# Silaheterocycles. 32.[1] Facile Synthesis of 3-Alkoxy-1-silacyclobutanes from the Trichlorovinylsilane/*t*-BuLi Reagent and Vinyl Ethers†

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Equimolar mixtures of trichlorovinylsilane and *t*-BuLi (**1**) were reacted with different vinyl ethers, $CH_2$=CH−OR (R = Et, *n*-Pr, *n*-Bu, *i*-Bu, *t*-Bu), to yield the silacyclobutanes **2**−**6**. NMR spectroscopic investigations showed the addition of the *formal* silene unit $Cl_2Si$=$CHCH_2t$-Bu to the vinyl group of the vinyl ethers to be stereo- and regiospecific, forming products of *E*-configuration. In contrast, in the presence of bisvinyl [$CH_2$=CH−O−$(CH_2)_n$−O−CH=$CH_2$ ($n$ = 2, 4, 6)] or cyclic vinyl ethers, such as 2,3-dihydrofuran and 3,4-dihydro-2*H*-pyran, the formation of silacylobutanes was suppressed and the formation of addition and SiCl/CHLi coupling products, such as $Cl_2$(R)$SiCH_2CH_2t$-Bu (R=Cl, **7**; *t*-Bu, **8**) and the tetrachloro-1,3-disilacyclobutane, $(Cl_2SiCHCH_2t\text{-}Bu)_2$ (**10**), was favored. Compounds **8** and **10** were characterized by single-crystal X-ray diffraction studies.



## Introduction

Monosilacyclobutanes have been investigated for several reasons. Their importance is mainly based on their ability to serve as precursors for the pyrolytic formation of transient silenes in the gas phase and their involvement in the production of new silicon-based materials by thermolysis, metathesis, and metal-catalyzed ring-opening polymerization reactions.[2] Furthermore, they serve as useful precursors for the formation of polysiloxanes containing silacyclobutane subunits in the silicon−oxygen-based backbone.[3] For these purposes a preparatively facile, preferably one-step, synthesis of such ring compounds was desired. Wiberg reported in 1986 the successful cycloaddition of silenes, $Me_2Si$=C(R)$SiMe_3$, to a vinyl ether to give a C3-alkoxy-substituted silacyclobutane.[4] During recent years we have investigated reactions of the trichlorovinylsilane/*t*-BuLi reagent[5] with suitable trapping agents as a route to 1,1-dichlorosilacyclobutanes. The dichlorosilylene functionality is useful for further modification of the silacyclobutanes via standard Si−Cl reactions.[2]

The reaction pathway leading to such silacyclic compounds is quite well understood: in general the reaction of organo-substituted chlorovinylsilanes $R^1R^2Si(Cl)CH$=$CH_2$ and *t*-BuLi leads to organolithium intermediates $R^1R^2Si(Cl)CH(Li)CH_2t$-Bu and via 1,2-LiCl-elimination to neopentylsilenes $R^1R^2Si$=$CHCH_2t$-Bu.[5]

Pursuing earlier work on the one-pot synthesis of monosilacyclobutanes, we describe here the preparation of 3-alkoxy-1-silacyclobutanes by reaction of equimolar amounts of trichlorovinylsilane, *t*-BuLi, and a small excess of a vinyl ether.[6]

## Results and Discussion

According to Scheme 1 *t*-BuLi adds to trichlorovinylsilane, initially forming the α-lithiated adduct, $Cl_3SiCH(Li)CH_2t$-Bu (**1**).[5,7] There are two possibilities for further reactions of **1**: (1) via intramolecular elimination of LiCl to give the silene $Cl_2Si$=$CHCH_2t$-Bu (path b), and (2) by direct reaction of the nucleophilic **1** with an electrophile (path a) (Scheme 1). At present we have no experimental evidence that favors either possibility in the reactions with vinyl ethers, and this question is the subject of studies currently in progress.[8] The reaction of the $Cl_3SiCH$=$CH_2$/*t*-BuLi reagent with vinyl ethers of the type $CH_2$=CHOR gives 3-alkoxy-1-silacyclobutanes in generally good yield.

The *formal* [2+2] cycloadducts **2**−**6** were isolated as colorless liquids (38−75% yield) and were characterized by their NMR spectra and mass spectrometry. Compared to other monosilacyclobutanes synthesized via the

† The experimental work described in this paper was performed at the Fachinstitut für Anorganische und Allgemeine Chemie der Humboldt-Universität zu Berlin, Hessische Strasse 1-2, 10115 Berlin.

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(1) Part 31: Auner, N.; Steinberger H.-U. *Z. Naturforsch.* **1994**, *49b*, 1743.

(2) Auner, N. *J. Prakt. Chem.* **1995**, *337*, 79, and relevant literature cited.

(3) Heikenwälder, C.-R. Ph.D. Thesis, Humboldt University Berlin, 1997.

(4) (a) R=$SiMe(t\text{-}Bu)_2$: Wiberg, N.; Wagner, G. *Chem. Ber.* **1986**, *119*, 1467. (b) R=$SiMe_3$: Wiberg, N.; Preiner, G. *Z. Naturforsch.* **1987**, *42b*, 1062.

(5) For reactions of diorgano-substituted vinylchlorosilanes and *t*-BuLi see: (a) Jones, P. R.; Lim, T. F. O.; Pierce, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 4970. (b) Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* **1977**, *99*, 8447. (c) Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* **1977**, *99*, 2013.

(6) The carbon analogue alkoxy-substituted cyclobutanes are well-known. For relevant literature see: Frauenrath, H. En-X-Verbindungen, in *Houben-Weyl, Methoden der Organischen Chemie, Vol. E15/1*; Kropf, H., Schaumann, E., Eds.; Thieme: Stuttgart, New York, 1993; p 332.

(7) This species can be trapped by $Me_3SiOSO_2CF_3$ to give $Cl_3SiCH(SiMe_3)CH_2t$-Bu: Auner, N.; Wolff, A. *Chem. Ber.* **1993**, *126*, 575.

(8) Ab initio calculations about competitive reactions of (neopentyl)-silenes and their corresponding lithiated equivalents are currently being carried out: Auner, N.; Apeloig, Y.; Müller, T.; Bendikov, M. In preparation.

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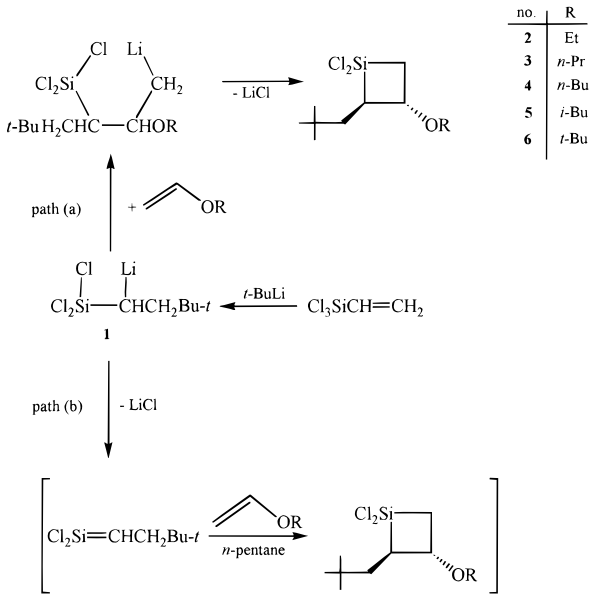
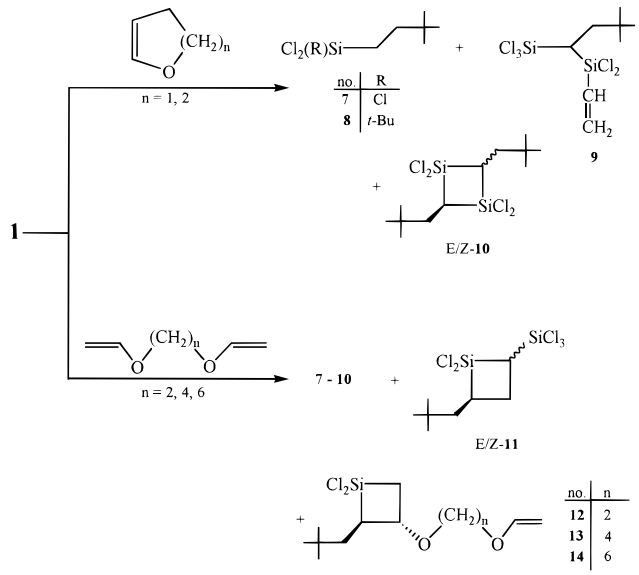
**Scheme 1**




**Scheme 2**




trichlorovinylsilane/*t*-BuLi reagent,[9−12] the NMR spectra of the products **2**−**6** were as expected. Especially the $^{29}$Si NMR resonance at ca. 14 ppm is very characteristic for *formal* [2+2] cycloaddition products resulting from reactions of this reagent with dienes[9,10,13,14] and permits quick identification of such compounds even in complex product mixtures. A full spectroscopic assignment for **5** by H,H-COSY, HSQC, and NOESY spectra is given as an example. The interpretation in the NMR spectroscopic part proves the stereo- and regiospecific addition of the silene unit to the vinyl group of the ethers.

In competition with silacyclobutane formation, in some cases compounds **7**−**11** (Scheme 2) were formed in various amounts. The formation of such products occurs via subsequent reactions of $Cl_3SiCH(Li)CH_2$*t*-Bu (**1**) in polar solvents[15] and results preferably from Si(Cl)/CH(Li) coupling to form **9**, solvent deprotonation to give **7**, and Si-chlorine → Si-*tert*-butyl replacement to yield **8**, respectively. Compounds **10** and **11** might alternatively be formed via the silene precursor. Using

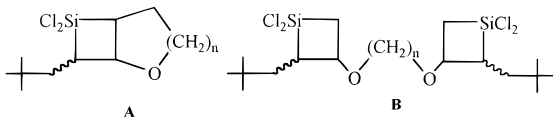



**Figure 1.** Silacyclobutanes, as expected from **1** and cyclic or bisvinyl ethers.

the bulky *tert*-butyl vinyl ether as reactant, the total amounts of **7**−**11** were ca. 25%. For ethyl or propyl vinyl ether these side reactions became even more prominent. However, the formation of **7**−**11** can be minimized or even avoided by using the vinyl ether reagents in high dilution.

With respect to the one-step preparation of precursors for the production of new silicon-based polymers, the facile synthesis of silacycles such as **A** and **B** (Figure 1) was of interest.

These compounds, in principle, should be easily prepared analogously to the syntheses of silacyclobutanes **2**−**6**, starting from equimolar amounts of trichlorovinylsilane, *t*-BuLi, and a small excess of respective cyclic vinyl ethers, e.g., 2,3-dihydrofuran and 3,4-dihydro-2*H*-pyran, or from bisvinyl ethers, $CH_2$=CH−O−$(CH_2)_n$−O−CH=$CH_2$ ($n$ = 2, 4, 6), respectively. However, the reaction of **1** with either the furan or the pyran led only to the formation of the compounds **7**−**10**; silacyclobutanes were not obtained.

With bisvinyl ethers as reaction partners for $Cl_3$-SiCH=$CH_2$/*t*-BuLi (**1**), similar results were obtained. From mixtures containing the ethers $CH_2$=CH−O−$(CH_2)_n$−O−CH=$CH_2$ ($n$ = 2, 4, 6) in a molar ratio of 1:1:1 and 2:2:1 the coupling products **7**−**11** were mainly formed, and only small amounts of the cycloadducts **12** and **13** could be isolated. The bulk of the vinyl ethers was recovered unchanged. Silacyclobutane **14** and "double cycloadducts" of the type **B** could not been detected, even by GC/MS analysis of the reaction mixtures.

For the characterization of **7**−**13** standard analytical and spectrosopic methods were used. The compounds **7**, **8**, and *E*/*Z*-**10** could be separated from the reaction mixtures; **8** and the *E*-isomer of **10** could be characterized by single-crystal X-ray analysis. The relative ratio of the products is given in Table 3 (Experimental Section) and depends mainly on the molar amounts of the starting materials used; for example, a small excess of *t*-BuLi led to the preferred formation of the *tert*-butyl-

(9) Sewald, N.; Ziche, W.; Wolff, A.; Auner, N. *Organometallics* **1993**, *12*, 4123.
(10) Ziche, W.; Sewald, N.; Seidenschwarz, C.; Herdtweck, E.; Popkova, V.; Auner, N. *Organometallics*, submitted.
(11) (a) Ziche, W.; Auner, N.; Behm, J. *Organometallics* **1992**, *11*, 2494. (b) Ziche, W.; Auner, N.; Behm, J. *Organometallics* **1992**, *11*, 3805.
(12) Auner, N.; Seidenschwarz, C.; Sewald, N. *Organometallics* **1992**, *11*, 1937.
(13) Auner, N.; Seidenschwarz, C.; Sewald, N.; Herdtweck, E. *Angew. Chem.* **1991**, *103*, 425; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 444.
(14) Ziche, W.; Seidenschwarz, C.; Auner, N.; Herdtweck, E.; Sewald, N. *Angew. Chem.* **1994**, *106*, 93; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 77.
(15) The reaction of equimolar amounts of trichlorovinylsilane and *t*-BuLi in THF results in nearly quantitative formation of (*E*/*Z*)-1,1,3,3-tetrachloro-2,4-neopentyl-1,3-disilacylobutane (**10**),[7] whereas the reaction in *n*-pentane yields more than one hundred products.[16a] In the presence of trapping agents in THF solution cycloadduct and disilacyclobutane formation compete, while in *n*-pentane the cycloadduct formation is strongly favored. Moreover, in most cases no tetrachloro-1,3-disilacyclobutane can be detected in the reaction mixtures.

**Table 1. Crystal Data and Details of the Structure Determination for 8 and *E*-10**

| | **8** | ***E*-10** |
|---|---|---|
| crystal system | monoclinic, 2/*m* | triclinic |
| space group | $P2_1/m$ (no. 11) | $P\bar{1}$ (no. 2) |
| lattice constants (Å, deg) | | |
| *a* | 6.0130(10) | 6.608(2) |
| *b* | 31.813(2) | 7.208(3) |
| *c* | 11.0050(10) | 9.755(4) |
| α | | 85.06(3) |
| *β* | 98.490(10) | 86.17(3) |
| *γ* | | 85.56(3) |
| *V* [Å$^3$] | 2082.1(4) | 460.7(3) |
| *Z* | 6 | 1 |
| $\rho_{obs}$, $\rho_{calc}$ (g/cm$^3$) | −, 1.155 | −, 1.320 |
| $F_{000}$ | 780 | 192 |
| $\mu_{Mo\ K\alpha}$ (mm$^{-1}$) | 0.5 | 0.8 |
| *R*, $R_w$, *S* | 0.0331, 0.0844, 1.029 | 0.0589, 0.1667, 1.13 |
| resd dens (e/Å$^3$) | −0.30, 0.355 | −0.37, 0.56 |

**Table 2. Preparation of Silacyclobutanes 2−6[a]**

| R | $CH_2$=CH−OR (g/mmol) | product | bp (°C/10$^{-2}$ mbar) | yield of product[b] (g/mmol/%) |
|---|---|---|---|---|
| Et | 4.32/60.00 | **2** | 45 | 5.99/23.50/39 |
| *n*-Pr | 5.17/60.00 | **3** | 50 | 6.19/23.00/38 |
| *n*-Bu | 6.01/60.00 | **4** | 53 | 12.74/45.00/75 |
| *i*-Bu | 6.01/60.00 | **5** | 43 | 12.17/43.00/72 |
| *t*-Bu | 6.01/60.00 | **6** | 46 | 12.74/45.00/75 |

[a] All silacyclobutanes are colorless liquids. [b] After distillation.

**Table 3. Reaction of 1 with Cyclic and Bisvinyl Ethers[a]**

| vinyl ether (g/mmol) | ratio of products (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **7** | **8** | **9** | E-**10** | *Z*-**10** | *E*-**11** | *Z*-**11** | CA[b] |
| 2H-furan | 46 | | 4 | 26 | 24 | | | |
| 4.32/60.00 | | | | | | | | |
| 2H-pyran | 49 | 18 | 2 | 16 | 15 | | | |
| 5.17/60.00 | | | | | | | | |
| ViO($CH_2$)$_2$OVi | | | | | | | | **12** |
| 6.84/60.00 | 45 | 2 | 1 | 26 | 26 | | | |
| 3.42/30.00 | 37 | | 20 | 14 | 16 | 5 | 2 | 6 |
| ViO($CH_2$)$_4$OVi | | | | | | | | **13** |
| 8.53/60.00 | 34 | 22 | | 13 | 13 | 6 | 3 | 9 |
| 4.26/30.00 | 10 | 6 | 4 | 24 | 13 | 11 | 6 | 26 |
| ViO($CH_2$)$_6$OVi | | | | | | | | **14** |
| 10.22/60.00 | 54 | 5 | 21 | 8 | 12 | | | |
| 5.11/30.00 | 14 | | 28 | 8 | 10 | 28 | 12 | |

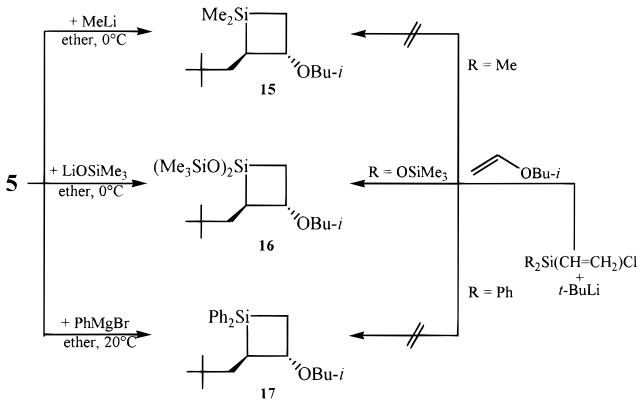
[a] **1** reacts with "double vinyl ethers" in ratios of 1:1 and 2:1. [b] Number and yield of isolated formal [2+2] cycloadduct.

substituted product **8** instead of **7**.[16] Characteristic $^{13}$C and $^{29}$Si NMR spectroscopic data of **12** and **13** are given in the NMR Spectroscopic Section; the assignment of the resonance signals conforms with those discussed for **5**.

In contrast to silene equivalent **1**, 1,1-diorgano-2-neopentyl-1-silenes, e.g., $Me_2Si$=$CHCH_2$*t*-Bu[5] and $Ph_2$-Si=$CHCH_2$*t*-Bu,[17] show a very different reactivity; their tendency to preferentially form [4+2] over [2+2] cycloadducts in the presence of suitable trapping agents is well documented, as is their much decreased dienophilicity.[2] The same is true for reactions of these silenes with vinyl ethers, as pointed out in Scheme 3.

As expected, the reaction of a small excess of isobutyl vinyl ether with equimolar amounts of chlorodimethylvinylsilane/*t*-BuLi and of chlorodiphenylvinylsilane/*t*-BuLi does not result in formation of the silacyclobutanes **15** and **17**. However, alternatively, the synthesis of **15** and **17** is possible via the "dichlorosilyl route". Thus, the reaction of **5** with 2 equiv of methyllithium yielded compound **15**, whereas the reaction with phenyl Grignard reagent gave silacyclobutane **17**. Only 2-neopentyl-1,1-bis(trimethylsiloxy)-1-silene[18] [from chlorobis(trimethylsiloxy)vinylsilane and *t*-BuLi] shows reactivity similar to that of silene equivalent **1**: it reacted with isobutyl vinyl ether to give silacyclobutane **16**. Alternatively, the same compound was obtained in the reaction of **5** with $LiOSiMe_3$ in diethyl ether. The silacyclobutanes **15**−**17** were characterized by the usual analytical and NMR spectroscopic methods, and the data fit well to those determined for compound **5**.

**Scheme 3**




These experiments, using differently organo-substituted neopentylsilenes and isobutyl vinyl ether as reaction partners, emphasize the outstanding utility of the mixture trichlorovinylsilane/*t*-BuLi as a reagent for the synthesis of silacyclobutanes.

## NMR Spectroscopic Section

The coupling reactions of **1** with vinyl ethers and the subsequent intramolecular ring closure led to (*E*)-3-alkoxy-1,1-dichloro-2-neopentyl-1-silacyclobutanes **2**−**6** stereo- and regiospecifically. The following section proves this statement and summarizes the results obtained from 1 D and 2 D NMR techniques, i.e., gradient selected H,H-COSY,[19] phase-sensitive gradient-selected HSQC,[20] and NOESY.[21] An assignment of the NMR

(16) For further information see: (a) Auner, N. *Z. Anorg. Allg. Chem.* **1988**, *558*, 55. (b) Auner, N.; Gleixner, R. *J. Organomet. Chem.* **1990**, *393*, 33.

(17) Auner, N.; Ziche, W.; Herdtweck, E. *J. Organomet. Chem.* **1992**, *426*, 1.

(18) Auner, N.; Heikenwälder, C.-R.; Ziche, W. *Chem. Ber.* **1993**, *126*, 2177.

(19) A total of one scan, preceded by eight dummy scans, was recorded into 2K data blocks for each of the 128 $t_1$ values with a relaxation delay of 1.5 s and a spectral widths of 1255.02 Hz. The data matrix was zero-filled to 1K×256w, and the apodization was performed with shifted square sine bell window functions in both dimensions: (a) Hurd, R. E. *J. Magn. Reson.* **1990**, *87*, 422. (b) von Kienlin, M.; Moonen, C. T. W.; van der Toorn, A.; van Zijl, P. C. M. *J. Magn. Reson.* **1991**, *93*, 423.

(20) A total of two scans, preceded by eight dummy scans, were recorded into 1K data block for each of the 256 $t_1$ values with a relaxation delay of 1.8 s and a spectral widths of 1990.44 Hz in $f_2$ and 12562.81 Hz in $f_1$. The data matrix was zero-filled to 2K × 512w and the apodization was performed with shifted square sine bell window functions in both dimensions: (a) Kay, L. E.; Keifer P.; Saarinen, T. *J. Am. Chem. Soc.* **1992**, *114*, 10663. (b) Kontaxis, G.; Stonehouse, J.; Laue, E. D.; Keeler, J. *J. Magn. Reson. Ser. A* **1994**, *111*, 70.

(21) A total of 56 scans, preceded by four dummy scans, were recorded into 2K data blocks for each of the 512 $t_1$ values with a relaxation delay of 2.0 s and spectral widths of 7246 Hz. The mixing time was set to 1.0 s and was varied randomly in the range of ±30 ms

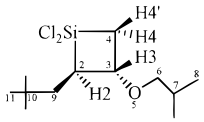



**Figure 2.** Numbering of the atoms in silacyclobutane **5**.

spectroscopic data is given for silacyclobutane **5** as an example. The numbering of the carbon and hydrogen atoms is shown in Figure 2. The NMR spectroscopic data are listed in the Experimental Section.

Starting the interpretation of the H,H-COSY with the most deshielded aliphatic signal, proton 3 (H3) is easy to localize at 3.66 ppm. This ring proton shows cross-peaks to H2 (2.21 ppm) and to both protons at C4 (1.69 and 2.23 ppm). The cross-peak of H2 leads to both protons at C9 (1.59 and 1.65 ppm), while H4′ at 2.23 ppm correlates with H4 (1.69 ppm) and H3. The protons at the neopentyl group (C9) have no further correlations.

Compared to $^{13}C$ NMR reference spectra of vinyl ethers, C3 (75.09 ppm) is in the characteristic range of aliphatic carbon atoms attached to oxygen. This proves the position of the butoxy substituent at the four-membered ring. The carbon atoms of the butoxy group are seen at 75.89 (C6, $CH_2$), 28.55 (C7, CH), and 19.49 (C8, $CH_3$) ppm and in agreement with the data of the isobutyl vinyl ether reference spectrum. The typical cross-peaks for the protons are available from the H,H-COSY spectrum, and the $^1H$ NMR shifts are given in the Experimental Section.

To determine the relative configuration of **5**, a NOESY[21] experiment was used. Starting the interpretation with the most deshielded aliphatic signal, a NOESY cross-peak is observed between H3 (3.66 ppm) and the protons of the $CH_2$ groups C6 (H6/H6′: 3.05/3.19 ppm) and C9 (H9/H9′: 1.59/1.65 ppm), whereas no cross-peak is observed between H3 and H2 (2.21 ppm). Furthermore, a weak NOE is noted for H3 and H4′ at 2.23 ppm. These results prove the *E*-configuration of silacyclobutane **5**.

**Single-Crystal X-ray Structure Analyses of 8 and *E*-10. 8.** From the reactions of the vinyltrichlorosilane/*t*-BuLi reagent with bisvinyl or cyclic vinyl ethers small portions of the chlorosilanes $Cl_2Si(R)CH_2CH_2t$-Bu (R = Cl, **7**; *t*-Bu, **8**) could be isolated. The crude solid product mixture was recrystallized from cold *n*-pentane, and **8** was obtained as a crystalline material that was suitable for X-ray diffraction analysis. The crystal data and details of the structure determination and refinement (together with *E*-**10**) are listed in Table 1. The molecular structure of **8** is shown in Figure 3. Bond distances and angles are listed in the caption.

The silicon center is surrounded by two alkyl and chlorine substituents each in a distorted tetrahedral fashion. Due to the steric demand of the alkyl groups, the angle C−Si−C of 115.98(8)° is slightly widened, while the Cl−Si−Cl angle of 105.73(3)° is slightly constricted relative to the ideal geometry. The average

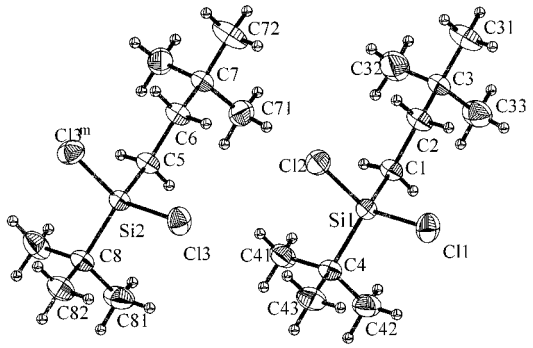



**Figure 3.** DIAMOND plot of the asymmetrical unit of 2,2,6,6-tetramethyl-3,3-dichloro-3-silaheptane (**8**) with numbering scheme. Ellipsoids are drawn at the 50% level. Selected bond distances (Å) and angles (deg): Cl1−Si1 2.0616(7), Cl2−Si1 2.0612(7), Si1−C1 1.8479(19), Si1−C4 1.8717(18), Cl1−Si1−Cl2 105.73(3), Cl1−Si1−C1 108.36(6), Cl1−Si1−C4 109.23(6), Cl2−Si1−C1 108.29(6), Cl2−Si1−C4 108.76(6), C1−Si1−C4 115.98(8); Cl3−Si2 2.0606(7), Si2−C8 1.871(2), Si2−C5 1.851(2). Atoms C82, C8, Si2, C5, C6, C7, and C72 occupy positions *x*, 0.25, *z* and −*x*, 0.75, −*z* (Wyckoff: 2e) on the mirror plane *m* of the monoclinic spacegroup $P2_1/m$ (no. 11).

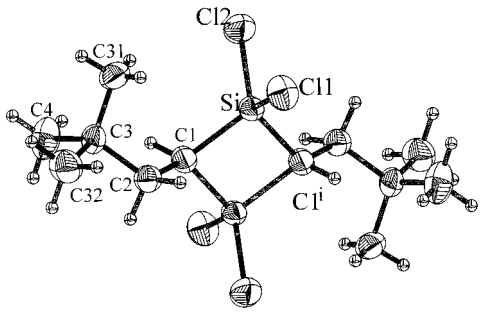



**Figure 4.** DIAMOND plot of the molecular structure of 1,1,3,3-tetrachloro-2,4-dineopentyl-1,3-disilacyclobutane (**10**) with numbering scheme. Ellipsoids are drawn at the 50% probability level (symmetry generator *i*: −*x*, −*y*, 1−*z*). Bond distances (Å) and angles (deg): Cl1−Si 2.034(2), Cl2−Si 2.034(2), Si−C1 1.887(4), Si−C1$^i$ 1.880(4), Si−Si$^i$ 2.561(2), C1−C2 1.524(6), C2−C3 1.542(5), C3−C4 1.525(7), C3−C31 1.523(6), C3−C32 1.546(6); Cl1−Si−Cl2 108.89(7), Cl1−Si−C1 113.94(14), Cl1−Si−C1$^i$ 111.38(13), C1−Si−C1$^i$ 94.36(17), Cl2−Si−C1 114.05(14), Cl2−Si−C1$^i$ 113.72(14), Si−C1−Si$^i$ 85.64(17), Si−C1−C2 124.2(3), C1−C2−C3 116.0(3), C2−C3−C4 112.6(3), C2−C3−C31 110.3(3), C2−C3−C32 106.3(3), C4−C3−C31 110.5(3), C4−C3−C32 108.7(4), C31−C3−C32 108.2(3).

Si−Cl and Si−C bond lengths are in the normal range for such bonds.

***E*-10.** From the reaction of vinyltrichlorosilane/*t*-BuLi (**1**) and 2,3-dihydrofuran a product mixture consisting of *E*-**10**/*Z*-**10**/**7**/**9** was formed in a relative molar ratio of 26:24:46:4. Crystals of the 1,3-disilacyclobutane *E*/*Z*-**10** were isolated by sublimation (50 °C/$10^{-2}$ mbar). The E/Z isomeric ratio was 52:48 and differed slightly from that reported in the literature (40:60[7,15,16]). Low-temperature recrystallization from *n*-pentane gave the pure single crystalline *E*-**10**, while the *Z* isomer remained in solution.

The centrosymmetric *E*-**10** crystallizes triclinic with one molecule in the unit cell. The molecular structure is shown in Figure 4, and bond distances and angles are listed in the caption. The core of the structure is

to suppress zero quantum coherence. The data matrix was zero-filled to 2K×1K, and the apodization was done with shifted square sine bell window functions in both dimensions: (a) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546. (b) States, D. J.; Haberkorn, R. A.; Ruben, D. J. *J. Magn. Reson.* **1982**, *48*, 286. (c) Bodenhausen, G.; Kogler, H.; Ernst, R. R. *J. Magn. Reson.* **1984**, *58*, 370.

best described as a diamond-shaped planar $Si_2C_2$ unit with two equal Si−C bond lengths. Since the silicon adopts a distorted tetrahedral coordination, the four Cl−Si−C angles are widened. The Cl−Si−Cl angle lies close to the ideal tetrahedral angle.

The crystal structure is characterized by weak intermolecular electrostatic interactions between the disilacyclobutane molecules reflected by a set of H···Cl distances of 3.2−3.7 Å between the methyl group hydrogen atoms of the neopentyl and the chlorine substituents. This leads to a three-dimensional network within the crystal structure.

## Experimental Section

**General Procedures.** All reactions were performed with exclusion of moisture and oxygen under an atmosphere of dry nitrogen. Solvents were dried by standard methods. Trichlorovinylsilane and chlorodimethylvinylsilane were obtained from Wacker Chemie GmbH (Burghausen, Germany); chlorodiphenylvinylsilane and chlorobis(trimethylsiloxy)vinylsilane were synthesized according to refs 17 and 18. The silanes were distilled from $K_2CO_3$ prior to use.

*t*-BuLi (1.7 M in *n*-pentane) and LiMe (1.6 M in diethyl ether) were obtained from Chemetall (Frankfurt/Main, Germany). Vinyl ethers, hexamethyldisiloxane, and bromobenzene were used as purchased from Aldrich-Chemie GmbH & Co KG (Steinheim, Germany).

Gas chromatography was carried out with a Varian Star 3400 CX with a 15 m column (J&W Scientific DB-1, Ø 0.32 mm). GC/MS analysis was performed with a Chrompack CP 9000 with a 12.5 m column (Chrompack CP Sil 5 CB-MS) coupled with a Finnigan MAT ion trap 800. Routine NMR spectra were recorded on a Bruker DPX 300 ($^1$H, $^{13}$C, and $^{13}$C DEPT) and Bruker AM 300 ($^{29}$Si). $CHCl_3$ was used as an internal standard in $^1$H and $^{13}$C NMR experiments ($^{29}$Si NMR: TMS as external standard).

All 2 D NMR experiments were done on a Bruker DPX 300 (H,H-COSY, HSQC) and a Bruker AMX 600 (NOESY) at 298 K in $CHCl_3$ as solvent and internal standard.

Elemental analyses were performed by Zentrales Elementaranalytisches Labor des Instituts für Chemie der Humboldt-Universität zu Berlin.

**General Procedure for the "One-Pot Synthesis" of C3-Alkoxy-Substituted Silacyclobutanes.** Trichlorovinylsilane (8.08 g, 50.0 mmol) and 60.0 mmol of the vinyl ether (exception: reaction of **1** with bisvinyl ethers in the ratio of 2:1) were dissolved in 200 mL of *n*-pentane, and the solution was cooled to −78 °C. An equimolar amount of *t*-BuLi (1.7 M in *n*-pentane) was added dropwise. The reaction mixture was allowed to warm to room temperature. The solution was filtered to remove precipitated LiCl. The solvent and excess trapping agent were distilled in vacuo at ambient temperature. The residue was distilled at $10^{-2}$ mbar. In general, colorless liquids were isolated. Only products containing no contamination by unknown substances as determined by GC and NMR spectroscopy were submitted for elemental analysis. The syntheses of C3-alkoxy-substituted monosilacyclobutanes are summarized in Tables 2 and 3.

**(*E*)-1,1-Dichloro-3-ethoxy-2-neopentyl-1-silacyclobutane (2):** $^1$H NMR ($CDCl_3$) $\delta$ 0.89 [s, 9H, C(C$H_3$)$_3$], 1.17 (t, $J$ = 7.1 Hz, 3H, C$H_3$), 1.58 (m, 2H, C$H_2$*t*-Bu), 1.71 (ddd, $J$ = 15.9/8.1/1.5 Hz, 1H, H4), 2.22 (m, 1H, H2), 2.24 (ddd, $J$ = 15.8/7.8/1.5 Hz, 1H, H4′), 3.37, 3.49 (q, $J$ = 6.8 Hz, 2H, OC$H_2$), 3.70 (dd, $J$ = 16.1/8.3 Hz, 1H, H3); $^{13}$C NMR ($CDCl_3$) $\delta$ 15.26 (C$H_3$), 29.44 [C(C$H_3$)$_3$], 30.51 [C(CH$_3$)$_3$], 32.02 (C4), 42.58 (C$H_2$*t*-Bu), 46.78 (C2), 64.34 (OC$H_2$), 74.76 (C3); $^{29}$Si NMR ($CDCl_3$) $\delta$ 13.89; MS (EI) *m*/*e* 208 (24), 193 (9), 178 (28), 129 (100), 115 (28). Anal. Calcd (found) for $C_{10}H_{20}Cl_2OSi$ (255.261): C, 47.05 (46.98); H, 7.90 (8.01); Cl, 27.78 (27.67).

**(*E*)-1,1-Dichloro-2-neopentyl-3-*n*-propoxy-1-silacyclobutane (3):** $^1$H NMR ($CDCl_3$) $\delta$ 0.90 (m, 3H, C$H_3$), 0.90 [s, 9H, C(C$H_3$)$_3$], 1.56 (m, 2H, C$H_2$*t*-Bu), 1.66 (m, 2H, C$H_2$CH$_3$), 1.69 (m, 1H, H4), 2.21 (m, 1H, H2), 2.23 (dd, $J$ = 15.0/8.4 Hz, 1H, H4′), 3.27, 3.41 (dt, $J$ = 9.0/6.4 Hz, 2H, OC$H_2$), 3.68 (ddd, $J$ = 8.4/8.2/8.1 Hz, 1H, H3); $^{13}$C NMR ($CDCl_3$) $\delta$ 10.74 (C$H_3$), 23.02 (C$H_2$CH$_3$), 29.62 [C(C$H_3$)$_3$], 30.55 [C(CH$_3$)$_3$], 32.03 (C4), 42.63 (C$H_2$*t*-Bu), 46.76 (C2), 70.65 (OC$H_2$), 73.85 (C3); $^{29}$Si NMR ($CDCl_3$) $\delta$ 14.03; MS (EI) *m*/*e* 269 ($M^+$ + 1, 8), 253 ($M^+$ − 15, 10), 215 (15), 125 (18), 95 (17), 57 (100). Anal. Calcd (found) for $C_{11}H_{22}Cl_2OSi$ (269.288): C, 49.06 (48.94); H, 8.23 (8.29); Cl, 26.33 (26.41).

**(*E*)-3-*n*-Butoxy-1,1-dichloro-2-neopentyl-1-silacyclobutane (4):** $^1$H NMR ($CDCl_3$) $\delta$ 0.88 (t, br, $J$ = 7.4 Hz, 3H, C$H_3$), 0.89 [s, 9H, C(C$H_3$)$_3$], 1.34 (sext, br, $J$ = 7.4 Hz, 2H, C$H_2$CH$_3$), 1.51 (quin, br, $J$ = 6.2 Hz, 2H, OCH$_2$C$H_2$), 1.59 (m, 2H, C$H_2$*t*-Bu), 1.66 (ddd, $J$ = 15.0/8.3/1.5 Hz, 1H, H4), 2.18 (m, 1H, H2), 2.20 (ddd, $J$ = 15.2/7.7/1.1 Hz, 1H, H4′), 3.27, 3.41 (dt, $J$ = 9.2/6.4 Hz, 2H, OC$H_2$), 3.64 (ddd, $J$ = 8.3/8.3/8.1 Hz, 1H, H3); $^{13}$C NMR ($CDCl_3$) $\delta$ 13.90 (C$H_3$), 19.38 (C$H_2$CH$_3$), 29.45 [C(C$H_3$)$_3$], 30.51 [C(CH$_3$)$_3$], 31.85 (OCH$_2$C$H_2$), 31.97 (C4), 42.60 (C$H_2$*t*-Bu), 46.74 (C2), 68.76 (OC$H_2$), 74.92 (C3); $^{29}$Si NMR ($CDCl_3$) $\delta$ 14.02; MS (EI) *m*/*e* 282 ($M^+$, 2), 263 (44), 209 (17), 191 (31), 151 (52), 123 (92), 95 (100), 81 (46). Anal. Calcd (found) for $C_{12}H_{24}Cl_2OSi$ (283.315): C, 50.82 (50.67); H, 8.54 (8.32); Cl, 25.06 (25.26).

**(*E*)-1,1-Dichloro-3-isobutoxy-2-neopentyl-1-silacyclobutane (5):** $^1$H NMR ($CDCl_3$) $\delta$ 0.88, 0.89 [d, $J$ = 1.5 Hz, 6H, H8,8′, CH(C$H_3$)$_2$], 0.90 [s, 9H, C(C$H_3$)$_3$], 1.59 (dd, $J$ = 14.3/7.5 Hz, 1H, H9/9′, C$H_2$*t*-Bu), 1.65 (dd, $J$ = 15.0/4.2 Hz, 1H, H9/9′, C$H_2$*t*-Bu), 1.69 (ddd, $J$ = 13.6/8.3/1.5 Hz, 1H, H4), 1.81 [non, $J$ = 6.6 Hz, 1H, C$H$(CH$_3$)$_2$], 2.21 (ddd, $J$ = 9.4/8.2/6.9 Hz, 1H, H2), 2.23 (ddd, $J$ = 14.3/7.8/0.9 Hz, 1H, H4′), 3.05, 3.19 (dd, $J$ = 8.8/6.6 Hz, 2H, H6,6′, OCH$_2$), 3.66 (ddd, $J$ = 9.4/8.3/7.8 Hz, 1H, H3); $^{13}$C NMR ($CDCl_3$) $\delta$ 19.49 [CH(C$H_3$)$_2$], 28.55 [CH-(CH$_3$)$_2$], 29.49 [C(C$H_3$)$_3$], 30.55 [C(CH$_3$)$_3$], 31.96 (C4), 42.65 (C$H_2$*t*-Bu), 46.75 (C2), 75.09 (C3), 75.89 (OCH$_2$); MS (EI) *m*/*e* 282 ($M^+$, 3), 267 ($M^+$ − 15,5), 263 (34), 209 (17), 191 (29), 151 (37), 123 (81), 95 (100), 81 (37); $^{29}$Si NMR ($CDCl_3$) $\delta$ 14.03. Anal. Calcd (found) for $C_{12}H_{24}Cl_2OSi$ (283.315): C, 50.87 (50.75); H, 8.54 (8.58); Cl, 25.03 (25.01).

**(*E*)-3-*tert*-Butoxy-1,1-dichloro-2-neopentyl-1-silacyclobutane (6):** $^1$H NMR ($CDCl_3$) $\delta$ 0.83 [s, 9H, C(C$H_3$)$_3$], 1.09 [s, 9H, OC(C$H_3$)$_3$], 1.40 (dd, $J$ = 13.3/3.8 Hz, 1H, C$H_2$*t*-Bu), 1.48 (dd, $J$ = 23.4/11.7 Hz, 1H, C$H_2$*t*-Bu), 1.70 (ddd, $J$ = 15.2/8.5/1.1 Hz, 1H, H4), 2.06 (m, 1H, H2), 2.08 (dd, $J$ = 15.2/7.1 Hz, 1H, H4′), 3.66 (ddd, $J$ = 8.6/8.6/8.1 Hz, 1H, H3); $^{13}$C NMR ($CDCl_3$) $\delta$ 28.62 [OC(C$H_3$)$_3$], 29.55 [C(C$H_3$)$_3$], 30.26 [C(CH$_3$)$_3$], 36.16 (C4), 41.90 (C$H_2$*t*-Bu), 47.96 (C2), 67.94 (C3), 73.58 [OC(CH$_3$)$_3$]; $^{29}$Si NMR ($CDCl_3$) $\delta$ 14.20; MS (EI) *m*/*e* 209 (9), 199 (13), 183 (20), 121 (100), 105 (43), 83 (89). Anal. Calcd (found) for $C_{12}H_{24}Cl_2OSi$ (283.315): C, 50.87 (50.81); H, 8.54 (8.44); Cl, 25.03 (25.10).

**1,1,1-Trichloro-4,4-dimethyl-1-silapentane (7):** $^1$H NMR ($CDCl_3$) $\delta$ 0.93 [s, 9H, C(C$H_3$)$_3$], 1.39 (m, 4H, C$H_2$); $^{13}$C NMR ($CDCl_3$) $\delta$ 19.73 (C2), 28.83 [C(C$H_3$)$_3$], 30.90 [C(CH$_3$)$_3$], 35.67 (C3); $^{29}$Si NMR ($CDCl_3$) $\delta$ 14.21; MS (EI) *m*/*e* 203 ($M^+$ − 15, 44), 183 ($M^+$ − 35, 6), 177 (55), 161 (13), 133 (100), 98 (19). Anal. Calcd (found) for $C_6H_{13}Cl_2Si$ (219.597): C, 32.82 (32.78); H, 5.97 (6.03); Cl, 48.42 (48.61).

**3,3-Dichloro-2,2,6,6-tetramethyl-3-silaheptan (8):**[22] $^{13}$C NMR ($CDCl_3$) $\boldsymbol{\delta}$ 11.63 (C4), 25.30 (C1), 28.83 (C7), 31.27 (C2), 31.68 (C6), 36.48 (C5); $^{29}$Si NMR ($CDCl_3$) $\boldsymbol{\delta}$ 21.14; MS (EI) *m*/*e* 240 ($M^+$, 2), 225 ($M^+$ − 15, 15), 205 ($M^+$ − 35, 3), 184 (22), 155 (18), 113 (100).

**3,3-Dichloro-4-trichlorosilyl-6,6-dimethyl-3-silahept-1-**

(22) This compound could only be isolated in traces together with **7** or **10**. For complete experimental data see: Wagner, C. Ph.D. Thesis, Technische Universität München, 1995.

**ene (9):**[23] $^1$H NMR ($CDCl_3$) $\delta$ 0.90 [s, 9H, C(C$H_3$)$_3$], 1.39 (m, 1H, H4), 1.88 (d, $J$ = 4.1 Hz, 2H, C$H_2$*t*-Bu), 6.26 (d, $J$ = 14.4 Hz, 1H, H1), 6.27 (d, $J$ = 10.0 Hz, 1H, H1′), 6.28 (dd, $J$ = 14.4/10.0 Hz, 1H, H2); $^{13}$C NMR ($CDCl_3$) $\delta$ 23.76 (C4), 29.67 [C(*C*H$_3$)$_3$], 31.89 [*C*(CH$_3$)$_3$], 36.21 (C5), 131.81 (C2), 138.91 (C1); MS (EI) *m*/*e* 342 ($M^+$, 10), 250 (3), 57 (100); $^{29}$Si NMR ($CDCl_3$) $\delta$ 12.75 ($SiCl_3$), 29.37 ($SiCl_2$). Anal. Calcd (found) for $C_8H_{15}Cl_5Si_2$ (344.645): C, 27.88 (27.21); H, 4.39 (4.19); Cl 51.43 (51.67).

**(*E*/*Z*)-1,1,3,3-Tetrachloro-2,4-dineopentyl-1,3-disilacyclobutane (10).**[23] ***E*-10:** $^1$H NMR ($CDCl_3$) $\delta$ 0.76 [s, 18H, C(C$H_3$)$_3$], 0.84 (dd, $J$ = 14.4/5.2 Hz, 2H, C*H*), 1.30 (dd, $J$ = 12.0/5.2 Hz, 2H, C$H_2$*t*-Bu), 1.75 (dd, $J$ = 14.4/12.0 Hz, 2H, C$H_2$*t*-Bu); $^{13}$C NMR ($CDCl_3$) $\delta$ 29.03 [C(*C*H$_3$)$_3$], 31.17 [*C*(CH$_3$)$_3$], 35.61 (CH), 38.20 (*C*H$_2$*t*-Bu); $^{29}$Si NMR ($CDCl_3$) $\delta$ 21.20; MS (EI) *m*/*e* 350 (13), 309 (100), 267 (22), 133 (69), 105 (75).

***Z*-10:** $^1$H NMR ($CDCl_3$) $\delta$ 0.79 [s, 18H, C(C$H_3$)$_3$], 0.92 (dd, $J$ = 13.1/4.7 Hz, 2H, C*H*), 1.28 (dd, $J$ = 12.0/4.7 Hz, 2H, C$H_2$*t*-Bu), 1.75 (dd, $J$ = 13.1/12.0 Hz, 2H, C$H_2$*t*-Bu); $^{13}$C NMR ($CDCl_3$) $\delta$ 29.15 [C(*C*H$_3$)$_3$], 31.03 [*C*(CH$_3$)$_3$], 33.87 (CH), 38.05 (*C*H$_2$*t*-Bu); $^{29}$Si NMR ($CDCl_3$) $\delta$ 18.67; MS (EI) *m*/*e* 350 (13), 308 (93), 265 (19), 133 (67), 105 (100). Anal. Calcd (found) for $C_{12}H_{24}Cl_4Si_2$ (366.308): C, 39.35 (39.31); H, 6.60 (6.71); Cl, 38.72 (38.68).

**(*E*/*Z*)-1,1-Dichloro-4-neopentyl-2-trichlorosilyl-1-silacyclobutane (11). *E*-11:** $^1$H NMR ($CDCl_3$) $\delta$ 0.90 [s, 9H, C(C$H_3$)$_3$], 1.46, 1.68 (dd, $J$ = 12.6/4.7 Hz, 2H, C$H_2$*t*-Bu), 1.95 (dd, $J$ = 9.4/1.9 Hz, 1H, H3), 2.38 (dd, $J$ = 10.1/5.2 Hz, 1H, H2), 2.52 (ddd, $J$ = 9.4/5.1/0.9 Hz, 1H, H4), 2.68 (m, 1H, H3′); $^{13}$C NMR ($CDCl_3$) $\delta$ 23.88 (C3), 29.56 [C(*C*H$_3$)$_3$], 30.81 [*C*(CH$_3$)$_3$], 33.40 (C2), 38.35 (C4), 44.17 (*C*H$_2$*t*-Bu); $^{29}$Si NMR ($CDCl_3$) $\delta$ 8.58 ($Si_{cycl.}$), 12.21 (*Si*Cl$_3$).

***Z*-11:** $^1$H NMR ($CDCl_3$) $\delta$ 0.95 [s, 9H, C(C$H_3$)$_3$], 1.46, 1.68 (dd, $J$ = 12.6/4.7 Hz, 1H, C$H_2$*t*-Bu), 1.82 (dd, $J$ = 10.5/1.1 Hz, 1H, H3), 2.18 (dd, $J$ = 12.0/9.8 Hz, 1H, H2), 2.45 (dd, $J$ = 14.6/9.8 Hz, 1H, H4), 2.64 (m, 1H, H3′); $^{13}$C NMR ($CDCl_3$) $\delta$ 24.78 (C3), 29.67 [C(*C*H$_3$)$_3$], 30.77 [*C*(CH$_3$)$_3$], 33.10 (C2), 39.02 (C4), 43.90 (*C*H$_2$*t*-Bu); $^{29}$Si NMR ($CDCl_3$) $\delta$ 7.88 ($Si_{cycl.}$), 11.51 (*Si*Cl$_3$). Anal. Calcd (found) for $C_8H_{15}Cl_5Si_2$ (344.645): C, 27.88 (27.21); H, 4.39 (4.19); Cl 51.43 (51.67).

**(*E*)-1,1-Dichloro-2-neopentyl-3-(2-vinyloxyethoxy)-1-silacyclobutane (12):**[24] $^1$H NMR ($CDCl_3$) $\delta$ 0.86 [s, 9H, C(C$H_3$)$_3$], 1.51 (m, 2H, C$H_2$*t*-Bu), 1.59 (m, 1H, H4), 1.95 (m, 1H, H2), 1.98 (dd, $J$ = 14.5/7.7 Hz, 1H, H4′), 3.51, 3.61 (m, 2H, OC$H_2$), 3.63 (m, 1H, H3), 3.76 (m, 2H, OCH$_2$C$H_2$), 3.93 (dd, $J$ = 6.8/1.5 Hz, 1H, OCH=C$H_2$), 4.12 (dd, $J$ = 13.9/1.5 Hz, 1H, OCH=C$H_2$), 6.42 (dd, $J$ = 13.9/6.8 Hz, 1H, OC*H*=CH$_2$); $^{13}$C NMR ($CDCl_3$) $\delta$ 29.47 [C(*C*H$_3$)$_3$], 30.53 [*C*(CH$_3$)$_3$], 30.84 (C4), 42.66 (*C*H$_2$*t*-Bu), 44.28 (C2), 67.31 (OCH$_2$*C*H$_2$), 67.39 (O*C*H$_2$CH$_2$), 75.33 (C3) 86.60 (OCH=*C*H$_2$), 151.81 (O*C*H=CH$_2$); $^{29}$Si NMR ($CDCl_3$) $\delta$ 13.04; MS (EI) *m*/*e* 261 ($M^+$ − 35, 2), 213 (7), 172 (31), 157 (22), 129 (31), 115 (100), 97 (48).

**(*E*)-1,1-Dichloro-2-neopentyl-3-(4-vinyloxybutoxy)-1-silacyclobutane (13):**[24] $^1$H NMR ($CDCl_3$) $\delta$ 0.84 [s, 9H, C(C$H_3$)$_3$], 1.55 (m, 2H, C$H_2$*t*-Bu), 1.59 (m, 1H, H4), 1.63 (m, 4H, OCH$_2$C$H_2$C$H_2$CH$_2$), 2.14 (m, 1H, H2), 2.16 (dd, $J$ = 15.1/7.5 Hz, 1H, H4′), 3.26, 3.39 (dt, $J$ = 9.3/6.0 Hz, 1H, OC$H_2$), 3.58 (m, 1H, H3), 3.60 (t, br, $J$ = 6.3 Hz, 2H, C$H_2$OCH=CH$_2$), 3.87 (dd, $J$ = 6.8/1.9 Hz, 1H, OCH=C$H_2$), 4.06 (dd, $J$ = 14.3/1.9 Hz, 1H, OCH=C$H_2$), 6.36 (dd, $J$ = 14.4/6.8 Hz, 1H, OC*H*=CH$_2$); $^{13}$C NMR ($CDCl_3$) $\delta$ 25.92 (OCH$_2$*C*H$_2$), 26.29 (OCH$_2$-CH$_2$*C*H$_2$), 29.39 [C(*C*H$_3$)$_3$], 30.46 [*C*(CH$_3$)$_3$], 31.87 (C4), 42.53 (*C*H$_2$*t*-Bu), 46.67 (C2), 67.39 (O*C*H$_2$), 68.50 (*C*H$_2$OCH=CH$_2$), 74.89 (C3) 86.18 (OCH=*C*H$_2$), 151.73 (O*C*H=CH$_2$); $^{29}$Si NMR ($CDCl_3$) $\delta$ 13.96; MS (EI) *m*/*e* 309 ($M^+$ − 15, 11), 267 (4), 133 (11), 105 (15), 57 (100).

**(*E*)-3-Isobutoxy-1,1-dimethyl-2-neopentyl-1-silacyclobutane (15).** Compound **5** (4.25 g, 15 mmol) in 100 mL of *n*-pentane was cooled to 0 °C, and 18.75 mL of 1.6 M LiMe/diethyl ether (30 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature. The solution was filtered to remove LiCl, and the solvents were removed at reduced pressure at ambient temperature. The residue was distilled at $10^{-2}$ mbar to give **15** as a colorless liquid (2.21 g, 9 mmol, 65% yield, bp 23 °C at $10^{-2}$ mbar): $^1$H NMR ($CDCl_3$) $\delta$ 0.03, 0.16 [s, 3H, Si(C$H_3$)$_2$], 0.74 [s, 9H, C(C$H_3$)$_3$], 0.77 [d, $J$ = 3.3 Hz, 3H, CH(C$H_3$)$_2$], 0.78 [d, $J$ = 4.1 Hz, 3H, CH(C$H_3$)$_2$], 1.22 (dd, $J$ = 11.9/2.8 Hz, 1H, C$H_2$*t*-Bu), 1.31 (ddd, $J$ = 14.9/8.9/1.3 Hz, 1H, H4), 1.52 (d, $J$ = 10.4 Hz, 1H, C$H_2$*t*-Bu), 1.69 (m, 1H, H2), 1.70 [non, $J$ = 6.6 Hz, 1H, C*H*(CH$_3$)$_2$], 1.71 (m, 1H, H4′), 2.86, 3.11 (dd, $J$ = 8.8/6.6 Hz, 2H, OCH$_2$), 3.35 (ddd, $J$ = 9.0/9.0/8.1 Hz, 1H, H3); $^{13}$C NMR ($CDCl_3$) $\delta$ −4.21, 0.13 [Si(*C*H$_3$)$_2$], 19.46 [CH(*C*H$_3$)$_2$], 20.74 (C4), 28.43 [*C*H(CH$_3$)$_2$], 29.60 [C(*C*H$_3$)$_3$], 30.44 [*C*(CH$_3$)$_3$], 35.02 (C2), 43.66 (*C*H$_2$*t*-Bu), 74.46 (O*C*H$_2$), 78.48 (C3); $^{29}$Si NMR ($CDCl_3$) $\delta$ −2.84; MS (EI) *m*/*e* 241 ($M^+$ − 1, 2), 185 (11), 169 (33), 131 (46), 95 (92), 75 (100). Anal. Calcd (found) for $C_{14}H_{30}OSi$ (242.479): C, 69.35 (69.21); H, 12.47 (12.55).

**(*E*)-3-Isobutoxy-2-neopentyl-1,1-bis(trimethylsiloxy)-1-silacyclobutane (16).** At 0 °C, 2.88 g (30 mmol) of LiOSi(CH$_3$)$_3$,[25] dissolved in 50 mL of diethyl ether, was added with stirring to 4.25 g (15 mmol) of **5** in 100 mL of *n*-pentane. The reaction mixture was allowed to warm slowly to room temperature and was stirred at reflux for an additional 8 h. After filtration and evaporation of the solvent, distillation of the residue under reduced pressure ($10^{-2}$ mbar) gave **16** as a colorless liquid (3.50 g, 9 mmol, 60% yield, bp 62 °C at $10^{-2}$ mbar): $^1$H NMR ($CDCl_3$) $\delta$ 0.10, 0.11 [s, 9H, OSi(C$H_3$)$_3$], 0.84 [s, 9H, C(C$H_3$)$_3$], 0.86, 0.88 [d, $J$ = 3.0 Hz, 6H, CH(C$H_3$)$_2$], 1.07 (ddd, $J$ = 14.3/8.6/1.1 Hz, 1H, H4), 1.42 (dd, $J$ = 12.8/1.5 Hz, 1H, C$H_2$*t*-Bu), 1.52 (dd, $J$ = 12.8/4.5 Hz, 1H, C$H_2$*t*-Bu), 1.61 (m, 1H, H2), 1.62 (ddd, $J$ = 14.3/7.9/0.7 Hz, 1H, H4′), 1.80 [non, $J$ = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$], 3.02, 3.18 (dd, $J$ = 9.0/6.8 Hz, 2H, OC$H_2$), 3.37 (ddd, $J$ = 8.6/8.3/8.3 Hz, 1H, H3); $^{13}$C NMR ($CDCl_3$) $\delta$ 1.85, 1.94 [OSi(*C*H$_3$)$_3$], 19.61, 19.63 [CH(*C*H$_3$)$_2$], 27.61 (C4), 28.64 [*C*H(CH$_3$)$_2$], 29.63 [C(*C*H$_3$)$_3$], 30.53 [*C*(CH$_3$)$_3$], 42.59 (C2), 43.32 (*C*H$_2$*t*-Bu), 75.18 (C3), 75.79 (OCH$_2$); MS (EI) *m*/*e* 391 ($M^+$ + 1, 1), 325 (1), 295 (13), 207 (100), 191 (13), 169 (33), 95 (56); $^{29}$Si NMR ($CDCl_3$) $\delta$ −36.09 ($Si_{cycl.}$), 8.29, 9.46 [O*Si*(CH$_3$)$_3$]. Anal. Calcd (found) for $C_{18}H_{42}O_3Si_3$ (390.789): C, 55.32 (54.75); H, 10.83 (10.92).

**(*E*)-3-Isobutoxy-2-neopentyl-1,1-diphenyl-1-silacyclobutane (17).** At room temperature PhMgBr (50 mmol in 100 mL of diethyl ether) was added to **5** (4.25 g, 15 mmol) in 100 mL of *n*-pentane at room temperature. After refluxing the mixture for 8 h it was stirred for an additional 12 h at room temperature. Filtration of the precipitate, evaporation of the solvents, and distillation of the residue under reduced pressure ($10^{-2}$ mbar) afforded **17** as a white solid (1.13 g, 0.3 mmol, 20% yield, mp 148 °C): $^1$H NMR ($CDCl_3$) $\delta$ 0.76 [s, 9H, C(C$H_3$)$_3$], 0.84, 0.85 [d, $J$ = 1.5 Hz, 6H, CH(C$H_3$)$_2$], 1.47 (m, 2H, H4), 1.79 [non, $J$ = 6.6 Hz, 1H, C*H*(CH$_3$)$_2$], 1.83 (m, 1H, H2), 1.78 (m, 2H, C$H_2$*t*-Bu), 3.46 (m, 1H, H3), 3.32, 3.35 (dd, $J$ = 8.8/6.6 Hz, 2H, OC$H_2$), 7.50−7.90 (m, 10H, C$H_{aromat.}$); $^{13}$C NMR ($CDCl_3$) $\delta$ 19.03 [CH(*C*H$_3$)$_2$], 19.94 (C4), 28.97 [CH(CH$_3$)$_2$], 29.14 [C(*C*H$_3$)$_3$], 30.91 [*C*(CH$_3$)$_3$], 44.34 (C2), 47.12 (*C*H$_2$*t*-Bu), 67.62 (C3), 70.10 (O*C*H$_2$), 127.77 ($C_{aromat.}$), 129.69, 129.90, 133.81 (*C*H$_{aromat.}$), 134.14 ($C_{aromat.}$), 134.25, 135.13, 135.95 (*C*H$_{aromat.}$); $^{29}$Si NMR ($CDCl_3$) $\delta$ 6.72. Anal. Calcd (found) for $C_{24}H_{36}OSi$ (368.637): C, 78.20 (77.98); H, 9.84 (9.73).

**X-ray Crystallography. 8:** A colorless needle of the approximate dimensions 0.08 × 0.08 × 0.4 [mm] was mounted to the goniometer of a CAD4 automated single-crystal diffractometer (NONIUS-ENRAF, Mo K$\alpha$ radiation, graphite mono-

(23) The formation of **9** and **10** is also observed in the reaction of **1** with furans.[7]

(24) Elemental analysis of a mixture of **9**, **11**, and **12** and of **9**, **11**, and **13** after separation from **7**, **8**, and **10**.

(25) For preparation of $LiOSiMe_3$ see: Seyferth, D.; Alleston, D. L. *Inorg. Chem.* **1963**, *2*, 418.

chromator, 0.8 mm collimator diameter, lead beam stop) equipped with a cold gas stream at 214(2) K. The initial lattice constants were refined by use of 25 accurately centered reflections at high angles, $15° < 2\theta < 25°$. After *Lp* correction of the raw intensities, a set of 9447 reflections remained with $(F_{rel})^2 > 0$ in the range of $3.17° < \theta < 26.93°$ ($\pm h = 7$, $\pm k = 40$, $l = 14$), out of which 4589 reflections were independent ($R_{int} = 0.0204$). With a threshold of $I > 2\sigma_I$ 3398 reflections were observed. On these bases the structure solution and the structure refinements were performed.

**10:** From a set at open air of quickly hydrolizing colorless crystals cooled to 200(2) K in a cold gas stream, one irregularly formed single-crystal sample of approximate dimensions 0.4 × 0.4 × 0.5 [mm] was glued with silicone grease to the tip of the goniometer of an imaging plate diffractometer (IPDS, STOE, Mo Kα radiation, graphite monochromator, 1.2 [mm] collimator diameter, lead beam stop), equipped with a cold gas stream (OXFORD CRYOSTREAM) at 200(2) K. A tilt angle of approximately 9° between the axis along the largest crystal diameter and the X-ray beam was chosen. The data collection was performed by $\varphi$-rotation measurements. The crystal rotated by an increment of 3° for each frame. A total rotation angle of 231.0° was chosen; after 9 h, a total of 77 exposures resulted with an irradiation time of 3 min at 50 kV/40 mA each. After data reduction and *Lp* correction a total of 5054 reflections remained with a mean value of $I/\sigma(I) = 71.4$. From these, 2051 independent reflections out of 2244 expected reflections in the range $1.90° < \theta < 28.15°$ survived and were used for structure solution and refinements.

The structures were solved by direct methods in SHELXS97 included in the program package SHELX97.2[26] and refined by subsequent full matrix least-squares calculations based on $\Delta F^2$ syntheses (SHELXL97). Atom form factors for neutral atoms were taken from the literature.[27] DIAMOND plots were used for molecule structure representations in this work.[28] Further details of the crystal structure analyses have been deposited (without structure factor listings) with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140507 (***E*-8**) and 140508 (**10**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (phone: + 44-1223/336-033, fax: + 44-1223/336-033, e-mail: deposit@ccdc.cam.ac.uk, WWW: http://www.ccdc.cam.ac.uk).

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**Supporting Information Available:** Tables of atomic coordinates, all bond distances and angles, and anisotropic thermal factors for **8** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0001725

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