Synthesis and Structural Characterization of Novel Silenes Stabilized by Intramolecular Coordination of a Dialkylamino Group[**]

Martin Mickoleit,[a] Rhett Kempe,[b] and Hartmut Oehme*[a]

Abstract: Two intramolecularly donor-stabilized silenes, 1-(8-dimethylamino-1-naphthyl)-1,2,2-tris(trimethylsilyl)silene (**6a**) and 1-(2-dimethylaminomethylphenyl)-1,2,2-tris(trimethylsilyl)silene (**6b**), were synthesized according to a novel one-step process by the reaction of (dichloromethyl)tris(trimethylsilyl)silane (**1**) with a twofold molar excess of 8-dimethylamino-1-naphthyllithium or 2-(dimethylaminomethyl)phenyllithium, respectively. Compounds **6a** and **6b** are thermally stable compounds. X-ray structural analyses of both silenes revealed strong donor–acceptor interactions between the dialkylamino groups and the electrophilic silene silicon atoms (Si–N distances: **6a**: 1.751(3) Å; **6b**: 1.749(3) Å) that lead to pyramidalization at the silicon centers. In contrast, the configuration at the silene carbon atoms was found to be planar. The Si=C distances (**6a**: 1.751(3) Å; **6b**: 1.749(3) Å) fit with literature data of comparable compounds. Addition of water or methanol to the Si=C bonds of **6a,b** afforded the silanols **7a,b** and the methoxysilanes **8a,b**, respectively. The compound 1-(8-dimethylaminomethyl-1-naphthyl)-1,2,2-tris(trimethylsilyl)silene (**6c**), generated following the same procedure by the reaction of **1** with 8-(dimethylaminomethyl)-1-naphthyllithium (molar ratio 1:2) proved to be unstable at room temperature and underwent rapid insertion of the Si=C group into a methylene C–H bond of the dimethylaminomethylnaphthyl ligand to afford the 1-silaacenaphthene **9**.

Keywords: donor–acceptor systems · main group elements · silenes · silicon · structure elucidation

Introduction

Silenes are extremely labile compounds, which, in absence of trapping agents, usually undergo rapid dimerizations or oligomerizations. By means of bulky substituents attached to the Si=C group, a kinetic stabilization of the systems can be achieved, and in recent years some highly congested silenes were isolated and, in part, structurally characterized.[1] As early as 1986, Wiberg et al. found that silenes are effectively stabilized by bases, such as amines, THF, or fluoride ions,[2a, b] and he succeeded in the isolation of an amine adduct of a silene, which is unstable in absence of the donor molecule.[2c] This concept of stabilization by base coordination to the electrophilic silicon atom is not confined to silenes, but is applicable to, for example, Si=N systems to silanimines.[3] An intensification of the effect is expected, when substituents with additional donor groups are introduced to the Si=C unit, which permits an intramolecular interaction with the electrophilic silicon center. In the case of silanethiones and of silylium salts, intramolecular base coordination proved to cause a tremendous increase in the stability of these unsaturated silicon compounds and allowed the isolation of some derivatives with insignificant steric congestion.[4] Intramolecularly donor-stabilized silenes were unknown till now, possibly because of the lack of suitable synthetic methods. A stable dibenzosilafulvene with an 8-dimethylaminomethyl-1-naphthyl group at the silicon atom, which could possibly be regarded as a silene with intramolecular amine coordination, was isolated by Chernyshev and co-workers;[5] however, there is no X-ray crystal structure analysis of the compound. From theoretical calculations, performed in the group of Gusel'nikov, a definite stabilization of the Si=C bond of silenes by intramolecular N → Si coordination was concluded.[6]

Recently we obtained 1-(8-dimethylamino-1-naphthyl)-1,2,2-tris(trimethylsilyl)silene (**6a**) by the reaction of (dichloromethyl)tris(trimethylsilyl)silane (**1**) with 8-dimethylamino-1-naphthyllithium (molar ratio 1:2), and we succeeded in performing its X-ray structural analysis, which clearly characterized the compound as an intramolecularly donor-stabilized silene.[7] Meanwhile, the synthetic route applied for the preparation of **6a** proved to be a general method for the

---

[a] Prof. Dr. H. Oehme, Dipl.-Chem. M. Mickoleit
Fachbereich Chemie der Universität Rostock
18051 Rostock (Germany)
Fax: (+49) 381-498-1765
E-mail: hartmut.oehme@chemie.uni-rostock.de

[b] Priv.-Doz. Dr. R. Kempe
Institut für Organische Katalyseforschung
an der Universität Rostock, 18055 Rostock (Germany)

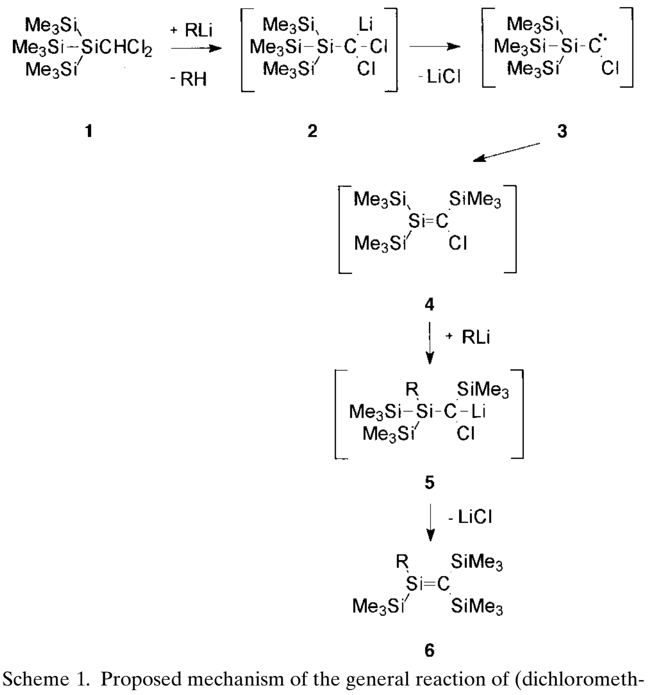
[**] Intramolecularly Donor-Stabilized Silenes, Part 2; for Part 1 see: ref. [7].

synthesis of donor-stabilized as well as of kinetically stabilized silenes,[8] and in the present paper we describe the generation of three novel silenes with strong intramolecular N → Si donor–acceptor interactions; two of the silenes are indefinitely stable at room temperature, but the third one undergoes a rapid rearrangement by insertion of the Si=C group into a C–H bond to form a 1-silaacenaphthene.

Results and Discussion

The synthesis of the intramolecularly donor-stabilized silenes 6a and 6b: The method, successfully applied to the synthesis of novel silenes and to be described in this paper, consists of the treatment of (dichloromethyl)tris(trimethylsilyl)silane (**1**) with suitably functionalized organolithium compounds. Compound **1** is easily obtained by the reaction of tris(trimethylsilyl)silane with chloroform in the presence of potassium *tert*-butoxide. Treatment of **1** with organolithium compounds leads to the deprotonation of the dichloromethyl group, and this initiates a remarkable sequence of elimination, isomerization, and addition steps; the structures of the resultant final products depend on the groups R introduced by the organolithium derivatives used.[8, 9]

Our proposal for the mechanism of the whole reaction (molar ratio **1**:RLi is 1:2) is outlined in Scheme 1. Loss of lithium chloride from the carbenoid **2** and subsequent silylcarbene–silene rearrangement[9] of **3** afford the transient silene **4**, which in the presence of an excess of the organolithium compound is immediately trapped to give the new carbenoids **5**. Repeated elimination of LiCl from **5** and renewed 1,2-Si–C-trimethylsilyl migration afford the Si=C systems **6**.

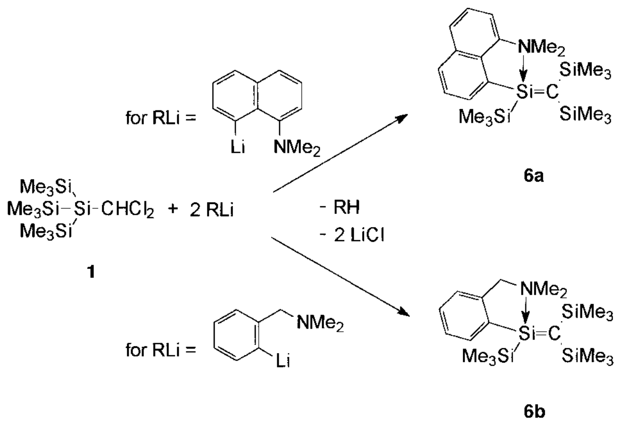


Scheme 1. Proposed mechanism of the general reaction of (dichloromethyl)tris(trimethylsilyl)silane (**1**) with organolithium reagents RLi.

In the case of the reaction of **1** with simple organolithium derivatives RLi (R = Me, *n*Bu, Ph, and Mes; molar ratio 1:3), the sterically more or less unprotected silenes $R(Me_3Si)Si{=}C(SiMe_3)_2$ (**6**) rapidly add a further equivalent of RLi to produce the organolithium intermediates $R_2(Me_3Si)Si{-}CLi(SiMe_3)_2$, which after hydrolytic workup afford the silanes $R_2(Me_3Si)Si{-}CH(SiMe_3)_2$.[9] The same end products are obtained, when the ratio of the reactants is reduced, for example, to 1:2. We assume the deprotonation of **1** to be a slow process compared with the subsequent steps; thus, the intermediate silenes always meet an effective excess of RLi and undergo the reactions described. But when, for the reaction with **1**, highly congested organolithium compounds RLi, such as 2,4,6-triisopropylphenyllithium or 2-*tert*-butyl-4,5,6-trimethylphenyllithium, were used, further addition of RLi to the silene double bond of **6** was prevented, and kinetically stabilized silenes could be synthesized and characterized.[8]

The efficiency of the method with respect to the synthesis of Si=C systems is best demonstrated by the reaction of **1** with dimethylamino-functionalized aryllithium derivatives. For that purpose, we have chosen and describe here the treatment of **1** with 8-dimethylamino-1-naphthyllithium, with 2-(dimethylaminomethyl)phenyllithium, and with 8-(dimethylaminomethyl)-1-naphthyllithium, respectively; the reaction leads to two novel intramolecularly donor-stabilized silenes and an unexpected silene resultant product.

In a preliminary communication we already described the synthesis and structure of 1-(8-dimethylamino-1-naphthyl)-1,2,2,-tris(trimethylsilyl)silene (**6a**) (Scheme 2), which is formed in a very straightforward one-pot reaction of **1** with two molar equivalents of 8-dimethylamino-1-naphthyllithium; the reaction follows the general route shown in Scheme 1.[7] The isolation of the silene is complicated by the presence of one equivalent of 1-dimethylaminonaphthalene in the product mixture. But, fortunately, **6a** proved to be sufficiently thermally stable, so that the amine could be removed by distillation in vacuo. After recrystallization from *n*-pentane, **6a** was obtained as a yellow solid (yield 80%), which was indefinitely stable at room temperature, and also



Scheme 2. Synthesis of the intramolecularly donor-stabilized silenes **6a** and **6b** by the reaction of **1** with 8-dimethylamino-1-naphthyllithium or 2-(dimethylaminomethyl)phenyllithium, respectively.

© WILEY-VCH Verlag GmbH, D-69451 Weinheim, 2001

heating for a short time to 140 °C left the compound unchanged. On exposure to air, **6a** gradually decomposes. Obviously, stabilization of the silene system by intramolecular N → Si coordination prevents the attack of excess organolithium reagent to the Si=C group, excludes dimerization reactions, and allows the isolation of **6a**.

With the use of the same synthetic pathway, 1-[2-(dimethylaminomethyl)phenyl]-1,2,2-tris(trimethylsilyl)silene (**6b**) was prepared by treatment of **1** with two equivalents of 2-(dimethylaminomethyl)phenyllithium in ether/THF (Scheme 2). After the reaction had ceased, the solvents and benzyldimethylamine were distilled off at moderate temperature (30–40 °C/0.01 mbar), and the silene was isolated by recrystallization from pentane (yield 74 %). Compound **6b** is a white solid. In the absence of air, it was found to be thermally stable up to at least 130 °C.

Unfortunately, attempts to extend the studies to the synthesis of further donor-stabilized silenes with a modified substitution pattern, failed. With the aim of introducing a further carbon substituent to the silene silicon atom, we investigated the behavior of the (dichloromethyl)oligosilanes $R(Me_3Si)_2Si{-}CHCl_2$ (R = Me, Ph) towards 8-dimethylamino-1-naphthyllithium or 2-(dimethylaminomethyl)phenyllithium, respectively. The two dichloromethylsilanes are known to react with simple organolithium compounds, such as methyllithium or phenyllithium; the reaction follows the pattern discussed above (Scheme 1).[8] But as a result of their interaction with the dimethylamino-functionalized aryllithium compounds, we obtained complex mixtures of products. A silene or any resultant silene product could not be isolated.

The structures of 6a and 6b: The structural elucidation of the two synthesized silenes was performed by NMR and MS studies as well as by X-ray structural analyses (see Experimental Section). The ^{29}Si and ^{13}C chemical shifts of the silicon and carbon atoms of the Si=C groups of **6a,b** are given in Table 1. For comparison, the data reported by Wiberg and coworkers for the acyclic silene amine adducts $Me_3N \cdot Me_2Si{=}C(SiMe_3)_2$[2b] and $Me_2EtN \cdot Me_2Si{=}C(SiMe_2Ph)_2$[2c] were additionally included. The ^{29}Si chemical shifts of all compounds mentioned are in good agreement, and the data obtained appear to be typical for silenes stabilized by amine coordination. The ^{13}C chemical shifts of **6a** and **6b** are close to each other, but differ significantly from those reported for the acyclic derivatives.

Table 1. δ^{29}Si and δ^{13}C NMR chemical shifts of the Si=C atoms in **6a**, **6b**, and two acyclic amine silene adducts.

	^{29}Si	^{13}C	Literature
6a	39.4	22.4	ref. [7]
6b	33.4	18.8	
$Me_3N \cdot Me_2Si{=}C(SiMe_3)_2$	36.9	56.5	ref. [2b]
$Me_2EtN \cdot Me_2Si{=}C(SiMe_2Ph)_2$ ref. [2c]	35.4	100.1	

The results of the X-ray structural analyses of **6a** and **6b** confirmed the expected picture of intramolecularly amine-stabilized silenes with four-coordinate silicon centers. Strong interactions of the dimethylamino groups with the silene silicon atoms under formation of five-membered cyclic systems are obviously the reason for the high stability of the two compounds. Expectedly, the N → Si coordinations lead to a pyramidalization at the central silicon atoms. This can be clearly seen for **6b** in Figure 1; for **6a** the situation is quite comparable.[7] The N1–Si1 distances as well as the sums of angles at the central silicon atoms of **6a** and **6b** are given in Table 2, which also includes the bond parameters of the ethyldimethylamine adduct of $Me_2Si{=}C(SiMe_2Ph)_2$.[2c] In **6a** and **6b** as well as in Wiberg's acyclic amine–silene adduct, the configuration at the silene carbon atoms is almost planar. The Si=C distances in all three compounds are comparable and generally slightly longer than that of the uncomplexed similarly substituted stable silene $Me_2Si{=}C(SiMe_3)(SiMe\textit{t}Bu_2)$.[10] This is consistent with the observation, made by Wiberg et al., that coordination of donor molecules to the silene silicon atom generally leads to an elongation of the Si=C bond.[2] The Si=C distances for the uncomplexed

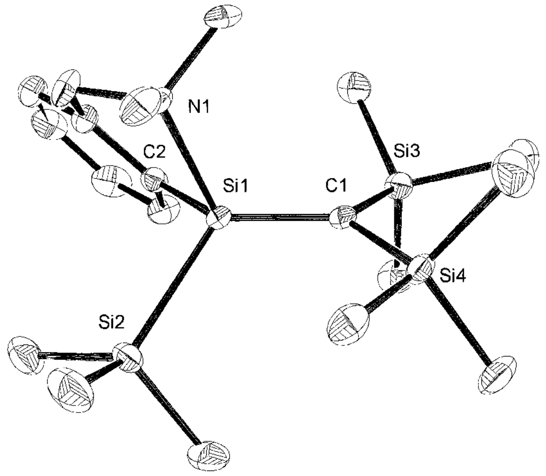
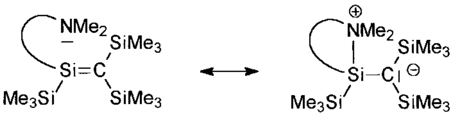


Figure 1. Molecular structure of **6b** in the crystal (ORTEP, 30 % probability, H atoms omitted for clarity); selected bond lengths [Å] and angles [°]: Si1–C1 1.749(3), C1–Si3 1.833(3), C1–Si4 1.823(3), Si1–C2 1.891(3), Si1–Si2 2.3809(12), Si1–N1 2.004(2); Si1-C1-Si3 120.3(2), Si1-C1-Si4 121.3(2), Si3-C1-Si4 117.7(2), C1-Si1-C2 121.30(13), C1-Si1-Si2 121.69(10), C2-Si1-Si2 100.62(10), C1-Si1-N1 113.30(12), C2-Si1-N1 85.97(12), 107.82(8).

Table 2. Selected structural data of the silenes **6a**, **6b**, and the acyclic compound $Me_2EtN \cdot Me_2Si{=}C(SiMe_2Ph)_2$.[2c]

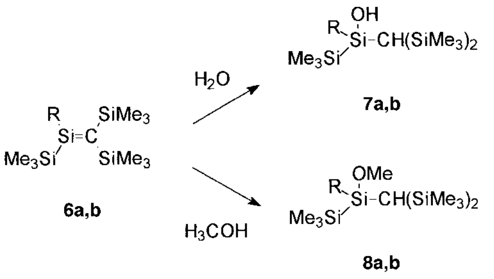
	Si=C distance [Å]	Si1–N1 distance [Å]	sum of angles Si1 [°]	sum of angles C1 [°]
6a	1.751(3)	2.069(2)	345.5	358.9
6b	1.749(3)	2.004(2)	343.6	359.3
$Me_2EtN \cdot Me_2Si{=}C(SiMe_2Ph)_2$	1.761(4)	1.988(4)	341.8	359.2

kinetically stabilized silenes $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$ (1.746 Å, Ad = 1-adamantyl)[11] and $(Me_3Si)_2Si{=}CAd'$ (1.741 Å, Ad' = 2-adamantylidene)[12] are longer and almost alike those of **6a** and **6b**, but these elongations were found to be due to electronic effects of the substituents.[12, 13] Thus, the structural data found agree with our notion about the ylide-like nature of the two donor-stabilized silenes **6a** and **6b**.



6a,b **6a,b**

For chemical characterization, **6a** and **6b** were treated with water and methanol, respectively. In a manner typical for reactive silenes,[1] water was added to the polar Si=C double bond of **6a** or **6b** to afford the silanols **7a** and **7b**. Similarly, **6a** and **6b** were converted by addition of methanol to give the methoxysilanes **8a** and **8b** (Scheme 3).

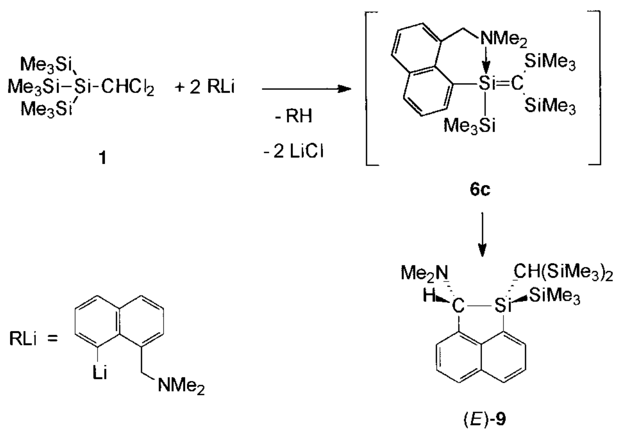


a: R = 8-dimethylamino-1-naphthyl
b: R = 2-dimethylaminomethylphenyl

Scheme 3. Conversion of the silenes **6a,b** with water into the silanols **7a,b** and with methanol into the methoxysilanes **8a,b**.

We are continuing the studies on the chemical reactivity of the intramolecularly donor-stabilized silenes **6a** and **6b**, which, as preliminary results show, are characterized by pronounced ylid-like behavior. This will be communicated elsewhere.

The reaction of (dichloromethyl)tris(trimethylsilyl)silane (1) with 8-(dimethylaminomethyl)-1-naphthyllithium: Under the same conditions applied for the synthesis of **6a** and **6b**, the dichloromethylsilane **1** was treated with 8-(dimethylaminomethyl)-1-naphthyllithium (1:2). But, to our surprise, the white crystalline product obtained did not prove to be a silene but the 1-silaacenaphthene **9** (Scheme 4). Its structure was proved on the basis of NMR and MS data (see Experimental Section). Unfortunately, the crystal quality was insufficient for an X-ray crystal structure analysis. NOE experiments that showed strong correlations between the C1 proton and the NCH_3 and $CSiCH_3$ protons but no correlation between NCH_3 and $SiSiCH_3$ revealed the *E* configuration of the compound isolated.



Scheme 4. Reaction of **1** with 8-dimethylaminomethyl-1-naphthyllithium; this affords finally the 1-silaacenaphthene **9**.

The formation of **9** is understood as proceeding through the same steps depicted in Schemes 1 and 2 for the synthesis of **6a** and **6b**, respectively, but, evidently, the silene **6c** is unstable and undergoes rapid insertion of the Si=C unit into a methylene C–H bond. Compound **9** is best isolated by Kugelrohr distillation at approximately 200 °C/0.06 mbar, and we assumed the formation of **9** to be due to the extreme workup conditions. But repeated reactions of **1** with 8-dimethylaminomethyl-1-naphthyllithium at −78 °C and careful workup at room temperature (removal of the solvent in vacuo and addition of *n*-heptane) similarly afforded **9** as the only identified product. Also attempts of quenching **6c** by addition of water to the cold solution of the products, following the procedure successfully applied to the synthesis of **7a,b**, gave no silanol **7c**, but a complex mixture of products, from which no definite compound could be isolated. The experiments indicate that **6c** is unstable, even at room temperature.

Actually, rearrangements of silenes by intramolecular insertion reactions of the Si=C groups into C–H bonds have occasionally been observed,[14] but in contrast to the thermal stability of **6b**, the behavior of **6c** is rather surprising. The rapid isomerization of **6c** into **9** indicates the still high reactivity of the Si=C unit in donor-stabilized silenes of type **6**, in particular with respect to intramolecular conversions. We assume, the remarkable differences in the stability of the two silenes to be due to the favorable ring size of the insertion product formed by isomerization of **6c** and, on the other hand, the disadvantageous four-membered ring system, which would be the result of the rearrangement of **6b**.

Experimental Section

All reactions which involve organometallic reagents were carried out under purified argon. NMR experiments: Bruker AC 250 or Bruker ARX 300, temperature 30 °C and tetramethylsilane as internal standard. IR experiments: Nicolet 205 FT-IR. MS experiments: Intectra AMD 402 (EI with 70 eV or chemical ionization with isobutane). (Dichloromethyl)tris(trimethylsilyl)silane[9] and 2-(dimethylaminomethyl)phenyllithium[15] were prepared as described in the literature. Compound 8-(dimethylaminomethyl)-1-naphthyllithium was made following the procedure given by Corriu et al.,[16] but was isolated as a brown amorphous powder. The data concerning the syntheses of **6a**, **7a**, and **8a** and the X-ray structural analysis of **6a** were communicated previously.[7] 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 (SiC formation). Therefore, high-resolution mass spectra were performed.

1-(2-Dimethylaminomethylphenyl)-1,2,2-tris(trimethylsilyl)silene (6b): At −78 °C, **1** (2.27 g, 6.85 mmol) was added gradually to a suspension of 2-(dimethylaminomethyl)phenyllithium (2.46 g, 17.4 mmol) in ether/THF (20 mL/5 mL). After warming up to room temperature, stirring was continued for 48 h, afterwards lithium chloride was separated, the solution evaporated, and the benzyldimethylamine distilled off in vacuo (30–40 °C/0.01 mbar). Recrystallization of the residue from pentane afforded white crystals (2.0 g, 74 %). M.p. 118–120 °C. ^{1}H NMR ([D$_6$]benzene): $\delta = 0.10$, 0.27, and 0.54 (3s, 3 × 9H; SiCH$_3$), 1.83 and 2.06 (2s, 2 × 3H; NCH$_3$), 2.89 and 3.31 (2d, $^{2}J = 14.5$ Hz, 2 × 1H; NCH$_2$), 6.62–6.66 (m, 1H; aryl–H), 7.03–7.07 (m, 2H; aryl–H), 7.63–7.67 (m, 1H; aryl–H); ^{13}C NMR ([D$_6$]benzene): $\delta = 1.7$, 7.7, and 8.1 (SiCH$_3$), 18.8 (Si=C), 45.2 and 45.9 (NCH$_3$), 64.7 (NCH$_2$), 123.7, 127.7, 129.0 and 135.1 (arom. CH), 139.3 and 141.8 (quart. arom. C); ^{29}Si NMR ([D$_6$]benzene): $\delta = -20.1$ (Si*Si*Me$_3$), −8.9 and −8.3 (CSiMe$_3$), 33.4 (Si=C); UV/Vis (*n*-heptane): λ_{max} (ε) = 248 nm (1540); MS (CI): *m*/*z* (%): 393 (100) $[M]^+$, 378 (45) $[M-CH_3]^+$, 320 (70) $[M-SiMe_3]^+$; elemental analysis calcd (%) for $C_{19}H_{39}NSi_4$ (393.87): C 57.94, H 9.98, N 3.56; found C 56.26, H 9.93, N 3.40; HRMS calcd for $C_{18}H_{36}NSi_4$ ($[M-CH_3]^+$): 378.192; found 378.189.

Silanol (7b): Water was added to the solution in ether/THF of the reaction mixture obtained from **1** (2.60 g, 7.9 mmol) and 2-(dimethylaminomethyl)phenyllithium (2.33 g, 16.5 mmol) following the procedure given for the synthesis of **6b**, and the organic phase was separated, dried, and evaporated. Kugelrohr distillation at 125–128 °C/5 × 10^{-2} mbar gave a colorless oil (yield: 2.1 g, 64 %). ^{1}H NMR ([D$_6$]benzene): $\delta = 0.00$ (s, 1H; Si$_3$CH), 0.20, 0.29, and 0.36 (3s, 3 × 9H; SiCH$_3$), 1.84 (s, 6H; NCH$_3$), 3.12 and 3.58 (2d, $^{2}J = 11.7$ Hz, 2 × 1H; NCH$_2$), 6.84–6.89 (m, 1H; aryl–H), 7.04–7.13 (m, 2H; aryl–H), 7.55–7.57 (m, 1H; aryl–H), 8.37 (br s, 1H; OH); ^{13}C NMR ([D$_6$]benzene): $\delta = 0.1$ (CH), 4.1 (SiSiCH$_3$), 7.9 (CSi*C*H$_3$), 44.1 (NCH$_3$), 65.9 (NCH$_2$), 126.6, 128.6, 132.0 and 136.8 (arom. CH), 142.6 and 144.0 (quart. arom. C); ^{29}Si NMR ([D$_6$]benzene): $\delta = -21.5$ (Si*Si*Me$_3$), −0.7 and 0.0 (CSiMe$_3$), 3.7 (SiOH); IR (cap.): $\tilde{\nu} = 3440$ cm^{-1} (br, OH$_{ass}$); MS (CI): *m*/*z* (%): 412 (100) $[M+H]^+$, 395 (95) $[MH-OH]^+$, 351 (62) $[MH-SiMe_2]^+$, 336 (33) $[MH-SiMe_3]^+$; elemental analysis calcd (%) for $C_{19}H_{41}NOSi_4$ (411.88): C 55.41, H 10.03, N 3.40; found C 54.83, H 9.87, N 3.19; HRMS calcd: 411.227; found 411.222.

Methoxysilane (8b): Methanol (1 mL) was added to a solution of **6b**, made from **1** (2.15 g, 6.4 mmol) and 2-(dimethylaminomethyl)phenyllithium (1.93 g, 13.5 mmol) following the procedure given above, and after stirring for 1 h, the mixture was evaporated. The residue was extracted with *n*-heptane, LiCl was filtered off, and the solution was again evaporated. Recrystallization of the residue from methanol gave **8b** (1.38 g, 50 %). M.p. 115 °C. ^{1}H NMR ([D$_6$]benzene): $\delta = 0.17$, 0.21 and 0.29 (3s, 3 × 9H; SiCH$_3$), 0.62 (s, 1H; Si$_3$CH), 2.15 (s, 6H; NCH$_3$), 3.41 and 3.62 (2d, $^{2}J = 13.2$ Hz, 2 × 1H; NCH$_2$), 3.45 (s, 3H; OCH$_3$), 7.16–7.20 (m, 2H; aryl–H), 7.46–7.50 (m, 1H; aryl–H), 7.67–7.71 (m, 1H; aryl–H); ^{13}C NMR ([D$_6$]benzene): $\delta = 1.1$, 3.70, and 3.73 (SiCH$_3$), 7.4 (Si$_3$CH), 44.9 (NCH$_3$), 52.2 (OCH$_3$), 64.0 (NCH$_2$), 126.3, 128.9, 130.3 and 135.9 (arom. CH), 141.1 and 143.6 (quart. arom. C); ^{29}Si NMR ([D$_6$]benzene): $\delta = -22.1$ (Si*Si*Me$_3$), −0.9 and 1.3 (CSiMe$_3$), 9.1 (SiOMe); IR (Nujol): $\tilde{\nu} = 1108$ cm^{-1} (SiOC); MS (EI): *m*/*z* (%): 424 (1) $[M-H]^+$, 410 (10) $[M-CH_3]^+$, 352 (100) $[M-SiMe_3]^+$, 306 (21) $[M-MeOSiMe_3]^+$; elemental analysis calcd (%) for $C_{20}H_{43}NOSi_4$ (425.91): C 56.40, H 10.18, N 3.29; found C 55.79, H 10.20, N 3.37; HRMS calcd for $C_{20}H_{40}NOSi_4$ ($[M-CH_3]^+$): 410.219; found 410.215.

(*E*)-2-Dimethylamino-1-trimethylsilyl-1-[bis(trimethylsilyl)methyl]-1-sila-acenaphthene (9): At −78 °C, **1** (1.15 g, 3.5 mmol) was added to a suspension of 8-(dimethylaminomethyl)-1-naphthyllithium (1.36 g, 7.1 mmol) in ether (50 mL). After warming up to room temperature and stirring for 48 h, the solution was concentrated, and the lithium chloride filtered off. Evaporation of the filtrate and Kugelrohr distillation at 200–210 °C/0.06 mbar gave oily **9** (0.78 g, 51 %). Crystallization from *n*-heptane afforded white crystals, m.p. 82–83 °C. ^{1}H NMR ([D$_6$]benzene): $\delta = -0.30$, 0.34, and 0.36 (3s, 3 × 9H; SiCH$_3$), −0.09 (s, 1H; Si$_3$CH), 2.19 (s, 6H; NCH$_3$), 4.29 (s, 1H; NCH), 7.29–7.70 (m, 6H; aryl–H); ^{13}C NMR ([D$_6$]benzene): $\delta = 0.5$, 3.2, and 3.5 (SiCH$_3$), 0.7 (Si$_3$CH), 44.6 (NCH$_3$), 63.0 (NCH), 125.6, 126.0, 126.1, 126.2, 128.3, and 132.9 (arom. CH), 132.8, 141.4, 142.0, and 144.6 (quart. arom. C); ^{29}Si NMR ([D$_6$]benzene): $\delta = -17.8$ (Si*Si*Me$_3$), −9.1 (aryl–Si), −0.2 and 0.4 (CSiMe$_3$); MS (EI): *m*/*z* (%): 443 (7) $[M]^+$, 428 (54) $[M-CH_3]^+$, 370 (78) $[M-SiMe_3]^+$, 73 (100) $[SiMe_3]^+$; elemental analysis calcd (%) for $C_{23}H_{41}NSi_4$ (443.93): C 62.23, H 9.31, N 3.16; found C 61.22, H 9.26, N 3.03; HRMS calcd for $C_{22}H_{38}NSi_4$ ($[M-CH_3]^+$): 428.208; found 428.208.

Crystal structure determination of 6b: X-ray diffraction data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo$_{K\alpha}$ radiation. Crystals from *n*-pentane, crystal size 0.6 × 0.3 × 0.2 mm, formula $C_{19}H_{39}NSi_4$, formula weight 393.87, orthorhombic, space group *Pbca*, $a = 15.978(3)$ Å, $b = 15.993(3)$ Å, $c = 19.275(4)$ Å, $V = 4925.5(17)$ Å^3, $Z = 8$, $T = 200(2)$ K, $m = 0.244$ mm^{-1}, $F(000) = 1728$, Θ range 2.09–24.19°, index ranges $-18 \leq h \leq 17$, $-18 \leq k \leq 18$, $0 \leq 1 \leq 16$, $\rho_{calcd} = 1.062$ g cm^{-3}, peak/hole 0.44/−0.22 e Å^{-3}, measured reflections 12293, independent reflections 3524, observed reflections 2240, *R*(int) 0.056, no. parameters 217, $R1$ $[I > 2\sigma(I)]$ 0.041, $\omega R2$ (all data) 0.087. The structure was solved by direct methods (SHELXS-86)[17] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[18] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145940. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the State of Mecklenburg-Vorpommern, by the Deutsche Forschungsgemeinschaft, and by the Fonds der Chemischen Industrie. We thank Prof. M. Michalik, Dr. W. Baumann, and Prof. N. Stoll for recording NMR and mass spectra.

---

[1] Reviews: A. G. Brook, M. A. Brook, *Adv. Organomet. Chem.* **1996**, *39*, 71–158; T. Müller, W. Ziche, N. Auner in *The Chemistry of Organic Silicon Compounds, Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, New York, **1998**, pp. 857–1062.

[2] a) N. Wiberg, H. Köpf, *J. Organomet. Chem.* **1986**, *315*, 9–18; b) N. Wiberg, G. Wagner, G. Reber, J. Riede, G. Müller, *Organometallics* **1987**, *6*, 35–41; c) N. Wiberg, K.-S. Joo, K. Polborn, *Chem. Ber.* **1993**, *126*, 67–69.

[3] N. Wiberg, K. Schurz, *J. Organomet. Chem.* **1988**, *341*, 145–163; G. Reber, J. Riede, N. Wiberg, K. Schurz, G. Müller, *Z. Naturforsch. B Chem. Sci.* **1989**, *44*, 786–795; S. Walter, U. Klingebiel, D. Schmidt-Bäse, *J. Organomet. Chem.* **1991**, *412*, 319–326.

[4] Silanethiones: P. Arya, J. Boyer, F. Carré, P. Corriu, G. Lanneau, J. Lapasset, M. Perrot, C. Priou, *Angew. Chem.* **1989**, *101*, 1069–1071; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1016–1018; J. Belzner, H. Ihmels, B. O. Kneisel, R. Herbst-Irmer, *Chem. Ber.* **1996**, *129*, 125–130. Silylium salts: C. Chuit, R. Corriu, A. Mehdi, C. Reyé, *Angew. Chem.* **1993**, *105*, 1372–1375; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1311–1314; C. Brelière, F. Carré, R. Corriu, M. Wong Chi Man, *J. Chem. Soc. Chem. Commun.* **1994**, 2333–2334; M. Chauhan, C. Chuit, R. J. P. Corriu, A. Mehdi, C. Reyé, *Organometallics* **1996**, *15*, 4326–4333; J. Belzner, D. Schär, B. O. Kneisel, R. Herbst-Irmer, *Organometallics* **1995**, *14*, 1840–1843.

[5] N. N. Zemljanskii, I. V. Borisova, A. K. Shestakova, Y. A. Ustynyuk, E. A. Chernyshev, *Izv. Akad. Nauk. Ser. Khim.* **1998**, *47*, 486–491; N. N. Zemljanskii, I. V. Borisova, A. K. Shestakova, Y. A. Ustynyuk, E. A. Chernyshev, *Russ. Chem. Bull.* **1998**, *47*, 469–474.

[6] V. G. Avakyan, L. E. Gusel'nikov, V. A. Pestunovich, A. A. Bagaturyants, N. Auner, *Organometallics* **1999**, *18*, 4692–4699.

[7] M. Mickoleit, K. Schmohl, R. Kempe, H. Oehme, *Angew. Chem.* **2000**, *112*, 1679–1681; *Angew. Chem. Int. Ed.* **2000**, *39*, 1610–1612.

[8] K. Schmohl, H. Reinke, H. Oehme, *Eur. J. Inorg. Chem.* **2001**, 481–489.

[9] K. Schmohl, T. Gross, H. Reinke, H. Oehme, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1100–1104.

[10] N. Wiberg, G. Wagner, J. Riede, G. Müller, *Organometallics* **1987**, *6*, 32–35.
[11] A. G. Brook, S. C. Nyburg, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. K. M. R. Kallury, Y. C. Poon, Y.-M. Chang, W. Wong-Ng, *J. Am. Chem. Soc.* **1982**, *104*, 5667–5672.
[12] Y. Apeloig, M. Bendikov, M. Yuzefovich, M. Nakash, D. Bravo-Zhivotovskii, D. Bläser, R. Boese, *J. Am. Chem. Soc.* **1996**, *118*, 12228–12229.
[13] Y. Apeloig, M. Karni, *J. Am. Chem. Soc.* **1984**, *106*, 6676–6682.
[14] A. G. Brook, H.-J. Wessely, *Organometallics* **1985**, *4*, 1487–1488; K. M. Baines, A. G. Brook, R. R. Ford, P. D. Lickiss, A. K. Saxena, W. J. Chatterton, J. F. Sawyer, B. A. Behnam, *Organometallics* **1989**, *8*, 693–709; U. Klingebiel, S. Pohlmann, L. Skoda, *J. Organomet. Chem.* **1985**, *291*, 277–284; F. Luderer, H. Reinke, H. Oehme, *Chem. Ber.* **1996**, *129*, 15–20.
[15] N. Auner, R. Probst, F. Hahn, E. Herdtweck, *J. Organomet. Chem.* **1993**, *459*, 25–41.
[16] R. Corriu, G. Lanneau, C. Priou, *Angew. Chem.* **1991**, *103*, 1153–1155; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1130–1132.
[17] G. M. Sheldrick, *SHELXS-86*, University of Göttingen (Germany), **1986**.
[18] G. M. Sheldrick, *SHELXL-93*, University of Göttingen (Germany), **1993**.

Received: July 6, 2000 [F2588]

© WILEY-VCH Verlag GmbH, D-69451 Weinheim, 2001