Organometallics **2002,** *21,* 2049−2054

Thermal Transformation of a 1,2-Disilacyclobutane to a Trisilacyclobutane†

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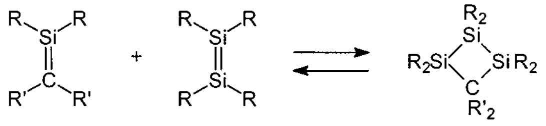
Received August 30, 2001

Thermolysis of 1,1,2,2-tetrakis(trimethylsilyl)dispiro[3,3′,4,4′-biadamantane-1,2-disilacyclobutane] (**6**) yields (75%) the stable 1,1,2,2,3,3-hexakis(trimethylsilyl)spiro[(4,4′-adamantane)-trisilacyclobutane] (**5**). The structure of **5** was determined by X-ray analysis. Thermolysis of **6** probably proceeds via the simultaneous formation of two transients, bis(trimethylsilyl)adamantylidenesilene (**7**) and tetrakis(trimethylsilyl)disilene (**11**), which then undergo cycloaddition to form **5**. Photolysis of **5** leads to a [2+2] cycloreversion reaction producing the silene **7** and the disilene **11**. This is the first demonstration that a silene and a disilene can be generated simultaneously from a single precursor.

Introduction

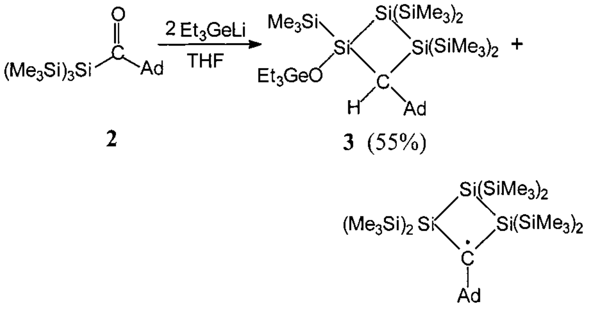
Exciting progress has been made in the field of multiply bonded silicon compounds in the past decades, in particular in revealing the rich chemistry of silenes[1] and disilenes.[2] Several stable compounds with C═Si[1] and Si═Si[2] double bonds have recently been isolated, but usually these compounds are formed as highly reactive intermediates. Unless they are sterically protected, both silenes and disilenes undergo very facile dimerization reactions or additions to other types of double bonds.[1,2] However, the reaction between a silene and a disilene, leading to the formation of a trisilacyclobutane **1** (eq 1), is still unknown, probably because it is difficult to produce these highly reactive species simultaneously at sufficiently high concentrations in the same reaction flask.



(1)

1

Interest in trisilacyclobutanes stems not only from their strained ring[3] but also from their potential fragmentation reactions, which can produce simultaneously silenes and disilenes (eq 1).[4] The first report on the preparation of a trisilacyclobutane derivative (i.e., **1**, R = CH_3, R′ = H), by Fritz and Gunert, indicated that this compound is unstable under ambient conditions.[5] Trisilacyclobutanimines with bulky *tert*-butyl groups attached to the silicon atoms and the vinylic carbon atoms of the ring were the first known family of stable trisilcyclobutanes.[6] In two earlier studies[7,8] we suggested that the trisilacyclobutanes **3** and **4** isolated in the reaction of acylsilane **2** with Et_3GeLi (eq 2) are formed via a reaction between a silene and a disilene of the type shown in eq 1. However, this suggestion was only tentative and could not be supported by other evidence.[7,8]



2

3 (55%)

4 (10%)

(2)

In this paper we report the preparation and the X-ray structure of a novel stable trisilacyclobutane, i.e., 1,1,2,2,3,3-hexakis(trimethylsilyl)spiro[(4,4′-adamantane)-

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† Dedicated to Professor Michael Voronkov, a pioneer in main group chemistry, on the occasion of his 80th birthday.

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[1] Müller, T.; Ziche, W.; Auner, N.; in *The Chemistry of Organic Silicon Compounds;* Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; Vol. 2, Chapter 16.

[2] (a) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231, and references therein. (b) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds;* Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 2001; Vol. 3, Chapter 5.

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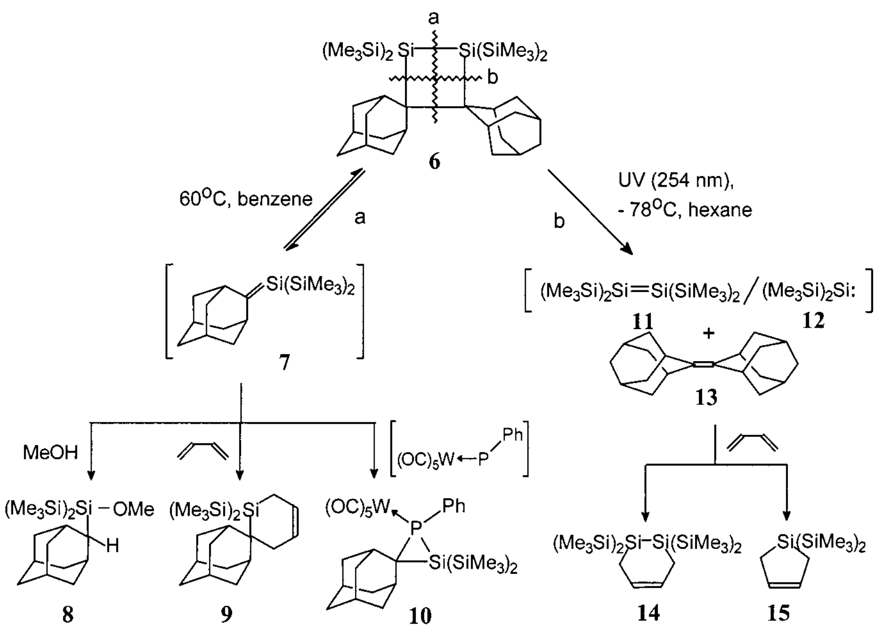
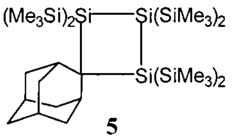
10.1021/om0107690 CCC: $22.00
Publication on Web 04/18/2002

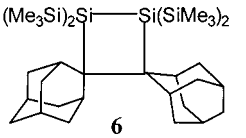
Scheme 1



trisilacyclobutane] (TSCB, **5**). **5** was synthesized by the solvent-free thermolysis of a 1,2-disilacyclobutane, i.e., 1,1,2,2-tetrakis(trimethylsilyl)dispiro[3,3′,4,4′-biadamantane-1,2-disilacyclobutane][9] (DSCB, **6**). We suggest that **5** is formed via a cycloaddition reaction of a silene and a disilene. We also report preliminary results which show that the photolysis of the novel **5** leads to its cleavage to a silene and a disilene.



5



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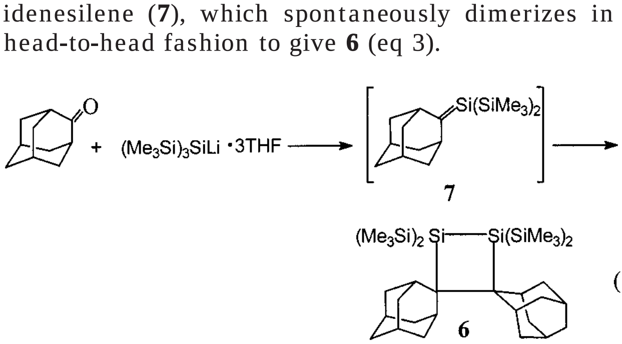
Results and Discussion

Synthesis of the Trisilacyclobutane (TSCB) 5. The disilacyclobutane (DSCB) **6** was synthesized previously by our group by the reaction of $(Me_3Si)_3SiLi\cdot 3THF$ with 2-adamantanone.[9] This reaction proceeds via the reactive intermediate bis(trimethylsilyl)adamantylidenesilene (**7**), which spontaneously dimerizes in a head-to-head fashion to give **6** (eq 3).



(3)

Earlier we showed[9,10] that **6**, which is stable under ambient conditions, can undergo cleavage along two pathways. In benzene at 60 °C (path a, Scheme 1) DSCB **6** exists in equilibrium with silene **7**. In the presence of trapping reagents, known to react with silenes, such as methanol or 1,3-butadiene, **7** forms the expected trapping products **8** and **9**, respectively.[9] In the presence of in situ generated complexed phosphinidene the phosphasilirane **10** was isolated (Scheme 1).[11] Thermal equilibrium with the corresponding silenes is known also for other 1,2-disilacyclobutanes with bulky substituents.[12] In contrast to thermolysis, photolysis of **6** in hexane at −78 °C (path b, Scheme 1) produces the tetrakis(trimethylsilyl)disilene **11** (which under further irradiation dissociates to the bis(trimethylsilyl)silylene **12**) and diadamantylidene **13**. In the presence of 1,3-butadiene the corresponding trapping products of **11** and **12**, i.e., **14** and **15** respectively, are formed (Scheme 1).[10]

Now we found that thermolysis of neat **6** at 150−180 °C (in a sealed degassed ampule) leads to the formation of a mixture of the novel trisilacyclobutane (TSCB) **5**, along with diadamantylidene **13** and polymer **16**, as shown in Scheme 2. After 3 h the transformation of **6** to products was essentially complete. A typical procedure is given in the Experimental Section. The thermolysis products could be easily separated by preparative gel permeation chromatography (GPC). The yield of the pure TSCB **5** is ca. 75%. Thermolysis of **6** in hydrocarbon solutions leads to a significantly lower yield of **5**.

The polymer **16**, which amounts to ca. 20% of the total weight of the reaction products, is formally the product of copolymerization of DSCB **6** and TSCB **5** in an approximate ratio of 2:1. In the ^1H and ^{13}C NMR spectra of polymer **16** only two groups of broad signals (belonging to the Me_3Si and adamantyl units), which are similar in their position to those of **6**, were observed. This indicates the presence of the $(Me_3Si)_2Si$ and adamantyl (Ad) units in the polymer. Taking into consideration that elemental analysis of the polymer showed

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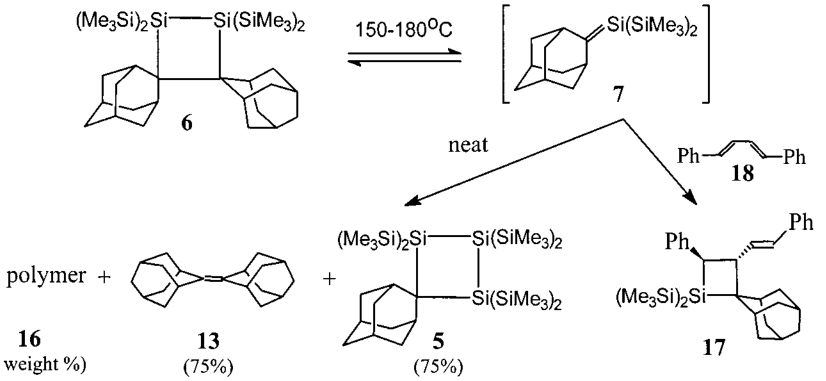
Scheme 2

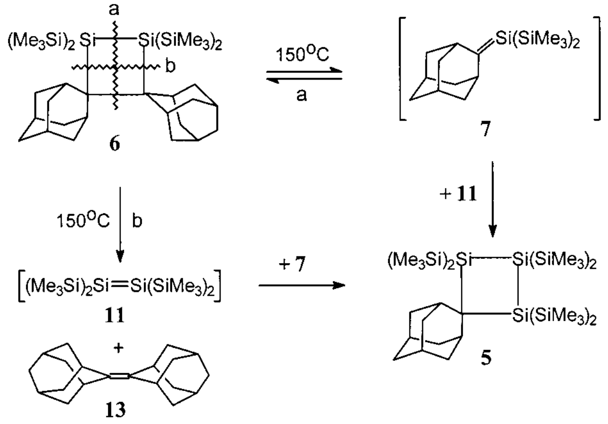


a smaller percentage of C (58.63%) than that expected for pure **6** (62.26%), the composition of the polymer may be formally represented by the "average" formula $[-\text{DSCB}_2-\text{TSCB}-]_n$. This suggests the incorporation of fragments of the type $[-(\text{Me}_3\text{Si})_2\text{Si}-\text{Si}(\text{Me}_3\text{Si})_2-]$ into the polymer. The ^{29}Si NMR spectrum of the polymer, revealing three different ranges of resonances, also points to the presence of polysilicon fragments.[13]

Thermolysis of **6** in the presence of *trans*,*trans*-1,4-diphenyl-1,3-butadiene (**18**) leads (in addition to **5**, **13**, and **16**, formed in the thermolysis of neat **6**) to the formation of **17**, the corresponding [2+2] trapping product of silene **7** (Scheme 2). The assigment of the NMR spectroscopic data of **17** was made by selective ^{1}H decoupling, ^{1}H−^{1}H-COSY, and ^{1}H−^{13}C-HETCOR experiments. The stereochemistry of **17** was determined by comparison of the J(H,H) coupling constants, measured for **17** (i.e., $J = 15.8$ Hz for olefin protons and $J = 11.4$ Hz for cyclic protons), with those known for the very similar 3-vinyl-4-phenyl-1-silacyclobutanes, for which a full detailed analysis of the NMR spectra was given.[14] When the starting molar ratio of **6**:**18** is 1:2, **17** is the major (90%) thermolysis product; that is, under these conditions the trapping of **7** by **18** depresses the formation of the other thermolysis products (**5**, **13**, and **16**). On the basis of these trapping experiments and on the behavior of **6** in benzene (Scheme 1, path a), we believe that the intermediacy of silene **7** in the thermolysis of **6**, as shown in Scheme 2, is established.

How is the trisilacyclobutane **5** formed in the thermolysis of **6**? In previous work[7] we have already suggested that the trisilacyclobutane ring (eq 2) could be formed by the cycloaddition reaction between a silene and a disilene. We suggest that the thermolytic conversion of **6** to **5** proceeds in two steps (Scheme 3). In the first step, **6** is cleaved simultaneously along two competing routes: path a (cleavage of the Si−Si and C−C bonds), which produces silene **7**,[9] and path b (cleavage of the C−Si bonds), leading to the formation of disilene **11** and diadamantylidene **13**. We assume that cleavage along path b, which occurs under UV irradiation,[10] may also occur under thermolytic conditions at 150 °C. The second step involves the cycloaddition reaction of silene **7** with disilene **11** to give TSCB **5** (Scheme 3). The fact that disilene **11** was not trapped by **18** during the thermolysis of **6** in the presence of **18** can be explained by assuming that under these experimental conditions **7** is a much more reactive "trapping agent" for **11** than **18**. To the best of our knowledge this is the first clear example of a [2+2] cycloadition of a silene and a disilene, as well as the first demonstration that a silene and a disilene can be generated simultaneously from a single precursor.

Scheme 3



Photolysis of TSCB 5. Photolysis of TSCB **5** in hexane with a 150 W middle-pressure Hg lamp (254 nm) for 1.5 h in the presence of 1,3-butadiene (Scheme 4) leads to a complex mixture of products, from which **9** and **14** were isolated. **9** and **14** are the known trapping products of silene **7** and disilene **11** with butadiene, respectively. This experiment strongly suggests that upon photolysis, TSCB **5** dissociates to produce the silene **7** and the disilene **11**. Recently, **7** and **11** were directly detected in flash-laser photolysis of **5**.[15] These flash-laser experiments will be reported elsewhere. The results of the photolysis of **5** support the idea that silene **7** and disilene **11** can be produced simultaneously from **6** under thermolysis. The photoreaction of **5** is rather unusual because cyclic as well as linear polysilanes with three adjacent Si atoms are known to extrude the silylene under irradiation.[16]

Molecular Structure of TSCB 5. The structure of **5** was determined by X-ray crystallography, and it is shown in Figure 1. The important structural features

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[13] The detailed analysis of the structure and the mechanism of formation of polymer **16** will be reported in a separate paper.

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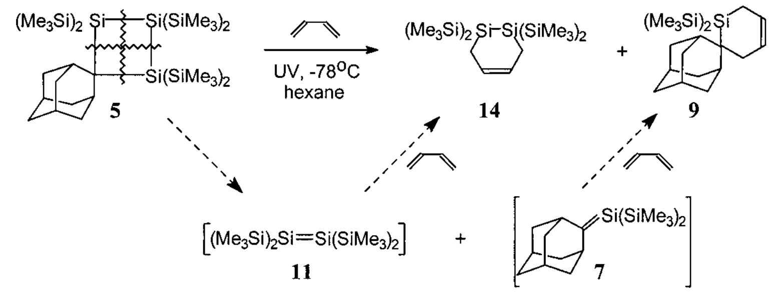
Table 1. Comparison of Bond Lengths (Å) and Angles (deg) for TSCB and DSCB

selected geometrical parameters	TSCB (**5**)	TSCB (**3**)[a]	DSCB (**6**)[b]	standard values[c]
endocyclic Si−Si bond	2.398	2.391 2.389	2.333	2.34
endocyclic Si−C bond	1.973	1.948 1.924	2.008	1.90
endocyclic C−C bond			1.647	1.54
exocyclic Si−Si bond	2.409; 2.392 2.384; 2.365	2.375; 2.365 2.370; 2.364	2.42 2.38	2.34
ring Si−Si−Si angle	76.5	77.2	77.3 (Si−Si−C)	
ring Si−Si−C angle	91.8	88.3		
ring Si−C−Si angle	97.6	105.8	95.8 (C−C−Si)	
ring dihedral angle	15.7[d]	14.3[d]	39.6[e]	

[a] From ref 7. [b] From ref 9. [c] From ref 17. [d] The inner-ring CSiSiSi dihedral angle. [e] The inner-ring CCSiSi dihedral angle.

Scheme 4



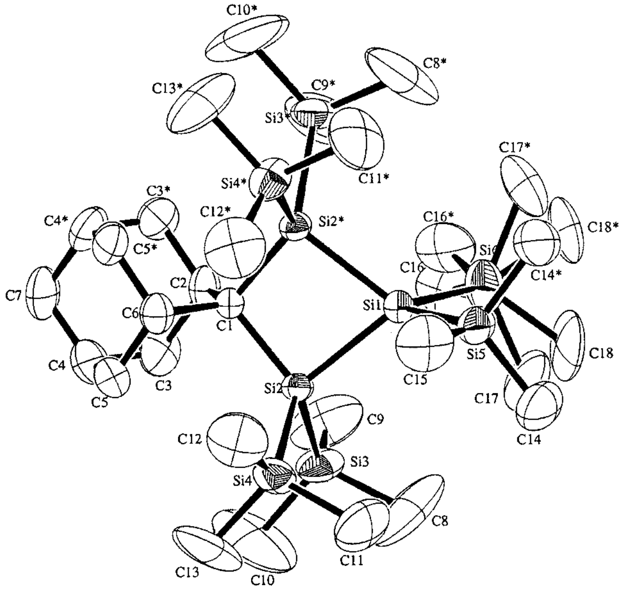


Figure 1. Molecular structure of TSCB (**5**) Selected bond lengths (Å) and bond angles (deg): C1−Si2 = 1.973, Si1−Si2 = 2.398, Si1−Si5 = 2.365, Si1−Si6 = 2.384, Si2−Si3 = 2.392, Si2−Si4 = 2.409, C1−C2 = 1.55, C1−C6 = 1.57; Si2−C1−Si2* = 97.6, Si2−Si1−Si2* = 76.5, C1−Si2−Si1 = 91.8, Si2−Si1−Si5 = 121.0, Si5−Si1−Si6 = 102.2, Si1−Si2−Si3 = 111.8, C1−Si2−Si3 = 120.8, Si2−C1−C6 = 114.1, Si2*−C1−C2 = 113.4. The dihedral angle between the planes defined by Si2−Si2*-C1 (P1) and Si1−Si2−Si2* (P2) is 15.7°. Hydrogen atoms omitted for clarity.

are shown in Table 1, where selected bond lengths and angles of two TSCBs, **5** and **3**, and of DSCB **6** are listed for comparison. TSCB **5** exhibits structural features similar to other known strained silacyclobutanes.[7,12] The full crystallographic details of **5** are given in the Supporting Information. The following points are of interest: (1) the endocyclic (and some exocyclic) bonds are longer than the "standard values" of similar nonstrained silicon compounds; (2) the trisilacyclobutane ring is puckered (the inner-ring CSiSiSi dihedral angle is 15.7°). The characteristic structural features of **5** and **3** are similar, indicating similar ring strain in these two rings.

Comparison between the geometries of **5** and of **6** suggests that the TSCB ring of **5** is less strained than the DSCB ring of **6**. While the endocyclic Si−Si and Si−C bonds in **5** are 0.05−0.07 Å longer than the corresponding "standard values", the elongation of the endocyclic Si−C and C−C bonds in **6** is larger, i.e., by about 0.1 Å (the ring Si−Si bond in **6** is not elongated). The exocyclic Si−Si bonds in **5** and **6** are similar. The inner valence angles at the Si atoms are small in both **5** and **6** (76.5° and 77.3°) and are among the smallest observed in silacyclobutanes.[7] However, the TSCB ring in **5** is much less puckered than the four-memberd ring in **6** (inner-ring dihedral angles of 15.7° and 39.6°, respectively).

Conclusions

Thermolysis of 1,2-disilacyclobutane **6** at 150−180 °C in the absence of trapping agents leads to the formation in 75% yield of the stable trisilacyclobutane **5**. The thermolysis probably proceeds via the simultaneous formation of two transients, the silene **7** and the disilene **11**, which then undergo cycloaddition (Scheme 3). Photolysis of **5** at −78 °C also leads to the simultaneous formation of a silene and a disilene, and both intermediates can be trapped by 1,3-butadiene, to give the expected [4+2] cycloaddition products.

Experimental Section

All reactions and processes involving air-sensitive materials were carried out using standard Schlenk techniques. Solvents were kept under $CaCl_2$ for a few days before use, unless otherwise specified. THF was refluxed over potassium and benzophenone and distilled under argon prior to use. Commercially available reagents were used without additional purification.

The NMR spectra were obtained at room temperature in C_6D_6 or $CDCl_3$ solutions. ^{1}H and ^{13}C spectra were measured with a Bruker EM-200 instrument. ^{29}Si NMR spectra were recorded on a Bruker-400 instrument using the INEPTRD program or on a Bruker DMX-500 instrument using the INVGATE program. Chemical shifts are referenced to TMS or to C_6D_6. Gel permeation chromatography (GPC) was performed using a Thermal Separation Products P-100 pump and a Labomatic refractive index detector, with toluene as an eluent. Phenomenex Phenogel 300 × 7.8 columns (MXL Mixed or 2 × 100 Å set) with an elution rate of 1 mL/min were used for the analytical measurements. A Phenogel 500 Å 300 × 21.2 column with an elution rate of 5 mL/min was used for preparative GPC separations. The preparative column chromatography was performed on silica gel (15 mesh) with hexane/ether gradient elution (flow rate 20 mL/min), using a Labomatic MD-100 pump. Mass spectroscopy measurements were performed on a Finnigan MAT TSQ 45 triple stage quadrupole mass spectrometer. Elemental analysis was performed in the analytical laboratory of the University of Frankfurt-on-Main. We are thankful to Professor N. Auner for the elemental analysis measurements.

Thermolysis of 6. A typical procedure is as follows: 0.5 g of DSCB **6** was placed in a Pyrex tube (8 mm × 15 cm). To avoid the presence of traces of water, prior to thermolysis the tube contaning DSCB was first degassed at 0.05 Torr and then heated at 80 °C for 24 h under vacuum. The tube was then sealed and heated in a furnace at 150 °C for 3 h. The tube then was opened in air (no internal pressure was developed during the heating), and the resulting white-yellow sticky powder was unloaded. The crude product obtained was characterized by NMR analysis and GPC. The conversion of **6** was complete, according to NMR data. The individual products were separated by preparative GPC. After drying 0.260 g of **5** (75%), 0.110 g of diadamantylidene **13** (75%), and 0.110 g of polymer **16** (23 wt % of the total weight of the crude product) were obtained.

Trisilacyclobutane (TSCB) (5). TSCB can be easily separated from the crude product, obtained by thermolysis of **6**, using preparative GPC. The yield of TSCB **5** was 75%. ^{1}H NMR (C_6D_6): δ 0.43 (18H, s, $Me_3Si{-}SiSiC$), 0.50 (36H, s, $Me_3Si{-}SiC$), 1.6−2.3 (14H, m, Ad). ^{13}C NMR (C_6D_6): δ 4.79 (12C, $Me_3Si{-}SiC$), 5.90 (6C, $Me_3Si{-}SiSiC$), 28.07, 35.79, 37.34 (Ad). ^{29}Si NMR (C_6D_6): δ −8.87 (2Si, $Me_3\mathit{Si}$-SiSiC), −11.60 (4Si, $Me_3Si{-}SiC$), −35.42 (ring C*Si*Si), −126.10 (ring Si*Si*Si). MS (CI): *m*/*z* 583 ($M^+ - Me_3Si$, 40); 409 ($M^+ - Si(SiMe_3)_3$, 10); 348 ($M^+ - (Me_3Si)_2Si{=}Ad$, 100). Anal. Calcd for $C_{28}H_{68}Si_9$: C, 51.14; H, 10.42. Found: C, 51.61; H, 10.33. Mp: 270 °C.

Polymer 16. The polymeric fraction was separated from the crude product, obtained in the thermolysis of **6**, using preparative GPC of a toluene solution. The isolated polymer is a white-yellow sticky powder highly soluble in toluene, hexane, THF, and chloroform. The polymer has a bimodal molecular weight distribution with a M_w = 11 800 (using polystyrene standards) and $M_w/M_n = 1.4$. ^{1}H NMR (C_6D_6): δ 0.2−0.8 very broad (Me_3Si), 1.5−2.7 very broad (Ad). ^{13}C NMR (C_6D_6): δ 1.0−5.0 very broad (Me_3Si), 28.4, 29.0, 31.5, 35.6, 38.1, 41.1 (all broad, Ad). ^{29}Si NMR (C_6D_6): δ −11.5 br, −16.0 br (*Si*−Si−Si), −35.0 br (Si−*Si*−Si), −75.0 br (Si_2−*Si*−Si). Anal. Calcd for $C_{92}H_{196}Si_{21}$ (as for $[-DSCB_2-TSCB-]_n$): C, 58.40; H, 10.44. Found: C, 58.63; H, 10.27.

Diadamantylidene (13). 13 was separated by preparative GPC from the crude product obtained in the thermolysis of **6**. Measured analytical and spectroscopic data of **13** were identical to those known for diadamantylidene.[18] ^{1}H NMR (C_6D_6): δ 1.72, 1.78, 1.83, 1.89 (24H, br), 2.92 (4H, s, HC−C=C−). ^{13}C NMR (C_6D_6): δ 29.05, 32.40, 37.68, 39.97 (18C), 133.64 (C=C). MS (CI): *m*/*z* 267 ($M^+ - H$, 100). Mp: 185 °C.

Thermolysis of 6 in the Presence of 1,4-Diphenyl-1,3-butadiene (18). A 0.06 g sample of DSCB **6** and 0.04 g of **18** (**6**:**18** molar ratio of 1:2) were placed in a Pyrex tube (8 mm × 15 cm). After preliminary drying at 80 °C for 24 h under vacuum, the tube was sealed and heated in a furnace at 150 °C for 2 h, resulting in full conversion of **6**. The obtained crude product was characterized by NMR spectroscopy and GPC. According to NMR data, the final product consisted mainly of **17** (ca. 90%), with small amount of TSCB **5** and diadamantylidene **13** (ca. 3−5% each). Traces of polymer **16** were also detected.

(*E*,*E*)-1,1-Bis(trimethylsilyl)-3-ethyl(2′-phenyl)-4-phenylspiro[2,2-adamantane-1-silacyclobutane] (17). A 0.054 g sample of grease-like **17** (yield 54%) was isolated by column chromatography on silica gel from the crude product, obtained after thermolysis of **6** in the presence of **18**. ^{1}H NMR (C_6D_6): δ 0.10 (9H, s, Me_3Si), 0.34 (9H, s, Me_3Si), 1.6−2.4 (14H, m, Ad), 3.2 (1H, d, $J = 11.4$ Hz, HC−Si), 3.75 (1H, dd, $J = 11.4$, 8.2 Hz, HC−Ad), 6.48 (1H, d, $J = 15.8$ Hz, Ph−CH=C), 6.56 (1H, dd, $J = 15.8$, 8.2 Hz, Ph−C=CH), 6.9−7.3 (10H, m, Ph). ^{13}C NMR (C_6D_6): δ 0.76, 1.72 (6C, Me_3Si), 28.29, 28.93, 32.77, 32.89, 35.09, 38.59, 39.84, 40.41, 40.73, 51.02 (10C, Ad), 32.24 (1C, HC−Si), 56.75 (1C, HC−Ad), 124.31, 126.52, 127.04, 128.33, 128.62, 128.76, 138.32, 143,88 (8C, Ph) 126.76, 135.58 (2C, HC=CH). ^{29}Si NMR (C_6D_6): δ −15.05, −15.15 (2Si, Me_3Si), −14.00 (ring Si). MS(CI): *m*/*z* 515 (M^+, 10); 411 ($M^+ -$ CH=CH−Ph, 8); 367 ($M^+ - (Me_3Si)_2$, 8); 334 ($M^+ -$ CH=CH−Ph, − Ph, 10); 321 ($M^+ -$ CH=CH−Ph, − CH−Ph, 100); 265 ($M^+ -$ Ad−CH−CH=CH−Ph, 30); 249 ($M^+ - (Me_3Si)_2Si$−CH−Ph, 30). Anal. Calcd for $C_{32}H_{46}Si_3$: C, 74.64; H, 9.00. Found: C, 74.90; H, 8.78.

Photolysis of TSCB (5) in the Presence of 1,3-Butadiene. A 0.1 g (0.15 mmol) sample of **5** and 0.08 g (1.5 mmol) of 1,3-butadiene in 15 mL of dry hexane were degassed and placed in a quartz ampule under vacuum. The solution was irradiated at −78 °C for 1.5 h by a medium-pressure mercury immersion lamp TQ 150 (254 nm) with a distance of 1 cm between the lamp and the ampule. The conversion of TSCB (**5**) was about 80%. The solvent was evaporated, the residue was washed in methanol and dried, and the products were separated by column chromatography on silica gel. **9** and **14** (ca. 30% each according to NMR analysis), the expected trapping products of silene **7** and disilene **11**, were found among the reaction products. The NMR data of **9** and **14** were reported previously.[9,10] The other products (about 20%) were not identified.

X-ray Structure Analysis of 5. Crystals of **5** suitable for X-ray diffraction studies were grown from a hexane solution of **5** by slow evaporation of solvent at room temperature. Crystal data: transparent prism, crystal size 0.15 × 0.25 × 0.33 mm, formula unit $C_{28}H_{68}Si_9$, $a = 11.253(5)$ Å, $b = 18.647(9)$ Å, $c = 10.050(5)$ Å, $\beta = 102.88(5)°$, monoclinic, space group $P2_1/m$ (no. 11), $Z = 2$. Four-circle diffractometer Philips PW 1100/20, wavelength Mo Kα, $\lambda = 0.71069$ Å, method of data collection $\omega/2\theta$, total number of data collected 3932, $R_{int} = 0.075$, $2\theta = 50.0°$, $R(I{>}2\sigma(I)) = 0.093$, wR2 = 0.171, refinement on F^2. All nonhydrogen atoms were refined anisotropically and hydrogens isotropically. Methyl hydrogens were placed at calculated positions and refined using the riding model. A crystallographic mirror plane bisects the molecule through C(15), Si(5), Si(6), C(1), C(6), C(7). Also, the three methyl carbons of the trimethylsilyl group at Si(6) were found

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to be disordered by taking two orientations about the mirror plane with occupancies of 0.5. Structure solution was carried out by SHELXS-97,[19] and structure refinement by SHELXL-97.[20] Molecular graphics were performed by TEXSAN.[21]

Acknowledgment. This research was supported by the Israel Science Foundation administrated by the Israel Academy of Science and Humanities, by the Fund for the Promotion of Research at the Technion, and by the Minerva Foundation in Münich. D.B.-Z. is grateful to the Israel Ministry of Immigrant Absorption for Kamea and Gileadi scholarships.

Supporting Information Available: Details of the X-ray crystal structure analysis of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0107690

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