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Palladium-Catalyzed Reactions of 4,5,10-Trisilabicyclo[6.3.0]undeca-1(11),8-diene-2,6-diyne with Acetylenes

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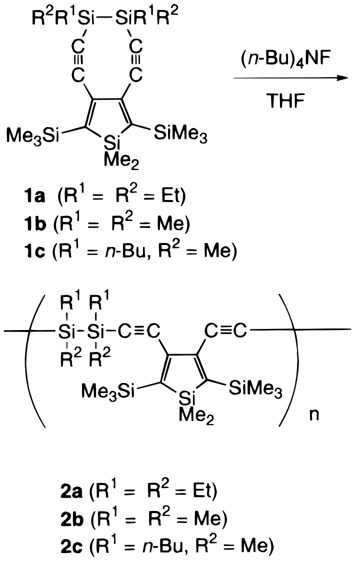
Pd(II)-catalyzed insertion reactions of phenyl- and diphenylacetylene, 1-hexyne, and 1,4-diphenylbutadiyne into the Si−Si bond of the 4,5,10-trisilabicyclo[6.3.0]undeca-1(11),8-diene-2,6-diyne **1a** gave the 4,7,12-trisilabicyclo[8.3.0]trideca-1(13),5,10-triene-2,8-diynes **3**−**6**. With 1,4-bis(trimethylsilyl)butadiyne, 1,4-bis-silylation of the butadiyne occurred specifically to afford the 4,9,14-trisilabicyclo[10.3.0]pentadeca-1(15),5,6,7,12-pentaene-2,10-diyne **7**.

Introduction

Dissociative addition of a silicon−silicon linkage to unsaturated carbon units is well-known as the bis-silylation reaction.[1] In general, disilanes having electron-withdrawing groups such as dichloro- or tetrachlorodisilanes are readily activated with transition-metal catalysts and add to olefins and acetylenes to afford products functionalized with bis(silyl) moieties, and thus the reactions are widely used as synthetic tools for various organic compounds. On the other hand, the bis-silylation reaction with simple disilanes hardly occurs unless the Si−Si linkage possesses a considerable strain.

Recently, we have found that cyclic disilanes involving a silole unit in their eight-membered rings, 4,5,10-trisilabicyclo[6.3.0]undeca-1(11),8-diene-2,6-diynes **1a**−**c**, undergo anionic ring-opening polymerization due to their strained-ring systems to give poly[(1,2-diethynylenedisilanylene)(1-silacyclopenta-2,4-diene-3,4-diyl)]s **2a**−**c**, as shown in Scheme 1.[2] Accordingly, we expected that the strained Si−Si bonds in **1** may be activated readily with transition metals and add to unsaturated C−C bonds, thus providing a new synthetic method for the silole-containing medium-ring systems. Siloles have attracted much attention because of their unique optical and electronic properties.[3] We herein report the Pd-catalyzed bis-silylation reactions of compound **1a** with acetylenes and 1,3-diynes which produce cyclic adducts. Addition to the butadiyne units takes place regiospecifically, depending on the nature of substituents on the triple bonds.

Scheme 1



1a (R^1 = R^2 = Et)
1b (R^1 = R^2 = Me)
1c (R^1 = *n*-Bu, R^2 = Me)

2a (R^1 = R^2 = Et)
2b (R^1 = R^2 = Me)
2c (R^1 = *n*-Bu, R^2 = Me)

Results and Discussion

Compound **1a** was prepared as reported previously.[2] As expected, reactions of **1a** with terminal acetylenes in the presence of a Pd(II) catalyst proceed quite smoothly to give 4,7,12-trisilabicyclo[8.3.0]trideca-1(13),5,10-triene-2,8-diyne derivatives **3** and **4**, which are produced by insertion of the alkynes into the Si−Si bond of **1a** (Scheme 2, Table 1). For example, the reaction of **1a** with phenylacetylene in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$ in benzene under reflux gave **3** in 74% yield. The reaction of **1a** with an internal acetylene, diphenylacetylene, gave the cyclic adduct **5** under similar conditions, although a longer reaction time was required.

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[1] Reviews for bis-silylation: (a) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317. (b) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351.

[2] Toyoda, E.; Kunai, A.; Ishikawa, M. *Organometallics* **1995**, *14*, 1089.

[3] Reviews for siloles: (a) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215. (b) Colomer, E.; Corriu, R. J. P.; Lheureux, M. *Chem. Rev.* **1990**, *90*, 265.

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Scheme 2

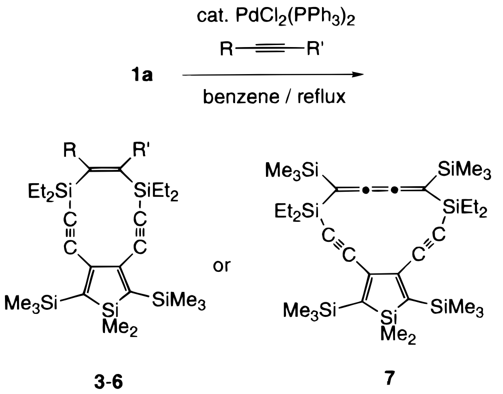

Table 1. Pd-Catalyzed Reactions of Silole 1a with Acetylenes

entry no.	R	R′	product	yield (%)
1	Ph	H	**3**	74
2	n-Bu	H	**4**	93
3	Ph	Ph	**5**	67
4	Ph	C≡CPh	**6**	79
5	Me$_3$Si	C≡CSiMe$_3$	**7**	66

The present reaction can also be applied to the insertion of conjugated acetylenes, such as 1,4-diphenyl- and 1,4-bis(trimethylsilyl)butadiynes. In the case of 1,4-diphenylbutadiyne, the 1,2-bis-silylated enyne derivative **6** was obtained as the cyclic adduct by insertion of one acetylene unit into the Si−Si bond of **1a** (Table 1, entry 4). The assignment of the structure of **6** was performed by ^{1}H, ^{13}C, and ^{29}Si NMR, mass, and IR spectrometry. The ^{1}H and ^{29}Si NMR spectra showed resonances due to two nonequivalent Me$_3$Si and Et$_2$Si groups. In addition, six respective signals for acetylenic and ethylenic carbons were observed in the ^{13}C NMR spectrum. These data support the unsymmetric structure of **6**.

Interestingly, the reaction of **1a** with 1,4-bis(trimethylsilyl)butadiyne under similar conditions gave the 4,9,14-trisilabicyclo[10.3.0]pentadeca-1(15),5,6,7,12-pentaene-2,10-diyne **7** selectively as orange crystals (Table 1, entry 5). The formation of a tetrasilylbutatriene unit in **7** indicated that the formal 1,4-bis-silylation of the butadiyne by the Si−Si bond of **1a** had occurred. In this case, a 1,2-bis-silylated enyne derivative was not detected. The assignment of the structure of **7** was also performed by ^{1}H, ^{13}C, and ^{29}Si NMR and mass spectrometry. The ^{1}H and ^{29}Si NMR spectra showed the presence of one kind of Et$_2$Si group and two kinds of Me$_3$Si groups. The ^{13}C NMR spectrum of **7** showed a signal due to the internal carbons of an allenic unit at δ 210.36. These data prove the symmetric structure of butatriene **7**. Ultimately, the structure of **7** was confirmed by X-ray crystallographic analysis.

A single crystal of **7** suitable for the X-ray crystallographic analysis was obtained from ethanol. An ORTEP drawing of **7** whose non-hydrogen atoms were refined isotropically is shown in Figure 1. The crystal data and the selected bond lengths and angles are summarized in Tables 2 and 3, respectively. These data clearly prove that the molecule has the structure as discussed below.

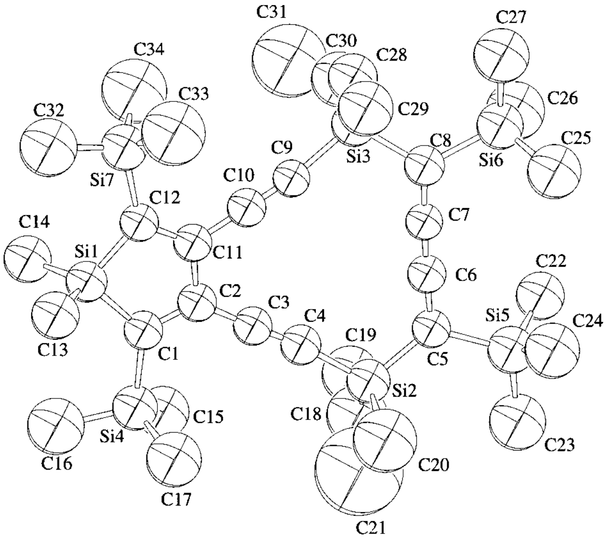

Figure 1. ORTEP drawing of compound **7**. All non-hydrogen atoms were refined isotropically. Protons are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Table 2. Crystal Data, Experimental Conditions, and Summary of Structural Refinement for 7

mol formula	C$_{34}$H$_{62}$Si$_7$
mol wt	667.46
space group	$P2_1/a$ (No. 14)
cell dimens	
a, Å	12.736(4)
b, Å	27.70(1)
c, Å	13.416(8)
β, deg	108.47(4)
V, Å^3	4490(3)
Z	4
D_{calcd}, g/cm^3	0.987
F_{000}	1456.00
cryst size, mm^3	0.20 × 0.20 × 0.03
cryst color	orange
μ(Mo Kα), cm^{-1}	2.31
diffractometer	Rigaku AFC7R
temp, K	298
wavelength (Mo Kα), Å	0.710 69
monochromator	graphite cryst
scan type	ω
scan speed, deg/min	16
scan width, deg	$5 \le 2\theta \le 45$
range of h, k, l	
h	$0 \le h \le 11$
k	$0 \le k \le 23$
l	$-12 \le l \le 10$
no. of unique rflns	4409
no. of obsd rflns ($I > 2.9\sigma(I)$)	1260
rfln/param ratio	7.64
R (R_w)^a	0.103 (0.106)

[a] The weighting scheme is $(\sigma(F_o)^2 + 0.0004|F_o|^2)^{-1}$.

We compared the arrangement around the butatriene units (C(5−8)) in **7** with that reported for tetrakis(trimethylsilyl)butatriene (**8**).[4,5] The terminal and internal C=C bond lengths in **7** (1.31(3), 1.25(3) Å and 1.33(3) Å) are similar to those in **8** (1.319(6) and 1.276(8) Å).[4] The terminal sp^2 carbons in **7** have narrow angles of 112(1)° for Si(5)−C(5)−C(6) and 115(1)° for Si(6)−C(8)−C(7), probably due to steric repulsion of bulky alkyl silyl groups on C(5) and C(8), as has been observed for **8**. The ethynyl units in **7** are bent markedly (172(2)°

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(4) Morimoto, Y.; Higuchi, Y.; Wakamatsu, K.; Oshima, K.; Utimoto, K.; Yasuoka, N. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 639.

(5) (a) Kusumoto, T.; Hiyama, T. *Tetrahedron Lett.* **1987**, *28*, 1807. (b) Kusumoto, T.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3103.

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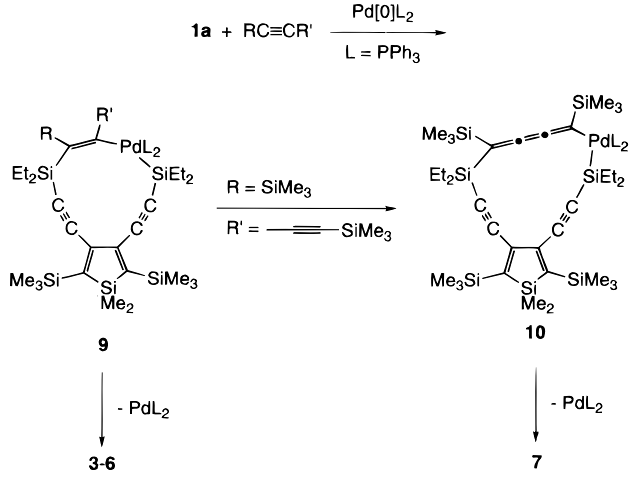
Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 7 with Their Esd's in Parentheses

Si(1)−C(1)	1.83(2)	Si(1)−C(12)	1.83(2)	Si(1)−C(13)	1.84(3)
Si(1)−C(14)	1.83(3)	Si(2)−C(4)	1.81(3)	Si(2)−C(5)	1.84(2)
Si(3)−C(8)	1.87(2)	Si(3)−C(9)	1.86(2)	Si(4)−C(1)	1.89(2)
Si(5)−C(5)	1.91(2)	Si(6)−C(8)	1.92(2)	Si(7)−C(12)	1.86(2)
C(1)−C(2)	1.36(3)	C(2)−C(3)	1.42(3)	C(2)−C(11)	1.48(3)
C(3)−C(4)	1.20(3)	C(5)−C(6)	1.31(3)	C(6)−C(7)	1.25(3)
C(7)−C(8)	1.33(3)	C(9)−C(10)	1.21(3)	C(10)−C(11)	1.45(3)
C(11)−C(12)	1.38(3)				

C(1)−Si(1)−C(12)	93(1)	C(1)−Si(1)−C(13)	109(1)
C(1)−Si(1)−C(14)	115(1)	C(12)−Si(1)−C(13)	113(1)
C(12)−Si(1)−C(14)	112(1)	C(13)−Si(1)−C(14)	110(1)
C(4)−Si(2)−C(5)	109(1)	C(8)−Si(3)−C(9)	109(1)
Si(1)−C(1)−Si(4)	129(1)	Si(1)−C(1)−C(2)	109(1)
Si(4)−C(1)−C(2)	121(1)	C(1)−C(2)−C(3)	126(2)
C(1)−C(2)−C(11)	112(2)	C(3)−C(2)−C(11)	120(2)
C(2)−C(3)−C(4)	177(2)	Si(2)−C(4)−C(3)	172(2)
Si(5)−C(5)−Si(2)	123(1)	Si(5)−C(5)−C(6)	112(1)
Si(2)−C(5)−C(6)	124(1)	C(5)−C(6)−C(7)	177(2)
C(6)−C(7)−C(8)	176(2)	Si(6)−C(8)−Si(3)	122(1)
Si(6)−C(8)−C(7)	115(1)	Si(3)−C(8)−C(7)	120(1)
Si(3)−C(9)−C(10)	172(2)	C(9)−C(10)−C(11)	173(2)
C(2)−C(11)−C(10)	117(2)	C(2)−C(11)−C(12)	120(2)
C(10)−C(11)−C(12)	122(2)	Si(7)−C(12)−Si(1)	128(1)
Si(7)−C(12)−C(11)	126(1)	Si(1)−C(12)−C(11)	104(1)

Scheme 3

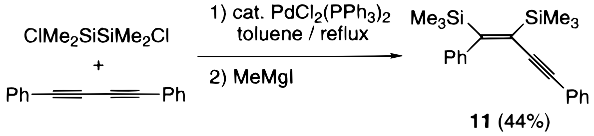


for C(3)≡C(4)−Si(2) and 172(2)° for C(10)≡C(9)−Si(3)) by the skeletal restriction of the 12-membered-ring system.

The IR spectra of **3**−**7** each showed a peak at 2134−2137 cm^{-1} assignable to the acetylene unit, as described in the Experimental Section. The lower frequency for that of **1a** (2108 cm^{-1})[2] in comparison to those for **3**−**7** suggests that the strain energy of **1a** would be an important driving force for the bis-silylation of acetylenes.

The reaction pathway affording **3**−**7** can be understood by a mechanism involving silyl(silylethenyl)palladium species **9** as the reactive intermediate (Scheme 3). 1,2-Bis-silylated adducts **3**−**6** would be generated by the reductive elimination of palladium from **9**. On the other hand, butatriene **7** would be produced by a 1,3-metal shift in **9** to give **10**, followed by the elimination of palladium from **10**.

Scheme 4



It has been reported that the bis-silylation of 1,4-bis(trimethylsilyl)butadiyne by several noncyclic disilanes using Pd(II) catalysts gives 1,1,2,4-tetrasilylbut-1-en-3-yne as the major product and 1,1,4,4-tetrasilylbutatriene as the minor one.[5] When the above reports are considered, the selective formation of either enyne **6** or butatriene **7**, depending on the nature of the butadiynes, would be extremely interesting. To obtain more information about regioselectivity, we carried out the reaction of $ClMe_2SiSiMe_2Cl$ with 1,4-diphenylbutadiyne in the presence of $PdCl_2(PPh_3)_2$. The product obtained after methylation of the reaction mixture was (*Z*)-1,4-diphenyl-1,2-bis(trimethylsilyl)but-1-ene-3-yne (**11**) in 44% yield (Scheme 4). No product arising from 1,4-bis-silylation was detected in the reaction mixture. The result clearly indicates that *cis*-1,2-bis-silylation is more advantageous in the case of diphenylbutadiyne than formal 1,4-bis-silylation, regardless of the disilanes used.

In conclusion, we have found that the Si−Si bond of silole **1a** is readily activated with a Pd(II) catalyst and reacts with acetylene compounds to give bis-silylated cyclic adducts. The reaction proceeds in two different manners, depending on the nature of the acetylene used. With phenyl- and diphenylacetylene, 1-hexyne, or diphenylbutadiyne, 1,2-addition occurs to give **3**−**6**, while formal 1,4-addition takes place with bis(trimethylsilyl)butadiyne to give butatriene **7** exclusively.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry nitrogen. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on JEOL Model JNM-EX 270 and JEOL Model JNM-LA 400 spectrometers. EI mass spectra were measured with Shimadzu GCMS QP-1000, Hitachi M-80B, and JEOL Model JMS-700 spectrometers. UV spectra were measured on a Hitachi U-3210 spectrophotometer, and IR spectra were measured on a Perkin-Elmer FT-IR Model 1600 spectrometer.

Materials. THF, benzene, and toluene were dried over sodium−potassium alloy, lithium aluminum hydride, and sodium metal, respectively, and distilled just before use. Compound **1a** was prepared as reported in the literature.[2]

Reaction of 1a with Phenylacetylene. A mixture of 167 mg (0.353 mmol) of **1a**, 69 mg (0.676 mmol) of phenylacetylene, and 5 mg (0.007 mmol, 2 mol %) of $PdCl_2(PPh_3)_2$ in 5 mL of benzene was heated at 80 °C for 1 h. The resulting mixture was concentrated and chromatographed on silica gel using hexane as the eluent to give 150 mg (0.26 mmol, 74%) of adduct **3**: colorless crystals; ^1H NMR ($CDCl_3$, δ) 0.24 (s, 9H), 0.26 (s, 9H), 0.27 (s, 6H), 0.78 (q, $J = 8$ Hz, 4H), 0.87 (q, $J = 8$ Hz, 4H), 0.97 (t, $J = 8$ Hz, 6H), 1.09 (t, $J = 8$ Hz, 6H), 6.44 (s, 1H), 7.06−7.30 (m, 5H); ^{13}C NMR ($CDCl_3$, δ) −3.62, −0.48, −0.44 (SiMe), 6.60, 6.79, 7.48, 7.50 (Et), 99.47, 100.50, 107.27, 107.49 (C≡C), 125.99, 126.37, 127.87, 146.30, 146.90, 147.05, 149.68, 150.16, 150.53, 163.05 (sp^2 carbon); ^{29}Si NMR ($CDCl_3$, δ) −23.65, −20.10, −7.46, −7.26, 26.83; IR $\nu_{C\equiv C}$ 2136 cm^{-1}. Anal. Calcd for $C_{32}H_{50}Si_5$: C, 66.82; H, 8.76. Found: C, 66.66; H, 8.75.

Reaction of 1a with 1-Hexyne. A mixture of 159 mg (0.336 mmol) of **1a**, 270 mg (3.287 mmol) of 1-hexyne, and 17 mg (0.024 mmol, 7 mol %) of $PdCl_2(PPh_3)_2$ in 3 mL of benzene was heated at 80 °C for 5 h. The resulting mixture was concentrated and chromatographed on silica gel using hexane

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as the eluent to give 174 mg (0.313 mmol, 93%) of adduct **4**: colorless crystals; ^{1}H NMR ($CDCl_3$, δ) 0.196 (s, 29H), 0.20 (s, 9H), 0.21 (s, 6H), 0.73−1.56 (m, 9H), 6.29 (s, 1H); ^{13}C NMR ($CDCl_3$, δ) −3.65, −0.48 (2Si) (SiMe), 5.97, 6.60, 7.46, 7.75, 13.98, 22.48, 32.62, 43.87 (Et and *n*-Bu), 100.04, 100.95, 107.12, 107.19 (C≡C), 140.50, 147.04, 147.21, 149.16, 149.90, 161.83 (sp^2 carbon); ^{29}Si NMR ($CDCl_3$, δ) −24.47, −19.24, −7.57, −7.37, 26.61; IR $\nu_{C\equiv C}$ 2137 cm^{-1}. Anal. Calcd for $C_{30}H_{54}Si_5$: C, 64.90; H, 9.80. Found: C, 64.84; H, 10.17.

Reaction of 1a with Diphenylacetylene. A mixture of 50.7 mg (0.107 mmol) of **1a**, 414 mg (0.232 mmol) of diphenylacetylene, and 7.0 mg (0.010 mol, 9 mol %) of $PdCl_2(PPh_3)_2$ in 5 mL of benzene was heated at 80 °C for 20 h. The resulting mixture was concentrated and chromatographed on silica gel using hexane as the eluent to give 46.4 mg (0.0712 mmol, 67%) of adduct **5**: pale yellow oil; ^{1}H NMR ($CDCl_3$, δ) 0.24 (s, 18H), 0.27 (s, 6H), 0.65 (q, J = 8 Hz, 8H), 0.94 (t, J = 8 Hz, 12H), 6.6−6.7 (m, 4H), 6.8−7.0 (m, 6H); ^{13}C NMR ($CDCl_3$, δ) −3.57, −0.41 (SiMe), 6.64, 7.60 (Et), 101.00, 108.28 (C≡C), 124.68, 127.07, 127.97, 145.15, 147.37, 149.68, 157.01 (sp^2 carbon); ^{29}Si NMR ($CDCl_3$, δ) −20.79, −7.35, 26.82; IR $\nu_{C\equiv C}$ 2135 cm^{-1}. Anal. Calcd for $C_{38}H_{54}Si_5$: C, 70.08; H, 8.36. Found: C, 69.86; H, 8.53.

Reaction of 1a with 1,4-Diphenylbutadiyne. A mixture of 106 mg (0.223 mmol) of **1a**, 105 mg (0.518 mmol) of 1,4-diphenylbutadiyne, and 14 mg (0.020 mmol, 9 mol %) of $PdCl_2(PPh_3)_2$ in 5 mL of benzene was heated at 80 °C for 11 h. The resulting mixture was concentrated and separated by using recycle GPC with benzene solution to give 113 mg (0.167 mmol, 79%) of adduct **6**: yellow crystals; mp 114−117 °C; ^{1}H NMR ($CDCl_3$, δ) 0.26 (s, 9H), 0.287 (s, 9H), 0.290 (s, 6H), 0.71 (q, J = 8 Hz, 4H), 0.98 (t, J = 8 Hz, 6H), 1.05−1.25 (m, 10H), 6.9−7.4 (m, 10H); ^{13}C NMR ($CDCl_3$, δ) −3.62, −0.44, −0.42 (SiMe), 6.73, 6.84, 7.50, 7.59 (Et), 92.96, 99.59, 100.15, 100.91, 107.83, 108.04 (C≡C), 123.88, 125.75, 127.18, 127.78, 127.82, 128.04, 131.29, 135.55, 147.01, 147.05, 147.35, 149.97, 150.34, 167.09 (sp^2 carbon); ^{29}Si NMR ($CDCl_3$, δ) −20.71, −20.56, −7.30, −7.27, 26.98; UV (THF) λ_{max}/nm (ϵ) 249 (35 000), 276 (sh, 29 000), 310 (sh, 27 000), 323 (sh, 26 000), 353 (sh, 5800); IR $\nu_{C\equiv C}$ 2134 cm^{-1}. Anal. Calcd for $C_{40}H_{54}Si_5$: C, 71.15; H, 8.06. Found: C, 71.27; H, 8.28.

Reaction of 1a with 1,4-Bis(trimethylsilyl)butadiyne. A mixture of 106 mg (0.224 mmol) of **1a**, 95.9 mg (0.493 mmol) of 1,4-bis(trimethylsilyl)butadiyne, and 14 mg (0.019 mmol, 9 mol %) of $PdCl_2(PPh_3)_2$ in 5 mL of benzene was heated at 80 °C for 19 h. The resulting mixture was concentrated and separated using recycle GPC with benzene solution to give 98.7 mg (0.148 mmol, 66%) of adduct **7**: orange crystals; mp 170−173.5 °C; ^{1}H NMR ($CDCl_3$, δ) 0.197 (s, 36H), 0.204 (s, 6H), 0.8−0.9 (q, J = 8 Hz, 8H), 1.06 (t, J = 8 Hz, 12H); ^{13}C NMR ($CDCl_3$, δ) −3.81, −0.68, 0.50 (SiMe), 7.26, 7.79 (Et), 97.50, 104.89 (C≡C), 146.11, 152.26, 153.90 (sp^2 carbon), 210.36 (sp carbon); ^{29}Si NMR ($CDCl_3$, δ) −17.22, −8.43, −6.31, 25.23; UV (THF) λ_{max}/nm (ϵ) 250 (28 000), 291 (sh, 19 000), 306 (25 000), 335 (sh, 3700); IR $\nu_{C\equiv C}$ 2135 cm^{-1}. HRMS: calcd for $C_{34}H_{62}Si_7$, 666.3233; obsd, 666.3260.

X-ray Crystallographic Analysis of 7. All unique diffraction maxima with $5 < 2\theta < 45°$ for **7** were recorded on a Rigaku AFC-7R automated four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Refractions with $I > 2.9\sigma(I)$ were used in the least-squares refinement. The structure was solved by SIR92 direct methods[6] and expanded using DIRDIF94 Fourier techniques.[7] The non-hydrogen atoms were refined isotropically. Hydrogen atoms were included but not refined. No absorption correction or decay correction was applied. Neutral atom scattering factors were taken from Cromer and Waber.[8] Anomalous dispersion effects were included in Fcalc;[9] the value for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[10] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[11] All calculations were performed using the teXsan[12] crystallographic software package of Molecular Structure Corp.

Reaction of 1,4-Diphenylbutadiyne with $ClMe_2SiSiMe_2Cl$. A mixture of 1.17 g (6.25 mmol) of $ClMe_2SiSiMe_2Cl$, 224 mg (1.11 mmol) of 1,4-diphenylbutadiyne, and 63.8 mg (0.161 mmol, 7.8 mol %) of $PdCl_2(PPh_3)_2$ in 10 mL of toluene was heated under reflux for 13 h. At 0 °C the reaction mixture was added into an Et_2O solution of MeMgI, which was prepared by mixing Mg (343 mg, 22.3 mmol), MeI (2.41 g, 17.0 mmol), and Et_2O (40 mL). After it was stirred at 0 °C for 1 h and at room temperature for 2 h, the mixture was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with hexane. The organic layer and the extracts were combined, washed with water and brine, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure, and the residue was chromatographed on silica gel using hexane as the eluent to give 176 mg (0.505 mmol, 44%) of (*Z*)-1,4-diphenyl-1,2-bis(trimethylsilyl)-1-buten-3-yne (**11**). **11**: pale yellow crystals; mp 75−76 °C; ^{1}H NMR ($CDCl_3$, δ) 0.18 (s, 9H), 0.45 (s, 9H), 6.93−7.00 (m, 2H), 7.01−7.07 (m, 2H), 7.14−7.21 (m, 3H), 7.21−7.28 (m, 1H), 7.33−7.41 (m, 2H); ^{13}C NMR ($CDCl_3$, δ) 1.30, 1.32 (SiMe), 93.33, 99.48 (C≡C), 124.24, 125.30, 126.83, 127.53, 127.68, 127.96, 131.29, 137.18, 148.29, 169.59 (sp^2 carbon); ^{29}Si NMR ($CDCl_3$, δ) −6.92, −6.05; MS *m*/*z* 348 (M^+). Anal. Calcd for $C_{22}H_{28}Si_2$: C, 75.79; H, 8.10. Found: C, 75.73; H, 8.24.

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Supporting Information Available: Tables of atomic coordinates and bond lengths and angles for compound **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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