

Synthesis of the first long-lived bis-silene

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Abstract

The sila-olefination reaction has been used to synthesize the first long-lived bis-silene *t*-BuMe₂Si(Me₃Si)Si=(2,6-Ad)=Si(SiMe₃)SiMe₂Bu-*t* (**1**). In this paper, we report the synthesis, spectroscopic data and some reactions of **1**. Our experiments show that the elimination step of sila-olefination reaction is strongly accelerated in diethyl ether (and other ethers) relative to toluene and by increasing the steric bulk around the silicon center undergoing elimination.

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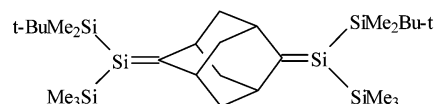
Keywords: Lithium; Silaethenes; Silicon; Silanes; Silenes

1. Introduction

The first stable silene was synthesized only in 1981 [1] after decades of intensive unsuccessful attempts [2]. However, despite intensive recent research, only a few methods for the synthesis of stable silenes are currently known and only a small number of stable silenes have so far been isolated [2].

Difunctional systems are very useful in synthesis, e.g. as polymer precursors, as ligands in organometallic complexes, etc. Stable or persistent compounds containing two silicon–carbon double bonds, i.e. bis-silenes, are not yet known [2]. Several attempts to generate such species resulted only in the possible formation of transient bis-silenes [3–5]. The synthesis of a bis-amine complex of a bis-silene, which has a relatively long lifetime ($t_{1/2} = 29–41$ h at room temperature), was briefly reported in a review [5c], but to the best of our knowledge detailed experimental data on this compound were not yet reported. The other bis-silenes reported are extremely reactive species [3–5]. In this paper, we report the synthesis, spectroscopic data and some reactions of

the first long-lived bis-silene, *t*-BuMe₂Si(Me₃Si)Si=(2,6-Ad)=Si(SiMe₃)SiMe₂Bu-*t* (**1**).



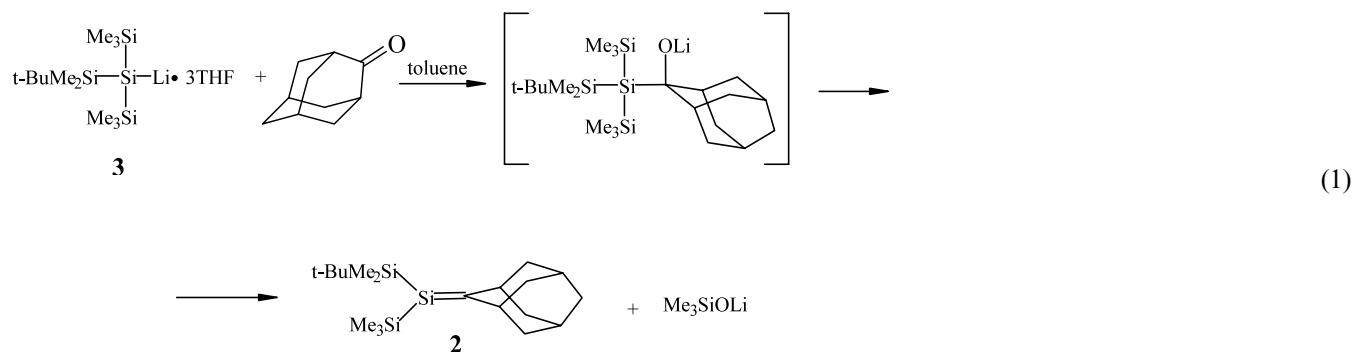
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2. Result and discussion

Our group reported recently the synthesis, using a sila-olefination reaction (Eq. (1)), of a new stable silene *t*-BuMe₂Si(Me₃Si)Si=2-Ad (**2**) and reported its X-ray structure [6]. In this reaction, 2-adamantanone was reacted in toluene with the THF-complexed silyl anion **3** (Eq. (1)). The analogous Peterson olefination is a well-known reaction for the preparation of alkenes from α -silyl carbanions and carbonyl compounds [7]. In analogy to the Peterson olefination reaction [7], also the sila-olefination reaction is believed to follow a multistep mechanism as shown in Eq. (1), involving a silyl transfer from carbon to oxygen, followed by elimination of the silanolate [6].

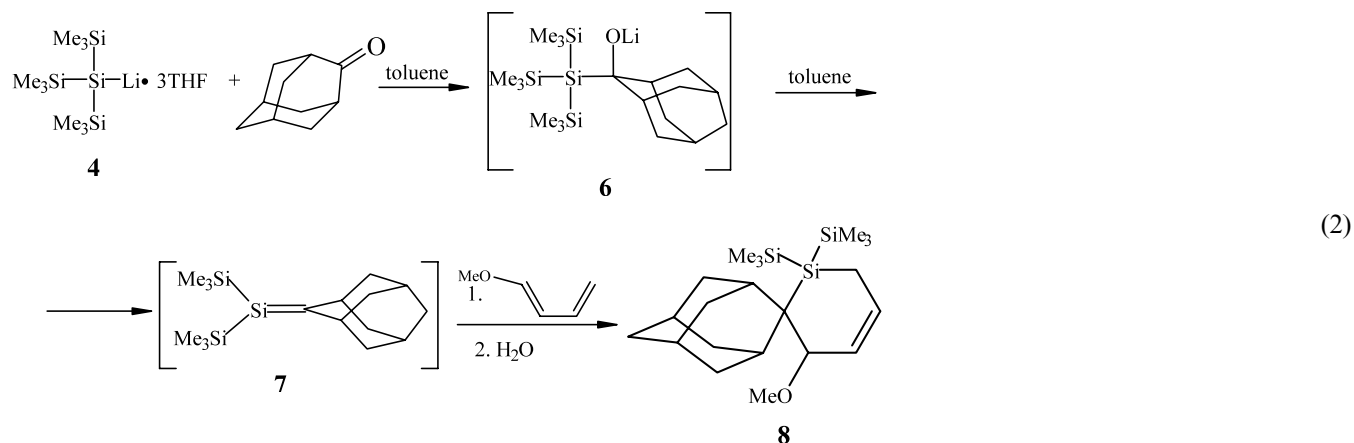
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Our first attempt to prepare a bis-silene used an analogous reaction to that in Eq. (1), i.e. the reaction in toluene of adamantanone with 2 mol of THF-complexed hypersilyllithium reagent **4**. The reaction yielded the corresponding bis-adduct **5** in 85% yield. However, **5** was found to be stable towards elimination

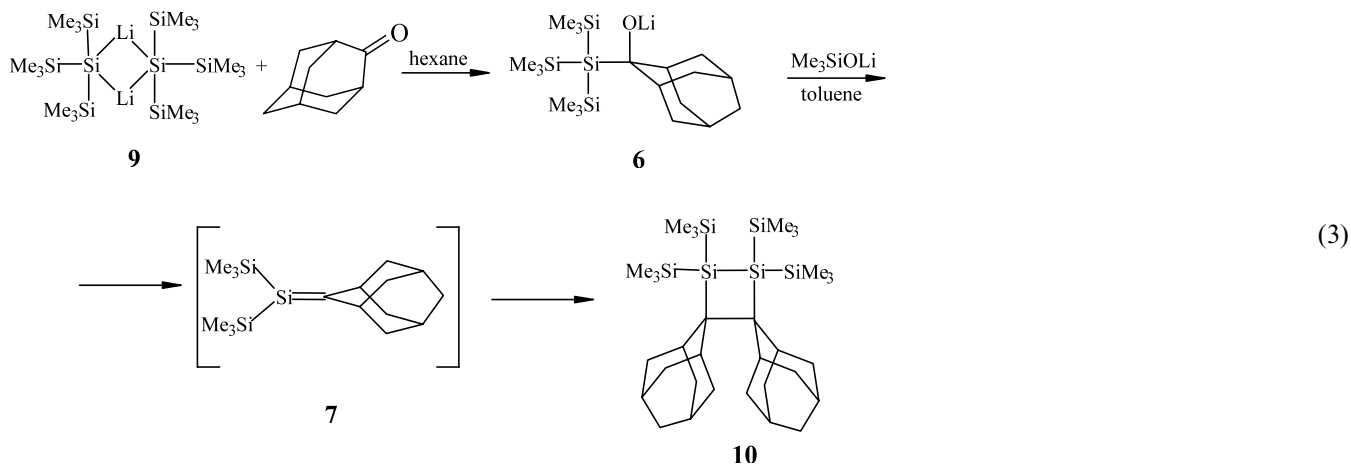
In an attempt to promote elimination of Me_3SiOLi from **5**, we have examined the effect of the solvent and of the complexing molecules of the silyl anion on the sila-olefination reaction. The non-solvated dimeric hypersilyl anion **9** reacts with 2-adamantanone in non-coordinating solvents (e.g. hexane) to give the stable



and it remains unchanged even after heating at 75 °C for 24 h (Scheme 1). This contrasts to behavior of the closely related mono-adduct **6**, which spontaneously eliminates Me_3SiOLi under these conditions, producing silene **7** as supported by the isolation of its trapping product with 1-methoxy-1,3-butadiene (**8**) (Eq. (2)) [8].

adduct **6** (Eq. (3)). The reaction shown in Eq. (3) is the first in which the intermediate alcoholate **6** could be isolated, and this allowed us to study the rate of its elimination reaction.

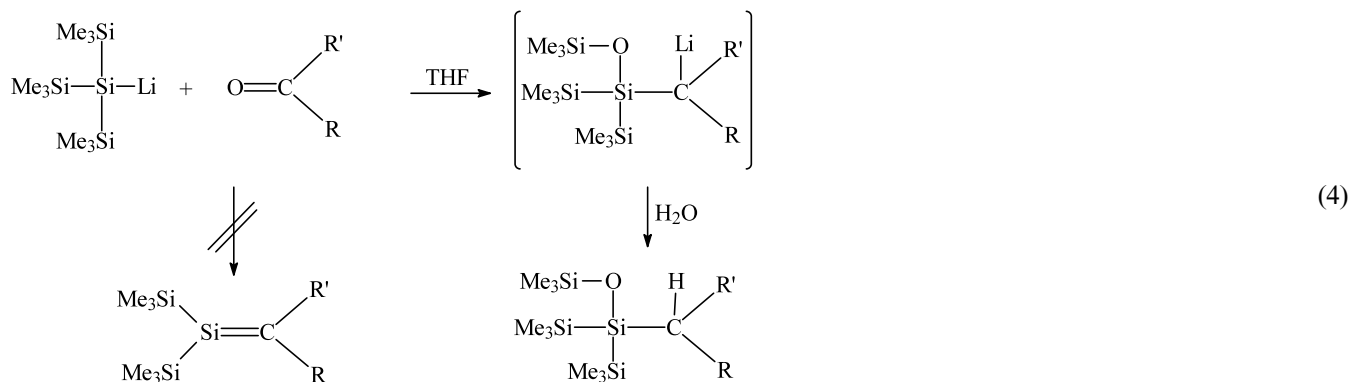
In toluene, the alcoholate **6** slowly eliminates Me_3SiOLi to give the corresponding transient silene **7**, which

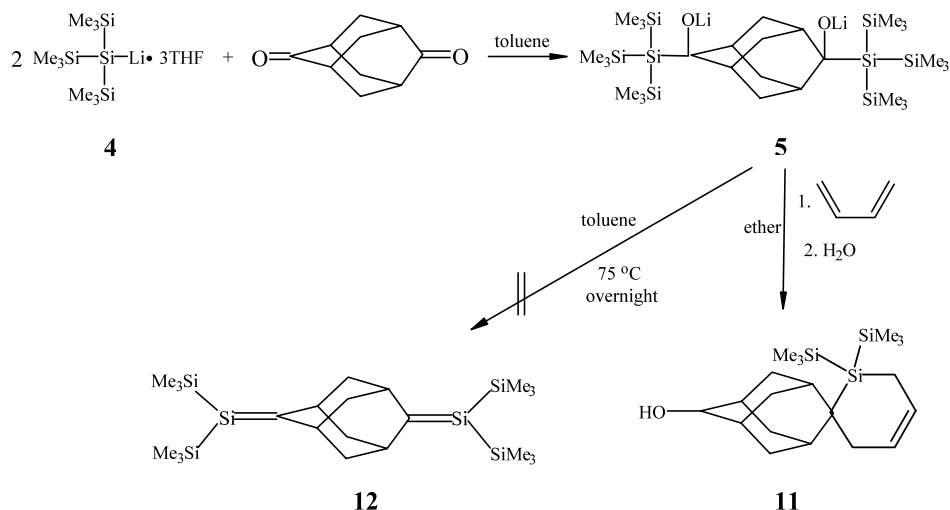


instantaneously dimerizes to the corresponding 1,2-disilacyclobutane (**10**). In the presence of 1,3-butadiene, the expected [4+2] adduct [**6**] is obtained. The half-life of **6** in benzene or in toluene at room temperature is approximately 2 days. When the elimination is carried out in the presence of one equivalent of THF the reaction is much faster, with a half-lifetime of 0.5–1 h. However, when three equivalents of THF are present the elimination occurs instantaneously. Similarly, we found previously [8] that in the reaction of 2-adamantanone with $(\text{Me}_3\text{Si})_3\text{SiLi}\cdot 3\text{THF}$ in toluene the elimination is spontaneous and the alcoholate adduct **6** could not be isolated. Oehme and coworkers [9] have previously found that in THF solution the silolefination reaction proceeds by a different pathway leading to rearrangement instead of elimination (Eq. (4)).

The results presented above suggest that the rate of elimination of the silanolate from the alcoholate **6** is accelerated by increasing the solvating ability of the media or the coordinating ability of the added molecules. Following this clue, adamantane-2,6-dione was reacted with THF-coordinated hypersilyllithium **4** in diethyl ether solution in the presence of 1,3-butadiene. Adduct **11** (Scheme 1) is obtained in a moderate yield (30% after separation by liquid chromatography). We do not yet fully understand the reaction pathway which leads to **11**. However, the isolation of **11** indicates that under these conditions elimination to produce the corresponding silene (which is trapped by butadiene) occurs.

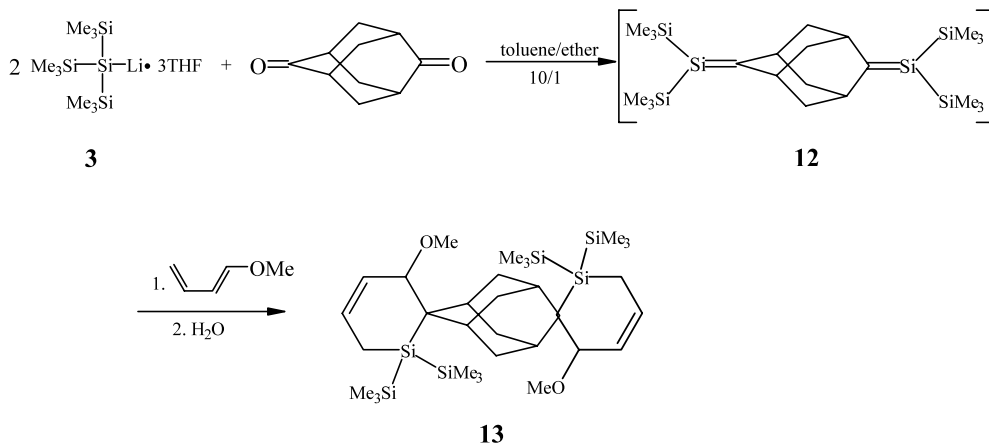
The desired reaction can be achieved by a minor change in the solvent. When adamantane-2,6-dione is reacted with THF-coordinated hypersilyllithium reagent





Scheme 1.

4 (in the presence of 1-methoxy-1,3-butadiene) in an ether–toluene (1:10) solution, the bis-adduct **13** is obtained in 60% yield (Scheme 2). This strongly indicates that the desired bis-silene **12** is formed as an intermediate and that it is trapped by two molecules of 1-methoxy-1,3-butadiene to produce **13** (Scheme 2).



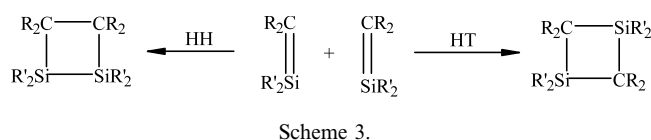
Scheme 2.

The structure of **13** was determined in analogy to the very similar mono-cycloaddition product **8** obtained from the transient silene **7** and 1-methoxy-1,3-butadiene (Eq. (2)) [8]. The close similarity of the ^1H - and ^{13}C -NMR chemical shifts associated with the six-membered rings of **13** and **8** strongly support the structure assigned to **13** (Scheme 2). The single peak related to the OMe group in the ^1H - and ^{13}C -NMR spectra (at 3.06 and 54.8 ppm, respectively) of the crude reaction mixture suggests that **13** is the only product, indicating that this cycloaddition reaction of bis-silene **12** is highly regioselective (Scheme 2).

Attempts to isolate the bis-silene **12** or to record its NMR were not successful. In the absence of trapping

reagents a polymer is formed. Most silenes dimerize in a head-to-tail (HT) fashion (Scheme 3), a process which is usually thermodynamically more favorable than the alternative head-to-head (HH) process [2].

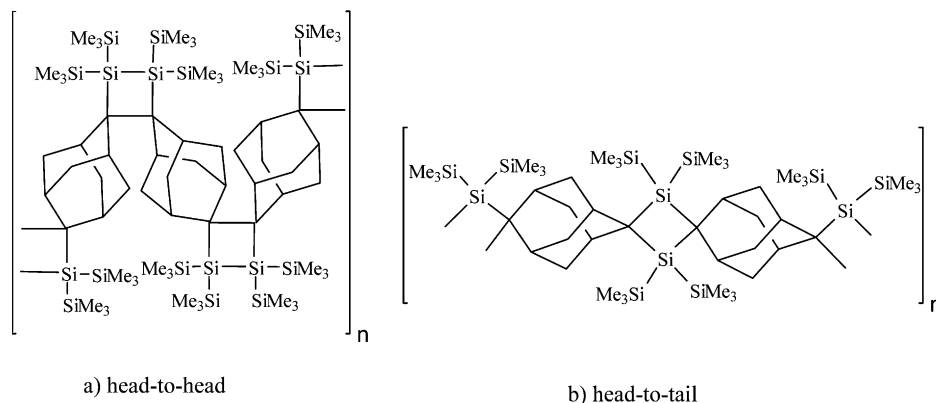
According to the solid-state NMR spectroscopy, the polymer obtained from **12** possesses exclusively units



Scheme 3.

resulting from a head-to-head dimerization of the $\text{C}=\text{Si}$ bonds. The proposed structure of the polymer is shown in Scheme 4a.

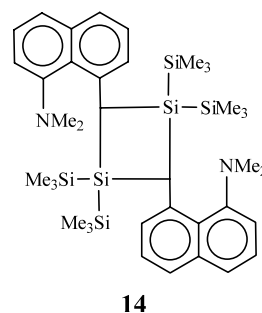
The assignment of the repeating unit of the polymer as being head-to-head is based on the almost identical



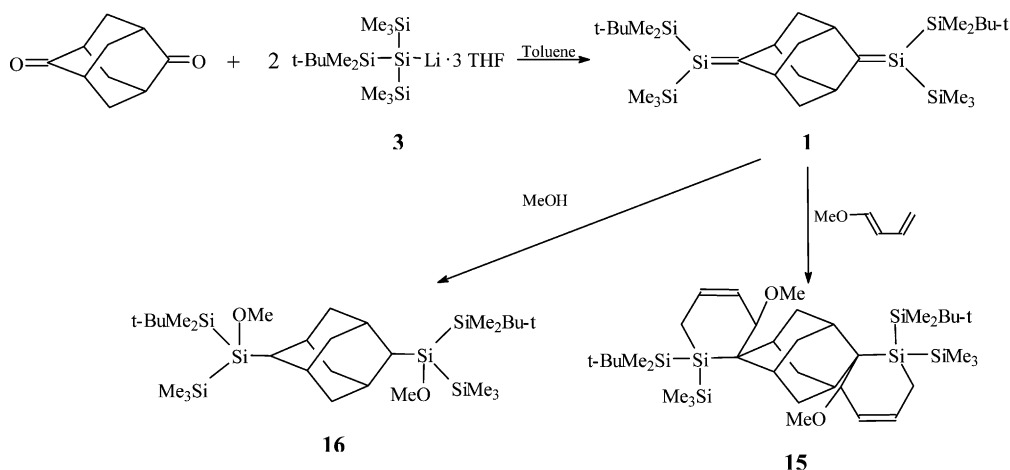
Scheme 4.

chemical shifts in the ^{13}C - and ^{29}Si -NMR spectra of the polymer product resulting from bis-silene **12** and those of **10** (see Section 4 for more details; **10** was characterized by X-ray crystallography). The polymer resulting from head-to-tail dimerization (Scheme 4b) is expected to have a very different ^{29}Si -NMR chemical shift of the endocyclic central silicon atom, as a result of the smaller number of silicon atoms bonded to it, i.e. in the head-to-tail repeating unit only two silyl substituents are bonded to the ring silicon atom, while in the head-to-head structure each of the ring silicon atom is connected to three silicon atoms.

For example, Oehme et al. [9c] reported recently the synthesis of the 1,3-disilacyclobutane (**14**). The ^{29}Si -NMR chemical shift of the endocyclic central silicon atom in **14** is 2.3 ppm, while in the polymer resulting from dimerization of bis-silene **12** the ^{29}Si chemical shift of the endocyclic central silicon atom appears at -44 ppm. The fact that bis-silene **12** reacts in a head-to-head fashion is consistent with the behavior of the transient silene **7** which in the absence of trapping agents spontaneously dimerizes in a head-to-head fashion to give **10**.



The highly reactive bis-silene **12** can be stabilized by using more bulky silyl substituents. Thus, when one of the methyl groups in **4** is substituted by a *t*-butyl group and the resulting **3** reacts with adamantane-2,6-dione in toluene the long-lived bis-silene **1** is obtained (Scheme 5). The fact that the bis-adduct resulting from the reaction of **3** with adamantane-2,6-dione eliminates spontaneously two Me_3SiOLi groups in toluene solution while the closely related bis-adduct **5** is highly stable under this conditions indicates that increase of the steric repulsion around the silicon center strongly accelerates



Scheme 5.

the elimination reaction. The bis-silene **1** is stable in hexane or toluene solution for several months at room temperature. Addition of 1-methoxy-1,3-butadiene yields the expected [4+2] bis-cycloaddition product **15**. Addition of methanol to the bis-silene solution produces the expected bis-ether **16** (Scheme 5). These trapping experiments strongly support the conclusion that the bis-silene **1** is present in solution. Further evidence for the proposed structure of **1** comes from the close similarity of the ^1H -, ^{13}C - and ^{29}Si -NMR spectra of **1** to those of the analogous silene **2**. Thus, the chemical shifts of the doubly bonded silicon and carbon atoms are 52.8 and 169.6 ppm, respectively, in **1** compared to 51.7 and 169.8 ppm, respectively, in **2**. The close similarity of these chemical shifts also indicates that there is no significant interaction between the two C=Si double bonds of **1**.

The synthesis of **1** was repeated six times in order to obtain suitable crystals for X-ray analysis. In two cases, crystallization lead to colorless crystals which we believed were suitable for X-ray analysis. Unfortunately, the crystals of **1** appear to be very sensitive and so far our attempts to solve the X-ray structure of **1** were unsuccessful.

It is interesting to note that the bis-silene **1** is a chiral molecule, which belongs to the C_2 point-group symmetry, since its two double bonds occupy two perpendicular planes. We have not yet attempted to separate **1** into its enantiomers, but this is an interesting goal for future work.

3. Conclusions

In this paper, we report the synthesis and the ^1H -, ^{13}C - and ^{29}Si -NMR spectra of the first long-lived bis-silene **1**. **1** exhibits a similar NMR spectra and reactivity to those of related silenes. We also found that the elimination step of sila-olefination reaction is strongly accelerated (relative to toluene) in better coordinating media such as diethyl ether and by increasing the steric bulk around the silicon center undergoing elimination.

4. Experimental

Standard Schlenk techniques were used for all syntheses and all sample manipulations. NMR spectra were recorded at room temperature (r.t.) in C_6D_6 solution using a Bruker EM-200 or Bruker-400 instruments. Mass spectroscopy (MS) data were obtained with a Finnigan MAT TSQ 70 triplestage quadrupole mass spectrometer (CI was produced with isobutene carrier gas).

Adamantane-2,6-dione was synthesized according to a procedure reported previously [10].

4.1. Preparation of $(\text{Me}_3\text{Si})_3\text{Si}(\text{OLi})\text{Ad}(\text{OLi})\text{Si}(\text{SiMe}_3)_3$ (**5**)

1 g (2.1 mmol) of **4** in 30 ml of dry toluene was placed in a Schlenk flask under vacuum and 0.1 g (0.6 mmol) of adamantane-2,6-dione in 10 ml of dry toluene was added at -78°C . The reaction was allowed to reach r.t. and stirring was continued for 2 h. During this time, a powder precipitated. The toluene solution was decanted and the powder was washed three times with 10 ml of dry hexane. The combined organic solution was evaporated under vacuum to give **5** at 65% yield. ^1H -NMR (C_6D_6): δ 0.32 (s, 54H, $\text{Si}(\text{SiMe}_3)_3$), 1.07–2.78 (m, 10H, Ad); ^{13}C -NMR (C_6H_6): δ 3.53 ($\text{Si}(\text{SiMe}_3)_3$), 32–54 (Ad), 90.10 (C–OLi); ^{29}Si -NMR (C_6D_6): δ -66.3 ($\text{Si}(\text{SiMe}_3)_3$), -13.2 ($\text{Si}(\text{SiMe}_3)_3$). Hydrolyze of **5** lead to the corresponding di alcohol. ^1H -NMR (C_6H_6): δ 0.29 (s, 54H, $\text{Si}(\text{SiMe}_3)_3$), 1.07–2.78 (m, 10H, Ad); ^{13}C -NMR (C_6H_6): δ 2.88 ($\text{Si}(\text{SiMe}_3)_3$), 25.30, 29.81, 34.17, 38.10, 38.22 (Ad), 81.04 (C–OH); ^{29}Si -NMR (C_6H_6): δ -61.5 ($\text{Si}(\text{SiMe}_3)_3$), -13.0 ($\text{Si}(\text{SiMe}_3)_3$). MS (CI): *m/e* 643 [$\text{MH}^+ - \text{OH}$], 629 [$\text{MH}^+ - \text{MeOH}$].

4.2. Preparation of **11**

0.1 g (0.21 mmol) of **4** in 10 ml of dry diethyl ether and 0.1 ml of butadiene was placed in a Schlenk flask under vacuum, and 0.01 g (0.06 mmol) of adamantane-2,6-dione in 2 ml of dry diethyl ether was added at -78°C . The reaction was allowed to reach r.t. and was stirred overnight. After addition of water the organic layer was separated and dried over magnesium sulfate and the solvent was evaporated giving a yellow oil. The crude product was separated by HPLC liquid chromatography on a reverse phase silica in methanol to give **11** in 30% yield. ^1H -NMR (CDCl_3): δ 0.13 (s, 18H, $\text{Si}(\text{SiMe}_3)_2$), 1.49 (d, 2H, $\text{CH}_2\text{-Si}$), 1.75–2.4 (m, 13H, Ad), 2.35 (d, 2H, $\text{CH}_2\text{-Ad}$), 5.67 (q, 1H, $=\text{CH-CH}_2\text{-Si}$), 5.93 (q, 1H, $=\text{CH-CH}_2\text{-Ad}$). MS (CI): *m/e* 361 [M-OH], 288 [$\text{M-SiMe}_3\text{OH}$].

4.3. Trapping experiments of the transient bis-silene **12**

1 g (2.1 mmol) of **4** in 27 ml of toluene solution and 0.3 ml of methoxybutadiene was placed in a Schlenk flask under vacuum, and 0.1 g (0.6 mmol) of adamantane-2,6-dione in 3 ml of dry diethyl ether was added at -78°C . The reaction was allowed to reach r.t. and stirred overnight. After addition of water the organic layer was separated and dried over magnesium sulfate and the solvent was evaporated giving a yellow oil. The crude was separated by HPLC liquid chromatography on the reverse phase silica in methanol to give **12** in 65% yield. ^1H -NMR (C_6D_6): δ 0.26, 0.31 (s, 18H, Me_3Si), 1.37–2.39 (m, 14 H, Ad and CH_2Si), 3.06 (s, 6H, OCH_3), 4.40 (d, 2H, CH-OCH_3), 5.57–5.62 (m, 2H,

CH=CH–CH–OCH₃), 6.13–6.18 (m, 2H, CH₂–CH=CH); ¹³C-NMR (C₆D₆): δ 1.02, 1.41 (Me₃Si), 11.20 (CH₂Si), 24.50, 32.14, 32.83, 35.54, 39.12, 50.46 (Ad), 54.80 (OCH₃), 78.78 (CH–OCH₃), 128.30 (CH=CH–CH–OCH₃), 133.37 (CH₂–CH=CH); ²⁹Si-NMR (C₆D₆): δ –12.7, –14.0 (Si(SiMe₃)₂), –43.6 (Si(SiMe₃)₂). MS (CI): *m/e* 648 [M⁺], 633 [M⁺–Me], 617 [M⁺–OMe], 575 [M⁺–SiMe₃].

4.4. Polymer product obtained from 12

GPC 5600, *M_w* = 4385, *M_n* = 2840, *P*(*M_w*/*M_n*) = 1.54. ¹H-NMR (C₆D₆): δ 0.44 (br m, 18H, Me₃Si), 1.90–3.15 (br m, 12H, Ad); ¹³C-NMR (C₆D₆): δ 3.82, 5.97 (Me₃Si), 22–40 (Ad). ²⁹Si SS-NMR: δ –12.7, –13.6 (Si(SiMe₃)₂), –44.2 (Si(SiMe₃)₂).

4.5. *t*-BuMe₂Si(Me₃Si)Si=(2,6-Ad)=Si(SiMe₃)SiMe₂Bu-*t* (1)

3.0 g (5.9 mmol) of **3** in 50 ml of dry toluene was placed in a Schlenk flask under vacuum and 0.46 g (2.8 mmol) of adamantane-2,6-dione in 20 ml of dry toluene was added. The reaction mixture was stirred overnight at r.t. (complete conversion was detected by NMR), the toluene was removed and 50 ml of dry pentane was added. The mixture was cooled to –78 °C and after 24 h white crystals of Me₃SiOLi precipitated and were separated. The solution was concentrated to 5 ml and at –5 °C colorless crystals of **1** were formed. ¹H-NMR (C₆D₆): δ 0.18 (s, 12H, *t*-BuMe₂Si), 0.26 (s, 18H, Me₃Si), 0.93 (s, 18H, *t*-Bu), 2.01–2.45 (br m, 6H, Ad), 3.35 (m, 4H, CH=C=Si); ¹³C-NMR (C₆D₆): δ –2.11 (*t*-BuMe₂Si), 2.44 (Me₃Si), 18.4 (Me₃C), 27.53 (Me₃C), 42.31, 42.86, 45.69, 45.88 (Ad), 196.60 (C=Si); ²⁹Si-NMR (C₆D₆): δ –14.3 (Me₃Si), 1.2 (*t*-BuMe₂Si), 52.8 (Si=C).

4.6. Trapping reactions of 1

4.6.1. Reaction with 1-methoxy-2,4-butadiene

The reaction mixture of **3** with adamantane-2,6-dione (see above) was stirred overnight and then 2 mol equivalents of 1-methoxy-1,3-butadiene was added. The product **15** was separated by column chromatography with hexane as an eluent. ¹H-NMR (C₆D₆): δ 0.26 (s, 6H, *t*-BuMe₂Si), 0.31 (s, 18H, Me₃Si), 1.08 (s, 18H, *t*-Bu), 1.58, 1.50 (m, each 2H, CH₂Si), 1.98–2.56 (m, 12H, Ad), 3.04 (s, 6H, OCH₃), 4.49 (d, 2H, CH–OCH₃), 5.50–5.70 (m, 2H, CH=CH–CH–OCH₃), 6.10–6.3 (m, 2H, CH₂–CH=CH); ¹³C-NMR (C₆D₆): δ –1.68 (*t*-BuMe₂Si), 1.84 (Me₃Si), 13.27 (CH₂Si), 19.60 (Me₃C), 28.38 (Me₃C), 29.04, 31.91, 33.05, 36.36 (Ad), 54.75 (OCH₃), 79.07 (CH–OCH₃), 128.08 (CH=CH–CH–OCH₃), 133.28 (CH₂–CH=CH); ²⁹Si-NMR (C₆D₆): δ –3.7, –12.2, –42.0.

4.6.2. Reaction with methanol

Methanol was added to a toluene solution of **1**. The reaction mixture was washed by water. The organic layer was separated, dried over MgSO₄, the volatile materials were evaporated under vacuum and **17** was obtained in nearly quantitative yield. **16** was recrystallized from hexane. ¹H-NMR (CDCl₃): δ 0.06 (s, 6H, *t*-BuMe₂Si), 0.09 (s, 6H, *t*-BuMe₂Si), 0.14 (s, 18H, Me₃Si), 0.92 (s, 18H, *t*-Bu), 1.66–2.27 (m, 12H, Ad), 3.45 (3H, s, OMe); ¹³C-NMR (CDCl₃): δ –3.50 (*t*-BuMe₂Si), –3.25 (*t*-BuMe₂Si), 0.70 (Me₃Si), 27.81 (Me₃C), 29.63, 32.04, 33.05, 37.45 (Ad); ²⁹Si-NMR (CDCl₃): δ –19.84 (Me₃Si), –7.65 (*t*-BuMe₂Si), 19.36 (SiOMe).

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References

- [1] (a) A.G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst, R.K.J. Kallury, Chem. Soc. Chem. Commun. (1981) 191.; (b) A.G. Brook, S.C. Nyburg, F. Abdesaken, B. Gutekunst, G. Gutekunst, R.K.M.R. Kallury, Y.C. Poon, Y. Chang, W. Wong-Ng, J. Am. Chem. Soc. 104 (1982) 5668.
- [2] (a) G. Raabe, J. Michl, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organosilicon Compounds (Chapter 17), Wiley, Chichester, UK, 1989 (Chapter 17); (b) T. Müller, W. Ziche, N. Auner, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2, Wiley, New York, 1998; (c) J. Escudie, C. Couret, H. Ranaivonjatovo, Coord. Chem. Rev. 178–180 (1998) 565; (d) T.L. Morkin, W.J. Leigh, Acc. Chem. Res. 34 (2001) 129.
- [3] M. Ishikawa, H. Sakamoto, T. Tabuchi, Organometallics 10 (1991) 3173.
- [4] V. Volkova, L. Gusel'nikov, E. Volnina, E. Buravtseva, Organometallics 13 (1994) 4603.
- [5] (a) W. Ando, H. Yoshida, K. Kurishima, M. Sugiyama, J. Am. Chem. Soc. 113 (1991) 7790; (b) W. Ando, M. Sugiyama, T. Suzuki, C. Kato, Y. Arakawa, Y. Kabe, J. Organomet. Chem. 499 (1995) 99; (c) W. Ando, Bull. Chem. Soc. Jpn. 69 (1996) 1; (d) V.Ya. Lee, M. Ichinohe, A. Sekiguchi, J. Am. Chem. Soc. 122 (2000) 12604; (e) D. Ostendorf, W. Saak, D. Haase, M. Weidenbruch, J. Organomet. Chem. 636 (2001) 7.
- [6] Y. Apeloig, M. Bendikov, M. Yuzefovich, M. Nakash, D. Bravo-Zhivotovskii, D. Blaser, R. Boese, J. Am. Chem. Soc. 118 (1996) 12228.
- [7] D.J. Ager, Org. React. 38 (1990) 4.
- [8] D. Bravo-Zhivotovskii, V. Braude, A. Stanger, M. Kapon, Y. Apeloig, Organometallics 11 (1992) 2326.

- [9] (a) C. Krempner, H. Reinke, H. Oehme, Chem. Ber. 128 (1995) 143;
(b) C. Krempner, H. Oehme, J. Organomet. Chem. 464 (1994) C7;
(c) H. Oehme, R. Wustrack, A. Heine, G.M. Sheldrick, D. Stalke, J. Organomet. Chem. 452 (1993) 33;
(d) C. Krempner, H. Reinke, H. Oehme, Angew. Chem. Int. Ed. Engl. 33 (1994) 1615;
(e) C. Krempner, H. Reinke, H. Oehme, Chem. Ber. 128 (1995) 1083;
(f) F. Luderer, H. Reinke, H. Oehme, Chem. Ber. 129 (1996) 15.
- [10] H.W. Geluk, J.L.M.A. Schlatmann, Recl. Trav. Chim. Pays-Bas 90 (1971) 516.