates from the nitrogen atom to the silene carbon atom with simultaneous formation of a cyclic aminosilane. The rearrangement can be interpreted as an expected nucleophilic methylation of the silene carbon atoms by methyl iodide, but the resultant silylium salts are unstable, the iodide anion attacks one *N*-methyl group regenerating methyl iodide and forming an aminosilane function. The strong  $\text{N}\rightarrow\text{Si}$  donor-acceptor interaction in **1a**, **1b**, and **1d** as well as in the intermediate silylium ions makes the nitrogen atom a good leaving group and the *N*-methyl substituent easily susceptible to a nucleophilic attack by the iodide anion. For



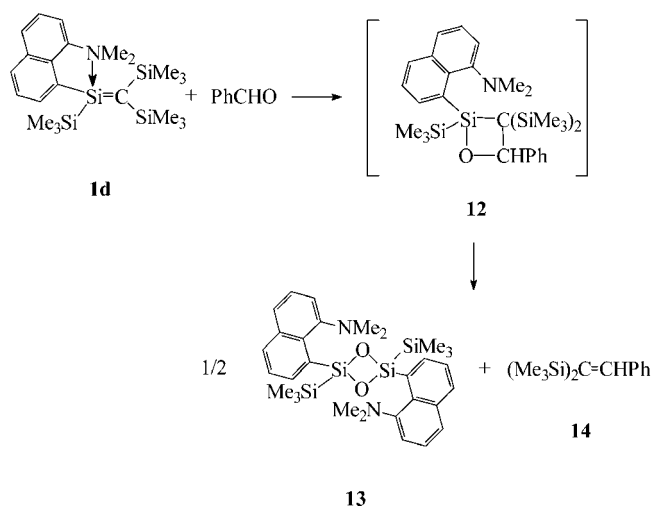
Scheme 3. The methyl iodide induced isomerization of the intramolecularly donor-stabilized silenes **1a**, **1b**, and **1d** into the cyclic aminosilanes **11a**, **11b**, and **11d**.

a complete conversion of **1a**, **1b**, and **1d** into **11a**, **11b**, and **11d**, respectively, only catalytic quantities of methyl iodide were necessary. Indeed, the results of the experiments are independent of the molar ratio of silene to methyl iodide. In order to attempt to ethylate or allylate the silene carbon atom, **1d** was treated with ethyl iodide or allyl iodide, respectively. Surprisingly, however, even with excesses of these reagents only **11d**, the methylated derivative, could be isolated in high yield. The ethyl or allyl analogues of **11d** could not be detected. This indicates that the nucleophilic reaction of the silene with the liberated methyl iodide proceeds considerably faster than with ethyl iodide or allyl iodide.

The structures of **11a**, **11b**, and **11d** were elucidated on the basis of NMR and MS spectroscopic studies (see Exp. Sect.). The compounds proved to be stable towards water and solutions of **11a**, **11b**, and **11d** in THF/water remained unchanged.

Silenes normally react with carbonyl compounds to give an olefin and silanone oligomers.<sup>[1]</sup> In some cases 2-oxasiletanes and [2 + 2] cycloadducts were isolated and, in particular, when aromatic ketones were used, [4 + 2] cycloadducts and a variety of their isomerization products were also isolated.<sup>[1]</sup> Uncomplexed, kinetically stabilized 2,2-bis(trimethylsilyl)silenes, recently synthesized by the reaction of **4c** or **4d**, respectively, when treated with 2,4,6-triisopropylphenyllithium (1:2) afforded, after subsequent treatment with benzaldehyde, stable substituted 2-oxasiletanes.<sup>[4]</sup> Treatment of intramolecularly amine-coordinated silenes of the type described in this paper with carbonyl compounds are of particular interest, since this could be a promising route to intramolecularly donor-stabilized silanones.

Unfortunately, the reactivity of the intramolecularly donor-stabilized silenes towards carbonyl compounds proved to be rather low. In THF solution **1d** and **2**, which were chosen for these studies, did not react with benzaldehyde. The reaction of **1d** with benzaldehyde in heptane at room temperature required three days to proceed to completion;



Scheme 4. The reaction of silene **1d** with benzaldehyde

at 80 °C 5–6 h were needed. In both cases a colorless solid was obtained, which was identified as a mixture of the two isomeric forms of the cyclodisiloxane **13** (Scheme 4). Furthermore, 2,2-bis(trimethylsilyl)styrene (**14**) was isolated in an almost quantitative yield.

The suggested reaction path is outlined in Scheme 4 and is consistent with the standard course of the reaction of silenes with simple aromatic aldehydes.<sup>[1]</sup> The silene carbon atom attacks the carbonyl carbon atom and subsequent Si–O interaction leads to the formation of the oxasiletane **12**. The long reaction times are due to the strong nitrogen–silicon interaction in **1d** reducing the electrophilic properties of the silene silicon atom. Clearly, **12** is unstable and decomposes spontaneously producing the olefin **14** and a mixture of the two diastereomers of the cyclodisiloxane **13**, which may be considered as a dimer of an originally formed transient silanone. The two isomers of **13** could not be separated, but <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data as well as MS data of the mixture unambiguously confirmed the proposed structures. A comparable cyclodisiloxane was recently obtained by Belzner et al. as the result of an oxygen transfer from isocyanates to bis[2-(dimethylaminomethyl)-phenyl]silylene and was presumed to be the cyclodimer of an initially generated silanone.<sup>[9]</sup> The analytical data obtained for **14** proved to be identical to those reported for 2,2-bis(trimethylsilyl)styrene in the literature.<sup>[10]</sup> The reaction of **2** with benzaldehyde under comparable conditions similarly led to **14** but the respective disiloxane could not be identified.

## Experimental Section

**General:** All reactions involving organometallic reagents were carried out under purified argon. NMR: Bruker AC 250 or Bruker ARX 300 instruments were used, temperature 30 °C, tetramethylsilane as internal standard. IR: Nicolet 205 FT-IR instrument. MS: Intectra AMD 402 spectrometer (EI with 70 eV or chemical ionization with isobutane). (Dichloromethyl)methylbis(trimethylsilyl)silane (**4a**),<sup>[4]</sup> *tert*-butyl(dichloromethyl)bis(trimethylsi-



lyl)silane (**4b**),<sup>[11]</sup> and (dichloromethyl)phenylbis(trimethylsilyl)silane (**4c**)<sup>[4]</sup> as well as 1-[8-(dimethylamino)-1-naphthyl]-1,2,2-tris(trimethylsilyl)silene (**1d**),<sup>[3a]</sup> and 1-(2-dimethylaminophenyl)-1,2,2-tris(trimethylsilyl)silene (**2**)<sup>[3b]</sup> were prepared as described previously. 8-(dimethylaminomethyl)-1-naphthyllithium was prepared following the procedure given by Corriu et al.,<sup>[12]</sup> but was isolated as a brown amorphous powder. All yields given refer to amounts obtained after chromatographic separation and purification or recrystallization. The results of the elemental analyses of the compounds prepared were unsatisfactory in some cases (SiC formation). Therefore, high resolution mass spectra were recorded.

**1-[8-(Dimethylamino)-1-naphthyl]-1-methyl-2,2-bis(trimethylsilyl)silene (1a):** At  $-78^{\circ}\text{C}$ , **4a** (1.50 g, 5.4 mmol) was added gradually to a suspension of 8-(dimethylamino)-1-naphthyllithium–diethyl ether (3.00 g, 11.7 mmol) in diethyl ether (30 mL). After warming to room temperature and stirring overnight, the solvent was removed in vacuo. Pentane was added and LiCl separated by filtration. The orange-yellow filtrate was concentrated and 1-(dimethylamino)naphthalene was removed by distillation in vacuo ( $80^{\circ}\text{C}/5 \cdot 10^{-4}$  mbar). The residue was purified by kugelrohr distillation ( $150^{\circ}\text{C}/5 \cdot 10^{-4}$  mbar). Care has to be taken not to exceed a temperature of  $155^{\circ}\text{C}$ , otherwise decomposition reactions take place. Silene **1a** was obtained as a glassy oil. Crystallization from pentane gave yellow crystals. Yield 1.83 g (52%); m.p.  $140\text{--}142^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = 0.23$  and  $0.57$  [2 broad s,  $2 \times 9$  H,  $\text{Si}(\text{CH}_3)_3$ ],  $0.34$  (s, 3 H,  $\text{SiCH}_3$ ),  $2.27$  and  $2.52$  (2s,  $2 \times 3$  H,  $\text{NCH}_3$ ),  $6.63\text{--}7.82$  (m, 6 H, aryl-H) ppm.  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = 5.0$  ( $\text{C}=\text{SiCH}_3$ ),  $7.6$  and  $8.0$  ( $\text{Si}=\text{CSiCH}_3$ , broad),  $14.5$  ( $\text{Si}=\text{C}$ ),  $45.6$  and  $52.8$  ( $\text{NCH}_3$ ),  $115.5$ ,  $125.8$ ,  $127.6$ ,  $127.7$ ,  $128.4$  and  $132.5$  (arom. CH),  $132.3$ ,  $132.9$ ,  $138.1$  and  $147.4$  (quat. arom. C) ppm.  $^{29}\text{Si}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = -16.1$  and  $-7.0$  ( $\text{SiMe}_3$ ),  $36.0$  ( $\text{Si}=\text{C}$ ) ppm. UV/Vis (*n*-heptane):  $\lambda_{\text{max}}$  ( $\epsilon$ ) =  $304$  nm ( $14800$ ). MS ( $70$  eV):  $m/z$  (%) =  $372$  (100)  $[\text{MH}]^+$ ,  $357$  (14)  $[\text{MH} - \text{CH}_3]^+$ .  $\text{C}_{20}\text{H}_{33}\text{NSi}_3$  (371.8): calcd. C 64.62, H 8.95, N 3.77; found C 64.18, H 8.92, N 3.74.

**1-tert-Butyl-1-[8-(dimethylamino)-1-naphthyl]-2,2-bis(trimethylsilyl)silene (1b):** As described for **1a**. Compound **4b** (1.63 g, 5.17 mmol) and 8-(dimethylamino)-1-naphthyllithium–diethyl ether (2.60 g, 10.33 mmol) afforded, after separation of 1-(dimethylamino)naphthalene,  $0.85$  g (41%) of oily **1b**, which gradually solidified.  $^1\text{H}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = 0.34$  and  $0.68$  (2s,  $2 \times 9$  H,  $\text{SiCH}_3$ ),  $0.84$  (s, 9 H,  $\text{CCH}_3$ ),  $2.48$  and  $2.52$  (2s,  $2 \times 3$  H,  $\text{NCH}_3$ ),  $6.50\text{--}7.94$  (m, 6 H, aryl-H) ppm.  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = 9.24$  and  $9.19$  ppm ( $\text{SiCH}_3$ ),  $24.6$  ( $\text{CCH}_3$ ),  $28.7$  ( $\text{Si}=\text{C}$ ),  $29.4$  ( $\text{CCH}_3$ ),  $43.8$  and  $56.2$  ( $\text{NCH}_3$ ),  $109.2$ ,  $113.9$ ,  $125.3$ ,  $127.5$ ,  $127.8$  and  $132.5$  (arom. CH),  $133.7$ ,  $134.8$ ,  $136.3$  and  $148.4$  (quat. arom. C) ppm.  $^{29}\text{Si}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = -10.2$  and  $-7.8$  ( $\text{SiMe}_3$ ),  $43.6$  ( $\text{Si}=\text{C}$ ) ppm. UV/Vis (*n*-heptane):  $\lambda_{\text{max}}$  ( $\epsilon$ ) =  $308$  nm ( $40660$ ). MS ( $70$  eV):  $m/z$  (%) =  $413$  (8)  $[\text{M}]^+$ ,  $398$  (26)  $[\text{M} - \text{CH}_3]^+$ ,  $356$  (100)  $[\text{M} - \text{C}(\text{CH}_3)_3]^+$ . HRMS calcd. for  $\text{C}_{23}\text{H}_{39}\text{NSi}_3$   $413.23904$ ; found  $413.23850$ .

**1,3-Bis[8-(dimethylamino)-1-naphthyl]-1,3-dimethyl-1,3-bis[bis(trimethylsilyl)methyl]disiloxane (8):** Wet diethyl ether was added to a yellow ethereal solution of **1a** (2.0 g, 4.66 mmol) until the color had completely disappeared. After evaporation, the residue was recrystallized from acetone to give a mixture of two diastereomeric forms of **8** (ratio of 40:60). Yield  $1.66$  g (81%), m.p.  $214\text{--}217^{\circ}\text{C}$ . The separation of the two diastereomers failed, but the NMR spectra of the mixture allowed the assignment of the signals of both forms. **Diastereomer 1:**  $^1\text{H}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = -0.31$ ,  $0.48$  [2s,  $2 \times 9$  H,  $\text{Si}(\text{CH}_3)_3$ ],  $0.38$  (s, 1 H, CH),  $1.17$  (s, 3 H,  $\text{OSiCH}_3$ ),  $2.15$  and  $2.60$  (2s,  $2 \times 3$  H,  $\text{NCH}_3$ ),  $7.05\text{--}8.75$  (m, 5 H aryl-H) ppm.  $^{13}\text{C}$

NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = 3.6$  and  $5.1$  ( $\text{SiMe}_3$ ),  $4.3$  ( $\text{Si}_3\text{C}$ ),  $9.1$  ( $\text{OSiCH}_3$ ),  $43.3$  and  $51.4$  ( $\text{NCH}_3$ ),  $117.0$ ,  $125.3$ ,  $125.57$ ,  $125.63$ ,  $130.5$  and  $138.1$  (arom. CH),  $135.1$ ,  $136.3$ ,  $137.7$  and  $153.5$  (quat. arom. C) ppm.  $^{29}\text{Si}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = -5.5$  ( $\text{SiOSi}$ ),  $-1.0$  and  $0.8$  ( $\text{SiMe}_3$ ) ppm. **Diastereomer 2:**  $^1\text{H}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = -0.07$ ,  $0.38$  [2s,  $2 \times 9$  H,  $\text{Si}(\text{CH}_3)_3$ ],  $0.44$  (s, 1 H, CH),  $0.75$  (s, 3 H,  $\text{OSiCH}_3$ ),  $2.32$  and  $2.46$  (2s,  $2 \times 3$  H,  $\text{NCH}_3$ ),  $7.05\text{--}8.75$  (m, 5 H), aryl-H ppm.  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = 3.9$  and  $5.4$  ( $\text{SiMe}_3$ ),  $4.3$  ( $\text{Si}_3\text{C}$ ),  $9.2$  ( $\text{OSiCH}_3$ ),  $45.8$  and  $48.8$  ( $\text{NCH}_3$ ),  $116.6$ ,  $124.9$ ,  $125.3$ ,  $126.0$ ,  $130.3$  and  $138.5$  (arom. CH),  $134.9$ ,  $136.1$ ,  $138.1$  and  $153.3$  (quat. arom. C) ppm.  $^{29}\text{Si}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = -5.3$  ( $\text{SiOSi}$ ),  $-0.6$  and  $0.8$  ( $\text{SiMe}_3$ ). **For the Mixture:** MS ( $70$  eV):  $m/z$  (%) =  $760$  (38)  $[\text{M}]^+$ ,  $745$  (5)  $[\text{M} - \text{CH}_3]^+$ ,  $590$  (16)  $[\text{M} - \text{C}_{10}\text{H}_6]^+$ ,  $372$  (100)  $[(\text{Me}_2\text{NC}_{10}\text{H}_6)\text{MeSiCH}(\text{SiMe}_3)_2]^+$ . HRMS calcd. for  $\text{C}_{40}\text{H}_{68}\text{N}_2\text{OSi}_6$   $760.39471$ ; found  $760.39430$ .

**[8-(Dimethylamino)-1-naphthyl]methyl[bis(trimethylsilyl)methyl]silanol (9a):** An ethereal solution of **1a** (2.0 g, 4.66 mmol) was added to a mixture of THF/water (1:1). After a few minutes, the organic layer was separated and the solvents evaporated. The residue was purified by kugelrohr distillation ( $130^{\circ}\text{C}/2 \cdot 10^{-2}$  mbar). Colorless oil, yield  $1.04$  g (57%).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = -0.14$  (s, 1 H, CH),  $0.00$  and  $0.27$  [2s,  $2 \times 9$  H,  $\text{Si}(\text{CH}_3)_3$ ],  $0.74$  (s, 3 H,  $\text{OSiCH}_3$ ),  $2.28$  and  $2.39$  (2s,  $2 \times 3$  H,  $\text{NCH}_3$ ),  $6.32$  (br.s, 1 H, OH),  $6.92\text{--}7.91$  (m, aryl-H) ppm.  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = 3.2$ ,  $3.5$ ,  $6.1$  and  $7.74$  ( $\text{SiCH}$  and  $\text{SiCH}_3$ ),  $44.6$  and  $48.3$  ( $\text{NCH}_3$ ),  $116.9$ ,  $125.0$ ,  $125.4$ ,  $127.0$ ,  $130.4$  and  $136.0$  (arom. CH),  $134.1$ ,  $136.7$ ,  $139.8$  and  $151.5$  (quat. arom. C) ppm.  $^{29}\text{Si}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = -0.3$  and  $0.2$  ( $\text{SiMe}_3$ ),  $3.0$  ( $\text{SiOH}$ ) ppm. IR (cap.):  $\tilde{\nu} = 3439$   $\text{cm}^{-1}$  (br.,  $\text{OH}_{\text{ass}}$ ). MS ( $70$  eV):  $m/z$  (%) =  $389$  (100)  $[\text{M}]^+$ ,  $374$  (23)  $[\text{M} - \text{CH}_3]^+$ ,  $230$  (68)  $[\text{M} - \text{CH}(\text{SiMe}_3)_2]^+$ .  $\text{C}_{22}\text{H}_{41}\text{NOSi}_4$  (389.8): calcd. C 61.63, H 9.05, N 3.59; found C 61.69, H 9.04, N 3.57.

**tert-Butyl[8-(dimethylamino)-1-naphthyl]bis(trimethylsilyl)methylsilanol (9b):** As described for **1a**. Compound **4b** (1.1 g, 3.49 mmol) was treated with 8-(dimethylamino)-1-naphthyllithium–diethyl ether (1.75 g, 6.97 mmol), but silene **1b** was not isolated. Instead, after separation of LiCl, water was added to the pentane solution. Separation of the organic layer, evaporation of the solvent and kugelrohr distillation of the residue ( $140^{\circ}\text{C}/2 \cdot 10^{-2}$  mbar) gave  $0.80$  g (53.1%) of **9b** in the form of a viscous oil.  $^1\text{H}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = 0.06$  and  $0.45$  (2s,  $2 \times 9$  H,  $\text{SiCH}_3$ ),  $0.08$  (s, 1 H, CH),  $1.13$  (s, 9 H, *t*Bu),  $2.37$  and  $2.43$  (2s,  $2 \times 3$  H,  $\text{NCH}_3$ ),  $7.0\text{--}7.96$  (m, 6 H, aryl-H),  $10.0$  (s, 1 H,  $\text{SiOH}$ ) ppm.  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = 4.7$  and  $5.2$  ( $\text{SiCH}_3$ ),  $4.3$  (CH),  $22.1$  ( $\text{CCH}_3$ ),  $28.7$  ( $\text{CCH}_3$ ),  $46.9$  and  $47.4$  ( $\text{NCH}_3$ ),  $119.4$ ,  $124.0$ ,  $125.3$ ,  $128.3$ ,  $128.8$  and  $131.0$  (arom. CH),  $136.6$ ,  $138.4$ ,  $151.6$  and  $154.2$  (quat. arom. C) ppm.  $^{29}\text{Si}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = -0.4$  and  $0.0$  ( $\text{SiMe}_3$ ),  $5.4$  ( $\text{SiOH}$ ) ppm. MS ( $70$  eV):  $m/z$  (%) =  $431$  (5)  $[\text{M}]^+$ ,  $416$  (10)  $[\text{M} - \text{CH}_3]^+$ ,  $374$  (100)  $[\text{M} - \text{CMe}_3]^+$ ,  $358$  (4)  $[\text{M} - \text{SiMe}_3]^+$ . HRMS calcd. for  $\text{C}_{23}\text{H}_{41}\text{NOSi}_3$   $431.24958$ ; found  $431.24913$ .

**[8-(Dimethylamino)-1-naphthyl]phenyl[bis(trimethylsilyl)methyl]silanol (9c):** As described for **1a**. Compound **4c** (1.23 g, 3.6 mmol) was gradually added to a suspension of 8-(dimethylamino)-1-naphthyllithium–diethyl ether (2.00 g) in diethyl ether (60 mL) at  $-78^{\circ}\text{C}$ . After warming to room temperature and stirring overnight water (5 mL) was added. The organic layer was separated, evaporated and the residue was recrystallized from acetonitrile. Colorless crystals, m.p.  $125\text{--}126^{\circ}\text{C}$ , yield  $1.12$  g (69%).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = 0.00$  and  $0.17$  [2s,  $2 \times 9$  H,  $\text{Si}(\text{CH}_3)_3$ ],  $0.11$  (s, 1 H, CH),  $1.74$  and  $2.35$  (2s,  $2 \times 3$  H,  $\text{NCH}_3$ ),  $6.83\text{--}8.11$  (11 H, aryl-H) ppm.  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta = 3.1$  and  $3.3$  ( $\text{SiCH}_3$ ),  $7.5$  (CH),  $43.9$  and  $49.2$  ( $\text{NCH}_3$ ),  $117.4$ ,  $124.6$ ,  $125.5$ ,  $127.3$ ,  $127.7$ ,  $129.0$ ,  $130.9$ ,  $134.9$  and  $137.0$  (arom. CH),  $134.2$ ,  $136.4$ ,  $137.3$ ,  $142.4$  and

151.2 (quat. arom. C) ppm.  $^{29}\text{Si}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = -5.2$  (SiOH), 0.2 and 0.3 (SiMe<sub>3</sub>) ppm. MS (70 eV):  $m/z$  (%) = 451 (54)  $[\text{M}]^+$ , 292 (100)  $[\text{M} - \text{CH}(\text{SiMe}_3)_2]^+$ . C<sub>25</sub>H<sub>37</sub>NOSi<sub>3</sub> (451.2): calcd. C 66.46, H 8.25, N 3.10; found C 65.63, H 8.25, N 3.10. HRMS calcd. for C<sub>25</sub>H<sub>37</sub>NOSi<sub>3</sub> 451.21829; found 451.21910.

**[8-(Dimethylamino)-1-naphthyl](methoxy)phenyl[bis(trimethylsilyl)-methyl]silane (10):** At  $-78^\circ\text{C}$  **4c** (1.3 g, 3.8 mmol) was added to a suspension of 8-(dimethylamino)-1-naphthyllithium–diethyl ether (2.1 g, 1.05 mmol) in diethyl ether (60 mL). After warming to room temperature and stirring overnight the solvent was replaced by pentane and lithium chloride was filtered off. Addition of methanol (2 mL) to this solution and evaporation gave a viscous oil which was purified by kugelrohr distillation ( $170$ – $180^\circ\text{C}/4 \times 10^{-2}$  mbar). Yield 1.4 g (83%).  $^1\text{H}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = 0.04$  and  $0.08$  ppm (2s,  $2 \times 9$  H, SiCH<sub>3</sub>),  $0.70$  (s, 1 H, CH),  $1.99$  and  $2.30$  (2s,  $2 \times 3$  H, NCH<sub>3</sub>),  $3.51$  (s, 3 H, OCH<sub>3</sub>),  $7.03$ – $8.19$  (m, 12 H, aryl-H) ppm.  $^{13}\text{C}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = 3.1$  (Si<sub>3</sub>C),  $3.9$  and  $4.2$  (SiCH<sub>3</sub>),  $46.8$  and  $47.8$  (NCH<sub>3</sub>),  $51.9$  (OCH<sub>3</sub>),  $117.8$ ,  $125.1$ ,  $125.8$ ,  $126.2$ ,  $127.3$ ,  $128.6$ ,  $131.0$ ,  $135.4$  and  $138.5$  (arom. CH),  $132.9$ ,  $136.0$ ,  $136.1$ ,  $139.7$  and  $153.6$  (quat. arom. C) ppm.  $^{29}\text{Si}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = -5.6$  (SiOMe),  $-1.2$  and  $0.4$  (SiMe<sub>3</sub>) ppm. IR (cap.):  $\tilde{\nu} = 1101\text{ cm}^{-1}$  (SiOCH<sub>3</sub>). MS (70 eV):  $m/z$  (%) = 465 (53)  $[\text{M}]^+$ , 450 (13)  $[\text{M} - \text{CH}_3]^+$ , 388 (18)  $[\text{M} - \text{Ph}]^+$ , 306 (100)  $[\text{M} - \text{CH}(\text{SiMe}_3)_2]^+$ . HRMS calcd. for C<sub>26</sub>H<sub>39</sub>NOSi<sub>3</sub> 465.23395; found 465.22990.

**1,2-Dimethyl-2-[1,1-bis(trimethylsilyl)ethyl]-1-aza-2-silaacenaphthene (11a):** To a solution of **4a** (1.75 g, 4.70 mmol) in dichloromethane (20 mL) was added methyl iodide (1 mL, 1.53 g, 10.8 mmol) and the solution was stirred for 48 h at room temperature. Evaporation of the solution and purification of the residue by column chromatography (silica gel, heptane) gave a yellow oil, yield 0.7 g (40%).  $^1\text{H}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = -0.13$  ppm and  $0.13$  [2s,  $2 \times 9$  H, Si(CH<sub>3</sub>)<sub>3</sub>],  $0.35$  (s, 3 H, SiCH<sub>3</sub>),  $1.22$  (s, 3 H, CCH<sub>3</sub>),  $2.78$  (s, 3 H, NCH<sub>3</sub>),  $6.34$ – $7.74$  (m, 6 H, arom. CH) ppm.  $^{13}\text{C}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = -1.0$ ,  $0.5$ ,  $1.3$  and  $3.4$  (SiC),  $13.7$  (CCH<sub>3</sub>),  $31.6$  (NCH<sub>3</sub>),  $101.8$ ,  $115.2$ ,  $126.5$ ,  $128.5$ ,  $128.6$  and  $129.9$  (arom. CH),  $132.5$ ,  $134.4$  and  $152.3$  (one signal hidden, quat. arom. C) ppm.  $^{29}\text{Si}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = 2.6$  and  $3.9$  (CSiMe<sub>3</sub>),  $10.4$  (ring-Si) ppm. MS (70 eV):  $m/z$  (%) = 371 (100)  $[\text{M}]^+$ , 356 (28)  $[\text{M} - \text{CH}_3]^+$ , 298 (14)  $[\text{M} - \text{SiMe}_3]^+$ . HRMS calcd. for C<sub>20</sub>H<sub>33</sub>NSi<sub>3</sub> 371.19203; found 371.18654.

**2-tert-Butyl-1-methyl-2-[1,1-bis(trimethylsilyl)ethyl]-1-aza-2-silaacenaphthene (11b):** **11b** can be obtained from **1b** and methyl iodide as described for **11a**. It can be prepared more easily, however, by treatment of the crude product mixture obtained after treatment of **4b** with 8-(dimethylamino)-1-naphthyllithium. A typical procedure follows: **4b** (0.93 g, 2.94 mmol) was added at  $-78^\circ\text{C}$  to a suspension of 8-(dimethylamino)-1-naphthyllithium–diethyl ether (1.48 g, 5.89 mmol) in diethyl ether (30 mL). The mixture was warmed to room temperature and was stirred for 12 h. After replacement of the solvent by *n*-pentane, LiCl was separated, the yellow solution evaporated and 1-(dimethylamino)naphthalene was removed by distillation at  $100^\circ\text{C}/10^{-2}$  mbar. The residue was dissolved in dichloromethane (20 mL), methyl iodide (2.0 g, 14 mmol) was added and the solution was stirred for 24 h. Evaporation and recrystallization from acetonitrile gave 0.75 g (62%) pale greenish crystals of **11b**, m.p.  $129$ – $132^\circ\text{C}$ .  $^1\text{H}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = -0.02$  ppm and  $0.08$  (2s,  $2 \times 9$  H, SiCH<sub>3</sub>),  $0.96$  [s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>],  $1.44$  (s, 3 H, CCH<sub>3</sub>),  $2.90$  (s, 3 H, NCH<sub>3</sub>),  $6.33$ – $7.71$  (6 H, aryl-H) ppm.  $^{13}\text{C}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = 1.8$  and  $2.1$  (SiCH<sub>3</sub>),  $4.3$  (CMe),  $13.9$  (CCH<sub>3</sub>),  $25.1$  (CMe<sub>4</sub>),  $28.2$  (*t*Bu CH<sub>3</sub>),  $32.4$  (NCH<sub>3</sub>),  $101.3$ ,  $115.1$ ,  $126.5$ ,  $128.3$ ,  $128.5$  and  $129.8$  (arom. CH),  $132.5$ ,  $134.3$ ,  $135.0$  and

$154.3$  (quat. arom. C) ppm.  $^{29}\text{Si}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = 3.4$  and  $4.1$  (SiMe<sub>3</sub>),  $10.5$  (ring-Si) ppm. MS (70 eV):  $m/z$  (%) = 413 (15)  $[\text{M}]^+$ , 398 (14)  $[\text{M} - \text{CH}_3]^+$ , 356 (100)  $[\text{M} - \text{CMe}_3]^+$ . HRMS calcd. for C<sub>23</sub>H<sub>39</sub>NSi<sub>3</sub> 413.23904; found 413.23692.

**1-Methyl-2-trimethylsilyl-2-[1,1-bis(trimethylsilyl)ethyl]-1-aza-2-silaacenaphthene (11d):** As described for **11a**. Compound **1d**<sup>[3a,3b]</sup> (2.0 g, 4.66 mmol) and methyl iodide (1 mL, 1.53 g, 10.8 mmol) were stirred in dichloromethane (20 mL) for 48 h at room temperature. After evaporation a solid was obtained, which was recrystallized from acetonitrile. Pale yellow crystals, yield 1.28 g (64%), m.p.  $165^\circ\text{C}$ .  $^1\text{H}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = -0.07$ ,  $0.02$  and  $0.12$  (3s,  $3 \times 9$  H, SiCH<sub>3</sub>),  $1.36$  (s, 3 H, CCH<sub>3</sub>),  $2.84$  (s, 3 H, NCH<sub>3</sub>),  $6.30$ – $7.70$  (m, 6 H, aryl-H) ppm.  $^{13}\text{C}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = -0.2$ ,  $0.7$  and  $1.2$  (SiCH<sub>3</sub>),  $4.8$  (Si<sub>3</sub>C),  $14.2$  (CCH<sub>3</sub>),  $33.0$  (NCH<sub>3</sub>),  $101.4$ ,  $114.7$ ,  $126.7$ ,  $128.6$  and  $129.6$  (arom. CH, one signal hidden),  $133.0$ ,  $135.6$ ,  $135.7$  and  $153.5$  (quat. arom. C) ppm.  $^{29}\text{Si}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = -17.2$  (SiSiMe<sub>3</sub>),  $3.0$ ,  $4.1$  and  $4.4$  (CSiMe<sub>3</sub> and ring-Si) ppm. MS (70 eV):  $m/z$  (%) = 429 (15)  $[\text{M}]^+$ ,  $414$  (6)  $[\text{M} - \text{CH}_3]^+$ ,  $356$  (100)  $[\text{M} - \text{SiMe}_3]^+$ . C<sub>22</sub>H<sub>39</sub>NSi<sub>4</sub> (429.9): calcd. C 61.47, H 9.14, N 3.26; found C 61.02, H 9.16, N 3.27.

**The Reaction of 1d with Benzaldehyde:** Benzaldehyde (1.18 g, 11.6 mmol) was added to a solution of **1d** (5.00 g, 11.6 mmol) in *n*-heptane (120 mL) and the mixture was stirred for 6 h at  $80^\circ\text{C}$ . After cooling to room temperature 1,3-bis[8-(dimethylamino)-1-naphthyl]-1,3-bis(trimethylsilyl)cyclodisiloxane (**13**) in the form of the mixture of the two diastereomers crystallized from the solution and was separated by filtration (2.04 g, 61%). The filtrate was evaporated and the residue purified by column chromatography (silica gel, heptane) to give 2.77 g (96%) of 2,2-bis(trimethylsilyl)vinylbenzene (**14**).<sup>[10]</sup>

Attempts to separate the two diastereomers of **14** failed, but  $^1\text{H}$  and  $^{13}\text{C}$  NMR studies of the mixture (80:20) allowed the assignment of the signals to both forms. **Diastereomer 1:**  $^1\text{H}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = -0.07$  ppm [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>],  $2.75$  and  $2.92$  (2s,  $2 \times 3$  H, NCH<sub>3</sub>) ppm.  $^{13}\text{C}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = -0.3$  (SiMe<sub>3</sub>),  $43.3$  and  $54.0$  (NCH<sub>3</sub>),  $114.2$ ,  $125.5$ ,  $125.6$ ,  $125.8$ ,  $128.2$ ,  $128.7$ ,  $134.0$ ,  $135.9$ ,  $137.6$  and  $141.4$  (arom. C) ppm. **Diastereomer 2:**  $^1\text{H}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = 0.01$  [s, 9 H, Si(CH<sub>3</sub>)<sub>3</sub>],  $2.69$  and  $2.76$  (2s,  $2 \times 3$  H, NCH<sub>3</sub>) ppm.  $^{13}\text{C}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = 0.0$  (SiMe<sub>3</sub>),  $43.4$  and  $53.2$  (NCH<sub>3</sub>),  $114.3$ ,  $125.6$ ,  $125.8$ ,  $129.3$ ,  $134.8$ ,  $135.1$ ,  $136.5$ ,  $137.1$  and  $151.7$  (one signal hidden, arom. C) ppm. **For the Mixture:**  $^1\text{H}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = 6.91$ – $8.86$  (m, 6 H, arom. CH) ppm.  $^{29}\text{Si}$  NMR ( $[\text{D}_6]$ benzene):  $\delta = -35.9$  and  $-35.4$  (OSiO),  $-22.1$  and  $-18.7$  (SiMe<sub>3</sub>). MS (CI, isobutane):  $m/z$  (%) = 575 (50)  $[\text{M} + \text{H}]^+$ ,  $559$  (15)  $[\text{M} - \text{CH}_3]^+$ ,  $501$  (100)  $[\text{M} - \text{SiMe}_3]^+$ . C<sub>30</sub>H<sub>42</sub>N<sub>2</sub>O<sub>2</sub>Si<sub>4</sub> (575.0): calcd. C 62.66, H 7.36, N 4.87; found C 62.31, H 7.21, N 4.53.

## Acknowledgments

We gratefully acknowledge the support of our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Dr. W. Baumann and Prof. N. Stoll for recording NMR and mass spectra.

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Received September 4, 2003

Early View Article

Published Online March 5, 2004