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Journal of Organometallic Chemistry 598 (2000) 395–402

Journal of Organo metallic Chemistry

Head-to-head versus head-to-tail dimerizations of transient silenes — the generation and dimerization behavior of 2-(2-dimethylaminoaryl)-1,1-bis(trimethylsilyl)silenes

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Received 24 September 1999; accepted 22 November 1999

Dedicated to Professor Manfred Meisel on the occasion of his 60th birthday

Abstract

The transient silenes $(Me_3Si)_2Si{=}CR^1R^2$ (**4**: $R^1 = H$, $R^2 = 2\text{-}Me_2N\text{-}5\text{-}Me{-}C_6H_3$; **11**: $R^1 = Me$, $R^2 = 2\text{-}Me_2N{-}C_6H_4$; **15**: $R^1 = 3,5\text{-}Me_2{-}C_6H_3$, $R^2 = 2\text{-}Me_2N{-}C_6H_4$; **18**: $R^1 = Me$, $R^2 = 2\text{-}Me_2N\text{-}5\text{-}Me{-}C_6H_3$) were generated following the mechanism of the sila-Peterson reaction. Thus, **4** was obtained by base-induced trimethylsilanol elimination from (2-dimethylamino-5-methylphenyl)tris(trimethylsilyl)silylmethanol (**3**). Addition of methyllithium or 3,5-dimethylphenyllithium, respectively, to the carbonyl group of 2-dimethylaminobenzoyl-tris(trimethylsilyl)silane (**10**) and subsequent elimination of Me_3SiOLi led to **11** and **15**, respectively. Similarly, (2-dimethylamino-5-methylbenzoyl)-tris(trimethylsilyl)silane (**17**) and MeLi gave **18**. The silene **4** underwent a spontaneous head-to-tail cyclodimerization to give a 1,3-disilacyclobutane (**5**), whereas **11** afforded a linear head-to-head dimer (**12**). The dimerization rates of **15** and **18** proved to be slow, thus, under the conditions of the sila-Peterson reaction readdition products of eliminated trimethylsilanolate to the Si=C bond of the silenes were obtained (**16**, **19**). The structures of the compounds prepared were elucidated on the basis of comprehensive NMR and MS studies; for **5** also the results of an X-ray structural analysis are given. Possible reasons for the different behavior of the similarly structured silenes are discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Silicon; Silenes; Silene dimerization; 1,2-Disilacyclobutanes; 1,3-Disilacyclobutanes

1. Introduction

In a recently published paper we described the generation of the transient 2-(2-dimethylaminophenyl)-1,1-bis(trimethylsilyl)silene (**1**) by a modified Peterson reaction and its spontaneous dimerization to 2,4-bis(2-dimethylaminophenyl) - 1,1,3,3 - tetrakis(trimethylsilyl)-1,3-disilacyclobutane (**2**) [1]. The formation of the 1,3-disilacyclobutane **2**, the formal head-to-tail cyclodimer of the silaethene **1**, was a rather unexpected result of the studies, since 1,1-bis(trimethylsilyl)silenes were generally found to dimerize in a head-to-head mode, affording products whose individual structures depend on the substitution pattern of the transient Si=C system [2–5]. The unusual behavior of **1** was attributed to the donor properties of the 2-dimethylamino group of the 2-aryl substituent causing an intermolecular interaction with the electrophilic silene silicon atom of a neighboring silene molecule, thus initiating a head-to-tail dimerization through a cyclic seven-membered transition state [1,5]. This picture could successfully be applied to the dimerization behavior of 2-(dimethylaminonaphthyl)-1,1-bis(trimethylsilyl)silenes [6] and proved to be worthwhile in understanding the solvent-dependent regiospecifity of the cyclodimerization of 2-(2-methoxyphenyl)-1,1-bis(trimethylsilyl)silene [5]. In this paper we describe the generation of some new transient 2 - (dimethylaminophenyl) - 1,1 - bis(trimethylsilyl)silenes and demonstrate that slight changes in the molecular

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PII: S0022-328X(99)00740-8

structure of the silaethenes may lead to a fundamentally different reaction behavior.

2. Results and discussion

2-(2-Dimethylamino-5-methylphenyl)-1,1-bis(trimethylsilyl)silene (**4**) was prepared according to our standard method by deprotonation of (2-dimethylamino-5-methylphenyl)-tris(trimethylsilyl)silylmethanol (**3**) with methyllithium in ether following the mechanism of the modified Peterson reaction. In the absence of scavenger reagents, silene **4** proved to be unstable and underwent rapid cyclodimerization to afford the two stereoisomeric 1,3-disilacyclobutanes *E*-**5** and *Z*-**5** in a total yield of 82%.

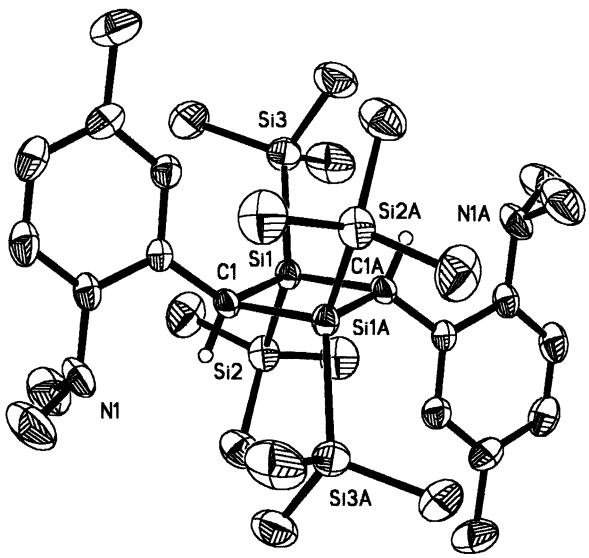
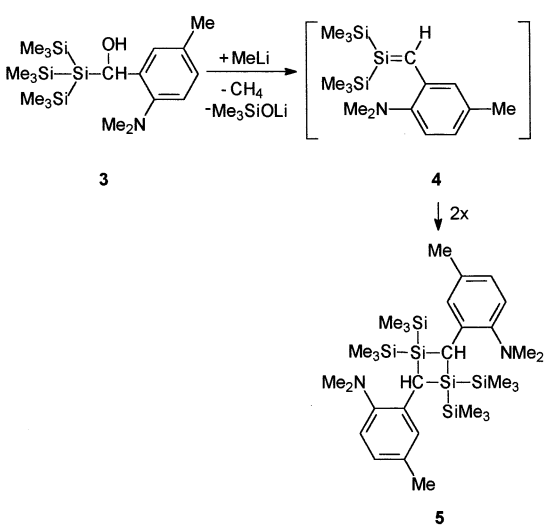


Fig. 1. Molecular structure of **5** in the crystal (ORTEP, 30% probability, H atoms, except ring-CH, omitted for clarity); selected bond lengths (Å) and angles (°): C1–Si1, 1.922(2); Si1–Si2, 2.3616(11); Si1–Si3, 2.6365(10); C1–Si1–C1A, 91.60(9); Si1–C1-Si1A, 88.40(9).



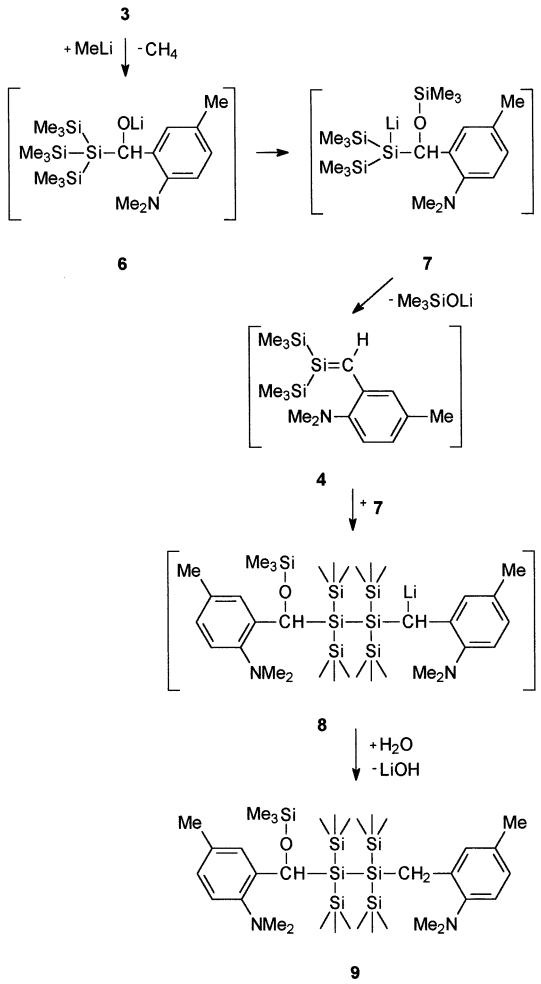
Scheme 1. Generation and head-to-tail cyclodimerization of the transient silene **4**.

The structures of *E*-**5** and *Z*-**5**, which are indicative for the head-to-tail mode of the dimerization of **4**, were elucidated on the basis of NMR and MS studies. For *E*-**5** also an X-ray structural analysis was performed, which revealed a planar 1,3-disilacyclobutane system (Fig. 1). Apart from slightly elongated ring Si–C distances, which are considered as being due to steric congestion, the bond parameters are in the expected region.

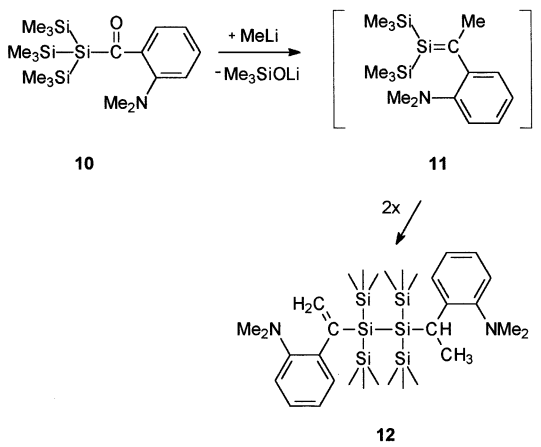
The 1,3-disilacyclobutane **5** is the expected dimer of **4**, since its formation is fully consistent with the conversion of **1** into **2**, and the observed regiospecifity of the dimerization can easily be explained following the proposed mechanism outlined in the introductory remarks. Obviously, the unusual head-to-tail dimerization is effected by the *ortho*-dimethylamino group of the phenyl substituent in **4**. With the intention to confirm the concept and to possibly reverse the dimerization regiospecifity of the Si=C system by ruling out the donor properties of the dimethylamino group through complexation, the procedure used for the generation of **4** was repeated in the presence of triethylborane as a lone-pair acceptor. Actually, deprotonation of **3** with methyllithium in ether in the presence of equimolar quantities of $Et_3B{\cdot}THF$ gave no head-to-tail cycloadduct **5** nor the head-to-head dimer of the silene **4**, but afforded the hexasilane **9** in a yield of 63% (Schemes 1 and 2). Its structure was elucidated by comprehensive NMR and MS studies (see Section 3).

The formation of **9** as the outcome of the conversion of deprotonated **3** was really surprising and the observed reaction course unique for all reactions of the sila-Peterson type we studied. The generation of **9** can easily be understood following the sequence given in Scheme 2. Deprotonation of **3**, isomerization of **6** by a 1,3-Si,O-trimethylsilyl migration to give **7** and subsequent trimethylsilanolate elimination leads to the silene **4**, which is trapped by addition of the silyl lithium compound **7** to the Si=C group resulting in the formation of **8**. Hydrolysis of **8** during the aqueous workup affords **9**. The lithium silanide **7** is considered to be an intermediate in the course of the silene generation. We suppose, in presence of triethylborane, the elimination of trimethylsilanolate from **7** under formation of **4** to be a comparatively slow process due to the complexation of the silaanion by Et_3B. Thus, the transient silene, forming gradually, always meets an effective excess of nucleophilic **7** and adduct formation dominates prior to silene dimerization.

The isolation of compound **9**, i.e. the proof of the intermediate formation of the organolithium derivative **8**, is of particular interest with respect to the general discussion of the mechanism of the formation of 1,2-disilacyclobutanes as the formal head-to-head dimers of



Scheme 2. Generation of the silene **4** by a sila-Peterson reaction and addition of the precursor lithium silanide **7** to the Si=C bond.



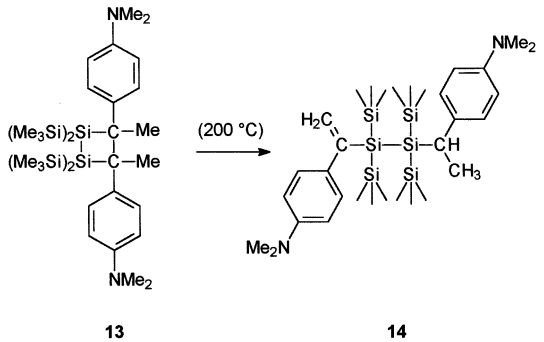
Scheme 3. Generation of the transient silene **11** and its spontaneous head-to-head reaction affording the linear dimer **12**.

transient silenes. It is generally accepted that the dimerization involves Si–Si bond formation as a first step giving a carbon centered 1,4-biradical, which subsequently stabilizes to give the four-membered ring [7]. But under conditions of the sila-Peterson reaction also the addition of silene precursors of type **7** to the Si=C bond of the transient silene and subsequent ring closure with intramolecular elimination of lithium trimethylsilanolate might be a way conceivable to 1,2-disilacyclobutanes. But, actually, in the case of the reaction of **3** with MeLi in presence of Et_3B no head-to-head cyclodimer of **4** was found. Also, prolonged heating of the reaction mixture prior to hydrolysis — even after exchange of the solvent from ether to toluene and refluxing for several hours — always gave compound **9** (after aqueous workup) as the final product exclusively. Consequently also, the related mechanism proposed by Auner and co-workers [10], for the formation of the formal [2 + 2] and [2 + 4] cyclodimers of 2-mesityl-1,1-bis(trimethylsilyl)silene [9], appears not to be very likely.

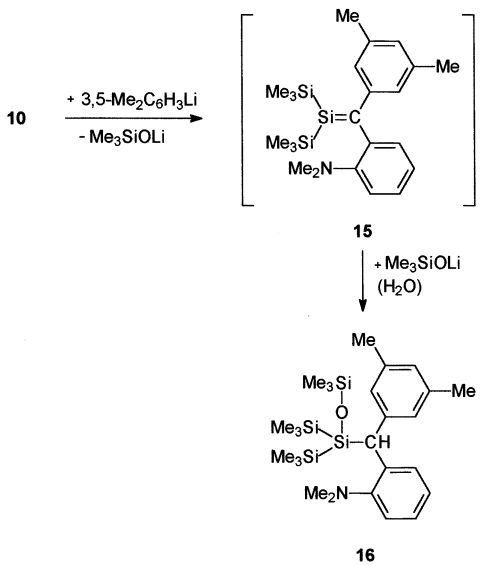
2-Methyl-2-(2-dimethylaminophenyl)-1,1-bis(trimethylsilyl)silene (**11**) was generated by addition of methyllithium to the carbonyl function of 2-dimethylaminobenzoyl-tris(trimethylsilyl)silane (**10**), giving an intermediate alkoxide, which spontaneously eliminated lithium trimethylsiloxide establishing the Si = C system. Also silene **11** is unstable and as the final product of the reaction we isolated 1-[1-(2-dimethylaminophenyl)-ethenyl] - 2[1 - (2 - dimethylaminophenyl)ethyl] - 1,1,2,2-tetrakis(trimethylsilyl)disilane (**12**), a product of an obvious head-to-head dimerization of **11** (Scheme 3). This type of silene dimerization is not uncommon; it is typical for 1,1-bis(trimethylsilyl)silenes with 'allylic' hydrogen atoms [3,4,8,9]. But the remarkable point is that the replacement of one hydrogen atom at the silene C atom of compound **1** by a methyl group leads to a reversed regiospecifity of the silene dimerization. The reason for this surprising behavior is not clear, and in view of the small difference in the spacial demand of the hydrogen atom in **1** and the methyl group in **11**, respectively, a change of the dimerization mode due to steric reasons is hardly conceivable.

Depending on the substitution pattern, the biradicals formed by Si–Si coupling of transient silenes may stabilize to afford 1,2-disilacyclobutanes, tetrahydro-2,3-disilanaphthalenes or (in the presence of 'allylic hydrogen') linear dimers of type **12**, respectively [5,7]. For some cases it was proved that both 1,2-disilacyclobutanes and tetrahydro-2,3-disilanaphthalenes exist in a temperature-dependent equilibrium with the monomeric silenes [11,12]. Recently we found that on heating to 200°C, the formerly described 1,2-disilacyclobutane **13**, the formal [2 + 2] head-to-head cyclodimer of 2-(4-dimethylaminophenyl)-1,1-bis(trimethylsilyl)silene [1], is quantitatively converted into the linear dimer **14** (Scheme 4).

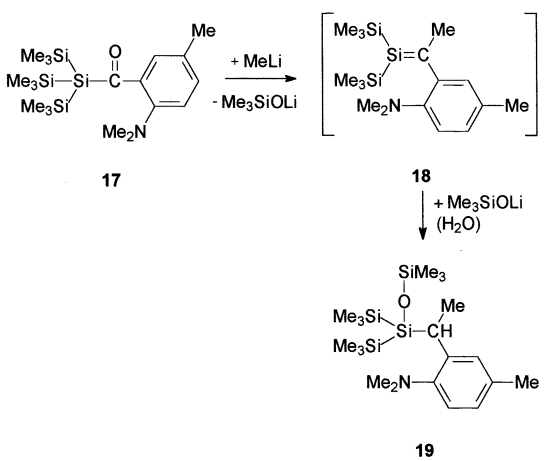
In the case of the dimerization of **11**, hydrogen transfer in the above mentioned 1,4-biradical under



Scheme 4. Thermal isomerization of a 1,2-disilacyclobutane **13**, the formal [2 + 2] cyclodimer of 2-(4-dimethylaminophenyl)-1,1-bis(trimethylsilyl)silene, into the linear silene dimer **14**.



Scheme 5. Generation of the transient silene **15** by a sila-Peterson reaction and readdition of Me_3SiOLi to the Si=C bond.



Scheme 6. Generation of the transient silene **18** by a sila-Peterson reaction and readdition of Me_3SiOLi to the Si=C bond.

formation of **12** makes the reaction irreversible and the formation of alternative products is excluded. Methyllithium is an unfavourable reagent in the reaction with **10**, since in this way 'allylic' hydrogen is introduced into the silene structure. To avoid this disadvantage, lithium derivatives possessing no hydrogen at the carbanionic C-atom were used in the addition reaction with the acylsilane **10**. But after treatment of **10** with *tert*butyllithium or mesityllithium, respectively, the acylsilane was recovered unchanged. Obviously, the nucleophilic attack of the bulky organolithium reagents at the sterically encumbered carbonyl group of **10** is completely prevented. The reaction of **10** with phenyllithium gave a complex mixture of unidentified, presumably oligomeric or polymeric products. This is in agreement with our general experience that silenes with an unsubstituted phenyl group at the silene C-atom do not undergo a clean dimerization but give complex mixtures of products. 3,5-Dimethylphenyllithium reacts with **10** to afford the siloxane **16** (Scheme 5).

The structure of **16** is easily understood as the result of an addition of trimethylsilanolate, just eliminated from the lithium alkoxide obtained through addition of 3,5-dimethylphenyllithium to the carbonyl group of **10**, at the Si=C bond of the generated silene **15**. The readdition of trimethylsilanolate is a general and expected side reaction of the silene synthesis according to the sila-Peterson process and was observed several times, particularly in the case of sterically highly congested silenes [4b,13]. Due to the kinetic stabilization, the dimerization of these silenes becomes a comparatively slow reaction, making the silanolate addition the dominant process. Summarizing the results of these experiments, we have to state that silenes, obtained by replacement of the 2-hydrogen atom in **1** by other groups, do not dimerize in a head-to-tail mode following the mechanism discussed above, and the question concerning the reason for the opposite regiospecifity of the two similarly structured silenes **1** and **11** remains unanswered.

Interestingly, the reaction of (2-dimethylamino-5-methylbenzoyl)-tris(trimethylsilyl)silane (**17**) with methyllithium under the same conditions applied in the reaction of **10** with MeLi, gave no silene dimer, but again a readdition product of eliminated trimethylsilanolate at the Si=C bond of the generated silene **18** (Scheme 6).

The insignificant increase of the steric bulk, caused by introduction of a methyl group into the 5-position of the aryl substituent of **11** (giving **18**), again leads to a fundamental change in the behavior of the respective silene.

The conclusion drawn from the experiments described in this paper is that slight variations in the structures of the 2-(dimethylaminophenyl)silenes funda-

mentally influence the mode of dimerization. Deviating from the usual dimerization behavior of 1,1-bis-(trimethylsilyl)silenes, 2-(2-dimethylaminophenyl)-1,1-bis(trimethylsilyl)silene (**1**) and 2-(2-dimethylamino-5-methylphenyl)-1,1-bis(trimethylsilyl)silene (**4**) undergo a formal [2 + 2] head-to-tail dimerization to give the 1,3-disilacyclobutanes **2** and **5**, respectively. On the other hand, 2-methyl-2-(2-dimethylaminophenyl)-bis(trimethylsilyl)silene (**11**) affords a linear head-to-head dimer, a behavior that was similarly also observed for the 4-dimethylaminophenyl isomer [1]. Unfortunately, attempts to replace the 2-methyl substituent in **11** by a group bearing no α-hydrogen atom were unsuccessful. Thus, the idea that hydrogen transfer in the biradical Si–Si coupling product of **11**, leading to the linear dimer **12**, might be a trap in the silene dimerization equilibria preventing the formation of head-to-head or head-to-tail cyclodimers, could not be deepened. Increasing steric protection of the Si=C system reduces the dimerization rate and in the case of a silene generation according to the sila-Peterson reaction, the readdition of trimethylsilanolate gains importance. Thus, for **15** and **18**, this reaction type dominates.

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, chemical ionization with isobutane as the reactant gas. $(Me_3Si)_3SiLi{\cdot}3THF$ was prepared as reported in the literature [14]. All yields given refer to amounts obtained after chromatographic separation and purification.

3.1. (2-Dimethylamino-5-methylphenyl)-tris(trimethylsilyl)silylmethanol (3)

A total of 5.00 g (10.6 mmol) of $(Me_3Si)_3SiLi{\cdot}3THF$, dissolved in 30 ml of ether, were added to a suspension of an equimolar quantity (2.75 g) of $MgBr_2{\cdot}OEt_2$ in 20 ml of ether. After stirring for 0.5 h at room temperature (r.t.), the mixture was cooled to −78°C and 1.73 g (10.6 mmol) of 2-dimethylamino-5-methylbenzaldehyde, dissolved in 20 ml of ether, were added within 1 h. The stirred solution was allowed to warm up overnight, water was added, the ethereal extracts were dried with $MgSO_4$ and the solvent was removed in vacuo. Chromatographic purification of the residue (silica gel; heptane–ethyl acetate, 20:1) and recrystallization from acetonitrile afforded 2.6 g (59%) of **3**, m.p. 72–75°C. IR (nujol): $\tilde{\nu} = 3552\ cm^{-1}$ (OH_{free}). ^{1}H-NMR (benzene-d_6): $\delta = 0.33$ (s, $SiCH_3$, 27H), 2.22 (s, aryl-CH_3, 3H), 2.40 (s, NCH_3, 6H), 3.37 (br s, COH, 1H), 5.62 (s, HCO, 1H), 6.81–6.83 (m, aryl-H, 2H), 7.31 (s, aryl-6CH, 1H). ^{13}C-NMR (benzene-d_6): $\delta = 1.8$ ($SiCH_3$), 2.7 (aryl-CH_3), 45.5 (NCH_3), 65.4 (HCO), 119.9, 127.9 and 130.6 (aryl-CH), 133.3, 141.1 and 148.7 (quart. aryl-C). ^{29}Si-NMR (benzene-d_6): $\delta = -68.9$ (*Si*$SiMe_3$), −12.5 ($SiMe_3$). MS *m/z* (%): 411 (5) [M^+], 396 (7) [M^+-CH_3], 338 (10) [M^+-SiMe_3], 164 (100) [$M^+-Si(SiMe_3)_3$]. Anal. Found: C, 55.34; H, 9.96; N, 3.31. Calc. for $C_{19}H_{41}NOSi_4$ (411.88): C, 55.41; H, 10.03; N, 3.40%.

3.2. 2,4-Bis(2-dimethylamino-5-methylphenyl)-1,1,3,3-tetrakis(trimethylsilyl)-1,3-disilacyclobutane (5)

To a stirred solution of 0.5 g (1.2 mmol) of **3** in 30 ml of ether, the equimolar quantity of methyllithium was added at −78°C. After warming up to r.t., water was added, the ethereal layer was separated, dried with magnesium sulfate and evaporated. After treatment of the residue with some *n*-heptane *E*-**5** separated in the form of colorless crystals (0.19 g). Chromatographic separation of the evaporated mother liquor (silica gel; heptane–ethyl acetate, 20:1) gave 0.13 g of the *Z*-isomer. Total yield 0.32 g (82%).

E-**5**: m.p. >230°C dec. ^{1}H-NMR (benzene-d_6): $\delta = 0.29$ (s, $SiCH_3$, 36H), 2.36 (s, aryl-CH_3, 6H), 2.55 (s, NCH_3, 12H), 4.14 (s, ring-CH, 2H), 6.77 (dd, $^3J = 7.93$ Hz, $^4J = 2.13$ Hz, aryl-4CH, 2H), 6.88 (d, $^3J = 7.95$ Hz, aryl-3CH, 2H), 7.62 (d, $^4J = 2.15$ Hz, aryl-6CH). ^{13}C-NMR (benzene-d_6): $\delta = 0.7$ ($SiCH_3$), 8.9 (ring-C), 20.6 (aryl-CH_3), 45.6 (NCH_3), 119.9, 124.5 and 131.6 (aryl-CH), 132.5, 140.9 and 149.1 (quart. aryl-C). ^{29}Si-NMR (benzene-d_6): $\delta = -14.2$ ($SiMe_3$), −8.7 (ring-Si). MS *m/z* (%): 642 (29) [M^+], 627 (10) [M^+-CH_3], 569 (100) [M^+-SiMe_3], 321 (62) [$(Me_3Si)_2Si{=}CH(C_6H_3Me\text{-}NMe_2)^+$]. Anal. Found: C, 59.47; H, 9.67; N, 4.36. Calc. for $C_{32}H_{62}N_2Si_6$ (643.37): C, 59.74; H, 9.71; N, 4.35%.

Z-**5**: m.p. = 205°C dec. ^{1}H-NMR (benzene-d_6): $\delta = 0.25$ and 0.36 (2s, $SiCH_3$, 2 × 18 H), 2.36 (s, aryl-CH_3, 6H), 2.57 (s, NCH_3, 12H), 3.80 (s, ring-CH, 2H), 6.77 (dd, $^3J = 8.23$ Hz, $^4J = 2.13$, aryl-4CH, 2H), 6.89 (d, $^3J = 7.93$, aryl-3CH, 2H), 7.62 (d, $^4J = 1.83$ Hz, aryl-6CH, 2H). ^{13}C-NMR (benzene-d_6): $\delta = -0.1$ and 1.7 ($SiCH_3$), 10.1 (ring-C), 20.6 (aryl-CH_3), 45.7 (NCH_3), 119.8, 124.8 and 132.2 (aryl-CH), 132.4, 139.9 and 149.3 (quart. aryl-C). ^{29}Si-NMR (benzene-d_6): $\delta = -14.4$ and −13.9 ($SiMe_3$), −6.9 (ring-Si). MS *m/z* (%): 642 (44) [M^+], 627 (10) [M^+-CH_3], 569 (100) [M^+-SiMe_3], 321 (39) [$(Me_3Si)_2Si{=}CH(C_6H_3Me\text{-}NMe_2)^+$]. Anal. Found: C, 59.50; H, 9.57; N, 4.33. Calc. for $C_{32}H_{62}N_2Si_6$ (643.37): C, 59.74; H, 9.71; N, 4.35%.

3.3. 1-(2-Dimethylamino-5-methylbenzyl)-2-[2-dimethylamino-5-methyl-(α-trimethylsiloxy)benzyl]-1,1,2,2-tetrakis(trimethylsilyl)disilane (**9**)

A total of 0.5 g (1.2 mmol) of **3** were dissolved in 30 ml of ether. The solution was cooled to −78°C and equimolar quantities of first BEt_3·THF and then of methyllithium were added. After stirring for 0.5 h the solution was allowed to warm up gradually to r.t., water was added and the ethereal phase was separated, dried and concentrated. Chromatography of the residue (silica gel; heptane–ethyl acetate, 20:1) gave 0.28 g (63%) of **9**, m.p. 132–134°C. ^{1}H-NMR (benzene-d_6): $\delta = 0.08$, 0.13, 0.36, 0.44 and 0.66 (5s, $SiSiCH_3$ and $OSiCH_3$, 5 × 9H), 2.26 and 2.29 (2s, aryl-CH_3, 2 × 3H), 2.51 and 2.57 (2s, NCH_3, 2 × 6H), 2.90 and 2.98 (2d, $^2J = 13.0$ Hz, $SiCH_2$, 2 × 1H), 6.07 (s, SiCH, 1H), 6.86–6.88 (m, aryl-CH, 4H), 7.27 (d, $^4J = 1.8$ Hz, aryl-CH, 1H), 7.59 (s, aryl-CH, 1H). ^{13}C-NMR (benzene-d_6): $\delta = 2.1$, 2.6, 2.9 and 3.0 ($SiSiCH_3$), 4.2 ($OSiCH_3$), 15.5 and 20.8 (aryl-CH_3), 45.6 and 46.5 (NCH_3), 66.9 ($SiCH_2$), 119.7, 120.4, 126.3, 127.6, 127.8, 128.3, 131.8, 132.7, 133.1, 137.9, 141.9, 147.8 and 149.8 (aromat-C and SiCH). ^{29}Si-NMR (benzene-d_6): $\delta = -64.8$ and −51.1 (SiSiMe$_3$), −13.5, −12.6 and −12.3 (two signals) (SiSiMe$_3$), 14.5 (OSiMe$_3$). MS m/z (%): 732 (23) [M^+], 717 (28) [M^+-CH_3], 643 (25) [$M^+-OSiMe_3$], 584 (17) [$M^+-CH_2C_6H_3MeNMe_2$], 236 (100) [$Me_3SiOCHC_6H_3MeNMe_2^+$]. Anal. Found: C, 57.17; H, 10.04; N, 3.82. Calc. for $C_{35}H_{72}N_2OSi_7$ (733.57): C, 57.31; H, 9.89; N, 3.82%.

3.4. 2-Dimethylaminobenzoyl-tris(trimethylsilyl)silan (**10**)

At r.t., 5.00 g (10.6 mmol) of $(Me_3Si)_3SiLi$·3THF, dissolved in 30 ml of ether, were added to an ethereal solution of 1.90 g (10.6 mmol) of methyl 2-dimethylaminobenzoate. After 2 h, stirring water was added, the organic layer separated, the aqueous phase extracted with ether, and the combined ethereal solutions were dried with $MgSO_4$ and evaporated. Chromatographic separation (silica gel; heptane–ethyl acetate, 20:1) of the residue gave 2.6 g (62%) of a yellow oil, which gradually crystallized. IR (cap.): $\tilde{\nu} = 1599$ cm^{-1} (CO). ^{1}H-NMR (benzene-d_6): $\delta = 0.28$ (s, $SiCH_3$, 27H), 2.47 (s, NCH_3, 6H), 6.66–7.21 (m, aryl-CH, 4H). ^{13}C-NMR (benzene-d_6): $\delta = 1.3$ ($SiCH_3$), 45.3 (NCH_3), 117.5, 120.7, 126.8 and 130.0 (aryl-CH), 142.9 and 149.3 (quart. aryl-C), 209.0 (CO). ^{29}Si-NMR (benzene-d_6): $\delta = -71.8$ (SiSiMe$_3$), −11.8 (SiMe$_3$). MS m/z (%): 395 (8) [M^+], 380 (60) [M^+-CH_3], 322 (17) [M^+-SiMe_3], 73 (100) [$SiMe_3^+$]. Anal. Found: C, 53.70; H, 9.44; N, 3.29. Calc. for $C_{18}H_{37}NOSi_4$ (395.84): C, 54.62; H, 9.42; N, 3.54%.

3.5. 1-[1-(2-Dimethylaminophenyl)ethenyl]-2[1-(2-dimethylaminophenyl)ethyl]-1,1,2,2-tetrakis(trimethylsilyl)disilane (**12**)

An equimolar quantity of methyllithium was added to a stirred solution of 0.5 g (1.27 mmol) of **10** in 20 ml of ether at −78°C. After gradual warming up to r.t., water was added and the organic layer separated, dried with $MgSO_4$ and evaporated. Chromatographic separation (silica gel; heptane–ethyl acetate, 20:1) of the residue afforded 0.29 g (71%) of **12** as a colorless oil, which gradually crystallized, m.p. 95–98°C. ^{1}H-NMR (benzene-d_6): $\delta = 0.10$, 0.32, 0.38 and 0.56 (4s, $SiCH_3$, 4 × 9H), 1.78 (d, $^3J = 7.63$ Hz, CHCH_3, 3H), 2.49 and 2.55 (2s, NCH_3, 2 × 6H), 3.76 (q, $^3J = 7.63$ Hz, CHCH$_3$, 1H), 5.93 and 6.25 (2d, $^2J = 3.05$ Hz, CCH_2, 2H), 6.89–7.51 (m, aryl-CH, 8H). ^{13}C-NMR (benzene-d_6): $\delta = 2.9$, 3.1 and 4.8 (two signals) ($SiCH_3$), 20.2 (CHCH_3), 24.8 (CHCH$_3$), 45.6 and 46.2 (NCH_3), 119.4, 119.9, 123.0, 124.3, 126.1, 127.5, 130.9, 131.0, 134.6, 143.2, 144.0, 149.8, 151.5 and 151.8 (olef. and aromat. C). ^{29}Si-NMR (benzene-d_6): $\delta = -62.7$ and-52.2 (SiSiMe$_3$), −13.6, −12.9, −12.3 and −12.2 (SiMe$_3$). MS m/z (%): 642 (7) [M^+], 627 (3) [M^+-CH_3], 494 (5) [$M^+-Me_2NC_6H_4CHCH_3$], 322 (70) [$Si(SiMe_3)_2$-$CHCH_3C_6H_4NMe_2^+$], 320 (100) [$Si(SiMe_3)_2CCH_2$-$C_6H_4NMe_2^+$]. Anal. Found: C, 59.71; H, 9.70; N, 4.32. Calc. for $C_{32}H_{62}N_2Si_6$ (643.37): C, 59.74; H, 9.71; N, 4.35%.

3.6. [(2-Dimethylaminophenyl)(3,5-dimethylphenyl)-methyl]-trimethylsiloxy-bis(trimethylsilyl)silane (**16**)

To 0.5 g (1.27 mmol) of **10**, dissolved in 20 ml of ether, an equimolar quantity of an ethereal 3,5-dimethylphenyllithium solution was added at −78°C. After gradual warming up to r.t., water was added and the organic layer was separated, dried with $MgSO_4$ and evaporated. Chromatography of the residue (silica gel; heptane–ethyl acetate, 20:1) gave **16** in form of a pale yellow oil, yield 0.39 g (61%). IR (cap.): $\tilde{\nu} = 1053$ cm^{-1} (SiO). ^{1}H-NMR (benzene-d_6): $\delta = 0.05$ and 0.11 (2s, $SiSiCH_3$, 2 × 9H), 2.55 (s, $OSiCH_3$, 9H), 2.21 (s, aryl-CH_3, 6H), 2.46 (s, NCH_3, 6H), 4.72 (s, SiCH, 1H), 6.69 (s, aryl-CH, 1H), 6.94–6.98 (m, aryl-CH, 1H), 7.08–7.12 (m, aryl-CH, 2H), 7.30 (s, aryl-CH, 2H), 7.78–7.82 (m, aryl-CH, 1H). ^{13}C-NMR (benzene-d_6): $\delta = -0.8$ and −0.6 ($SiSiCH_3$), 2.5 ($OSiCH_3$), 21.5 (aryl-CH_3), 40.1 (SiCH), 45.5 (NCH_3), 120.4, 123.5, 126.4, 126.8, 126.9 132.4, 137.6, 138.0, 144.0 and 153.2 (aromat. C). ^{29}Si-NMR (benzene-d_6): $\delta = -19.7$ and −19.6 (SiSiMe$_3$), −13.1 (SiSiMe$_3$), 7.0 (OSiMe$_3$). MS m/z (%): 501 (4) [M^+], 486 (13) [M^+-CH_3], 428 (100) [M^+-SiMe_3], 263 (85) [$Me_3SiOSi(SiMe_3)_2^+$]. Anal. Found: C, 61.65; H, 9.24; N, 2.98. Calc. for $C_{26}H_{47}NOSi_4$ (502.01): C, 62.21; H, 9.44; N, 2.79%.

3.7. (2-Dimethylamino-5-methylbenzoyl)tris-(trimethylsilyl)silane (17)

As described for the synthesis of **10**, 5.0 g (10.6 mmol) of $(Me_3Si)_3SiLi{\cdot}3THF$ and 2.1 g (10.6 mmol) of methyl 2-dimethylamino-5-methylbenzoate gave 2.4 g (55%) of **17** in the form of a yellow oil, which slowly crystallized. IR (Nujol): $\tilde{\nu} = 1606\ cm^{-1}$ (CO). ^{1}H-NMR (benzene-d_6): $\delta = 0.29$ (s, $SiCH_3$, 27H), 2.13 (aryl-CH_3, 3H), 2.50 (s, NCH_3, 6H), 6.67 (d, $^3J = 8.25$ Hz, aryl-CH, 1H), 6.90 (dd, $^3J = 8.23$ Hz, $^4J = 2.43$ Hz, aryl-CH, 1H), 6.99 (d, $^4J = 2.35$ Hz, aryl-CH, 1H). ^{13}C-NMR (benzene-d_6): $\delta = 1.3$ ($SiCH_3$), 20.3 (aryl-CH_3), 45.5 (NCH_3), 117.8, 127.1, 130.2, 130.4, 143.4 and 147.2 (aromat. C), 208.7 (CO). ^{29}Si-NMR (benzene-d_6): $\delta = -72.1$ (SiSiMe$_3$), -11.9 (SiMe$_3$). MS m/z (%): 409 (3) [M^+], 394 (22) [M^+-CH_3], 336 (6) [M^+-SiMe_3], 247 (2) [$Si(SiMe_3)_3^+$], 73 (100) [$SiMe_3^+$]. Anal. Found: C, 55.43; H, 9.60; N, 3.46. Calc. for $C_{19}H_{39}NOSi_4$ (409.87): C, 55.68; H, 9.59; N, 3.42%.

3.8. [2-Dimethylamino-5-methyl(α-methyl)benzyl]-trimethylsiloxy-bis(trimethylsilyl)silane (19)

To 0.5 g (1.22 mmol) of **17**, dissolved in 20 ml of ether, the equimolar quantity of methyllithium was added at −78°C. After gradual warming up to r.t., water was added and the organic phase was separated, dried with $MgSO_4$ and evaporated. Chromatographic separation (silica gel; heptane–ethyl acetate, 20:1) afforded the siloxane **19** in the form of a colorless oil, yield 0.23 g (44%). ^{1}H-NMR (benzene-d_6): $\delta = 0.11$ (s, $OSiCH_3$, 9H), 0.20 and 0.21 (2s, $SiSiCH_3$, 2×9 H), 1.61 (d, $^3J = 7.65$ Hz, CHCH_3, 3H), 2.26 (s, aryl-CH_3, 3H), 2.51 (s, NCH_3, 6H), 3.19 (q, $^3J = 7.63$, SiCH, 1H), 6.86–7.22 (m, aryl-CH, 3H). ^{13}C-NMR (benzene-d_6): $\delta = -0.8$ and -0.6 ($SiSiCH_3$), 2.3 ($OSiCH_3$), 19.0 (CHCH_3), 20.9 (SiCH), 24.5 (aryl-CH_3), 45.4 (NCH_3), 119.3, 126.3, 130.4, 132.6, 141.5 and 149.2 (aromat. C). ^{29}Si-NMR (benzene-d_6): $\delta = -20.4$ and -19.7 (SiSiMe$_3$), 2.3 (SiSiMe$_3$), 6.9 (OSiMe$_3$). MS m/z (%): 425 (2) [M^+], 410 (10) [M^+-CH_3], 352 (100) [M^+-SiMe_3], 263 (30) [$Me_3SiOSi(SiMe_3)_2^+$]. Anal. Found: C, 56.69; H, 10.07; N, 3.54. Calc. for $C_{20}H_{43}NOSi_4$ (425.91): C, 56.64; H, 10.18; N, 3.30%.

3.9. Crystal-structure determination of 5

X-ray diffraction data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo–K_α radiation. Crystals from heptane, crystal size $0.4 \times 0.3 \times 0.3$ mm^3, formula $C_{32}H_{62}N_2Si_6$, formula weight 643.38, monoclinic, space group $C2/c$, $a = 20.655(4)$, $b = 12.581(3)$, $c = 16.066(3)$ Å; $\beta = 98.32(3)°$; $V = 4131.0(15)$ Å^3; $Z = 4$; temperature 293(2) K, $\mu = 0.223\ mm^{-1}$, $F(000) = 1408$, Θ range 1.9–24.33°; index ranges $-23 \le h \le 23$, $-18 \le k \le 18$, $-14 \le l \le 14$; $d_{calc} = 1.034\ g\ cm^{-3}$, peak/hole 0.65/−0.43 e Å^{-3}, measured reflections 10 815, independent reflections 3305, observed reflections 2344, R_{int} 0.04, number of parameters 212, R_1 [$I = 2\sigma(I)$] 0.043, wR_2 (all data) 0.110. The structure was solved by direct methods (SHELXS-86) [15] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93) [16]. 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, CCDC no. 132657. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We gratefully acknowledge the support of our research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Professor M. Michalik, Dr W. Baumann and Professor N. Stoll for recording the NMR and MS spectra, respectively.

References

[1] C. Krempner, D. Hoffmann, H. Oehme, R. Kempe, Organometallics 16 (1997) 1828.
[2] A.G. Brook, K.M. Baines, Adv. Organomet. Chem. 25 (1986) 1.
[3] D. Bravo-Zhivotovskii, V. Brande, A. Stanger, M. Kapon, Y. Apeloig, Organometallics 11 (1992) 2326.
[4] (a) J.Ohshita, Y. Masaoka, M. Ishikawa, Organometallics 10 (1991) 3775. (b) J. Ohshita, Y. Masaoka, M. Ishikawa, T. Takeuchi, Organometallics 12 (1993) 876.
[5] K. Schmohl, M. Blach, H. Reinke, R. Kempe, H. Oehme, Eur. J. Inorg. Chem. (1998) 1667 and literature cited therein.
[6] D. Hoffmann, H. Reinke, H. Oehme, J. Organomet. Chem. 585 (1999) 189.
[7] T. Müller, W. Ziche, N. Auner, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2, John Wiley, New York, 1998, p. 927.
[8] (a) A.G. Brook, J.W. Harris, J. Lennon, M. ElSheikh, J. Am. Chem. Soc. 101 (1979) 83. (b) K. Baines, A.G. Brook, Organometallics 6 (1987) 692.
[9] C. Krempner, H. Reinke, H. Oehme, Chem. Ber. 128 (1995) 143.
[10] T. Müller, W. Ziche, N. Auner, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2, John Wiley, New York, 1998, p. 919.

[11] A.G. Brook, S.C. Nyburg, W.F. Reynolds, Y.C. Poon, Y.-M. Chang, J.-S. Lee, J. Am. Chem. Soc. 101 (1979) 6750.
[12] C. Krempner, R. Kempe, H. Oehme, Z. Naturforsch. 52b (1997) 815.
[13] F. Luderer, H. Reinke, H. Oehme, J. Organomet. Chem. 510 (1996) 181.
[14] G. Gutekunst, A.G. Brook, J. Organomet. Chem. 225 (1982) 1.
[15] G.M. Sheldrick, SHELXS-86, University of Göttingen, Germany, 1986.
[16] G.M. Sheldrick, SHELXL-93, University of Göttingen, Germany, 1983.