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Reactions of Silylenes with Acetylenes and 1,3-Diacetylenes Linked by C−C Multiple-Bond Units[1,2]

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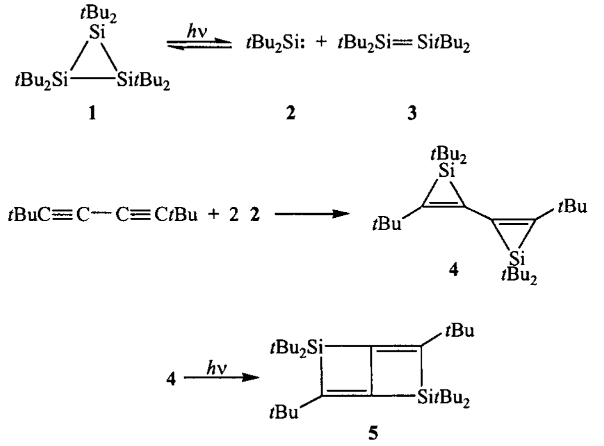
The reaction of di-*tert*-butylsilylene (**2**), generated photochemically from hexa-*tert*-butylcyclotrisilane (**1**), with a (*Z*)-3-hexene-1,5-diyne furnishes a product built up of two silirene rings linked by an olefinic double bond. A similar reaction of **2** with (*Z*)-6-dodecene-2,4,8,10-tetrayne yields two rearranged 2,5-disilabicyclo[2.2.0]hexane-1(6),3-diene units linked by a C−C double bond. The oligoene frameworks of both compounds adopt the all-trans configuration. Treatment of 1,3,5-tris((trimethylsilyl)ethynyl)benzene and 1,2-diethynylbenzene with **1** affords a 1,3,5-tris(silacyclopropenyl)benzene and a 1*H*-indeno[2,1-*b*]silete derivative with an exocyclic $t\mathrm{Bu}_2\mathrm{SiH}$ group at position 7 of the tricyclic system.

Introduction

Silirenes, three-membered-ring compounds containing a silicon atom and a C−C double bond, have been known for more than 25 years.[3,4] An Si−Si-linked bis(silirene)[5] as well as the C−C-linked compound **4**[6] were first prepared much later, the latter by double [2 + 1] cycloaddition of the silylene **2**, generated photolytically from the cyclotrisilane **1**,[7] to the triple bonds of the 1,3-diyne. Compound **4** is thermally stable but undergoes rearrangement to afford the bicyclic system **5** upon renewed photolysis (Scheme 1). We recently even obtained a quatersilirene by cycloaddition of four molecules of **2** to a 1,3,5,7-tetrayne. This product is also thermally stable but, similar to **4**, undergoes rearrangement upon longer photolysis.[8]

We have now examined the question if the partial replacement of the conjugated C−C triple bonds in the oligoynes by C−C double bonds would lead to molecules containing both silirene and silirane increments next to each other or whether the cycloadditions of **2** to only one of these types of multiple bonds would be preferred. In this context we now report on the reactions of **1** with an enediyne and with an enetetrayne as well as its cycloadditions to 1,3,5-triethynyl- and 1,2-diethynylbenzenes.

Scheme 1



Results and Discussion

Photolysis of **1** in the presence of 1,6-bis(trimethylsilyl)-(*Z*)-3-hexene-1,5-diyne (**6**)[9,10] resulted in the formation of yellow crystals in 76% yield. The analytical and spectral data indicate the formations of the bis(silirene) **7** with an olefinic double-bond linkage. Of high diagnostic value are the ^{13}C NMR spectrum, showing only signals for olefinic carbon atoms in the low-field part of the spectrum, and the ^{29}Si NMR spectrum, exhibiting only a high-field signal at −71.88 ppm in the typical range for silirenes with this substitution pattern[6,8,11,12] (Scheme 2).

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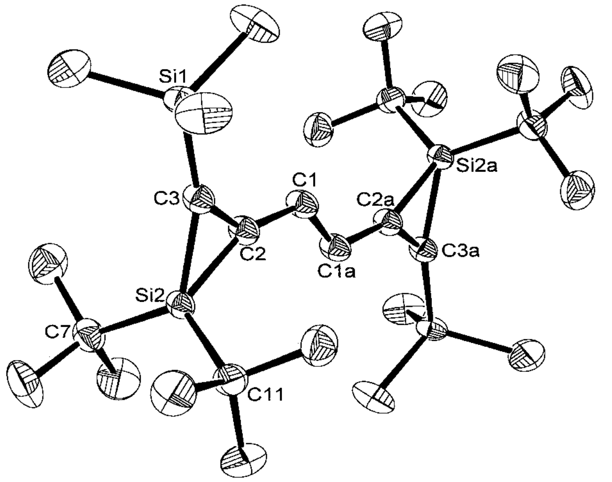


Figure 1. Molecule of **7** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C(1)−C(1a) = 1.334(3), C(1)−C(2) = 1.4475(17), C(2)−C(3) = 1.3506(18), C(2)−Si(2) = 1.8039(12), C(3)−Si(2) = 1.8355(12); C(2)−Si(2)−C(3) = 43.56(6), Si(2)−C(2)−C(3) = 69.47(7), Si(2)−C(3)−C(2) = 66.97(7).

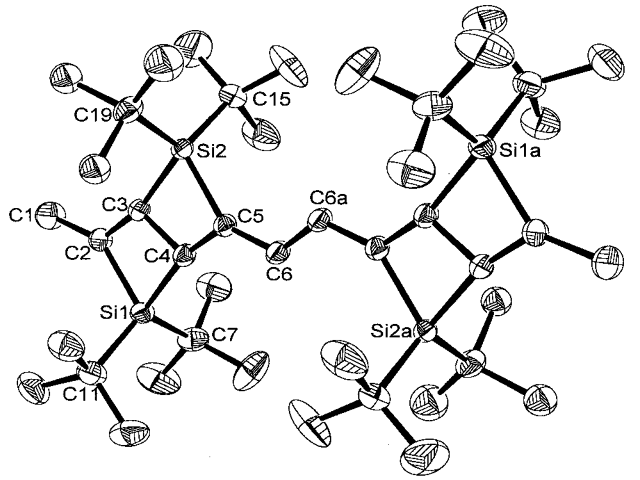
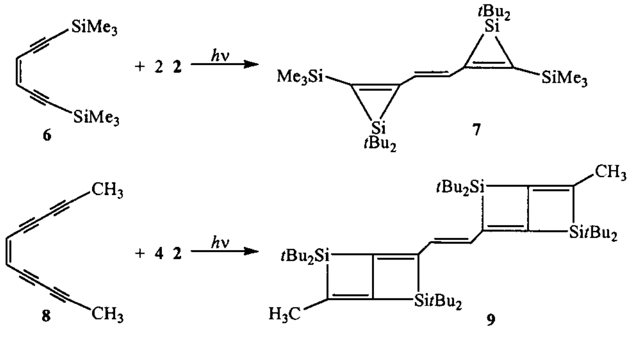


Figure 2. Molecule of **9** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): C(2)−C(3) = 1.355(3), C(3)−C(4) = 1.483(2), C(4)−C(5) = 1.364(3), C(5)−C(6) = 1.435(2), C(6)−C(6a) = 1.343(4); C(2)−Si(1)−C(4) = 75.11(8), C(3)−Si(2)−C(5) = 75.36(8).

Scheme 2



An X-ray crystallographic analysis (Figure 1) additionally revealed that the double bonds in **7** adopt the all-trans configuration.

Two remarkable features are apparent from the reaction of **1** with **6**: first, the triple bonds appear to be more reactive toward the silylene **2** than the also present double bond. Second, of the two products formed upon photolysis of **1** only the silylene **2,** but not the concomitantly formed disilene **3**, undergoes cycloadditions to the multiple bonds of **6**. Indeed, not only from this reaction but also from those described below, varying amounts of hepta-*tert*-butylcyclotetrasilane are always isolated; this compound is formed by dimerization of two molecules of **3** with simultaneous elimination of isobutene whenever a suitable reaction partner for the only marginally stable disilene **3** is not available.[13]

The low reactivity of **3** toward molecules of this type is also seen in the cophotolysis of **1** with (*Z*)-dodeca-6-ene-2,4,8,10-tetrayne (**8**),[9,10] which possesses an extended system of conjugated multiple bonds. As a consequence of the photochemical lability of **8** the product was obtained as light yellow crystals in a yield of merely 5%. The analytical and spectroscopic data were in accord with the rearranged structure **9**. Thus, the ^{13}C NMR spectrum contained only signals for olefinic skeletal carbon atoms. The ^{29}Si NMR spectrum is more informative, showing two deshielded signals at 36.70 and 38.99 ppm, in the same range as those for bicyclic systems of the type **5** (Scheme 2).[6,8]

The assumptions based on these analytical findings were confirmed by the X-ray crystal structure analysis that demonstrated the existence of the two 2,5-disilabicyclo[2.2.0]hexadiene units linked by a C−C double bond (Figure 2). In analogy to **7**, the double bonds of **9** also adopt an all-trans arrangement. These molecules apparently behave like polyacetylenes, where the all-trans forms are more stable than the all-cis configuration.[14]

In addition to the above acetylenes linked by olefinic double bonds, we have also examined the reactivity of oligoacetylenes separated by one or two aromatic multiple bonds.

Photolysis of **1** in the presence of 1,3,5-tris((trimethylsilyl)ethynyl)benzene (**10**)[15] resulted in the formation of colorless crystals in 71% yield, the analytical and spectroscopic data of which indicate the formation of the tris(silirenyl)benzene **11** (Scheme 3). Similar to compound **7** only signals for the olefinic carbon atoms can be seen in the low-field part of the ^{13}C NMR spectrum. The ^{29}Si NMR spectrum is more informative, containing a signal shifted to the high-field region typical for silirenes at −71.53 ppm in addition to a signal for the $SiMe_3$ groups.

Again the constitution for **11** deduced from the spectroscopic data was confirmed by an X-ray crystallographic analysis (Figure 3). The terminal trimethylsilyl groups appear to be important for the smooth addition of **2** to the triple bonds of **10**, since attempts to react **1** with 1,3,5-triethynylbenzenes bearing *t*Bu groups

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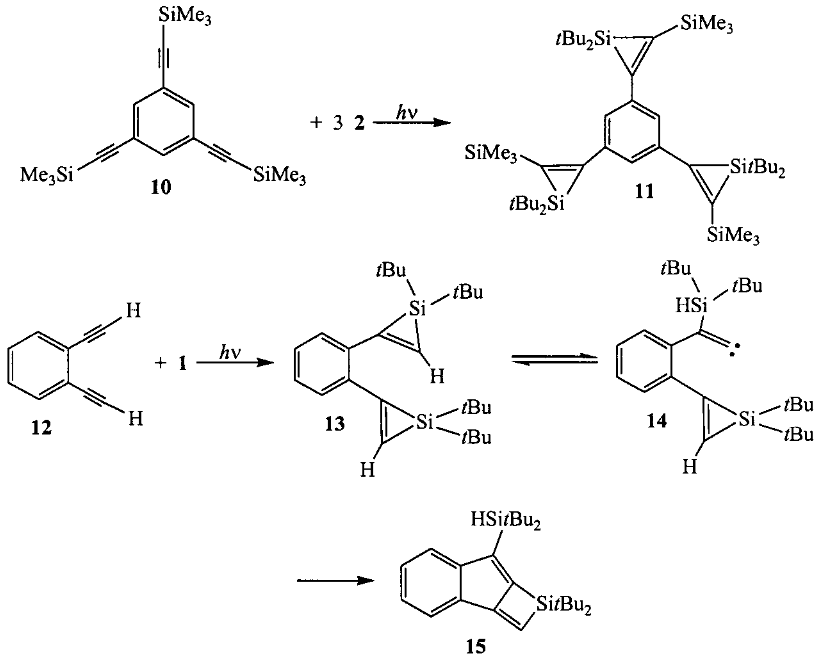
Scheme 3



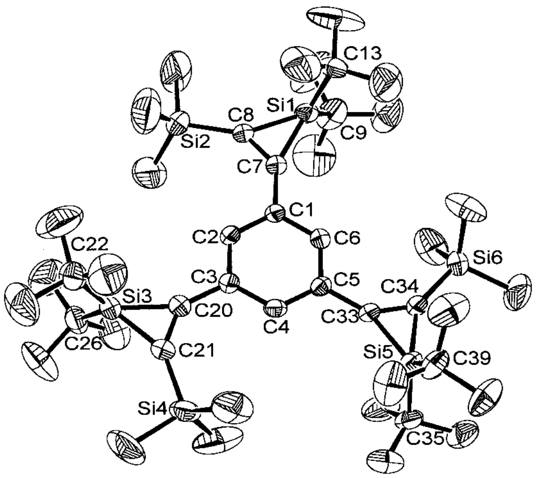


Figure 3. Molecule of **11** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Si(1)–C(7) = 1.814(4), Si(1)–C(8) = 1.824(4), C(7)–C(8) = 1.345(6), C(7)–C(1) = 1.472(5); C(7)–Si(1)–C(8) = 43.38(18), Si(1)–C(7)–C(8) = 68.7(3), Si(1)–C(8)–C(7) = 67.9(3), C(1)–C(7)–Si(1) = 154.3(3).

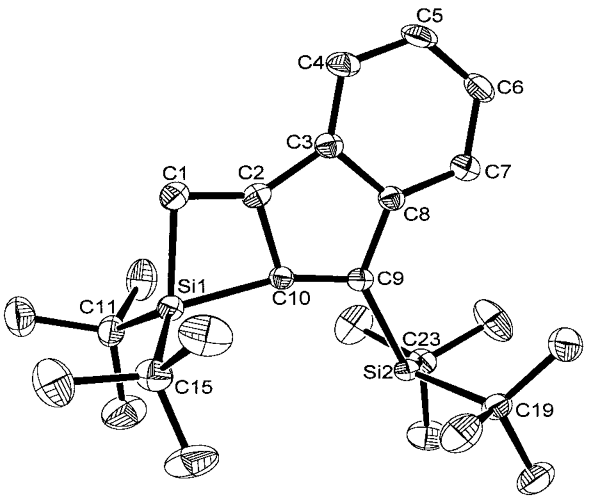


Figure 4. Molecule of **15** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Si(1)–C(1) = 1.891(4), Si(1)–C(10) = 1.885(3), C(1)–C(2) = 1.347(5), C(2)–C(10) = 1.478(4), C(10-C(9) = 1.352(4), C(9)–C(8) = 1.488(5), C(3)–C(8) = 1.424(4), C(9)–Si(2) = 1.878(2); C(1)–Si(1)–C(10) = 74.48(14), Si(1)–C(10)–C(2) = 87.00(19), C(10)–C(2)–C(1) = 107.9(3), C(2)–C(1)–Si(1) = 90.6(2).

or hydrogen atoms as end groups did not produce any useful results.

The cophotolysis of **1** with 1,2-diethynylbenzene (**12**)[16] followed an unexpected course to furnish yellow crystals in 9% yield. Elemental analysis and the absence of signals for acetylenic carbon atoms in the ^{13}C NMR spectrum at first suggested the existence of a 1,2-bis(silirenyl)benzene. However, this assumption was not supported by the ^{29}Si NMR spectrum, which showed two signals at 13.3 and 26.14 ppm. Furthermore, an absorption band at 2109 cm^{-1} typical for an Si–H bond was observed in the IR spectrum.

The structure of the isolated crystalline compound was finally elucidated by X-ray crystallography (Figure 4), which demonstrated the formation of the tricyclic system **15** with an exocyclic $t\mathrm{Bu_2SiH}$ group (Scheme 3). Again, it can be assumed that the reaction sequence is initiated by a 2-fold cycloaddition of **2** to the C–C triple bonds to afford compound **13**, followed by a 1,2-hydrogen shift to give the vinylidene derivative **14**. Insertion of this carbene intermediate into the silicon–carbon bond of the other silirene unit should then furnish the isolated compound **15**. A similar type of reaction was previously observed by the insertion of isonitriles into the Si–C bonds of siliranes.[17]

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Table 1. Crystallographic Data for 7, 9, 11, and 15

	7	9	11	15
empirical formula	$C_{28}H_{56}Si_4$	$C_{44}H_{80}Si_4$	$C_{45}H_{84}Si_6$	$C_{26}H_{42}Si_2{\cdot}CDCl_3$
fw	505.09	721.44	793.66	529.14
a (Å)	7.7683(5)	8.7423(7)	14.9910(8)	8.4052(6)
b (Å)	10.0800(7)	11.6824(9)	26.3400(15)	12.2900(14)
c (Å)	12.0377(8)	13.7924(11)	55.045(3)	16.2456(16)
α (deg)	96.979(8)	113.124(9)	90	72.334(12)
β (deg)	94.730(8)	91.046(10)	90.092(4)	87.475(11)
γ (deg)	111.425(7)	109.724(9)	90	71.056(11)
V (Å^3)	862.72(10)	1200.81(16)	21735(2)	1509.7(3)
Z	1	1	4	2
d(calcd) (g cm^{-3})	0.972	0.998	0.970	1.166
cryst size (mm)	0.55 × 0.44 × 0.37	0.25 × 0.20 × 0.12	0.30 × 0.25 × 0.20	0.95 × 0.17 × 0.10
cryst syst	triclinic	triclinic	monoclinic	triclinic
temp (K)	193(2)	193(2)	293(2)	193(2)
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$
$2\theta_{max}$ (deg)	52	52	129	52
no. of rflns measd	10486	15240	34182	18457
no. of unique rflns	3110	4373	11627	5478
lin abs coeff (mm^{-1})	0.185	0.150	ψ-scan	0.396
no of params	145	214	922	293
R ($I > 2\sigma(I)$)	0.0289	0.0415	0.0679	0.0518
wR2 (all data)	0.0790	0.1095	0.1877	0.0972
GOF (F^2)	1.022	0.951	1.100	0.783

Experimental Section

General Procedures. All manipulations were carried out in oven-dried glassware under an atmosphere of dry argon. Photolyses were carried out at room temperature using a high-pressure mercury immersion lamp (Heraeus TQ 150).

The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM 300 spectrometer using C_6D_6 as solvent. The ^{29}Si NMR spectra were recorded on a Bruker AMX 300 spectrometer. IR spectra were taken on a Bio-Rad FTS-7 spectrometer. The mass spectra were recorded on a Finnigan MAT 212 spectrometer. Elemental analyses were performed by Analytische Laboratorien, D-51789 Lindlar, Germany.

2-[(*E*)-2-[1,1-Di-*tert*-butyl-3-(trimethylsilyl)silacycloprop-2-en-2-yl]ethenyl]-1,1-di-*tert*-butyl-3-(trimethylsilyl)silacycloprop-2-ene (7). A solution of **1** (1.00 g, 2.3 mmol) and **6** (0.67 g, 2.3 mmol) in *n*-hexane (80 mL) was irradiated for 6 h at room temperature. After this time the solution was concentrated to a volume of 5 mL and cooled to −30 °C for 3 days to furnish 0.88 g (76% yield) of yellow crystals of **7**: mp 109 °C; ^{1}H NMR δ 0.29 (s, 18 H, SiCH$_3$), 1.09 (s, 36 H, *t*Bu), 7.27 (s, 2 H, CH); ^{13}C NMR δ 0.37 (C$_p$, SiCH$_3$), 21.04 (C$_q$, *t*Bu), 30.48 (C$_p$, *t*Bu), 134.58, 162.9, 172.18 (C$_p$, C$_t$, C$_q$ refer to primary, tertiary, and quaternary carbon atoms); ^{29}Si NMR δ −71.83, −12.59; MS (CI, isobutane) m/z (%) 561 $[M + C_4H_9]^+$ (100), 505 $[MH]^+$ (70); IR (KBr) ν 1561 (C=C) cm^{-1}. Anal. Calcd for $C_{28}H_{56}Si_4$: C, 66.58; H, 11.17. Found: C, 66.42; H, 11.30.

2,2,5,5-Tetra-*tert*-butyl-3-methyl-6-{(*E*)-2-[2,2,5,5-tetra-*tert*-butyl-6-methyl-2,5-disilabicyclo[2.2.0]hexa-3,6-dien-3-yl]ethenyl}-2,5-disilabicyclo[2.2.0]hexa-3,6-diene (9). A solution of **1** (1.00 g, 2.3 mmol) and **8** (0.18 g, 1.2 mmol) in *n*-hexane (80 mL) was irradiated for 6 h at room temperature. After this time the solution was concentrated to a volume of 5 mL and cooled to −30 °C to yield 29 mg (5%) of pale yellow crystals of **9**: mp >400 °C; ^{1}H NMR δ 1.16 (s, 36 H, *t*Bu), 1.21 (s, 36 H, *t*Bu), 2.00 (s, 6 H, C−CH$_3$), 6.33 (s, 2 H); ^{13}C NMR δ 20.61 (C$_p$, C−*C*H$_3$), 28.40 (C$_p$, *t*Bu), 28.54 (C$_p$, *t*Bu), owing to the low solubility of **9** the C$_q$ signals of the *t*Bu groups could not be observed, 135.37, 151.74, 155.14, 177.98; ^{29}Si NMR δ 36.70, 38.89; MS (CI, isobutane) m/z (%) 720 $[M]^+$ (100); IR (KBr) ν 1654, 1629 (C=C) cm^{-1}. Anal. Calcd for $C_{44}H_{80}Si_4$: C, 73.25; H, 11.28. Found: C, 72.60; H. 11.15.

2-{3,5-Bis[1,1-di-*tert*-butyl-3-(trimethylsilyl)silacycloprop-2-en-2-yl]phenyl}-1,1-di-*tert*-butyl-3-(trimethylsilyl)-silacycloprop-2-ene (11). A solution of **1** (1.00 g, 2.3 mmol) and **10** (0.30 g, 0.82 mmol) in *n*-hexane (80 mL) was irradiated for 5 h at room temperature. The solvent was distilled off and the residue redissolved in 5 mL of toluene. Cooling of this solution to −40 °C furnished 0.46 g (71%) of colorless crystals of **11**: mp 244 °C; ^{1}H NMR δ 0.42 (s, 27 H, SiCH$_3$), 1.15 (s, 54 H, *t*Bu), 7.99 (s, 3 H); ^{13}C NMR δ 0.74 (C$_p$, SiCH$_3$), 21.19 (C$_q$, *t*Bu), 30.67 (C$_p$, *t*Bu), 130.17, 137.90, 158.37, 174.11; ^{29}Si NMR δ −13.46, −71.53; IR (KBr) ν 1581, 1551 (C=C) cm^{-1}. Anal. Calcd for $C_{45}H_{84}Si_6$: C, 68.10; H, 10.67. Found: C, 67.69; H. 10.93.

7-(Di-*tert*-butylsilyl)-1,1-di-*tert*-butyl-1*H*-indeno[2,1-*b*]-silete (15). A solution of **1** (1.00 g, 2.3 mmol) and **12** (0.30 g, 2.4 mmol) in *n*-hexane (80 mL) was irradiated for 5 h at room temperature. The solution was concentrated to a volume of 5 mL and chromatographed on silica gel with *n*-hexane as eluent to give unreacted **1** and then a pale yellow solution. The solvent was distilled off and the residue redissolved in a minimum amount of *n*-hexane. Cooling at −25 °C for several hours afforded 90 mg (9%) of yellow crystals of **15**: mp 211−212 °C; ^{1}H NMR δ 1.14 (s, 18 H, *t*Bu), 1.20 (s, 18 H, *t*Bu), 4.20 (s, 1 H, Si−H), 7.02 (m, 1 H), 7.21 (m, 1 H), 7.35 (s, 1 H, C−H), 7.60 (m, 2 H); ^{13}C NMR δ 19.97 (C$_q$, *t*Bu), 21.07 (C$_q$, *t*Bu), 28.69 (C$_p$, *t*Bu), 30.10 (C$_p$, *t*Bu), 122.69, 123.80, 124.44, 129.39, 133.91, 138.11, 141.70, 154.89, 164.48, 172.54; ^{29}Si NMR (C_7D_8) δ 13.3 (broad), 26.14; MS (CI, isobutane) m/z (%) 467 $[M + C_4H_{10}]^+$ (100), 411 $[M]^+$ (88); IR (KBr) ν 2108 (Si−H), 1653, 1604 (C=C) cm^{-1}. Anal. Calcd for $C_{26}H_{42}Si_2$: C, 76.02; H, 10.31. Found: C, 75.75; H, 10.27. Single crystals suitable for X-ray diffraction analysis were obtained from trichloromethane.

Crystallographic Analyses. Crystal and numerical data of the structure determinations are given in Table 1. In each case the crystal was mounted in an inert oil. Data collection was performed with a Stoe IPDS area detector (**7**, **9**, **15**) using graphite-monochromated Mo Kα radiation (0.710 73 Å) or with a Bruker-AXS CCD area detector (**11**) using Cu Kα radiation (1.541 84 Å). The structures were solved by direct phase determination and refined by full-matrix least-squares techniques against F^2 with the SHELXL-97 program system.[18] Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically. The carbon atoms C19−C22 of **9** and the carbon atoms C88−C90 of **11** are disordered and were refined on two positions with an occupancy factor of 0.5 each. The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-169074 (**7**), CCDC-169072 (**9**), CCDC-169073 (**11**), and CCDC-169071 (**15**).

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Supporting Information Available: Listings of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **7**, **9**, **11**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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