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Intramolecularly donor-stabilized silenes: Part 6. The synthesis of 1-[2,6-bis(dimethylaminomethyl)phenyl]silenes and their reaction with aromatic aldehydes ☆

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Abstract

The intramolecularly donor-stabilized silenes $ArR^1Si{=}C(SiMe_3)_2$ (**3a**–**d**) (**3a**: $R^1 = Me$; **3b**: $R^1 = t\text{-Bu}$; **3c**: $R^1 = Ph$; **3d**: $R^1 = SiMe_3$; $Ar = 2,6\text{-}(Me_2NCH_2)_2C_6H_3$) were prepared by treatment of the (dichloromethyl)oligosilanes $(Me_3Si)_2R^1Si\text{–}CHCl_2$ (**1a**–**d**), with 2,6-bis(dimethylaminomethyl)phenyllithium (molar ratio 1:2). For **3c** and **3d**, X-ray structural analyses were performed indicating that only one dimethylamino group of the tridentate ligand is coordinated to the electrophilic silene silicon atoms, i.e., the central silicon atoms are tetracoordinated. The $N \rightarrow Si$ donation leads to pyramidalization at the silene silicon atoms; the configuration at the silene carbon atoms is planar. For a chemical characterization **3a** and **3c** were treated with water to give the silanols $ArR^1Si(OH)\text{–}CH(SiMe_3)_2$ (**5a,c**). Studies of the reactions of **3a** and **3c** with benzaldehyde, 4-chlorobenzaldehyde or 4-methoxybenzaldehyde, respectively, revealed an unexpected reaction path leading to the substituted 2-oxa-1-sila-1,2,3,4-tetrahydronaphthalenes **12a**, **12c**, **13** and **14**. Both **12a** and **12c** were structurally characterized by X-ray analyses. The formation of these six-membered cyclic compounds, which is discussed in detail, gives support to a dipolar mechanism for the general reaction of silenes with carbonyl derivatives.
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1. Introduction

Intramolecular amine coordination proved to be an effective tool in stabilizing derivatives of three-coordinate silicon, such as silanthiones [2], silanimines [3], silaphosphenes [3] as well as silylium ions [4]. In this context, the tridentate 2,6-bis(dimethylaminomethyl)-phenyl ligand is of particular interest, since one or both amino groups may coordinate to the electrophilic silicon atom. Recently, we were able to describe the synthesis of the isolable intramolecularly donor-stabilized 1-[2,6-bis(dimethylaminomethyl)phenyl]-1,2,2-tris(trimethylsi-

lyl)silene (**3d**) [5]. The compound is obtained in a multi-step but simple one-pot reaction by treatment of (dichloromethyl)tris(trimethylsilyl)silane (**1d**) with 2,6-bis(dimethylaminomethyl)phenyllithium (molar ratio 1:2). The reaction path leading to **3d**, which similarly applies to a series of further intramolecularly donor-stabilized silenes bearing other dialkylaminoaryl substituents, was discussed in detail [6] and is outlined in an abbreviated form in Scheme 1. NMR studies as well as the X-ray structural analysis of **3d** revealed a strong intramolecular coordination, but only one dimethylamino group of the ligand is coordinated to the silene Si atom of **3d**, i.e., the silene silicon atom is tetracoordinated in solution as well as in the solid state.

In the case of silyl cations, substituted and stabilized by the 2,6-bis(dimethylaminomethyl)phenyl ligand,
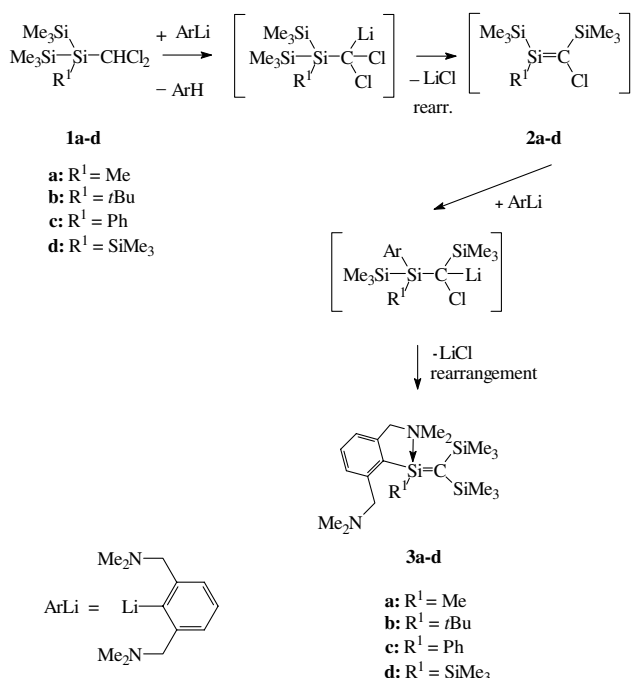
Scheme 1. The reaction of the (dichloromethyl)oligosilanes (**1a–d**) with 2,6-bis(dimethylaminomethyl)phenyllithium (1:2) producing the intramolecularly donor-stabilized silenes **3a–d**.

pentacoordination at the central silicon atom was observed. Thus, silyl cations bearing at least one Si–H bond are siliconium ions with chelation of both dimethylamino groups to the silicon atom. But generally, the number of dimethylamino groups coordinated to the silicon atom is varying depending on substituents, the counterion and the solvent [4b].

In the present paper, we pursue the question, whether a change in the substitution pattern of silene **3d**, e.g., the replacement of the 1-trimethylsilyl group by a more electronegative carbon substituent, may increase the coordination number at the silene silicon atom. For that purpose, we synthesized some new silenes bearing the 2,6-bis(dimethylaminomethyl)phenyl group (**3a–c**) using the established method mentioned above. Furthermore, we studied the behavior of these Si=C-systems towards aromatic aldehydes and describe an unexpected reaction path leading to products whose structures shed some light on the mechanism of the general reaction of silenes with carbonyl compounds.

2. Results and discussion

2.1. Synthesis and structure of the 1-[bis(dimethylaminomethyl)phenyl]silenes 3a–d

The (dichloromethyl)oligosilanes $(Me_3Si)_2R^1Si–CHCl_2$ (**1a–d**) (**a**: $R^1 = Me$; **b**: $R^1 = t$-Bu; **c**: $R^1 = Ph$; **d**: $R^1 = Me_3Si$) react with 2,6-bis(dimethylaminomethyl)phenyl

phenyllithium (molar ratio 1:2) to give the stable silenes **3a–d** (Scheme 1). As discussed previously [5], the reaction proceeds through a deprotonation of the dichloromethyl group of **1a–d**, lithium chloride elimination and trimethylsilyl migration producing the transient silenes **2a–d**. Addition of a second molar equivalent of 2,6-bis(dimethylaminomethyl)phenyllithium across the polar Si=C bond of **2a–d**, repeated loss of LiCl and a further Si–C shift of a Me₃Si group, affords the silenes **3a–d**. Using the same method, treatment of **1d** with 2,6-bis(diethylaminomethyl)phenyllithium gave **4**, the diethylaminomethyl analogue of **3d**. Complexes **3a,c,d** and **4** were isolated as pale yellow crystalline solids (yields between 49% and 78%). Complex **3b** was obtained only in an impure oily form, but could be identified by characteristic NMR data.

For **3c** and **4** X-ray structural analyses were performed, which unambiguously confirm the proposed structures. The results of the structural elucidation of **3d** were reported previously [5]. The structural data obtained reveal, that in all compounds investigated only one dimethylamino group (in **4** one diethylamino group) is coordinated to the silene silicon atom. This is clearly to be seen in Fig. 1, which exemplarily shows the results of the X-ray analysis of **3c**.

Some characteristic bond parameters are summarized in Table 1. The data obtained for the new compounds **3c** and **4** largely agree with those already reported for **3d** [5]
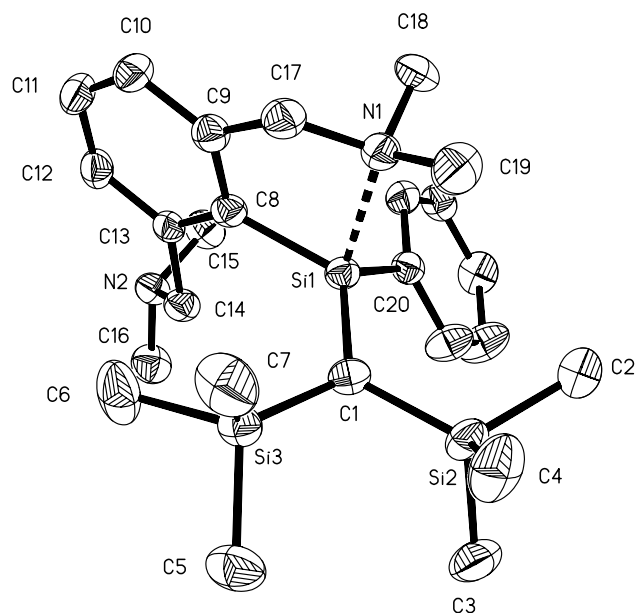
Fig. 1. Molecular structure of **3c** in the crystal (ORTEP, 30% probability level, H atoms omitted for clarity; see also Table 2 for additional crystallographic information). Selected bond lengths (Å): Si(1)–C1 1.744(2), Si1–C8 1.888(2), Si1–C20 1.891(2), Si1–N1 2.043(2), Si1–N2 4.709; C1–Si2 1.840(2), C1–Si3 1.838(2). Selected bond angles (°): C1–Si1–C8 122.01(10), C1–Si1–C20 120.14(10), C8–Si1–C20 106.70(10), Si1–C1–Si2 123.04(13), Si1–C1–Si3 121.47(12), Si2–C1–Si3 114.87(11).

Table 1
Selected structural data of the silenes **3c**, **3d** and **4** and, for comparison, of the acyclic silene amine adduct $Me_2EtN \cdot Me_2Si=C(SiMe_2Ph)_2$ [7]

Compound	Distances (Å)		Sum of angles (°)	
	Si=C	Si1–N1	Si1	C1
3c	1.744(2)	2.043(2)	348.9	359.4
3d [5]	1.759(3)	2.035(3)	348.5	359.9
4	1.764(2)	2.077(2)	345.7	359.5
$Me_2EtN \cdot Me_2Si=C(SiMe_2Ph)_2$ [7]	1.761(4)	1.988(4)	341.8	359.2

Atomic numbering analogously **3c**.

and are similarly consistent with those reported by Wiberg et al. [7] for the acyclic silene amine adduct $Me_2Et-N \cdot Me_2Si=C(SiMe_2Ph)_2$. For all compounds Si1–N1 distances of approximately 2.04 Å were found. These figures appear to be typical for amine-coordinated silenes. The distances between the silene silicon atoms and the nitrogen atoms of the second dimethylamino group are considerably longer (for **3c** 4.709 Å). The donation of the nitrogen lone pair to the silene silicon atom leads to pyramidalizations at the Si1 atoms. In contrast, the configuration at the silene carbon atoms is trigonal planar. The similarities also apply to the Si1–C1 distances. Si=C bond lengths of approximately 1.75 Å prove to be standard values for amine coordinated silenes (see also [6b]). A comparison of these structural data with those of kinetically stabilized uncomplexed silenes was discussed previously [6b].

Tetracoordination of the silene silicon atoms was proved for **3a–d** also in solution. Whereas the ^{1}H NMR spectra of **3a–d** at room temperature show only one signal for both NMe_2 groups, at low temperatures two signals for the dimethylamino groups appear and, additionally, one of the NMe_2 signals is split into two peaks (for **3d** in THF-d_8 the coalescence temperature was found to be 233 K). Thus, the signal pattern of the low temperature ^{1}H NMR spectra agrees with the solid-state structure. At room temperature rapid exchange processes lead to the magnetic equivalence of the two dimethylamino groups.

Summarizing the results of the structural investigations, we have to conclude that independent of the second substituent at the silene silicon atoms in **3a–d** and **4**, respectively, only one dialkylamino group is coordinated to the electrophilic Si1 atoms, i.e., in the solid state as well as in solution the silene silicon atoms are always tetracoordinated.

2.2. Reactivity of the intramolecularly donor-stabilized silenes 3a–d

Compared with uncomplexed silenes, the reactivity of **3a–d** or **4**, respectively, is reduced dramatically. Rapid dimerization is a typical behavior of reactive Si=C systems [8], but even after prolonged heating, no dimers of the newly synthesized silenes could be detected; **3a–d**

and **4** were recovered unchanged. Similar results were obtained after treatment of the stable silenes with 2,3-dimethyl-1,3-butadien. The reaction, which in case of uncomplexed silenes through a [2 + 4] cycloaddition step normally leads to silacyclohexenes, is frequently used for the chemical characterization of silenes [8]. But in this particular case no reaction occurred.

The addition of water across the Si=C double bond to give silanols is considered to be a typical reaction of silenes [8]. Actually, the reaction of **3a** and **3c** with excess water produced the expected silanols ArR^1-$Si(OH)CH(SiMe_3)_2$ (**5a,c**) (**5a**: R^1 = Me; **5c**: R^1 = Ph; Ar = 2,6-$(Me_2NCH_2)_2C_6H_3$). The silene **3a** proved to be extraordinarily moisture sensitive and is converted by traces of water into the disiloxane $[(Me_3Si)_2CH]$-$ArMeSi–O–SiMeAr[CH(SiMe_3)_2]$ (**6a**) (Ar = 2,6(Me_2-$NCH_2)_2C_6H_3$). Addition of water to the silene **4** gave the silanol $[2,6-(Et_2NCH_2)_2C_6H_3][(Me_3Si)][(Me_3Si)_2CH]$-SiOH (**7**). In these reactions, the behavior of **3a–c** and **4** is in full agreement with the previously described properties of **3d** [5]. For **5c** and **6a** also X-ray structural analyses were performed. Details of the synthesis and structure of **5–7** are given below (see Section 3).

Particularly, high hopes we had of studies on the interaction of the newly synthesized silenes with carbonyl compounds. Normally, silenes react with aldehydes and ketones in a formal [2 + 2] cycloaddition step to give 1,2-oxasiletanes [8]. Only in a few cases these four-membered ring systems can be isolated [6a,9]. Usually, they undergo spontaneous cycloreversions into an olefin and a transient silanone, which rapidly forms oligomeric products.

As already verified for other derivatives of three-coordinate silicon, also silanones are expected to be stabilized by amine coordination to the electrophilic silanone silicon atom. While intramolecularly donor-stabilized silanethiones could be isolated and proved to be stable [2], comparable Si=O systems are unknown. Expectations on the stabilization of silanones by intramolecular amine coordination must not be exaggerated. Belzner et al. [2b] succeeded in the generation of the silanone $Ar_2Si=O$ (Ar = 2-dimethylaminomethylphenyl) by the reaction of the silylene Ar_2Si: with isocyanates, but the compound proved to be labile and the product isolated he identified as the respective cyclotrisiloxane $(Ar_2SiO)_3$, the silanone trimer. Silanones bearing a

2,6-bis(dialkylaminomethyl)phenyl substituents might be interesting model compounds, and additional kinetic stabilization by suitable bulky substituents may finally lead to stable silanones. In this context the reaction of **3a**–**d** and **4** or any related silene with aldehydes or ketones might be a promising route to intramoleculaly donor-stabilized silanones.

Unfortunately, the reactivity of the silenes **3a**–**d** and **4** towards carbonyl compounds is very low. This, obviously, is due to the strong N → Si coordination. Complexes **3a**, **3c** and **3d** were chosen for studies of their reaction with benzaldehyde. The components were dissolved in heptane and the solutions were heated for three days at 80 °C. Aqueous workup of the heptane solutions and chromatographic separation of the reaction mixtures always gave the olefin **9** in yields of 33–69%. Its analytical data proved to be identical with those described for 2,2-bis(trimethylsilyl)styrene in the literature [10]. The silanone oligomers **8a**, **8c** and **8d**, respectively, were not isolated as pure compounds, but NMR and IR studies of the chromatographically separated product mixtures strongly refer to the proposed structures. In most cases varying quantities of the respective silanols **5a,c,d** were isolated, indicating that considerable quantities of the starting silenes remained unchanged. Both **8a,c,d** and **9** are the expected products of the reaction of the silenes **3a**, **3c** and **3d** with benzaldehyde (Scheme 2).

In case of the reaction of **3a** and **3c**, respectively, with benzaldehyde, besides **8a**, **8c** and **9** two unexpected products were isolated, to which we assign the structures of the 2-oxa-1-sila-1,2,3,4-tetrahydronaphthalenes (**12a** and **12c**). Whereas **12a** was isolated as a pure diastereo-

mer, **12c** could be separated into the two stereoisomers *trans,cis*-**12c** and *cis,trans*-**12c**, which differ in the relative configurations of the 4-dimethylamino groups and the 3-phenyl groups with reference to the substituents at the ring silicon atoms. All three isolated species are colorless solids, whose structures were elucidated on the basis of NMR and MS studies and, in particular, by X-ray structural analyses. Fig. 2 shows the results of the X-ray analysis of *trans,cis*-**12c**, the outcome of the X-ray analysis of *cis,trans*-**12c** is demonstrated in Fig. 3. Complex **12a** may similarly be described as the *trans,cis*-derivative, however, there are two symmetry independent molecules in the asymmetric unit, hence the number of molecules within the triclinic unit cell is 4. The six membered rings are slightly folded (torsional angles O1–Si1–C8–C9: **12a** 13.34(19)° and −6.7(2)° for the corresponding atoms O31–Si31–C38–C39 in the second molecule; *trans,cis*-**12c** 10.1(3)°, *cis,trans*-**12c** 26.98(12)°; C8–C9–C17–C20: **12a** 17.5(3)° and 24.5(3)° for the corresponding atoms C38–C39–C47–C50 in the second molecule, *trans,cis*-**12c** 28.9(5)°, *cis,trans*-**12c** −55.32(15)°; atomic numbering for **12a** analogously **12c**). In all structures the obtained bond lengths and angles are in agreement with standard values. The reaction of **3d** with benzaldehyde gave **8d** and **9** exclusively.

Our proposal on the reaction path to **12a,c** is summarized in Scheme 3. Obviously, the aldehyde attacks the silene system of **3a,c** with the nucleophilic carbonyl oxygen atom at the silene silicon atom to form the zwitterionic structures **15a,c**. Ring closure to **16a,c** is the expected way of stabilization of **15a,c**, and the oxasiletane systems formed undergo spontaneous cycloreversions leading finally to the olefin **9** and the silanone

9 (R² = H)
10 (R² = Cl)
11 (R² = OCH₃)

3a,c,d

8a,c,d

12a (R¹ = Me; R² = H)

12c (R¹ = Ph; R² = H)

13 (R¹ = Ph; R² = Cl)

14 (R¹ = Ph; R² = OCH₃)

Scheme 2. The reaction of the intramolecularly donor-stabilized silenes **3a** and **3c**, respectively, with benzaldehyde.
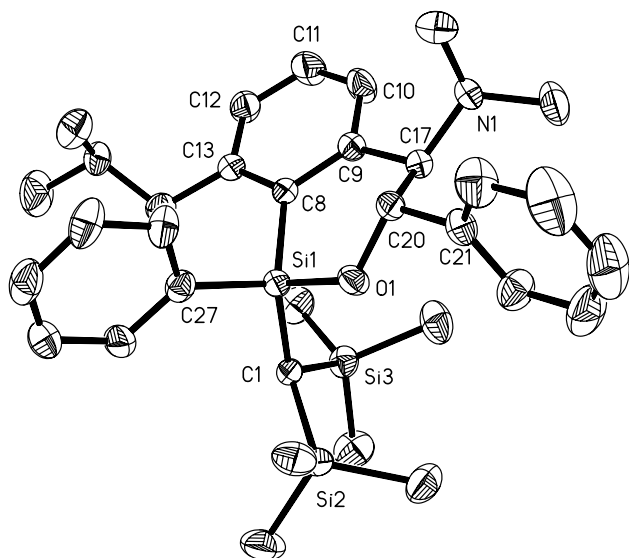
Fig. 2. Molecular structure of *trans,cis*-**12c** in the crystal (ORTEP, 30% probability level, H atoms omitted for clarity; see also Table 2 for additional crystallographic information). Selected bond lengths (Å): Si1–C1 1.874(4), Si1–C27 1.887(4), Si1–O1 1.654(3), C8–C9 1.418(5), C9–C17 1.556(5), C17–C20 1.541(5), C20–O1 1.440(4). Selected bond angles (°): O1–Si1–C8 102.65(15), O1–C20–C17 108.7(3), C9–C17–C20 112.2(3), C20–O1–Si1 123.4(2).
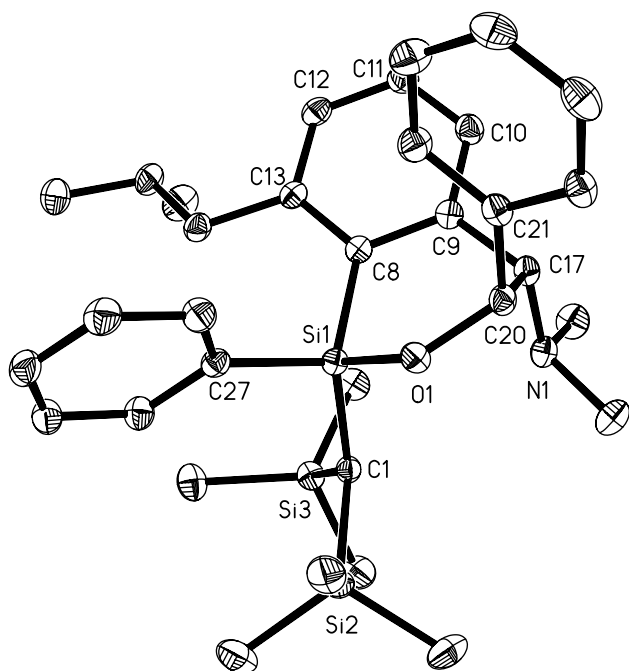

Fig. 3. Molecular structure of *cis,trans*-**12c** in the crystal (ORTEP, 30% probability level, H atoms omitted for clarity; see also Table 2 for additional crystallographic information). Selected bond lengths (Å): Si1–C1 1.8686(15), Si1–C8 1.8983(15), Si1–C27 1.8811(15), Si1-O1 1.6594(10), C8–C9 1.417(2), C9–C17 1.517(2), C17–C20 1.540(2), C20–O1 1.4282(17). Selected bond angles (°): O1–Si1–C8 101.27(6), O1–C20–C17 111.23(12), C9–C17–C20 110.35(12), C20–O1–Si1 127.45(9).

oligomers **8a,c** (Way A). But in a competing reaction one proton is abstracted intramolecularly from the benzylic methylen group by the tris(silyl)carbanionic centres of **15a,c** to produce the new zwitterions **17a,c**, which stabilize under ring closure to give **12a,c** (Way B).

The proposed mechanism is supported by studies of the reaction of **3c** with benzaldehyde in different solvents. Increasing polarity of the solvent should enhance the stability of the zwitterion **15c**, facilitating the proton transfer **15c** → **17c**, thus favoring Way B and the formation of **12c**. Actually, the results of the reactions of **3c** with benzaldehyde in heptane, toluene and THF, respectively, indicate that with increasing polarity of the solvent used the yield of **12c** (i.e., the mixture of the isomers) increases on the expense of the olefin **9** [yields in heptane: **9** 33%, **12c** 24%; in toluene: **9** 12%, **12c** 49% (mixture of isomers); in THF: **9** 4%, **12c** 52% (mixture of isomers)]. After the reaction of **3d** with benzaldehyde neither in heptane nor in THF the expected six-membered system **12d** could be found, i.e., the reaction proceeds along Way A exclusively. Probably, due to the extraordinary steric congestion at the central silicon atom in **15d** (R = SiMe$_3$) and a restricted rotation around the Si–CSi$_2$ bond a suitable conformation necessary for the proton transfer is excluded.

Moderately stable "silenes of the Brook type" [8b] react with aromatic aldehydes to give mixtures of diastereomeric oxasiletanes [9]. Concerning the reaction path, three alternative ways were taken into consideration: a concerted one-step [2 + 2] addition or two-step processes involving either a diradical intermediate or a dipolar intermediate both resulting from primary interactions of the carbonyl oxygen atom with the silene silicon atom. The radical mechanism could widely be excluded, and Brook et al. [9] favor a dipolar mechanism with intermediates structurally comparable with **15a,c,d**, but were unable to present any trapping products. The formation of the intermediates **17a,c** by an irreversible proton transfer from **15a,c**, identified by the isolation of **12a,c**, may be considered as an indication of a dipolar intermediate in the course of the reaction of **3a,c,d** with benzaldehyde. Despite a considerable weakening of the electrophilic properties of the central silicon atoms due to the intramolecular amine coordination in **3a,c,d**, the primary attack of the aldehyde with its nucleophilic oxygen atom is directed towards the silene silicon atoms. Thus, the reasonable interpretation of the formation of **12a,c** strongly supports a dipolar mechanism for the reaction of silenes with carbonyl compounds, as proposed by Brook et al. [9].

In view of the ylidic character of intramolecularly amine coordinated silenes and the proved pronounced nucleophilic properties of their silene carbon atoms [6c], one may also assume the reaction of **3a,c,d** with benzaldehyde to proceed through an initial attack of the silene carbon atom at the carbonyl carbon atom,
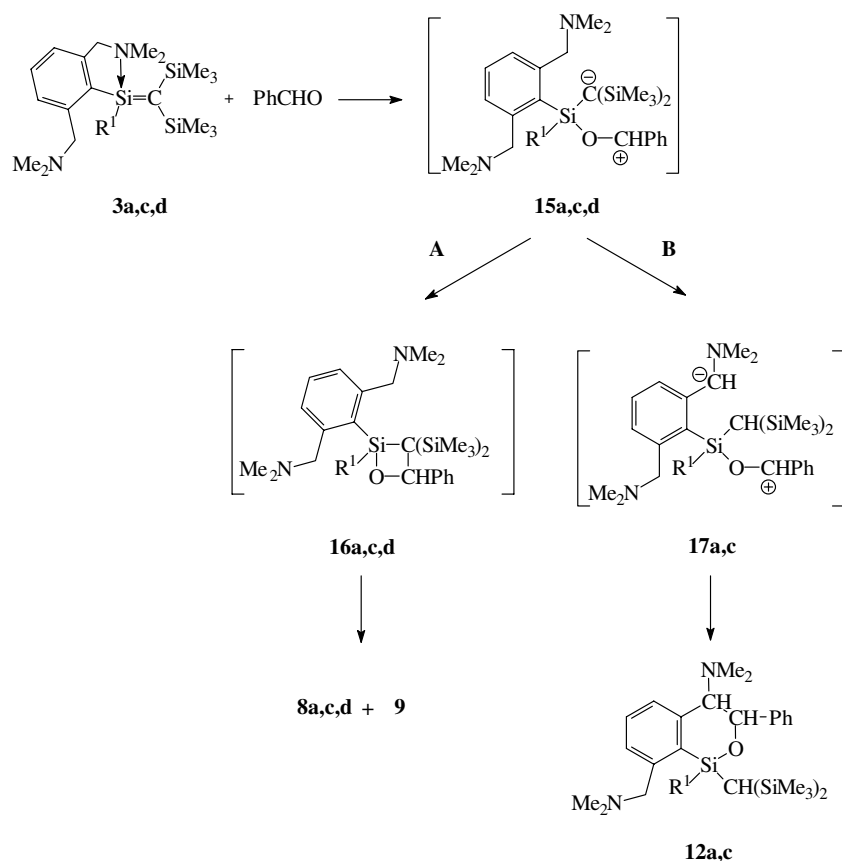
Scheme 3. Proposed reaction path of the formation of the 2-oxa-1-sila-1,2,3,4-tetrahydronaphthalenes (**10a** and **10c**) by the interaction of the silenes **3a** and **3c**, respectively, with benzaldehyde.

and **8a,c,d** and **9** might be produced through the intermediate oxasiletanes **16a,c,d** along a Peterson-type mechanism. Under these circumstances no **12a,c** can be formed, i.e., **8a,c,d** and **9** on the one hand and **12a,c** on the other are products of different reaction paths. But this idea could easily be excluded by studies of the reaction of **3c** with 4-chlorobenzaldehyde or 4-methoxybenzaldehyde, respectively. Whereas the conversion of the intermediate zwitterions of the type **15** (Way A or B) should not be significantly influenced by the nature of the carbonyl compound used, 4-chlorobenzaldehyde should favor a Peterson-type mechanism, 4-methoxybenzaldehyde should favor the mechanism described in Fig. 3. Actually, the reaction of **3c** with 4-chlorobenzaldehyde in heptane produced 32% of the 2-oxa-1-silatetrahydronaphthalene **13** besides 9% of the olefin **10**. Under the same conditions, complex **3c** was converted with 4-methoxybenzaldehyde to give 19% of **14** and 46% of **11** (Scheme 2). Both **13** and **14** proved to be pure diastereomers and X-ray structural analyses, performed for the two compounds, justify a description as *c*-3-(4-chlorophenyl)-*t*-4-dimethylamino-8-(dimethylaminomethyl)-1-phenyl-*r*-1-[bis(trimethylsilyl)methyl]-2-oxa-1-sila-1,2,3,4-tetrahydronaphthalene (**13**) and *c*-3-(4-methoxyphenyl)-*t*-4-dimethylamino-8-

(dimethylaminomethyl)-1-phenyl-*r*-1-[bis(trimethylsilyl)methyl]-2-oxa-1-sila-1,2,3,4-tetrahydronaphthalene (**14**), respectively. The results of these experiments unambiguously exclude a significant role of a Peterson-type mechanism and support the proposed pathway described in Scheme 3.

As the outcome of the reaction of **3d** with 4-chlorobenzaldehyde and 4-methoxybenzaldehyde, respectively, the olefins **10** and **11** were isolated besides considerable quantities of the silanol $ArR^1Si(OH)CH(SiMe_3)_2$ (**5d**) ($R^1 = Me_3Si$, $Ar = 2,6(Me_2NCH_2)_2C_6H_3$). Again, the formation of the respective 2-oxa-1-sila-tetrahydronaphthalene systems did not occur.

3. Experimental

All reactions involving organometallic reagents were carried out under purified argon. NMR: Bruker AC 250 or Bruker ARX 300, temperature 30 °C, tetramethylsilane as internal standard. IR: Nicolet 205 FT-IR. MS: Intectra AMD 402 (EI with 70 eV or chemical ionization with isobutane). (Dichloromethyl)methylbis(trimethylsilyl)silane (**1a**) [6a], *tert* butyl(dichloromethyl)bis(trimethylsilyl)silane (**1b**) [11], (dichloromethyl)

phenylbis(trimethylsilyl)silane (**1c**) [6a], (dichloromethyl)tris(trimethylsilyl)silane (**1d**) [12] as well as 2,6-bis(dimethylaminomethyl)phenyllithium [13] were prepared as described in the literature. The synthesis of **3d** and **5d** previously [5]. All yields given refer to amounts obtained after chromatographic separation and purification or recrystallization.

3.1. General procedure for the synthesis of the silenes 3a–c and 4

At 0 °C, the respective (dichloromethyl)tris(trimethylsilyl)silane **1a**, **1b** or **1c**, respectively, was added to an ethereal suspension of 2,6-bis(dimethylaminomethyl)phenyllithium (in case of **4** to a solution of 2,6-bis(diethylaminomethyl)phenyllithium). The mixture was stirred for 48 h at room temperature, and after evaporation of the solution in vacuo pentane was added and the lithium chloride formed was separated by filtration. The residue obtained by evaporation of the filtrate was recrystallized from pentane.

3.1.1. 1-[2,6-Bis(dimethylaminomethyl)phenyl]-1-methyl-2,2-bis(trimethylsilyl)silene (3a)

1.00 g (3.65 mmol) of **1a** and 1.45 g (7.32 mmol) of 2,6-bis(dimethylaminomethyl)phenyllithium gave 0.77 g (78%) of **3a**. Colorless crystals, m.p. 190–194 °C. ^{1}H NMR (benzene-d_6): $\delta = -0.15$ and 0.18 (2s, Si(CH$_3$)$_3$, 2×9H), 0.13 (s, SiCH$_3$, 3H), 1.80 (s, NCH$_3$, 12H), 2.75 and 3.41 (2d, $^2J = 13.4$ Hz, CH$_2$, 2×2H), 6.77–6.93 (m, aryl-CH, 3H). ^{13}C NMR (benzene-d_6): $\delta = 1.7$ (SiCH$_3$), 6.8 and 8.0 (Si(CH$_3$)$_3$), 22.7 (Si=C), 45.9 (NCH$_3$), 64.2 (CH$_2$), 125.7, 127.7, 128.3, 129.7, 139.6 and 143.4 (arom. C). ^{29}Si NMR (benzene-d_6): $\delta = -10.6$ and -7.7 (SiMe$_3$), 30.3 (Si=C). MS (EI, m/z, %): 392 (100) [M$^+$], 377 [M$^+$ – CH$_3$]. Anal. Calc. for C$_{20}$H$_{40}$N$_2$Si$_3$ (392.80): C, 61.15; H, 10.26; N, 7.13. Found: C, 60.95; H, 10.52; N, 7.31%.

3.1.2. 1-tert-Butyl-1-[2,6-bis(dimethylaminomethyl)-phenyl]-2,2-bis(trimethylsilyl)silene (3b)

The compound could not be isolated in a pure form. Therefore, only the characteristic NMR data are given. ^{1}H NMR (benzene-d_6): $\delta = 0.14$ and 0.53 (2s, SiCH$_3$, 2×9H), 1.11 (s, CCH$_3$, 9H), 2.15 (s, NCH$_3$, 12H), 3.57 (pseudo-t, $^2J = 15.6$ Hz, CH$_2$, 4H), 6.88–7.42 (aryl-CH, 3H). ^{13}C NMR (benzene-d_6): $\delta = 7.1$ and 8.4 (SiCH$_3$), 26.8 (Si=C), 29.6 (CCH$_3$), 44.1 (NCH$_3$), 63.9 (CH$_2$), 124.2–147.5 (aryl-C). ^{29}Si NMR (benzene-d_6): $\delta = -10.6$ and -8.8 (SiMe$_3$), 39.0 (Si=C).

3.1.3. 1-[2,6-Bis(dimethylaminomethyl)phenyl]-1-phenyl-2,2-bis(trimethylsilyl)silene (3c)

2.09 g (6.22 mmol) of **1c** and 2.46 g (12.45 mmol) of 2,6-bis(dimethylaminomethyl)phenyllithium afforded 1.80 g (54%) of yellow crystals, m.p. 189–193 °C. ^{1}H

NMR (benzene-d_6): $\delta = 0.28$ and 0.62 (2s, Si(CH$_3$)$_3$, 2×9H), 1.99 (s, NCH$_3$, 12H), 3.13 and 3.66 (2d, $^2J = 14.0$ Hz, CH$_2$, 2×2H), 6.93–7.70 (m, aryl-CH, 8H). ^{13}C NMR (benzene-d_6): $\delta = 7.68$ and 9.1 (Si(CH$_3$)$_3$), 22.7 (Si=C), 46.4 (NCH$_3$), 64.2 (CH$_2$), 125.6, 127.1, 129.1, 130.0, 136.7, 137.0, 138.0 and 144.5 (arom. C). ^{29}Si NMR (benzene-d_6): $\delta = -9.6$ and -8.9 (SiMe$_3$), 23.9 (Si=C). MS (EI, m/z, %): 454 (44) [M$^+$], 439 (75) [M$^+$ – CH$_3$]. Anal. Calc. for C$_{25}$H$_{42}$N$_2$Si$_3$ (454.27): C, 66.01; H, 9.31; N, 6.16. Found: C, 65.82; H, 9.58; N, 6.17%.

3.1.4. 1-[2,6-Bis(diethylaminomethyl)phenyl]-1,2,2-tris(trimethylsilyl)silene (4)

Following the procedure described above, 0.65 g (1.97 mmol) of **1d** and 1.00 g (3.94 mmol) of 2,6-bis(diethylaminomethyl)phenyllithium gave 0.48 g (49%) of **4**. Pale yellow crystals, m.p. 74–78 °C. ^{1}H NMR (benzene-d_6): $\delta = 0.19, 0.28$ and 0.57 (3s, SiCH$_3$, 3×9H), 0.90 (t, $^3J = 7.2$ Hz, CCH$_3$, 12H), 2.58 (dq, $^2J = 13.0$ Hz, $^3J = 7.0$ Hz, CCH$_2$N, 4H), 2.79 (dq, $^2J = 13.1$ Hz, $^3J = 7.0$ Hz, CCH$_2$N, 4H), 3.64 (d, $^2J = 15.3$, ArCH$_2$, 2H), 3.73 (d, $^2J = 15.3$, ArCH$_2$, 2H), 7.23–7.24 (m, aryl-CH, 3H). ^{13}C NMR (benzene-d_6): $\delta = 3.1$ (SiSiCH$_3$), 7.1 and 8.1 (CSiCH$_3$), 10.5 (CCH$_3$), 21.7 (Si=C), 46.4 (CCH$_2$), 58.7 (ArCH$_2$N), 124.5, 129.6, 140.3 and 143.5 (arom. C). ^{29}Si NMR (benzene-d_6): $\delta = -20.0$ (Si*Si* Me$_3$), -8.35 and 8.40 (CSiMe$_3$), 36.7 (Si=C). MS (EI, m/z, %): 506 (3) [M$^+$], 477 (38) [M$^+$ – CH$_2$CH$_3$]. Anal. Calc. for C$_{26}$H$_{54}$N$_2$Si$_4$ (507.06): C, 61.59; H, 10.73; N, 5.52. Found: C, 61.65; H, 10.99; N, 5.62%.

3.2. General procedure for the reaction of 3a, 3c or 4 with water

Ethereal solutions of the respective silenes were added to excess water/THF mixtures (1:1). After stirring for half an hour the organic layer was separated and the aqueous phase extracted with ether. The collected and dried organic solutions were evaporated and the residues obtained were purified by recrystallization from heptane (**5c**) or by Kugelrohr-distillation (**5a** and **7**).

3.2.1. [2,6-Bis(dimethylaminomethyl)phenyl]-methyl-[bis(trimethylsilyl)methyl]-silanol (5a)

1.25 g (3.19 mmol) of the silene **3a** produced 0.88g (67%) of **5a**. Colorless oil. ^{1}H NMR (benzene-d_6): $\delta = 0.24$ and 0.47 (2s, SiCH$_3$, 2×9H), 0.31 (s, SiCH, 1H), 0.70 (s, OSiCH$_3$, 3H), 1.96 (s, NCH$_3$, 12H), 3.32 and 3.64 (2d, $^2J = 12.2$ Hz, 2×2H), 6.84–7.30 (m, aryl-CH, 3H), 8.0 (br s, OH, 1H). ^{13}C NMR (benzene-d_6): $\delta = 1.4$ (OSiCH$_3$), 3.2 and 3.8 (CSiCH$_3$), 5.3 (SiCH), 44.4 (NCH$_3$), 65.9 (CH$_2$), 126.0, 127.8, 128.1, 131.5, 143.4 and 143.8 (arom. C). ^{29}Si NMR

(benzene-d_6): δ = 0.5 and 0.6 (SiMe$_3$), 1.9 (SiOH). MS (EI, m/z, %): 410 (3) [M$^+$], 395 (81) [M$^+$ − CH$_3$], 393 [M$^+$ − OH]. Anal. Calc. for C$_{20}$H$_{42}$N$_2$OSi$_3$ (410.26): C, 58.47; H, 10.30; N, 6.82. Found: C, 58.20; H, 10.20; N, 6.74%.

3.2.2. [2,6-Bis(dimethylaminomethyl)phenyl]-phenyl-[bis(trimethylsilyl)methyl]-silanol (5c)

1.43 g (3.15 mmol) of silene **3c** gave 0.67 g (88%) of **5c**, colorless crystals (from heptane), m.p. 168–171 °C. IR (nujol): $\tilde{v}$ = 3424 cm^{-1} (SiOH). ^{1}H NMR (benzene-d_6): δ = 0.21 and 0.37 (2s, SiCH$_3$, 2 × 9H), 0.64 (s, CH, 1H), 1.98 (s, NCH$_3$, 12H), 2.73 and 4.00 (2br d, CH$_2$, 2 × 2H), 6.84–7.30 (m, aryl-CH, 8H), 9.7 (br s, SiOH, 1H). ^{13}C NMR (benzene-d_6): δ = 3.2 and 3.4 (SiCH$_3$), 4.7 (SiCH), 44.3 and 45.5 (NCH$_3$), 63.4 and 65.4 (CH$_2$), 125.6, 127.8, 129.1, 130.0, 136.7, 137.0, 138.0 and 144.5 (arom. CH). ^{29}Si NMR (benzene-d_6): δ = −8.7 (SiOH), 0.2 and 1.1 (SiMe$_3$). MS (EI, m/z, %): 472 (76) [M$^+$], 457 (100) [M$^+$ − CH$_3$], 412 (38) [M$^+$ − CH$_2$NMe$_2$]. Anal. Calc. for C$_{25}$H$_{44}$N$_2$OSi$_3$ (472.89): C, 63.50; H, 9.38; N, 5.92. Found: C, 63.86; H, 9.49; N, 5.41%.

3.3. 1,3-Bis[2,6-bis(dimethylaminomethyl)phenyl]-1,3-dimethyl-1,3-bis[bis(trimethylsilyl)methyl]disiloxane (6a)

Wet ether was added to an ethereal solution of 2.0 g (5.51 mmol) of **3a** until the solution had completely decolorized. Evaporation and recrystallization of the residue from acetonitrile gave colorless crystals, m.p. 168–173 °C, yield 3.87 g (84%). ^{1}H NMR (benzene-d_6): δ = 0.05 and 0.49 (2s, SiCH$_3$, 2 × 18H), 0.29 (s, OSiCH$_3$, 6H), 1.30 (s, CH, 2H), 2.04 and 2.23 (2s, NCH$_3$, 2 × 6H), 2.75 and 3.08 (2d, ^2J = 13.4 Hz, CH$_2$, 2 × 2H), 3.01 and 4.55 (2d, ^2J = 12.5 Hz, CH$_2$, 2 × 2H), 7.07–7.37 (m, arom CH). ^{13}C NMR (benzene-d_6): δ = 1.4 (OSiCH$_3$), 3.4 and 5.3 (SiCH$_3$), 8.3 (SiCH), 45.4 and 45.5 (NCH$_3$), 65.4 and 65.8 (CH$_2$), 130.4, 132.6 and 147.6 (arom. CH), 143.5, 144.1 and 144.5 (quart. arom. C). ^{13}C NMR (benzene-d_6): δ = −1.51, 0.12 and 0.93 (SiMe$_3$ and SiO). MS (EI, m/z, %): 802 (33) [M$^+$], 787 (35) [M$^+$ − CH$_3$], 758 (31) [M$^+$ − NMe$_2$], 611 (62) [M$^+$ − C$_6$H$_3$(NMe$_3$)$_2$]. Anal. Calc. for C$_{40}$H$_{82}$N$_4$OSi$_6$ (803.62): C, 59.78; H, 10.28; N, 6.97. Found: C, 58.58; H, 10.37; N, 6.72%.

3.3.1. [2,6-Bis(diethylaminomethyl)phenyl]-trimethylsilyl-[bis(trimethylsilyl)methyl]silanol (7)

Treatment of 1.04 g (2.05 mmol) of **4** with water produced 0.77 g (77%) of **7** in form of a colorless oil. IR (nujol): $\tilde{v}$ = 3350–3500 cm^{-1} (br, SiOH) ^{1}H NMR (benzene-d_6): δ = 0.16, 0.30 and 0.49 (3s, SiCH$_3$, 3 × 9H), 0.84 and 1.03 (2t, ^3J = 7.02 Hz, CCH$_3$, 2 × 6H), 0.96 (s, CH, 1 H), 2.40–2.70 (m, NCH$_2$C, 8H), 3.26 and 4.11 (dd, ^2J = 11.9 Hz, PhCH$_2$N, 2H), 3.66 and 3.97 (dd, ^2J = 14.9 Hz, PhCH$_2$N, 2H), 6.87–7.92 (m, aryl-CH, 3H) 8.38 (br s, OH, 1H). ^{13}C NMR (benzene-d_6): δ = 1.4, 3.8 and 4.3 (SiCH$_3$), 6.7, 10.0, 12.2 and 12.9 (CCH$_3$), 30.2 (SiCH), 44.8 and 46.8 (CH$_2$CH$_3$), 59.5 and 61.2 PhCH$_2$N, 126.2, 127.2 and 132.1 (arom. CH), 127.7, 128.5 and 143.6 (quart. arom. C). ^{13}C NMR (benzene-d_6): δ = −19.7 (SiSiMe$_3$), 0.8 and 1.5 (CSiMe$_3$), 2.3 (SiOH). MS (EI, m/z, %): 524 (1) [M$^+$], 509 (29) [M$^+$ − CH$_3$], 496 (6) [M$^+$ − C$_2$H$_5$]. Anal. Calc. for C$_{26}$H$_{56}$N$_2$OSi$_4$ (525.08): C, 59.47; H, 10.75; N, 5.34. Found: C, 59.65; H, 10.78; N, 5.55%.

3.4. General procedure of the reaction of the silenes 3a, 3c and 3d, respectively, with aromatic aldehydes

The reactions were carried out in heptane, THF or toluene. Approximately 2 mmol of the respective silene were dissolved in 100 ml of the solvent and after addition of the equimolar quantity of the aldehyde the mixture was heated under stirring for 3 days (reaction temperature in heptane 80 °C, in THF 61 °C, in toluene 105 °C). Subsequently, the solvent was removed in vacuo and the residue was separated by column chromatography. The respective styrenes were eluted with pure hexane. The silanols were obtained by elution with heptane/ethyl acetate (50:1), and elution with heptane/ethyl acetate (5:1) gave the 2-oxa-1-silatetrahydronaphthalenes. The products obtained were recrystallized from acetonitrile.

3.4.1. Reaction of 3a with benzaldehyde in heptane

Separation of the product mixture obtained after the reaction of 1.06 g (2.71 mmol) of **3a** with 0.29 g (2.71 mmol) of benzaldehyde afforded 0.46 g (69%) of **9**, 0.05 g (4.5%) of **5a** and 0.15 g (11.5%) of **12a**.

3.4.1.1. c-4-Dimethylamino-8-(dimethylaminomethyl)-1-methyl-c-3-phenyl-r-1-bis(trimethylsilyl)-2-oxa-1-sila-1,2,3,4-tetrahydronaphthalene (12a)

Colorless crystals, m.p. 98–100 °C. IR (nujol): $\tilde{v}$ = 1034 cm^{-1} (SiOC). ^{1}H NMR (benzene-d_6): δ = 0.13 and 0.29 (2s, Si(CH$_3$)$_3$, 2 × 9H), 0.035 (s, Si$_3$CH, 1H), 0.76 (s, SiCH$_3$, 3H), 1.96 (s, NCH$_3$, 6H), 2.11 (s, NCH$_3$, 6H), 3.42 and 3.92 (2d, ^2J = 12.8 Hz, NCH$_2$, 2 × 1H), 4.40 (d, ^3J = 9.9 Hz, NCH, 1H), 5.19 (d, ^3J = 9.9 Hz, OCH, 1H), 7.12–7.86 (m, aryl-H, 8H). ^{13}C NMR (benzene-d_6): δ = 2.9 (SiCH$_3$), 3.1 and 3.8 (Si(CH$_3$)$_3$), 4.6 (Si$_3$C), 41.4 and 45.2 (NCH$_3$), 65.8 (NCH$_2$), 71.3 (NCH), 75.0 (OCH), 127.0, 127.9, 128.2, 128.7, 129.3 and 130.0 (arom. CH), 132.9, 138.4 143.2 and 149.5 (arom. quart. C). ^{29}Si NMR (benzene-d_6): δ = 0.44 (SiO), 0.83 and 2.96 (SiMe$_3$). MS (CI, m/z, %): 498 (M$^+$), 483 [M$^+$ − CH$_3$]. Anal. Calc. for C$_{27}$H$_{46}$N$_2$OSi$_3$ (498.92): C, 65.00; H, 9.29; N, 5.61. Found: C, 65.58; H, 9.41; N, 5.56%.

3.4.2. Reaction of 3c with benzaldehyde

The reaction of 1.2 g (2.6 mmol) of **3c** with 0.28 of benzaldehyde in heptane gave 0.21 g (33%) of **9** and 0.36 g (24%) of *trans,cis*-**12c**. The same reaction carried out with 0.90 g (2.0 mmol) of **3c** and 0.21 g of benzaldehyde in toluene afforded 0.06 g (12.5%) of **9**, 0.06 g (3%) of **5c**, 0.30 g (27%) of *trans,cis*-**12c** and 0.04 g (3%) of *cis trans*-**12c**. In THF 1.0 g (2.2 mmol) of **3c** and 0.23 g (2.2 mmol) of benzaldehyde produced 0.02 g (4.0%) of **9**, 0.38 g (31%) of *trans,cis*-**12c** and 0.11 g (8%) of *cis trans*-**12c**.

3.4.2.1. t-4-Dimethylamino-8-(dimethylaminomethyl)-1,c-3-diphenyl-r-1-[bis(trimethylsilyl)methyl]-2-oxa-1-sila-1,2,3,4-tetrahydronaphthalene (trans,cis-12c).
Colorless crystals, m.p. 137–141 °C. IR (nujol): $\tilde{v} = 1035$ cm^{-1} (SiOC). ^{1}H NMR (benzene-d_6): $\delta = 0.10$ and 0.26 (2s, SiCH$_3$, 2×9H), 0.74 (s, Si$_3$CH, 1H), 1.96 and 2.11 (2s, NCH$_3$, 2×6H), 3.42 (d, $^2J = 12.8$ Hz, 1H), 3.95 (d, $^2J = 12.8$ Hz, 1H), 4.40 (d, $^3J = 9.9$ Hz, NCH, 1H), 5.18 (d, $^3J = 10.0$ Hz, OCH, 1H), 7.09–7.86 (m, aryl-CH, 13H). ^{13}C NMR (benzene-d_6): $\delta = 3.3$ and 3.7 (SiCH$_3$), 4.7 (SiO), 41.1 and 45.0 (NCH$_3$), 65.3 (CH$_2$), 70.7 (NCH), 76.1 (OCH), 121.4, 128.7, 129.8, 135.3, 136.3, 139.9, 143.2, 144.5 and 149.8 (arom. CH), 128.2, 128.3, 128.8, 129.7 and 135.4 (quart. arom. C). ^{29}Si NMR (benzene-d_6): $\delta = -3.48$ (SiO), 0.39 and 1.25 (SiMe$_3$). MS (CI, m/z, %): 560 (15) [M$^+$], 545 (32) [M$^+$ – CH$_3$], 516 (23) [M$^+$ – N(CH$_3$)$_2$], 454 (100) [M$^+$ – C$_6$H$_5$CHO]. Anal. Calc. for C$_{32}$H$_{48}$N$_2$OSi$_3$ (560.99): C, 68.51; H, 8.62; N, 4.99. Found: C, 67.05; H, 8.78; N, 4.46%.

3.4.2.2. c-4-Dimethylamino-8-(dimethylaminomethyl)-1,t-3-diphenyl-r-1-[bis(trimethylsilyl)methyl]-2-oxa-1-sila-1,2,3,4-tetrahydronaphthalene (cis,trans-12c).
Colorless crystals, m.p. 120–126 °C. IR (nujol): $\tilde{v} = 1040$ cm^{-1} (SiOC). ^{1}H NMR (benzene-d_6): $\delta = 0.24$ and 0.33 (2s, SiCH$_3$, 2×9H), 1.35 (s, Si$_3$CH, 1H), 1.97 and 2.14 (2s, NCH$_3$, 2×6H), 3.41 (d, $^3J = 14.0$ Hz, CH$_2$, 1H), 3.51 (d, $^3J = 14.0$ Hz, CH$_2$, 1H), 3.33 (d, $^3J = 3.7$ Hz, NCH, 1H), 5.58 (d, $^3J = 3.7$ Hz, OCH, 1H), 6.95–7.99 (m, aryl-H, 13H). ^{13}C NMR (benzene-d_6): $\delta = 3.7$ and 4.0 (SiCH$_3$), 7.1 (SiO), 43.3 and 47.9 (NCH$_3$), 64.8 (CH$_2$), 74.2 (NCH), 75.4 (OCH), 121.0, 122.7, 125.6, 127.4, 127.5, 128.1, 129.6, 135.8 and 136.0 (arom. CH), 137.6, 141.0, 143.6, 144.8 and 145.7 (quart. arom. C). ^{29}Si NMR (benzene-d_6): $\delta = -9.11$ (SiO), -1.55 and -0.58 (SiMe$_3$). MS (CI, m/z, %): 560 (2) [M$^+$], 545 (17) [M$^+$ – CH$_3$], 516 (2) [M$^+$ – N(CH$_3$)$_2$], 454 (100) [M$^+$ – C$_6$H$_5$CHO]. Anal. Calc. for C$_{32}$H$_{48}$N$_2$OSi$_3$ (560.99): C, 68.51; H, 8.62; N, 4.99. Found: C, 67.80; H, 8.67; N, 4.79%.

3.4.3. Reaction of 3c with 4-chlorobenzaldehyde

0.85 g (1.9 mmol) of **3c** and 0.25 g (1.9 mmol) of 4-chlorobenzaldehyde gave besides unidentified material 0.05 g (9.5%) of **10** and 0.60 g (32%) of **13**.

3.4.3.1. 1-(4-Chlorophenyl)-2,2-bis(trimethylsilyl)ethylene (10).
Colorless oil. ^{1}H NMR (benzene-d_6): $\delta = 0.01$ and 0.21 (2s, SiCH$_3$, 2×9H), 7.68 (s, CH, 1H), 6.85 (d, $^3J = 8.0$ Hz, aryl-CH, 2H), 7.04 (d, $^3J = 8.0$ Hz, aryl-CH, 2H). ^{13}C NMR (benzene-d_6): $\delta = 0.6$ and 2.2 (SiCH$_3$), 30.2 (Si$_2$C), 113.5 and 129.6 (arom. CH), 155.6 and 155.8 (arom. quart. C), 159.5 (olef. C). ^{29}Si NMR (benzene-d_6): $\delta = -8.1$ and -0.7 (SiCH$_3$). MS (CI, m/z, %): 282 (44) [M$^+$], 267 (76) [M$^+$ – CH$_3$], 209 (20) [M$^+$ – SiMe$_3$]. Anal. Calc. for C$_{14}$H$_{23}$ClSi$_2$ (282.96): C, 59.43; H, 8.19. Found: C, 59.55; H, 8.36%.

3.4.3.2. c-3-(4-chlorophenyl)-t-4-dimethylamino-8-(dimethylaminomethyl)-1-phenyl-r-1-[bis(trimethylsilyl)-methyl]-2-oxa-1-sila-1,2,3,4-tetrahydronaphthalene (13)
Colorless crystals, m.p. 123–127 °C. IR (nujol): $\tilde{v} = 1062$ cm^{-1} (SiOC). ^{1}H NMR (benzene-d_6): $\delta = 0.10$ and 0.24 (2s, SiCH$_3$, 2×9H), 0.74 (s, Si$_3$CH, 1H), 1.89 and 2.10 (2s, NCH$_3$, 2×6H), 3.39 and 3.93 (2d, $^2J = 12.82$ Hz, CH$_2$, 2H), 4.25 (d, $^3J = 10.07$ Hz, NCH, 1H), 5.04 (d, $^3J = 10.07$ Hz, OCH, 1H), 7.16–7.82 (m, aryl-CH, 12 H). ^{13}C NMR (benzene-d_6): $\delta = 3.3$ and 3.7 (SiCH$_3$), 4.6 (Si$_3$C), 41.1 and 44.9 (NCH$_3$), 65.3 (CH$_2$), 70.7 (NCH), 75.3 (OCH), 119.8, 128.1, 128.6, 129.0, 129.3, 129.8, 135.2 and 135.4 (arom. CH), 133.6, 136.2, 139.6, 143.1, 143.2, 149.3 (quart. arom. C). ^{29}Si NMR (benzene-d_6): $\delta = -3.1$ (SiO), 0.4 and 1.2 (SiMe$_3$). MS (CI, m/z, %): 594 (3) [M$^+$], 579 [M$^+$ – CH$_3$], 550 (3) [M$^+$ – N(CH$_3$)$_2$]. Anal. Calc. for C$_{32}$H$_{47}$ClN$_2$OSi$_3$ (595.44): C, 64.55; H, 7.96; N, 4.70. Found: C, 63.49; H, 7.96; N, 4.57%. HRMS calc.: 594.2685; found: 594.2665.

3.4.4. Reaction of 3c with 4-methoxybenzaldehyde

0.85 g (1.9 mmol) of **3c** and 0.25 g (1.9 mmol) of 4-methoxybenzaldehyde gave besides unidentified material 0.24 g (46%) **11** and 0.21 g (19%) of **14**.

3.4.4.1. 1-(4-Methoxyphenyl)-2,2-bis(trimethylsilyl)ethylene (11).
Colorless oil. ^{1}H NMR (benzene-d_6): $\delta = 0.14$ and 0.27 (2s, SiCH$_3$, 2×9H), 3.38 (s, OCH$_3$, 3H), 6.71 (d, $^3J = 8.55$ Hz, arom. CH, 2H), 7.12 (d, $^3J = 8.55$ Hz, arom. CH, 2H), 7.90 (s, CH, 1H). ^{13}C NMR (benzene-d_6): $\delta = 0.8$ and 2.4 (SiCH$_3$), 30.2 (Si$_2$C), 54.7 (OCH$_3$), 113.5 (CH), 113.5 and 129.6 (arom. CH), 155.6 and 155.8 (quart. arom. C), 159.5 (olef. C). ^{29}Si NMR (benzene-d_6): $\delta = -8.3$ and -1.0 (SiCH$_3$). MS (CI, m/z, %): 278 (44) [M$^+$], 263 (28) [M$^+$ – CH$_3$], 205 (16) [M$^+$ – SiMe$_3$]. Anal. Calc. for C$_{15}$H$_{26}$OSi$_2$ (278.15): C, 64.68; H, 9.41. Found: C, 64.28; H, 9.53%.

Table 2
Crystal and structure refinement data for **3c** and isomers of **12c**

Compound	**3c**	*trans,cis*-**12c**	*cis,trans*-**12c**
Formula weight	454.88	560.99	560.99
T (K)	200(2)	293(2)	173(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group (H.-M.)	$P\bar{1}$	$P2_1/n$	$C2/c$
Space group (Hall)	$-P\,1$	$-P\,2yn$	$-C\,2yc$
Unit cell dimensions			
a (Å)	8.8750(18)	10.600(3)	18.7836(4)
b (Å)	10.725(2)	27.508(11)	19.7861(5)
c (Å)	15.473(3)	12.341(4)	17.8214(4)
α (°)	101.71(3)	90	90
β (°)	105.03(3)	109.990(10)	91.7680(10)
γ (°)	101.35(3)	90	90
V (Å^3)	1343.5(5)	3382(2)	6620.2(3)
Z	2	4	8
D_{calc} (Mg m^{-3})	1.124	1.102	1.126
Absorption coefficient (mm^{-1})	0.191	0.166	0.169
$F(000)$	496	1216	2432
Crystal size (mm^3)	$0.4 \times 0.3 \times 0.3$	$0.58 \times 0.4 \times 0.24$	$0.68 \times 0.36 \times 0.22$
θ Range for data collection (°)	2.01–24.21	1.91–22.00	3.10–25.00
Index ranges	$-10 \leqslant h \leqslant 9$,	$-1 \leqslant h \leqslant 11$,	$-22 \leqslant h \leqslant 22$,
	$-12 \leqslant k \leqslant 12$,	$-28 \leqslant k \leqslant 1$,	$-22k \leqslant 23$,
	$0 \leqslant l \leqslant 17$	$-13 \leqslant l \leqslant 12$	$-21 \leqslant l \leqslant 21$
Reflections collected	4019	5189	32067
Independent reflections (R_{int})	4019	4128 (0.0338)	5833 (0.0252)
Completeness to $\theta/(\%)$	24.21°/92.7	22.00°/100	25.00°/99.8
Data/restraints/parameters	4019/0/271	4128/0/343	5833/0/343
Goodness-of-fit on F^2	0.998	1.062	1.084
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0385$, $wR_2 = 0.0953$	$R_1 = 0.0471$, $wR_2 = 0.1070$	$R_1 = 0.0345$, $wR_2 = 0.0900$
R indices (all data)	$R_1 = 0.0533$, $wR_2 = 0.1000$	$R_1 = 0.0914$, $wR_2 = 0.1385$	$R_1 = 0.0412$, $wR_2 = 0.0977$
Largest difference in peak/hole (e Å^{-3})	0.291/-0.188	0.277/-0.223	0.297/-0.204

3.4.4.2. c-3-(4-methoxyphenyl)-t-4-dimethylamino-8-(di-methylaminomethyl)-1-phenyl-r-1-[bis(trimethylsilyl) me-thyl]-2-oxa-1-sila-1,2,3,4-tetrahydronaphthalene (14)
Colorless crystals, m.p. 150–156 °C. IR (nujol): $\tilde{v} = 1061$ cm^{-1} (SiOC). ^{1}H NMR (benzene-d_6): $\delta = 0.12$ and 0.28 (2s, SiCH$_3$, 2×9H), 0.74 (s, Si$_3$CH, 1H), 2.02 and 2.11 (2s, NCH$_3$, 2×6H), 3.30 (s, OCH$_3$, 3H), 3.43 and 3.96 (2d, $^2J = 12.8$ Hz, CH$_2$, 2H), 4.41 (d, $^3J = 10.0$ Hz, NCH, 1H), 5.19 (d, $^3J = 9.8$ Hz, OCH, 1H), 6.83–7.91 (m, aryl-CH, 12H). ^{13}C NMR (benzene-d_6): $\delta = 3.3$ and 3.7 (SiCH$_3$), 4.6 (Si$_3$C), 41.1 and 44.9 (NCH$_3$), 54.7 (OCH$_3$), 65.3 (CH$_2$), 70.7 (NCH), 75.6 (OCH), 113.9, 127.4, 128.8, 129.1, 129.7, 129.9, 135.3 and 135.4 (arom. CH), 136.3, 136.6, 140.1, 143.2, 150.0 and 159.8 (arom. quart. C). ^{29}Si NMR (benzene-d_6): $\delta = -3.6$ (SiO), 0.4 and 1.3 (SiMe$_3$). MS (CI, m/z, %): 590 (1) [M$^+$], 575 (12) [M$^+ -$ CH$_3$]. Anal. Calc. for C$_{33}$H$_{50}$N$_2$O$_2$Si$_3$ (591.02): C, 67.06; H, 8.53; N, 4.74. Found: C, 67.21; H, 8.72; N. 4.54%.

3.5. Crystal structure determination of 3c, trans,cis-12c and cis,trans-12c

The X-ray investigations were performed with three different diffractometer systems. For **3c** and **4**, a STOE imaging plate detecting system, for the *trans–cis* isomer of **12c** a Bruker P4 four-circle diffractometer and for all other compounds an X8Apex area detector system was used. All investigations were carried out with Mo Kα-radiation (graphite monochromator). The structures were solved with the Bruker SHELXTL software package and refined with full-matrix least-squares methods (Bruker SHELXTL) on F^2. All non-hydrogen atoms were refined anisotropically, while the hydrogens were put into theoretical positions and refined according to the riding model. Due to the low absorption coefficients no absorption correction was performed. Further, crystallographic and structure refinement data for the compounds shown in Figs. 1–3 can be taken from Table 2. CCDC Nos. 252260–252262 contain the corresponding supplementary crystallographic data.

4. Supplementary material

Acknowledgements

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