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Silaheterocycles. 21.[1] Silene to Silene Rearrangement: Intramolecular [1,3]-Migration of Alkoxy Groups

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By addition of *tert*-butyllithium to 1-(trichlorosilyl)-1-(*tert*-butoxydimethylsilyl)ethene (**2**) and subsequent LiCl elimination the intermediate 2-(*tert*-butoxydimethylsilyl)-1,1-dichloro-2-neopentylsilene (**5**) is formed. Fast intramolecular [1,3]-migration of the *tert*-butoxy group yields the unexpected 2-(*tert*-butoxydichlorosilyl)-1,1-dimethyl-2-neopentylsilene (**6**), which is trapped by methoxytrimethylsilane, dienes, and quadricyclane. Blocking the target position of the migration by bulky *tert*-butoxy groups in the silenes $Cl_{2-n}(OBu^t)_nSi{=}C(SiMe_2OBu^t)CH_2Bu^t$ (n = 1, **20**; n = 2, **27**) cannot prevent the rearrangement from taking place. X-ray diffraction studies of the quadricyclane cycloadduct from 2-(di-*tert*-butoxychlorosilyl)-1,1-dimethyl-2-neopentylsilene (**25**, $C_{23}H_{43}ClO_2Si_2$) and NMR spectroscopic studies support these findings. Compound **25** crystallizes in the monoclinic space group $P2_1/n$ and a = 1000.7 (3) pm, b = 1463.5 (3) pm, c = 1780.9 (7) pm, β = 98.02 (1)°, $V = 2583 \times 10^6$ pm^3, and Z = 4. A model explaining the reactivity of the *C*-alkoxysilyl-substituted silenes **5**, **17a**, **20**, and **27** is proposed.

Introduction

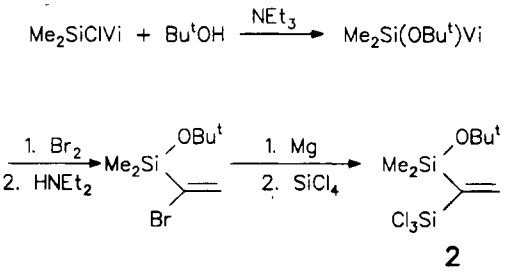
The reactivity of 1,1-dichlorosilenes is quite different from that of 1,1-diorganosilenes, as the studies of 1,1-dichloro-2-neopentylsilene have shown.[2] In a previous paper we described the cycloaddition behavior of 1,1-dichloro-2-neopentyl-2-(trimethylsilyl)silene (**1**), an investigation that showed the great influence of the trimethylsilyl group.[3] These studies were supported by qualitative MO calculations of HOMO and LUMO levels, eigenvector coefficients, and bond polarities.[4] In order to gain more insight into the factors governing silene reactivity, we have introduced additional substituents at the Si=C moiety. In this paper we report the cycloaddition reactions of silene **5** in which a methyl group of **1** has been replaced by a *tert*-butoxy group and of analogous silenes in which one or both of the chloro atoms of **5** are replaced by *tert*-butoxy groups (**20** and **27**).

Results

Synthesis and Reactivity of 1,1-Dichloro-2-(*tert*-butoxydimethylsilyl)-2-neopentylsilene (5). The synthesis of 1-(*tert*-butoxydimethylsilyl)-1-(trichlorosilyl)-ethene (**2**) is shown in Scheme I.

Reaction of **2** with *tert*-butyllithium at −78 °C in pentane initially yields the α-lithiated species **4** (Scheme II). In contrast to the case for $Cl_3SiCH(Li)CH_2Bu^t$ (prepared from trichlorovinylsilane and *tert*-butyllithium), **4** cannot be trapped by trimethylsilyl triflate.[5] Lithium chloride is eliminated from **4** over a temperature range of −5 to 0 °C, and the silene **5** is formed. Analysis of the ^{29}Si NMR spectroscopic data of trapping products shows that **5** must have rearranged by intramolecular [1,3]-migration of the *tert*-butoxy group to give **6**, which undergoes reactions with silene traps (Scheme II).[6]

Scheme I. Synthesis of the Silene Precursor 2



To establish the identity of compound **2** and thus to exclude the possibility that the OBu^t group might have migrated during the Grignard synthesis of **2** (yielding $Me_2Si(Cl)C(SiCl_2OBu^t){=}CH_2$ as a silene precursor), it was derivatized with $MeOH/NEt_3$.[7]

Another possible alternative reaction pathway leading to **6** is the initial elimination of $LiOBu^t$ from **4** to give $Me_2Si{=}C(SiCl_3)CH_2Bu^t$ followed by a chlorine → butoxide exchange. Two experimental findings exclude this mode of reaction. (1) When *tert*-butoxydimethylvinylsilane, $Me_2Si(OBu^t)(CH{=}CH_2)$, is reacted with Bu^tLi at 35 °C in pentane for 24 h, no 1,1-dimethyl-2-neopentylsilene ($Me_2Si{=}CHCH_2Bu^t$) is formed. The expected and well-known products of dimerization, the E/Z isomeric tetramethyldisilacyclobutanes $(Me_2Si(CHCH_2Bu^t))_2$,[8] were not found. (2) Later in this text we will show in detail that chlorine/*tert*-butoxy exchange does not take place under the mild conditions used for silene trapping reactions, even when lithium alkoxide is used.

6 is formed so rapidly that the efficient silene trap methoxytrimethylsilane traps just this silene and not **5**. The identity of **7** was established by mild derivatization with $MeOH/NEt_3$. The permethoxy derivative **8** shows

(1) Part 20: Auner, N.; Penzenstadler, E.; Herdtweck, E. *Z. Naturforsch.*, in press.

(2) (a) Auner, N.; Seidenschwarz, C.; Herdtweck, E.; Sewald, N. *Angew. Chem.* **1991**, *103*, 425; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 444. (b) Auner, N.; Seidenschwarz, C.; Herdtweck, E. *Angew. Chem.* **1991**, *103*, 1172; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1151. (c) Auner, N.; Seidenschwarz, C.; Sewald, N. *Organometallics* **1992**, *11*, 173. (d) Seidenschwarz, C. Dissertation; TU München, 1991.

(3) Ziche, W.; Auner, N.; Behm, J. *Organometallics* **1992**, *11*, 2494.

(4) (a) Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676. (b) Nagase, S.; Kudo, T.; Ito, K. In *Applied Quantum Chemistry*; Smith, V. H., Jr., Schaefer, H. F., III, Morokuma, K., Eds.; Reidel: Dordrecht, The Netherlands, 1986; p 249. (c) Gordon, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 4352.

(5) Wolff, A. Dissertation; TU München, 1991. Adding trimethylsilyl triflate to a clear solution of **2** and *tert*-butyllithium at −10 °C only leads to the formation of at least 20 compounds of undefined composition.

(6) Ziche, W.; Auner, N.; Kiprof, P. *J. Am. Chem. Soc.* **1992**, *114*, 4910.

(7) The product **3** shows just one resonance for the methoxy groups in ^{1}H as well as in ^{13}C NMR spectra. The $Si(OMe)_3$ fragment is quite prominent in the mass spectrum. In contrast, 1-[(Dimethylamino)dimethylsilyl]-1-bromoethene cannot be metalated in any way (LiR, Mg, Li), as excessive migration of the dimethylamino group takes place.

(8) (a) Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* **1977**, *99*, 2013. (b) Auner, N.; Seidenschwarz, C.; Herdtweck, E. X-ray structure in preparation.

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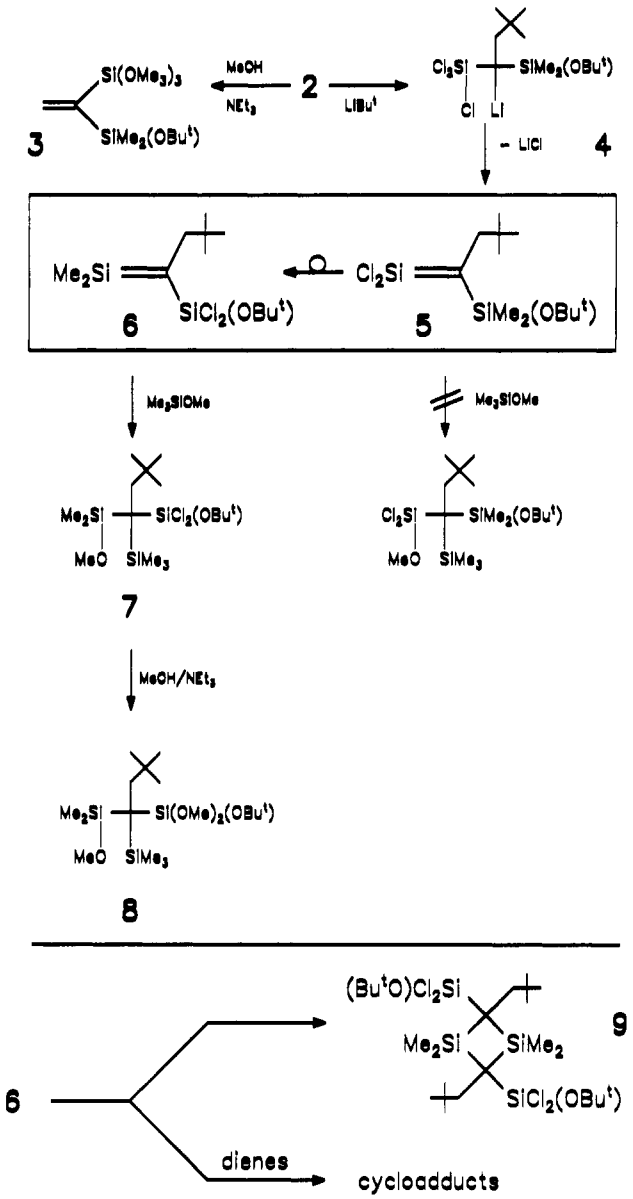
Scheme II. Synthesis and Reactivity of Silenes 5 and 6

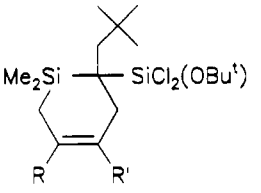


two ^{13}C as well as two ^{1}H NMR resonances (ratio of integrals 2:1) for the different methoxy groups.

When no trapping reagents are present, cyclodimerization of **6** takes place: GC/MS and NMR spectroscopic analyses show the main product to be the *E* isomer of the dimer **9** (5% *Z* isomer). This distinguishes **6** from dimethylneopentylsilene, which yields the 1,1,3,3-tetramethyl-2,4-dineopentyl-1,3-disilacyclobutanes in a *E*/*Z* ratio of 47/53.[8] These findings confirm a general trend: The amount of the *E* isomer increases when the substituents R of the silene $R_2Si{=}CHCH_2Bu^t$ increase in bulk. When R = OBu^t, a ratio of 64/36 is observed;[9] for R = Ph it is 86/14.[10] The 1,3-disilacyclobutane **9** is obtained as the pure *E* isomer after recrystallization; an X-ray crystallographic study could not be carried out, as the crystals were twinned.

Electron-rich but sterically more congested dienes such as anthracene and pentamethylcyclopentadiene do not react with **6**; in these reactions only the 1,3-disilacyclobutanes are formed.

6 reacts regiospecifically with 1,3-dimethylbutadiene (DMB), isoprene (MBD), and butadiene (BD) to give the Diels–Alder products **10–12** by [4 + 2] cycloaddition reactions.



R=R'=Me : **10**
R=Me, R'=H : **11**
R=R'=H : **12**

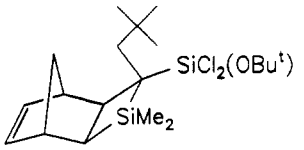
Thus, **6** behaves as a typical silene, unlike 1,1-dichloro-2-neopentyl-2-(trimethylsilyl)silene, which gives both Diels–Alder and [2 + 2] cycloadducts with butadienes.[3]

Our investigations on the reactivity and cycloaddition behavior of **1** have shown that the tendency to yield [2 + 2] cycloadducts increases with diminishing electron density in the butadienes (DMB > MBD > BD).[3] **6**, however, only gives the Diels–Alder adducts: The energy difference $HOMO_{diene}$–$LUMO_{dienophile}$ is obviously in favor of this reaction; i.e., no critical value is exceeded.[11] This is due to **6** having two alkyl groups at the silicon atom and a silyl group at the carbon atom of the Si=C system, leading to a lowering of the $LUMO_{dienophile}$ energy.

With MBD **6** yields only *one* Diels–Alder adduct, **11**. Our investigations on the cycloaddition behavior of 1,1-dichloro-2-neopentylsilene with dienes[2,12] have shown the addition of the silene to be strictly regioselective; i.e. the silicon atom of the Si=C fragment always attacks the carbon atom of the diene having the largest orbital coefficients. The structure of **11** can be established from the ^{13}C NMR peaks for the ring methylene carbon atoms, Si–CH_2 at 19.56 ppm and –CH_2– at 29.16 ppm. In **12** the two corresponding resonances are found at 14.44 and 28.93 ppm and in **10** at 21.74 and 36.57 ppm. Thus, the Si–CH_2 resonance of **11** is similar to that of the dimethyl compound **10**, while the other ring CH_2 signal is close to that of the dihydrogen compound **12**. These observations support the structure shown for **11**,[13,14] which is in accord with the expected regiochemistry. No trace of a second isomer was detected by GC/MS analysis.

Electron-deficient dienophiles can be trapped well by quadricyclane.[15] Theoretical[16] and experimental work[15,17] predicts the formation of the exo-[$2_\pi + 2_\sigma + 2_\sigma$] isomeric cycloadduct from **6** and quadricyclane. This compound (**13**) is obtained as a crystalline solid whose structure was determined by X-ray crystallography.[6] This is the first crystal structure of an exo-[2 + 2 + 2] cycloadduct of quadricyclane with a double-bond π system[18] (tricyclo-

(9) Grobe, J.; Schröder, H.; Auner, N. *Z. Naturforsch.* **1990**, *45B*, 785.
(10) Auner, N.; Ziche, W.; Herdtweck, E. *J. Organomet. Chem.* **1992**, *426*, 1.
(11) Sauer, J.; Sustmann, R. *Angew. Chem.* **1980**, *92*, 773; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.
(12) Auner, N.; Wolff, A.; Sewald, N. Manuscript in preparation.
(13) Wiberg, N.; Wagner, S.; Fischer, G. *Chem. Ber.* **1986**, *119*, 3498. Wiberg isolated two regioisomeric [4 + 2] cycloadducts from the reaction between MBD and $Me_2Si{=}C(SiMe_3)_2$. The methyl group stemming from MBD is preferentially found in position 3 of the six-membered ring; the other isomer (methyl group at C4) constitutes 8% of the isomer mixture.
(14) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C NMR-Spektroskopie*; Thieme Verlag: Stuttgart, Germany, 1984.
(15) (a) Smith, C. D. *J. Am. Chem. Soc.* **1966**, *88*, 4273. (b) Kaupp, G.; Prinzbach, H. *Chem. Ber.* **1971**, *104*, 182.
(16) Haselbach, E.; Martin, H.-D. *Helv. Chim. Acta* **1974**, *57*, 472.
(17) Paquette, L. A.; Kesselmayer, M. A.; Künzer, H. *J. Org. Chem.* **1988**, *53*, 5183.



13

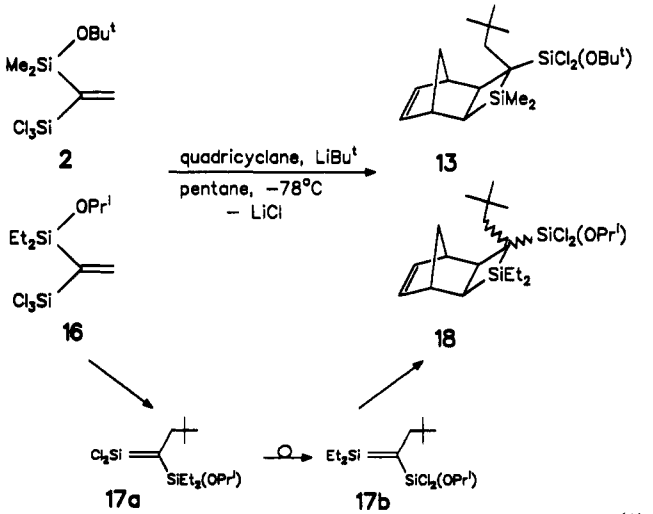
[4.2.0.1^{2,5}]non-3-ene structure). The ORTEP representation is given in Figure 1.

The structure of the cycloadduct **13** shows little distortion as far as the bicyclo[2.2.1]heptene fragment stemming from quadricyclane is concerned. The silacyclobutane ring is nearly planar (maximum 0.5-pm deviation from an ideal plane). Like all silacyclobutanes[2b,c,d,6,19] it is distorted: the transannular distance Si1···C4 of 243 pm is shorter than C3···C5 with 247 pm. The endocyclic angle C3–Si1–C5 is 81.39° and is smaller than the angle C3–C4–C5, which is 102.2°. The endocyclic bond distances are slightly longer than the exocyclic ones between similar atoms. The interbond angle of the *tert*-butoxydichlorosilyl group and the neopentyl group, Si2–C3–C11, is larger than the tetrahedral angle by 5°; in part this may be a consequence of the small endocyclic angle Si1–C3–C4.

The regioselectivity of silene reactions is well established in cycloadditions of other neopentylsilenes.[2,12] Surprising and unprecedented is the high stereoselectivity of the reaction that results in the exclusive syn position of the neopentyl group in **13**. We explain this by assuming a donor coordination of the oxygen atom of the *tert*-butoxy group to the dimethylsilene: the preferred (and in this case obviously exclusive) orientation during the cycloaddition is determined by steric factors (see Figure 2).

A cross experiment using a 1-(trichlorosilyl)-1-(isopropoxydiethylsilyl)ethene (**16**)/**2** mixture in the cycloaddition with quadricyclane shows the reaction to be intramolecular, as no products originating from intermolecular alkoxy group migration between the corresponding silenes could be detected by GC/MS analysis.

In contrast to the case for **6**, the silene **17** prepared from **16**/Bu^{t}Li yields two isomeric cycloadducts (**18**) with quadricyclane (eq 1). The loss of stereoselectivity can be



(1)

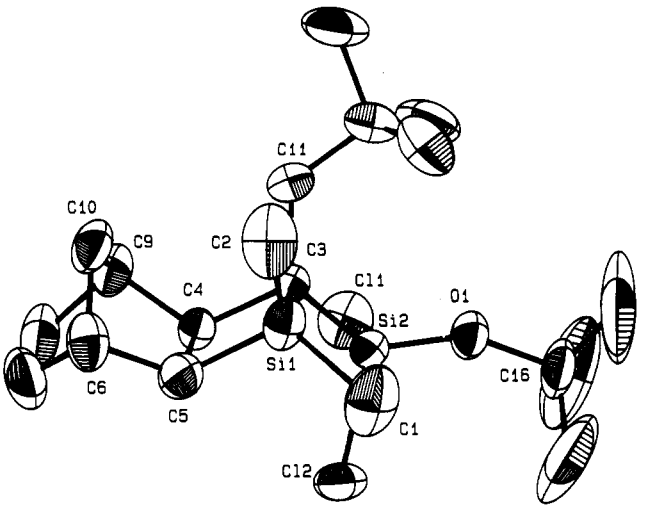


Figure 1. ORTEP representation of **13** (50% probability, hydrogens omitted for clarity). The labeling of atoms is different in ref 6; it has been changed to coincide with that of **25**.

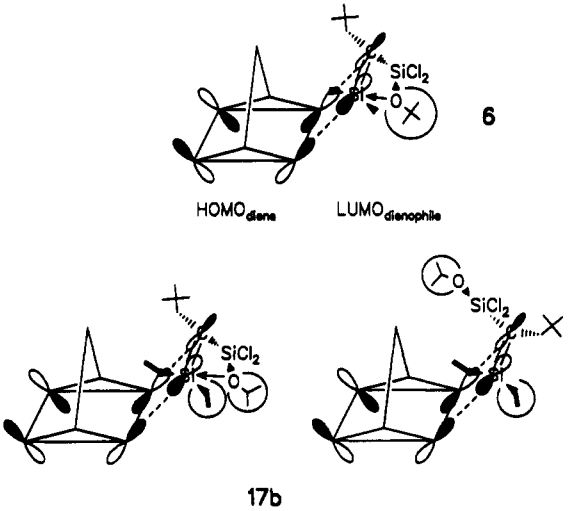
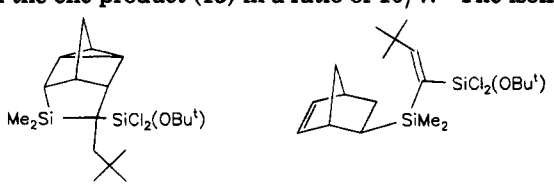


Figure 2. Steric interactions in transition states for silenes **6** and **17b**.

explained by steric factors: the repulsion between the isopropyl and ethyl groups in silene **17b** may lead to a lesser degree of donor coordination and consequently to equally favorable orientations of the silene in the transition state of the cycloaddition reaction (Figure 2).

The reaction of **6** with the classically nonconjugated diene norbornadiene (NBD) is not so straightforward. On the one hand, because of homoconjugation of its localized π orbitals[20] NBD can form δ-cyclane derivatives by [2_π + 2_π + 2_π] cycloaddition; on the other hand, it may act as a strained ene component and react with **6** as an enophile. An experiment shows that both reaction pathways are followed: The [2 + 2 + 2] cycloadduct (**14**) is isolated along with the ene product (**15**) in a ratio of 10/7. The isomers



14 15

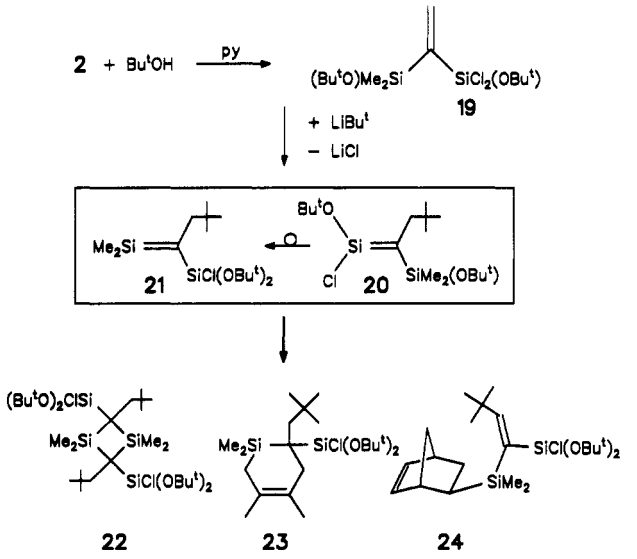
cannot be separated by distillation; a minor amount (<5%) of an unknown substance contaminates the mixture of **14**

(18) (a) Tricyclo[4.2.0.1^{2,5}]nona-3,7-diene system: Lehr, K. H.; Werp, J.; Bingmann, H.; Krüger, C.; Prinzbach, H. *Chem. Ber.* **1982**, *115*, 1835. (b) *endo*-Tricyclo[4.2.0.1^{2,5}]-3-nonene structure: Bats, J. W.; Billinger, O.; Ried, W. *Acta Crystallogr., Sect. C, Cryst. Struct. Commun.* **1984**, *C40*, 184.

(19) D'yachenko, O. A.; Sokolova, Y. A.; Atovmyan, L. O.; Ushakov, N. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 1030.

(20) Ferguson, L. N.; Nnadi, J. C. *J. Chem. Educ.* **1965**, *42*, 529.

Scheme III. Synthesis of 20 and Reactivity of Silene 21



and **15**. Identification of the products is easily achieved from characteristic ^{13}C NMR spectroscopic resonances. **14** shows three resonances of the cyclopropane ring (12–14 ppm); **15** exhibits a specific pattern in the region of sp^2 C atoms (133.67, 138.47 (HC=CH); 130.38 (*C*=CH); and especially 175.52 ppm (*C*H=C)). We assume that the *tert*-butoxydichlorosilyl group takes the anti position, in analogy to the quadricyclane cycloadduct **13**.

Synthesis and Reactivity of 1-Chloro-1-*tert*-butoxy-2-(*tert*-butoxydimethylsilyl)-2-neopentylsilene. It was interesting to see if the intramolecular [1,3]-migration of the *tert*-butoxy group could be prevented by blocking the electrophilic Si target atom by bulky substituents. To investigate this contention, we synthesized 1-(*tert*-butoxydichlorosilyl)-1-(*tert*-butoxydimethylsilyl)-ethene (**19**) from **2** and *tert*-butyl alcohol and reacted this with *tert*-butyllithium to give silene **20**, in the presence of DMB or NBD (Scheme III).

The results show, however, that the attempted blockade was in vain and that the alkoxy group migration still takes place, with silene **20** rearranging into **21**. The presence of a di-*tert*-butoxychlorosilyl group in all products is documented by the $^{29}Si\{^1H\}$ NMR spectroscopic data. The resonances of lower intensity for the di-*tert*-butoxychlorosilyl group are found between ca. −50 and −60 ppm. In comparison to the values found for the cycloadducts from **6**, there is a characteristic high-field shift of $\delta^{29}Si(ClSi(OBu^t)_2)$ of ca. 30 ppm. No change is registered for the ^{29}Si NMR spectroscopic resonances of the dimethylsilyl group, whose signals are found between +5 and +10 ppm.

In the absence of trapping reagents **21** dimerizes exclusively to (*E*)-1,3-disilacyclobutane **22**. With DMB the [4 + 2] cycloadduct **23** is formed, and with NBD just one product is found. The Si=C bond in **21** is obviously sterically quite congested, so that no [2 + 2 + 2] cycloaddition takes place and only the ene product **24** is formed.

21 and quadricyclane yield the crystalline exo-$[2_\sigma + 2_\sigma + 2_\pi]$ cycloadduct **25**, whose structural features do not differ much from those of **13**. A decent single crystal was obtained by crystallization from pentane, and the structure was elucidated by X-ray diffraction analysis (Figure 3). Crystallographic data are listed in Table I, and selected bond lengths and angles for **13** and **25** are found in Table II.

The molecular structure of **25** shows no significant distortions in the bicyclo[2.2.1]heptene fragment originating from quadricyclane. Interesting properties are observed for the slightly folded silacyclobutane ring[2b-d,6,19] (dihedral angle between planes C3–C4–C5 and C3–Si1–C5: 6.4 (9)°) that is distorted by the silicon atom and the large substituents at C3. The transannular distance Si1···C4 (244.8 pm) is shorter than C3···C5 (248.3 pm). Again the endocyclic distances are a little longer than those of their exocyclic congeners. As expected, the endocyclic angle C3–C4–C5 at 102.6° is larger than its counterpart C3–Si1–C5 at 81.22°. The steric interactions of the bulky

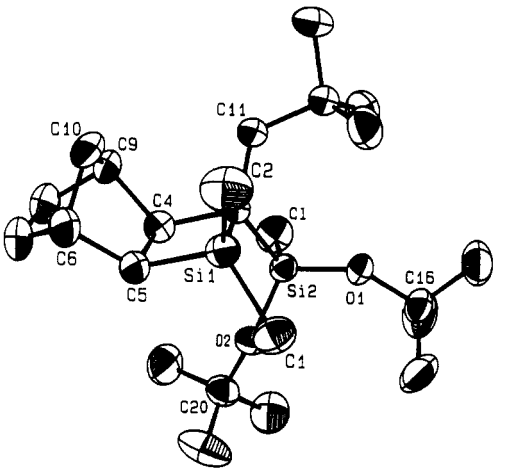


Figure 3. ORTEP representation of **25** (50% probability, hydrogens omitted for clarity).

Table I. Crystallographic Data for 25

formula	$C_{23}H_{43}ClO_2Si_2$
mol wt	443.2
cryst color	colorless
cryst dimens, mm	0.70 × 0.15 × 0.18
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, pm	1000.7 (3)
b, pm	1463.5 (3)
c, pm	1780.9 (7)
β, deg	98.02 (1)
cell vol, pm^3	2583 × 10^6
Z	4
D(calcd), g/cm^3	1.14
radiation	Mo Kα, μ = 2.5 cm^{-1}
scan type	ω scan
scan time, s	max 60
scan width, deg	1.00 + 0.30(tan θ)
no. of collcd rflns	4869
no. of indep rflns	4076
no. of obsd rflns with $I > \sigma(I)$	3798
no. of params refined	257
R^a	0.047
$R_w{}^b$	0.037
goodness of fit^c	3.587
resid electron density, e/Å^3	+0.31, −0.32

$^a R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. ^{c}GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

Table II. Selected Bond Lengths (Å) and Angles (deg) for 13 and 25

	bond lengths			bond angles	
	13	**25**		**13**	**25**
Si1–C3	1.920 (2)	1.922 (1)	C3–Si1–C5	81.39 (7)	81.22 (6)
Si1–C5	1.874 (2)	1.880 (1)	C3–C4–C5	102.2 (1)	102.65 (10)
C3–C4	1.609 (3)	1.609 (2)	Si1–C3–C4	86.7 (1)	86.48 (7)
C4–C5	1.571 (2)	1.562 (2)	Si1–C5–C4	89.4 (2)	89.31 (8)
Si2–C3	1.851 (1)	1.858 (1)	Si2–C3–C11	114.6 (2)	117.74 (8)
Si1–C2	1.864 (2)	1.874 (2)	C3–C11–C12	123.5 (1)	122.94 (11)
C3–C11	1.567 (3)	1.554 (2)	O1–Si2–C3	113.11 (6)	109.24 (5)
Si1···C4	2.43 (1)	2.448 (3)	O2–Si2–C3		110.09 (5)
C3···C5	2.47 (3)	2.483 (1)			

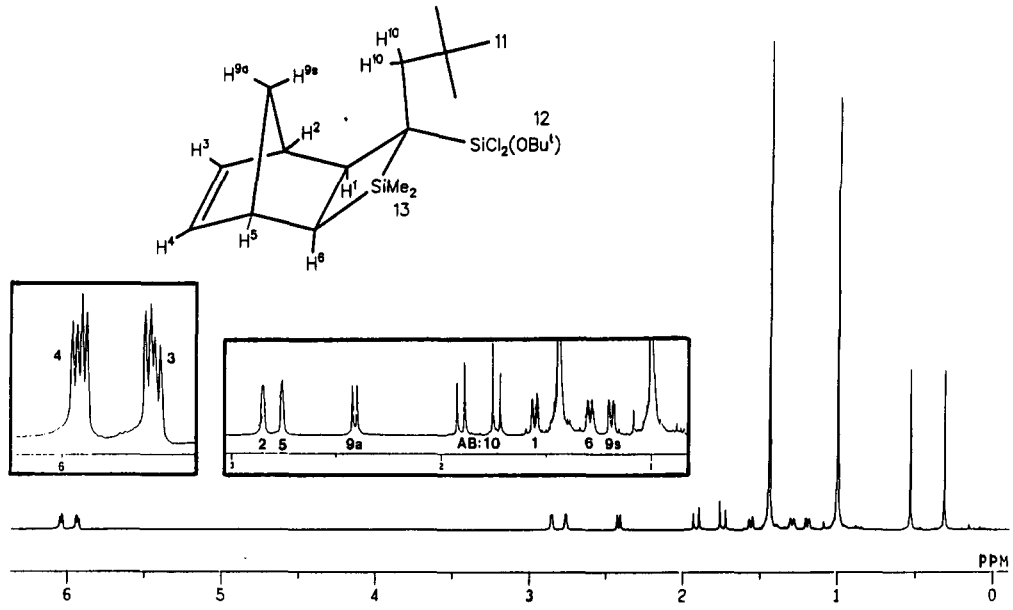


Figure 4. ^1H NMR spectrum of **13**.

groups at C3 are again shown more by distorted angles than by elongated bonds. The angle Si2–C3–C11 between those two substituents is quite large at 117.7°; this is made possible by the small endocyclic angle Si1–C3–C4 (86.48°). Si2–C3–C11 is larger by 3° when moving from **13** to **25**; this is obviously the effect of the additional *tert*-butoxy group at the silyl group, because the angle Si1–C3–C4 is not very much smaller than in **13** (86.48 vs 86.7°).

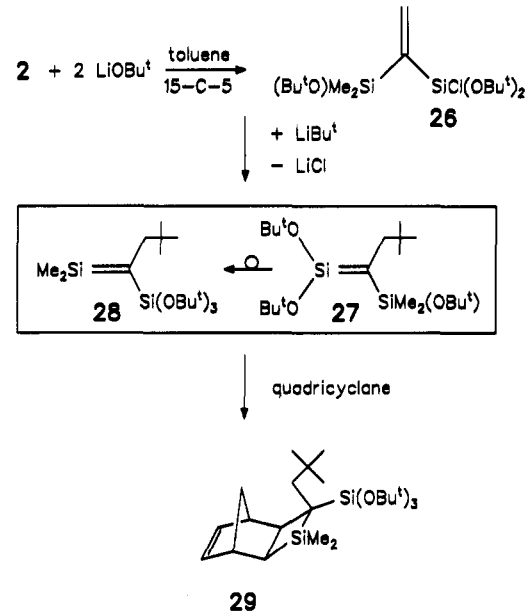
The intramolecular [1,3]-migration of the *tert*-butoxy group that transforms the silenes **5** and **20** into **6** and **21**, respectively, obviously occurs rapidly under mild conditions: the first visible LiCl elimination from the α-lithio adducts begins between −5 and 0 °C. In all reactions no products other than the cycloadducts are found (exception **6**/NBD) and the yields are astonishingly high (60–80%).

Synthesis and Reactivity of 1,1-Di-*tert*-butoxy-2-(*tert*-butoxydimethylsilyl)-2-neopentylsilene. The speed with which the silene → silene rearrangement occurs is contrasted by the difficulties encountered when synthesizing 1-(di-*tert*-butoxychlorosilyl)-1-(*tert*-butoxydimethylsilyl)ethene (**26**) from **2**. Only the monosubstituted product **19** is formed when **2** is refluxed in excess *tert*-butyl alcohol and pyridine. **26** is however obtained when **2** is refluxed with 2 equiv of $LiOBu^t$ in toluene in the presence of catalytic amounts of crown ether (15-C-5)[21] for 2 days (Scheme IV).

The reaction of **26** with $LiBu^t$ in the absence of trapping agents leads to a multitude of products, as can be proved by GC/MS analysis. None of these, however, seems to be the expected disilacyclobutane.

From the mixture **26**/$LiBu^t$ with quadricyclane a crystalline [2 + 2 + 2] cycloadduct (**29**) is again obtained. The resonance having the minor intensity in the ^{29}Si NMR spectrum at −75.68 ppm is assigned to a tri-*tert*-butoxy group. That signal is a high-field shift of 25 ppm compared to the di-*tert*-butoxy group of **25**. The more intense resonance for the dimethylsilyl fragment appears at 9.98 ppm. These values clearly show that the intramolecular 1,3-migration takes place even for silene **27**. The driving force of the rearrangement **27** → **28** is great enough to place the sterically quite demanding tri-*tert*-butoxysilyl group at the α-carbon atom of silene **28**. Additional proof is provided

Scheme IV. Synthesis and Reactivity of Silene 27



29

by finding just one resonance for the *tert*-butoxy groups in **29** in ^1H as well as in ^{13}C NMR spectra.

The structural similarity between **13** and **29** is also shown by their ^1H NMR (Figure 4 for **13**) and ^1H–^1H COSY NMR spectra (Figure 5 for **13**); the ^{13}C–^1H NMR correlation spectra were helpful for the assignment of the resonances for H^1, H^6, and H^{9s}.

Discussion

The silenes $Cl_{2-n}(OBu^t)_nSi{=}C(SiMe_2OBu^t)CH_2Bu^t$ (type A; n = 0 (**5**), 1 (**20**), 2 (**27**)), produced primarily by addition of Bu^tLi to the precursors $(Me_2Bu^tOSi)(Cl_{3-n}(Bu^tO)_nSi)C{=}CH_2$ (*n* = 0 (**2**), 1 (**19**), 2 (**26**)), rearrange by fast intramolecular [1,3]-migration to the silenes $Me_2Si{=}C[SiCl_{2-n}(OBu^t)_{n+1}]CH_2Bu^t$ (type B; **6**, **21**, and **28**). This also applies for the conversion **17a** → **17b**.

In silene chemistry intramolecular [1,3]-migrations of silyl,[22] phenyl,[23] methyl,[24] and ethoxy groups[25] are known;

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(22) Ishikawa, M.; Nishimura, K.; Ochiai, H.; Kumada, M. *J. Organomet. Chem.* **1982**, *236*, 7.

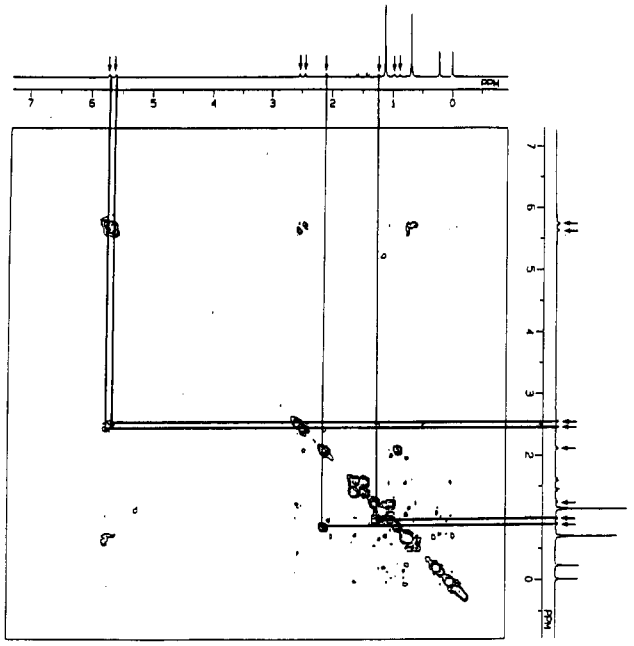
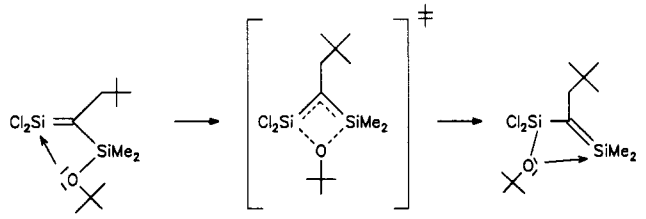


Figure 5. ^1H–^1H COSY spectrum of **13**.

Scheme V. Intramolecular [1,3]-Migration of the *tert*-Butoxy group shown for 5 → 6



A B

the last reaction results, however, in loss of the silene function.

We propose the following mechanism for the rearrangement. It is well-known that the electron-deficient silicon atoms in the inherently polar silenes can be coordinated by external[26] and internal[1,6] donors. This stabilization is also observed for other electrophilic sp^2 Si centers, e.g. in silylenemetal complexes (as "heterosilenes").[27,28] The *tert*-butoxy group can coordinate to the silene silicon atom to give a bridged intermediate (Scheme V). Similar intermediates have been proposed for other intramolecular 1,3-migrations.[24,25]

The silene silicon atom in A should be much more electrophilic than those in the resulting silenes B. Since the electronic influences of chloro and alkoxy groups are nearly equal (both are π donors),[29] the unchanged tendency to migration with increasing *tert*-butoxy substitution at the silenes' A silicon atom is not surprising. Astonishingly, steric factors hardly play a role.

A and B may be considered as bridged species: The suggestion has been made that the structure discussed as the transition state might well be the ground-state structure of the silenes.[30] This contention is understandable when we consider the reactivity of the silenes B with quadricyclane, which is quite different from that of other diorganosilenes which do not react (e.g. $R_2Si{=}CHCH_2Bu^t$; R = Me,[31] Ph[10]). The results of the cycloadditions, however, support the assymetric structure B. A comparable bridging structure has been isolated and proved by X-ray diffraction in the case of a disilanyliron compound.[32]

The stereospecificity of the cycloaddition reactions of the silenes **6**, **21**, and **28** with quadricyclane can also be explained by donor coordination in the transition state. That this effect is not very strong is proved by the loss of stereospecificity when the substituents are slightly altered (e.g. changing from **6** to **17**).

These results confirm the directive effects of substituents at the silene moiety in cycloaddition reactions and show that a controlled synthesis of cycloadducts with defined regio- and stereochemistry may be possible in future work.

Experimental Section

All reactions were carried out with exclusion of moisture and oxygen. Solvents were dried by the usual methods. Dienes and trapping reagents were used as purchased; chlorosilanes were distilled from K_2CO_3 prior to use.

Gas chromatography was carried out with a Chrompack CP 9000 with a 10-m Chrompack CP Sil 5 CB column. GC–MS analysis was carried out with a Chrompack CP 9000 coupled with a Finnigan MAT Ion Trap 800. Chemical ionization (CI) used methanol as reactant gas. NMR spectra were recorded on JEOL JNM GX 270 and JEOL JNM GX 400 (^1H,^{29}Si) and Bruker WP100SY instruments (^{13}C and ^{13}C DEPT). $CDCl_3$ was used as internal standard. Mass spectra were obtained with a Finnigan MAT 311A spectrometer.

X-ray Structure Determination. The X-ray measurements were made on an Enraf-Nonius CAD-4 diffractometer (graphite monochromator) at room temperature. Crystal data and details of measurement are summarized in Table I. The structures were solved by using direct methods followed by difference Fourier syntheses and subsequent least-squares refinement. The analysis was based on scattering factors for neutral atoms taken from ref 33. Anomalous dispersion was considered.[34] For all calculations the SDP program package was used.[35] All atoms but the hydrogens were refined anisotropically. The positions of the hydrogen atoms were calculated.

Synthesis of 2. *tert*-Butoxydimethylvinylsilane. In a 2-L three-necked flask equipped with a mechanical stirrer and a reflux condenser are placed 74 g (1.0 mol) of Bu^tOH, 120 g (1.0 mol) of $Me_2SiCl(CH{=}CH_2)$, 101 g (1.0 mol) of NEt_3, and 1 L of pentane. The mixture is refluxed for 24 h. The precipitated ammonium salt is dissolved by adding 10% hydrochloric acid until the aqueous phase is acidic. The organic phase is washed twice with water and dried over $MgSO_4$. Distillation yields 121 g (0.77 mol, 77%) of a colorless liquid boiling at 85 °C/300 mbar. ^1H NMR ($CDCl_3$):

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(29) Ziche, W. Dissertation; TU München, 1992.
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(31) Jones, P. R.; Lim, T. F. O.; Pierce, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 4970.
(32) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415.
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(34) Cromer, D. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.
(35) Schmidt, R. E.; Birkhahn, M.; Massa, W.; Kiprof, P.; Herdtweck, E. "Strux-III, a Program System for the Refinement of X-ray Data"; Universität Marburg, 1980, and TU München, 1985–1989, Germany.

δ 0.60 (s, 6 H, $Si(CH_3)_2$), 1.69 (s, 9 H, $C(CH_3)_3$), 6.00–6.85 (m, 3 H, $CH=CH_2$). ^{13}C NMR ($CDCl_3$): δ 0.94 ($Si(CH_3)_2$), 32.27 ($C(CH_3)_3$), 72.45 ($C(CH_3)_3$), 131.36 (CH_2), 140.67 (CH).

Bromination of *tert*-butoxydimethylvinylsilane and subsequent elimination of HBr are carried out according to the literature.[36]

(1,2-Dibromoethyl)-*tert*-butoxydimethylsilane. ^1H NMR ($CDCl_3$): δ 0.29 (s, 6 H, $Si(CH_3)_2$), 1.21 (s, 9 H, $C(CH_3)_3$), 1.67–1.75 (m, 1 H, $CHCH_2$), 3.19–4.22 (m, 2 H, $CHCH_2$). ^{13}C NMR ($CDCl_3$): δ −1.47, 0.17 ($Si(CH_3)_2$), 31.04 (CH), 31.75 ($C(CH_3)_3$), 36.79 (CH_2), 73.55 ($C(CH_3)_3$).

(1-Bromoethenyl)-*tert*-butoxydimethylsilane. ^1H NMR ($CDCl_3$): δ 0.26 (s, 3 H, $Si(CH_3)_2$), 0.27 (s, 3 H, $Si(CH_3)_2$), 1.26 (s, 9 H, $C(CH_3)_3$), 6.23–6.29 (m, 2 H, $=CH_2$). ^{13}C NMR ($CDCl_3$): δ −0.03 ($Si(CH_3)_2$), 31.71 ($C(CH_3)_3$), 73.12 ($C(CH_3)_3$), 129.59 (CH_2), 137.99 (C). MS (CI): *m/e* 238 (0.7%, M^+), 223 (100), 195 (6.3), 131 (13.4).

1-(*tert*-Butoxydimethylsilyl)-1-(trichlorosilyl)ethene (2). The vinyl bromide is added fast enough to activated magnesium (by $BrCH_2CH_2Br$) in THF to maintain gentle reflux. After the addition is complete, the mixture is refluxed for 3 h. The Grignard reagent is added to a 30% excess of freshly distilled $SiCl_4$ (from K_2CO_3). After 3 h of reflux the mixture is allowed to cool. Most of the THF is recovered by distillation. The product is extracted with three 150-mL portions of pentane. Distillation yields 101.6 g (0.35 mol, 65%) of **2**, a colorless liquid, bp 40 °C/10^{-2} mbar. ^1H NMR ($CDCl_3$): δ 0.30 (s, 6 H, $Si(CH_3)_2$), 1.27 (s, 9 H, $C(CH_3)_3$), 6.65 , 6.81 (AB, *J* = 16.0 Hz, CH_2). ^{13}C NMR ($CDCl_3$): δ 1.97 ($Si(CH_3)_2$), 31.45 ($C(CH_3)_3$), 73.02 ($C(CH_3)_3$), 147.56 ($=CH_2$), 150.53 (=C). ^{29}Si NMR ($CDCl_3$): δ −40.54 ($SiCl_3$), −2.51 ($Si(CH_3)_2$). MS (70 eV): *m/e* 290 (0%, M^+), 275 (26.6), 219 (45.5), 183 (15.7), 131 (25.7), 75 (100), 57 (61.3). Anal. Found: C, 32.58; H, 5.35; Cl, 36.20; Si, 18.86. Calcd for $C_8H_{17}Cl_3OSi_2$ (291.75): C, 32.94; H, 5.87; Cl, 36.46; Si, 19.25.

1-(*tert*-Butoxydimethylsilyl)-1-(trimethoxysilyl)ethene (3). **2** is stirred 4 h with an excess of pyridine and methanol at ambient temperatures. The precipitate of pyridinium chloride is then dissolved in aqueous HCl, and the product is extracted with pentane. Distillation (47 °C/10^{-2} mbar) gives a colorless liquid in nearly quantitative yield. ^1H NMR ($CDCl_3$): δ 0.13 (s, 6 H), 1.24 (s, 9 H), 4.01 (s, 9 H), 6.36–6.54 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 0.73 ($SiCH_3$), 31.43 ($C(CH_3)_3$), 49.96 ($OC(CH_3)_3$), 50.20 (OCH_3), 128.69 (=C), 131.93 ($=CH_2$). MS (70 eV): *m/e* 278 (0%, M^+), 233 (<1), 205 (64.08), 173 (63.51), 121 (100), 113 (27.01), 105 (14.37). Anal. Found: C, 47.19; H, 9.33. Calcd for $C_{11}H_{26}O_4Si_2$ (278.50): C, 47.44; H, 9.41.

(*tert*-Butoxydichlorosilyl)(methoxydimethylsilyl)neopentyl(trimethylsilyl)methane (7). 2.90 g of **2** (10.0 mmol) in 50 mL of pentane is cooled to −78 °C. A 5.88-mL amount of 1.7 M $LiBu^t$/pentane (10.0 mmol) is added dropwise. The clear solution is warmed to −10 °C, and then 4.10 mL of Me_3SiOMe (3.12 g, 30.0 mmol) is added. A colorless solid immediately precipitates. After the solids are removed by filtration, **7** is distilled at 70 °C/10^{-2} mbar as a colorless liquid, yield 3.55 g (8.5 mmol, 85%). ^1H NMR ($CDCl_3$): δ 0.28 (s, 9 H, $Si(CH_3)_3$), 0.34 (s, 6 H, $Si(CH_3)_2$), 1.09 (s, 9 H, $C(CH_3)_3$), 1.45 (s, 9 H, $C(CH_3)_3$), 1.96, 2.16 (AB, 2 H, *J* = 14.9 Hz), 3.38 (s, 3 H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 1.33, 1.93 ($Si(CH_3)_2$), 3.21 ($Si(CH_3)_3$), 20.32 (SiCSi), 31.36, 31.70 ($C(CH_3)_3$), 33.38 ($CC(CH_3)_3$), 42.79 (CH_2), 49.55 (OCH_3), 79.40 ($OC(CH_3)_3$). ^{29}Si NMR ($CDCl_3$): δ −23.34 ($SiCl_2OC(CH_3)_3$), 5.06 ($Si(CH_3)_3$), 16.21 ($Si(CH_3)_2OCH_3$). MS (CI): *m/e* 416 (0%, M^+), 401 (0.5), 381 (25), 347 (100), 324 (73), 288 (38). Anal. Found: C, 45.76; H, 9.12. Calcd for $C_{16}H_{38}Cl_2O_2Si_3$ (417.64): C, 46.02; H, 9.17.

(*tert*-Butoxydimethoxysilyl)(methoxydimethylsilyl)neopentyl(trimethylsilyl)methane (8). Stirring **7** for 2 h at room temperature in NEt_3/MeOH gives **8**: bp 85 °C/10^{-2} mbar; colorless liquid. ^1H NMR ($CDCl_3$): δ 0.18 (s, 6 H, $Si(CH_3)_2$), 0.23 (s, 9 H, $Si(CH_3)_3$), 1.03 (s, 9 H, $C(CH_3)_3$), 1.40 (s, 9 H, $C(CH_3)_3$), 3.33 (s, 3 H, OCH_3), 3.51 (s, 6 H, $Si(OCH_3)_2$), 1.93, 2.08 (AB, 2 H, *J* = 15.1 Hz). ^{13}C NMR ($CDCl_3$): δ 1.51, 1.71 ($Si(CH_3)_2$), 2.98 ($Si(CH_3)_3$), 20.16 (SiCSi), 31.48, 31.87 ($C(CH_3)_3$), 33.19 ($CC(CH_3)_3$), 42.62 (CH_2), 49.32, 50.17 (OCH_3), 79.23 ($OC(CH_3)_3$). Anal. Found: C, 52.57; H, 10.73. Calcd for $C_{18}H_{44}O_4Si_3$ (408.81): C, 52.89; H, 10.85.

1-(*tert*-Butoxydichlorosilyl)-1-(*tert*-butoxydimethylsilyl)ethene (19). A 29.0-g (100.0-mmol) amount of **2** is refluxed for 8 h with 7.5 g (101.4 mmol) of *tert*-butyl alcohol in 250 mL of pyridine/hexane (1:1). The solvents are exchanged for pentane, and the precipitated salts are removed by filtration. Distillation yields 28.5 g (87.0 mmol, 87%) of a colorless liquid, bp 55 °C/10^{-2} mbar. ^1H NMR ($CDCl_3$): δ 0.29 (s, 6 H); 1.27 (s, 9 H); 1.44 (s, 9 H); 6.60, 6.70 (AB, 2 H, *J* = 4.6 Hz). ^{13}C NMR ($CDCl_3$): δ 2.91 ($Si(CH_3)_2$), 31.89, 32.65 ($C(CH_3)_3$), 73.45, 78.90 ($OC(CH_3)_3$), 147.43 ($=CH_2$), 148.73 (=C). ^{29}Si NMR ($CDCl_3$): δ −33.39 ($SiCl_2$), −3.31 ($Si(CH_3)_2$). MS (70 eV): *m/e* 313 (1.42%, M^+ − 16), 257 (10.26), 199 (17.68), 75 (40.24), 57 (100). Anal. Found: C, 44.03; H, 8.13. Calcd for $C_{12}H_{26}Cl_2O_2Si_2$ (329.42): C, 43.75; H, 7.96.

1-(Di-*tert*-butoxychlorosilyl)-1-(*tert*-butoxydimethylsilyl)ethene (26). A 14-g (48.3-mmol) amount of **2** is mixed with 100.0 mmol of a solution of lithium 2-methyl-2-propanolate (from 7.4 g (100.0 mmol) of *tert*-butyl alcohol in 50 mL of toluene/ether and 58.8 mL of 1.7 M *n*-BuLi/pentane (100.0 mmol)[21]). The low-boiling solvents are removed by distillation, and 1 drop of 15-C-5 is added. After 2 days of reflux toluene is replaced by pentane and the solids are filtered off. Distillation yields 9.15 g (25.0 mmol, 51.8%) of a colorless liquid, bp 123 °C/10^{-2} mbar. ^1H NMR ($CDCl_3$): δ 0.37 (s, 6 H), 1.36 (s, 9 H), 1.45 (s, 18 H), 6.64, 6.75 (AB, 2 H, *J* = 5.5 Hz). ^{13}C NMR ($CDCl_3$): δ 2.48 ($Si(CH_3)_2$), 31.46, 32.09 ($C(CH_3)_3$), 72.39, 75.24 ($OC(CH_3)_3$), 145.59 ($=CH_2$), 149.88 (=C). ^{29}Si NMR ($CDCl_3$): δ −55.25 (SiCl), −3.34 ($Si(CH_3)_2$). MS (70 eV): *m/e* 351 (0.12%, M^+ − 15), 313 (1.95), 295 (8.00), 257 (9.02), 239 (18.62), 201 (14.70), 183 (35.34), 75 (44.14), 57 (100). Anal. Found: C, 52.33; H, 9.32. Calcd for $C_{16}H_{35}ClO_3Si_2$ (367.08): C, 52.35; H, 9.61.

General Procedure for Silene Cycloaddition Reactions. A 5.80-g (20.0-mmol) amount of **2** and a 3–10-fold excess of diene/ene are dissolved in 150 mL of pentane (exception: anthracene in toluene) and cooled to −78 °C (exception: anthracene in toluene, +60 °C). An 11.8-mL portion of 1.7 M $LiBu^t$/pentane (20.0 mmol) is added dropwise. The reaction mixture is warmed up (cooled down). The solution is freed from precipitated LiCl by filtration. The solvent and excess diene are removed at ambient temperature and 10^{-2} mbar (anthracene is sublimed at +80 °C). The residue is distilled at 10^{-2} mbar or recrystallized from pentane. Only products containing no contamination by unknown substances as determined by GC and NMR spectroscopy were submitted to elemental analysis.

(*E*)-2,4-Bis(*tert*-butoxydichlorosilyl)-1,1,3,3-tetramethyl-2,4-dineopentyl-1,3-disilacyclobutane (9): colorless solid; 3.8 g (60%); mp 135 °C. ^1H NMR ($CDCl_3$): δ 0.54 (s, 12 H), 0.96 (s, 18 H), 1.33 (s, 18 H), 1.89 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 4.32, 4.33 ($Si(CH_3)_2$), 19.49 (SiCSi), 31.50, 31.90 ($C(CH_3)_3$), 32.72 ($C(CH_3)_3$), 43.82 (CH_2), 79.75 ($OC(CH_3)_3$). ^{29}Si NMR ($CDCl_3$): δ −23.54 ($SiCl_2$), 9.73 ($Si(CH_3)_2$). MS (CI): *m/e* 613 (1.94%, M^+ − 14), 591 (5.74), 539 (9.32), 499 (11.30), 479 (100), 421 (25.96), 313 (2.21), 279 (17.56). Anal. Found: C, 45.77; H, 8.21. Calcd for $C_{24}H_{52}Cl_4O_2Si_4$ (626.83): C, 45.99; H, 8.36.

(*Z*)-2,4-Bis(*tert*-butoxydichlorosilyl)-1,1,3,3-tetramethyl-2,4-dineopentyl-1,3-disilacyclobutane. ^{13}C NMR ($CDCl_3$): δ 3.60, 4.89 ($Si(CH_3)_2$), 20.08 (SiCSi), 31.33, 32.19 ($C(CH_3)_3$), 32.80 ($C(CH_3)_3$), 46.74 (CH_2), 79.30 ($OC(CH_3)_3$). ^{29}Si NMR ($CDCl_3$): δ −9.90 ($SiCl_2$), 8.79 ($Si(CH_3)_2$).

6-(*tert*-Butoxydichlorosilyl)-1,1,3,4-tetramethyl-6-neopentyl-1-sila-3-cyclohexene (10): colorless liquid; 3.1 g (79%); bp 100 °C/10^{-2} mbar. ^1H NMR ($CDCl_3$): δ 0.05 (s, 3 H), 0.16 (s, 3 H), 1.01 (s, 9 H), 1.22 (s br, 6 H), 1.40 (s, 9 H), 1.53–2.07 (m, 6 H). ^{13}C NMR ($CDCl_3$): δ −2.36, −1.81 ($Si(CH_3)_2$), 2.45 (SiCSi), 21.74 ($CH_2Si(CH_3)_2$), 21.97, 23.83 (CH_3), 31.21, 32.20 ($C(CH_3)_3$), 33.53 ($C(CH_3)_3$), 36.57 (CH_2), 43.44 ($CH_2C(CH_3)_3$), 78.56 ($OC(CH_3)_3$), 125.57, 126.76 (C=C). ^{29}Si NMR ($CDCl_3$): δ −22.38 ($SiCl_2$), 1.18 ($Si(CH_3)_2$). MS (70 eV): *m/e* 394 (0.41%, M^+), 338 (4.2), 321 (5.5), 281 (6.0), 199 (10.4), 57 (100). Anal. Found: C, 53.93; H, 8.75; Si, 13.91. Calcd for $C_{18}H_{36}Cl_2OSi_2$ (395.56): C, 54.66; H, 9.17; Si, 14.20.

6-(*tert*-Butoxydichlorosilyl)-1,1,3-trimethyl-6-neopentyl-1-sila-3-cyclohexene (11): colorless liquid; 2.8 g (74%); bp 85 °C/10^{-2} mbar. ^1H NMR ($CDCl_3$): δ 0.10 (s, 3 H), 0.21 (s, 3 H), 1.00 (s, 9 H), 1.26 (s, 3 H), 1.38 (s, 9 H), 1.57–2.05 (m, 4 H),

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2.37–2.68 (m, 2 H), 5.22–5.42 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ −2.36, −1.99 ($Si(CH_3)_2$), 19.56 ($CH_2Si(CH_3)_2$), 21.87 (SiCSi), 28.32 (CH_3), 29.16 (CH_2), 31.15, 32.20 ($C(CH_3)_3$), 33.59 ($C(CH_3)_3$), 42.69 ($CH_2C(CH_3)_3$), 78.57 ($OC(CH_3)_3$), 121.73 (=CH), 134.28 (C). ^{29}Si NMR ($CDCl_3$): δ −21.79 ($SiCl_2$), 1.04 ($Si(CH_3)_2$). MS (70 eV): *m/e* 365 (0.54%, M^+ − 15), 309 (2.54), 267 (7.72), 227 (3.78), 199 (4.39), 57 (100). Anal. Found: C, 53.41; H, 8.96; Cl, 18.48. Calcd for $C_{17}H_{34}Cl_2OSi_2$ (381.54): C, 53.52; H, 8.98; Cl, 18.58.

6-(*tert*-Butoxydichlorosilyl)-1,1-dimethyl-6-neopentyl-1-sila-3-cyclohexene (12): colorless liquid; 2.8 g (77%); bp 75 °C/10^{-2} mbar. ^{1}H NMR ($CDCl_3$): δ 0.09 (s, 3 H), 0.22 (s, 3 H), 1.00 (s, 9 H), 1.27 (m,2 H), 1.39 (s, 9 H), 1.61–2.05 (m, 2 H), 2.41–2.66 (m, 2 H), 5.44–5.85 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ −2.71, −1.92 ($Si(CH_3)_2$), 14.44 ($CH_2Si(CH_3)_2$), 22.20 (SiCSi), 28.93 (CH_2), 31.14, 32.19 ($C(CH_3)_3$), 33.70 ($C(CH_3)_3$), 42.46 ($CH_2C(CH_3)_3$), 78.50 ($OC(CH_3)_3$), 127.25, 127.60 (C=C). ^{29}Si NMR ($CDCl_3$): δ −22.07 ($SiCl_2$), 0.04 ($Si(CH_3)_2$). MS (70 eV): *m/e* 351 (0.50%, M^+ − 15), 253 (3.48), 217 (4.49), 199 (6.07), 57 (100). Anal. Found: C, 51.93; H, 8.45; Si, 15.32. Calcd for $C_{16}H_{32}Cl_2OSi_2$ (367.51): C, 52.29; H, 8.78; Si, 15.29.

8-(*tert*-Butoxydichlorosilyl)-7,7-dimethyl-8-neopentyl-7-silatricyclo[4.2.0.1^{2,5}]non-3-ene (13): colorless crystals; 2.7 g (67%); bp 110 °C/10^{-2} mbar; mp 115 °C. ^{1}H NMR ($CDCl_3$): δ 0.31 (s, 3 H), 0.52 (s, 3 H), 1.00 (s, 9 H), 1.21 (d, br, 1 H, *J* = 8.60 Hz), 1.29 (d, br, 1 H, *J* = 8.55 Hz), 1.44 (s, 9 H), 1.55 (d, br, 1 H, *J* = 8.55 Hz), 1.73, 1.91 (AB, 2 H, *J* = 14.34 Hz), 2.41 (d, 1 H, *J* = 8.55 Hz), 2.76 (s, br, 1 H), 2.45 (s, br, 1 H), 5.93 (dd, 1 H, *J* = 5.49, 3.06 Hz), 6.43 (dd, 1 H, *J* = 5.49, 2.44 Hz). ^{13}C NMR ($CDCl_3$): δ 0.44, 2.57 ($Si(CH_3)_2$), 23.56 (SiCSi), 29.27 (SiCH), 30.65 ($C(CH_3)_3$), 31.32, 31.41 ($C(CH_3)_3$), 40.64 ($CH_2C(CH_3)_3$), 40.94, 42.24, 44.04 (CH), 45.86 (CH_2), 79.15 ($OC(CH_3)_3$), 134.79, 138.37 (CH=CH). ^{29}Si NMR ($CDCl_3$): δ −25.37 ($SiCl_2OC(CH_3)_3$), 7.36 ($Si(CH_3)_2$). MS (70 eV): *m/e* 347 (1.03%, M^+ − 57), 256 (1.34), 225 (2.77), 199 (5.74), 57 (100). Anal. Found: C, 56.23; H, 8.39; Cl, 17.52; Si, 14.19. Calcd for $C_{19}H_{34}Cl_2OSi_2$ (405.56): C, 56.27; H, 8.45; Cl, 17.48; Si, 13.85.

4-(*tert*-Butoxydichlorosilyl)-3,3-dimethyl-4-neopentyl-3-silatetracyclo[6.1.0^{2,6}.0^{1,8}.0^{5,9}]nonane (14): colorless liquid; 2.5 g (61%, 14 and 15); bp 140 °C. ^{1}H NMR ($CDCl_3$; along with resonances of **15**): δ 0.29, 0.31, 0.35, 0.45 (s), 0.98, 1.09, 1.43, 1.47 (s), 1.2 –2.7 (div m). ^{13}C NMR ($CDCl_3$; along with resonances of **15**): δ −1.44, 0.60, 1.61, 2.00 ($Si(CH_3)_2$), 27.87, 29.70 (SiCH), 30.51, 31.33, 31.83, 31.92 ($C(CH_3)_3$), 33.94, 46.17, 47.20 (CH_2), 39.70, 42.46, 43.51, 49.02 (CH), 78.59, 78.91 ($OC(CH_3)_3$); only **14** δ 12.07, 12.51, 13.77 (CHCHCH), 25.90 (SiCSi), 37.04 ($C(CH_3)_3$). ^{29}Si NMR ($CDCl_3$): δ −25.39 ($SiCl_2$), 9.76 ($Si(CH_3)_2$). MS (CI): *m/e* 369 (4%, M^+ − 35), 335 (5), 313 (28), 257 (100).

5-[2′-(*tert*-Butoxydichlorosilyl)-3′-*tert*-butyl-1′,1′-dimethyl-1′-sila-2′-propenyl]bicyclo[2.2.1]-2-heptene (15). ^{1}H NMR ($CDCl_3$): δ 5.01 (dd, 1 H, *J* = 5.8, 2.9 Hz), 5.23 (dd, 1 H, *J* = 5.8, 2.7 Hz), 6.39 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ 130.38 (C=CH), 133.67, 138.47 (HC=CH), 175.52 (CH=C). ^{29}Si NMR ($CDCl_3$): δ −9.02 ($SiCl_2$), 19.53 ($Si(CH_3)_2$). MS (CI): *m/e* 369 (0.3%, M^+ − 35), 349 (63), 313 (100), 119 (10).

(*E*)-2,4-Bis(di-*tert*-butoxychlorosilyl)-1,1,3,3-tetramethyl-2,4-dineopentyl-1,3-disilacyclobutane (22): colorless solid; 4.3 g (62%); mp 167 °C. ^{1}H NMR ($CDCl_3$): δ 0.57 (s, 12 H), 1.02 (s, 18 H), 1.39 (s, 36 H), 2.02 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 4.79 ($Si(CH_3)_2$), 16.68 (SiCSi), 31.89, 32.02 ($C(CH_3)_3$), 32.66 ($C(CH_3)_3$), 76.16 ($OC(CH_3)_3$). ^{29}Si NMR ($CDCl_3$): δ −58.00 (SiCl), 11.85 ($Si(CH_3)_2$). MS (70 eV): *m/e* 459 (2.72%, M^+ − 243), 401 (10.27), 383 (5.25), 365 (5.11), 239 (9.58), 163 (15.34), 57 (100). Anal. Found: C, 54.59; H, 10.24. Calcd for $C_{32}H_{70}Cl_2O_4Si_4$ (702.16): C, 54.74; H, 10.05.

6-(Di-*tert*-butoxychlorosilyl)-1,1,3,4-tetramethyl-6-neopentyl-1-sila-3-cyclohexene (23): colorless liquid; 3.2 g (75%); bp 115 °C/10^{-2} mbar. ^{1}H NMR ($CDCl_3$): δ 0.099 (s, 3 H), 0.22 (s, 3 H), 1.14 (s, 9 H), 1.44 (s, 9 H), 1.45 (s, 9 H), 1.66 (s, br, 6 H), 2.44 (m, 2 H), 1.4–1.6 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ −2.62, −0.34 ($Si(CH_3)_2$), 19.36 (SiCSi), 21.42 ($CH_2Si(CH_3)_2$), 21.79, 23.92 (CH_3), 31.89, 32.24 ($C(CH_3)_3$), 33.73 ($C(CH_3)_3$), 36.60 (CH_2), 43.99 ($CH_2C(CH_3)_3$), 75.78, 75.96 ($OC(CH_3)_3$), 125.19, 126.75 (C=C). ^{29}Si NMR ($CDCl_3$): δ −51.86 ($SiCl_2$), 2.10 ($Si(CH_3)_2$). MS (70 eV): *m/e* 432 (0.22%, M^+), 356 (1.72), 320 (6.22), 263 (8.00), 222 (9.91), 57 (100). Anal. Found: C, 60.55; H, 10.24. Calcd for $C_{22}H_{45}ClO_2Si_2$ (433.22): C, 60.99; H, 10.47.

5-[2′-(Di-*tert*-butoxychlorosilyl)-3′-*tert*-butyl-1′,1′-dimethyl-1′-sila-2′-propenyl]bicyclo[2.2.1]-2-heptene (24): colorless liquid; 2.8 g (63%); bp 135 °C/10^{-2} mbar. ^{1}H NMR ($CDCl_3$): δ −0.80 (m, 1 H), −0.64 (s, 3 H), −0.69 (s, 3 H), 0.12 (s, 9 H), 0.35 (s, 9 H), 0.36 (s, 9 H), 0.37–0.44 (m, 4 H), 1.83 (m, 2 H), 4.88 (dd, 1 H, *J* = 5.6, 2.8 Hz), 5.13 (dd, 1 H, *J* = 5.5, 2.8 Hz), 6.34 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ 1.69, 2.09 ($Si(CH_3)_2$), 26.07 (CH_2), 27.88 (CHSi), 30.52, 31.57, 31.94 ($C(CH_3)_3$), 36.87 ($C(CH_3)_3$), 42.47, 43.55 (CH), 47.22 (CH_2), 72.91, 75.37 ($OC(CH_3)_3$), 131.22 (=C), 133.61, 138.62 (HC=CH), 173.39 (C=CH). ^{29}Si NMR ($CDCl_3$): δ −51.69 (SiCl), −7.30 ($Si(CH_3)_2$). MS (70 eV): *m/e* 350 (2.51%, M^+ − 92), 293 (22.83), 237 (52.66), 57 (100). Anal. Found: C, 61.88; H, 9.72. Calcd for $C_{23}H_{43}ClO_2Si_2$ (443.22): C, 62.33; H, 9.78.

8-(Di-*tert*-butoxychlorosilyl)-7,7-dimethyl-8-neopentyl-7-silatricyclo[4.2.0.1^{2,5}]non-3-ene (25): colorless crystals; 2.6 g (59%); mp 195 °C. ^{1}H NMR ($CDCl_3$): δ 0.28 (s, 3 H), 0.49 (s, 3 H), 1.01 (s, 9 H), 1.69 (s, 9 H), 1.80 (s, 9 H), 1.10 (s, br, 1 H), 1.62–1.8 (m, 3 H), 1.83 (s, br, 1 H), 1.94 (s, br, 1 H), 2.07 (d, 1 H, *J* = 1.05 Hz), 2.48 (d, br, 1 H, *J* = 8.7 Hz), 2.77 (d, br, 1 H, *J* = 7.8 Hz), 5.87 (dd, 1 H, *J* = 5.43, 3.01 Hz), 6.03 (dd, 1 H, *J* = 5.55, 2.6 Hz). ^{13}C NMR ($CDCl_3$): δ 0.24, 2.59 ($Si(CH_3)_2$), 28.97 (SiCH), 30.84 (SiCSi), 31.50, 31.63, 31.92 ($C(CH_3)_3$), 32.12 ($C(CH_3)_3$), 40.98 ($CH_2C(CH_3)_3$), 45.83 (CH_2), 40.98, 42.27, 43.45 (CH), 74.37, 77.01 ($OC(CH_3)_3$), 134.40, 138.39 (HC=CH). ^{29}Si NMR ($CDCl_3$): δ −50.73 (SiCl), 9.89 ($Si(CH_3)_2$). MS (70 eV): *m/e* 385 (1.25, M^+ − 57), 328 (2.34), 237 (40.79), 57 (100). Anal. Found: C, 61.97; H, 9.70. Calcd for $C_{23}H_{43}ClO_2Si_2$ (443.22): C, 62.33; H, 9.78.

8-(Tri-*tert*-butoxysilyl)-7,7-dimethyl-8-neopentyl-7-silatricyclo[4.2.0.1^{2,5}]non-3-ene (29): colorless crystals; 2.9 g (61%), mp 290 °C. ^{1}H NMR ($CDCl_3$): δ 0.21 (s, 3 H), 0.43 (s, 3 H), 1.00 (s, 9 H), 1.35 (s, 27 H), 1.47–1.81 (m, 4 H), 2.22–2.57 (m, 2 H), 2.58–2.98 (m, 2 H), 5.84 (dd, 1 H, *J* = 5.50, 3.00 Hz), 5.99 (dd, 1 H, *J* = 5.53, 2.63 Hz). ^{13}C NMR ($CDCl_3$): δ 1.52, 2.64 ($Si(CH_3)_2$), 17.52 (SiCSi), 28.80 (SiCH), 30.83 ($C(CH_3)_3$), 32.07 ($CC(CH_3)_3$), 32.29 ($C(CH_3)_3$), 39.17 ($CH_2C(CH_3)_3$), 41.03, 42.33, 43.28 (CH), 45.58 (CH_2), 73.38 ($OC(CH_3)_3$), 134.42, 137.79 (HC=CH). ^{29}Si NMR ($CDCl_3$): δ −75.68 ($Si(OC(CH_3)_3)_3$), 9.98 ($Si(CH_3)_2$). MS (CI): *m/e* 481 (2.52, M^+ + 1), 447 (2.50), 425 (100), 409 (14.52), 369 (89.71), 313 (85.13), 135 (48.34). Anal. Found: C, 67.12; H, 10.67. Calcd for $C_{27}H_{52}O_3Si_2$ (480.86): C, 67.44; H, 10.90.

Synthesis of 16. Chlorodiethylvinylsilane: colorless liquid; bp 137 °C. ^{1}H NMR ($CDCl_3$): δ 0.69–1.57 (m, 10 H), 6.07 (m, 3 H). ^{13}C NMR ($CDCl_3$): δ 6.30 (CH_3), 7.78 (CH_2), 133.42 (CH=), 134.87 (=CH_2). MS (70 eV): *m/e* 148 (24.32%, M^+), 135 (2.01), 119 (34.92).

Diethylisopropoxyvinylsilane: colorless liquid; bp 85 °C/100 mbar. ^{1}H NMR ($CDCl_3$): δ 0.73–1.75 (m, 16 H), 4.87 (sept, 1 H, *J* = 7.3 Hz), 6.04 (m, 3 H). ^{13}C NMR ($CDCl_3$): δ 5.02 (CH_2), 6.41 (CH_3), 25.60 (CH_3), 64.88 (OCH), 133.22 (CH_2=), 135.64 (C=).

1-Bromo-1-(diethylisopropoxysilyl)ethene: colorless liquid; bp 65 °C/10^{-2} mbar. ^{1}H NMR ($CDCl_3$): δ 0.67–1.52 (m, 16 H), 4.22 (sept, 1 H, *J* = 6.4 Hz), 6.45 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 4.05 (CH_2), 6.24 (CH_3), 25.51 (CH_3), 65.65 (OCH), 131.78 (CH_2=), 134.30 (C=). MS (CI): *m/e* 253 (30.5%, M^+), 251 (32.1), 225 (71.3), 223 (82.4), 211 (79.8), 209 (64.2), 119 (100).

1-(Trichlorosilyl)-1-(diethylisopropoxysilyl)ethene (16): colorless liquid; bp 58 °C/10^{-2} mbar. ^{1}H NMR ($CDCl_3$): δ 0.64–1.43 (m, 16 H), 4.53 (sept, 1 H, *J* = 7.1 Hz), 6.55 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 5.83 (CH_2Si), 8.75 (CH_3CH_2Si), 24.98 (($CH_3)_2CHO$), 69.17 (CHO), 111.67 (C=CH_2), 151.25 (C=CH_2). ^{29}Si NMR ($CDCl_3$): δ 26.78 ($SiCl_3$), −43.92 ($SiEt_2OPr^i$). MS (CI): *m/e* 304 (15.2%, M^+), 289 (21.6), 275 (10.9), 159 (33.3). Anal. Found: C, 34.98; H, 6.17. Calcd for $C_9H_{19}Cl_3OSi_2$ (305.78): C, 35.35; H, 6.26.

***syn*-/*anti*-8-(Isopropoxydichlorosilyl)-7,7-diethyl-8-neopentyl-7-silatricyclo[4.2.0.1^{2,5}]non-3-ene (18)**. The synthesis is analogous to other cycloadditions described in this paper: colorless liquid; bp 150 °C/10^{-2} mbar. ^{1}H NMR ($CDCl_3$): δ 0.70–1.06 (m, 11 H), 1.16–1.29 (m, 15 H), 1.40–2.70 (m, 7 H), 4.05 (sept, 0.5 H, *J* = 6.84 Hz), 4.48 (sept, 0.5 H, *J* = 6.80 Hz), 5.9–6.1 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 4.25, 4.86, 6.69, 8.01 ($SiCH_2$), 7.12, 7.28, 7.59, 7.71 (CH_2CH_3), 22.51, 27.93 (SiCSi), 24.41, 24.66, 25.26, 25.64 (($CH_3)_2CHO$), 26.55, 28.13 (SiCH), 30.39, 33.97 ($C(CH_3)_3$), 31.24, 31.92 ($C(CH_3)_3$), 40.83, 45.47 ($CH_2C(CH_3)_3$), 41.54, 42.35, 42.45, 43.70, 45.67, 48.08 (CH), 45.86, 48.06 (CH_2), 68.32, 68.92

(CHO), 134.86, 135.69, 137.46, 137.99 (HC=CH). ^{29}Si NMR ($CDCl_3$): δ -17.56, -12.84 ($SiCl_2OPr^i$), 12.89, 17.24 ($SiEt_2$). MS (70 eV): m/e 418 (0%, M^+), 375 (1.08), 319 (2.97), 253 (12.28), 57 (100). Anal. Found: C, 57.32; H, 8.77. Calcd for $C_{20}H_{36}Cl_2OSi_2$ (419.59): C, 57.25; H, 8.65.

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Supplementary Material Available: Tables of bond lengths and angles, least-squares planes, atomic coordinates, root-mean-square amplitudes of thermal vibration, and thermal parameters for compound **25** (15 pages). Ordering information is given on any current masthead page.

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Transition-Metal-Catalyzed Decomposition of Silylated Diazoacetic Esters: Influence of Silicon Substituents, Catalyst, and Solvent on Product Formation

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The catalytic decomposition of silylated diazo esters, $R^1R^2R^3SiC(N_2)COOMe$ ($R^1R^2R^3Si$ = Me_3Si, Et_3Si, Me_2tBuSi, iPr_3Si, Ph_2tBuSi, $Me_3SiSiMe_2$), by copper(I) triflate, dirhodium tetraacetate, and dirhodium tetrakis(perfluorobutyrate) ($Rh_2(pfb)_4$) in inert solvents has been studied. The efficiency of the catalysts is CuOTf > $Rh_2(pfb)_4$ ≫ $Rh_2(OAc)_4$. With $Rh_2(pfb)_4$, ketenes $R^2R^3(OMe)SiC(R^1)=C=O$ are formed in all cases. With CuOTf, the formal carbene dimers, azines, 5,5-dimethoxy-3,4-bis($SiR^1R^2R^3$)-2(5*H*)-furanones, and the ketenes mentioned before can be obtained; the result depends on the nature of the silyl substituent and on the solvent (carbon tetrachloride or toluene). The X-ray crystal structures of (*E*)-**2a** ($C_{12}H_{24}O_4Si_2$, orthorhombic space group *Pbca*, a = 8.987 (1) Å, b = 12.076 (1) Å, c = 15.329 (7) Å, Z = 4) and of **4d** ($C_{24}H_{48}O_4Si_2$, monoclinic space group $P2_1/c$, a = 15.220 (4) Å, b = 8.503 (3) Å, c = 22.247 (3) Å, β = 103.75 (2)°, Z = 4) have been determined.

In the last few years, transition-metal-catalyzed decomposition of diazocarbonyl and related diazo compounds has become a standard tool in synthetic organic chemistry, especially since significant progress has been made in terms of efficient chemo-, stereo-, and even enantioselective inter- and intramolecular reactions derived from metal–carbene intermediates.[1] α-Diazo-α-silylcarbonyl compounds have hardly participated in this development, except for some α-diazo-α-silyl ketones, the Cu- or Pd-assisted decomposition of which resulted in intramolecular carbene chemistry.[2-4]

Extrusion of dinitrogen from silylated diazoacetic esters has so far been induced by UV irradiation or by thermal means in nearly all cases.[5] Photolysis of ethyl diazo(trimethylsilyl)acetate generates the corresponding carbene, which is able to cyclopropanate alkenes and to insert into alkane C–H bonds.[6] When the same diazo compound is photolyzed in an alcohol, a complex mechanistic scenery arises, which is dominated by direct carbene interaction with the alcohol, Wolff rearrangement, and a 1,2(Si→C)-methyl shift resulting in a silene.[7] This silene is prone to further rearrangement but can be trapped by the alcohol present. The carbene → silene isomerization constitutes the exclusive pathway when ethyl diazo(pentamethyldisilanyl)acetate is photolyzed in an inert solvent.[8]

With the fact in mind that the mode of decomposition of diazo compounds very often alters the yields, the identity, and the diastereomer ratio of the products, we embarked on the transition-metal-catalyzed decomposition of various silylated methyl diazoacetates, all of which are easily accessible by electrophilic substitution of methyl diazoacetate with silyl triflates. The purpose of this study was to reveal the steric and electronic influence of silicon-attached substituents on the decomposition and subsequent carbene chemistry of these diazo esters. In particular, the following questions were to be answered: (a) What catalyst is needed for efficient decomposition, when sterically demanding silyl groups are present? (b) Does steric shielding by the silyl group entail different carbene-derived products? (c) Is the 1,2(Si→C)-substituent shift observed for the free carbenes also possible in the corresponding metal–carbene intermediates?

Results

Decomposition of Silylated Methyl Diazoacetates 1 in the Absence of a Trapping Reagent. Diazo esters **1a–f** were chosen for the present study since the size of

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