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Intramolecularly donor-stabilized silenes: Part 5. Generation and conversion of 1-[2,6-bis(alkoxymethyl)phenyl]- and 1-(8-alkoxynaphthyl)-1,2,2-tris(trimethylsilyl)silenes ☆

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Abstract

1-(8-Methoxy-1-naphthyl)-1,2,2-tris(trimethylsilyl)silene (**10**) and the 1-[2,6-bis(alkoxymethyl)phenyl]-1,2,2-tris(trimethylsilyl)silenes (**12a–d**) were generated by the reaction of (dichloromethyl)tris(trimethylsilyl)silane (**1**) with two molar equivalents of 8-methoxy-1-naphthyllithium or 2,6-bis(alkoxymethyl)phenyllithium (**8a–d**), respectively, but proved to be unstable. **10** was trapped with excess of the applied naphthyllithium reagent to give 1,1-bis(8-methoxy-1-naphthyl)-1-[bis(trimethylsilyl)methyl]-2,2,2-trimethyldisilane (**11**); and **12a–d** underwent spontaneous conversions and formed two types of substituted 2-oxa-1-silaindane derivatives (**13a**,**b** and **14b–d**). Whereas silenes with an intramolecular amine coordination are thermally stable compounds which can be isolated, the intramolecular coordination of an ether group to the electrophilic silene silicon atom does not provide a comparable stabilization to the Si=C system and the respective derivatives generated were converted into resultant products.

Keywords: Insertion reactions; Rearrangements; Silaethenes; Silanes; Silenes

1. Introduction

The reaction of (dichloromethyl)tris(trimethylsilyl)silane (**1**) with organolithium compounds proved to be a versatile and straightforward method for the synthesis of silenes. The deprotonation of **1** by RLi initiates a sequence of elimination and isomerization steps leading to 1,2,2-tris(trimethylsilyl)silenes (**2**) (Scheme 1). In case of RLi=MeLi, *n*-BuLi, PhLi and MesLi the resulting sterically more or less unprotected silenes $R(Me_3Si)Si{=}C(SiMe_3)_2$ (**2**) (R=Me, nBu, Ph, Mes) are unstable with respect to further addition of RLi across the polarized Si=C bond and are trapped by excess RLi to give finally – after hydrolytic workup – [bis(trimethylsilyl)methyl]silanes $R_2(Me_3Si)Si[CH(SiMe_3)_2]$ (**3**) [1]. In these cases, for the whole reaction three molar equivalents of RLi are necessary, but, unfortunately, a decrease of the molar ratio **1**/RLi to 1:2 does not prevent formation of **3**. Obviously, the deprotonation of **1** is a slow process compared with the subsequent steps, and therefore the intermediate silenes **2** always meet an effective excess of RLi. But, when organolithium compounds are chosen with groups R, which, when introduced to the silene silicon atom of **2**, provide sufficient stabilization, e.g. by their steric bulk, the reaction stops at this stage and stable silenes **2** can be isolated [1b].

The efficiency of the new method was best demonstrated by the synthesis of stable intramolecularly amine-coordinated silenes [2]. Thus, e.g. **4**, **5** and **6** were prepared in high yields by a simple one-pot reaction of **1** with two molar equivalents of 8-dimethyl-

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☆ For Part 4, see [2d].

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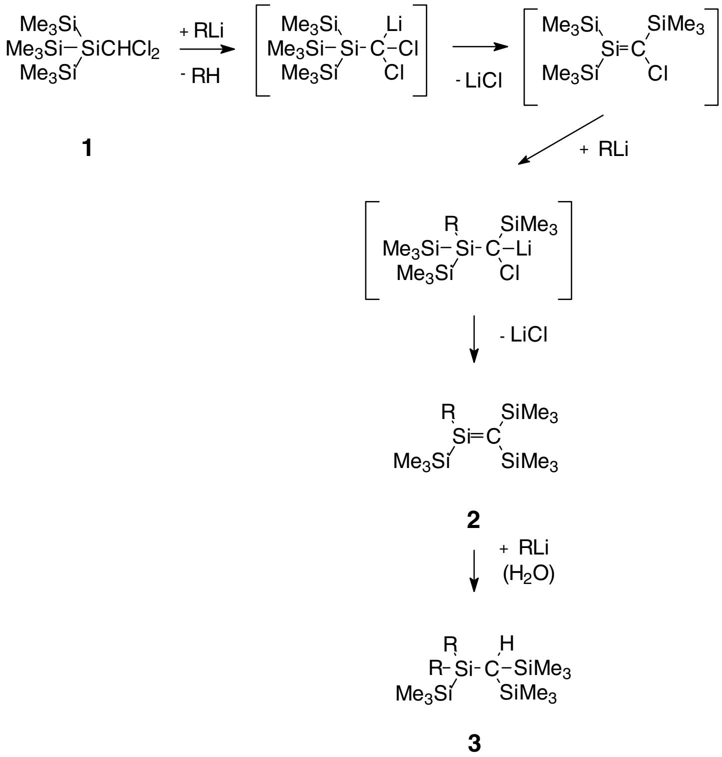
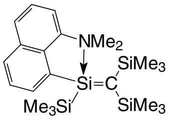


Scheme 1. The reaction of (dichloromethyl)tris(trimethylsilyl)silane (**1**) with organolithium compounds.

amino-1-naphthyllithium, 2-(dimethylaminomethyl) phenyllithium or 2,6-bis (dimethylaminomethyl)phenyllithium, respectively.



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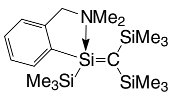

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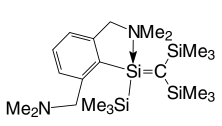

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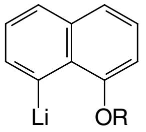
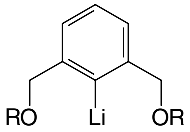
The high stability of silenes of the type **4**–**6** is attributed to a strong donor–acceptor interaction between the nitrogen lone pairs and the silene silicon atoms reducing the electrophilic properties of the Si=C systems. This way further addition reactions of a third equivalent of the applied dialkylaminoaryllithium compounds to the silene groups are prevented and **4**–**6** could be isolated and characterized by X-ray structural analyses [2a,2b,2c].

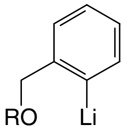
In this paper we pursue the question whether intramolecularly donor-stabilized silenes are accessible, in which the dialkylamino groups of **4**–**6** are replaced by alkoxy groups. For that purpose we have chosen the alkoxyaryl- and (alkoxymethyl)aryl lithium compounds **7**–**9** and studied their reactions with (dichloromethyl)tris(trimethylsilyl)silane (**1**).



7a-c



8a-d



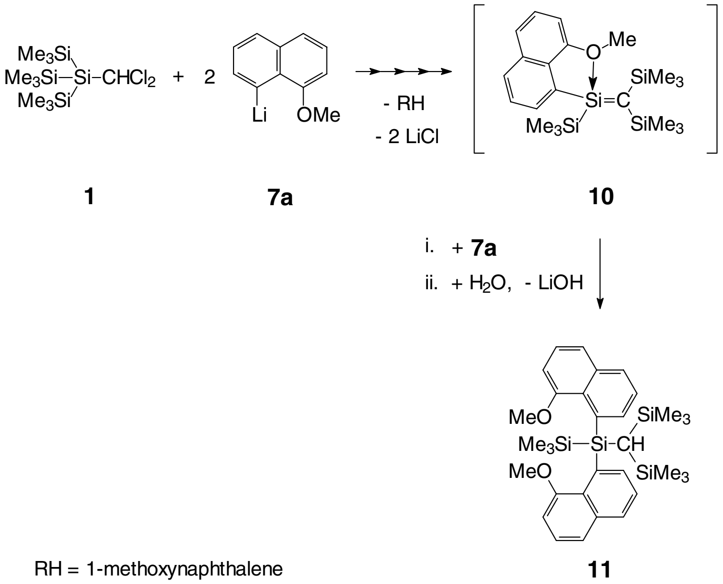
9a-c

(**a**: R=Me; **b**: R=Et; **c**: R=iPr; **d**: R=tBu)

2. Results and discussion

The reaction of the dichloromethylsilane **1** with 8-methoxy-1-naphthyllithium (**7a**) (1:2), made by direct metalation of 1-methoxynaphthalene with tertbutyllithium, afforded 1,1-bis(8-methoxy-1-naphthyl)-1-[bis (trimethylsilyl)methyl]-2,2,2-trimethyldisilane (**11**). As shown in Scheme 2, the expected silene **10** was formed along the discussed reaction path, but excess 8-methoxy-1-naphthyllithium (**7a**) was added across the Si=C double bond of **10** giving after hydrolysis the silane **11**. Obviously, the stabilization of the silene system by an electron pair donation from the methoxy group to the silene silicon atom of **10** is insufficient in preventing nucleophilic attack of the organolithium compound.

The structure of **11** was proved on the basis of NMR and MS data (see Section 3). Also an X-ray structural analysis was performed which characterizes the com-



Scheme 2. The reaction of (dichloromethyl)tris(trimethylsilyl)silane (**1**) with 8-methoxy-1-naphthyllithium (**7a**).

pound as a sterically considerably congested silane (Fig. 1). All three Si–C bonds starting with the central silicon atom are elongated by about 4.0%. The Si–SiMe$_3$ bond (2.398 Å) was found to be about 2.0% longer than the standard value. Also the non-equivalence of the two CHSiMe$_3$ groups in the NMR spectra of **11** agrees with the picture of an extremely congested molecule. Interestingly, the Si1–O1 distance (2.875 Å) as well as the Si1–O2 distance (2.903 Å) is considerably shorter than the sum of the van der Waals radii (3.60 Å). Probably, there might be some donor–acceptor interaction between the ether oxygen atoms and the originally tetracoordinate central silicon atom, but the main reason for the short interatomic distances is the structure of the 1,8-disubstituted naphthalene ligands.

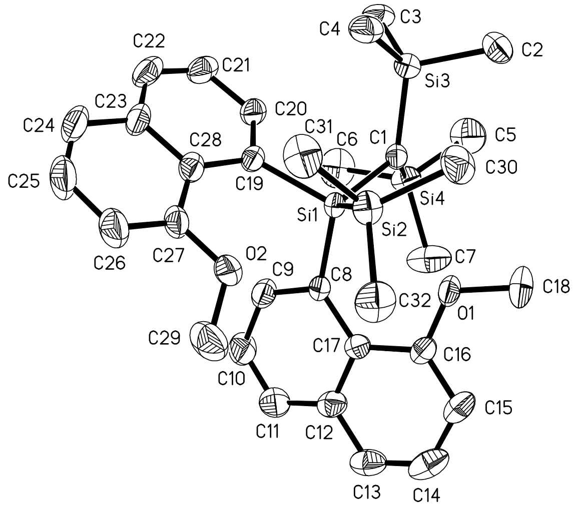
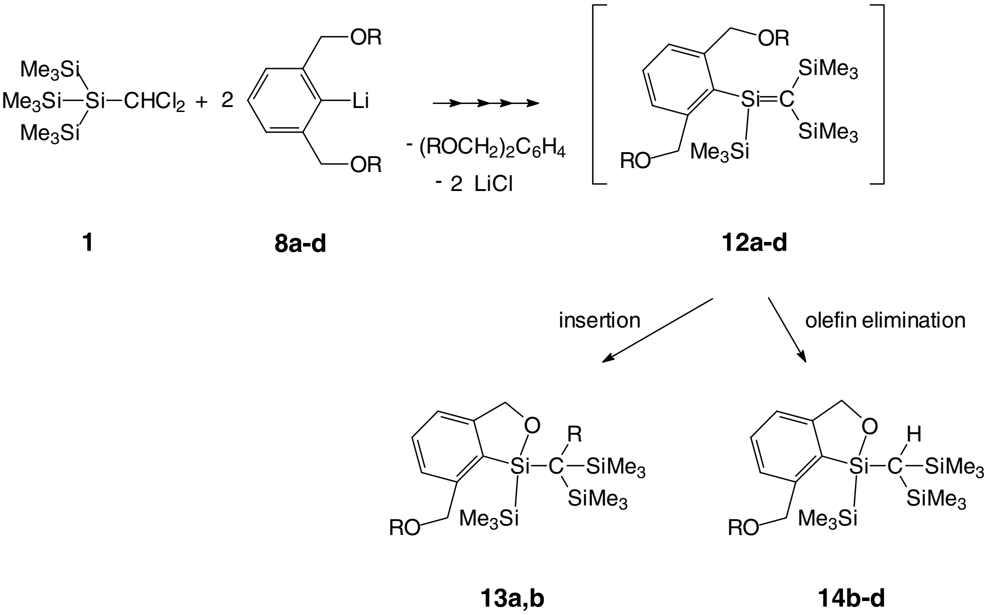


Fig. 1. Molecular structure of **11** in the crystal (ORTEP, 30% probability level, H atoms omitted for clarity). Selected bond lengths (Å): Si1–C1 1.921(5), Si1–C8 1.915(5), Si1–C19 1.936(5), Si1–Si2 2.398(2), Si1–O1 2.875(4), Si1–O2 2.903(4). Selected bond angles (°): C1–Si1–C8 112.7(2), C1–Si1–C19 106.0(2), C1–Si1–Si2 109.99(17), C8–Si1–C19 105.4(2), C8–Si1–Si2 113.53(18), C19–Si1–Si2 108.75(18).

With the aim of improving the stability of silenes of type **10**, we tried to increase the steric bulk of the alkoxynaphthyl substituent in these compounds, thus, eventually preventing the attack of the naphthyllithium derivative to the Si=C double bond. But preliminary results showed that the generation of the precursor organolithium reagents **7b** or **7c** by metalation of 1-ethoxynaphthalene and 1-isopropoxynaphthalene, respectively, following the procedure given by Shirley and Cheng for the direct metalation of 1-methoxynaphthalene [3], gave mixtures of the 2- and 8-lithio derivatives. Thus, as the result of the reaction of **1** with lithiated 1-ethoxynaphthalene (molar ratio 1:2) we obtained 43% of 1-(1-ethoxy-2-naphthyl)-1-(8-ethoxy-1-naphthyl)-2,2,2-trimethyl-1-[bis(trimethylsilyl)methyl]disilane. This was proved by an X-ray structural analysis. The uncertainty of the regiospecifity of the metalation of 1-alkoxynaphthalenes led us to stop these studies.

The reactivity of the bis(alkoxymethyl)phenyllithium compounds **8a**–**d** towards **1** proved to be unexpectedly low. In ether, also after prolonged reaction times, no reaction occurred. In THF in presence of TMEDA at 55 °C the reaction required one week to come to completion. As the result of the interaction of **1** with **8a**–**d** under these conditions two different types of products were obtained, and the structures of both indicate that always the intermediate silenes **12a**–**d** were formed first (Scheme 3). Obviously, **12a**–**d** are unstable, but no addition of excess organolithium compound across the silene double bond occurred. Instead, in most likely



Scheme 3. The reaction of (dichloromethyl)tris(trimethylsilyl)silane (**1**) with 2,6-bis(alkoxymethyl)phenyl lithium derivatives **8a**–**d**.

intramolecular processes the silenes **12a**–**d** stabilized by either a formal insertion of the Si=C bond into the carbon oxygen bond of the ether group (**13a**,**b**) or by elimination of the ether alkyl group in form of an olefin producing **14b**–**d**. In both cases 2-oxa-1-silaindane systems were formed.

The mode of conversion of **12a**–**d** is determined by the nature of the ether alkyl substituents. In case of **12a**, i.e. after reaction of **1** with **8a** (1:2), the insertion product **13a** was obtained exclusively. Treatment of **1** with **8b** produced a mixture of **13b** and **14b** and the reaction of **1** with **8c** and **8d** led to the elimination products **14c** and **14d**, respectively. This behavior is easily understood. The insertion reaction can be described as a nucleophilic attack of the negatively charged silene carbon atom at one methoxy group of **12a**. A certain intramolecular donor–acceptor interaction of the ether oxygen atom with the electrophilic silene silicon atom increases the nucleophilic activity of the silene carbon atom and makes the benzyloxy function a good leaving group. Thus, a formal shift of the ether methyl group of **12a** to the silene carbon atom and a simultaneous formation of a silicon oxygen bond leads to the formation of the oxasilaindane **13a**. Obviously, with increasing bulkiness of the ether alkyl groups this reaction is disfavored. On the other hand, **12b**–**d** are easily converted into **14b**–**d** by attack of the silene carbon atoms at a β-hydrogen atom of the ether alkyl groups. In a β-elimination process the cyclic siloxanes **14b**–**d** are formed under simultaneous generation of the respective olefin. Propylene and isobutene, the expected byproducts in the reactions of **1** with **8c** and **8d**, respectively, were unambiguously detected by GC–MS experiments. Silene **12b**, bearing a bis(ethoxymethyl)phenyl substituent, decomposes along both discussed routes. Unfortunately, a complete chromatographic purification of the two compounds **13b** and **14b** failed. But NMR experiments with the two products, which proved to be slightly contaminated with unknown material, allowed an unambiguous assignment of the proposed structures.

Insertion reactions of silenes into polar single bonds have frequently been observed. Thus, alkoxysilanes were used as scavenger reagents for silenes [4]. Also intramolecular insertions of Si=C units into C–H bonds are known [5]. To our knowledge, cleavage reactions of ether groups by silenes have not yet been described.

These results reveal remarkable differences in the behavior of the bis(alkoxymethyl)phenylsilenes **12a**–**d** and the structurally comparable bis(dimethylaminomethyl)-phenylsilene **6**. Whereas intramolecular amine coordinations in **6** as well as in **4** and **5** cause a significant stabilization of the Si=C systems allowing the isolation and structural elucidation of these derivatives, **12a**–**d** proved to be labile. Actually, no dimers of **12a**–**d** were found and no addition reactions of excess **8a**–**d** across the Si=C bonds of **12a**–**d** could be detected. The high reactivity of the silenes described in this paper may partially be attributed to the expectedly weaker donor properties of the ether group. But, furthermore, also the activation of the alkoxy groups by the electronegative ether oxygen atom, which will be strengthened by some donor–acceptor interaction with the silene silicon atom, may contribute to the discussed rapid conversions of **12a**–**d**.

Studies of the reactions of **1** with the 2-(alkoxymethyl)phenyllithium derivatives **9a–c** remained unsuccessful. In all experiments complex mixtures of products were obtained. There are indications (NMR) that the intermediate silene, obtained by treatment of **1** with 2-(methoxymethyl)phenyllithium (1:2) undergoes a similar insertion reaction as described for the conversion **12a** → **13a**, but the isolation of really pure products failed.

3. Experimental

All reactions involving organometallic reagents were carried out under purified argon. NMR: Bruker AC 250 or Bruker ARX 300, tetramethylsilane as internal standard. IR: Nicolet 205 FT-IR. MS: Intectra AMD 402 (EI with 70 eV or chemical ionization with isobutane). (Dichloromethyl)tris(trimethylsilyl)silane (**1**) was synthesized as described previously [1a]. 8-Methoxy-1-naphthyllithium (**7a**) was made by direct metalation of 1-methoxynaphthalene with tertbutyllithium [3] and was isolated as a greyish amorphous powder. The aryllithium derivatives **8a–d** were obtained by metal halogen exchange reactions of the respective 2,6-bis(alkoxymethyl)bromobenzenes with *n*-butyllithium in THF and the resulting solutions were used directly. The application of the method, described by Hellwinkel [6] for the synthesis of 2,6-bis(methoxymethyl)bromobenzene [6], similarly led to 2,6-bis(ethoxymethyl)bromobenzene and 2,6-bis(isopropoxymethyl)bromobenzene (yields 70% and 85%, respectively). 2,6-Bis(tertbutoxymethyl) bro-mobenzene was prepared by the reaction of 2,6-bis(bromomethyl)bromobenzene [7] with potassium tertbutoxide [8].

3.1. *1.1-bis(8-methoxy-1-naphthyl)-1-[bis(trimethylsilyl)-methyl]-2,2,2-trimethyldisilane (**11**)*

Under stirring, a THF solution of 0.34 g (1.0 mmol) of **1** was added at −78 °C to a solution of 0.5 g (3.0 mmol) of 8-methoxy-1-naphthyllithium (**7a**) in 50 ml ether/THF (4:1). After continued stirring at room temperature for 48 h, water was added and the organic layer separated, dried and evaporated. The residue was crystallized from ethyl acetate and gave a colorless solid, m.p. 239 °C, yield 0.61 g (52%). IR (KBr): $\tilde{\nu} = 1113$ cm^{-1} (COC). ^{1}H NMR (benzene-d_6): $\delta = 0.02$, 0.19 (broad) and 0.42 (3s, $SiCH_3$, 3×9H), 0.59 (s, Si_3CH, 1H), 2.24 and 3.59 (2s, OCH_3, 2×3H), 6.26–7.77 (m, arom. CH, 12H). ^{13}C NMR (benzene-d_6): 1.5–2.2, 4.0 and 5.1 ($SiCH_3$), 2.3 (Si_3CH), 56.1 and 56.2 (OCH_3), 122.3, 122.5, 124.7, 125.3, 125.7, 125.8, 128.5, 130.3, 137.5 and 138.8 (arom. CH), 131.2, 131.4, 135.0, 135.9, 136.3, 138.1, 157.4 (quart. arom. C). ^{29}Si NMR (benzene-d_6): −21.8 (Si*Si*Me$_3$), 14.5 (*Si*SiMe$_3$), −1.1 and 1.1 (CSiMe$_3$). MS *m/z* (%): 574 (0.1) [M$^+$], 559 [M$^+$–CH$_3$], 501 (100) [M$^+$–SiMe$_3$]. Anal. Found: C, 66.74; H, 7.92. Calcd. for $C_{32}H_{46}O_2Si_4$ (575.05): C, 66.84; H, 8.06%.

3.2. *7-Methoxymethyl-1-trimethylsilyl-1-[1,1-bis(trimethylsilyl)ethyl]-2-oxa-1-silaindane (**13a**)*

About 5.1 ml of a 1.6 M hexane solution of *n*-butyllithium were added at −78 °C to a solution of 2.0 g (8.2 mmol) of 2.6-bis(methoxymethyl)bromobenzene in 25 ml of THF. After stirring for 3 h, 1.3 g (3.9 mmol) of **1** and 0.1 ml of TMEDA, dissolved in 25 ml of THF, were added to the cold solution. The mixture was stirred for 7 days at 55 °C. Afterwards water was added and the organic layer separated dried and evaporated. 1,3-Bis(methoxymethyl)benzene was distilled off at 60 °C/ 1×10^{-3} mbar and the residue was purified by column chromatography (silica gel; heptane/toluene 10:1) to give a colorless solid, m.p. 76 °C, yield 1.1 g (30%). ^{1}H NMR (benzene-d_6): $\delta = -0.07$, 0.16 and 0.40 (3s, $SiCH_3$, 3×9H), 1.35 (s, CCH_3, 3H), 3.12 (s, OCH_3, 3H), 4.25 and 4.39 (2d, $^2J = 12.8$ Hz, OCH_2, 2H), 4.94 and 5.15 (2d, $^2J = 14.7$ Hz, OCH_2, 2 H), 6.78 (d, $^3J = 7.3$ Hz, arom. CH, 1H), 6.98 (d, $^3J = 7.3$ Hz, arom. CH, 1H), 7.10 ("t", $^3J = 7.3$ Hz, arom. CH, 1H). ^{13}C NMR (benzene-d_6): $\delta = 0.4$, 0.6 and 1.6 ($SiCH_3$), 5.7 (*C*CH$_3$), 12.4 (C *C*H$_3$), 58.4 (OCH_3), 72.0 (OCH_2), 75.8 (OCH_2), 120.3, 124.2 and 129.1 (arom. CH), 136.0, 142.5 and 150.4 (quart. Arom. C). ^{29}Si NMR (benzene-d_6): $\delta = -17.8$ (Si*Si*Me$_3$), 4.4 and 5.2 (CSiMe$_3$), 28.0 (OSi). MS *m/z* (%): 424 (11) [M$^+$–H], 409 (100) [M$^+$–SiMe$_3$]. Anal. Found: C, 56.49; H, 9.53. Calcd. for $C_{20}H_{40}O_2Si_4$ (424.89): C, 56.54; H, 9.49%.

3.3. *7-Isopropoxymethyl-1-trimethylsilyl-1-[bis(trimethylsilyl)methyl]-2-oxa-1-silaindane (**14c**)*

As described for **13a**, 4.6 g (15.3 mmol) of 2,6-bis(isopropoxymethyl)bromobenzene, 9.5 ml of 1.6 M *n*-butyllithium solution and 2.5 g (7.5 mmol) of **1** gave after chromatographic separation and recrystallization from heptane a colorless solid, m.p. 34.5 °C, yield 1.65 g (50%). ^{1}H NMR (benzene-d_6): $\delta = 0.02$ (s, Si_3CH, 1H), 0.03, 0.17 and 0.41 (3s, $SiCH_3$, 3×9H), 1.14 (d, $^3J = 6.1$ Hz, CCH_3, 6H), 3.52 (sept, $^3J = 6.1$ Hz, 1H), 4.39 and 4.57 (2d, $^2J = 12.2$ Hz, OCH_2, 2H), 5.03 and 5.21 (2d, $^2J = 14.6$ Hz, OCH_2, 2H), 6.81 (d, $^3J = 7.6$ Hz, arom. CH, 1H), 7.13 ("t", $^3J = 7.6$ Hz, arom. CH, 1H), one arom. CH signal hidden by solvent signals. ^{13}C NMR (benzene-d_6): $\delta = -0.1$, 3.1, 3.8 ($SiCH_3$), 7.2 (Si_3CH), 22.0 and 22.5 (OC*C*H$_3$), 71.9 (OCH_3), 72.4 (O*C*CH$_3$), 72.7 (OCH_2), 120.4, 125.0 and 129.3 (arom. CH), 136.9, 142.9 and 149.7 (quart. arom. C). ^{29}Si NMR (benzene-d_6): $\delta = -19.2$ (Si*Si*Me$_3$), −0.1 and 1.1 (CSiMe$_3$), 25.5 (OSi). MS *m/z* (%): 438 (19) [M$^+$], 423 (100) [M$^+$–CH$_3$], 366 (50) [M$^+$–SiMe$_3$]. Anal. Found: C, 56.97; H, 9.41. Calcd. for $C_{21}H_{42}O_2Si_4$ (438.91): C, 57.47; H, 9.65%.

*3.4. 7-tertButoxymethyl-1-trimethylsilyl-1-[bis(trimethylsilyl)methyl]-2-oxa-1-silaindane (**14d**)*

As described before, 3.2 g (9.7 mmol) of 2,6-bis(tertbutoxymethyl)bromobenzene, 6.1 ml of 1.6 M *n*-butyllithium solution and 1.6 g (4.9 mmol) of **1** gave after chromatographic separation and recrystallization from heptane 0.6 g (27%) of colorless crystalline **14d**, m.p. 87 °C. ^{1}H NMR (benzene-d_6): $\delta = -0.04$ (s, Si_3CH, 1H), 0.04, 0.19 and 0.39 (3s, $SiCH_3$, 3×9H), 1.22 (s, CCH_3, 9H), 4.46 and 4.55 (2d, $^2J = 11.2$ Hz, OCH_2, 2H), 5.05 and 5.21 (2d, $^2J = 14.3$ Hz, OCH_2, 2H), 6.82 (d, $^3J = 7.6$ Hz, arom. CH, 1H), 7.19 (“t”, $^3J = 7.6$ Hz, arom. CH), 7.40 (d,$^3J = 7.6$ Hz, arom. CH, 1H). ^{13}C NMR (benzene-d_6): $\delta = -0.3$, 3.1 and 3.8 ($SiCH_3$), 7.9 (Si_3CH), 27.8 ($C\mathit{C}H_3$), 66.3 (OCH_2), 73.1 (OCH_2), 73.4 ($O\mathit{C}$ CH_3), 120.5, 126.2 and 129.6 (arom. CH), 137.8, 143.3 and 149.3 (quart. arom. C). ^{29}Si NMR (benzene-d_6): $\delta = -19.8$ ($Si\mathit{Si}Me_3$), 0.0 and 1.1 ($CSiMe_3$), 26.4 (OSi). MS *m*/*z* (%): 452 (6) [M^+], 395 (99) [M^+–CMe_3], 379 (50) [M^+–$SiMe_3$]. Anal. Found: C, 58.27; H, 9.60. Calcd. for $C_{22}H_{44}$ O_2Si_4 (452.93): C, 58.34; H, 9.79%.

*3.5. The reaction of (dichloromethyl)tris(trimethylsilyl)silane (**1**) with (2,6-bis(ethoxymethyl)phenyllithium (**8b**)*

About 1.6 g (4.8 mmol) of **1** were added to a solution of **8b**, made by treatment of 2.7 g (9.8 mmol) of 2,6-bis(ethoxymethyl)bromobenzene), dissolved in 25 ml of THF, with 6.1 ml of a 1.6 M hexane solution of *n*-butyllithium. Workup as described above and chromatographic separation (silica gel/heptane) led to two slightly contaminated products. By NMR and MS studies the two products were unambiguously identified as 7-ethoxy-1-trimethylsilyl-1-[1,1-bis(trimethylsilyl)propyl]-2-oxa-1-silaindane (**13b**) (1.1 g, 46%) and 7-ethoxymethyl-1-trimethylsilyl-1-[bis(trimethylsilyl)methyl]-2-oxa-1-silaindane (**14b**) (0.1 g, 4.5%).

13b: ^{1}H NMR (benzene-d_6): $\delta = 0.04$, 0.18 and 0.44 (3s, $SiCH_3$, 3×9H), 0.98 (t, $^3J = 7.2$ Hz, $CCH_2\mathit{CH}_3$, 3H),1.19 (t, $^3J = 7.1$ Hz, $OCH_2\mathit{CH}_3$, 3H), 1.37 (q, $^3J = 7.2$ Hz, $C\mathit{CH}_2CH_3$, 2H), 3.51 (m, OCH_2, 2H), 4.55 and 4.66 (2d, $^2J = 11.3$ Hz, OCH_2, 2H), 4.95 and 5.18 (2d, $^2J = 14.5$ Hz, OCH_2, 2H), 6.78 (d, $^3J = 7.3$ Hz, arom. CH, 1H), 7.54 (d, $^3J = 7.7$ Hz, arom. CH, 1H), one arom. CH signal hidden. ^{13}C NMR (benzene-d_6): $\delta = 0.5$, 2.3 and 3.5 ($SiCH_3$), 14.1 and 15.0 ($C\mathit{C}H_3$), 66.7, 72.7 and 75.9 (OCH_2), 120.2, 123.3 and 129.1 (arom. CH), 135.7, 142.7 and 150.3 (quart. Arom. C). ^{29}Si NMR (benzene-d_6): $\delta = -17.4$ ($Si\mathit{Si}Me_3$), 3.2 and 4.8 ($CSiMe_3$), 27.8 (OSi). MS *m*/*z* (%): 452 (10) [M^+], 423 (21) [M^+–C_2H_5], 379 (53) [M^+–$SiMe_3$].

14b: ^{1}H NMR (benzene-d_6): $\delta = 0.01$, 0.15 and 0.44 (3s, $SiCH_3$, 3×9H), 1.07 (t,$^3J = 7.0$ Hz, CCH_3, 3H), 3.35 (…, $^3J = 7.0$ Hz, $O\mathit{CH}_2Me$, 2H), 4.29 and 4.44 (2d, $^2J = 13.1$ Hz, OCH_2, 2H), 5.02 and 5.21 (2d, $^2J = 14.3$ Hz. OCH_2, 2H), 6.82 (d, $^3J = 7.6$ Hz, arom. CH, 1H), 6.88 (d, $^3J = 7.6$ Hz, arom. CH, 1H), 7.11 (“t”, $^3J = 7.6$ Hz, arom. CH, 1H). ^{13}C NMR (benzene-d_6): $\delta = -0.2$, 2.9 and 3.8 ($SiCH_3$), 6.4 (Si_3CH), 14.8 ($CH_2\mathit{C}H_3$), 66.5, 72.2 and 72.7 (OCH_2), 120.2, 123.3 and 129.1 (arom. CH), 135.7, 142.7 and 150.3 (quart. Arom. C). ^{29}Si NMR (benzene-d_6): $\delta = -18.6$ ($Si\mathit{Si}Me_3$), 0.0 and 0.8 ($CSiMe_3$), 23.2 (OSi). MS *m*/*z* (%): 424 (16) [M^+], 409 (89) [M^+–CH_3], 395 (57) [M^+–C_2H_5].

*3.6. Crystal structure determination of **11***

The crystal structure determination of **11** was done on a Bruker P4 four-circle diffractometer equipped with a molybdenum X-ray tube ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal quality was checked by a rotational photo prior to the determination of a suitable reduced cell by the Bruker SHELXTL software. The structure was solved by direct methods and refined by the full-matrix least-squares method against F^2. CCDC-223188 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Further details of the crystal structure and the refinement calculations for **11** – molecular formula: $C_{32}H_{46}O_2Si_4$, formula weight: 575.05, temperature: 293(2) K, crystal system: monoclinic, space group (H.-M.): $P2_1/c$, space group (Hall): $P\bar{2}ybc$, cell dimensions: $a = 17.315(4)$ Å, $b = 11.145(3)$ Å, $c = 17.897(5)$ Å, $\alpha = \gamma = 90°$, $\beta = 100.06(2)$, cell volume: 3400.6(15) Å^3, $Z = 4$, $F(000) = 1240$, density (calcd.): 1.123 Mg/m^3, absorption coefficient $\mu = 0.200$ mm^{-1}, crystal size: $0.60 \times 0.50 \times 0.10$ mm^3 Θ-range for data collection: 2.16–22.00°, completeness to $\Theta = 22°$: 99,9%, index ranges: $-1 \leqslant h \leqslant 18$, $-1 \leqslant k \leqslant 11$, $-18 \leqslant l \leqslant 18$, independent reflections: 4171 [$R(\text{int}) = 0.0466$], data/restraints/parameters: 4171/0/343, goodness-of-fit on F^2: 1.026, final R indices (obs. refl.): $R_1 = 0.0615$, $wR_2 = 0.1401$, observation criterion: $I > 2\sigma(I)$, R indices (all data): $R_1 = 0.1181$, $wR_2 = 0.1814$, largest diff. peak/hole: 0.252/−0.337 e/Å^3.

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References

[1] (a) K. Schmohl, T. Gross, H. Reinke, H. Oehme, Z. Anorg. Allg. Chem. 626 (2000) 1100;
(b) K. Schmohl, H. Reinke, H. Oehme, Eur. J. Inorg. Chem. (2001) 481.

[2] (a) M. Mickoleit, K. Schmohl, R. Kempe, H. Oehme, Angew. Chem. 112 (2000) 1679;
(b) M. Mickoleit, K. Schmohl, R. Kempe, H. Oehme, Angew. Chem., Int. Ed. Engl. 39 (2000) 1610;
(c) M. Mickoleit, R. Kempe, H. Oehme, Chem. Eur. J. (2001) 987;
(d) M. Pötter, U. Bäumer, M. Mickoleit, R. Kempe, H. Oehme, J. Organomet. Chem. 621 (2001) 261;
(e) M. Mickoleit, K. Schmohl, M. Michalik, H. Oehme, Eur. J. Inorg. Chem., in press.

[3] D.A. Shirley, C.F. Cheng, J. Organomet. Chem. 20 (1969) 251.

[4] G. Raabe, J. Michl, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, vol. 1, Wiley, New York, 1989, p. 1085;
T. Müller, W. Ziche, N. Auner, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2, Wiley, New York, 1998, p. 937.

[5] A.G. Brook, H.-J. Wessely, Organometallics 4 (1985) 1487;
K.M. Baines, G. Brook, R.R. Ford, P.D. Lickiss, A.K. Saxena, W.J. Chatterton, J.F. Sawyer, B. Behnam, Organometallics 8 (1989) 693;
U. Klingebiel, S. Pohlmann, L. Skoda, J. Organomet. Chem. 291 (1985) 277;
F. Luderer, H. Reinke, H. Oehme, Chem. Ber. 129 (1996) 15.

[6] D. Hellwinkel, W. Krapp, Chem. Ber. 111 (1978) 13.

[7] D. Hellwinkel, W. Krapp, Chem. Ber. 110 (1977) 693.

[8] R. Jambor, L. Dostal, A. Ruzicka, I. Cisarova, J. Brus, M. Holcapek, J. Holecek, Organometallics 21 (2002) 3996.