Silaheterocycles. 26.[1] Facile Synthesis of Silicon Dichloro Substituted 3-Vinyl-1-silacyclobutanes from Silene/Butadiene [2 + 2] Cycloaddition Reactions: Model Compounds for Vinylsilacyclobutane → Silacyclohexene Rearrangements

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The reaction between in situ formed 1,1-dichloro-2-neopentylsilene, $Cl_2Si{=}CHCH_2$-*t*-Bu (**1**), and 1,3-butadienes leads almost solely to the formation of monosilacyclobutanes (**2, 5, 6, 10, 14, 15, 16**). NMR spectroscopic investigations of the products prove the periselective addition of the silene unit to the dienes. The reaction does, however, not proceed stereospecifically: the neopentyl and vinyl groups on the carbon skeleton of the silacyclobutane give rise to *E*/*Z* isomerism. On thermolysis the *E* configured 3-vinylsilacyclobutanes undergo ring expansion to the [4 + 2] cycloadducts; the *Z* isomers undergo retro ene reactions involving the neopentyl and vinyl groups which lead to cleavage of the silacyclobutane rings and give allylvinylsilanes. Appropriate substituents of a cycloadduct (**14**) disfavor the retro ene reaction and lead to the unexpected formation of nearly only the Diels–Alder products. The results obtained from cycloaddition reactions of **1** characterized the silene to have a high polarity and a lower HOMO as compared to diorganosilenes: both properties lead us to suggest a stepwise, strongly dipolar reaction pathway in the formation of the silacyclobutanes. Zwitterionic species are involved in their thermolysis reactions leading to the [4 + 2] cycloadducts. The retro ene reaction proceeds via a different reaction pathway: this can be deduced from the ratios of isomers *before* and *after* thermolysis reactions.

Introduction

Four membered ring compounds containing silicon and carbon atoms such as monosilacyclobutanes, monosilacyclobutenes, and 1,3-disilacyclobutanes have been investigated in organosilicon research for several reasons. Theoreticians are interested in their structures;[2] their cleavage, e.g., by Lewis acids leads to carbosilanes substituted by organoelement groups[3] and their pyrolytic and photolytic degradation has been a source of silenes for many years.[4] First studies on pentacoordinated silicon anions in the gas phase have been carried out with silacyclobutanes,[5] and quite recently, it has been discussed that such intermediates participate in anionic ring opening polymerization reactions of silacyclobutanes[6] and silacyclobutenes[7] in solution. In the past years silicon- and carbon-containing four membered ring compounds have become useful for the synthesis of polycarbosilanes by thermolysis,[8] metathesis,[9] and transition metal catalyzed ring opening polymerization reactions[10] and for the application of these polymers as preceramics. For these purposes an easy, preferably one-step synthesis of such ring compounds is desired. Further transformations (e.g. dehalogenation, substitution, and coupling reactions) at the silicon atom require readily replaceable substituents, e.g., chlorine. Furthermore, the variation of substituents at the carbon skeleton of the cyclic compounds should be easily possible so that (i) correspondingly substituted polycarbosilanes are available by ROMP reactions[11] and (ii) the properties of polysiloxanes and silicones containing the Si—C—C—C skeleton can be modified easily.[12,13] If these substituents are functional groups, e.g., vinyl or phenyl,[14] then even more subsequent reactions are conceivable, e.g., polymerization or hydrosilylation of the vinyl group or cleavage of the phenyl group.

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(1) Part 25: Auner, N.; Heikenwälder, C.; Ziche, W. *Chem. Ber.* **1993**, *126*, 2177.

(2) Savin, A.; Flad, H.-J.; Flad, J.; Preuss, H.; von Schnering, H. G. *Angew. Chem.* **1992**, *104*, 185; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 185. Rempfer, B.; Pfafferott, G.; Oberhammer, H.; Auner, N.; Boggs, J. E. *Acta Chem. Scand.* **1988**, *A42*, 352.

(3) Auner, N.; Grobe, J. *Z. Anorg. Allg. Chem.* **1983**, *500*, 132.

(4) For recent reviews on silenes see: Raabe, G.; Michl, J. In *The chemistry of organic silicon compounds*; Patai, S., Rappoport, Z., Eds.; J. Wiley & Sons: New York, 1989; pp 1015. Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. For mechanisms of pyrolysis of 1,3-disilacyclobutane and derivatives see: Auner, N.; Davidson, I. M. T.; Ijadi-Maghsoodi, S.; Lawrence, F. T. *Organometallics* **1986**, *5*, 431.

(5) Sullivan, S. A.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1981**, *103*, 480. DePuy, C. H.; Damrauer, R.; Bowie, J. H.; Shelton, J. C. *Acc. Chem. Res.* **1987**, *20*, 127.

(6) Liao, C. X.; Weber, W. P. *Polym. Bull.* **1992**, *28*, 281.

(7) Theunig, M.; Weber, W. P. *Polym. Bull.* **1992**, *28*, 17.

(8) Nametkin, N. S.; Vdovin, V. M. *J. Polym. Sci. C* **1963**, 1043. Vdovin, V. M.; Pushchevaya, T. S.; Petrov, A. D. *Dokl. Akad. Nauk SSSR* **1961**, *141*, 843.

(9) Finkel'shtein, E. Sh.; Ushakov, N. V.; Portuykh; E. B. *J. Mol. Catal.* **1992**, *76*, 133.

(10) Weyenberg, D. R.; Lee, L. E. *J. Org. Chem.* **1965**, *30*, 2618. Makovetsky, K. L.; Finkel'shtein, E. Sh.; Ostrovskaya, I. Ya.; Portuykh, E. B.; Gorbacheva, L. I.; Golberg, A. I.; Ushakov, N. V.; Yampolsky, Y. P. *J. Mol. Catal.* **1992**, *76*, 107.

(11) Investigations on ROMP and anionic ring polymerization reactions are being conducted: Steinberger, U.; Auner, N. Unpublished results.

(12) Baney, R. H.; Bilfrien, C. J.; Burns, G. T.; Fiedler, L. D.; Lee, C. L. U.S. Pat. No. 5,049,611, 1991.

(13) For the synthesis of monosilacyclobutanes from $(Me_3SiO)_2$-$Si{=}CHCH_2$-*t*-Bu see ref 1.

(14) Auner, N.; Seidenschwarz, C.; Herdtweck, E.; Popkova, V.; Sewald, N.; Ziche, W. Manuscript in preparation.

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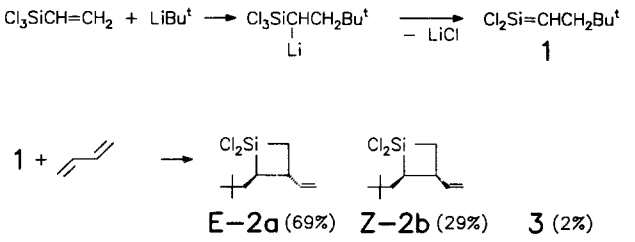
Scheme I



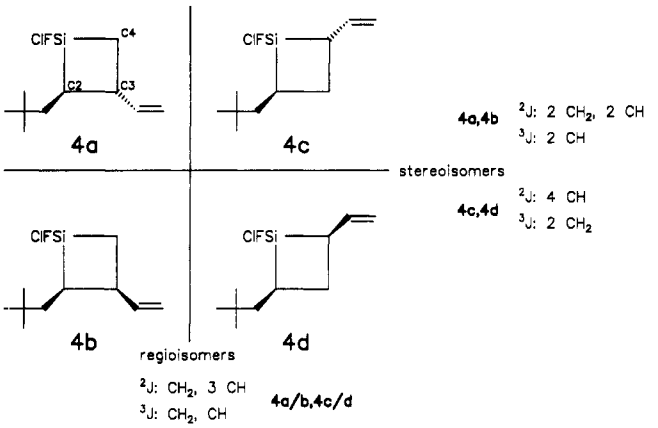
In earlier work we have reported on the simple one-step preparation of 1,1,3,3-tetrachloro-2,4-dineopentyl-1,3-disilacyclobutane[15,16] and of silicon dichloro substituted silacyclobutenes.[17] P. R. Jones described the one-step synthesis of silicon dimethyl substituted monosilacyclobutanes from $Me_2Si{=}CHCH_2$-*t*-Bu and butadiene.[18] In this paper we will describe the facile synthesis of silacyclobutanes from equimolar amounts of trichlorovinylsilane and Li-*t*-Bu and an excess of butadiene. The products contain a dichlorosilyl group and a vinyl group and are useful building blocks for the preparation of Si-containing new materials.[6–13] Furthermore they serve as model compounds for mechanistic studies, because they give silicon dichlorinated silacyclohexenes and catenated products upon thermolysis and silacyclopentenes are obtained by pyrolysis reactions.[19]

Results

Cycloaddition Reactions. The reaction of trichlorovinylsilane and *tert*-butyllithium initially leads to the α-lithiated adduct $Cl_3SiCH(Li)CH_2$-*t*-Bu[20] which eliminates LiCl to form dichloroneopentylsilene, $Cl_2Si{=}CHCH_2$-*t*-Bu (**1**), as an intermediate. This can be trapped by polar compounds such as methoxytrimethylsilane[21] or by dienes (e.g., 1,3-cyclohexadiene[21]); even dienes of only low dienophilic activity such as furans[16] and naphthalene[22] react with **1**. Furthermore, **1** can be trapped by aldehydes.[23] From the reactions with imines 2-silaazetidines are available,[24] while silacyclobutenes are obtained with diorganosubstituted acetylenes.[17]

When 1,3-butadiene is used as a trapping reagent for silene **1** the *E*/*Z* isomeric 2-neopentyl-3-vinyl-1-silacyclobutanes **2a** and **2b** are formed in about 80% yield. The product mixture contains ca. 2% of another compound **3** (Scheme I); NMR spectroscopy reveals the presence of the sequences CH_2—CH=CH—CH_2, CH_2—CH_2, and CH_2 but no sensible assignment is possible. The Diels–Alder and ene products are not formed.

Chart I



By distillation fractions are obtained that are highly enriched by either one of the two stereoisomeric [2 + 2] cycloadducts **2a** and **2b**, but a complete separation is not possible.[25] Attempted gas chromatography of the product mixture shows that partial decomposition or rearrangement takes place during the analysis (temperature of split injector is 200 °C), but the registration of mass spectra is possible. Thus GC/MS analysis to determine product ratios has to be conducted with the dimethoxy substituted derivatives (easily obtained by using methanol/triethylamine as the solvent and reagent for GC analysis). The NMR spectroscopic characterization of **2** has therefore to be carried out with the product mixture. An excellent tool to discriminate between [4 + 2] and [2 + 2] products is ^{29}Si NMR spectroscopy: while Diels–Alder adducts of **1** show chemical shifts at ca. 30 ppm[16,21,26] the resonances for [2 + 2] adducts are observed at 16–19 ppm.[21] The approximate signal intensities of the ^{29}Si{^{1}H} NMR spectra of **2a** and **2b** coincide with those obtained by GC techniques. A full NMR spectroscopic assignment for the stereoisomeric mixture of **2** is made by ^{1}H^{1}H-COSY and ^{1}H^{13}C correlation spectra. The stereochemistry of **2a** and **2b** was determined by a NOESY experiment (see Spectroscopic Section).

Another method for the determination of the regiochemistry utilizes fluorination of the silicon atom in **2**. The monofluorinated compounds **4a** and **4b** are quantitatively formed when **2** is reacted with antimony trifluoride in C_6D_6 as solvent. In contrast to the corresponding monofluorinated derivatives formed from the 2-methylbutadiene and 2,3-dimethylbutadiene cycloadducts of **1** (vide infra), the additional *E*/*Z* isomerism in **4** (F at silicon vs neopentyl and vinyl at the carbon skeleton) does not appear in the ^{13}C NMR spectrum.

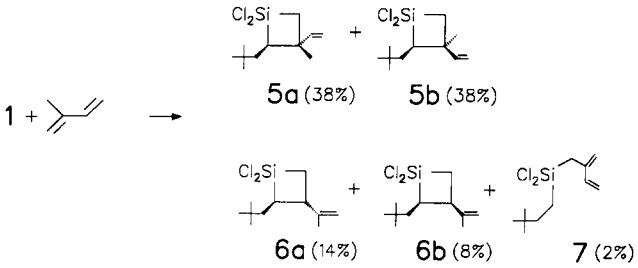
The important features in **4** are the ^2J and ^3J coupling constants between ^{19}F and ^{13}C nuclei in the proton decoupled ^{13}C NMR spectrum. Mixtures of *regioisomers* (e.g. **4a**/**4c**) should show a significantly different pattern as compared to *stereoisomers* (**4a**/**4b**) (Chart I).

The coupling constants $J(^{13}C\ ^{19}F)$ are taken from the ^{13}C DEPT NMR spectrum. Two resonances for methylene groups (C4) are found with ^2J = 12 Hz;[27] two signals with

(15) Auner, N.; Gleixner, R. *J. Organomet. Chem.* **1990**, *393*, 33.
(16) The reaction of equimolar amounts of $Cl_3SiCH{=}CH_2$ and Li-*t*-Bu in *THF* as solvent results in the nearly quantitative formation of $(Cl_2SiCHCH_2$-*t*-Bu$)_2$: Auner, N.; Wolff, A. *Chem. Ber.* **1993**, *126*, 575.
(17) Auner, N.; Seidenschwarz, C.; Herdtweck, E. *Angew. Chem.* **1991**, *103*, 1172; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1151. Synthesis of monosilacyclobutenes from $Cl_2Si{=}C(R)CH_2$-*t*-Bu (R = H, Ph) and $(Me_3SiO)_2Si{=}CHCH_2$-*t*-Bu: Auner, N.; Heikenwälder, C.; Wagner, C. Following article in this issue.
(18) Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* **1977**, *99*, 8447. Jones, P. R.; Lim, T. F. O.; Pierce, R. A. *Ibid.* **1980**, *102*, 4970. The yield of the [2 + 2] cycloadducts is comparatively low, and no further derivatization at the silicon atom is possible.
(19) Weingartner, A. Dissertation, München, **1992**.
(20) This species can be trapped by $Me_3SiOSO_2CF_3$ to give $Cl_3SiCH(SiMe_3)CH_2$-*t*-Bu.[16]
(21) Auner, N.; Seidenschwarz, C.; Sewald, N. *Organometallics* **1992**, *11*, 1137.
(22) Auner, N.; Seidenschwarz, C.; Sewald, N.; Herdtweck, E. *Angew. Chem.* **1991**, *103*, 425; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 444.
(23) Auner, N.; Seidenschwarz, C. *Z. Naturforsch.* **1990**, *45B*, 909.
(24) Auner, N.; Weingartner, A. W.; Bertrand, G. *Chem. Ber.* **1993**, *126*, 581.

(25) The best separation possible was **2a**:**2b** = 9:1 and 2:8 by spaltrohr distillation; attempts to improve the method are underway.
(26) Auner, N. *J. Organomet. Chem.* **1988**, *353*, 275.
(27) $^2J(^{13}C, ^{19}F)$ is usually found to be 8–12 Hz. ^3J depends on the dihedral angle α(F–Si–C2–C3); a rough calculation is possible by the equation $^3J = 5.5 \cos 2\alpha + 5.5$. (Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C-NMR-Spektroskopie*; Thieme Verlag: Stuttgart, 1984.) A determination of α in **4** is made with the molecular modeling program ALCHEMY II; it is found to be ca. 120–125°, this gives $^3J \sim 2.7$–3.6 Hz.

Scheme II



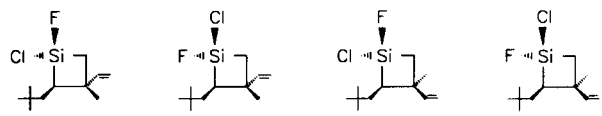
^3J = 2.5 and 1.8 Hz are assigned to methine groups (C3). The other two methine groups (C2) show ^2J coupling (9.4, 8.4 Hz).

These findings unequivocally prove the unique formation of **4a** and **4b** and thus also of **2a** and **2b** when it is assumed that fluorination does not change the constitution of the latter compounds. This can be ruled out, as the results obtained coincide with the conclusions drawn from the 2D NMR spectroscopic experiments. By these investigations we showed that the reaction of **1** with 1,3-butadiene proceeds regiospecifically.[28]

Modification of substituents on the skeleton atoms of the silacyclobutane ring should essentially be possible by two reaction routes: (i) variation of the substitution pattern at C2/C3 in the 1,3-butadienes used as trapping reagents for silene **1** leads to variation of substituents at the carbon atoms C3 and C4 of the resulting ring, while (ii) the introduction of organo groups at the α-C-atom of the silene unit should result in a disubstitution at C2 of the silacyclobutane.[29] But investigations on the cycloaddition behavior of the silenes $Cl_2Si{=}C(R)CH_2$-*t*-Bu (R = $SiMe_3$, Ph, $SiMe_2O$-*t*-Bu) show that with 1,3-butadienes the Diels–Alder and ene reactions predominate over the silacyclobutane formation. An alternative reaction pathway leading to C3 organo substituted silacyclobutane derivatives requires silenes of the formula $R^1R^2Si{=}CR^3(CR^4R^5$-*t*-Bu) and their [2 + 2] cycloaddition to 1,3-butadiene, but when organo substituents are introduced at the β-atom of the vinyl group of the silene precursor, silene formation and cycloaddition reactions are not observed. Vinylchlorosilanes of the general formula $R^1R^2ClSi{-}C(R^3){=}CR^4R^5$ preferentially undergo substitution of chlorine by a *tert*-butyl group when treated with *tert*-butyllithium when R^4 and R^5 are not a hydrogen atom. Competitive addition of the lithium organyl to the vinyl group also takes place but does not lead to silenes.[19,30]

Treating silene **1** with 2-methyl-1,3-butadiene gives five products that are obtained in an overall yield of 80%. In this case the *stereo*- and *regioisomeric*[31] [2 + 2] cycloadducts **5** and **6**[32] are formed along with a minor amount of the ene product **7** (Scheme II). Observations equivalent to the formation of the "false" isomers **6** have also been made by Wiberg with $Me_2Si{=}C(SiMe_3)_2$[33] and A. G. Brook with $(Me_3Si)_2Si{=}C(OSiMe_3)$ad;[34] these are silenes that yield mixtures of regioisomeric [4 + 2] cycloadducts (para/meta substitution) along with small amounts of the ene products. The ratio of para:meta methylated silacyclohexenes resembles that of catalyzed Diels–Alder reactions[35] like the [4 + 2] cycloaddition reactions of 2-methylbutadiene with methylacrylate (95:5) and acroleine (96:4).

Again, a full separation of the product mixture **5/6/7** failed but samples containing different ratios of the cycloadducts facilitate the gas chromatographic and NMR spectroscopic characterization of the product mixtures. ^{29}Si NMR spectroscopy again proves the sole formation of [2 + 2] cycloadducts. An extensive discussion of $^1H^1H$-COSY, NOESY, and $^1H^{13}C$ correlation spectra is found in the Spectroscopic Section. Elemental and GC/MS analyses[36] confirm the identity of **5–7**. Monofluorination of the product mixture leads to the well characterized derivatives **8a,b** (from **5a**) and **9a,b** (from **5b**).[37]



8a **8b** **9a** **9b**

The additional isomers due to the possible *E/Z* isomerism of the fluorine atom at silicon vs the vinyl and neopentyl groups at the four membered ring unit in **8** and **9** is not established by the observation of the double set of resonances in the ^{13}C NMR spectra. Only the methyl group at C3 displays two different NMR signals (ratio 1:1) for **8a,b** (**9a,b**). The same arguments that were used for the butadiene cycloadducts **4** also hold for **8** and **9** and confirm the results of the above mentioned NMR experiments.

Known silene cycloaddition reactions with 2,3-dimethyl-1,3-butadiene yield the [4 + 2] cycloadducts and in some cases the ene products.[38] Quite different from the dimethyl analogue ($Me_2Si{=}CHCH_2$-*t*-Bu), **1** and 2,3-dimethyl-1,3-butadiene give the *E/Z* isomeric cycloadducts **10a,b** along with a minor amount of the ene product **11** in an overall yield of about 75% (Scheme III).[39]

NMR spectroscopic investigations on **10** and **12**—the latter again obtained from **10** and SbF_3 in C_6D_6 solution—establish the presence of stereoisomers. An extensive discussion of the 2D NMR spectra of **10** is given in the NMR Spectroscopic Section. The reasoning that was used for the fluorinated derivatives **4**, **8**, and **9** is also applied to **12** and confirms the results derived from the other NMR spectroscopic data. Not altogether surprising,

(28) P. R. Jones also found regiospecificity in the reaction of $Me_2Si{=}CHCH_2$-*t*-Bu with 1,3-butadiene.[18] The methylation of **2** with methyl Grignard reagent leads to products identical with those obtained by Jones.

(29) Silenes of the type $Cl_2Si{=}C(R)CH_2$-*t*-Bu are formed from the precursor vinylchlorosilanes $Cl_3Si{-}C(R){=}CH_2$: (R = $SiMe_3$) Ziche, W.; Auner, N.; Behm, J. *Organometallics* **1992**, *11*, 2494. (R = Ph) Auner, N.; Wagner, C. Manuscript in preparation. (R = $SiMe_2$(O-*t*-Bu)) Ziche, W.; Auner, N.; Kiprof, P. *J. Am. Chem. Soc.* **1992**, *114*, 4910. Ziche, W.; Auner, N.; Behm, J. *Organometallics* **1992**, *11*, 3805.

(30) Schröder, H. Dissertation, Münster, 1991.

(31) Note that with isoprene two different forms of regioisomerism are possible. The silene's silicon atom, however, always attacks at the terminal carbon atoms of the 1,3-diene systems.

(32) For the isoprene frontier orbitals there are differences in the orbital coefficients at the terminal carbon atoms. Coefficients for the HOMO are given in: Alston, P. V.; Ottenbrite, R. M. *J. Org. Chem.* **1975**, *40*, 1111.

(33) Wiberg, N.; Preiner, G.; Schieda, O. *Chem. Ber.* **1986**, *119*, 3498.

(34) Brook, A. G.; Verspohl, K.; Ford, R. R.; Hesse, M.; Chatterton, W. J. *Organometallics* **1987**, *6*, 2128.

(35) Inukai, T.; Kojima, T. *J. Org. Chem.* **1971**, *36*, 924. Williamson, K. L.; Hsu, Y. L. *J. Am. Chem. Soc.* **1970**, *92*, 7385.

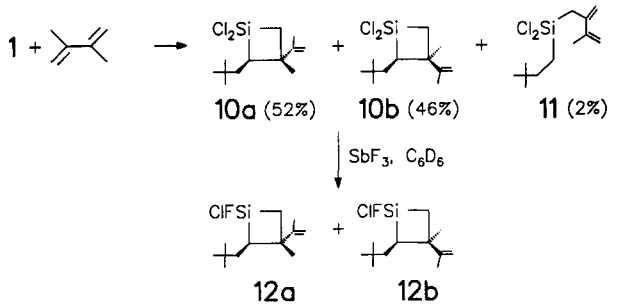
(36) The silicon dichloro substituted products again rearrange or partly decompose during GC analysis. Correct product ratios are obtained from the dimethoxy derivatives. The mass spectrometric fragmentation pattern of **5** and **6** also shows differences between [2 + 2] and [4 + 2] adducts; the latter show more intense fragment ions.

(37) The splitting of resonances by $J(^{13}C, ^{19}F)$ prohibit the concise assignment of the resonances belonging to the derivatives of **6**. These are therefore omitted in the spectroscopic discussion.

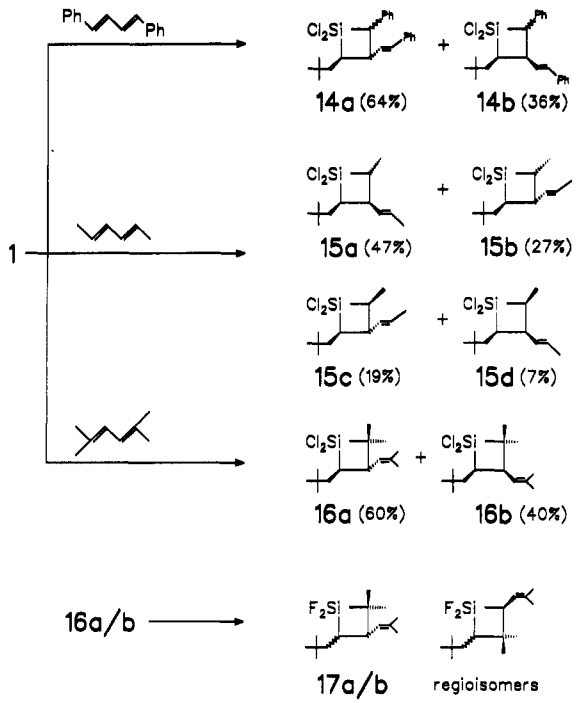
(38) Wiberg's $Me_2Si{=}C(SiMe_3)_2$:[33] 80% [4 + 2], 20% ene. Brook's $(Me_3Si)_2Si{=}C(OSiMe_3)$ad:[34] 60% [4 + 2], 40% ene. Jones' $Me_2Si{=}CHCH_2$-*t*-Bu:[18] 100% [4 + 2]. A [4 + 2] cycloadduct is obtained from $Me_2Si{=}CH_2$ and butadiene: Nametkin, N. S.; Guselnikov, L. E.; Ushakova, R. L.; Vdovin, V. M. *Dokl. Akad. Nauk SSSR* **1971**, *201*, 1365.

(39) The product ratios were again obtained by GC analysis of the dimethoxy derivatives; 2D NMR spectroscopic studies were carried out with the product mixture.

Scheme III



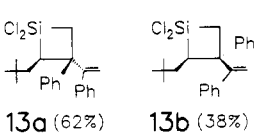
Scheme IV



considering the hitherto obtained results, the reaction forming **10a,b** proceeds regiospecifically.

Steric reasons are probably responsible for the low yield (3%) of the products **13a** and **13b** formed from **1** and 2,3-diphenyl-1,3-butadiene.

The isolated mixture of cycloadducts contains some byproducts, and fluorination is not successful. The identification is, however, possible by ^{13}C NMR spectroscopy, as enough data for comparison are already available from other cycloadducts of **1** (e.g. **2**, **5**, or **10**).



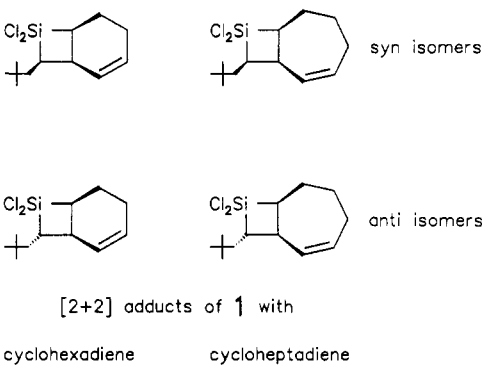
1,4 substituted butadienes react with **1** to form the stereoisomeric [2 + 2] cycloadducts (Scheme IV) as shown by the use of *all-trans*-2,5-hexadiene, 2,5-dimethyl-2,5-hexadiene, and 1,4-diphenyl-1,3-butadiene as trapping agents for **1**.[39]

The identity of the isomeric mixture of **15** was established by 2D NMR methods (see Spectroscopic Section). It is surprising that the neopentyl and vinyl groups in the major isomer **15a** are mutually *Z* to each other; obviously, this is due to additional steric hindrance by the methyl group at C4 as compared to [2 + 2] cycloadducts without substitution at this carbon atom.

While the attempted fluorination of **14** leads to decomposition, **16** is easily transformed to the difluoro derivatives **17**. The ^{19}F–^{13}C couplings in the $^{13}C\{^1H\}$ NMR spectrum prove that the two compounds **17a/b** are stereoisomers.[40]

Thermolysis Reactions. Investigations on vinylcyclobutanes[41] and bicyclic monosilacyclobutanes (from **1** and 1,3-cyclohexadiene[21]) showed that thermally and solvent induced rearrangements lead to silacyclohexenes via zwitterionic intermediates. In the latter case a retro ene reaction between peripheral groups on the SiC_3 moiety (neopentyl and vinyl) also yields catenated products.

Additional investigations on related compounds (e.g., the [2 + 2] adduct from **1** and 1,3-cycloheptadiene and 1,3,5-cycloheptatriene[42]) confirm the need to have the dichlorosilyl group in the γ-position to a C–C double bond within the bicyclic silaheterocycle for both intramolecular rearrangements; furthermore, the rearrangements require both *E and Z* isomerism of substituents at the carbon skeleton (α- and β-position to silicon) of the monosilacyclobutane subunit.[21]



As the cycloaddition reactions of silene **1** with butadienes give no Diels–Alder products, the C3 vinyl substituted [2 + 2] adducts seem to be simple monocyclic model compounds for extensive studies of the silacyclobutane → silacyclohexene/allylvinylsilane conversion. Furthermore thermolysis reactions[43] possibly are an easy synthetic route for the preparation of dichlorosilyl functionalized cyclohexenes.

When stereoisomeric mixtures of the [2 + 2] cycloadducts (**2, 5, 10, 14–16**) are sealed in glass tubes and subjected to temperatures up to 240 °C for 3–7 days (**14** was heated under vacuum to 500 °C for 6 h; detailed thermolysis conditions are given in the Experimental Section), in all cases the formal Diels–Alder adducts are formed (**18–20, 24, 26, 28**) along with the products resulting from retro ene reactions (**21–23, 25, 27, 29**).

The product mixtures cannot be separated by distillation but the unambigous identification of the compounds is possible by GC/MS analysis[36] and NMR spectroscopic investigations. The ^{29}Si NMR spectroscopic data allow a

(40) ^2J(C2–F) and ^2J(C4–F) range from 12.1 to 14.3 Hz; ^3J coupling is observed to the exocyclic methyl groups and to the methylene unit of the neopentyl group. Long range coupling proves the spatial proximity of the vinyl substituent to the fluorine nuclei. It is surprising that no ^3J coupling is observed for C3 because in fluorocyclobutane it is quite large with 19.1 Hz.

(41) The [2 + 2] cycloreversion reactions of donor–acceptor substituted vinylcyclobutanes and their stereospecificity are dependent on temperature, solvent polarity, and acid catalysis: Gruseck, U.; Heuschmann, M. *Chem. Ber.* **1990**, *123*, 1911.

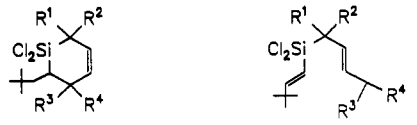
(42) Ziche, W.; Seidenschwarz, C.; Auner, N.; Herdtweck, E.; Sewald, N. *Angew. Chem.*, in press.

(43) The influence of solvents of different polarity on the isomerization behavior of the silacyclobutanes described in this paper is being investigated in our laboratories.

18 $R^1=R^2=H$ 21

19 $R^1=Me$, $R^2=H$ 22

20 $R^1=R^2=Me$ 23



24 $R^1=R^4=Ph$, $R^2=R^3=H$ 25

26 $R^1=R^4=Me$, $R^2=R^3=H$ 27

28 $R^1=R^2=R^3=R^4=Me$ 29

quick determination of the constitution of the products: The [4 + 2] cycloadducts of 1 exhibit chemical shifts of ca. 30 ppm (the resonances for [2 + 2] educts are found at 16–19 ppm), while the resonances of the retro ene products are detected at 10–15 ppm.

To elucidate the reaction pathway of the rearrangements, several thermolysis reactions of **2** (enriched by either the *E* or *Z* isomer[25]) were carried out and showed that the ratios of products (formal [4 + 2] adducts **18** vs retro ene products **21**) as determined by GC/MS and NMR spectroscopic methods clearly reflect the initial *E*:*Z* ratios of the [2 + 2] cycloadducts **2a**/**2b**. It follows that the silacyclohexenes originate from the *E* isomers while the *Z* isomers suffer retro ene reactions;[44] this coincides with the results obtained from the thermolysis reactions with the monosilacyclobutanes **5**, **10**, **15**, and **16**. From **2** two isomeric retro ene products are obtained; ^{1}H NMR shows the *E*/*Z* isomerism of the Si—CH=CH—*t*-Bu unit.

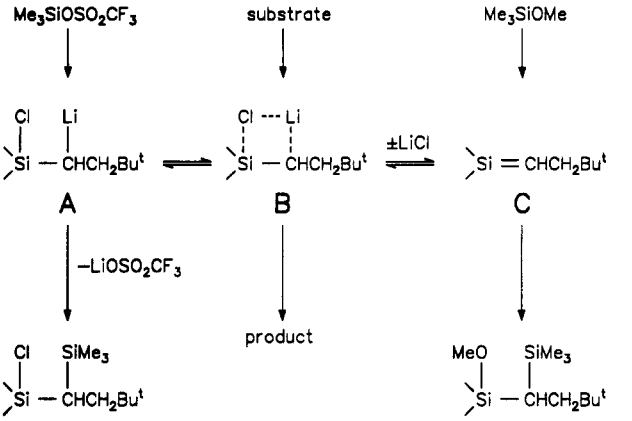
16 is surprisingly stable: When a sample of these [2 + 2] cycloadducts is treated for 5 days at 240 °C, ca. 80% of the distillable thermolysis products (yield 35%) is found to be **16**. The ^{29}Si NMR spectrum shows the formation of a silacyclohexene (**28**) and the retro ene product (**29**).

To complicate matters, the result from the thermolysis reaction of **14** does not comply with those mentioned above. Refluxing **14** for 6 h in vacuo results in the nearly quantitative formation of Diels–Alder products (**24**, 94%). ^{29}Si NMR spectroscopy reveals the presence of four isomers (ratio 79:5:5:5) along with a minor amount of two isomers of the retro ene product (**25**, 6%).

Such clearly proceeding reactions are not observed as soon as the dichloro substituents at silicon are no longer present. The corresponding dimethyl derivatives of **2**[45] give complex mixtures of decomposition products and polymeric material upon thermolysis[46] and the monofluorinated species **4**, **8**, **9**, and **12** yield only minor amounts of a ring opened product but are otherwise surprisingly stable (after 200 °C/14 days).[47]

In order to trap zwitterionic (or radical) intermediates formed by thermally induced carbon–carbon bond cleavage, the thermolysis reactions of **2** and **5** were also carried out in the presence of methyl iodide, chlorotrimethylsilane, thiophenol, and trimethylsilyl triflate, but the nature of the products did not change, only the yields were diminished by a few percent.

Scheme V



Discussion

(a) Silene Formation and Cycloaddition Reactions. Silene **1** is formed by addition of Li-*t*-Bu to the vinyl group of trichlorovinylsilane (utilization of the silicon β effect[49]) to give the α-lithiated species **A**. The reaction possibly proceeds via the LiCl/silene adduct **B**, and subsequent 1,2-elimination of lithium chloride yields the free silene **C**. In accord with this formulation we find reactions typical of organolithium compounds (**A**/$Me_3SiOSO_2CF_3$[20]) or of silenes (**C**/Me_3SiOMe) (Scheme V).

The temperature at which a cycloaddition reaction of a neopentylsilene takes place (detected by the elimination of LiCl) is dependent on the diene added as substrate. This implies that an interaction between the substrate and **A** or **B** or the substrate and **C** occurs somewhere along the reaction pathway depicted above. For the system $Cl_3SiCH{=}CH_2$/Li-*t*-Bu/$R_2C{=}NR'$ it was observed that the imine initiates and supports the salt elimination from the species **A**/**B**.[24,50] On the basis of the knowledge that silenes are stabilized by external donors,[15,51,52] we conclude that with carbon unsaturated compounds π-donor interactions instead of σ-donor complexes may be possible for the lithiated species (**D**) as well as for the silene itself (**E**).

(44) Only the *Z* isomers possess the necessary conformation to allow a thermally induced retro ene reaction leading to the catenated compounds via a six elctron transition state. Molecular models show the distance from H to $=CH_2$ to be more than 4 Å for the *E* isomer; the corresponding value is ca. 2 Å for the *Z* isomer.

(45) These are obtained by methylation of **2** with methyl Grignard reagent.

(46) This differs significantly from the isomerization behavior of silicon diorgano substituted (*Z*)-8-neopentyl-7-silabicyclo[4.2.0]-2-octenes which are converted into their *E* stereoisomers upon heating and very slowly even at room temperature.[21]

(47) Obviously, the fluoro substituent at silicon stabilizes the silacyclobutane. Pyrolysis of $F_2Si{-}CH_2CH_2CH_2$ to yield $F_2Si{=}CH_2$ requires significantly higher temperatures than are needed in the case of $Cl_2Si{=}CH_2$.[48]

(48) Auner, N.; Grobe, J. *J. Organomet. Chem.* **1981**, *222*, 33.

(49) Bassindale, A. R.; Taylor, P. G.Activating and directive effects of silicon. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, U.K., 1989.

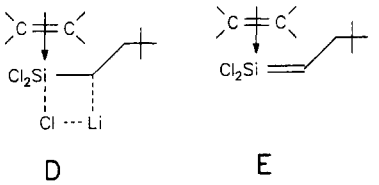
(50) Such interactions are also discussed for the stereoselective synthesis of 1-amino-2-neopentylsilenes: Auner, N.; Weingartner, A. W.; Herdtweck, E. *Z. Naturforsch.* **1993**, *48B*, 318.

(51) *Inter*molecular silene ← donor adducts: Wiberg, N.; Wagner, G.; Reber, G.; Riede, J.; Müller, G. *Organometallics* **1987**, *6*, 35. *Intra*molecular silene–donor interactions initiate following reactions involving the silene unit: see ref 29 (R = $SiMe_2O$-*t*-Bu). See also: Auner, N.; Penzenstadler, E.; Herdtweck, E. *Z. Naturforsch.* **1992**, *47B*, 1377.

(52) In accord with this is the experimental finding that the formation of **1** from $Cl_3SiCH{=}CH_2$/Li-*t*-Bu (i.e. the elimination of LiCl) *and* the following reaction to give 1,1,3,3-tetrachloro-2,4-dineopentyl-1,3-disilacyclobutane does not take place in the absence of a trapping substrate and with *n*-pentane as solvent.[53] Only when triethylamine is added to the reaction mixture is the dimerization of the silene the sole reaction pathway.[15]

(53) Auner, N. *Z. Anorg. Allg. Chem.* **1988**, *558*, 55.

This postulate is supported indirectly by the first example of an isolated alkene/alkylaluminum chloride π-complex.[54]



D E

The choice of reaction conditions for the system vinylchlorosilane/Li-*t*-Bu/substrate (e.g., temperatures, solvents[55]) determines *where* and *when* a reaction takes place on the silene forming pathway; consequently, both sides of the system (**A** or **C**) can be utilized for organosilicon synthesis. In spite of these mechanistical considerations, all results we obtained from cycloaddition reactions of vinylchlorosilane/Li-*t*-Bu mixtures and dienes in nonpolar solvents can be interpreted with no additional assumptions by considering the free silene **C** as the only reactive intermediate.

It is obvious that the exceptional behavior of 1 (=**C**) is caused by the influence of the two chlorine atoms bound to the silicon atom. An insight into the properties of 1 can be gained by considering ab initio calculations on substituted silenes.[56-58] It follows that π-donors (like chlorine[59]) enhance the polarity of the Si=C bond and the electrophilicity of the silicon atom as compared to the basic system $Me_2Si{=}CH_2$. Considering the participation of 1 in cycloaddition reactions, the fact that the energy of the π-orbital (HOMO) of 1 is lower than that in diorgano substituted silenes ($Me_2Si{=}CH_2$, -7.8 eV;[56] $F_2Si{=}CH_2$, -9.1 eV;[58] $Me_2Si{=}CHMe$, -7.5;[60] $Cl_2Si{=}CHMe$; -8.5 eV[60]) is most important.

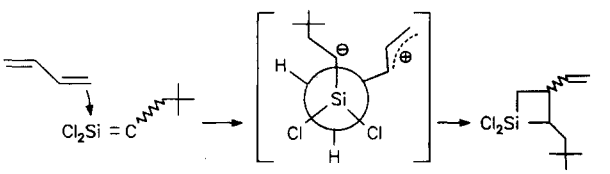
The route that a cycloaddition takes ([2 + 2] vs [4 + 2] reaction) depends on the energy difference ΔE ($HOMO_{dienophile} - LUMO_{diene}$).[61] The greater ΔE, the greater is the activation barrier for synchronous [4 + 2] reactions and the more probable is a reaction pathway leading to [2 + 2] cycloadducts.[62] For 1 ΔE is obviously large enough to cause the exclusive formation of [2 + 2] cycloadducts with 1,3-butadienes.

The [2 + 2] cycloaddition reactions of 1 most probably proceed stepwise via strongly asymmetric transition states. Calculations on the course of [2 + 2] cycloadditions of strongly polar π-systems show the interaction of just two centers of the reaction partners in the early stages of the reaction.[63-66] The regiochemistry is governed by the size of the eigenvector coefficients: in the case of 1 the electrophilic silicon atom interacts with the most nucleophilic atom of the diene system, i.e., one of the terminal carbon atoms of the 1,3-butadiene moiety.

An alternative description of the reactivity of 1 is that of a strong electrophile: ab initio calculations[56-58] also support this view. The relevant orbital for such a reaction is the LUMO of the electrophile;[63] for silenes having a p-donor at the silicon atom the orbital coefficients are increased at the silicon atom, thus rendering them more electrophilic than diorgano substituted silenes.

In both cases an intermediate zwitterion is formed that should be strongly favored by the chlorine substituents on the silicon atom. The allylic carbocation is mostly stabilized by conjugation with the C–C double bond, while the α carbanion is stabilized by hyperconjugation and inductive effects of the dichlorosilyl group.[69] In organic chemistry such species (1,4-dipoles) were either observed spectroscopically or trapped.[67,68] As 1 is synthesized from a chlorosilane and *tert*-butyllithium, these traps (e.g., alcohols) cannot be used. A spectroscopic observation has not been made.

Asymmetric transition states may also explain the formation of almost equal amounts of the *E*/*Z* isomers of the [2 + 2] cycloadducts, as rotation of the vinyl and neopentyl groups is still possible. That steric encumbrance is of minor influence is shown by the formation of substantial amounts of the *E* isomer. The final ring closure may be considered merely a following reaction of the crucial first step of electrophilic attack of the silene at the diene system.



(b) Thermolysis Reactions. The thermolysis reactions of **2**, **5**, **10**, **15**, and **16** will be discussed for the butadiene cycloadducts **2** because separation of the stereoisomers is possible in this case; for similar rearrangements see ref. 21.

The stereochemistry of the vinyl and neopentyl groups determines the rearrangement pathway. A retro ene reaction is possible for the *Z* isomer **2b**,[44] as shown. As a carbon–carbon bond of the silacyclobutane ring is involved in this conversion, the four membered ring is cleaved and the catenated compound **21** is formed. The *E* isomer **2a** is rearranged by a different route: the cleavage of the carbon carbon bond in the β position to the silicon

(54) Schnöckel, H.; Leimkühler, M.; Lotz, R.; Mattes, R. *Angew. Chem.* **1986**, *98*, 929; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 921. Dohmeier, C.; Mattes, R.; Schnöckel, H. *J. Chem. Soc., Chem. Commun.* **1990**, 358.

(55) **A** is stabilized by polar solvents like THF;[16] **C** is preferably formed in nonpolar solvents (e.g. pentane, toluene). With mixtures of $Cl_3SiCH{=}CH_2$/Li-*t*-Bu/imines products of imine/Li-*t*-Bu reactions are obtained at -78 °C. Addition of the imine to $Cl_3SiCH{=}CH_2$/Li-*t*-Bu mixtures at -20 °C yields 2-silaazetidines.[24]

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

(57) 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.

(58) Gordon, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 4352.

(59) Note that chlorine is a weaker π-donor than fluorine, which is used in most of the calculations as substituent: Schleyer, P. v. R.; Jemmis, E. D.; Spitznagel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6393.

(60) These values were supplied by Prof. Janoschek, University of Graz, and will be published elsewhere.

(61) Cycloadditions with inverse electron demand are assumed for silenes, as their π- and π^*-orbitals are generally 1–2.5 eV higher in energy than is the case for their alkene congeners.[56]

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

(63) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, Beccles, and Colchester, U.K., 1978.

(64) Inagaki, S.; Fukui, K. *J. Am. Chem. Soc.* **1975**, *97*, 7480.

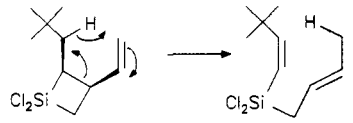
(65) Gordon, M. S.; Truong, T. N. *Chem. Phys. Lett.* **1975**, *8*, 361.

(66) A trans arrangement of the reaction partners is also calculated for the reaction of silene, $H_2Si{=}CH_2$, with H_2: Gordon, M. S.; Truong, T. N. *Chem. Phys. Lett.* **1987**, *142*, 110.

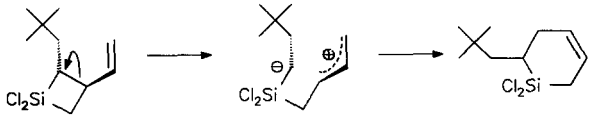
(67) Alcohols, ketones as traps: Brannock, K. C.; Bell, A.; Burpitt, R. D.; Kelly. C. A. *J. Org. Chem.* **1964**, *29*, 801. Gompper, R.; Elser, W; Müller, H.-J. *Angew. Chem.* **1967**, *79*, 473. Huisgen, R.; Schug, R.; Steiner, G. *Angew. Chem.* **1974**, *86*, 47, 48. Schug, R.; Huisgen, R. *J. Chem. Soc., Chem. Commun.* **1975**, 60. Hall, H. K., Jr.; Ykman, P. *J. Am. Chem. Soc.* **1975**, *97*, 800.

(68) Thiophenol was used: Kataoka, F.; Shimizu, N.; Nishida, S. *J. Am. Chem. Soc.* **1980**, *102*, 711.

(69) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.



atom is the reversal of the last step of the silacyclobutane formation reaction. The intermediate zwitterion then collapses to yield the formal [4 + 2] cycloadduct **18** of **1** with butadiene. The attempted trapping of the dipolar species was not successful.[70]

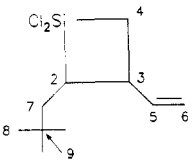


The results of the thermolysis reactions of **14** and **16** show that the steric and/or electronic influence of substituents on the carbon skeleton may not be neglected. It seems that as soon as the retro ene rearrangement is disfavored (in the case of **14**), the route to the [4 + 2] products is also possible for the *Z* configured [2 + 2] isomers. Steric hindrance may also explain the stability of **16** and the formation of 65% of polymers in the thermolysis reaction.

NMR Spectroscopic Section

The NMR spectroscopic results for the products **2**, **5**, **6**, **10**, and **15** are summarized and discussed in detail in the following section to give a comprehensive description of the reasoning that shows the regioselectivity of the [2 + 2] cycloaddition reactions of **1**. Further analytical data on these compounds are given in the Experimental Section.

The numbering scheme of the atoms is



The periselectivity of the reaction of 1,1-dichloro-2-neopentylsilene (**1**) with butadiene and substituted 1,3-butadienes can be proved by the multiplicity of the vinylic ^{13}C NMR signals of the cycloadducts (Tables III and IV).

Two *E*/*Z* isomeric [2 + 2] cycloadducts (**2a**, **2b**) are obtained in the case of 1,3-butadiene, both having one olefin CH group and one olefin CH_2 group, whereas the [4 + 2] cycloadduct should have two olefin CH groups (Table III).

Four isomers (**5a**, **5b**, **6a**, **6b**) are formed on reaction of 1,1-dichloro-2-neopentylsilene with isoprene (2-methyl-1,3-butadiene). A vinylic CH_2 group and a vinylic CH group are present in the two major isomers (**5a**, **5b**) while the two minor isomers (**6a**, **6b**) give rise to ^{13}C DEPT NMR signals corresponding to one olefin methylene group and one quaternary olefin carbon atom each, whereas only an olefin CH group and a quaternary olefin carbon atom would be expected for the two possible [4 + 2] regioisomers (Table III).

Furthermore, only one set of signals should be observed for the enantiomeric mixture of the [4 + 2] cycloadducts of 1,1-dichloro-2-neopentylsilene (**1**) to 1,3-butadiene or 2,3-dimethyl-1,3-butadiene, as different regioisomers (as with isoprene) are not possible.

With 2,3-dimethyl-1,3-butadiene, two isomers (**10a**, **10b**) are observed having a vinylic CH_2 group and a vinylic quaternary carbon atom each, while two quaternary olefin carbon atoms would be expected for the [4 + 2] cycloadduct (Table III).

In the case of 2,4-hexadiene, four cycloadducts (**15a**, **15b**, **15c**, **15d**) are detected with two olefin CH groups for each isomer. Both the [2 + 2] and [4 + 2] adducts should give rise to two signals representing a CH group each. Therefore, in this case no prediction on the periselectivity can be made according to the ^{13}C DEPT NMR spectra (Table IV).

These preliminary results indicate the exclusive formation of the [2 + 2] cycloadducts **2**, **5**, **6**, **10**, and **15**. Two-dimensional NMR techniques, double-quantum filtered H,H-COSY (DQF-COSY[71]), H,C-COSY,[72] and NOESY,[73] were used to assign the ^1H and ^{13}C NMR signals of the product mixtures and to establish both the regiochemistry and the stereochemistry of the cycloadducts.

The sample of the 1,3-butadiene adducts to **1** contained mainly two products (**2a**, **2b**) in a ratio of 70:30. The DQF-COSY of **2a**/**2b** are shown in Figures 1–3. The ^1H NMR assignment of **2** is given in Table I.

The product mixture of the reaction of **1** with isoprene contained mainly four compounds (**5a**, **5b**, **6a**, **6b**) in a ratio 38:38:15:9. The ^1H NMR assignment of **5**/**6** is given in Table I. The main components of the sample of the 2,3-dimethyl-1,3-butadiene adducts to **1** (**10a**, **10b**) were present in a ratio of 53:47. The ^1H NMR assignment of **10** is given in Table I. This sample also contained the ene product (**11**), which was identified by NMR spectroscopy. The sample of the 2,4-hexadiene cycloadducts contained four products (**15a**, **15b**, **15c**, **15d**) in a ratio 47:27:19:7. The ^1H NMR assignment of **15** is given in Table I.

The sequence CH_2—CH—CH(—CH_2)—CH=CH_2, which represents the skeleton C7—C2—C3(—C4)—C5=C6, is found in the DQF-COSY spectrum of both 1,3-butadiene cycloadducts (**2a**, **2b**) proving that the vinyl substituent is placed at C3 (Figures 1–3).

A similar spin system (CH_2—CH—CH—CH_2) is found for the two minor isoprene cycloadducts (**6a**, **6b**) in the DQF-COSY; whereas only three isolated spin systems CH_2—CH, CH_2, and CH=CH_2 (representing C7—C2, C4, and C5=C6) are registered for the two major isoprene cycloadducts (**5a**, **5b**).

The two 2,3-dimethyl-1,3-butadiene adducts (**10a**, **10b**) similarily give rise to three isolated signal patterns CH_2—CH, CH_2, and CH_3—C=CH_2 (C7—C2, C4, and CH_3—C5=C6). Consequently, both a vinyl and a methyl substituent are attached to C3 in these cases.

The alternative regiochemistry would require the sequences CH_2—CH—CH_2—CH—CH=CH_2 for 1,3-butadiene, CH_2—CH—CH_2—C(CH_3)—CH=CH_2 or CH_2—CH—CH_2—CH—C(CH_3)=CH_2 for isoprene, and CH_2—CH—CH_2—C(CH_3)—C(CH_3)=CH_2 for 2,3-dimethyl-1,3-butadiene. None of these spin patterns are found in the 2D NMR spectra of the product mixtures examined; this regiochemistry is also unlikely according to mechanistic

(70) A zwitterion could be trapped by thiophenol during the rearrangement reaction of another dichlorosilene [2 + 2] cycloadduct (see first reference in ref 29).

(71) (a) Marion, D.; Wuethrich, K. *Biochem. Biophys. Res. Commun.* **1983**, *113*, 967. (b) Rance, M.; Soerensen, O. W.; Bodenhausen, G.; Wagner, G.; Ernst, R. R.; Wuethrich, K. *Biochem. Biophys. Res. Commun.* **1983**, *117*, 479.

(72) (a) Bax, A. *J. Magn. Reson.* **1983**, *53*, 517. (b) Rutar, V. *J. Magn. Reson.* **1984**, *58*, 306.

(73) Bodenhausen, G.; Kogler, H.; Ernst, R. R. *J. Magn. Reson.* **1984**, *58*, 370.

Table I. ^{1}H NMR Assignment of the [2 + 2] Cycloadducts 2, 5, 6, and 10

	E isomers							
	2a		**5a**		**6a**		**10a**	
no.	δ[ppm]	*J*[Hz]	δ[ppm]	*J*[Hz]	δ[ppm]	*J*[Hz]	δ[ppm]	*J*[Hz]
2	1.69, m		2.01, dd	12.7/3.1	2.01, m		2.28, ddbr	12.8/2.8
3	2.14, m				2.24, m			
3Me			1.04, s				1.12, sbr	
4	1.35, dd	15.0/11.2	1.48, m[a]		1.38, dd	15.0/11.5	1.57, m	
	1.72, ddd	15.0/8.3/1.2	1.70, m[a]		1.67, m		1.80, m	
5	5.52, m		5.93, dd (ABX)					
5Me					1.52, s		1.59, dbr	0.9
6	4.81, m		4.83, dd (ABX)		4.63, m		4.62, m	
	4.82, m		4.91, dd (ABX)		4.66, m		4.66, sbr	
7/7′	1.25, m		1.12, dd	13.0/3.1	1.31, dd	13.9/3.2	1.28, dd	13.2/2.8
	1.49, m		1.50, dd	13.0/12.7	1.57, m		1.56, dd	13.2/12.8
8	0.83, s		0.88, s		0.87, s		0.87, s	
	Z isomers							
	2b		**5b**		**6b**		**10b**	
no.	δ[ppm]	*J*[Hz]	δ[ppm]	*J*[Hz]	δ[ppm]	*J*[Hz]	δ[ppm]	*J*[Hz]
2	2.18, m		1.86, ddm	13.0/3.1	2.19, m		1.92, ddq	12.6/2.4/1.0
3	2.94, ddddbr	10.3/10.3/10.3/2.5			2.77, m			
3Me			1.04, s				1.26, sbr	
4	1.48, ddd	16.0/2.3/1.0	1.52, m[a]		1.66, m		1.54, d	16.2
	1.85, ddd	16.0/10.3/0.9	1.80, m[a]		1.66, m		2.15, dd	16.2/1.0
5	5.74, m		5.58, dd (ABX)					
5Me					1.52, s		1.65, dbr	0.9
6	4.83, m		4.74, dd (ABX)		4.63, m		4.74, sbr	
	4.88, m		4.75, dd (ABX)		4.82, m		4.82, m	
7/7′	1.15, dd	14.0/3.8	1.06, dd	13.0/3.1	1.14, dd	13.9/2.4	1.17, dd	13.7/2.4
	1.44, dd	14.0/12.2	1.51, dd	13.0/13.0	1.50, m		1.53, dd	13.7/12.6
8	0.82, s		0.87, s		0.83, s		0.82, s	

[a] Assignment uncertain.

Table II. ^{1}H NMR Assignment of the Hexadiene [2 + 2] Cycloadducts 15

	15a 2*R*,3*R*,4*R*/2*S*,3*S*,4*S*		**15b** 2*R*,3*S*,4*R*/2*S*,3*R*,4*S*		**15c** 2*R*,3*S*,4*S*/2*S*,3*R*,4*R*		**15d** 2*R*,3*R*,4*S*/2*S*,3*S*,4*R*	
no.	δ[ppm]	*J*[Hz]	δ[ppm]	*J*[Hz]	δ[ppm]	*J*[Hz]	δ[ppm]	*J*[Hz]
2	2.39, dddd	12.0/10.6/3.6/1.5	2.03, m		1.65, m		2.20, m	
3	2.67, ddd	10.6/8.6/4.8	2.52, m		1.80, m		3.22, m	
4	1.93, ddq	4.8/1.5/7.5	2.27, m		2.20, m		1.70, m	
4Me	1.23, d	7.5	1.00, d	7.4	1.12, d	7.4	1.10, d	7.4
5	5.23–5.48, m		5.23–5.48, m		5.23–5.48, m		5.23–5.48, m	
6	5.23–5.48, m		5.23–5.48, m		5.23–5.48, m		5.23–5.48, m	
6Me	1.70, d		1.70, d		1.70, d		1.70, d	
7	1.27, dd	14.2/3.6	1.33, m		1.24, m		1.37, m	
	1.52, dd	14.2/12.0	1.56, m		1.52, m		1.47, m	
8	0.90, s		0.90, s		0.90, s		0.90, s	

evidence: Only electrophilic attack of the silicon atom to the terminus of the conjugated system creates a stabilized zwitterion. Therefore, the cycloaddition of symmetrically substituted 1,3-butadienes to 2,2-dichloro-1-neopentylsilene 1 proceeds with complete peri- and regioselectivity.

One of the geminal protons at C4 of the major isoprene adducts (**5a**, **5b**) and of the 2,3-dimethyl-1,3-butadiene adducts (**10a**, **10b**) shows a correlation to a methyl group, which is therefore supposed to be attached to C3. The second pair of methyl groups in the 2,3-dimethyl-1,3-butadiene adducts (**10a**, **10b**) resonating at lower field is shown to be placed at C5 according to crosspeaks between these methyl groups and olefin protons in the DQF-COSY.

There is spectroscopic evidence that the four products of the reaction of 2,4-hexadiene with 1 are the four possible *Z*/*E* isomers (**15a**, **15b**, **15c**, **15d**), regarding the stereochemistry of the ring skeleton. *Z*/*E* isomerism at the vinyl substituent should exert only little influence on the chemical environment of the silacyclobutane ring. In two isomers (**15a**, 47%; **15c**, 7%) the full spin pattern CH_2—CH—CH(CH=CH—CH_3)—CH—CH_3, representing C7—C2—C3(C5=C6—CH_3)—C4—CH_3, is found, while for the other isomeric pair only the patterns CH_2—CH—CH(CH=CH—CH_3) and CH—CH_3, i.e. C7—C2—C3(C5=C6—CH_3) and C4—CH_3, appear in the DQF-COSY spectrum. However, no correlation is found between the protons at C4 and olefin protons, as should be expected for the [4 + 2] cycloadducts. It can be assumed that all four products are the diastereoisomeric [2 + 2] adducts between 2,4-hexadiene and 1 with the vinyl group being placed at C3.

The protons and carbon atoms of all compounds were assigned by a combination of DQF-COSY and H,C-COSY data. The complete assignment is listed in Tables I and II (^{1}H NMR) and III and IV (^{13}C NMR). In some cases signals could not be assigned unambiguously to certain isomers; this is, however, irrelevant to structure determination.

The relative stereochemistry of the compounds was determined by evaluation of the intensities of characteristic NOESY crosspeaks. Considering the ratio of the diastereoisomeric 1,3-butadiene adducts (major isomer:minor isomer) to be 70:30, the absolute NOE ratio $2^{major}/3^{major}$: $2^{minor}/3^{minor}$ is 0.8, which means that protons 2 and 3 are

Table III. ^{13}C NMR Assignment of the [2 + 2] Cycloadducts 2, 5, 6, and 10

	E isomers							
	2a		**5a**		**6a**		**10a**	
no.	δ[ppm]		δ[ppm]		δ[ppm]		δ[ppm]	
2	45.08	CH	47.38	CH	42.21	CH	45.45	CH
3	39.54	CH	40.67[a]	C	42.25	CH	42.48	*C*
3Me			22.48	CH_3			23.79	CH_3
4	30.44	CH_2	38.30[a]	CH_2	29.94	CH_2	38.20	CH_2
5	141.22	CH	142.65	CH	145.68	*C*	152.14	*C*
5Me					19.38	CH_3	19.20	CH_3
6	113.44	CH_2	112.43	CH_2	110.00	CH_2	108.78	CH_2
7	42.79	CH_2	39.30	CH_2	43.19	CH_2	40.14	CH_2
8	29.77	CH_3	29.58	CH_3	29.57	CH_3	29.82	CH_3
9	30.63	*C*	30.23[a]	*C*	30.51[a]	C	30.65	C
	Z isomers							
	2b		**5b**		**6b**		**10b**	
no.	δ[ppm]		δ[ppm]		δ[ppm]		δ[ppm]	
2	42.67	CH	50.51	CH	41.16	CH	50.56	CH
3	38.44	CH	39.67[a]	C	39.77	CH	43.48	C·
3Me			28.82	CH_3			32.00	CH_3
4	30.52	CH_2	37.90[a]	CH_2	28.59	CH_2	37.39	CH_2
5	139.13	CH	147.52	CH	144.20	C	147.87	C
5Me					22.44	CH_3	22.27	CH_3
6	115.42	CH_2	109.45	CH_2	112.77	CH_2	112.77	CH_2
7	40.91	CH_2	40.69	CH_2	38.14	CH_2	40.42	CH_2
8	29.79	CH_3	29.62	CH_3	29.54	CH_3	29.69	CH_3
9	30.63	C	30.23[b]	C	30.51[a]	C	30.55	C

[a] Assignment uncertain.

Table IV. ^{13}C NMR Assignment of the Hexadiene [2 + 2] Cycloadducts 15

	15a		**15b**		**15c**		**15d**	
no.	δ[ppm]		δ[ppm]		δ[ppm]		δ[ppm]	
2	39.19	CH	41.20	CH	41.95	CH	39.50	CH
3	46.56	CH	42.61	CH	47.49	CH	44.05	CH
4	39.41	CH	36.37	CH	35.81	CH	39.01	CH
4Me	14.66	CH_3	10.03	CH_3	10.12	CH_3	12.18	CH_3
5	131.37[a]	CH	129.66[a]	CH	133.15[a]	CH	128.70[a]	CH
6	125.83[a]	CH	126.59[a]	CH	125.33[a]	CH	128.23[a]	CH
6Me	17.91[a]	CH_3	18.02[a]	CH_3				
7	39.67	CH_2	42.34	CH_2	42.38	CH_2	40.27	CH_2
8	29.62	CH_3	29.62	CH_3	29.62	CH_3	29.62	CH_3
9	30.38[a]	C	30.44[a]	C	30.54[a]	C	30.47[a]	C

[a] Assignment uncertain.

closer in the minor isomer. Similarly, the absolute NOE ratio $3^{major}/7^{major}:3^{minor}/7^{minor}$ is about 4.0, indicating that protons 3 and 7 are closer in the major isomer. Therefore, the major isomer is the *E* isomer and the minor one is the *Z* isomer (Table V).

The *E* [2 + 2] cycloadducts of 1,3-cyclohexa-1,3-diene to 1,1-dichloro-2-neopentylsilene (**1**) were shown previously to be thermodynamically more stable than the corresponding *Z* isomers. The relative stereochemistry of one of the major isoprene cycloadducts (**5a**) was assigned by the presence of a NOE crosspeak between the methyl group placed at C3 and the proton at C2. Therefore, this isomer should have *Z* configuration, referring to the orientation of the neopentyl group and the vinyl group. No correlation is found between the corresponding protons of the other isomer.

Comparison of the shift values of the major *Z* isoprene adduct to the values found for both dimethylbutadiene adducts renders the stereochemical assignment of the latter compounds possible. The ratio *Z*:*E* in the 2,3-dimethyl-1,3-butadiene adducts and the major isomeric pair of the isoprene adducts is nearly 1, reflecting the similar steric demands of the methyl and vinyl groups.

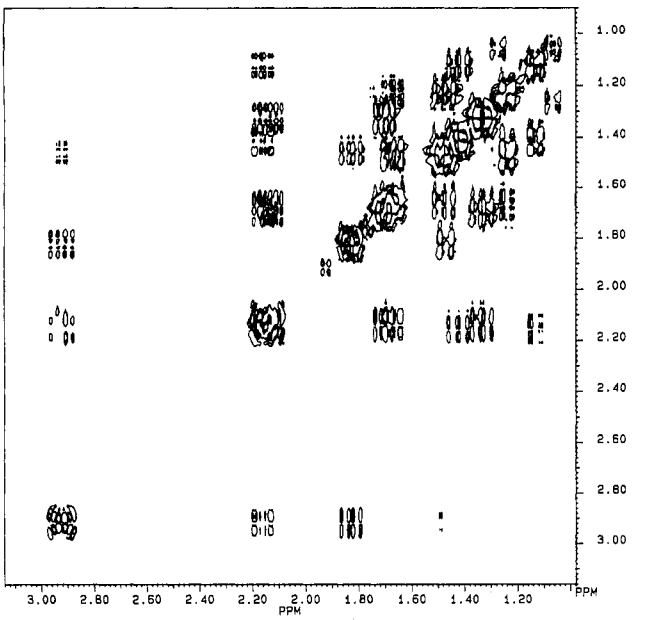


Figure 1. High-field crosspeak region of the DQF-COSY of the mixture **2a/2b**.

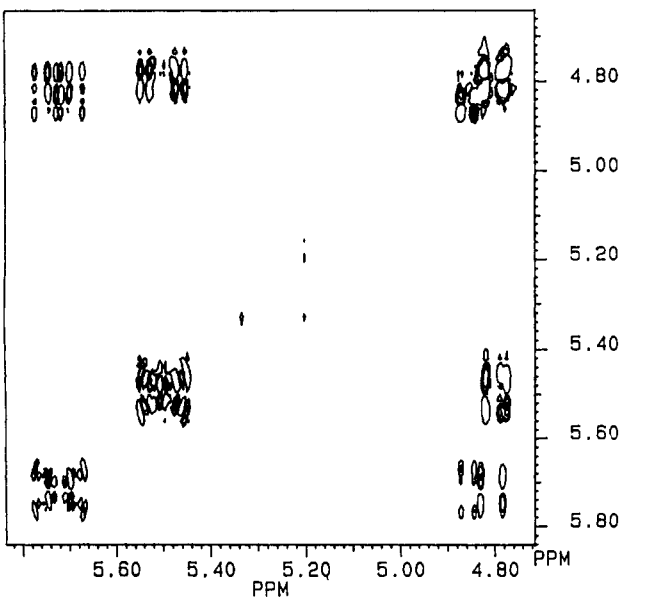


Figure 2. Low-field crosspeak region of the DQF-COSY of the mixture **2a/2b**.

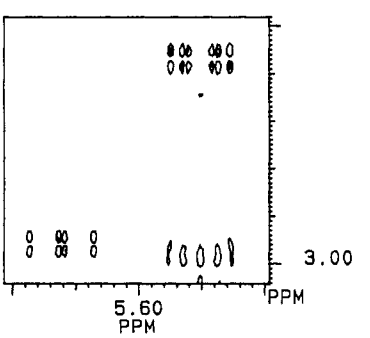


Figure 3. High-field/low-field crosspeak region of the DQF-COSY of the mixture **2a/2b**.

Comparison of the shift values of the butadiene cycloadducts (**2a, 2b**) with the values of the minor isomeric pair (**6a, 6b**) of the isoprene adducts, which have nearly the same ring substitution pattern, shows that again the more abundant one is the *E* isomer **6a** (product ratio 15:9).

Table V. Intensity Ratios of Characteristic NOE Crosspeaks (1,3-Butadiene Adducts 2, Major Isomer 2a:Minor Isomer 2b)

relation	product ratio	NOE ratio	
		relative	absolute
7/7′	2.33	2.44	1.05
2/3	2.33	1.85	0.80
3/7	2.33	9.10	3.90

In the case of compounds **15**, the NOESY crosspeaks indicate that the most abundant isomer (**15a**, 47%) is the 2*R*,3*R*,4*R*/2*S*,3*S*,4*S* enantiomeric pair regarding the stereochemistry at the ring skeleton. The proton attached to C3 in **15a** shows a strong NOE to the proton at C2, a very weak one to the proton at C4, and a strong one to the methyl group at C4. In the least abundant isomer (**15d**, 7%) the NOESY crosspeak between the protons at C3 and C2 is of equal intensity to the crosspeak between the protons at C3 and C4, showing that the stereochemistry of this compound is 2*R*,3*R*,4*S*/2*S*,3*S*,4*R*. Compound **15b** (27%) apparently is also a [2 + 2] adduct (NOE crosspeak between the protons at C3 and C4) having the configuration 2*R*,3*S*,4*R*/2*S*,3*R*,4*S* because of NOE crosspeaks between the protons at C3 and C7. NOE signals between the protons at C3 and C7 and between the proton at C3 and the methyl group at C4 (this also proves the silacyclobutane structure) in compound **15c** (19%) show that the stereochemistry of this enantiomeric pair is 2*R*,3*S*,4*S*/2*S*,3*R*,4*R*. Obviously, the steric hindrance between the neopentyl group and the methyl group at C4 exerts a stronger effect on the thermodynamic stability of the [2 + 2] cycloadducts **15** than the hindrance between the neopentyl group and the vinyl group at C3 does.

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. 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 the reactant gas. Routine NMR spectra were recorded on a JEOL JNM GX 270 (^{1}H,^{29}Si) and Bruker WP100SY (^{13}C and ^{13}C-DEPT). $CDCl_3$ and C_6D_6 were used as internal standards. Mass spectra were obtained with a Finnigan MAT 311A.

All 2D NMR experiments were done on a Bruker AM 360 spectrometer (^{1}H, 360 MHz; ^{13}C, 90 MHz) at 298 K in C_6D_6 or $CDCl_3$ (2,4-hexadiene cycloadducts). The samples were degassed in several freeze–thaw cycles and sealed. Chemical shifts are referenced internally to solvent peaks (C_6D_6(^{1}H) 7.15 ppm, (^{13}C) 128.00 ppm; $CDCl_3$ (^{1}H) 7.26 ppm, (^{13}C) 77.00 ppm). Quadrature detection in f_1 was achieved using the TPPI method (DQF-COSY, NOESY). A 180° composite ^{13}C pulse was used for ^{1}H decoupling in the H,C-COSY. NOESY spectra were edited with the Bruker UXNMR software on a Bruker X32 workstation.

NMR Parameters for the 1,3-Butadiene Cycloadducts 2. DQF-COSY. A total of 16 scans, preceded by 2 dummy scans, were recorded into 2K data blocks for each of the 512 t_1 values with a relaxation delay of 1.5 s and spectral widths of 2873.56 Hz. The data matrix was zero-filled to 4K*1K and apodized with shifted square sine bell window functions in both dimensions.

H,C-COSY. A total of 32 scans were recorded into 2K data blocks for each of the 400 t_1 values with a relaxation delay of 1.4 s and spectral widths of 14285.71 Hz in f_2 and 3599.70 Hz in f_1. The data matrix was zero-filled to 2K*1K and apodized with sine bell window functions in both dimensions.

NOESY. A total of 8 scans, preceded by 2 dummy scans, were recorded into 1K data blocks for each of the 256 t_1 values with a relaxation delay of 2.0 s and spectral widths of 2873.56 Hz. The average longitudinal relaxation time T_1 was determined in an inversion-recovery experiment. The mixing time was set to 1.5 s and was varied randomly in the range of ±30 ms to suppress zero quantum coherence. The data matrix was zero-filled to 2K*2K and apodized with shifted square sine bell window functions in both dimensions. After Fourier transformation and phase correction, a baseline correction in both dimensions was applied.

NMR Parameters for the 2-Methyl-1,3-butadiene Cycloadducts 5/6. DQF-COSY. A total of 16 scans, preceded by 2 dummy scans, were recorded into 2K data blocks for each of the 512 t_1 values with a relaxation delay of 1.4 s and spectral widths of 865.05 Hz. The data matrix was zero-filled to 2K*1K and apodized with shifted square sine bell window functions in both dimensions.

H,C-COSY. A total of 24 scans were recorded into 2K data blocks for each of the 512 t_1 values with a relaxation delay of 1.2 s and spectral widths of 14285.71 Hz in f_2 and 2873.56 Hz in f_1. The data matrix was zero-filled to 2K*1K and apodized with sine bell window functions in both dimensions.

NOESY. A total of 8 scans, preceded by 2 dummy scans, were recorded into 2K data blocks for each of the 512 t_1 values with a relaxation delay of 2.0 s and spectral widths of 2525.25 Hz. The average longitudinal relaxation time T_1 was determined in an inversion-recovery experiment. The mixing time was set to 1.5 s and was varied randomly in the range of ±30 ms to suppress zero quantum coherence. The data matrix was zero-filled to 4K*2K and apodized with shifted square sine bell window functions in both dimensions. After Fourier transformation and phase correction, a baseline correction in both dimensions was applied.

NMR Parameters for the 2,3-Dimethyl-1,3-butadiene Cycloadducts 10. DQF-COSY. A total of 16 scans, preceded by 2 dummy scans, were recorded into 2K data blocks for each of the 512 t_1 values with a relaxation delay of 1.9 s and spectral widths of 2525.25 Hz. The data matrix was zero-filled to 4K*2K and apodized with shifted square sine bell window functions in both dimensions.

H,C-COSY. A total of 32 scans were recorded into 2K data blocks for each of the 512 t_1 values with a relaxation delay of 2.0 s and spectral widths of 14285.71 Hz in f_2 and 2999.40 Hz in f_1. The data matrix was zero-filled to 4K*1K and apodized with sine bell window functions in both dimensions.

NMR Parameters for the 2,3-Hexadiene Cycloadducts 15. DQF-COSY. A total of 64 scans, preceded by 2 dummy scans, were recorded into 2K data blocks for each of the 512 t_1 values with a relaxation delay of 2.5 s and spectral widths of 1984.13 Hz. The data matrix was zero-filled to 2K*2K and apodized with shifted square sine bell window functions in both dimensions.

H,C-COSY. A total of 64 scans were recorded into 2K data blocks for each of the 256 t_1 values with a relaxation delay of 2.0 s and spectral widths of 13513.51 Hz in f_2 and 3067.48 Hz in f_1. The data matrix was zero-filled to 2K*1K and apodized with sine bell window functions in both dimensions.

NOESY. A total of 32 scans, preceded by 2 dummy scans, were recorded into 2K data blocks for each of the 256 t_1 values with a relaxation delay of 2.5 s and spectral widths of 2336.45 Hz. The average longitudinal relaxation time T_1 was determined in an inversion-recovery experiment. The mixing time was set to 0.8 s and was varied randomly in the range of ±25 ms to suppress zero quantum coherence. The data matrix was zero-filled to 4K*2K and apodized with shifted square sine bell window functions in both dimensions. After Fourier transformation and phase correction, a baseline correction in both dimensions was applied.

General Procedure for Silene Cycloaddition Reactions. A 9.60-g (60.0-mmol) sample of trichlorovinylsilane and a 3–10-fold excess of butadiene (exceptions: phenylated butadienes are used in equimolar amounts) are dissolved in 1000 mL of pentane, the solution is cooled to −78 °C. Then 35.3 mL of 1.7 M Li-*t*-Bu/pentane (60.0 mmol) is added dropwise. The reaction mixture is allowed to warm. The solution is freed from precipitated LiCl

by filtration. The solvent and excess diene are removed at ambient temperature and 10^{-2} mbar. The residue is distilled at 10^{-2} mbar. Only products containing no contamination by unknown substances as determined by GC and NMR spectroscopy were submitted to elemental analysis.

(E/Z)-1,1-Dichloro-2-neopentyl-3-vinyl-1-silacyclobutane (2). The ^1H and ^{13}C NMR spectra are discussed in the NMR Spectroscopic Section and are summarized in Tables I and III. Colorless liquid, 11.3 g (48 mmol, 80%) total yield. Anal. Calcd for $C_{10}H_{18}Cl_2Si$ (237.25): C, 50.63; H, 7.65. Found: C, 50.17, H, 7.55. *E* isomer: bp 40–41 °C/10^{-2} mbar; ^{29}Si NMR ($CDCl_3$) δ 20.57; MS(EI) *m/e* 236 (1.1%, M^+), 221 (3.2), 201 (3.5), 179 (12.1), 144 (3.9), 57 (100.0). *Z* isomer: bp 41–43 °C/10^{-2} mbar; ^{29}Si NMR ($CDCl_3$) δ 15.55; MS (EI) *m/e* 236 (1.1%, M^+), 221 (1.0), 201 (1.2), 179 (3.6), 144 (5.8), 57 (100.0).

Byproduct 3. ^{13}C NMR ($CDCl_3$): δ 121.98, 131.38, 131.84, 137.76 (=CH). ^{29}Si NMR ($CDCl_3$): δ 12.2. MS (EI): *m/e* 236 (3.0%, M^+), 210 (2.1), 201 (1.9), 183 (5.8), 117 (6.2), 57 (100.0).

1,1-Dichloro-3-methyl-2-neopentyl-3-vinyl-1-silacyclobutane (5) and 1,1-Dichloro-3-(1-methylethenyl)-2-neopentyl-1-silacyclobutane (6). The ^1H and ^{13}C NMR spectra are discussed in the NMR Spectroscopic Section and are summarized in Tables I and III. Colorless liquid, 12.8 g (48 mmol, 80%), bp 50 °C/10^{-2} mbar. ^{29}Si NMR ($CDCl_3$): δ 20.0 ((*E*)-**5**); 18.5 ((*Z*)-**5**). Anal. Calcd for $C_{11}H_{20}Cl_2Si$ (251.27): C, 52.58; H, 8.02. Found: C, 52.22; H, 8.01. **5**: MS (EI) *m/e* 250 (1.2%, M^+), 235 (3.7), 215 (6.6), 193 (11.9), 125 (10.4), 57 (100.0). **6**: MS (EI) *m/e* 250 (1.2%, M^+), 235 (3.7), 215 (6.6), 209 (6.7), 174 (1.4), 57 (100.0).

5,5-Dichloro-3,8,8-trimethyl-5-sila-1-nonene (7). ^{13}C NMR ($CDCl_3$): δ 15.72, 27.25 (Si—CH_2), 29.65 (C(CH_3)$_3$), 30.51 (*C*(CH_3)$_3$), 36.48 (*C*H_2—C(CH_3)$_3$), 115.85, 117.40 (=CH_2), 132.46, (=CH), 141.34 (=C). MS (EI) *m/e* 250 (1.2%, M^+), 223 (2.2), 215 (2.8), 193 (3.4), 125 (3.2), 57 (100.0).

1,1-Dichloro-3-(1-methylethenyl)-3-methyl-2-neopentyl-1-silacyclobutane (10). The ^1H and ^{13}C NMR spectra are discussed in the NMR Spectroscopic Section and are summarized in Tables I and III. Colorless liquid, 11.9 g (45.0 mmol, 75%), bp 70 °C/10^{-2} mbar. ^{29}Si NMR ($CDCl_3$): δ 19.4 (*E* isomer), 19.6 (*Z* isomer). MS (EI) *m/e* 264 (3.5%, M^+), 249 (2.8), 229 (3.1), 207 (2.9), 178 (3.8), 57 (100.0). Anal. Calcd for $C_{12}H_{22}Cl_2Si$ (265.30): C, 54.33; H, 8.36. Found: C, 53.95; H, 8.30.

5,5-Dichloro-2,3,8,8-tetramethyl-5-sila-1-nonene (11). ^{13}C NMR ($CDCl_3$): δ 15.22, 27.65 (Si—CH_2), 21.19 (CH_3), 29.84 (C(CH_3)$_3$), 31.01 (*C*(CH_3)$_3$), 36.41 (*C*H_2—C(CH_3)$_3$), 114.78, 114.80 (=CH_2); 141.20, 143.80 (=C). MS (EI) *m/e* 264 (10.4 %, M^+), 207 (8.6), 193 (2.9), 179 (6.6), 164 (6.4), 57 (100.0).

1,1-Dichloro-3-(1-phenylethenyl)-3-phenyl-2-neopentyl-1-silacyclobutane (13). Colorless liquid, 0.7 g (2.0 mmol, 3%), bp 250 °C/10^{-2} mbar. The low yield and the presence of side products prohibit the ^{29}Si and ^1H NMR spectroscopic characterization. ^{13}C NMR ($CDCl_3$): δ 28.6, 28.9 (C(*C*H_3)$_3$), 29.6 (*C*(CH_3)$_3$), 28.1, 29.4 (Si—*C*H—CH_2), 38.6, 40.1 (*C*H_2—C(CH_3)$_3$), 33.3 (Si—CH_2), 143.3, 144.2 (*C*(Ph)=CH_2), 107.2, 110.0 (C(Ph)=*C*H_2), 122.8, 126.1, 127.1, 128.1 (phenyl *C*H), 129.4 (phenyl *C*). MS (EI) *m/e* 338 (1.0%, M^+), 331 (1.1), 284 (2.5), 206 (94.7), 128 (65.3) 57 (100.0).

1,1-Dichloro-3-(2-phenylethenyl)-2-neopentyl-4-phenyl-1-silacyclobutane (14). Colorless liquid, 8.9 g (23 mmol, 38%), bp 250 °C/10^{-2} mbar. **14a**: ^1H NMR ($CDCl_3$) δ 0.97 (s, 9H, C(CH_3)$_3$), 1.25 (dd, *J* = 5.2, 12.0 Hz, 1H, CH_2), 1.48 (dd, *J* = 12.0, 12.1 Hz, 1H, CH_2), 1.58 (dd, br, *J* = 5.2, 12.2 Hz, 1H, Si—C*H*-CH_2), 2.72 (dd, br, *J* = 10.3, 12.2 Hz, 1H, Si—CH—C*H*), 3.30 (d, *J* = 12.2 Hz, 1H, Si—C*H*—Ph), 6.88 (dd, *J* = 10.3, 16.6 Hz, 1H, C*H*=CH—Ph), 7.34 (d, *J* = 16.6 Hz, 1H, CH=C*H*—Ph), 7.36–7.50 (m, 10H, Ph). **14b**: ^1H NMR ($CDCl_3$) δ 0.96 (s, 9H, C(CH_3)$_3$), 1.22 (dd, *J* = 5.6, 11.8 Hz, 1H, CH_2), 1.58 (dd, *J* = 10.5, 11.8 Hz, 1H, CH_2), 1.73 (dd, br, *J* = 5.6, 10.5 Hz, 1H, Si—C*H*—CH_2), 2.86 (ddd, *J* = 5.6, 6.8, 10.5 Hz, 1H, Si—CH—C*H*), 3.51 (d, *J* = 6.8 Hz, 1H, Si—C*H*—Ph), 6.71 (dd, *J* = 10.5, 16.1 Hz, 1H, C*H*=CH—Ph), 7.30 (d, *J* = 16.1 Hz, 1H, CH=C*H*—Ph), 7.36–7.50 (m, 10H, Ph). **14a** and **14b**: ^{13}C NMR ($CDCl_3$) δ 29.5 (C(CH_3)$_3$), 30.3 and 30.6 (*C*(CH_3)$_3$), 39.6 (*C*H_2—C(CH_3)$_3$), 40.0 and 40.9 (Si—CH-CH_2), 44.9 and 45.4 (Si—*C*H—Ph), 51.5 and 52.7 (Si—CH—*C*H), 129.2 and 129.5 (*C*H=CH—Ph), 131.3 and 132.8 (CH=*C*H—Ph), 126.3, 126.4, 126.8, 127.2, 127.4, 127.5, 128.5, and 128.6 (phenyl *C*H), 136.8, 137.3, and 138.6 (phenyl *C*); ^{29}Si NMR ($CDCl_3$) δ 14.60 (**14a**), 15.90 (**14b**); MS (EI) *m/e* 388 (1.02%, M^+), 331 (4.11), 206 (96.63), 177 (10.73), 128 (60.35), 91 (100.0). Anal. Calcd for $C_{22}H_{26}Cl_2Si$ (389.44): C, 67.85; H, 6.73. Found: C, 67.55; H, 6.77.

1,1-Dichloro-4-methyl-2-neopentyl-3-(1-propenyl)-1-silacyclobutane (15). The ^1H and ^{13}C NMR spectra are discussed in the NMR Spectroscopic Section and are summarized in Tables II and IV. ^{29}Si NMR ($CDCl_3$): δ 19.96, 17.61, 17.16, 17.01. MS (EI) *m/e* 264 (2.7%, M^+), 249 (3.6), 229 (4.7), 207 (5.3), 178 (3.4), 57 (100.0). Anal. Calcd for $C_{12}H_{22}Cl_2Si$ (265.30): C, 54.33; H, 8.36. Found: C, 54.04; H, 8.27.

1,1-Dichloro-3-(2,2-dimethylethenyl)-4,4-dimethyl-2-neopentyl-1-silacyclobutane (16). Colorless liquid, 7.0 g (24.0 mmol, 40%), bp 90 °C/10^{-2} mbar. ^1H NMR ($CDCl_3$): δ 0.88 (s, 18H), 0.89–0.98 (m, 6H), 1.32 (s, 6H), 1.62 (s, 6H), 1.75 (s, 6H), 1.77 (s, 6H), 2.39 (dd, *J* = 9.3, 9.4 Hz, 1H), 2.97 (tr, *J* = 11.2 Hz), 4.90 (d, *J* = 9.3 Hz), 5.18 (d, *J* = 11.2 Hz). ^{13}C NMR ($CDCl_3$): δ 18.44, 19.80, 23.32, 26.00, 26.07, 26.39, 28.71, 29.02 (CH_3), 29.51, 29.52 (C(*C*H_3)$_3$), 30.32, 30.40 (*C*(CH_3)$_3$), 39.54, 42.38 (CH_2), 36.59, 40.52 (Si—CH), 41.94, 41.96 (Si—C), 46.25, 46.73 (Si—CH—*C*H), 122.34, 122.97 (*C*H=C), 133.42, 135.02 (CH=*C*). ^{29}Si NMR ($CDCl_3$): δ 18.68; 21.27. MS (EI): *m/e* 292 (2.12%, M^+), 277 (0.50), 235 (4.23), 209 (3.23), 163 (9.95), 125 (6.70), 110 (21.99), 57 (100.0). Anal. Calcd for $C_{14}H_{26}Cl_2Si$ (293.36): C, 57.32; H, 8.93. Found: C, 57.01; H, 8.93.

Difluorination of the Cycloadducts 16. A 2.92-g sample of **16** (10.0 mmol) and 5.4 g of SbF_3 (30.0 mmol) are heated to 50 °C in *p*-xylene for 48 h. The solvent is removed in vacuo, and the product is extracted from the antimony salts with pentane. The product **17** is distilled. Just the ^{13}C and ^{29}Si NMR spectra were recorded, as they contained the coupling information needed as additional proof for regioselectivity in cycloaddition reactions of **1**.

1,1-Difluoro-3-(2,2-dimethylethenyl)-4,4-dimethyl-2-neopentyl-1-silacyclobutane (17). Colorless liquid, 2.47 g (9.5 mmol, 95%), bp 90 °C/10^{-2} mbar. ^{13}C NMR ($CDCl_3$): δ 18.31, 25.91, 26.05, 28.31 (=C(*C*H_3)$_2$), 24.77 (tr, *J* = 2.5 Hz), 22.46 (d, *J* = 1.1 Hz), 18.76 (d, *J* = 1.6 Hz), 17.20 (tr, *J* = 2.0 Hz, CH_3), 29.25 (C(*C*H_3)$_3$), 30.11, 30.05 (*C*(CH_3)$_3$), 42.21 (d, *J* = 2.2 Hz), 38.89 (d, *J* = 1.6 Hz, CH_2), 33.26 (dd, *J* = 10.5, 12.1 Hz), 37.22 (tr, *J* = 11.6 Hz, Si—CH), 40.50 (dd, *J* = 12.1, 13.8 Hz), 41.39 (dd, *J* = 13.2, 14.3 Hz, Si—C), 44.22, 44.05 (Si—CH—*C*H), 123.48 (dd, *J* = 8.0, 3.5 Hz), 122.26 (d, *J* = 1.7 Hz, *C*H=C), 135.00 (m), 133.20 (m) (CH=*C*). ^{29}Si NMR ($CDCl_3$): δ 25.31 (dd, *J* = 416.7, 422.1 Hz), 25.39 (dd, *J* = 358.5, 417.7 Hz). Anal. Calcd for $C_{14}H_{26}F_2Si$ (260.45): C, 64.57; H, 10.06. Found: C, 64.32; H, 10.00.

General Procedure for the Monofluorination of Silacyclobutanes. A 5.0-mmol sample of the dichloro cycloadducts and 2.7 g (15.0 mmol) of SbF_3 in 3.0 mL C_6D_6 are stirred for 48 h at room temperature. All material volatile at 10^{-2} mbar and the temperature given below is then condensed into an NMR tube. Just the ^{13}C and ^{29}Si NMR spectra were recorded, as they contained the coupling information needed as additional proof for regioselectivity in cycloaddition reactions of **1**.

1-Chloro-1-fluoro-2-neopentyl-3-vinyl-1-silacyclobutane (4). Colorless liquid, bp 20 °C/10^{-2} mbar. *E* isomer: ^{13}C NMR (C_6D_6) δ 36.52 (d, *J* = 9.4 Hz, Si—CH), 41.58 (d, *J* = 1.8 Hz, Si—CH—*C*H), 25.20 (d, *J* = 12.0 Hz, Si—CH_2), 42.19 (d, *J* = 1.9 Hz, *C*H_2—C(CH_3)$_3$), 30.02 (C(*C*H_3)$_3$), 29.23 (*C*(CH_3)$_3$), 112.91 (CH=*C*H_2), 142.00 and 142.25 (*C*H=CH_2); ^{29}Si NMR ($CDCl_3$) δ −21.66 (d, *J* = 394.2 Hz), −18.84 (d, *J* = 381.0 Hz). *Z* isomer: ^{13}C NMR (C_6D_6) δ 32.89 (d, *J* = 8.4 Hz, Si—CH), 39.01 (d, *J* = 2.5 Hz, Si—CH—*C*H), 25.67 (d, *J* = 12.1 Hz, Si—CH_2), 39.94 (d, *J* = 1.9 Hz, *C*H_2—C(CH_3)$_3$), 29.23 (C(*C*H_3)$_3$), 30.01 (*C*(CH_3)$_3$), 114.58 and 114.59 (CH=*C*H_2), 142.09 and 142.81 (*C*H=CH_2); ^{29}Si NMR ($CDCl_3$) δ −27.31 (d, *J* = 427.2 Hz), −21.44 (d, *J* = 370.2 Hz).

1-Chloro-1-fluoro-3-methyl-2-neopentyl-3-vinyl-1-silacyclobutane (8, 9). Colorless liquid, bp 30 °C/10^{-2} mbar. ^{13}C NMR

(C_6D_6): δ 46.94 (d, J = 9.5 Hz), 46.43 (d, J = 9.6 Hz, Si—CH), 35.95 (d, J = 1.0 Hz), 35.22 (d, J = 1.0 Hz, Si—CH—*C*), 33.27 (d, J = 11.4 Hz), 33.82 (d, J = 11.4 Hz, Si—CH_2); 39.43 (d, J = 2.0 Hz, *C*H_2—C(CH_3)$_3$), 29.14 (C(*C*H_3)$_3$), 29.66 (*C*(CH_3)$_3$), 27.95, 27.74, 28.25, 28.30 (CH_3), 111.88, 111.93 (CH=*C*H_2), 142.67, 142.72 (*C*H=CH_2). ^{29}Si NMR ($CDCl_3$): δ −16.60 (d, J = 383.4 Hz), −15.24 (d, J = 392.0 Hz), −17.20 (d, J = 397.4 Hz), −17.84 (d, J = 391.0 Hz).

1-Chloro-1-fluoro-3-(1-methylethenyl)-3-methyl-2-neopentyl-1-silacyclobutane (12). Colorless liquid, bp 50 °C/10^{-2} mbar. ^{13}C NMR (C_6D_6): δ 44.73 (d, J = 5.4 Hz, Si—CH), 31.51, 32.16 (Si—CH—*C*), 42.21 (d, J = 10.0 Hz, Si—CH_2), 38.77 (d, J = 1.5 Hz), 38.78 (d, J = 1.5 Hz, *C*H_2—C(CH_3)$_3$), 29.29 (C(*C*H_3)$_3$), 30.13 (*C*(CH_3)$_3$), 19.70, 19.72, 24.78, 24.98, 26.21, 26.23, 30.13, 30.15 (CH_3), 114.58, 115.27, 115.27, 116.15 (CH=*C*H_2), 141.57, 141.59 (*C*H=CH_2). ^{29}Si NMR ($CDCl_3$): δ −7.40 (d, J = 222.4 Hz), −2.20 (d, J = 232.8 Hz), −2.10 (d, J = 223.5 Hz), 4.30 (d, J = 228.4 Hz).

Thermolysis Reactions. Thermolysis of 14. A 3.9-g (10.0 mmol) sample of **14** is heated to reflux for 6 h at 10^{-2} mbar (ca. 500 °C). Distillation yielded 2.9 g (7.4 mmol, 74%) of products (**24, 25**): colorless liquid, bp 250 °C/10^{-2} mbar. The main isomer of **24** (79%) can be characterized without problems; for the other three isomers the ^{29}Si NMR resonances are given.

1,1-Dichloro-6-neopentyl-2,5-diphenyl-1-sila-3-cyclohexene (24). Main isomer: ^{1}H NMR (C_6D_6) δ 0.80 (s, 9H, C(C*H*$_3$)$_3$), 1.32 (dd, J = 14.0, 8.8 Hz, 1H, C*H*$_2$), 1.72 (dd, J = 14.0, 3.2 Hz, 1H, C*H*$_2$), 1.83 (m, 1H, Si—C*H*—CH_2), 2.56 (d, J = 11.3 Hz, 1H, Si—C*H*—Ph), 3.81 (dd, J = 5.3, 9.8 Hz, 1H, Si—CH—C*H*—Ph), 5.54 (dd, J = 11.3, 2.6 Hz, 1H, Si—CH—C*H*=CH), 5.73 (dd, J = 5.3, 2.6 Hz, 1H, Si—CH—CH=C*H*), 6.70–7.30 (m, Ph); ^{13}C NMR (C_6D_6) δ 29.0 (C(*C*H_3)$_3$), 32.0 (*C*(CH_3)$_3$), 35.7 (Si—*C*H—CH_2), 41.1 (*C*H_2—C(CH_3)$_3$), 72.8 and 84.2 (*C*H—Ph), 126.4 and 126.6 (*C*, phenyl), 128.0, 128.2, 128.6, and 128.8 (*C*H, phenyl), 130.1 and 134.8 (H*C*=*C*H); ^{29}Si NMR ($CDCl_3$) δ 22.5. Other isomers: ^{29}Si NMR ($CDCl_3$) δ 19.7, 21.2, 24.4.

5,5-Dichloro-8,8-dimethyl-1,4-diphenyl-5-sila-2,6-nonadiene (25). Characteristic signals for the Si—*C*H=*C*H—C(CH_3)$_3$ moiety are found in the ^{13}C NMR spectrum. The ^{29}Si NMR resonances also support the catenated structure. ^{13}C NMR (C_6D_6): δ 117.4, 117.5 (Si—*C*H=CH—C(CH_3)$_3$), 164.0, 164.1 (Si—CH=*C*H—C(CH_3)$_3$). ^{29}Si NMR ($CDCl_3$): δ 8.3, 8.5.

Thermolysis Reactions of 2, 5/6, 10, 15, and 16. The cycloadducts are sealed in a tube after degassing (three freeze, pump, thaw cycles) and heated up to 240 °C for several days. The products were distilled.

Thermolysis conditions for 2: 240 °C, 5 days; yield from 2.36 g of **2** (10.0 mmol), 1.96 g of **18** and **21** (8.3 mmol, 83%). Colorless liquid, bp 40 °C/10^{-2} mbar. Anal. Calcd for $C_{10}H_{18}Cl_2Si$ (237.25): C, 50.63; H, 7.65. Found: C, 50.44; H, 7.32.

1,1-Dichloro-6-neopentyl-1-sila-3-cyclohexene (18). ^{1}H NMR (C_6D_6): δ 0.95 (m, 3H), 0.98 (s, 9H), 1.56–1.63 (m, 2H), 1.77–1.85 (m, 2H), 4.08–4.20 (m, 1H), 5.61–5.74 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 19.02 (Si—*C*H_2), 22.56 (Si—*C*H), 29.59 (C(*C*H_3)$_3$), 31.60 (*C*(CH_3)$_3$), 32.62 (CH_2), 41.73 (*C*H_2—C(CH_3)$_3$), 123.11, 129.72 (H*C*=*C*H). ^{29}Si NMR ($CDCl_3$): δ 28.59.

5,5-Dichloro-8,8-dimethyl-5-sila-2,6-nonadiene (21). ^{1}H NMR (C_6D_6): δ 0.90 (AB, br, J = 4.09 Hz, 2H, Si—CH_2), 1.00 (s, 9H, C(CH_3)$_3$), 1.19 (s, br, 3H, CH_3), 4.19–4.23 (m, 1H, CH=), 5.36–5.38 (m, 1H, CH=), 5.45, 5.47 (d, J = 19.04 Hz, 1H, Si—C*H*=CH—C(CH_3)$_3$), 6.39, 6.41 (d, J = 19.04 Hz, 1H, Si—CH=C*H*—C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$): δ 12.93, 18.09 (CH_3), 21.88, 26.23 (Si—CH_2), 28.52 (C(*C*H_3)$_3$), 35.50 (*C*(CH_3)$_3$), 116.11, 120.83, 121.42, 125.89, 128.08 (CH=), 164.60, 164.70 (CH=*C*H—C(CH_3)$_3$). ^{29}Si NMR ($CDCl_3$): δ 13.44, 13.66.

Thermolysis conditions for 5/6: 240 °C, 5 days; yield from 2.50 g of **5/6** (10.0 mmol), 2.20 g of **19** and **22** (8.7 mmol, 87%). Ratio **19/22** = 50/50. Colorless liquid, bp 50 °C/10^{-2} mbar. Anal. Calcd for $C_{11}H_{20}Cl_2Si$ (251.27): C, 52.58; H, 8.02. Found: C, 52.47; H, 7.89.

1,1-Dichloro-3-methyl-6-neopentyl-1-sila-3-cyclohexene (18). ^{1}H NMR ($CDCl_3$): δ 0.82 (s, 9H, C(CH_3)$_3$), 1.08 (dd, J = 8.2, 2.4 Hz, 1H, C*H*$_2$—C(CH_3)$_3$), 1.43 (dd, J = 8.2, 8.3 Hz, 1H, C*H*$_2$—C(CH_3)$_3$), 1.45 (s, 3H, CH_3), 1.57 (d, J = 8.6 Hz, 1H, Si—C*H*$_2$), 1.59 (d, J = 8.6 Hz, 1H, Si—C*H*$_2$), 1.62 (m, 1H, Si—C*H*), 5.16 (d, J = 3.8 Hz, 1H, =C*H*), 2.23 (m, 2H, Si—CH—C*H*$_2$—CH=). ^{13}C NMR: 22.3 (Si—CH); 23.8 (Si—CH_2), 27.4 (CH_3), 29.6 (C(*C*H_3)$_3$), 31.7 (*C*(CH_3)$_3$), 32.4 (Si—CH—*C*H_2), 42.1 (*C*H_2—C(CH_3)$_3$), 123.9 (C=*C*H), 131.2 (*C*=CH). ^{29}Si NMR ($CDCl_3$): δ 29.30.

5,5-Dichloro-3,8,8-trimethyl-5-sila-2,6-nonadiene (22). ^{1}H NMR ($CDCl_3$): δ 0.84 (s, 9H, C(C*H*$_3$)$_3$), 1.46 (s, 3H, CH_3), 1.55 (d, J = 9.2 Hz, 1H, Si—C*H*$_2$), 1.62 (s, 3H, CH_3), 1.63 (d, J = 9.2 Hz, 1H, Si—C*H*$_2$), 4.82 (s, 1H, =C*H*—CH_3), 5.52 (d, J = 16.2 Hz, 1H, Si—C*H*), 6.42 (d, J = 16.2 Hz, 1H, Si—CH=C*H*). ^{13}C NMR ($CDCl_3$): δ 26.1, 26.2 (CH_3), 27.9 (Si—CH_2), 28.6 (C(*C*H_3)$_3$), 35.6 (*C*(CH_3)$_3$), 117.2, 120.7 (=CH), 128.6 (=C), 164.5 (=*C*H—C(CH_3)$_3$), 22.3 (Si—CH), 23.8, 27.4 (CH_3), 29.6, 31.7, 32.4 (Si—CH—*C*H_2), 42.1 (*C*H_2—C(CH_3)$_3$), 123.9 (C=*C*H), 131.2 (*C*=CH). ^{29}Si NMR ($CDCl_3$): δ 13.69.

Thermolysis conditions for 10: 200 °C, 5 days; yield from 2.64 g of **10** (10.0 mmol), 2.40 g of **20** and **23** (9.1 mmol, 91%). Colorless liquid, bp 70 °C/10^{-2} mbar. Anal. Calcd for $C_{12}H_{22}Cl_2Si$ (265.30): C, 54.33; H, 8.36. Found: C, 54.30; H, 8.34.

1,1-Dichloro-3,4-dimethyl-6-neopentyl-1-sila-3-cyclohexene (20). ^{1}H NMR ($CDCl_3$): δ 0.86 (s, 9H, C(C*H*$_3$)$_3$), 1.16 (dd, J = 12.0, 3.0 Hz, 1H, C*H*$_2$—C(CH_3)$_3$), 1.45 (dd, J = 12.0, 3.0 Hz, 1H, C*H*$_2$—C(CH_3)$_3$), 1.49 (s, 3H, C*H*$_3$), 1.59 (s, 3H, C*H*$_3$), 1.62 (d, J = 14.2 Hz, 1H, Si—C*H*$_2$), 1.65 (m, 1H, Si—C*H*), 1.86 (d, J = 14.2 Hz, 1H, Si—C*H*$_2$), 2.10 (d, J = 11 Hz, 2H, C*H*$_2$). ^{13}C NMR ($CDCl_3$): δ 21.33, 22.62 (CH_3), 23.31 (Si—CH), 25.97 (Si—CH_2), 29.61 (C(*C*H_3)$_3$), 31.46 (*C*(CH_3)$_3$), 39.49 (CH_2), 42.65 (*C*H_2—C(CH_3)$_3$), 122.99, 129.33 (C=C). ^{29}Si NMR ($CDCl_3$): δ 30.22.

5,5-Dichloro-2,3,8,8-tetramethyl-5-sila-2,6-nonadiene (23). ^{1}H NMR ($CDCl_3$): δ 0.90 (s, 9H, C(C*H*$_3$)$_3$), 1.52 (s, 3H, CH_3), 1.55 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.89 (d, J = 10.0 Hz, 1H, Si—C*H*$_2$), 2.04 (d, J = 10.0 Hz, Si—C*H*$_2$), 5.5 (d, J = 16.2 Hz, 1H, Si—C*H*=CH), 6.4 (d, J = 16.2 Hz, 1H, Si—CH=C*H*). ^{13}C NMR ($CDCl_3$): δ 20.68, 20.96, 21.49 (CH_3), 28.59 (C(*C*H_3)$_3$), 29.96 (Si—CH_2), 35.38 (*C*(CH_3)$_3$), 116.99 (Si—CH=CH), 120.0, 125.53 (C=C), 163.98 (Si—CH=*C*H). ^{29}Si NMR ($CDCl_3$): δ 13.93.

Thermolysis conditions for 15: 240 °C, 5 days; yield from 2.64 g of **10** (10.0 mmol), 2.20 g of **26** and **27** (8.3 mmol, 83%). Colorless liquid, bp 80 °C/10^{-2} mbar. Anal. Calcd for $C_{12}H_{22}Cl_2Si$ (265.30): C, 54.33; H, 8.36. Found: C, 54.24; H, 8.13.

1,1-Dichloro-6-neopentyl-2,5-dimethyl-1-sila-3-cyclohexene (26). ^{13}C NMR ($CDCl_3$): δ 14.00, 14.15 (Si—CH), 29.49 (C(*C*H_3)$_3$), 31.36 (*C*(CH_3)$_3$), 38.24, 38.87 (CH_3), 42.01 (*C*H_2—C(CH_3)$_3$), 47.37 (Si—CH—*C*H), 126.70, 132.51 (HC=CH). ^{29}Si NMR ($CDCl_3$): δ 31.29.

5,5-Dichloro-1,4,8,8-tetramethyl-5-sila-2,6-nonadiene (27). ^{13}C NMR ($CDCl_3$): δ 14.37 (Si—CH), 21.09 (CH_2), 26.02 (CH_3), 28.54 (C(*C*H_3)$_3$), 29.97 (CH_3), 35.52 (*C*(CH_3)$_3$), 114.91, 127.18, 133.02 (=CH), 165.06 (CH=*C*H—C(CH_3)$_3$). ^{29}Si NMR ($CDCl_3$): δ 15.19.

Thermolysis conditions for 16: 240 °C, 5 days; yield from 2.92 g of **16** (10.0 mmol), 1.02 g of **16, 28,** and **29** (3.5 mmol, 35%). Colorless liquid, bp 85 °C/10^{-2} mbar. Anal. Calcd for $C_{14}H_{26}Cl_2Si$ (293.36): C, 57.32; H, 8.93. Found: C, 57.22; H, 8.87.

1,1-Dichloro-6-neopentyl-2,2,5,5-tetramethyl-1-sila-3-cyclohexene (28). ^{29}Si NMR ($CDCl_3$): δ 30.33.

5,5-Dichloro-1,1,4,4,8,8-hexamethyl-5-sila-2,6-nonadiene (29). ^{29}Si NMR ($CDCl_3$): δ 13.90.

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