Silaheterocycles. 28.[1] Facile Synthesis of Silacyclobutenes from Silene/Acetylene [2 + 2] Cycloaddition Reactions

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The dichlorosilyl substituted silenes $Cl_2Si{=}CHCH_2$-*t*-Bu (**2a**) and $Cl_2Si{=}C(Ph)CH_2$-*t*-Bu (**2b**) and the bis(trimethylsiloxy) substituted derivative $(Me_3SiO)_2Si{=}CHCH_2$-*t*-Bu (**2c**) are formed from reactions of the corresponding chlorovinylsilanes $Cl_3SiCH{=}CH_2$ (**1a**), $Cl_3SiC(Ph){=}CH_2$ (**1b**), and $(Me_3SiO)_2Si(Cl)CH{=}CH_2$ (**1c**) with Li-*t*-Bu. The reaction of the silenes with a variety of diorgano substituted acetylenes $R^3C{\equiv}CR^4$ (R^3, R^4 = Me, $SiMe_3$, Ph) yields the silacyclobutenes **4a–9c** in a one step procedure; in some cases the ene products **5**α–**8**γ are formed in competition with the silene [2 + 2] cycloadducts. The substitution at C^4 of the silacyclobutene skeleton can be modified, when different silene units are used (e.g. **2a** → **2b**), while the substitution pattern at C^2 and C^3 will be modified by the use of different acetylenes. The dichlorosilyl functionality can be utilized for the synthesis of silicon substituted derivatives by simple reaction sequences. The silacylobutenes are thermally surprisingly stable and can be distilled in most cases under vacuum at temperatures up to 200 °C without decomposition.

Introduction

The synthesis, structure, and reactivity of monosilacylo*butanes* have been the subjects of numerous investigations in the past 30 years.[2] In comparison, very little has been reported about silacyclo*butenes*;[3] the obvious reason is their poor accessibility. They can be prepared on a laboratory scale, but only with great effort and in comparably low yield by multistep organosilicon synthesis[4] or by gas-phase pyrolysis of suitable precursors.[5]

This is also true in the case of cycloaddition reactions of silenes with acetylene derivatives.[6,7] Moreover, silacyclobutenes halogenated at the silicon atom were unknown up to 1991.[8] From these compounds substituted derivatives are accessible by simple reaction sequences so that technical applications and a possible use for the preparation of Si-containing polymers and preceramic materials are conceivable.[2,9] They may also serve as precursors for 1-silabutadienes.[10] We have described the facile one-step synthesis of monosilacyclobutanes[2] and of differently silicon 2,4-substituted 1,3-disilacyclobutanes[11] starting from equimolar mixtures of chlorovinylsilanes and *tert*-butyllithium and we now report the facile synthesis of monosilacyclobutenes with different substitution patterns at the silicon and carbon atoms of the unsaturated four membered ring skeleton. The synthesis is achieved by reacting vinylchlorosilanes, Li-*t*-Bu and diorganoacetylenes.

Results

In earlier work we have reported about the synthesis of silenes **2a–2c** from vinylchlorosilane precursors **1a–1c**. The synthesis of **1b** and **1c** follows Scheme I.

$Cl_3SiCH{=}CH_2$	$Cl_3SiC(Ph){=}CH_2$	$(Me_3SiO)_2Si(Cl)CH{=}CH_2$
1a	**1b**	**1c**
$Cl_2Si{=}CHCH_2tBu$	$Cl_2Si{=}C(Ph)CH_2tBu$	$(Me_3SiO)_2Si{=}CHCH_2tBu$
2a [12]	**2b** [1]	**2c** [13]

Investigations on the silenes cycloaddition potential characterize **2c** to be a true *synthetic* equivalent to **2a**, because both silenes show an extraordinary [2 + 2]

• Abstract published in *Advance ACS Abstracts*, September 15, 1993.

(1) Part 27: Auner, N.; Wagner, C.; Ziche, W. *Z. Naturforsch.*, submitted for publication.

(2) For a summary of relevant literature see: Sewald, N.; Ziche, W.; Wolff, A.; Auner, N. *Organometallics*, preceding article in this issue.

(3) The first publications on silacyclobutenes appeared in the sixties: Gilman, H.; Atwell, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 5589. *Ibid.* **1965**, *87*, 2678. For an overview see: Backer, M. Diplom-thesis, TU München, 1993.

(4) See ref 3. Eaborn, C.; Dalton, D. R. M.; Chan, M. *J. Organomet. Chem.* **1967**, *9*, 25. Valkovich, P. B.; Weber, W. P. *Tetrahedron Lett.* **1975**, *26*, 2153. Ishikawa, M. *Organometallics* **1990**, *9*, 205.

(5) Barton, T. J.; Groh, B. L. *J. Am. Chem. Soc.* **1985**, *107*, 8297. Burns, G. T.; Barton, T. J. *Ibid.* **1983**, *105*, 2006. Burns, S. A.; Burns, G. T.; Barton, T. J. *Ibid.* **1982**, *104*, 6140. Burns, G. T.; Barton, T. J. *J. Organomet. Chem.* **1981**, *216*, C5. Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1978**, *100*, 1630.

(6) Conlin, R. T.; Kwak, Y.-W.; Huffacker, H. B. *Organometallics* **1983**, *2*, 343. Brook, A. G.; Harris, J. W.; Lennon, J.; Sheitch, M. E. *J. Am. Chem. Soc.* **1979**, *101*, 83.

(7) In contrast *di*silacyclobutenes are available in good yields from disilene synthons and acetylene derivatives: Schäfer, A.; Weidenbruch, M.; Pohl, S. *J. Organomet. Chem.* **1985**, *282*, 305. Weidenbruch, M.; Schäfer, A.; Thom, K.-L. *Z. Naturforsch.* **1983**, *38B*, 1695. Weidenbruch, M.; Schäfer, A.; Marsmann, H. *J. Organomet. Chem.* **1988**, *354*, C12.

(8) In 1991 a short communication was published on the synthesis of silacyclobutenes from dichloroneopentylsilene and diorgano substituted acetylenes: Auner, N.; Seidenschwarz, C.; Herdtweck, E. *Angew. Chem.* **1991**, *103*, 1172; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1151.

(9) Theunig, M.; Weber, W. P. *Polym. Bull.* **1992**, *28*, 17. Anionic ring opening polymerization reactions with the silacyclobutenes described in this paper yield polymeric materials of high quality. These investigations and the transition metal induced ROMP reactions are being investigated in our group.

(10) Irradiation experiments with the silacyclobutenes presented in this paper show that methoxytrimethylsilane adds to 1-silabutadienes across the Si=C bond. Investigations are underway in our laboratories. For irradiation of silacyclobutene in the presence of acetone see: Valkovich, P. B.; Weber, W. P. *Tetrahedron Lett.* **1975**, 2153.

(11) Auner, N.; Gleixner, R. *J. Organomet. Chem.* **1990**, *393*, 33. For example, equimolar mixtures of $Cl_3SiCH{=}CH_2$, Li*t*Bu, and NEt_3 yield $(Cl_2SiCHCH_2tBu)_2$ in nearly quantitative amounts. For stepwise synthesis of the disilacylobutane see: Auner, N.; Wolff, A. *Chem. Ber.* **1993**, *126*, 575.

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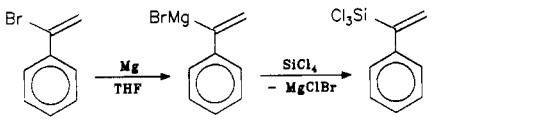
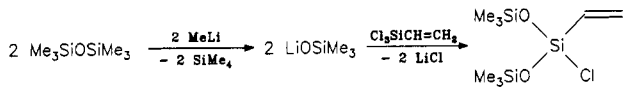
Scheme I



1b



1c

cycloaddition activity toward dienes and 2,5-norbornadiene as well as to compounds with activated or strained CC double bonds such as 2-norbornene.[12-14] Thus from **2a** mainly silicon dichlorinated monosilacyclobutanes are obtained, while **2c** yields the silicon bis(trimethylsiloxy) substituted four membered ring compounds. Compared with the reactivity of **2a** and **2c**, silene **2b** shows a significantly different cycloaddition behavior toward butadienes: pure stereoisomers of silacyclohexenes are obtained from *regio-* and *stereo*specific [4+2] addition.[1] Thus **2b** is characterized by a cycloaddition potential similar to that for silenes $Me_2Si{=}C[SiCl_{2-n}(O\text{-}t\text{-}Bu)_{n+1}]\text{-}CH_2\text{-}t\text{-}Bu$ (n = 0, 1),[15] and exhibits a lesser tendency toward [2 + 2] cycloaddition reactions than the α-C substituted analogue $Cl_2Si{=}C(SiMe_3)CH_2\text{-}t\text{-}Bu$ (**3**).[16] For a detailed comparative study on silene reactivity, the reaction partners (e.g. butadienes) always have to be considered.[16] This is clearly demonstrated in the reactivity of **2b** and **3** toward diorgano substituted acetylenes: while compound **3** does not react, silacyclobutenes are obtained from the phenyl substituted analogue **2b**. This proves that the silenes **2a–2c** are useful building blocks for the synthesis of silacyclobutenes.

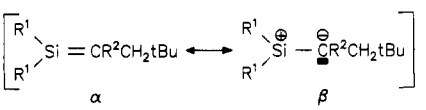
Using *one* acetylene derivative as the reaction partner for **2a–2c** Si- and C^4-modified silacyclobutenes are obtained; changing the acetylene component results in a modification of the substituents at C^2 and C^3 in the carbon skeleton.

According to Scheme II, the chlorovinylsilanes **1a–1c** add to Li-*t*-Bu forming α-lithio adducts; subsequent intramolecular 1,2-LiCl elimination liberates the silenes **2a–2c** which are allowed to react with the diorgano substituted acetylenes **4–9**, yielding silacyclobutenes **4a–9c** in a one-step procedure. Table II in the Experimental Section lists the conducted experiments and the numerical values of the yield of products, while the plot in Figure 1 clearly depicts a comparison from different silenes and acetylenes.

As can be seen, the synthesis of silacyclobutenes is determined not only by the electronic features of the silene unit but also by the steric demands of both the silene and the acetylene derivatives. Starting from **2a** the [2 + 2] cycloadducts are formed in 50–80% yield; this decreases to 30–60% using silene **2c** and even to 10–40% with compound **2b**. Evidently, the steric influence of the substituents at the silicon (in **2c**) or the α-carbon atom (in **2b**) of the Si=C-moieties are responsible for minimizing the yields of the silacylobutenes. With respect to the acetylene derivatives needed for the cycloaddition reaction, there is a similar trend: the highest yields of silacyclobutenes from **2a** and **2c** are obtained with tolan, while **2b** forms the ring compound **4b** in comparatively high yield only with the "smallest" acetylene (2-propyne) of the series.[17]

Surprisingly, the silacyclobutenes **4a–9c** are thermally very stable; they do not decompose even on heating for several days at 200 °C. They are obtained as highly viscous, colorless liquids, which can be distilled at temperatures up to 200 °C under vacuum;[17] only **8a** was isolated as a sublimable, crystalline solid and could be characterized by X-ray crystallography.[8]

The [2 + 2] cycloaddition reactions most likely proceed in two steps involving 1,4-dipoles of the general type $[R^1_2Si(\ddot{C}\text{-}R^2CH_2\text{-}t\text{-}Bu)C^+(R^3){=}C(R^4)]$, and proceed regiospecifically: isomeric products $R^1_2SiC(R^3){=}C(R^4)C(R^2)\text{-}CH_2\text{-}t\text{-}Bu$ cannot be detected in any case. The silenes **2a–2c** are polar with the positive partial charge localized at the silicon atom and the negative partial charge at the carbon atom. In comparison to silicon diorgano substituted silenes this polarity and the electrophilic character of the silenes are enhanced and can be attributed to the influence of the π-donor substituents at the silicon atom and the phenyl group as π-acceptor at the carbon atom (in **2b**).[2,18] The changes in orbital energies and coefficients lead to an enhanced propensity to participate in [2 + 2] cycloaddition reactions.[19] A simple model for the strongly polar silenes is given by the two mesomeric forms α and β.



An alternative reaction path for the formation of silacyclobutenes could involve a carbanionic attack on the acetylenes by the α-lithio compounds $R^1_2Si(Cl)CLi(R^2)\text{-}CH_2\text{-}t\text{-}Bu$, followed by cyclization and elimination of LiCl. However, performing the synthesis of silacyclobutenes in THF as solvent—this should stabilize the lithiated species[20]—does not result in the formation of silacyclobutenes;[21] moreover, $F_3SiCH(Li)CH_2\text{-}t\text{-}Bu$, which is markedly more stable than the chlorine analogue, does not react with dienes and acetylenes.[22]

(12) See refs 1, 2, and 8. Auner, N. *Z. Anorg. Allg. Chem.* **1988**, *558*, 55. Auner, N. *J. Organomet. Chem.* **1988**, *353*, 275. Auner, N.; Seidenschwarz, C. *Z. Naturforsch.* **1990**, *45B*, 909. Auner, N.; Seidenschwarz, C.; Sewald, N.; Herdtweck, E. *Angew. Chem.* **1991**, *103*, 425; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 444. Auner, N.; Seidenschwarz, C.; Sewald, N. *Organometallics* **1992**, *11*, 1137. Auner, N.; Weingartner, A. W.; Bertrand, G. *Chem. Ber.* **1993**, *126*, 581.

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

(14) Toward compounds of only low diene activity such as furans and naphthalene, **2c** shows a lower enophilic activity than **2a**; from these reactions no cycloaddition compounds are obtained.[13]

(15) Ziche, W.; Auner, N.; Kiprof, P. *J. Am. Chem. Soc.* **1992**, *114*, 4910. Ziche, W.; Auner, N.; Behm, J. *Organometallics* **1992**, *11*, 3805.

(16) Ziche, W.; Auner, N.; Behm, J. *Organometallics* **1992**, *11*, 2494. In the reactions of silenes $Cl_2Si{=}C(R)CH_2tBu$ interactions $R_2Si(Cl)\text{-}CR(Li)CH_2tBu$/substrate, silene/LiCl, and silene/substrate cannot been ruled out.[12]

(17) It should be mentioned that distillation of silacyclobutenes with high boiling points (>200 °C) reduces the yields because of thermal formation of polymeric material. Gas chromatographic investigations on the reaction solution mostly show peaks only for the acetylenes, silacyclobutenes, and the ene products. Purification of the compounds by column chromatography is prohibited by the chlorine substituents at the silicon.

(18) Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676.

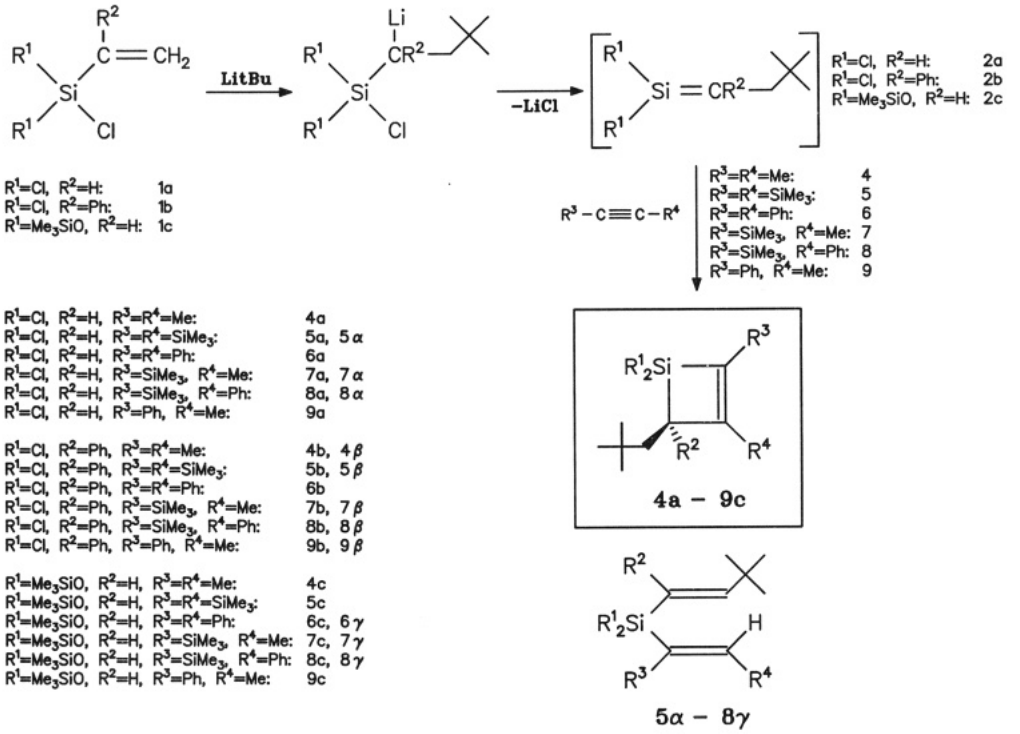
(19) Sauer, J.; Sustmann, R. *Angew. Chem.* **1980**, *92*, 773; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(20) Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* **1977**, *99*, 8447. See also ref 11.

(21) Wolff, A. Dissertation, TU München, 1991.

(22) Auner, N.; Seidenschwarz, C.; Wolff, A. Unpublished results.

Scheme II



R¹=Cl, R²=H, R³=R⁴=Me: 4a
R¹=Cl, R²=H, R³=R⁴=SiMe₃: 5a, 5α
R¹=Cl, R²=H, R³=R⁴=Ph: 6a
R¹=Cl, R²=H, R³=SiMe₃, R⁴=Me: 7a, 7α
R¹=Cl, R²=H, R³=SiMe₃, R⁴=Ph: 8a, 8α
R¹=Cl, R²=H, R³=Ph, R⁴=Me: 9a

R¹=Cl, R²=Ph, R³=R⁴=Me: 4b, 4β
R¹=Cl, R²=Ph, R³=R⁴=SiMe₃: 5b, 5β
R¹=Cl, R²=Ph, R³=R⁴=Ph: 6b
R¹=Cl, R²=Ph, R³=SiMe₃, R⁴=Me: 7b, 7β
R¹=Cl, R²=Ph, R³=SiMe₃, R⁴=Ph: 8b, 8β
R¹=Cl, R²=Ph, R³=Ph, R⁴=Me: 9b, 9β

R¹=Me₃SiO, R²=H, R³=R⁴=Me: 4c
R¹=Me₃SiO, R²=H, R³=R⁴=SiMe₃: 5c
R¹=Me₃SiO, R²=H, R³=R⁴=Ph: 6c, 6γ
R¹=Me₃SiO, R²=H, R³=SiMe₃, R⁴=Me: 7c, 7γ
R¹=Me₃SiO, R²=H, R³=SiMe₃, R⁴=Ph: 8c, 8γ
R¹=Me₃SiO, R²=H, R³=Ph, R⁴=Me: 9c

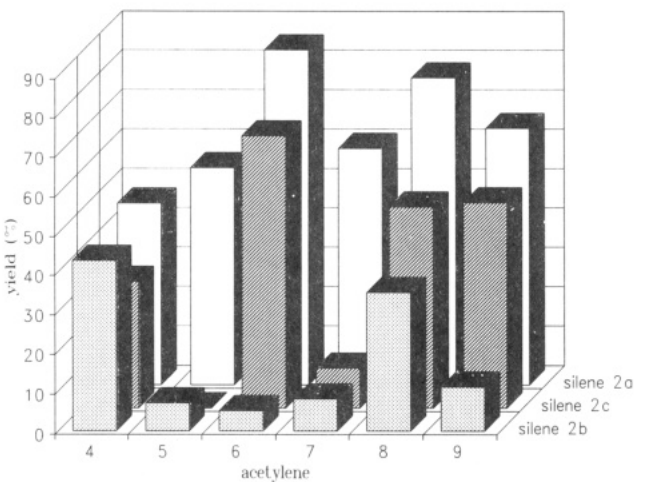


Figure 1.

Three reactions of silene **2a** lead to formation of the silacylobutenes **5a**, **7a**, and **8a** and, competitively, the *trans*-ethene compounds 5α, 7α, and 8α (cis orientation of R^3 and R^4). The latter were formed in amounts between 10 and 30%. Silene **2b** forms analogous compounds 4β–9β only in traces, while from silene **2c** the derivatives 6γ–8γ are obtained (Scheme II). The formation of 5α–8γ can be explained by an ene reaction, in which the silenes react with the diorgano substituted acetylenes as enophiles.[23] The ene reaction of silene **2b** with nearly all acetylenes used for silacyclobutene synthesis is obviously due to steric factors of both the silene *and* the C≡C unit; consequently, the formation of zwitterionic intermediates in the stepwise cycloaddition reactions seems to be hindered in these cases.

The silacyclobutenes **4a–9c** and the ene products 5α–8γ are characterized by the usual analytical and spectroscopic methods. Table I lists characteristic ^{13}C and ^{29}Si NMR spectroscopic features, i.e. the ^{13}C NMR spectroscopic shift of the carbon ring skeleton atoms of the silacyclobutenes and those for the unsaturated carbon atoms of the ene product divinyl subunit.

(23) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51. Wiberg, N. *J. Organomet. Chem.* **1984**, *272*, 141.

Experimental Section

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

Gas chromatography was carried out with a Chrompack CP 9000, equipped with a 10-m Chrompack CP Sil 5 CB. GC/MS analysis was carried out with a Chrompack CP 9000 coupled with a Finnigan MAT ion trap 800. Chemical ionization used methanol as the reactant gas. NMR spectra were recorded on JEOL JNM GX 270 and JEOL JNM GX 400 (^1H and ^{29}Si) and Bruker WP100SY (^1H, ^{13}C, and ^{13}C-DEPT). $CDCl_3$ was used as internal standard. Mass spectra were obtained with Finnigan MAT 311A. Elemental analyses were carried out at Mikroanalytisches Labor des Anorganisch-chemischen Instituts der Technischen Universität München, D-85747 Garching, Germany.

For the preparation and spectroscopic characterization of chlorovinylsilanes **1b** and **1c** see refs 1 and 13.

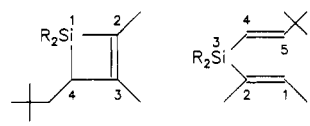
General Procedure for Cycloaddition Reactions of Silenes 2a–2c. Between 4 and 16 mmol of the chlorovinylsilanes **1a–1c** and a 2–10-fold excess of acetylene (see Table II) are dissolved in 150 mL of *n*-pentane, and the solution is cooled to –78 °C. An equimolar amount of Li-*t*-Bu (1.7 *m* in *n*-pentane) is added dropwise. The reaction mixture is allowed to warm up. The solution is freed from precipitated LiCl by filtration. The solvent and excess diene are removed at ambient temperatures. The residue is distilled at 10^{-2} mbar or—in the case of **8a**—recrystallized from pentane. Only products containing no contamination by unknown substances as determined by GC and NMR spectroscopy were submitted to elemental analysis. The syntheses of silacylobutenes **4a–9c** are summarized in Table II.

1,1-Dichloro-2,3-dimethyl-4-neopentyl-1-silacyclobut-2-ene, 4a: ^1H NMR ($CDCl_3$) δ 0.90 [s, 9H, C(C*H*$_3$)$_3$], 1.50 (m, 2H, C*H*$_2$), 1.80 and 1.90 (s, 3H, C*H*$_3$), 2.30 (m, 1H, C*H*); ^{13}C NMR ($CDCl_3$) δ 14.20 and 14.40 (*C*H$_3$), 28.70 [C(*C*H$_3$)$_3$], 30.90 [*C*(CH$_3$)$_3$], 40.60 (*C*H$_2$), 43.20 (C^4), 141.00 (C^3), 158.80 (C^2); ^{29}Si NMR ($CDCl_3$)

Table I. Characteristic ^{13}C and ^{29}Si NMR Spectroscopic Parameters for the Silacyclobutenes 4a–9c and the Ene Products 5α–8γ[a]

compd	C2	C3	C4	SiR_2	compd	C1	C2	C4	C5	SiR_2
4a	158.80	141.00	43.20	18.90						
5a	186.30	169.40	51.30	−1.30	**5α**	171.80	159.90	117.80	164.40	5.20
6a	157.10	143.60	42.10	−7.00						
7a	174.10	148.40	48.60	−6.80	**7α**[b]					
8a	173.00	149.50	46.30	−1.40	**8α**	141.00	164.67	117.70	166.00	−1.37
9a	157.90	141.60	42.10	−2.30						
4b	162.91	149.84	60.39	13.36	**4β**	149.98	138.26	141.31	165.21	8.43
5b	168.20	143.80	58.67	−6.18	**5β**	157.40	143.40	141.80	183.60	
6b	154.84	140.01	67.00	10.34						
7b	177.25	160.16	61.89	−5.45	**7β**	157.42	145.61	140.05	176.70	4.22
8b	178.34	167.09	67.37	14.29	**8β**	157.35	151.93	140.09	160.95	−0.95
9b	153.74	144.95	69.17	8.37	**9β**	144.95	154.50	154.50	165.06	
4c	140.02	132.06	36.56	−40.44						
5c[c]										
6c	156.35	146.07	41.08	−53.34	**6γ**	145.30	157.05	135.73	156.04	−42.50
7c	173.13	147.35	47.03	−53.16	**7γ**[c]					
8c	157.09	132.04	44.75	−53.69	**8γ**	132.04	167.18	120.17	160.17	−42.34
9c	156.89	142.67	39.59	−58.61						

[a] Numbering of the atoms:



[b] **7α** could only be characterized by ^1H NMR. [c] **5c** and **7γ** could only be detected by GC/MS analysis.

Table II. Preparation of Silacyclobutenes[a]

chlorovinylsilane [compd no./g/mmol]	LiⁱBu [mL/mmol]	acetylene [compd no./g/mmol]	products[b,c]	bp/mp [°C/HV]	yield[c] [g/mmol/%]
1a/2.42/15.00	8.82/15.00	**4**/2.43/45.00	**4a**	52	1.63/6.90/46
1a/2.42/15.00	8.82/15.00	**5**/7.67/45.00	**5a, 5α** (67/23)	87	2.92/8.25/55
1a/2.42/15.00	8.82/15.00	**6**/8.02/45.00	**6a**	200	4.61/12.75/85
1a/2.42/15.00	8.82/15.00	**7**/5.05/45.00	**7a, 7α** (96/4)	70	2.66/9.00/60
1a/2.42/15.00	8.82/15.00	**8**/7.67/45.00	**8a, 8α** (92/8)	mp 56	4.14/11.70/78
1a/2.42/15.00	8.82/15.00	**9**/5.23/45.00	**9a**	116	3.50/11.70/65
1b/0.98/4.12	2.67/4.53	**4**/0.33/06.19	**4b, 4β** (83/17)	118	0.55/1.76/43
1b/3.12/13.13	8.50/14.45	**5**/3.36/19.70	**5b, 5β** (79/21)	145	0.41/1.95/7
1b/3.42/14.38	9.30/15.82	**6**/2.87/15.82	**6b**	235	0.28/6.40/5
1b/3.42/14.38	9.30/15.82	**7**/1.78/15.82	**7b, 7β** (95/5)	129	0.44/1.18/8
1b/3.74/15.74	10.20/17.32	**8**/3.29/18.89	**8b, 8β** (91/9)	245	2.40/5.54/35
1b/3.42/14.38	9.3/15.82	**9**/1.84/15.82	**9b, 9β** (98/2)	120	0.58/1.54/11
1c/2.82/10.48	6.16/10.48	**4**/1.13/20.96	**4c**	136	1.16/3.37/32
1c/2.24/8.32	4.89/8.32	**5**/2.55/14.96	**5c**[d]		
1c/2.78/10.33	6.07/10.33	**6**/5.52/30.99	**6c, 6γ** (93/7)	143	3.34/7.13/69
1c/2.78/10.33	6.07/10.33	**7**/3.47/30.99	**7c, 7γ** (89/11)	85	0.42/1.33/10
1c/1.21/4.49	2.64/4.49	**8**/2.56/08.98	**8c, 8γ** (68/32)	160	1.06/2.28/51
1c/2.84/10.56	6.21/10.56	**9**/1.83/15.83	**9c**	154	2.23/5.48/52

[a] All silacyclobutenes are colorless, viscous liquids; only **8a** was isolated as a crystalline solid.[8] [b] The ene products cannot be separated from the silacyclobutenes by distillation. The product ratios are given in parentheses. The mixtures of isomers were subjected to elemental analysis (see Experimental Section). [c] Gas chromatography of the reaction mixtures showed only the compounds listed below. The yield is given for isolated product (Figure 1). [d] **5c** could only be detected by GC/MS analysis.

δ 18.90 ($SiCl_2$); MS (70 eV) *m/z* 236 (2, M^+), 193 (5), 137 (7), 83 (8), 57 (100). Anal. Calcd (found) for $C_{10}H_{18}Cl_2Si$ (237.21): C, 50.06 (49.98); H, 7.65 (7.58); Cl, 29.90 (29.95); Si, 12.39 (12.20).

1,1-Dichloro-4-neopentyl-2,3-bis(trimethylsilyl)-1-silacyclobut-2-ene, 5a: ^1H NMR ($CDCl_3$) δ −0.20 and −0.15 [s, 9H, $Si(CH_3)_3$], 0.80 [s, 9H, $C(CH_3)_3$], 1.30 (m, 2H, CH_2), 2.70 (m, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 0.30 and 0.50 [$Si(CH_3)_3$], 29.60 [$C(CH_3)_3$], 31.00 [$C(CH_3)_3$], 42.50 (CH_2), 51.30 (C^4), 169.40 (C^3), 186.30 (C^2); ^{29}Si NMR ($CDCl_3$) δ −12.90 and −7.30 [$Si(CH_3)_3$], −1.30 ($SiCl_2$); MS (70 eV) *m/z* 352 (3, M^+), 295 (5), 244 (10), 229 (6), 187 (52), 73 (100), 57 (68). Anal. Calcd (found) for $C_{14}H_{30}Cl_2Si_3$ (353.28): C, 47.59 (47.14); H, 8.49 (8.01); Cl, 20.07 (20.43); Si, 23.85 (23.28).

1,1-Dichloro-4-neopentyl-2,3-diphenyl-1-silacyclobut-2-ene, 6a: ^1H NMR ($CDCl_3$) δ 0.90 [s, 9H, $C(CH_3)_3$], 1.40 (m, 2H, CH_2), 3.00 (m, 1H, CH), 7.00 (m, 10H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 29.30 [$C(CH_3)_3$], 30.40 [$C(CH_3)_3$], 40.20 (CH_2), 42.10 (C^4), 127.80 (CH aromat), 128.00, 128.10, 128.50, and 128.60 (2CH aromat), 129.00 (CH aromat), 134.00 and 134.50 (C_q aromat), 143.60 (C^3), 157.10 (C^2); ^{29}Si NMR ($CDCl_3$) δ −7.00 ($SiCl_2$); MS (70 eV) *m/z* 360 (0.4, M^+), 178 (100), 105 (6), 89 (10), 76 (9). Anal. Calcd (found) for $C_{20}H_{22}Cl_2Si$ (316.39): C, 66.47 (66.39); H, 6.14 (6.08); Cl, 19.62 (19.70); Si, 7.77 (7.65).

1,1-Dichloro-3-methyl-4-neopentyl-2-(trimethylsilyl)-1-silacyclobut-2-ene, 7a: ^1H NMR ($CDCl_3$) δ 0.17 [s, 9H, $Si(CH_3)_3$], 0.95 [s, 9H, $C(CH_3)_3$], 1.80 (m, 2H, CH_2), 2.01 (d, ^4J = 1.0 Hz, 3H, CH_3), 2.33 (m, 1H, CH); ^{13}C NMR ($CDCl_3$) δ −0.40 [$Si(CH_3)_3$], 20.30 (CH_3), 29.50 [$C(CH_3)_3$], 30.50 [$C(CH_3)_3$], 40.90 (CH_2), 48.60 (C^4), 148.40 (C^3), 174.10 (C^2); ^{29}Si NMR ($CDCl_3$) δ −11.20 [$Si(CH_3)_3$], −6.80 ($SiCl_2$); MS (70 eV) *m/z* 294 (0.1, M^+), 237 (52), 109 (100), 98 (50), 73 (54). Anal. Calcd (found) for $C_{12}H_{24}Cl_2Si_2$ (295.402): C, 48.79 (48.71); H, 8.19 (8.13); Cl, 24.00 (24.09); Si, 19.02 (18.96).

1,1-Dichloro-4-neopentyl-3-phenyl-2-(trimethylsilyl)-1-silacyclobut-2-ene, 8a: ^1H NMR ($CDCl_3$) δ 0.02 [s, 9H, $Si(CH_3)_3$], 0.84 [s, 9H, $C(CH_3)_3$], 1.40 (m, 2H, CH_2), 3.20 (m, 1H, CH), 7.25 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ −0.20 [$Si(CH_3)_3$], 29.30 [$C(CH_3)_3$], 30.50 [$C(CH_3)_3$], 40.80 (CH_2), 46.30 (C^4), 127.60 and 128.30 (2CH aromat), 129.20 (CH aromat), 137.20 (C_q aromat), 149.50 (C^3), 173.00 (C^2); ^{29}Si NMR ($CDCl_3$) δ −12.40 [$Si(CH_3)_3$],

−1.40 ($SiCl_2$); MS (70 eV) m/z 356 (14, M^+), 299 (39), 191 (42), 73 (100), 57 (47). Anal. Calcd (found) for $C_{17}H_{28}Cl_2Si_2$ (357.23): C, 57.45 (57.50); H, 7.31 (7.38); Cl, 15.80 (16.13); Si, 19.44 (19.22).

1,1-Dichloro-3-methyl-4-neopentyl-2-phenyl-1-silacyclobut-2-ene, 9a: ^1H NMR ($CDCl_3$) δ 0.90 [s, 9H, $C(CH_3)_3$], 1.70 (m, 2H, CH_2), 2.10 (d, ^4J = 2.4 Hz, 3H, CH_3), 3.20 (m, 1H, CH), 7.30 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 13.00 (CH_3), 29.30 [$C(CH_3)_3$], 30.40 [$C(CH_3)_3$], 40.60 (CH_2), 42.10 (C^4), 128.00 and 128.50 (2CH aromat), 128.60 (CH aromat), 134.20 (C_q aromat), 141.60 (C^3), 157.90 (C^2); ^{29}Si NMR ($CDCl_3$) δ −2.30 ($SiCl_2$); MS (70 eV) m/z 298 (10, M^+), 283 (13, $M^+ - 15$), 241 (14), 171 (16), 57 (100). Anal. Calcd (found) for $C_{15}H_{20}Cl_2Si$ (299.11): C, 60.22 (60.19); H, 6.69 (6.57); Cl, 23.70 (23.69); Si, 9.39 (9.58).

3,3-Dichloro-6,6-dimethyl-1,2-bis(trimethylsilyl)-3-silahepta-(*E*)-1(*E*)-4-diene, 5α: ^1H NMR ($CDCl_3$) δ −0.05 and 0.04 [s, 9H, $Si(CH_3)_3$], 0.66 [s, 9H, $C(CH_3)_3$], 5.41 (d, 1H, Cl_2SiCH=), 6.25 (d, 1H, =CH-t-Bu, J_{AB} = 19.44 Hz), 6.57 [s, 1H, =CH-($SiMe_3$)]; ^{13}C NMR ($CDCl_3$) δ 0.70 and 1.90 [$Si(CH_3)_3$], 28.80 [$C(CH_3)_3$], 31.80 [$C(CH_3)_3$], 117.80 (C^4), 159.90 (C^2), 164.40 (C^5), 171.80 (C^1); ^{29}Si NMR ($CDCl_3$) δ −8.80 and −6.90 [$Si(CH_3)_3$], 5.20 ($SiCl_2$); MS (70 eV) m/z 352 (0.1, M^+), 337 (12, $M^+ - 15$), 297 (5), 244 (5), 187 (8), 73 (100).

4,4-Dichloro-7,7-dimethyl-3-(trimethylsilyl)-4-silaocta-(*E*)-2(*E*)-5-diene, 7α: This compound could not be isolated. The identification was possible by the characteristic AB spin pattern in the ^1H NMR spectrum: 5.71 (d, 1H, Cl_2SiCH=), 6.65 (d, 1H, =CH-t-Bu), J_{AB} = 18.66 Hz).

3,3-Dichloro-6,6-dimethyl-1-phenyl-2-(trimethylsilyl)-3-silahepta-(*E*)-1(*E*)-4-diene, 8α: ^1H NMR ($CDCl_3$) δ −0.03 [s, 9H, $Si(CH_3)_3$], 1.00 [s, 9H, $C(CH_3)_3$], 5.65 (m, 1H, Cl_2SiCH=), 6.19 (m, 1H, =CH-t-Bu), J_{AB} = 18.5 Hz), 6.80 [s, 1H, =CH-(Ph)], 7.30 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ −0.10 [$Si(CH_3)_3$], 29.10 [$C(CH_3)_3$], 35.70 [$C(CH_3)_3$], 117.70 (C^4), 127.60 and 128.30 (2CH aromat), 129.20 (CH aromat), 137.20 (C_q aromat), 141.00 (C^1), 164.67 (C^2), 166.00 (C^5); ^{29}Si NMR ($CDCl_3$) δ −6.63 [$Si(CH_3)_3$], −1.37 ($SiCl_2$); MS (70 eV) m/z 356 (4, M^+), 283 (53, $M^+ - 15$), 191 (35), 73 (100), 57 (30).

1,1-Dichloro-2,3-dimethyl-4-neopentyl-4-phenyl-1-silacyclobut-2-ene, 4b: ^1H NMR ($CDCl_3$) δ 0.90 [s, 9H, $C(CH_3)_3$], 2.00 (s, 3H, CH_3), 2.17 (m, 2H, CH_2), 2.21 (s, 3H, CH_3), 7.33 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 15.40 and 18.24 (CH_3), 29.72 [$C(CH_3)_3$], 32.37 [$C(CH_3)_3$], 42.94 (CH_2), 60.39 (C^4), 126.63 and 128.05 (2CH aromat), 131.81 (CH aromat), 138.19 (C_q aromat), 149.84 (C^3), 162.91 (C^2); ^{29}Si NMR ($CDCl_3$) δ 13.36 ($SiCl_2$); MS (70 eV) m/z 313 (100, $M^+ + 1$), 277 (62), 257 (23), 242 (20), 228 (13), 157 (25). Anal. Calcd (found) for $C_{16}H_{22}Cl_2Si$ (313.35): C, 61.33 (61.69); H, 7.08 (7.09); Cl, 22.63; Si, 8.96 (8.71).

1,1-Dichloro-4-neopentyl-4-phenyl-2,3-bis(trimethylsilyl)-1-silacyclobut-2-ene, 5b: ^1H NMR ($CDCl_3$) δ 0.22 and 0.38 [s, 9H, $Si(CH_3)_3$], 0.93 [s, 9H, $C(CH_3)_3$], 2.10 (m, 2H, CH_2); 7.39 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 0.74 and 1.70 [$Si(CH_3)_3$], 29.68 [$C(CH_3)_3$], 32.61 [$C(CH_3)_3$], 41.71 (CH_2), 58.67 (C^4), 127.50 (CH aromat), 128.60 and 129.00 (2CH aromat), 137.90 (C_q aromat), 143.80 (C^3), 168.20 (C^2); ^{29}Si NMR ($CDCl_3$) δ −12.68 and −11.87 [$Si(CH_3)_3$], −6.18 ($SiCl_2$); MS (70 eV) m/z 431 (100, $M^+ + 1$), 395 (13), 375 (8), 361 (5). Anal. Calcd (found) for $C_{20}H_{39}Cl_2Si_3$ (429.66): C, 55.91 (56.23); H, 7.98 (7.84); Cl, 16.50; Si, 19.61 (19.92).

1,1-Dichloro-4-neopentyl-2,3,4-triphenyl-1-silacyclobut-2-ene, 6b: ^1H NMR ($CDCl_3$) δ 1.13 [s, 9H, $C(CH_3)_3$], 2.23 (m, 2H, CH_2), 7.36 (m, 15H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 29.89 [$C(CH_3)_3$], 32.64 [$C(CH_3)_3$], 43.41 (CH_2), 67.00 (C^4), 126.04 and 126.71 (CH aromat), 127.33, 127.26, 128.21, 128.81, 130.11, and 131.42 (2CH aromat), 132.08 (CH aromat), 137.26, 138.84, and 139.49 (C_q aromat), 140.01 (C^3), 154.84 (C^2); ^{29}Si NMR ($CDCl_3$) δ 10.34 ($SiCl_2$); MS (70 eV) m/z 437 (100, $M^+ + 1$), 402 (5), 379 (23), 367 (12), 365 (12). Anal. Calcd (found) for $C_{26}H_{26}Cl_2Si$ (437.49): C, 70.38 (69.99); H, 5.99 (5.78); Cl, 16.21; Si, 6.42 (6.51).

1,1-Dichloro-3-methyl-4-neopentyl-4-phenyl-2-(trimethylsilyl)-1-silacyclobut-2-ene, 7b: ^1H NMR ($CDCl_3$) δ 0.37 [s, 9H, $Si(CH_3)_3$], 0.87 [s, 9H, $C(CH_3)_3$], 1.46 (s, 3H, CH_3), 2.13 (m, 2H, CH_2), 7.30 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 1.70 [$Si(CH_3)_3$], 28.61 (CH_3), 29.67 [$C(CH_3)_3$], 32.60 [$C(CH_3)_3$], 41.70 (CH_2), 61.89 (C^4), 126.61 (CH aromat), 128.61 and 128.99 (2CH aromat), 137.85 (C_q aromat), 160.16 (C^3), 177.25 (C^2); ^{29}Si NMR ($CDCl_3$) δ −5.45 ($SiCl_2$), 8.30 [$Si(CH_3)_3$]; MS (70 eV) m/z 371 (12, $M^+ + 1$), 335 (78), 314 (25), 301 (9), 299 (10), 263 (42). Anal. Calcd (found) for $C_{18}H_{28}Cl_2Si_2$ (371.50): C, 58.20 (58.34); H, 7.60 (7.57); Cl, 19.10; Si, 15.12 (14.98).

1,1-Dichloro-4-neopentyl-3,4-diphenyl-2-(trimethylsilyl)-1-silacyclobut-2-ene, 8b: ^1H NMR ($CDCl_3$) δ 0.08 [s, 9H, $Si(CH_3)_3$], 1.06 [s, 9H, $C(CH_3)_3$], 2.26 (m, 2H, CH_2), 7.47 (m, 10H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 1.32 [$Si(CH_3)_3$], 29.93 [$C(CH_3)_3$], 32.56 [$C(CH_3)_3$], 43.48 (CH_2), 67.37 (C^4), 126.05 (CH aromat), 127.39, 128.09 and 128.74 (2CH aromat), 130.45 (CH aromat), 132.13 (2CH aromat), 139.88 and 143.16 (C_q aromat), 167.09 (C^3), 178.34 (C^2); ^{29}Si NMR ($CDCl_3$) δ −4.83 ($SiCl_2$), 14.29 [$Si(CH_3)_3$]; MS (70 eV) m/z 433 (20, $M^+ + 1$), 418 (19), 397 (199), 377 (62), 342 (46), 305 (54), 282 (21). Anal. Calcd (found) for $C_{23}H_{30}Cl_2Si_2$ (433.57): C, 63.72 (63.73); H, 6.97 (7.08); Cl, 16.35; Si, 12.96 (13.11).

1,1-Dichloro-3-methyl-4-neopentyl-2,4-diphenyl-1-silacyclobut-2-ene, 9b: ^1H NMR ($CDCl_3$) δ 0.85 [s, 9H, $C(CH_3)_3$], 1.33 (s, 3H, CH_3), 2.04 (m, 2H, CH_2), 7.30 (m, 10H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 24.78 (CH_3), 29.65 [$C(CH_3)_3$], 32.56 [$C(CH_3)_3$], 41.69 (CH_2), 69.17 (C^4), 127.42 (2CH aromat), 128.65 and 131.81 (4CH aromat), 137.81 ($2C_q$ aromat), 144.95 (C^3), 153.74 (C^2); ^{29}Si NMR ($CDCl_3$) δ 8.37 ($SiCl_2$); MS (70 eV) m/z 376 (97, $M^+ + 1$), 340 (12), 318 (23), 305 (33), 219 (23). Anal. Calcd (found) for $C_{21}H_{24}Cl_2Si$ (375.42): C, 61.19 (60.86); H, 6.44 (6.31); Cl, 18.89; Si, 7.48 (7.59).

4,4-Dichloro-2,7,7-trimethyl-5-phenyl-4-silaocta-(*E*)-2(*E*)-5-diene, 4β: ^1H NMR ($CDCl_3$) δ 0.83 [s, 9H, $C(CH_3)_3$], 1.26 and 1.42 (s, 3H, CH_3), (m, 5H, C_6H_5);[24] ^{13}C NMR ($CDCl_3$) δ 11.40 and 13.88 (CH_3), 30.67 [$C(CH_3)_3$], 41.12 [$C(CH_3)_3$], 126.28 (CH aromat), 127.12 and 129.34 (2CH aromat), 137.79 (C_q aromat), 138.26 (C^3), 141.31 (C^5), 149.98 (C^2), 165.21 (C^6); ^{29}Si NMR ($CDCl_3$) 8.43 ($SiCl_2$); MS (70 eV) m/z 313 (10, $M^+ + 1$), 277 (78), 257 (14), 157 (72).

3,3-Dichloro-6,6-dimethyl-4-phenyl-1,2-bis(trimethylsilyl)-3-silahepta-(*E*)-1(*E*)-4-diene,[25] 5β: ^1H NMR ($CDCl_3$) δ 0.08 and 0.20 [s, 9H, $Si(CH_3)_3$], 0.83 [s, 9H, $C(CH_3)_3$], 7.38 (m, 5H, C_6H_5);[24] ^{13}C NMR ($CDCl_3$) δ −0.02 and 1.10 [$Si(CH_3)_3$], 31.66 [$C(CH_3)_3$], 38.62 [$C(CH_3)_3$], 126.60 (2CH aromat), 127.80 (CH aromat), 129.30 (2CH aromat), 137.90 (C_q aromat), 141.80 (C^4), 143.40 (C^2), 157.40 (C^1), 183.60 (C^5); MS (70 eV) m/z 395 (11), 374 (8), 357 (7).

4,4-Dichloro-7,7-dimethyl-5-phenyl-3-(trimethylsilyl)-4-silaocta-(*E*)-2(*E*)-5-diene, 7β: ^1H NMR ($CDCl_3$) δ 0.21 [s, 9H, $Si(CH_3)_3$], 0.77 [s, 9H, $C(CH_3)_3$], 1.33 (s, 3H, CH_3), 7.30 (m, 5H, C_6H_5);[24] ^{13}C NMR ($CDCl_3$) δ −0.51 [$Si(CH_3)_3$], 29.43 (CH_3), 31.58 [$C(CH_3)_3$], 41.14 [$C(CH_3)_3$], 126.16 and 127.45 (2CH aromat), 128.22 (CH aromat), 141.77 (C_q aromat), 140.05 (C^5), 145.61 (C^3), 157.42 (C^2), 176.70 (C^6); ^{29}Si NMR ($CDCl_3$) δ 4.22 ($SiCl_2$), 17.26 [$Si(CH_3)_3$]; MS (70 eV) m/z 371 (83, $M^+ + 1$), 335 (19), 315 (44), 301 (12), 299 (17), 263 (63).

3,3-Dichloro-6,6-dimethyl-1,4-diphenyl-2-(trimethylsilyl)-3-silahepta-(*E*)-1(*E*)-4-diene, 8β: ^1H NMR ($CDCl_3$) δ 0.03 [s, 9H, $Si(CH_3)_3$], 0.89 [s, 9H, $C(CH_3)_3$], 7.12 (m, 10H, C_6H_5);[24] ^{13}C NMR ($CDCl_3$) δ −0.67 [$Si(CH_3)_3$], 30.95 [$C(CH_3)_3$], 31.59 [$C(CH_3)_3$], 126.60 (CH aromat), 127.72, 127.80, and 128.27 (2CH aromat), 129.47 (CH aromat), 132.08 (2CH aromat), 134.57 and 139.05 (C_q aromat), 140.09 (C^4), 151.93 (C^2), 157.35 (C^1), 160.95 (C^5); ^{29}Si NMR ($CDCl_3$) δ −10.29 [$Si(CH_3)_3$], −0.95 ($SiCl_2$); MS (70 eV) m/z 433 (9, $M^+ + 1$), 418 (100), 397 (42), 377 (5), 305 (3), 282 (5).

4,4-Dichloro-7,7-dimethyl-3,5-diphenyl-4-silaocta-(*E*)-2(*E*)-5-diene,[25] 9β: ^1H NMR ($CDCl_3$) δ 0.97 [s, 9H, $C(CH_3)_3$], 1.31 (s, 3H, CH_3), 7.41 (m, 10H, C_6H_5);[24] ^{13}C NMR ($CDCl_3$) δ 28.59 (CH_3), 31.59 [$C(CH_3)_3$], 41.13 [$C(CH_3)_3$], 126.61 and 128.21 (4CH aromat), 128.97 (2CH aromat), 138.74 ($2C_q$ aromat), 144.95 (C^2), 154.50 (C^3), 154.50 (C^4), 165.06 (C^5); MS (70 eV) m/z 376 (2, $M^+ + 1$), 341 (1), 305 (19), 285 (40), 219 (25).

(24) The olefin protons are hidden by the resonances of the phenyl group.

(25) The compound is formed only in traces; it cannot be detected in the ^{29}Si NMR spectrum of the product mixture.

2,3-Dimethyl-4-neopentyl-1,1-bis(trimethylsiloxy)-1-silacyclobut-2-ene, 4c: ^{1}H NMR ($CDCl_3$) δ 0.15 [s, 18H, OSi(CH_3)$_3$], 0.85 [s, 9H, C(CH_3)$_3$], 0.93 and 1.02 (s, 3H, CH_3), 1.50 (m, 2H, CH_2), 2.30 (m, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 1.92 and 2.22 [OSi(CH_3)$_3$], 19.13 and 21.16 (CH_3), 30.08 [C(CH_3)$_3$], 30.84 [C(CH$_3$)$_3$], 36.56 (C^4), 45.11 (CH_2), 132.06 (C^3), 140.02 (C^2); ^{29}Si NMR ($CDCl_3$) δ -40.44 (Si), 8.65 [OSi(CH$_3$)$_3$]; MS (70 eV) m/z 329 (16, M$^+$ - 15), 287 (100, M$^+$ - 57), 273 (8), 257 (72), 207 (51). Anal. Calcd (found) for $C_{16}H_{36}O_2Si_3$ (344.72): C, 55.75 (55.70); H, 10.53 (10.46); O, 24.44;[26] Si, 9.28 (9.34).

4-Neopentyl-1,1-bis(trimethylsiloxy)-2,3-bis(trimethylsilyl)-1-silacyclobut-2-ene,[27] 5c: MS (70 eV) m/z 460 (11, M$^+$), 445 (44, M$^+$ - 15), 403 (100, M$^+$ - 57), 387 (9, M$^+$ - 73), 315 (37), 233 (43), 205 (24).

4-Neopentyl-2,3-diphenyl-1,1-bis(trimethylsiloxy)-1-silacyclobut-2-ene, 6c: ^{1}H NMR ($CDCl_3$) δ 0.46 [s, 18H, OSi(CH_3)$_3$], 1.18 [s, 9H, C(CH_3)$_3$], 1.70 (m, 2H, CH_2), 3.00 (m, 1H, CH), 7.00 (m, 10H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 1.18 and 2.29 [OSi(CH_3)$_3$], 29.66 [C(CH_3)$_3$], 30.45 [C(CH$_3$)$_3$], 41.08 (C^4), 41.23 (CH_2), 128.22 (4CH aromat), 128.23 (2CH aromat), 128.38 (4CH aromat), 137.15 (2C$_q$ aromat), 146.07 (C^3), 156.35 (C^2); ^{29}Si NMR ($CDCl_3$) δ -53.34 (Si), 9.92 [OSi(CH$_3$)$_3$]; MS (70 eV) m/z 468 (36, M$^+$), 453 (36, M$^+$ - 15), 411 (44, M$^+$ - 57), 397 (8), 321 (15), 263 (19), 207 (100). Anal. Calcd (found) for $C_{26}H_{40}O_2Si_3$ (468.86): C, 66.61 (66.42); H, 8.60 (8.77); O, 6.82;[26] Si, 17.97 (18.00).

3-Methyl-4-neopentyl-1,1-bis(trimethylsiloxy)-2-(trimethylsilyl)-1-silacyclobut-2-ene, 7c: ^{1}H NMR ($CDCl_3$) δ 0.08 [s, 9H, Si(CH_3)$_3$], 0.11 [s, 18H, OSi(CH_3)$_3$], 0.85 [s, 9H, C(CH_3)$_3$], 0.93 (s, 3H, CH_3), 1.00 (m, 2H, CH_2), 1.92 (m, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 0.29 [Si(CH_3)$_3$], 1.99 and 2.09 [OSi(CH_3)$_3$], 22.64 (CH_3), 29.77 [C(CH_3)$_3$], 30.47 [C(CH$_3$)$_3$], 42.03 (CH_2), 47.03 (C^4), 147.35 (C^3), 173.13 (C^2); ^{29}Si NMR ($CDCl_3$) δ -53.16 (Si), -40.60 [Si(CH$_3$)$_3$], 7.99 [OSi(CH$_3$)$_3$]; MS (70 eV) m/z 402 (4, M$^+$), 387 (92, M$^+$ - 15), 345 (100, M$^+$ - 57), 272 (3), 207 (50). Anal. Calcd (found) for $C_{18}H_{42}O_2Si_4$ (402.88): C, 53.66 (53.70); H, 10.51 (10.52); O, 7.94;[26] Si, 27.89 (27.80).

4-Neopentyl-3-phenyl-1,1-bis(trimethylsiloxy)-2-(trimethylsilyl)-1-silacyclobut-2-ene, 8c: ^{1}H NMR ($CDCl_3$) δ -0.03 [s, 9H, Si(CH_3)$_3$], 0.09 [s, 18H, OSi(CH_3)$_3$], 0.81 [s, 9H, C(CH_3)$_3$], 1.38 (m, 2H, CH_2), 2.68 (m, 1H, CH), 7.23 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 0.53 [Si(CH_3)$_3$], 2.02 and 2.24 [OSi(CH_3)$_3$], 29.57 [C(CH_3)$_3$], 30.43 [C(CH$_3$)$_3$], 41.75 (CH_2), 44.75 (C^4), 127.54 (CH aromat), 127.80 and 127.91 (2CH aromat), 132.04 (C^3), 139.87 (C$_q$ aromat), 157.09 (C^2); ^{29}Si NMR ($CDCl_3$) δ -53.59 (Si), -43.01 [Si(CH$_3$)$_3$], -15.14 [OSi(CH$_3$)$_3$]; MS (70 eV) m/z 464 (4, M$^+$), 449 (65, M$^+$ - 15), 407 (49, M$^+$ - 57), 393 (6), 391 (7), 387 (6), 221 (10), 207 (5). Anal. Calcd (found) for $C_{23}H_{44}O_2Si_4$ (464.95): C, 59.42 (59.40); H, 9.54 (9.57); O, 6.88;[26] Si, 24.16 (24.26).

3-Methyl-4-neopentyl-2-phenyl-1,1-bis(trimethylsiloxy)-1-silacyclobut-2-ene, 9c: ^{1}H NMR ($CDCl_3$) δ 0.16 [s, 18H, OSi(CH_3)$_3$], 0.89 [s, 9H, C(CH_3)$_3$], 1.48 (m, 2H, CH_2), 1.7 (s, 3H, CH_3), 2.82 (m, 1H, CH), 7.16 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 0.74 and 0.92 [OSi(CH_3)$_3$], 13.86 (CH_3), 29.78 [C(CH_3)$_3$], 30.43 [C(CH$_3$)$_3$], 39.59 (C^4), 41.75 (CH_2), 128.28 (2CH aromat), 128.55 (CH aromat), 131.83 (2CH aromat), 136.75 (C$_q$ aromat), 142.67 (C^3), 156.89 (C^2); ^{29}Si NMR ($CDCl_3$) δ -58.61 (Si), 1.87 [OSi(CH$_3$)$_3$]; MS (70 eV) m/z 391 (70, M$^+$ - 15), 349 (49, M$^+$ - 57), 295 (17), 250 (100), 236 (47). Anal. Calcd (found) for $C_{21}H_{38}O_2Si_3$ (406.79): C, 62.01 (62.22); H, 9.42 (9.56); O, 7.86;[26] Si, 20.71 (20.65).

6,6-Dimethyl-1,2-diphenyl-3,3-bis(trimethylsiloxy)-3-silahepta-(*E*)-1(*E*)-4-diene, 6γ: ^{1}H NMR ($CDCl_3$) δ 0.35 [s, 18H, OSi(CH_3)$_3$], 0.98 [s, 9H, C(CH_3)$_3$], 5.58, 6.02, and 6.30 (m, 1H, CH olefin), 7.00 (m, 10H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 2.04 and 2.92 [OSi(CH_3)$_3$], 29.92 [C(CH_3)$_3$], 31.70 [C(CH$_3$)$_3$], 126.45 (4CH aromat), 127.16 (2CH aromat), 127.70 (4CH aromat), 135.65 (2C$_q$ aromat), 135.73 (C^4), 145.30 (C^1), 156.04 (C^5), 157.05 (C^2); ^{29}Si NMR ($CDCl_3$) δ -42.50 (Si), 14.18 [OSi(CH$_3$)$_3$].

7,7-Dimethyl-3,3-bis(trimethylsiloxy)-3-(trimethylsilyl)-4-silaocta-(*E*)-2(*E*)-5-diene,[28] 7γ: MS (70 eV) m/z 402 (3, M$^+$), 387 (100, M$^+$ - 15), 345 (45, M$^+$ - 57), 272 (7), 207 (37).

6,6-Dimethyl-1-phenyl-3,3-bis(trimethylsiloxy)-3-(trimethylsilyl)-3-silahepta-(*E*)-1(*E*)-4-diene, 8γ: ^{1}H NMR ($CDCl_3$) δ -0.80 [s, 9H, Si(CH_3)$_3$], 0.11 [s, 18H, OSi(CH_3)$_3$], 0.97 [s, 9H, C(CH_3)$_3$], 5.55, 6.12, and 6.75 (m, 1H, CH olefin), 7.23 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 0.08 [Si(CH_3)$_3$], 1.70 and 1.73 [OSi(CH_3)$_3$], 28.97 [C(CH_3)$_3$], 30.94 [C(CH$_3$)$_3$], 120.75 (C^4), 127.16 (CH aromat), 128.25 and 128.51 (2CH aromat), 132.04 (C^1), 139.87 (C$_q$ aromat), 160.17 (C^5), 167.18 (C^2); ^{29}Si NMR ($CDCl_3$) δ -42.34 (Si), -8.71 [Si(CH$_3$)$_3$], 7.96 [OSi(CH$_3$)$_3$]; MS (70 eV) m/z 464 (20, M$^+$), 449 (100, M$^+$ - 15), 407 (17, M$^+$ - 57), 393 (4), 391 (3), 207 (26).

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(26) The determination of oxygen in the presence of silicon is not possible.

(27) A very complex product mixture is obtained and the silacyclobutene **5c** could not be isolated. A compound was detetced by GC/MS analysis whose molecular composition could be that of **5c**.

(28) A compound was detected by GC/MS analysis whose molecular composition could be that of the ene-product **7γ**.