

Intramolecularly donor-stabilized silenes[☆]

Part 3. Synthesis and structure of 1-[2,6-bis(dimethylaminomethyl)phenyl]-1,2,2- tris(trimethylsilyl)silene

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

Abstract

1-[2,6-Bis(dimethylaminomethyl)phenyl]-1,2,2-tris(trimethylsilyl)silene (**9**) was prepared by treatment of (dichloromethyl)tris(trimethylsilyl)silane (**3**) with 2,6-bis(dimethylaminomethyl)phenyllithium (molar ratio 1:2). **9** is a crystalline compound, indefinitely stable at room temperature. The X-ray structural analysis of **9** characterized the compound as an intramolecularly amine-stabilized silene with four-coordinate silicon, i.e. only one of the two amine groups of the bis(dimethylaminomethyl)phenyl substituent is coordinated to the electrophilic silicon center (Si–N distance 2.035(3) Å). Thus, the silene silicon atom is pyramidalized (sum of angles 348.49°), whereas the configuration at the silene carbon atom is trigonal planar (sum of angles 359.9°). The Si=C bond length was found to be 1.759(3) Å. Reaction of **9** with water or methanol led to the addition of these nucleophiles to the Si=C bond, producing the silanol **12** and the methoxysilane **13**, respectively. The reaction pathway leading to **9** is discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Derivatives of three-coordinate silicon, such as silenes, silanimines, silanethiones and silylium salts, are extremely labile compounds, but can effectively be stabilized by interaction of their electrophilic silicon atoms with bases. In 1986, Wiberg and coworkers described the stabilization of silenes by amines, THF and fluoride ions [1a], and they succeeded in isolating an amine adduct of a silene, which is unstable in the absence of

the donor molecule [1b]. Amines, THF and even benzophenone were found to coordinate to the silicon atom of silanimines, decreasing the dimerization tendency of these unsaturated silicon compounds [2]. A significant increase of the stability of three-coordinate silicon derivatives was achieved by introducing substituents providing an intramolecular N→Si coordination, which allowed the isolation and structural characterization of a silanethione and some silylium salts [3]. Intramolecularly donor-stabilized silenes were hitherto unknown. A stable dibenzosilafulvene with an 8-dimethylaminomethyl-1-naphthyl group at the silicon atom, which may be regarded as a silene with intramolecular amine coordination, was isolated by Chernychev and coworkers; however, there is no X-ray crystal structure analysis of the compound [4]. From

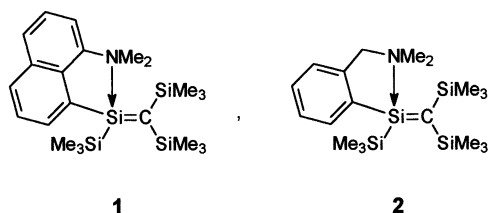
[☆] For Part 2, see Ref. [7].

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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 [5].

Using a new synthetic pathway, we recently succeeded in preparing 2-(8-dimethylamino-1-naphthyl)-1,2,2-tris(trimethylsilyl)silene (**1**) [6] and 1-(2-dimethylaminomethylphenyl)-1,2,2-tris(trimethylsilyl)silene (**2**) [6,7]. The X-ray structural analyses of **1** and **2** clearly characterized both compounds as intramolecularly amine-stabilized silenes with four-coordinate silicon centers. Obviously, the chelate-like coordination of the donor groups to the electrophilic silicon atoms dramatically decreases the reactivity of the silene systems, prevents dimerizations and allows the isolation of the, at most, moderately congested silenes **1** and **2**.



In the course of these studies, we replaced the dimethylamino functionalized groups of **1** or **2** by a 2,6-bis(dimethylaminomethyl)phenyl substituent and were particularly interested in the coordination number of the silicon atom in the resulting intramolecularly donor-stabilized silene. Thus, in the present paper we report the synthesis and structure of 1-[2,6-bis(dimethylaminomethyl)phenyl]-1,2,2-tris(trimethylsilyl)silene (**9**) and describe its reactions with water and methanol.

2. Results and discussion

Recently, we observed that dichloromethyltris(trimethylsilyl)silane (**3**) reacted with excess organolithium reagents RLi (R = Me, *n*-Bu, Ph, Mes) under substitution of the two chlorine atoms and a complete reorganization of the whole substitution pattern of the molecule to give (after hydrolytic workup) silanes of the type $R_2(Me_3Si)Si-CH(SiMe_3)_2$ (**11**) [8]. As shown in Scheme 1, the reaction is initiated by deprotonation of **3** by RLi to give the carbenoid **4**. Loss of LiCl and 1,2-Si,C migration of one trimethylsilyl group, following the pattern of the known silylcarbene–silene rearrangement [9], leads to the transient silene **6**, which is trapped by excess RLi. Repeated elimination of LiCl from **7** and renewed 1,2-Si,C-trimethylsilyl migration again leads to the formation of an Si=C system. In the case of the application of MeLi, *n*-BuLi, PhLi or MesLi, the sterically almost unprotected silenes **8** are trapped by excess RLi to afford the organolithium

derivatives **10**, which are protonated during the hydrolytic workup affording **11**, or which may be quenched by chlorotrimethylsilane to give the [tris(trimethylsilyl)methyl]silanes $R_2(Me_3Si)Si-C(SiMe_3)_3$ [8,9]. Independent of the molar ratio 3:RLi the reaction always proceeded through all intermediates outlined in Scheme 1 to the final products mentioned. Attempts to find dimers of the silenes **6** or **8**, by reducing the ratios of the reactants to 1:2 or 1:1, respectively, were unsuccessful. We assume that the deprotonation of **3**, producing the carbenoid **4**, is a slow process compared with the subsequent steps, and that the transient silenes **6** and **8**, formed in the course of the reaction, always meet an effective excess of the organolithium reagent to produce finally the congested silanes **11**.

When, by reaction of the dichloromethylsilane **3** with appropriate organolithium compounds, substituents R are introduced to the silene silicon atom of **8**, which by means of their bulkiness or by suitable donor groups provide a sufficient stabilization of the Si=C system, the silaethenes **8** can be isolated and characterized. Thus, treatment of **3** with two molar equivalents of 8-dimethylamino-1-naphthyllithium or 2-(dimethylaminomethyl)phenyllithium afforded the intramolecularly donor-stabilized silenes **1** and **2**, respectively [6,7]. Similarly, **3** and either 2,4,6-triisopropylphenyllithium or 2-*tert*-butyl-4,5,6-trimethylphenyllithium gave the kinetically stabilized silenes $(2,4,6-^iPr_3C_6H_2)(Me_3Si)Si=C(SiMe_3)_2$ or $(2-^tBu-4,5,6-Me_3C_6H)(Me_3Si)Si=C(SiMe_3)_2$, respectively; these could not be isolated in a pure form, but they were characterized by various consecutive reactions [10].

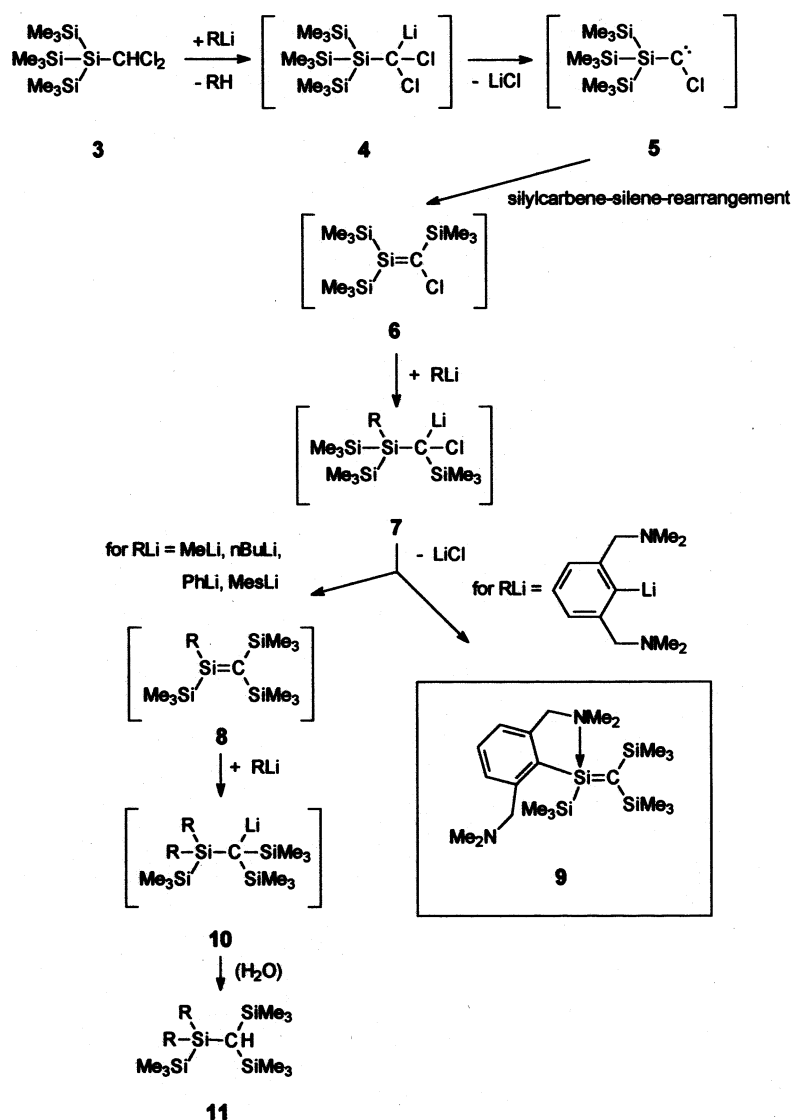
Continuing these studies, and using the same synthetic pathway, we introduced the tridentate 2,6-bis(dimethylaminomethyl)phenyl substituent to the silene silicon atom. In a very straightforward one-pot reaction, **3** is converted by 2,6-bis(dimethylaminomethyl)phenyllithium (1:2) to afford the silene **9** (Scheme 1). After addition of the organolithium reagent to the ethereal solution of **3** and stirring overnight, removal of the solvent, addition of pentane and separation of the lithium chloride that was formed, the compound crystallized from the concentrated solution as a colorless solid (yield 58%). At room temperature, in the absence of air, **9** is indefinitely stable; also 30 min heating of **9** in boiling toluene leaves the compound unchanged. Obviously, intramolecular amine-coordination to the silene silicon atom prevents the addition of excess organolithium reagent to the Si=C bond of **9** and excludes dimerization reactions.

The structure proposed for **9** is confirmed by NMR and MS studies (see Section 3). Of particular interest are the chemical shifts of the silene silicon and carbon atoms. The data found for **9** (^{13}C -NMR: $\delta = 17.5$ ppm; ^{29}Si -NMR: $\delta = 29.5$ ppm) are in reasonable agreement with those measured for **1** (^{13}C -NMR: $\delta = 22.4$ ppm, ^{29}Si -NMR: $\delta = 39.4$ ppm) [6] and **2** (^{13}C -NMR: $\delta =$

18.8 ppm, ^{29}Si -NMR: $\delta = 33.4$ ppm) [7]. The ^{29}Si chemical shift reported by Wiberg et al. for the silene silicon atom of the acyclic amine adduct $\text{Me}_3\text{N} \cdot \text{Me}_2\text{Si}=\text{C}(\text{SiMe}_3)_2$ ($\delta = 36.9$ ppm) is in the same area; the ^{13}C chemical shift of the silene carbon atom ($\delta = 56.5$ ppm) was found at slightly lower field [1b].

The X-ray structural analysis of **9** (single crystals from pentane) provided the picture of an intramolecularly donor-stabilized silene (Fig. 1). Some characteristic bond parameters are summarized in Table 1, which, for comparison, additionally includes the data for **1** and **2** and an acyclic amine silene adduct, described by Wiberg et al. [1c]. The structural investigations unambiguously revealed the $\text{N} \rightarrow \text{Si}$ interaction of only one of the two dimethylamino groups and a tetra-coordinate silene silicon atom. The Si1-N1 distance ($2.035(3)$ Å) was found to be in a region typical for silene amine

adducts. The Si1-N2 distance ($3.441(3)$ Å) is considerably longer. The chelate-like coordination of the dimethylamino group to the silene silicon atom leads to a pyramidalization at the Si1 atom of **9**. In contrast, the configuration at the silene carbon atom is almost trigonal-planar. Quite comparable configurations were described for the open-chain ethyldimethylamine adduct of the silene $\text{Me}_2\text{Si}=\text{C}(\text{SiMe}_2\text{Ph})_2$ [1c] and for **1** and **2** [6,7]. The Si1-C1 bond length in **9** was found to be $1.759(3)$ Å. This value is in perfect agreement with the $\text{Si}=\text{C}$ distances of the other compounds mentioned. Wiberg and coworkers found that coordination of donor molecules to the silene silicon atom generally leads to an elongation of the $\text{Si}=\text{C}$ bond [1b–d]. Thus, the slightly longer $\text{Si}=\text{C}$ distance in **9**, compared with the length of the $\text{Si}=\text{C}$ bond of the similarly substituted, uncomplexed stable silene $\text{Me}_2\text{Si}=\text{C}(\text{SiMe}_3)(\text{SiMe}'\text{Bu}_2)_2$



Scheme 1. Reaction of (dichloromethyl)tris(trimethylsilyl)silane (**3**) with organolithium reagents RLi, leading in the case of MeLi, *n*-BuLi, PhLi and MesLi to the congested silanes **11** and affording in the case of 2,6-bis(dimethylaminomethyl)phenyllithium the intramolecularly amine-stabilized silene **9**.

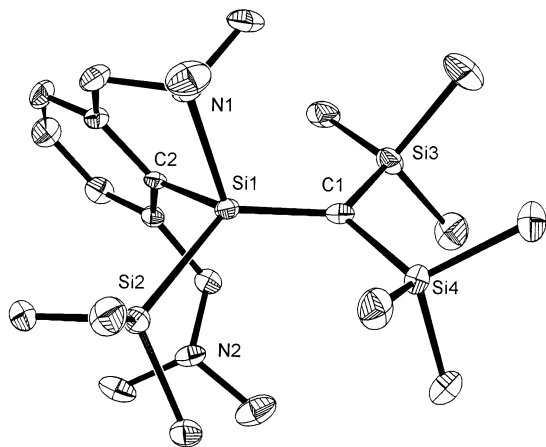


Fig. 1. Molecular structure of **9** in the crystal (ORTEP, 30% probability, H atoms omitted for clarity). Selected bond lengths (Å): Si1–C1, 1.759(3); Si1–Si2, 2.4024(13); Si1–N1, 2.035(3); Si1–N2, 3.441(3); Si1–C2, 1.892(4); C1–Si3, 1.839(3); C1–Si4, 1.837(4). Selected bond angles (°): C2–Si1–Si2, 101.43(10); C1–Si1–C2, 122.0(2); C1–Si1–Si2, 125.06(12); Si1–C1–Si3, 123.7(2); Si1–C1–Si4, 121.3(2); Si3–C1–Si4, 114.9(2); N1–Si1–C2 84.83(15).

Table 1

Selected structural data of the silenes **1**, **2** and **9** and of the acyclic amine silene adduct $\text{Me}_2\text{EtN} \cdot \text{Me}_2\text{Si}=\text{C}(\text{SiMe}_2\text{Ph})_2$ [2c]. Atomic numbering analogously **9**

Compound	Distance (Å)		Sum of angles (°)	
	Si=C	Si1–N1	Si1	C1
1	1.751(3)	2.069(2)	345.5	358.9
2	1.749(3)	2.004(2)	343.6	359.3
9	1.759(3)	2.035(3)	348.5	359.9
$\text{Me}_2\text{EtN} \cdot \text{Me}_2\text{Si}=\text{C}(\text{SiMe}_2\text{Ph})_2$	1.761(4)	1.988(4)	341.8	359.2

(1.741 Å, $\text{Ad}' = 2\text{-adamantylidene}$) [13] are longer and almost the same as that of **9**, but these elongations were found to be due to electronic effects of the substituents [13,14].

Whereas the results of the X-ray analysis of **9** unambiguously proved that only one dimethylamino group of the ligand is coordinated to the silene silicon atom, solution NMR spectra at room temperature in benzene- d_6 showed only one signal for two apparently equivalent dimethylaminomethyl substituents. But, interestingly, dynamic ^1H -NMR studies of **9** in $\text{THF}-d_8$ revealed that at ca. 233 K the NCH_3 signal is split into two peaks, one of which additionally splits into two signals. Thus, the results of the low-temperature ^1H -NMR spectra of **9** are in best agreement with the picture given by the X-ray analysis, indicating that, in solution also, the silene silicon atom is tetra-coordinated through $\text{N} \rightarrow \text{Si}$ interaction with one dimethylamino group, but at elevated temperatures rapid exchange processes lead to a magnetic equivalence of the two Me_2N substituents.

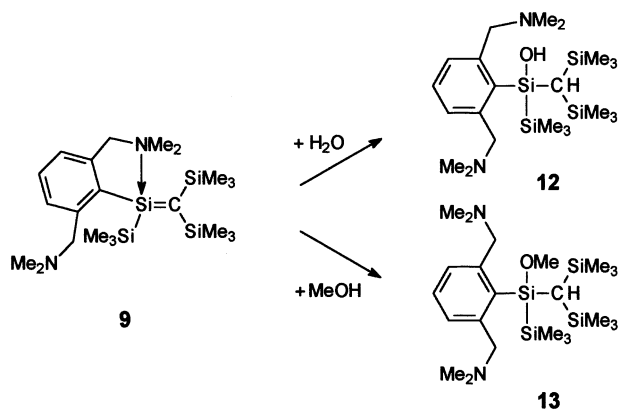
For a chemical characterization of **9**, we studied the behavior of the compound towards water and methanol. In a manner typical for reactive silenes [15], water is added to the polar $\text{Si}=\text{C}$ bond of **8** to afford the silanol **12**. Similarly, **9** is converted by methanol to give the methoxysilane **13** (Scheme 2). A broad OH-absorption band in the IR spectrum of **12** and the nonequivalence of the two dimethylamino groups and broadening of one of these signals in the ^1H -NMR spectrum point to strong hydrogen bonding between the silanol-OH group and a dimethylamino group. The results of detailed studies of the reactivity of **9** and related intramolecularly donor-stabilized silenes, which exhibit a pronounced ylide-like behavior, will be described elsewhere.

3. Experimental

All reactions involving organometallic reagents were carried out under purified argon. NMR: Bruker AC 250 or Bruker ARX 300, tetramethylsilane as internal standard. IR: Nicolet 205 FT-IR. MS: Intectra AMD 402 (EI with 70 eV). (Dichloromethyl)tris(trimethylsilyl)silane (**3**) [8] and 2,6-bis(dimethylaminomethyl)phenyllithium [16] were prepared as reported in the literature.

3.1. 1-[2,6-Bis(dimethylaminomethyl)phenyl]-1,2,2-tris(trimethylsilyl)silene (**9**)

At 0°C, 2.1 g (6.3 mmol) of **3** were added to an ethereal solution (150 ml) of 2.5 g (12.6 mmol) of 2,6-bis(dimethylaminomethyl)phenyllithium [16]. After gradual warming up to room temperature and stirring overnight, the solvent was removed in vacuo. Pentane



Scheme 2. Reaction of the silene **9** with water and methanol affording the silanol **12** and the methoxysilane **13**, respectively.

(1.702 Å) [11], is in good agreement with this observation. The $\text{Si}=\text{C}$ distances reported for the kinetically stabilized silenes $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{Ad}$ (1.764 Å, $\text{Ad} = 1\text{-adamantyl}$) [12] and $(\text{Me}_3\text{Si})(^t\text{BuMe}_2\text{Si})=\text{Ad}'$

was added and LiCl separated by filtration. The residue obtained by evaporation of the solution was recrystallized from pentane to give pale yellow prisms. Yield 1.6 g (57%), m.p. 81–82°C. $^1\text{H-NMR}$ (benzene- d_6): δ = 0.15, 0.27 and 0.57 (3s, SiCH_3 , $3 \times 9\text{H}$), 2.12 (s, NCH_3 , 12H), 3.19 (d, 2J = 14 Hz, CH_2 , 2H), 3.66 (d, 2J = 14 Hz, CH_2 , 2H), 6.95–7.30 (m, aryl-CH, 3H). $^{13}\text{C-NMR}$ (benzene- d_6): δ = 3.0, 7.2 and 8.3 (SiCH_3), 17.5 ($\text{Si}=\text{C}$), 45.7 (NCH_3), 64.1 (CH_2), 125.7, 127.8, 128.0 and 142.6 (arom. C). $^{29}\text{Si-NMR}$ (benzene- d_6): δ = –19.6 (SiSiMe_3), –8.3 (br, CSiMe_3), 29.5 ($\text{Si}=\text{C}$): (THF- d_8): δ = –19.4 (SiSiMe_3), –8.75 (CSiMe_3), –8.68 (CSiMe_3), 28.3 ($\text{Si}=\text{C}$). MS m/z (%): 452 (16) [$\text{M}^+ + 2\text{H}$], 451 (6) [$\text{M}^+ + \text{H}$], 408 (89) [$\text{M}^+ + 2\text{H} - \text{NMe}_2$], 395 (100) [$\text{M}^+ + 2\text{H} - \text{CH}_2\text{NMe}_2$]. Anal. Found: C, 58.83; H, 10.29; N, 6.51. Calc. for $\text{C}_{22}\text{H}_{46}\text{N}_2\text{Si}_4$ (450.96): C, 58.60; H, 10.28; N, 6.21%.

3.2. [2,6-Bis(dimethylaminomethyl)phenyl]-(trimethylsilyl)-[bis(trimethylsilyl)methyl]silanol (**12**)

Excess water was added to an ethereal solution of 1.0 g (2.2 mmol) of **9**. After stirring for 1 h, the organic phase was separated, dried with Na_2SO_4 and evaporated. Kugelrohr-distillation of the residue (110°C, 2×10^{-2} mbar) afforded a colorless oil, yield 0.7 g (67%). IR (cap.): $\tilde{\nu}$ = 3350–3440 cm^{-1} (br, OH_{ass}). $^1\text{H-NMR}$ (benzene- d_6): δ = 0.19, 0.23 and 0.49 (3s, SiCH_3 , $3 \times 9\text{H}$), 0.42 (s, CH, 1H), 1.93 and 2.14 (2s, NCH_3 , $2 \times 6\text{H}$), 3.16 and 3.77 (2 br s, CH_2 , $2 \times 2\text{H}$), 6.75–7.54 (m, aryl-CH). $^{13}\text{C-NMR}$ (benzene- d_6): δ = 1.4, 3.8 and 4.3 (SiCH_3), 7.1 (CH), 44.4 and 45.4 (NCH_3), 64.4 and 66.7 (CH_2), 128.9, 129.7, 130.1 and 145.1 (arom. C). $^{29}\text{Si-NMR}$ (benzene- d_6): δ = –19.4 (SiSiMe_3), –0.2 and 1.9 (CSiMe_3), 3.2 (SiOH). MS m/z (%): 467 (7) [$\text{M}^+ - \text{H}$], 423 (100) [$\text{M}^+ - \text{HNMe}_2$], 408 (100) [$\text{M}^+ - \text{CH}_2\text{NMe}_2$]. Anal. Found: C, 56.10; H, 10.06; N, 5.67. Calc. for $\text{C}_{22}\text{H}_{48}\text{N}_2\text{OSi}_4$ (468.98): C, 56.34; H, 10.32; N, 5.97%.

3.3. [2,6-Bis(dimethylaminomethyl)phenyl]-methoxy-(trimethylsilyl)-[bis(trimethylsilyl)methyl]silane (**13**)

Excess methanol (50 ml) was added to the ethereal solution of 0.17 g (0.37 mmol) of **9** and the solution was refluxed for 1 h. After evaporation the residue was recrystallized from methanol. Colorless crystals, m.p. 89°C, yield 0.15 g (84%). IR (nujol): $\tilde{\nu}$ = 1113 cm^{-1} (SiOCH_3). $^1\text{H-NMR}$ (benzene- d_6): δ = 0.14, 0.20 and 0.37 (3s, SiCH_3 , $3 \times 9\text{H}$), 1.22 (s, CH, 1H), 2.18 (br s, NCH_3 , 12H), 3.32–3.81 (m, CH_2 , 4H), 3.53 (s, OCH_3 , 3H), 7.22–7.50 (m, aryl-CH, 3H). $^{13}\text{C-NMR}$ (benzene- d_6): δ = 1.1, 3.2 and 3.7 (SiCH_3), 8.3 (CH), 45.3 (NCH_3), 52.0 (OCH_3), 64.1 (CH_2), 128.1, 128.2, 129.0 and 141.0 (arom. C). $^{29}\text{Si-NMR}$ (benzene- d_6): δ = –21.3 (SiSiMe_3), –0.8 and 2.5 (CSiMe_3), 10.2

(SiOMe). MS (CI, isobutane) m/z (%): 482 (6) [M^+], 467 (23) [$\text{M}^+ - \text{CH}_3$], 451 (51) [$\text{M}^+ - \text{OCH}_3$], 409 (100) [$\text{M}^+ - \text{SiMe}_3$]. Anal. Found: C, 56.91; H, 10.31; N, 6.07. Calc. for $\text{C}_{23}\text{H}_{50}\text{N}_2\text{OSi}_4$ (483.00): C, 57.19; H, 10.43; N, 5.80%.

3.4. Crystal-structure determination of **9**

X-ray diffraction data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo- K_α radiation. Crystals from pentane, crystal size $0.4 \times 0.2 \times 0.2 \text{ mm}^3$, formula $\text{C}_{22}\text{H}_{46}\text{N}_2\text{Si}_4$, formula weight 450.97, orthorhombic, space group $Pbcn$, a = 17.597(4), b = 20.506(4), c = 15.432(3) Å; V = 5568(2) Å³; Z = 8; temperature 200(2) K, μ = 0.224 mm^{-1} , $F(000)$ = 1984, θ range 1.99–24.19°; index ranges $-20 \leq h \leq 20$, $0 \leq k \leq 14$, $-17 \leq l \leq 17$; d_{calcd} = 1.076 g cm^{-3} , peak/hole 0.28/–0.22 e Å^{–3}, measured reflections 12 322, independent reflections 3504, observed reflections 2012, R_{int} = 0.060, no. of parameters 253, R_1 [$I > 2\sigma(I)$] 0.042, wR_2 (all data) 0.090. 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.

4. Supplementary material

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-145939. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (UK) (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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