Reaction of the (Dichloromethyl)oligosilanes $R(Me_3Si)_2Si-CHCl_2$ (R = Me, Ph, Me_3Si) with Organolithium Reagents and the Synthesis of Novel Kinetically Stabilized Silenes

Kathleen Schmohl,[a] Helmut Reinke,[a] and Hartmut Oehme*[a]

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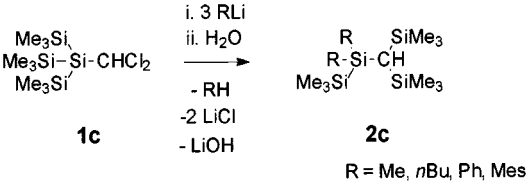
The dichloromethyloligosilanes $R^1(Me_3Si)_2Si-CHCl_2$ (**1a**,**b**) (**1a**: R^1 = Me; **1b**: R^1 = Ph), prepared by treatment of methylbis(trimethylsilyl)silane or phenylbis(trimethylsilyl)silane respectively, with chloroform and potassium *tert*-butoxide, treated with the organolithium reagents R^2Li (R^2 = Me, Ph) to produce the intermediate organolithium derivatives $R^1R^2_2Si-CLi(SiMe_3)_2$ (**10**). Hydrolysis of **10** during the aqueous workup afforded the [bis(trimethylsilyl)methyl]silanes $R^1R^2_2Si-CH(SiMe_3)_2$ (**2**); quenching of the reaction mixture with chlorotrimethylsilane gave the [tris(trimethylsilyl)methyl]silanes $R^1R^2_2Si-C(SiMe_3)_3$ (**11**). The formation of **10** is discussed as proceeding through a remarkable series of isomerization processes involving the transient silenes $R^1R^2Si=C(SiMe_3)_2$ (**7**), which in the presence of an effective excess of R^2Li are immediately trapped to give **10**. By the use of sterically congested organolithium derivatives, the nucleophilic addition of R^2Li to the Si=C bond of **7** can be prevented and kinetically stabilized silenes obtained. Thus, Ph(2,4,6-iPr$_3$C$_6$H$_2$)Si=C(SiMe$_3$)$_2$ (**8b**) was synthesized by the reaction of **1b** with 2,4,6-triisopropylphenyllithium (molar ratio 1:2). Similarly, (Me$_3$Si)(2,4,6-iPr$_3$C$_6$H$_2$)Si=C(SiMe$_3$)$_2$ (**8c**) and (Me$_3$Si)(2-tBu-4,5,6-Me$_3$C$_6$H)Si=C(SiMe$_3$)$_2$ (**9c**) were prepared from (dichloromethyl)tris(trimethylsilyl)silane (**1c**) and 2,4,6-triisopropylphenyllithium or **1c** and 2-*tert*-butyl-4,5,6-trimethylphenyllithium (1:2), respectively, but due to difficulties in the separation of starting material and side products, **8b**, **8c**, and **9c** were obtained in impure form only. Despite the steric congestion, the compounds are reactive and exhibit the usual behavior of silenes. Thus **8b**, **8c**, and **9c** were chemically characterized by the reaction with water to give silanols, by the addition of methanol to give methoxysilanes and by formal [2+2] cycloadditions with benzaldehyde to afford stable 1,2-oxasiletanes. 1-Methyl-1-(2,4,6-triisopropylphenyl)-2,2-bis(trimethylsilyl)silene (**8a**), produced as intermediate from **1a** and 2,4,6-triisopropylphenyllithium (1:2), proved to be unstable in the presence of excess aryllithium compound. Thus, only the addition product Me(2,4,6-iPr$_3$C$_6$H$_2$)$_2$SiCH(SiMe$_3$)$_2$ (**14**) was isolated (after hydrolysis).

Introduction

Silenes are known to be extremely labile compounds which can be isolated and handled under normal conditions only in those cases where structural influences cause an efficient stabilization of the Si=C system.[1] In numerous reactions transient silenes occur as reactive intermediates, but until now the number of synthetic methods affording stable, isolable silenes is rather limited. Brook and co-workers introduced the photochemical isomerization of acyloligosilanes as a versatile method for the generation of silenes, and in 1982 they were the first to isolate a stable silene, $(Me_3Si)_2Si=C(OSiMe_3)Ad$ (Ad = 1-adamantyl), and to perform an X-ray analysis of the compound.[2] In 1983 Wiberg and his group succeeded in applying the classical 1,2 salt elimination to the synthesis of the stable silene $Me_2Si=C(SiMe$*t*$Bu_2)SiMe_3$ and provided the results of its X-ray analysis.[3] Elimination of lithium chloride after addition of *tert*-butyllithium to the carbon−carbon double bond of chloro(vinyl)silanes is also the crucial step in establishing Si=C bonds in a method developed by the groups of Jones and Auner, which was successfully used by Couret et al. in 1994 in the preparation of the stable 1,1-dimesityl-2-neopentylsilene.[4] A further method, which has proved to be an efficient general route to silenes, is the sila Peterson reaction. We were able to contribute to the development of the process and generated a number of transient silenes and studied their mode of dimerization,[5] and in 1996 Apeloig and co-workers succeeded in preparing the stable derivative (tBuMe$_2$Si)$_2$Si=CAd′ (Ad′ = 2-adamantylidene) by this method.[6] A few further stable silenes have been isolated by the groups mentioned.[1] Of course, the structures of these compounds are related to their methods of preparation, and extension of the substitution pattern by introducing new synthetic pathways is desirable.

Recently we reported the reaction of (dichloromethyl)-tris(trimethylsilyl)silane (**1c**) with organolithium reagents RLi (R = Me, *n*Bu, Ph, Mes).[7] As the result of a remarkable sequence of isomerization and addition steps, and a complete reorganization of the substitution pattern of the starting compound, [bis(trimethylsilyl)methyl]silanes **2** were formed as end products [Equation (1)].



[a] Fachbereich Chemie der Universität Rostock,
18051 Rostock, Germany
Fax: (internat.) + 49-(0)381/498-1765
E-mail: hartmut.oehme@chemie.uni-rostock.de

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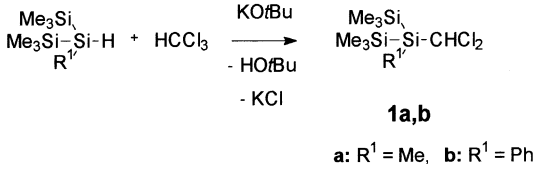
As outlined in Scheme 1 for the behavior of the (dichloromethyl)oligosilanes **1a−c** towards methyllithium or phenyllithium respectively, in the course of this reaction transient silenes occurred as intermediates, which in the presence of excess organolithium reagent were trapped to give the products mentioned. Increasing the bulkiness of the substituents of the organolithium derivatives used in this reaction is expected to afford kinetically stabilized silenes, sufficiently protected against the attack of excess lithium compound and stable with respect to dimerization. Thus, this paper describes the extension of the conversion depicted in Equation (1) for **1c** to (dichloromethyl)methylbis(trimethylsilyl)silane (**1a**) and (dichloromethyl)phenylbis(trimethylsilyl)silane (**1b**), as well as the generation of novel stable silenes along this new synthetic pathway.

Results and Discussion

Reaction of (Dichloromethyl)methylbis(trimethylsilyl)silane (1a) and (Dichloromethyl)phenylbis(trimethylsilyl)silane (1b) with Organolithium Derivatives

The dichloromethylsilanes **1a** and **1b** were prepared adapting a procedure reported by Weidenbruch et al. for the preparation of (dichloromethyl)tri-*tert*-butylsilane.[8] Thus, treatment of methylbis(trimethylsilyl)silane with chloroform in the presence of potassium *tert*-butoxide afforded **1a** in a yield of 36%. Compound **1b** was similarly obtained from phenylbis(trimethylsilyl)silane, $HCCl_3$ and KO*t*Bu (yield 41%) [Equation (2)]. The dichloromethylsilane **1a** has already been described by Sakurai et al., who obtained the compound from 2-chloroheptamethyltrisilane and dichloromethyllithium.[9]



In agreement with the described reaction of **1c** with organolithium compounds,[7] **1a** reacted with methyllithium at room temperature (molar ratio 1:3) to give, after hydrolytic workup, tris(trimethylsilyl)methane (**2ax**). Under the same conditions **1a** and phenyllithium afforded methyldiphenyl[bis(trimethylsilyl)methyl]silane (**2ay**). Similarly, reaction of **1b** with the same organolithium derivatives gave dimethylphenyl[bis(trimethylsilyl)methyl]silane (**2bx**) and triphenyl[bis(trimethylsilyl)methyl]silane (**2by**), respectively (Scheme 1). The structures of the compounds obtained were elucidated on the basis of NMR and MS data (see Experimental Section).

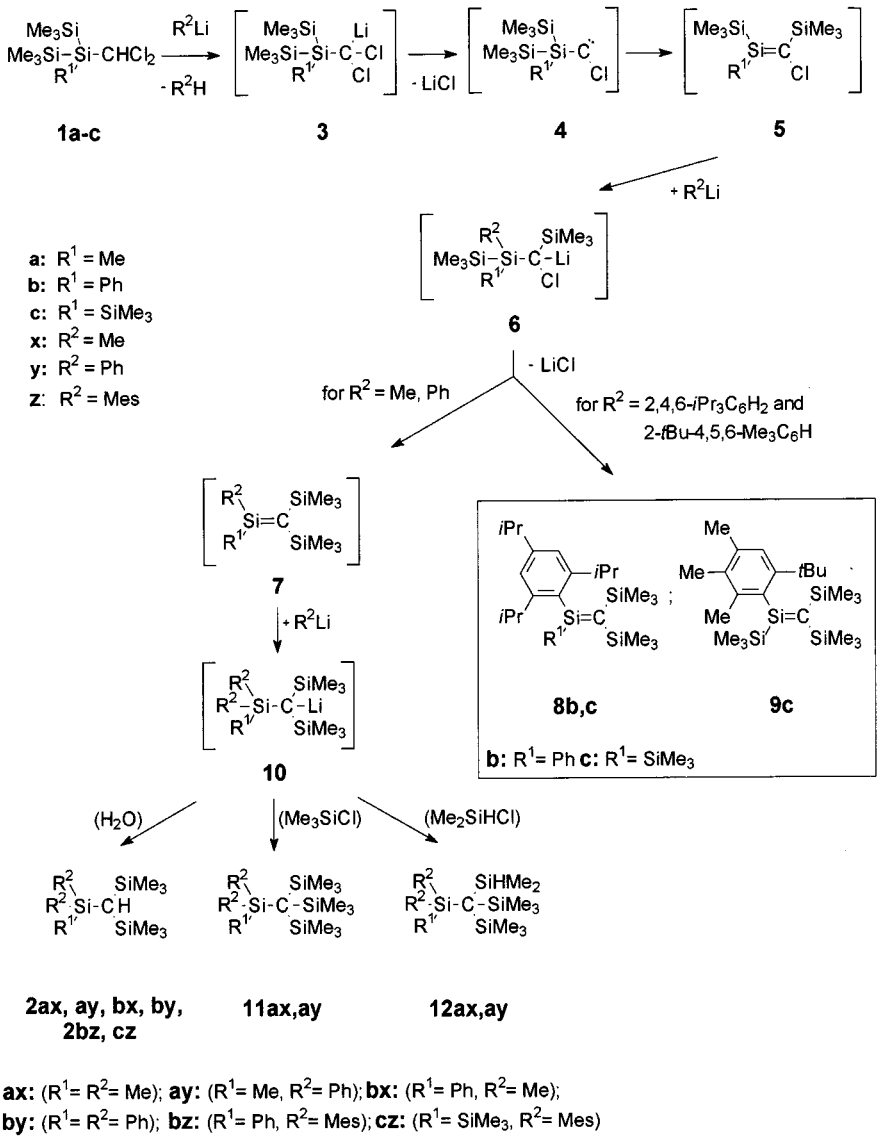
The conversion of **1a−c** to **2** by the means of organolithium compounds is a complex process. Two trimethylsilyl groups migrate from the central silicon atom to the neighboring carbon atom, formally replacing the two chlorine substituents, and the two organic groups introduced by the lithium derivatives occupy the former positions of the two trimethylsilyl substituents. Despite the unexpected outcome of the reaction, the conversion can be rationalized as a clear sequence of known steps. Our proposal for the reaction mechanism is outlined in Scheme 1, which also includes the formerly described conversion of **1c**.[7]

The dichloromethylsilanes **1a−c** are deprotonated by the organolithium reagents with generation of the silylcarbenoids **3**. Elimination of lithium chloride and migration of one trimethylsilyl group from the central silicon atom to the carbene carbon atom affords the intermediate silene **5**.

Rearrangements of silylcarbenes to silenes involving the shift of one substituent from the silicon atom to the neighboring carbene carbon atom are well-documented reactions and a standard method for the generation of transient silenes.[10] Hydrogen, alkyl, aryl, and silyl groups have been found to be suitable migrating substituents in this isomerization process; the migrating ability of the silyl groups exceeds that of the other groups mentioned.[11] In the presence of excess organolithium reagent the silenes **5** are immediately trapped to give the new carbenoids **6**. Repeated elimination of LiCl and a further 1,2-Si,C shift of one trimethylsilyl group affords the silenes **7**, which again undergo nucleophilic addition of a third equivalent of R^2Li, producing **10**. Hydrolysis during the aqueous workup affords **2**.

The intermediate existence of the chlorosilylcarbene **4** could not be proved and an intramolecular Me_3Si/Li exchange in **3**, followed by a 1,2 lithium chloride elimination, might be an alternative route to the silene **5**. Trapping experiments of the carbene **4** were abandoned, since it is well known that silylcarbenes, generated photochemically or thermally from the corresponding diazo compounds, very rapidly rearrange to the respective silenes, and in numerous experiments with different scavenger reagents only the silenes were detected.[11,12] The carbenoids **6** proved to be moderately stable at low temperatures. As described previously, we succeeded in trapping **6cy**, generated from **1c** and phenyllithium, with chlorotrimethylsilane to give $Ph(Me_3Si)_2Si-CCl(SiMe_3)_2$ and by quenching with water, affording $Ph(Me_3Si)_2Si-CHClSiMe_3$.[7] The intermediate organolithium compounds **10**, formed by addition of methyllithium or phenyllithium to the silene double bond of **7**, are suitable precursors for highly congested tris(silyl)-methyl-substituted silanes. Thus, addition of chlorotrimethylsilane to the product mixture obtained after the reaction of **1a**,**b** with MeLi or PhLi produced the [tris(trimethylsilyl)methyl]silanes **11**. Similarly, quenching of **10** with Me_2SiHCl gave the [dimethylsilylbis(trimethylsilyl)-methyl]silanes **12**.

Independent of the molar ratio **1a−c**/RLi, we found the reaction to proceed through all intermediates outlined in Scheme 1 to give the final products **2**, **11**, or **12**, respectively. Attempts to isolate dimers of the silenes **5** or **7** by reducing the ratio of the reactants to 1:2 or 1:1 were unsuccessful. We assume that the deprotonation of **1a−c**, producing the carbenoids **3**, is a slow process compared with the subsequent steps, and the transient silenes **5** and **7**, formed during the course of the reaction, always meet an effective ex-



Scheme 1. Reaction of the dichloromethyloligosilanes **1a−c** with organolithium reagents R^2Li

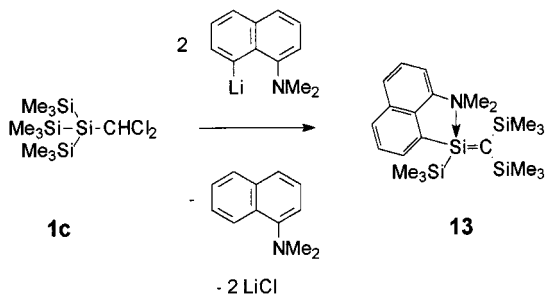
cess of the organolithium reagent, finally producing the congested silanes.

Reaction of the Dichloromethylsilanes 1a−c with 2,4,6-Triisopropylphenyllithium and of 1c with 2-*tert*-Butyl-4,5,6-trimethylphenyllithium − Synthesis and Behavior of the Stable Silenes 8b, 8c, and 9c

As discussed above, in the course of the reaction of the dichloromethylsilanes **1a−c** with methyllithium or phenyllithium, the transient silenes **5** and **7** occur as intermediates. As expected, in the presence of excess organolithium reagent, the almost unprotected, reactive silenes are immediately trapped to give the addition products **6** or **10**, respectively. However, if organolithium reagents are chosen with groups R^2, which, when introduced to the silene Si atom of **7**, provide sufficient stabilization of the silaethene by means of their steric bulk or by intramolecular donor-acceptor interactions, the reaction may stop at this stage and the resulting silenes may be expected to be stable. The high reactivity of silenes of type **5** also allows the addition of extremely congested organolithium derivatives to produce carbenoids **6**, which after loss of LiCl and subsequent isomerization may result in the formation of kinetically stabilized Si=C systems. Thus, we consider (dichloromethyl)oligosilanes and their reaction with organometallic bases as a promising tool in the synthesis of stable silenes.

Following this concept we studied the reaction of **1c** with 8-dimethylamino-1-naphthyllithium and obtained **13** in a straightforward one-pot reaction as a yellow, crystalline compound in a yield of 79% [Equation (3)].[13] The X-ray analysis of **13** confirmed the expected picture of an intramolecularly donor-stabilized silene with fourfold coordination at the silene silicon atom. Obviously, the 8-dimethylaminonaphthyl substituent dramatically decreases the electrophilic character of the silicon center and prevents further attack of organolithium reagent at the silene double bond. Thus, **13** is stable and can be isolated, and the reaction is highly recommended as an efficient and versatile method

for the synthesis of further intramolecularly donor-stabilized silenes.



For the synthesis of kinetically stabilized silenes of type **7** two options were taken into consideration. Firstly, bulky groups R^1 may be introduced at the silene Si atom by starting with appropriately substituted (dichloromethyl)silanes **1**, or secondly, space-demanding substituents R^2 may be introduced by the respective organolithium derivatives R^2Li in the reaction with **1a**−**c**. Concerning the first alternative, we tried to synthesize (dichloromethyl)mesitylbis(trimethylsilyl)silane following the standard method described above. Unfortunately, mesitylbis(trimethylsilyl)silane was recovered unchanged after treatment with chloroform and potassium *tert*-butoxide. No reaction between the H-silane and CCl_2 occurred, probably due to steric reasons. On the other hand, **1b** and **1c**, which were chosen for some preliminary experiments, reacted with mesityllithium (1:2) to give after hydrolysis the "normal" silene addition products $PhMes_2Si-CH(SiMe_3)_2$ (**2bz**) and $Me_3SiMes_2Si-CH(SiMe_3)_2$ (**2cz**),[7] respectively, (Scheme 1). Obviously, one *Si*-mesityl substituent and one *Si*-phenyl or *Si*-trimethylsilyl group at the silene silicon atom of **7** provides insufficient protection to the Si=C system against the attack of mesityllithium. Replacement of the mesityl group in **7** by a 2,4,6-tri-*tert*-butylphenyl substituent is expected to increase the kinetic stability of the silene. But 2,4,6-tri-*tert*-butylphenyllithium did not react with the (dichloromethyl)-silane **1c**. The components remained unchanged, i.e. no deprotonation of **1c** occurred, very likely due to the steric congestion in both the dichloromethylsilane and the organolithium compound. Also, the reaction of **1c** with *tert*-butyllithium in pentane gave unsatisfactory results. We obtained a complex mixture of products. Neither a silene, nor any product resulting from a silene, could identified.

However, treatment of **1b** and **1c** with 2,4,6-triisopropylphenyllithium (molar ratio 1:2) afforded in a clean reaction the indefinitely stable silenes **8b** and **8c**, respectively. Similarly, **1c** and 2-*tert*-butyl-4,5,6-trimethylphenyllithium (1:2) gave the silene **9c** (Scheme 1). The compounds were obtained by a straightforward one-pot reaction of the components in ether at room temperature. Unfortunately, we did not succeed in crystallizing the compounds, and in all cases complete separation of starting materials or side products from the oily silenes failed. In particular the quality of **8b** and **9c** did not allow an unambiguous assignment of e.g. their NMR signals, and therefore no spectroscopic data of the compounds are given. The silene **8c** was obtained as a pale yellow oil, only slightly contaminated with 1,3,5-triisopropylbenzene, after reaction of the components, removal of the solvent and extraction of the residue with pentane. Triisopropylbenzene, formed as by-product, was separated by repeated concentration of the pentane solution in vacuo, finally at 100 °C. Furthermore, under these conditions no silene dimerization or uncontrolled decomposition was observed. Compound **8c** could be characterized by its NMR and MS data (see Experimental Section). Indicative of the proposed structure is the ^{29}Si chemical shift of the silene silicon atom of **8c** (δ = 79.6). Silenes with comparable substitution patterns are unknown, but similarly structured derivatives, such as (*E*)-$(Me_3Si)TipSi=C(OSiMe_3)Ad$ ($\delta^{29}Si$ = 40.3; Ad = 1-adamantyl),[14] $Mes_2Si=CHCH_2tBu$ ($\delta^{29}Si$ = 77.6)[4] or $(Me_3Si)(tBuMe_2Si)Si=Ad'$ ($\delta^{29}Si$ = 51.7, Ad′ = 2-adamantylidene)[6] also show characteristic downfield shifts of the Si=C signals in their ^{29}Si NMR spectra. Unfortunately, the ^{13}C NMR signal of the silene carbon atom of **8c**, which is expected to appear with very low intensity, could not be assigned unambiguously.

To our surprise, the reaction of **1a** with 2,4,6-triisopropylphenyllithium (molar ratio 1:2) did not give the stable silene **8a**, but led after aqueous workup to methylbis(2,4,6-triisopropylphenyl)[bis(trimethylsilyl)methyl]silane (**14**) [Equation (4)]. Obviously, replacement of a phenyl group or a trimethylsilyl group in **8b** or **8c**, respectively, by the smaller methyl substituent, decreases the steric protection of the Si=C system and in the presence of excess organolithium reagent a second 2,4,6-triisopropylphenyl substituent is introduced at the silene silicon atom. Compound **14** is an extremely congested silane and structural data would be of particular interest. However, due to the poor crystal quality, the accuracy of the X-ray structural analysis was not very high. Thus, the connectivity of the structure proposed was

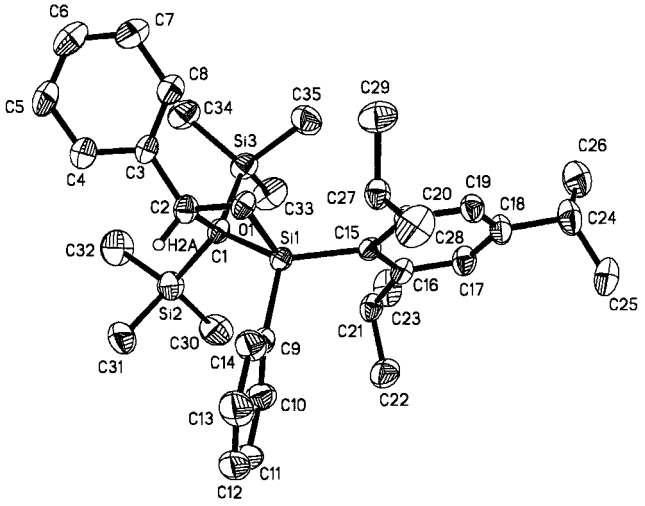
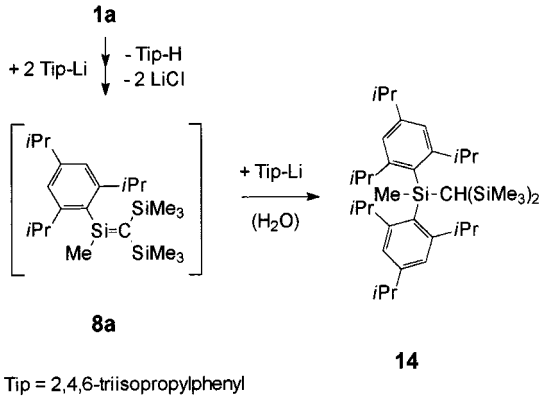
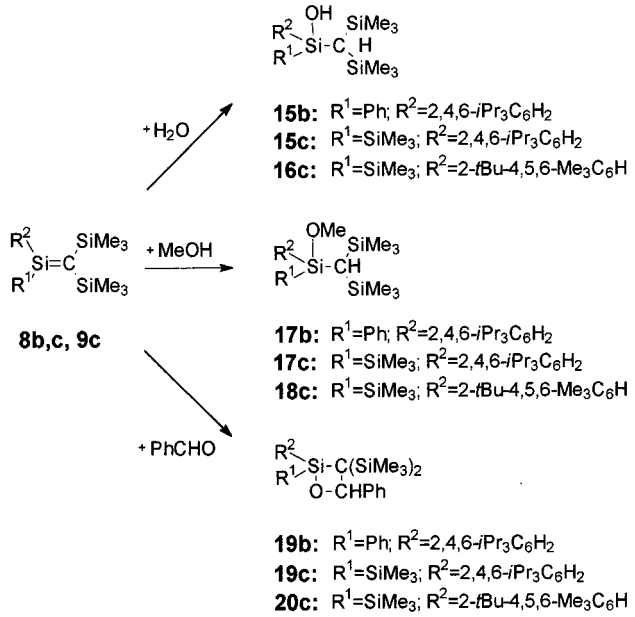


Figure 1. Molecular structure of **19b** in the crystal (H atoms omitted); selected bond lengths [Å] and angles [°]: Si1−O1 1.679(2), O1-C2 1.461(4), C2−C1 1.607(5), C1−Si1 1.924(3), Si1−C15 1.900(3), Si1−C9 1.890(3), C1−Si2 1.912(3), C1−Si3 1.915(4), C2−C3 1.495(5); Si1−O1−C2 112.6(2), O1−C2−C1 99.3(2), C2−C1−Si1 79.11(18), C1−Si1−O1 80.72(13), C9−Si1−C15 107.71(14), Si2−C1−Si3 111.86(17), torsion angle C1−C2−O1−Si1 25.9(2)

confirmed unambiguously, but a detailed discussion of bond parameters is excluded.



Despite the steric congestion, which prevents the dimerization of **8b**, **8c**, and **9c**, the compounds are reactive and exhibit the typical behavior of silenes. Thus, treatment with water led to the expected formation of the silanols **15b**, **15c**, and **16c** (Scheme 2). Similarly, methanol was added to the silene group to afford the methoxysilanes **17b**, **17c**, and **18c**. The results of the nucleophilic addition of methyllithium or phenyllithium to the Si=C unit, a reaction which we generally used for the characterization of transient silenes,[15] were unclear in case of **8b**, **8c**, and **9c**. We obtained complex mixtures of products, from which no compounds could be isolated. Further, reactions with 2,3-dimethyl-1,3-butadiene, which were intended to give [2+2] or [2+4] cycloadducts,[1] produced unsatisfactory results. The components were recovered unchanged. Both unsuccessful attempts at characterization are interpreted as an indication of the extreme steric shielding of the silene group.



Scheme 2. Conversion of the stable silenes **8b**, **8c**, and **9c** with water into the silanols **15b**, **15c**, and **16c**, with methanol into the methoxysilanes **17b**, **17c**, and **18c**, and with benzaldehyde into the 1,2-oxasiletanes **19b**, **19c**, and **20c**

Benzaldehyde adds to the Si=C functionality of **8b**, **8c**, and **9c** in a formal [2+2] reaction to afford the 1,2-oxasiletanes **19b**, **19c**, and **20c** (Scheme 2). 1,2-Oxasiletanes, generated as intermediates in the reaction of transient silenes with carbonyl compounds in most cases undergo rapid decyclizations to give oligomers of the respective silanones and an olefin.[16] But in case of relatively stable silenes of the "Brook-type",[1b] the formation of stable 1,2-oxasiletanes is common.[17] Compounds **19b**, **19c**, and **20c** were formed in low yields (besides large quantities of unidentified material), but could be isolated in crystalline form, and for all three compounds X-ray structural analyses were performed. The molecular structure of **19b**, which was chosen as an example of the comparable 1,2-oxasiletane systems, is shown in Figure 1. In all three structures the ring bonds are slightly longer than the usual acyclic values [Si−C: **19b**: 1.924(3), **19c**: 1.944(3), **20c**: 1.939(3); C−C: **19b**: 1.607(5), **19c**: 1.603(4), **20c**: 1.600(5); C−O: **19b**: 1.461(4), **19c**: 1.440(4), **20c**: 1.446(4); Si−O: **19b**: 1.679(2), **19c**: 1.684(2), **20c**: 1.680(2) Å]. These data are comparable with those reported for 1,2-oxasiletanes.[17] The four-membered rings in **19c** and **20c** are nearly planar, in **19b** the ring is folded, the torsion angle C1−C2−O1−Si1 being 25.9°.

Experimental Section

General: 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. − $Me(Me_3Si)_2SiH$, $Ph(Me_3Si)_2SiH$, and $(Me_3Si)_3SiH$ were prepared using the method described by Marschner.[18] − The syntheses and structures of **1c**, **2cx**, **2cy**, and **2cz** were described previously.[7] − Due to the formation of SiC, the results of the elemental analyses of some compounds were unsatisfactory. In these cases HRMS data are given.

(Dichloromethyl)methylbis(trimethylsilyl)silane (1a):[9] At room temperature, KO*t*Bu (1.42 g, 12.6 mmol) and chloroform (1.51 g, 12.6 mmol) were added gradually to a solution of methylbis(trimethylsilyl)silane (2.2 g, 11.5 mmol) in pentane (30 mL). After stirring for 12 h, water was added, the organic layer separated and the aqueous phase extracted with pentane. The collected extracts were dried and concentrated and the residue purified by kugelrohr distillation (50 °C/1.4·10^{-2} mbar) to give 1.14 g (36%) of **1a**. Colorless oil. − ^{1}H NMR ([D$_6$]benzene): δ = 0.16 [s, Si(CH$_3$)$_3$; 18 H], 0.20 (s, SiCH$_3$; 3 H), 5.28 (s, CH; 1 H). − ^{13}C NMR ([D$_6$]benzene): δ = −0.7 [Si(CH$_3$)$_3$], −8.4 (SiCH$_3$), 64.8 (CH). − ^{29}Si NMR ([D$_6$]benzene): δ = −23.2 (*Si*SiMe$_3$), −15.8 (SiMe$_3$). − $C_8H_{22}Cl_2Si_3$ (273.4): calcd. C 35.14, H 8.11, Cl 25.93; found C 35.35, H 8.39, Cl 24.94.

(Dichloromethyl)phenylbis(trimethylsilyl)silane (1b): As described for **1a**, phenylbis(trimethylsilyl)silane (2.2 g, 8.71 mmol), KO*t*Bu (1.1 g, 9.81 mmol) and chloroform (1.17 g, 9.81 mmol) afforded after kugelrohr distillation at 110 °C/2.2·10^{-1} mbar 1.2 g (41%) of a colorless oil. − ^{1}H NMR ([D$_6$]benzene): δ = 0.24 (s, SiCH$_3$; 18 H), 5.63 (s, CH; 1 H), 7.11−7.45 (m, arom. CH; 5 H). − ^{13}C NMR ([D$_6$]benzene): δ = −0.0 (SiCH$_3$), 63.6 (CH), 128.3, 129.2, and 135.3 (arom. CH), 133.8 (arom. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −24.2 (*Si*SiMe$_3$), −15.2 (Si*Si*Me$_3$). − MS (70 eV); *m*/*z* (%): 334 (1) [M]$^+$, 319 (3) [M − CH$_3$]$^+$, 299 (100) [M − Cl]$^+$. − $C_{13}H_{24}Cl_2Si_3$ (335.5): calcd. C 46.54, H 7.20, Cl 21.13; found C 46.79, H 7.13, Cl 21.38.

Tris(trimethylsilyl)methane (2ax): To a solution of **1a** (0.5 g, 1.83 mmol) in ether (30 mL), a threefold molar quantity of methyllithium was gradually added at room temperature. After stirring for 12 h, the mixture was hydrolyzed and the organic layer separated, dried and concentrated. Compound **2ax** was separated by column chromatography (silica gel, heptane) as a colorless oil, yield 0.3 g (70%). The spectral data measured for **2ax** agree with those described in the literature.[19]

Methyldiphenyl[bis(trimethylsilyl)methyl]silane (2ay): Similarly, **1a** (0.5 g, 1.83 mmol) and ethereal phenyllithium solution (5.5 mmol) afforded 0.45 g (68%) of **2ay**. Colorless crystals, m.p. 66−69 °C. − ^{1}H NMR ([D$_6$]benzene): δ = 0.02 [s, Si(CH$_3$)$_3$, 18 H], 0.04 (s, CH, 1 H), 0.74 (s, SiCH$_3$, 3 H), 7.13−7.52 (m, arom. CH, 10 H). − ^{13}C NMR ([D$_6$]benzene): δ = −2.2 (CH), 1.3 (SiCH$_3$), 3.4 [Si(CH$_3$)$_3$], 128.3, 129.0, and 134.8 (arom. CH), 140.4 (arom. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −9.6 (SiMe$_3$), −0.1. −(SiMe). − MS (70 eV); *m/z* (%): 356 (2) [M]$^+$, 341 (100) [M − CH$_3$]$^+$, 279 (5) [M − Ph]$^+$. − C$_{20}$H$_{32}$Si$_3$ (356.7): calcd. C 67.34, H 9.04; found C 67.04, H 9.07.

Dimethylphenyl[bis(trimethylsilyl)methyl]silane (2bx): As described for **2ax**, **1b** (0.5 g, 1.49 mmol), and MeLi (4.50 mmol) gave after chromatographic separation (silica gel, heptane) 0.73 g (84%) of **2bx**. Colorless oil. − ^{1}H NMR ([D$_6$]benzene): δ = −0.38 (s, CH, 1 H), 0.08 [s, Si(CH$_3$)$_3$, 18 H], 0.38 [s, Si(CH$_3$)$_2$, 6 H], 7.18−7.49 (m, arom. CH, 5 H). − ^{13}C NMR ([D$_6$]benzene): δ = −1.0 (CH), 1.8 [Si(CH$_3$)$_3$], 3.4 [Si(CH$_3$)$_2$], 128.8, 133.7, and 134.7 (arom. CH), 142.5 (arom. C). − ^{29}Si NMR ([D$_6$]benzene): δ = − 16.2 (SiMe$_2$Ph), − 0.3 (SiMe$_3$). − MS (70 eV); *m/z* (%): 279 (100) [M − CH$_3$]$^+$. − C$_{15}$H$_{30}$Si$_3$ (294.7): calcd. C 61.14, H 10.26; found C 61.16, H 10.26.

Triphenyl[bis(trimethylsilyl)methyl]silane (2by): As described for **2ax**, **1b** (0.5 g, 1.49 mmol), and PhLi (4.50 mmol) gave after chromatographic separation (silica gel, heptane) and recrystallization from methanol 0.44 g (70%) of **2by**. Colorless crystals, m.p. 82−84 °C. − ^{1}H NMR ([D$_6$]benzene): δ = 0.07 (s, SiCH$_3$, 18 H), 0.31 (s, CH, 1 H), 7.15−7.71 (m, arom. CH, 15 H). − ^{13}C NMR ([D$_6$]benzene): δ = 1.3 (CH), 3.8 (SiCH$_3$), 127.9, 129.4, and 136.7 (arom. CH), 137.9 (arom. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −10.0 (SiPh$_3$), −0.0 (SiMe$_3$). − MS (70 eV); *m/z* (%): 419 (2) [M + H]$^+$, 403 (48) [M − CH$_3$]$^+$, 341 (100) [M − Ph]$^+$, 264 (6) [M − Ph$_2$]$^+$, 259 (11) [M − CH(SiMe$_3$)$_2$]$^+$. − C$_{25}$H$_{34}$Si$_3$ (418.8): calcd. C 71.70, H 8.18; found 70.84, 8.05. HRMS calcd. for C$_{24}$H$_{31}$Si$_3$ (M − CH$_3$): 403.17337; found 403.17013.

Dimesitylphenyl[bis(trimethylsilyl)methyl]silane (2bz): At room temperature, a twofold molar excess of mesityllithium was added to a solution of **1b** (0.56 g, 1.65 mmol) in ether (30 mL). After stirring for 12 h, water was added and the organic phase was separated, dried and concentrated. Column chromatography of the residue (silica gel, heptane) and recrystallization of the product from methanol gave 0.1 g (12%) colorless crystals, m.p. 45−50 °C. − ^{1}H NMR ([D$_6$]benzene): δ = −0.07 and 0.05 (2 s, SiCH$_3$, 2 × 9 H), 0.33 (s, CH, 1 H), 2.09 and 2.22 (2 s, Mes-CH$_3$, 2 × 6 H), 2.33 and 2.34 (2 s, Mes-CH$_3$, 2 × 3 H), 6.70−7.86 (m, arom. CH, 9 H). − ^{13}C NMR ([D$_6$]benzene): δ = −0.4 and 4.7 (SiMe$_3$), 4.7 (CH), 20.9, 21.0, 21.1, 25.8, and 26.1 (aryl-CH$_3$), 127.4, 128.2, 128.9, 129.2, 130.0, 130.6, 136.3, 138.1, 138.5, 143.8, and 144.5 (arom. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −16.0 (aryl$_3$Si), 0.3 and 1.1 (SiMe$_3$). − MS (70 eV); *m/z* (%): 502 (1) [M]$^+$, 487 (5) [M − CH$_3$]$^+$; HRMS calcd. for C$_{31}$H$_{46}$Si$_3$ 502.25965, found 502.29074.

1-(2,4,6-Triisopropylphenyl)-1,2,2-tris(trimethylsilyl)silene (8c): To a solution of **1c** (0.5 g, 1.5 mmol) in ether (30 mL) a twofold molar excess of 2,4,6-triisopropylphenyllithium was gradually added at room temperature. After stirring for 12 h, the mixture was concentrated and the residue extracted with pentane. After filtration, the solution was repeatedly concentrated (with further addition of pentane) in vacuo, finally at 100 °C/10^{-2} mbar, to give 0.4 g (58%) of a pale yellow oil, which proved to be a mixture of **8c** and 1,3,5-triisopropylbenzene. − **8c:** ^{1}H NMR ([D$_6$]benzene): δ = 0.17, 0.24, and 0.49 (3 s, SiCH$_3$, 3 × 9 H), 1.17, 1.25, and 1.38 (3 d, ^3J = 6.7 Hz, *i*Pr-CH$_3$, 3 × 6 H), 2.72 (sept, ^3J = 6.7 Hz, *i*Pr-CH, 1 H), 3.33 (sept, ^3J = 6.7 Hz, *i*Pr-CH, 2 H), 7.00 (s, arom. CH, 2 H). − ^{13}C NMR ([D$_6$]benzene): δ = 1.3, 4.8, and 6.3 (SiCH$_3$), 24.1, 24.2, and 24.7 (*i*Pr-CH$_3$), 34.7 and 38.1 (*i*Pr-CH), 121.0 (arom. CH), 136.0, 151.7, and 152.4 (arom. C), the signal of the Si=C atom could not be assigned unambiguously. − ^{29}Si NMR ([D$_6$]benzene): δ = −15.4 (Si*Si*Me$_3$), −6.8 and −5.7 (CSiMe$_3$), 79.6 (Si=C). − MS (70 eV); *m/z* (%): 463 (88) [M + H]$^+$, 390 (5) [M − SiMe$_3$]$^+$; HRMS calcd. for C$_{25}$H$_{50}$Si$_4$ 462.29285, found 462.29895. − 1,3,5-*i*Pr$_3$C$_6$H$_3$: ^{1}H NMR ([D$_6$]benzene): δ = 1.24 (d, ^3J = 7.5 Hz, CCH$_3$, 18 H), 2.82 (sept, ^3J = 7.5 Hz, CHMe$_2$, 3 H), 6.99 (s, arom. CH, 3 H). − ^{13}C NMR ([D$_6$]benzene): δ = 24.4 (CH$_3$), 34.8 (CH), 122.4 (arom. CH), 149.1 (arom. C).

Tetrakis(trimethylsilyl)methane (11ax): To a solution of **1a** (0.5 g, 1.83 mmol) in ether (30 mL), MeLi (5.5 mol) was added at room temperature. The mixture was stirred for 12 h and subsequently chlorotrimethylsilane (0.5 g, 4.5 mmol) was added. Stirring was continued for further 12 h. After the addition of water, separation of the organic layer and concentration, the residue was purified by column chromatography (silica gel, heptane). Colorless crystals, yield 0.46 g (82%), m.p. 129−135 °C. The spectral data obtained for **11ax** are identical with those of authentic material.[20]

Methyldiphenyl[tris(trimethylsilyl)methyl]silane (11ay): Following the procedure for the synthesis of **11ax**, **1a** (0.5 g, 1.83 mmol), PhLi (5.5 mmol) and chlorotrimethylsilane (0.5 g, 4.5 mmol) gave after chromatography (silica gel, heptane) and recrystallization from ethanol gave colorless crystals (0.44 g), which proved to be a mixture of **11ay** and approx. 10% of **2ay**. The two compounds could not be cleanly separated, therefore only the NMR and MS data of **11ay** are given. − ^{1}H NMR ([D$_6$]benzene): δ = 0.10 (s, SiCH$_3$, 27 H), 0.32 (s, SiCH$_3$, 3 H), 7.13−7.79 (m, arom. H). − ^{13}C NMR ([D$_6$]benzene): δ = 0.8 (SiCH$_3$), 3.5 [Si(CH$_3$)$_3$], Si$_4$C could not be assigned unambiguously, 128.3, 128.9, and 136.3 (m, arom. CH), 140.1 (arom. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −13.1 (SiMePh$_2$), 2.2 (SiMe$_3$). − MS (70 eV); *m/z* (%): 413 (2) [M − CH$_3$]$^+$, 351 (1) [M − Ph]$^+$, 192 (100) [M − C(SiMe$_3$)$_3$]$^+$.

Dimethyl[tris(trimethylsilyl)methyl]silane (12ax): The preparation of **12ax** followed the procedure given for **11ax**, but chlorodimethylsilane was used instead of chlorotrimethylsilane. Thus, **1a** (0.5 g, 1.83 mmol), MeLi (5.5 mmol) and Me$_2$SiHCl (0.5 g, 5.5 mmol) gave after purification by column chromatography (silica gel, heptane) colorless crystals, yield 0.43 g (82%), m.p. 97−103 °C. − IR (KBr): $\tilde{\nu}$ = 2099 cm^{-1} (SiH). − ^{1}H NMR ([D$_6$]benzene): δ = 0.25 (s, SiCH$_3$, 27 H), 0.21 (d, ^3J = 3.0 Hz, SiCH$_3$, 3 H), 0.30 (d, ^3J = 3.0 Hz, SiCH$_3$, 3 H), 4.31 (br. q, ^3J = 3.0 Hz, SiH, 1 H). − ^{13}C NMR ([D$_6$]benzene): δ = −4.1 (quat. C), 1.6 (HSiCH$_3$), 4.5 [Si(CH$_3$)$_3$]. − ^{29}Si NMR ([D$_6$]benzene): δ = −16.9 (SiH), −1.3 (SiMe$_3$). − MS (70 eV): *m/z* (%): 289 (1) [M − H]$^+$, 275 (100) [M − CH$_3$]$^+$. − C$_{12}$H$_{34}$Si$_4$ (290.7): calcd. C 49.57, H 11.79; found C 49.50, H 11.58.

Methyldiphenyl[(dimethylsilyl)bis(trimethylsilyl)methyl]silane (12ay): Similarly, **1a** (0.5 g, 1.83 mmol), PhLi (5.5 mmol), and Me$_2$SiHCl (0.5 g, 5.5 mmol) afforded 0.3 g (40%) of **12ay**. Colorless crystals, m.p. 93−97 °C. − IR (KBr): $\tilde{\nu}$ = 2122 cm^{-1} (SiH). − ^{1}H

NMR ([D$_6$]benzene): δ = 0.18 [d, ^3J = 3.8 Hz, Si(CH$_3$)$_2$, 6 H], 0.22 [s, Si(CH$_3$)$_3$, 18 H], 0.91 (s, PhSiCH$_3$, 3 H), 5.08 (sept, ^3J = 3.8 Hz, SiH, 1 H), 7.14−8.01 (m, arom. CH, 10 H). − ^{13}C NMR ([D$_6$]benzene): δ = −1.8 (quat. C), 1.8 [Si(CH$_3$)$_2$], 5.6 [Si(CH$_3$)$_3$], 127.5, 129.2, and 136.8 (arom. CH), 139.6 (arom. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −16.0 and −15.5 (SiPh$_2$ and SiH), −0.8 (SiMe$_3$). − MS (70 eV); *m/z* (%): 399 (1) [M − H]$^+$, 336 (50) [M − C$_6$H$_5$, − H]$^+$, 321 (100) [M − C$_6$H$_5$, − CH$_3$, − H]$^+$, 264 (10) [M − C$_6$H$_5$, − SiMe$_3$]$^+$. − $C_{22}H_{38}Si_4$ (414.9): calcd. C 63.69, H 9.23; found C 63.65, H 9.13.

Methylbis(2,4,6-triisopropylphenyl)[bis(trimethylsilyl)methyl]silane (14): At room temperature a threefold molar excess of 2,4,6-triisopropylphenyllithium was added to **1a** (0.5 g, 1.8 mmol) in ether (30 mL). After stirring for 12 h, water was added and the organic layer separated, dried and concentrated. Chromatographic separation of the residue (silica gel, heptane) gave 0.42 g (44%) of **14**. Single crystals were obtained by recrystallization from heptane, m.p. 151−156 °C. − ^{1}H NMR ([D$_6$]benzene): δ = 0.11 and 0.38 (2 s, SiCH$_3$, 2 × 9 H), 0.22 (br. s, SiCH$_3$, 3 H), 0.46 (s, CH, 1 H), 1.40 (br. signal) and 1.12−1.23 (m, *i*Pr-CH$_3$, 36 H), 2.73 (m, *i*Pr-CH, 2 H), 3.23, 3.32, 3.59, and 3.73 (4 br. signals, *i*Pr-CH, 4 × 1 H), 6.90−7.20 (2 m, arom. CH, 4 H). − ^{13}C NMR ([D$_6$]benzene): δ = 4.3 and 5.7 [Si(CH$_3$)$_3$], 8.2 (CH), 9.2 (SiCH$_3$), 22.3, 23.0, 23.7, 23.9, 24.9, 25.7, 26.5, and 27.0 (*i*Pr-CH$_3$), 31.7, 32.4, 33.2, 34.1, and 35.3 (*i*Pr-CH), 122.7 (arom. CH), 138.1, 148.8, and 149.4 (arom. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −13.0 (SiMe), −1.4 and 0.6 (SiMe$_3$). − MS (70 eV); *m/z* (%): 608 (1) [M]$^+$, 593 (16) [M − CH$_3$]$^+$, 535 (1) [M − SiMe$_3$]$^+$, 449 (9) [M − CH(SiMe$_3$)$_2$]$^+$, 404 (89) [M − Tip, − H]$^+$, 201 (100) [M − 2 Tip, − H]$^+$. − $C_{38}H_{68}Si_3$ (609.2): calcd. C 74.92, H 11.25; found C 74.10, H 11.01.

General Procedure for the Preparation of the Silanols 15b, 15c, and 16c: To an ethereal solution of the dichloromethylsilane **1b** or **1c** a 2.2-fold molar excess of the respective organolithium compound was added at room temperature. After stirring for 12 h, the product was hydrolyzed by addition of water. The resulting silanols were extracted with ether and the solutions dried and concentrated. The residues were purified by chromatography (silica gel, heptane).

15b: Compound **1b** (0.5 g, 1.5 mmol) and 2,4,6-triisopropylphenyllithium (3.3 mmol) gave 0.4 g (55%) of silanol **15b**. Colorless oil. − IR (cap.): $\tilde{\nu}$ = 3682 cm^{-1}(OH). − ^{1}H NMR ([D$_6$]benzene): δ = 0.17 and 0.20 (2 s, SiCH$_3$, 2 × 9 H), 0.31 (s, CH, 1 H), 1.20 (d, ^3J = 6.7 Hz, *i*Pr-CH$_3$, 12 H), 1.23 (d, ^3J = 6.7 Hz, *i*Pr-CH$_3$, 6 H), 1.89 (s, OH, 1 H), 2.75 (sept, ^3J = 6.7 Hz, *i*Pr-CH, 1 H), 3.65 (sept, ^3J = 6.7 Hz, *i*Pr-CH, 2 H), 7.10−7.70 (m, arom. CH, 7 H). − ^{13}C NMR ([D$_6$]benzene): δ = 3.5 and 3.7 (SiCH$_3$), 7.8 (CH), 24.0, 24.8, and 25.7 (*i*Pr-CH$_3$), 33.3 and 34.5 (*i*Pr-CH), 121.9, 127.4, 129.4, and 133.1 (arom. CH), 135.1, 142.5, 150.5, and 155.3 (arom. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −2.8 (SiOH), −0.4 and 0.7 (SiMe$_3$). − MS (70 eV); *m/z* (%): 469 (70) [M − CH$_3$]$^+$, 467 (100) [M − OH]$^+$, 407 (20) [M − SiMe$_3$]$^+$. − $C_{28}H_{48}Si_3O$ (484.9): calcd. C 69.35, H 9.98; found C 66.87, H 9.80; HRMS calcd. for $C_{27}H_{45}OSi_3$ [M − CH$_3$] 469.26051, found 469.27783.

15c: Compound **1c** (0.5 g, 1.5 mmol) and 2,4,6-triisopropylphenyllithium (3.3 mmol) afforded 0.35 g (49%) of **15c**, colorless crystals, m.p. 54−57 °C (heptane). − IR (KBr): $\tilde{\nu}$ = 3681 cm^{-1} (OH). − ^{1}H NMR ([D$_6$]benzene): δ = 0.02 (s, CH, 1 H), 0.06, 0.20 and 0.30 (3 s, SiCH$_3$, 3 × 9 H), 1.35 (s, OH, 1 H), 1.21, 1.32 and 1.37 (3 d, ^3J = 6.7 Hz, *i*Pr-CH$_3$, 3 × 6 H), 2.77 (sept, ^3J = 6.7 Hz, *i*Pr-CH, 1 H), 3.50 (sept, ^3J = 6.7 Hz, *i*Pr-CH, 2 H), 7.09 (s, arom. CH, 2 H). − ^{13}C NMR ([D$_6$]benzene): δ = 0.7, 3.4, and 3.7 (SiCH$_3$), 9.2 (CH), 24.1, 25.6, and 26.0 (*i*Pr-CH$_3$), 32.5 and 32.4 (*i*Pr-CH), 121.7 (arom. CH), 134.9, 149.9, and 154.5 (arom. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −19.3 (Si*Si*Me$_3$), −0.6 and 1.8 (CSiMe$_3$), 7.6 (SiOH). − MS (70 eV); *m/z* (%): 465 (3) [M − CH$_3$]$^+$, 390 (1) [M − SiMe$_3$, − OH, − H]$^+$, 203 (100) [M − Tip, − SiMe$_3$, − H]$^+$. − $C_{25}H_{52}OSi_4$ (481.6): calcd. C 62.42, H 10.89; found C 62.14, H 10.87.

16c: Compound **1c** (0.5 g, 1.5 mmol) and 2-*tert*-butyl-4,5,6-trimethylphenyllithium (3.3 mmol) gave 0.3 g (44%) **16c**, colorless crystals, m.p. 50−56 °C. − IR (nujol): $\tilde{\nu}$ = 3695 cm^{-1} (OH). − ^{1}H NMR ([D$_6$]benzene): δ = −0.03, 0.19, and 0.38 (3 s, SiCH$_3$, 3 × 9 H), 0.32 (s, CH, 1 H), 1.48 (s, *t*Bu-CH$_3$, 9 H), 1.62 (s, OH, 1 H), 1.93, 2.12, and 2.16 (3 s, aryl-CH$_3$, 3 × 3 H), 7.23 (s, arom. CH, 1 H). − ^{13}C NMR ([D$_6$]benzene): δ = 0.2, 3.6, and 4.4 (SiCH$_3$), 6.1 (CH), 15.1, 21.1, and 24.0 (aryl-CH$_3$), 34.2 (*t*Bu-CH$_3$), 36.6 (*t*Bu-C), 127.0 (arom. CH), 132.4, 135.9, 136.3, 141.2, and 153.7 (arom. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −18.2 (Si*Si*Me$_3$), 0.5 (CSiMe$_3$), 1.5 (SiOH). − MS (70 eV); *m/z* (%): 437 (5) [M − CH$_3$]$^+$, 379 (37) [M − SiMe$_3$]$^+$; HRMS calcd. for $C_{23}H_{48}OSi_4$ 437.24907, found 437.25476.

General Procedure for the Preparation of the Methoxysilanes 17b, 17c, and 18c: At room temperature a 2.2-fold molar excess of the respective organolithium reagent was added to the ethereal solution of **1b** or **1c**, respectively After stirring for 12 h, excess methanol was added and stirring was continued for 2 h. The ethereal phases were separated and concentrated, and the residues were purified by chromatography (silica gel, heptane).

17b: Compound **1b** (0.5 g, 1.5 mmol) and 2,4,6-triisopropylphenyllithium (3.3 mmol) gave 0.45 g (60%) of **17b**, colorless oil. − IR (cap.): $\tilde{\nu}$ = 1103 cm^{-1} (SiOC). − ^{1}H NMR ([D$_6$]benzene): δ = 0.05 and 0.12 (2 s, SiCH$_3$, 2 × 9 H), 0.15 (s, CH, 1 H), 1.04, 1.07 and 1.13 (3 d, ^3J = 6.7 Hz, *i*Pr-CH$_3$, 3 × 6 H), 2.63 (sept, *i*Pr-CH, 1 H), 3.18 (s, OCH$_3$, 3 H), 3.45 (sept, *i*Pr-CH, 2 H), 7.04 (s, Tip-CH, 2 H), 6.95 and 7.54 (2 m, Ph-CH, 5 H). − ^{13}C NMR ([D$_6$]benzene): δ = 3.6 and 4.2 (SiCH$_3$), 8.4 (CH), 24.4, 24.6, and 26.3 (*i*Pr-CH$_3$), 32.3 and 34.5 (*i*PrCH), 51.8 (OCH$_3$), 121.9, 127.5, 129.6, and 132.3 (arom. CH), 136.5, 138.3, 150.5, and 155.6 (arom. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −0.8 and −0.7 (SiMe$_3$), 0.9 (SiOMe). − MS (70 eV): *m/z* (%): 497 (4) [M − H]$^+$, 483 (25) [M − CH$_3$]$^+$, 425 (8) [M − SiMe$_3$]$^+$, 295 (100) [M − Tip]$^+$. − $C_{29}H_{50}OSi_3$ (499.1): calcd. C 69.81, H 10.10; found C 70.09, H 10.11.

17c: Compound **1c** (0.5 g, 1.5 mmol) and 2,4,6-triisopropylphenyllithium (3.3 mmol) gave 0.3 g (40%) of **17c**, colorless crystals, m.p. 58−65 °C. − IR (nujol): $\tilde{\nu}$ = 1114 cm^{-1} (SiOC). − ^{1}H NMR ([D$_6$]benzene): δ = 0.02 (s, SiCH$_3$, 9 H), 0.10 (s, CH, 1 H), 0.33 (s, SiCH$_3$, 18 H),1.23 (d, ^3J = 6.7 Hz, *i*Pr-CH$_3$, 6 H), 1.36 (d, ^3J = 6.7 Hz, *i*Pr-CH$_3$, 12 H), 2.80 (sept, ^3J = 6.7 Hz, *i*Pr-CH, 1 H), 3.18 (sept, ^3J = 6.7 Hz, *i*Pr-CH, 2 H), 3.47 (s, OCH$_3$, 3 H), 7.09 (s, arom. CH), 2 H). − ^{13}C NMR ([D$_6$]benzene): δ = 2.1, 3.3, and 3.8 (SiCH$_3$), 9.9 (CH), 24.1, 25.9, and 26.2 (*i*Pr-CH$_3$), 33.3 and 34.4 (*i*Pr-CH), 52.2 (OCH$_3$), 121.9 (arom. CH), 135.9, 149.9, and 155.1 (arom. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −21.7 (Si*Si*Me$_3$), −0.2 and 1.8 (CSiMe$_3$), 10.4 (SiOMe). − MS (70 eV); *m/z* (%): 494 (8) [M]$^+$, 479 (59) [M − CH$_3$]$^+$, 291 (100) [M − Tip]$^+$; HRMS calcd. for $C_{26}H_{54}OSi_4$ 479.29319, found 479.30170. − $C_{26}H_{54}OSi_4$ (495.1): calcd. C 63.08, H 10.99; found C 63.00, H 10.85.

18c: Compound **1c** (0.5 g 1.5 mmol) and 2-*tert*-butyl-4,5,6-trimethylphenyllithium (3.3 mmol) afforded 0.3 g (43%) of **18c**, colorless crystals, m.p. 86−89 °C. − IR (nujol): $\tilde{\nu}$ = 1124 cm^{-1} (SiOC). − ^{1}H NMR ([D$_6$]benzene): δ = −0.05, 0.28, and 0.35 (3 s, SiCH$_3$, 3 × 9 H), 0.05 (s, CH, 1 H), 1.54 (s, *t*Bu-CH$_3$, 9 H), 1.92, 2.14, and 2.17 (3 s, aryl-CH$_3$, 3 × 3 H), 3.55 (s, OCH$_3$, 3 H), 7.26 (s, arom.

CH, 1 H). – ^{13}C NMR ([D$_6$]benzene): δ = 2.1, 3.5, and 4.3 (SiCH$_3$), 7.1 (CH), 15.1, 21.0, and 25.3 (aryl-CH$_3$), 33.5 (*t*Bu-CH$_3$), 37.4 (*t*Bu-CH), 52.8 (OCH$_3$), 127.3 (arom. CH), 128.3, 132.3, 135.8, 140.8, and 154.3 (arom. C). – ^{29}Si NMR ([D$_6$]benzene): δ = −18.6 (Si*Si*Me$_3$), −0.3 and 0.6 (CSiMe$_3$), 3.8 (SiOMe). – MS (70 eV); *m*/*z* (%): 466 (1) [M]$^+$, 451 (10) [M − CH$_3$]$^+$, 393 (100) [M − SiMe$_3$]$^+$; HRMS calcd. for $C_{23}H_{47}OSi_4$ [M − CH$_3$] 451.27550, found 451.27042. – $C_{24}H_{50}OSi_4$ (467.0): calcd. C 61.73, H 10.79; found C 61.90, H 10.58.

General Procedure for the Preparation of the 1,2-Oxasiletanes 19b, 19c, and 20c: At room temperature a 2.2-fold molar excess of the respective organolithium reagent was added to the ethereal solution of **1b** or **1c**, respectively. After stirring for 12 h, an equimolar quantity of benzaldehyde was added, stirring was continued for 2 h and the reaction quenched with water. The organic layer was separated, dried and concentrated and the residue was purified by chromatography (silica gel, heptane). Single crystals of the oxasiletanes were obtained by recrystallization from acetone.

19b: Compound **1b** (0.5 g, 1.5 mmol), 2,4,6-triisopropylphenyllithium (3.3 mmol) and benzaldehyde (0.16 g, 1.5 mmol) gave 0.1 g (12%) of **19b**, colorless crystals, m.p. 114−119 °C. – IR (cap.): $\tilde{\nu}$ = 1101 cm^{-1} (SiOC). – ^{1}H NMR ([D$_6$]benzene): δ = −0.07 and 0.17 (2 s, SiCH$_3$, 2 × 9 H), 1.17 (d, ^3J = 6.5 Hz, *i*Pr-CH$_3$, 6 H), 1.08, 1.37, 1.49, and 1.69 (4 d, ^3J = 6.5 Hz, *i*Pr-CH$_3$, 4 × 3 H), 2.84, 3.26, and 4.37 (3 sept, ^3J = 6.5 Hz, *i*Pr-CH, 3 × 1 H), 6.28 (s, PhCH, 1 H), 7.00−8.07 (m, arom. CH, 12 H). – ^{13}C NMR ([D$_6$]benzene): δ = 2.8 and 4.0 (SiCH$_3$), 23.9, 25.3, 25.5, 25.9, and 28.1 (*i*Pr-CH$_3$), 31.2, 34.5, and 36.5 (*i*Pr-CH), 36.2 (C(SiMe$_3$)$_2$), 81.3 (CH), 121.0, 123.3, 126.9, 128.2, 129.7, 132.4, and 134.5 (arom. CH), 134.8, 139.8, 151.4, 153.0, and 157.0 (arom. C). – ^{29}Si NMR ([D$_6$]benzene): δ = −2.2 and −0.4 (SiMe$_3$), 8.4 (ring-Si). – MS (70 eV); *m*/*z* (%): 572 (4) [M]$^+$, 557 (5) [M − CH$_3$]$^+$, 495 (2) [M − Ph]$^+$, 325 (100) [M − PhCC(SiMe$_3$)$_2$]$^+$; HRMS calcd. for $C_{35}H_{52}OSi_3$ 572.31011, found 572.33258.

19c: Compound **1c** (0.5 g, 1.5 mmol), 2,4,6-triisopropylphenyllithium (3.3 mmol) and benzaldehyde (0.16 g, 1.5 mmol) afforded 0.3 g (35%) of **19c**, colorless crystals, m.p. 153−155 °C. – IR (nujol): $\tilde{\nu}$ = 1009 cm^{-1} (SiOC). – ^{1}H NMR ([D$_6$]benzene): δ = 0.04, 0.20, and 0.29 (3 s, SiCH$_3$, 3 × 9 H), 1.22 (d, ^3J = 6.7 Hz, *i*Pr-CH$_3$, 6 H), 1.25, 1.39, 1.44, and 1.52 (4 d, ^3J = 6.7 Hz, *i*Pr-CH$_3$, 4 × 3 H), 2.75 (sept, ^3J = 6.7 Hz, *i*Pr-CH, 2 H), 4.13 (sept, ^3J = 6.7 Hz, *i*Pr-CH, 1 H), 6.26 (s, PhCH, 1 H), 7.03 and 7.24 (2 s, Tip-CH, 2 × 1 H), 7.11−7.82 (m, arom. CH). – ^{13}C NMR ([D$_6$]benzene): δ = 1.1, 2.6, and 3.4 (SiCH$_3$), 31.4 [C(SiMe$_3$)$_2$], 82.5 (PhCH), 24.1, 25.3, 25.9, 26.2, and 26.8 (*i*Pr-CH$_3$), 31.8, 34.5, and 35.0 (*i*Pr-CH), 120.3, 122.7, 126.6, and 127.1 (arom. CH), 135.9, 145.6, 150.8, 151.8, and 155.6 (arom. C). – ^{29}Si NMR ([D$_6$]benzene): δ = −15.0 (Si*Si*Me$_3$), −2.6 and 0.9 (CSiMe$_3$), 36.5 (ring-Si). – MS (70 eV); *m*/*z* (%): 553 (10) [M − CH$_3$]$^+$, 495 (69) [M − SiMe$_3$]$^+$; HRMS calcd. for $C_{31}H_{53}OSi_4$ [M − CH$_3$] 553.30991, found 553.31738.

20c: Compound **1c** (0.5 g, 1.5 mmol), 2-*tert*-butyl-4,5,6-trimethylphenyllithium (3.3 mmol), and benzaldehyde (0.16 g, 1.5 mmol) afforded 0.1 g (12%) of **20c**, colorless crystals, m.p. 170−175 °C. – IR (nujol): $\tilde{\nu}$ = 999 cm^{-1} (SiOC). – ^{1}H NMR ([D$_6$]benzene): δ = 0.04, 0.08, and 0.34 (3 s, SiCH$_3$, 3 × 9 H), 1.60 (s, *t*Bu-CH$_3$, 9 H), 1.93, 2.14, and 2.34 (3 s, aryl-CH$_3$, 3 × 3 H), 6.21 (s, PhCH, 1 H), 7.08−7.84 (m, arom. CH, 6 H). – ^{13}C NMR ([D$_6$]benzene): δ = 1.2, 2.9, and 4.7 (SiCH$_3$), 14.7, 21.1, and 23.3 (aryl-CH$_3$), 29.9 [C(SiMe$_3$)$_2$], 33.4 (*t*Bu-CH$_3$), 37.1 (*t*Bu-C), 79.8 (PhCH), 126.9, 127.3, 127.7, and 127.8 (arom. CH), 128.3, 131.6, 136.5, 137.2, 138.6, and 144.9 (arom. C). – ^{29}Si NMR ([D$_6$]benzene): δ = −16.2

Table 1. Crystal data and structure refinement data for compounds **19b**, **19c**, and **20c**

Compound	**19b**	**19c**	**20c**
Empirical formula	$C_{35}H_{52}OSi_3$	$C_{32}H_{56}OSi_4$	$C_{30}H_{52}OSi_4$
Molecular mass	573.04	569.13	541.08
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 9.440(2) Å b = 11.112(3) Å c = 18.440(6) Å α = 83.47(3)° β = 81.43(3)° γ =65.600(10)°	a = 20.740(4) Å b = 9.7790(10) Å c = 18.695(2) Å α = 90° β = 109.260(10)° γ = 90°	a = 21.048(4) Å b = 9.516(2) Å c = 16.667(6) Å α = 90° β = 100.31(2)° γ = 90°
Volume [Å^3]	1738.9(8)	3579.4(9)	3284.4(15)
Z	2	4	4
Density (calcd.) [Mg/m^3]	1.094	1.056	1.094
Absorption coeff. [mm^{-1}]	0.161	0.187	0.201
F(000)	624	1248	1184
Crystal size [mm^3]	0.82×0.52×0.36	0.66×0.46×0.32	0.80×0.40×0.35
Θ range for data coll.[°]	2.02 to 22.00	2.20 to 22.00	1.97 to 22.00
Index ranges	$-9 \le h \le 1$, $-11 \le k \le 11$, $-19 \le l \le 19$	$-21 \le h \le 20$, $-10 \le k \le 1$, $-1 \le l \le 19$	$-22 \le h \le 22$, $-10 \le k \le 1$, $-1 \le l \le 17$
Reflections collected	5219	5578	5170
Independent reflections	4261	4395	4018
[R(int)]	0.0322	0.0362	0.0400
Completeness to Θ = 22.00°	99.9%	99.9%	99.9%
Data/restraints/param.	4261/0/352	4395/0/334	4018/0/318
Goodness-of-fit on F^2	1.020	1.021	1.011
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0565 $wR2$ = 0.1512	$R1$ = 0.0493 $wR2$ = 0.1227	$R1$ = 0.0484 $wR2$ = 0.1225
R indices (all data)	$R1$ = 0.0691 $wR2$ = 0.1615	$R1$ = 0.0694 $wR2$ = 0.1354	$R1$ = 0.0679 $wR2$ = 0.1348
Largest diff. peak/hole [e·Å^{-3}]	0.390/−0.267	0.220/−0.174	0.226/−0.193

($Si\mathit{Si}Me_3$), −1.7 and 1.1 ($CSiMe_3$), 21.6 (ring-Si). − MS (70 eV); *m/z* (%): 525 (2) $[M - CH_3]^+$, 467 (11) $[M - SiMe_3]^+$; HRMS calcd. for $C_{29}H_{49}OSi_4$ $[M - CH_3]$ 525.27594, found 525.28607.

X-ray Structure Determinations of 19b, 19c, and 20c: Suitable crystals of the compounds were selected under a microscope and sealed onto a glass fiber. Afterwards rotational photos were taken and 13 reflections chosen to find reasonable reduced cells for the data collections. These data collections were done with a Siemens P4 four-circle diffractometer equipped with a graphite monochromator and using Mo-K_α radiation in a routine ω-scan. The structures were solved by direct methods (*SHELXTL*, Siemens Analytical X-ray Inst. Inc., **1990**) and refined by the full-matrix least-squares method of SHELXL-97 (G. M. Sheldrick, Universität Göttingen, **1997**). All non-hydrogen atoms were refined anisotropically . The H atoms were put into theoretical positions and refined using the riding model. Further details see Table 1. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143201 (**19b**), -143202 (**19c**), and -143203 (**20c**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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