Reaction of Polysilacycloalkynes with $CpCo(CO)_2$ and $CpMn(CO)_3$

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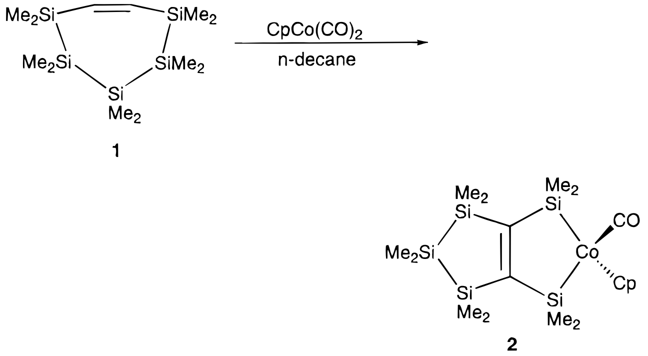
Reactions of a pentasilacycloheptyne and a hexasilacyclooctyne with $CpCo(CO)_2$ resulted in facile formation of metallapentene derivatives, and a tetrasilacyclohexyne gave a triene derivative. Photochemical reactions of $CpMn(CO)_3$ with the tetrasilacyclohexyne and the hexasilacyclooctyne gave vinylidene complexes. The vinylidene complex readily reacts with tetrasilacyclohexyne to yield the triene and a bis(allene) derivative. The structures of one of the metallapentenes and of the bis(allene) were determined by X-ray crystallographic analysis.

Introduction

The rearrangement of alkynes to vinylidenes in the coordination sphere of a transition metal has been intensively investigated in recent years.[1] The 1,2-silyl migration of a disilylacetylene to vinylidene complex proceeds analogously to the 1,2-hydrogen shift, and the corresponding manganese[2] and rhodium[3] vinylidene complexes have been isolated. The cyclotrimerization of alkynes in the presence of a $CpCoL_2$ catalyst to give benzene derivatives could be a synthetically useful reaction.[4] Intramolecular incorporation of an α,ω-diyne into a benzene derivative in the presence of a transition metal complex has been reported. Bis(trimethylsilyl)acetylene, which, as a result of steric factors, was prevented from undergoing cyclotrimerization, could be utilized as the third alkyne in the cyclization of α,ω-diynes to benzene derivatives in the presence of a $CpCoL_2$ complex.[5] Vollhardt et al. reported that, in the reaction of neat bis(trimethylsilyl)acetylene with $CpCo(CO)_2$, tetrakis(trimethylsilyl)butatriene was formed in low yield via a 1,2-silyl shift.[6] On the other hand, medium-ring cycloalkynes are the subjects of considerable current interest in view of their reactivity.[7] Recently, we have succeeded in the synthesis of polysilacycloalkynes which are highly reactive toward various compounds.[8] Herein we report the reactions of polysilacycloalkynes with $CpCo(CO)_2$ and $CpMn(CO)_3$.

Scheme 1



Results and Discussion

Reaction with $CpCo(CO)_2$. The reaction of the pentasilacycloheptyne **1** with $CpCo(CO)_2$ in boiling *n*-decane gave the metallapentene derivative **2** in 82% yield (Scheme 1); The yellow crystals of **2** are unstable toward oxygen. The structure of **2** was determined by spectroscopic and X-ray crystallographic analysis. In particular, the ^{29}Si NMR signal due to the silicon atom adjacent to the cobalt atom appears at 57.5 ppm. The structure of **2** is shown in Figure 1a (Tables 1 and 2). Notable features of the structure are as follows: (i) The length of the C=C double bond (=1.37(2) Å) of **2** is slightly longer than that of a normal double bond. (ii) The bond angle Si3−Si4−Si5 = 92.0° is found to be strained due to the small ring structure. $CpCo(CO)_2$ also reacted readily with hexasilacyclooctyne **3** to give yellow stable crystals, the metallapentene derivative **4**, in 52% yield (Scheme 2). The structure of **4** was determined by the spectral data. Typically, its ^{13}C NMR spectrum contains the characteristic sp^2 carbon signal at 194.1 ppm, the carbonyl carbon signal at 199.9 ppm, and resonances due to the six types of methyl groups. The ^{29}Si NMR spectrum contains three signals, two

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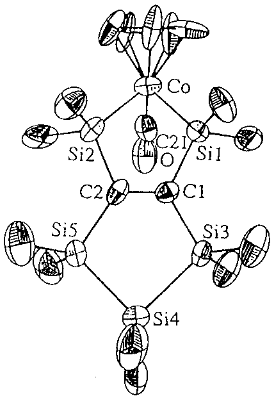


Figure 1. ORTEP drawing of metallapentene **2** showing the labeling scheme. Atoms are represented by thermal ellipsoids at the 50% level. Hydrogen atoms are omitted.

Table 1. Crystallographic Data for Diffraction Studies

	compd	
	2	**10**
empirical formula	$C_{18}H_{35}CoSi_{12}O$	$C_{30}H_{72}Si_{12}$
fw	466.84	769.94
cryst system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
lattice constants		
a, Å	7.226(1)	16.258(2)
b, Å	19.543(5)	18.221(2)
c, Å	18.338(3)	18.973(2)
α, deg		75.85(1)
β, deg	95.01(1)	71.41(1)
γ, deg		84.60(1)
V, Å^3	2579.6	5164.6
Z value	4	4
F(000)	992	1680
D_{calc}, g cm^{-3}	1.20	0.99
μ(Mo Kα), cm^{-1}	9.0	3.1
radiation (λ, Å)	Mo Kα (0.709 30)	Mo Kα (0.709 30)
$2\theta_{max}$, deg	50.0	41.8
temp, °C	23	23
no. of observns ($I > 3\sigma(I)$)	2985	8771
no. of variables	1678	8450
max shift/σ (last least-squares cycle)	2.72σ	2.48σ
largest peak in final diff map, e Å^{-3}	0.52(7)	0.65(8)
R, R_w	0.053, 0.060	0.089, 0.100

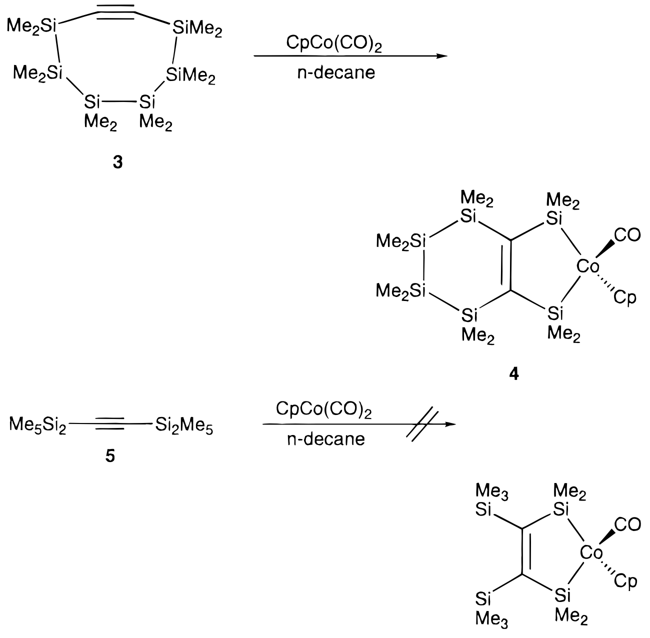
Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Metallapentene Derivative 2

Co−Si(1)	2.291(4)	Si(3)−C(1)	1.89(1)
Co−Si(2)	2.278(4)	Si(4)−Si(5)	2.339(5)
Si(1)−C(1)	1.88(1)	Si(5)−C(2)	1.88(1)
Si(2)−C(2)	1.90(1)	C(1)−C(2)	1.37(2)
Si(3)−Si(4)	2.346(5)		
Si(1)−Co−Si(2)	81.7(1)	Si(1)−C(1)−Si(3)	123.0(6)
Co−Si(1)−C(1)	108.5(4)	Si(1)−C(1)−C(2)	116.0(9)
Co−Si(2)−C(2)	108.8(4)	Si(3)−C(1)−C(2)	120.9(9)
Si(4)−Si(3)−C(1)	101.7(4)	Si(2)−C(2)−Si(5)	122.1(7)
Si(3)−Si(4)−Si(5)	92.0(2)	Si(2)−C(2)−C(1)	114.7(9)
Si(4)−Si(5)−C(2)	101.1(4)	Si(5)−C(2)−C(1)	123.2(9)

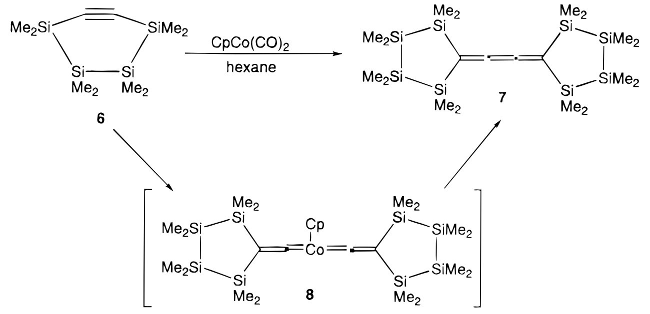
signals at −51.5 and −29.5 ppm, which are assigned as cyclic polysilane parts, and one signal at 61.0 ppm, indicative of a vinylsilane bound to cobalt. The reaction of the acyclic acetylene **5** with $CpCo(CO)_2$ under similar conditions did not give a metallapentene derivative, and only an as yet unidentified complex mixture was obtained. These results suggest that a ring structure is required for the formation of metallapentene derivative.

However, with tetrasilacyclohexyne **6** in boiling hexane, the triene derivative **7** was obtained in 52% yield (Scheme 3). No metallapentene derivative was isolated. The strucuture of **7** was determined by spectroscopic analysis. The $^{29}Si\{^1H\}$ NMR spectrum of **7** contains two types of dimethylsilyl groups, and the ^{13}C NMR spectrum shows resonances characteristic of the triene sp carbons at 207.6 and sp^2 carbon at 160.5 ppm. The IR C=C absorption was observed at 1545 cm^{-1}. Vollhardt and Day et al. reported the reaction of the bis(trimethylsilyl)acetylene with $CpCo(CO)_2$ to give the triene derivative, via a bis(vinylidene) complex, in low yield.[4] The bis(vinylidene) complex **8** might be formed in a 1,2-silyl shift of **6** to give **7**, probably because of the highly reactive acetylene function.

Scheme 2



Scheme 3



Reaction with $CpMn(CO)_3$. The photochemical reaction of **6** with $CpMn(CO)_3$ gave the vinylidene complex **9** and **7** in 46 and 11% yield, respectively, together with a small amount of trimer **10** (Scheme 4). Sakurai et al.[2] reported that both cyclic and acyclic acetylenes substituted by two silyl groups undergo a 1,2-silyl shift in their reactions with $CpMn(CO)_2(THF)$. The structure of **10** was determined by spectroscopic and X-ray crystallographic analysis. The ^{13}C NMR spectrum of **10** shows the characteristic allenic sp carbon resonance at 204.7 ppm and signals due to two types of sp^2 carbon atoms at 75.4 and 78.6 ppm, respectively. The IR spectrum shows the characteristic C=C=C absorption at 1879 cm^{-1}. The molecular structure of **10** is shown in Figure 2 (Tables 1 and 3). The bond lengths and angles of **10** are almost normal. The triene derivative **7** is considered to be formed by the reaction of **9**

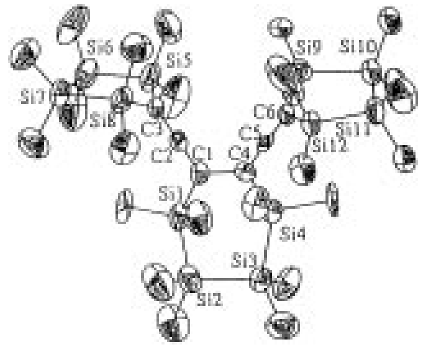


Figure 2. ORTEP drawing of bis(allene) **10** showing the labeling scheme. Atoms are represented by thermal ellipsoids at the 50% level. Hydrogen atoms are omitted. Only one of two molecules in the unit cell is shown.

Scheme 4

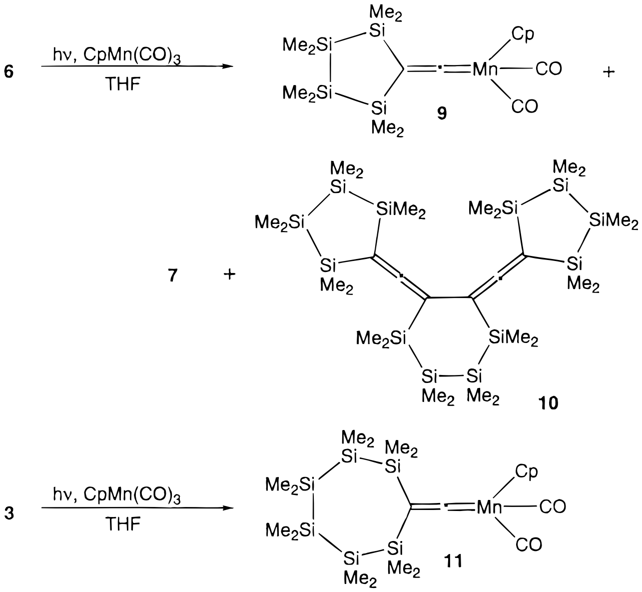


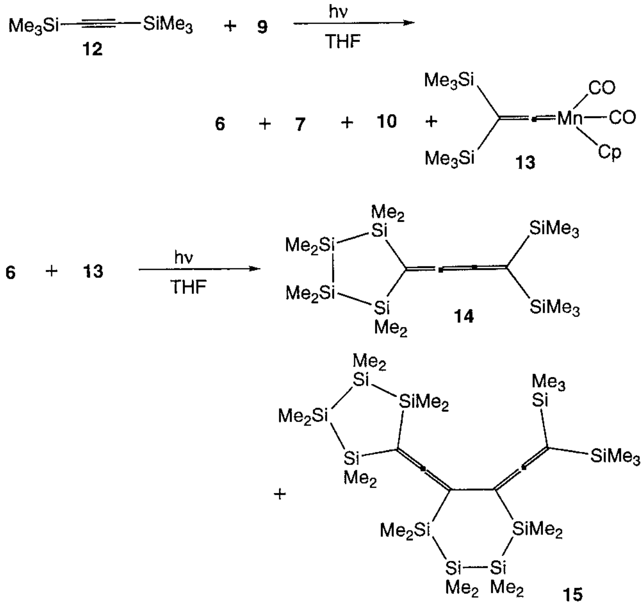
Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for Bis(allene) 10

Si(1)–Si(2)	2.348(8)	Si(9)–Si(10)	2.360(7)
Si(1)–C(1)	1.84(2)	Si(9)–C(6)	1.87(1)
Si(2)–Si(3)	2.321(7)	Si(10)–Si(11)	2.363(6)
Si(3)–Si(4)	2.330(7)	Si(11)–Si(12)	2.354(7)
Si(4)–C(4)	1.88(1)	Si(12)–C(6)	1.85(1)
Si(5)–Si(6)	2.326(7)	C(1)–C(2)	1.29(2)
Si(5)–C(3)	1.88(2)	C(1)–C(4)	1.59(2)
Si(6)–Si(7)	2.351(7)	C(2)–C(3)	1.32(2)
Si(7)–Si(8)	2.340(7)	C(4)–C(5)	1.30(2)
Si(8)–C(3)	1.86(1)	C(5)–C(6)	1.31(2)

Si(2)–Si(1)–C(1)	110.7(5)	Si(1)–C(1)–C(4)	120.5(9)
Si(1)–Si(2)–Si(3)	103.9(3)	C(2)–C(1)–C(4)	117(1)
Si(2)–Si(3)–Si(4)	103.7(2)	C(1)–C(2)–C(3)	177(1)
Si(3)–Si(4)–C(4)	110.6(5)	Si(5)–C(3)–Si(8)	118.8(7)
Si(6)–Si(5)–C(3)	102.7(5)	Si(5)–C(3)–C(2)	120(1)
Si(5)–Si(6)–Si(7)	100.9(3)	Si(8)–C(3)–C(2)	120(1)
Si(6)–Si(7)–Si(8)	100.4(3)	Si(4)–C(4)–C(1)	121(1)
Si(7)–Si(8)–C(3)	102.0(5)	Si(4)–C(4)–C(5)	118(1)
Si(10)–Si(9)–C(6)	102.1(4)	C(1)–C(4)–C(5)	120(1)
Si(9)–Si(10)–Si(11)	100.3(2)	C(4)–C(5)–C(6)	176(1)
Si(10)–Si(11)–Si(12)	100.7(2)	Si(9)–C(6)–Si(12)	119.6(9)
Si(11)–Si(12)–C(6)	102.5(5)	Si(9)–C(6)–C(5)	118.7(9)
Si(1)–C(1)–C(2)	122(1)	Si(12)–C(6)–C(5)	120(1)

with **6**. In fact, the photochemical reaction of **9** with **6** gave **7** and **10** in 30 and 18% yield, respectively. Similarly, hexasilacyclooctyne **3** reacted with CpMn(CO)$_3$ to give the vinylidene complex **11** in 36% yield. The vinylidene complex **9** is much more reactive toward acetylenes. When vinylidene complex **9** was irradiated in a solution of **3** with a high-pressure mercury lamp, the vinylidene complex **11** was formed in 30% yield together with traces of **6**, **7**, and **10**. Formation of **11** is thought to involve decomposition of **9** to give **6** and CpMn(CO)$_3$ followed by the reaction with **3**. In fact, vinylidene complex **11** is also obtained in the photochemical reaction of **3** in the presence of CpMn(CO)$_3$. The photochemical reaction of **9** with **12** yielded **13** together with traces of **6**, triene **7**, and **10** (Scheme 5).

Scheme 5

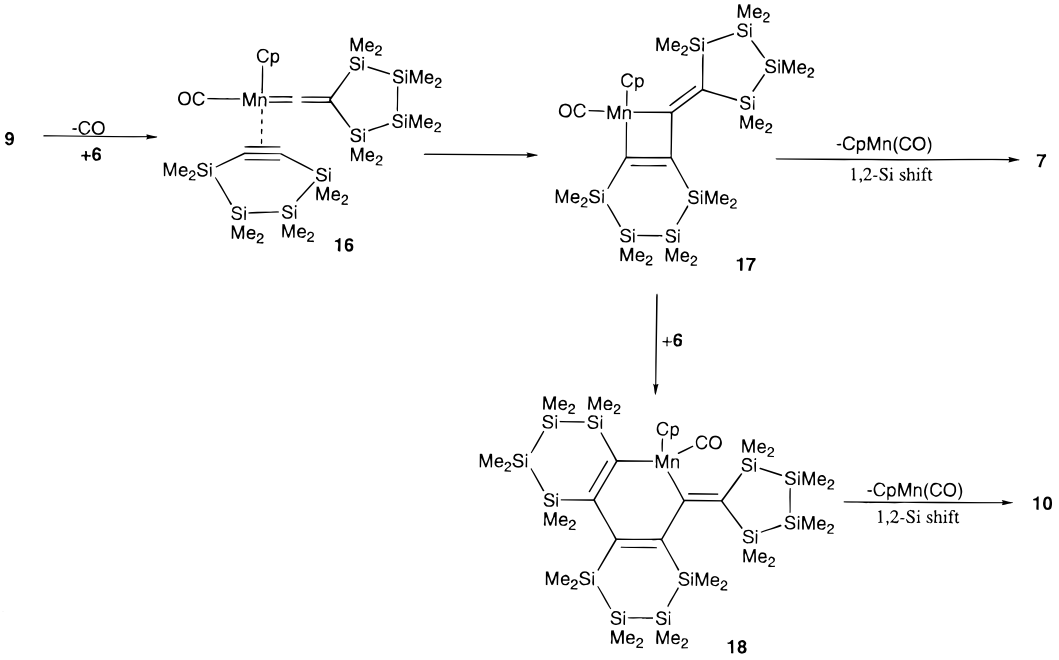


The vinylidene complex **13** reacts with **3** to give **12** and **11**, respectively, in 35% total yield, respectively. Nevertheless, no corresponding triene and bis(allene) derivatives were found. The vinylidene complex **13** also reacts with **6** to give **14** and **15** in 5 and 10% yield, respectively, together with traces of **9** and **12** (Scheme 5). The structures of compounds **14** and **15** were determined by spectroscopic analysis. The ^{1}H and ^{13}C NMR spectra of **14** show three types of silylmethyl groups. The ^{13}C NMR spectrum shows signals due to two types of triene sp carbon atoms and two types of sp^{2} carbon atoms. The ^{13}C NMR spectrum of **15** shows signals due to two types of allenic sp carbon atoms and four types of sp^{2} carbon atoms. These results indicate that only when **6** reacts with vinylidene complexes are triene and bis(allene) derivatives formed. The reaction mechanism of complex formation is shown in Scheme 6. A dissociation of a carbonyl ligand from **9** generates an alkyne vinylidene complex, **16**, which would be expected to form the metallacyclobutene **17**. The triene **7** was formed by reductive elimination reaction of **17** along with a 1,2-silyl shift. Insertion of a second molecule of **6** forms metallacyclohexadiene **18**. A reductive elimination reaction of **18** along with the 1,2-silyl shift results in the formation of **10**.

Experimental Section

Melting points were measured on a Yanaco micro melting point apparatus and are uncorrected. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a JEOL JNM-EX 90 (^{1}H, 90 MHz; ^{13}C, 22.5 MHz; ^{29}Si, 17.6 MHz), a Bruker AC-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{29}Si, 79.5 MHz), or a Bruker AC-300 (^{1}H, 300 MHz; ^{13}C, 75 MHz; ^{29}Si, 60 MHz) spectrometer. Infrared spectra were measured on a JASCO FT/IR-5000 spectrometer. UV–vis spectra were measured on a JASCO Ubest-50 spec-

Scheme 6



trometer with samples as either neat liquids or KBr disks. Mass and high-resolution mass spectra were obtained on a Shimadzu QP-2000 and JEOL JMS SX102A mass spectrometer, respectively. Gas chromatography was performed on a Hitachi G-3000 with a capillary column (OV1, 0.25 mm × 5 m). TLC and preparative TLC (PLC) were performed with Merck Kieselgel 60PF$_{254}$. Column chromatography was performed using a Merck Kieselgel 60. Gel-permeation chromatography (GPC) was performed using a JAI LC-08 and LC-908 liquid chromatography instrument with a JAIGEL-1H column (20 mm × 600 mm × 2) and toluene as eluent. All solvents were predried by standard methods, and all the reactions were carried out under an inert atmosphere.

Reaction of Pentasilacycloheptyne 1 with Cyclopentadienylcobalt Dicarbonyl. An *n*-decane solution (10 mL) of pentasilacycloheptyne **1**[8c] (30 mg 0.0953 mmol) was added to cyclopentadienylcobalt dicarbonyl (20 mg 0.111 mmol) at room temperature. The mixture was refluxed for 24 h. After removal of the solvent, 36.5 mg of metallapentene derivative **2**[8c] (82%) remained. It was purified by chromatography on silica gel (hexane) to give yellow crystals. Mp: 108−110 °C. HRMS (EI, 20 eV), *m/e*: Calcd for $C_{18}H_{35}OSi_5Co$, 466.0905; found, 466.0866. LRMS (EI, 70 eV): *m/e* 466 (M^+), 428 ($M^+ - CO$). ^1H NMR (C_6D_6, 400 MHz): δ 0.31 (s, 3H), 0.32 (s, 3H), 0.43 (s, 6H), 0.52 (s, 6H), 0.55 (s, 6H), 0.89 (s, 6H), 4.44 (s, 5H). ^{13}C NMR (C_6D_6, 100 MHz): δ −8.0 (q), −7.8 (q), −1.1 (q), −0.7 (q), 8.9 (q), 9.6 (q), 86.6 (d), 200.0 (s), 202.1 (s). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ −49.4, −11.3, 57.5. IR (KBr): 1970 (C=O) cm^{-1}.

Reaction of Hexasilacyclooctyne 3 with Cyclopentadienylcobalt Dicarbonyl. A similar reaction of hexasilacyclooctyne **3**[8c] (300 mg, 0.804 mmol) with cyclopentadienylcobalt dicarbonyl (145 mg 0.805 mmol) gave compound **4** (305 mg, 72% yield). **4** was purified by TLC on silica gel (hexane) giving yellow crystals. Mp: 96−98 °C. Anal. Calcd for $C_{20}H_{41}OSi_6Co$: C, 45.75; H, 7.87. Found: C, 45.52; H, 7.66. HRMS (EI, 20 eV), *m/e*: Calcd for $C_{20}H_{41}OSi_6Co$, 524.1105; found, 524.1065. LRMS (EI, 70 eV): *m/e* 524 (M^+), 496 ($M^+ - CO$). ^1H NMR (C_6D_6, 300 MHz): δ 0.332 (s, 6H), 0.328 (s, 6H), 0.46 (s, 6H), 0.54 (s, 6H), 0.60 (s, 6H), 0.96 (s, 6H), 4.43 (s, 5H). ^{13}C NMR (C_6D_6, 75 MHz): δ −6.1 (q), −5.9 (q), −0.2 (q), 0.7 (q), 9.1 (q), 11.8 (q), 87.0 (d), 194.1 (s), 199.9 (s). ^{29}Si NMR (C_6D_6, 60 MHz): δ −51.5, −29.5, 61.0. IR (KBr): 1970 (C=O) cm^{-1}.

Reaction of Tetrasilacyclohexyne 6 with Cyclopentadienylcobalt Dicarbonyl. A hexane solution (10 mL) of tetrasilacyclohexyne **6** (100 mg, 0.390 mmol) was added to cyclopentadienylcobalt dicarbonyl (70.2 mg, 0.390 mmol) at room temperature. The mixture was heated at reflux for 30 min. After removal of the solvent, 52.1 mg of triene derivative **7** (52%) remained. It was purified by chromatography on silica gel (hexane) to yield pinkish crystals. Mp: 99−101 °C. Anal. Calcd for $C_{20}H_{48}Si_8$: C, 46.80; H, 9.43. Found: C, 47.02; H, 9.44. HRMS (EI, 20 eV), *m/e*: Calcd for $C_{20}H_{48}Si_8$, 512.1910; found, 512.1921. LRMS (EI, 70 eV): *m/e* 512 (M^+), 497 ($M^+ - CO$). ^1H NMR (C_6D_6, 400 MHz): δ 0.34 (s, 24H), 0.49 (s, 24H). ^{13}C NMR (C_6D_6, 100 MHz): δ −6.4 (q), −1.6 (q), 160.5 (s), 207.6 (s). ^{29}Si NMR (C_6D_6, 17.6 MHz): δ −46.3, −18.3. IR (neat): 1545 (C=C) cm^{-1}. UV (hexane): 339 (5100), 306 (5200) nm.

Photochemical Reaction of Tetrasilacyclohexyne 6 with Cyclopentadienylmaganese Tricarbonyl. A THF solution (30 mL) of **6** (192 mg, 0.748 mmol), cyclopentadienylmaganese tricarbonyl (256 mg, 1.25 mmol), and *n*-decane as an internal standard was irradiated with a high-pressure mercury lamp (400 W) through a Pyrex filter for 1 h. After removal of the solvent, the reaction mixture was purified by HPLC to give 149 mg of **9** (46%), 21.1 mg of **7** (11%), and 3.21 mg of **10** (2%), respectively. **9**: yellow crystals; mp 55−57 °C. Anal. Calcd for $C_{17}H_{29}O_2Si_4Mn$: C, 47.18; H, 6.76. Found: C, 46.94; H, 6.57. HRMS (EI, 20 eV), *m/e*: Calcd for $C_{17}H_{29}$O2Si$_4$Mn, 432.0161; found, 432.0625. LRMS (EI, 70 eV): *m/e* 432 (M^+), 496 ($M^+ - CO$). ^1H NMR (C_6D_6, 300 MHz): δ 0.28 (s, 12H), 0.52 (s, 12H), 4.42 (s, 5H). ^{13}C NMR (C_6D_6, 75 MHz): δ −6.7 (q), −0.7 (q), 85.7 (d), 109.7 (s), 229.3 (s), 332.0 (s). ^{29}Si NMR (C_6D_6, 60 MHz): δ −43.8, −6.3. IR (KBr): 1980 (C=O), 1918 (C=O) cm^{-1}. **10**: colorless crystals; mp 137−139 °C. LRMS (EI, 70 eV): *m/e* 768 (M^+). ^1H NMR (C_6D_6, 300 MHz): δ 0.374 (s, 12H), 0.377 (s, 12H), 0.39 (s, 12H), 0.43 (s, 12H), 0.48 (s, 12H), 0.49 (s, 12H). ^{12}C NMR (C_6D_6, 75 MHz): δ −6.2 (q), −6.1 (q), −5.8 (q), −2.0 (q), −1.3 (q), 0.35 (q), 75.4 (s), 78.6 (s), 204.7 (s). ^{29}Si NMR (C_6D_6, 60 MHz): δ −47.8, −46.0, −21.0, −14.3. IR (KBr): 1879 (C=C=C) cm^{-1}.

Photochemical Reaction of Hexasilacyclooctyne 3 with Cyclopentadienylmaganese Tricarbonyl. A THF solution (30 mL) of hexasilacyclooctyne **3** (287 mg, 0.770 mmol), cyclopentadienyltricarbonylmanganese (157 mg, 0.769 mmol), and *n*-decane as an internal standard was irradiated with a high-pressure mercury lamp (400 W) through a Pyrex filter for 12 h. After removal of the solvent, the reaction mixture was purified by HPLC to give 150 mg of **11** (35%): yellow crystals; mp 84−85 °C. Anal. Calcd for $C_{21}H_{41}O_2Si_6Mn$: C, 45.94; H, 7.53. Found: C, 45.82; H, 7.38. LRMS (EI, 70 eV): *m*/*e* 548 (M^+), 492 ($M^+ - 2CO$). ^{1}H NMR (C_6D_6, 400 MHz): δ 0.34 (s, 12H), 0.36 (s, 12H), 0.50 (s, 12H), 4.42 (s, 5H). ^{13}C NMR (C_6D_6, 100 MHz): δ −5.3 (q), −4.8 (q), 1.1 (q), 86.2 (s), 229.4 (s), 335.4 (s). ^{29}Si NMR (C_6D_6, 80 MHz): δ −42.81, −42.78, −17.9. IR (KBr): 1975 (C═O), 1923 (C═O) cm^{-1}.

Photochemical Reaction of Tetrasilacyclohexyne 6 with Triene 7. A THF solution (5 mL) of tetrasilacyclohexyne **6** (50 mg 0.195 mmol) and triene **7** (28 mg, 0.0546 mmol) was irradiated with a high-pressure mercury lamp (400 W) through a Pyrex filter for 13 h. Trimer **10** was not observed on GLC analysis. After removal of the solvent, the reaction mixture was purified by TLC on silica gel (hexane). The triene derivative (25 mg, 0.048 mmol) was isolated (89%).

Photochemical Reaction of Tetrasilacyclohexyne 6 with Vinylidene Complex 9. A THF solution (15 mL) of **6** (56 mg, 0.220 mmol), **9** (115 mg, 0.266 mmol) and *n*-decane as an internal standard was irradiated with a high-pressure mercury lamp (400 W) through a Pyrex filter for 3 h. After removal of the solvent, the reaction mixture was purified by HPLC to give 41 mg of unreacted **9**, 26 mg of **7** (30% yield), and 15 mg of **10** (18% yield).

Photochemical Reaction of Hexasilacyclooctyne 3 with Vinylidene Complex 9. A THF solution (5 mL) of **3** (44 mg, 0.116 mmol), **9** (50 mg, 0.116 mmol), and *n*-decane as an internal standard was irradiated with a high-pressure mercury lamp (400 W) through a Pyrex filter for 3 h. After removal of the solvent, the reaction mixture was purified by HPLC to give 30 mg of **11** (30% yield). Traces of **6**, **7**, and **10** were observed by GLC.

Photochemical Reaction of Bis(trimethylsilyl)acetylene (12) with Vinylidene Complex 9. A THF solution (5 mL) of **12** (28 mg, 0.164 mmol), **9** (71 mg, 0.164 mmol), and *n*-decane as an internal standard was irradiated with a high-pressure mercury lamp (400 W) through a Pyrex filter for 3 h. Traces of **6**, **7**, **10**, and **13** were observed by GLC and NMR spectroscopy.

Photochemical Reaction of Hexasilacyclooctyne 3 with Vinylidene Complex 13. A THF solution (15 mL) of **3** (118 mg, 0.316 mmol), **13** (110 mg, 0.318 mmol), and *n*-decane as an internal standard was irradiated with a high-pressure mercury lamp (400 W) through a Pyrex filter for 3 h. After removal of the solvent, the reaction mixture was purified by HPLC to give 60 mg of **11** (35% yield); **12** was observed by GLC.

Photochemical Reaction of Tetrasilacyclohexyne 6 with Vinylidene Complex 13. A THF solution (15 mL) of **6** (106 mg, 0.413 mmol), **13** (143 mg, 0.413 mmol), and *n*-decane as an internal standard was irradiated with a high-pressure mercury lamp (400 W) through a Pyrex filter for 3 h. After removal of the solvent, the reaction mixture was purified by HPLC to give 25 mg of **9**, 22 mg of **13**, 9 mg of triene derivative **14** (5% yield), and 14 mg of trimer **15** (10% yield). **14**: pinkish crystals; mp 79−81 °C. Anal. Calcd for $C_{18}H_{42}Si_6$: C, 50.62; H, 9.91. Found: C, 50.95; H, 9.61. HRMS (EI, 20 eV), *m*/*e*: Calcd for $C_{18}H_{42}Si_6$, 426.1902; found, 426.1884. LRMS (EI, 70 eV): *m*/*e* 426 (M^+). ^{1}H NMR (C_6D_6, 400 MHz): δ 0.35 (s, 12H), 0.39 (s, 18H), 0.48 (s, 12H). ^{13}C NMR (C_6D_6, 100 MHz): δ −6.5 (q), −1.4 (q), 0.8 (q), 157.7 (s), 160.2 (s), 206.0 (s), 209.2 (s). ^{29}Si NMR (C_6D_6, 17.6 MHz): δ −46.5, −17.1, −7.9. IR (neat): 1545 (C═C) cm^{-1}. UV (cyclohexane): 305 (25 000), 525 (220), 480 (sh, 60) nm. **15**: colorless crystals; mp 100−103 °C. LRMS (EI, 70 eV): *m*/*e* 682 (M^+). HRMS (EI, 20 eV), *m*/*e*: Calcd for $C_{28}H_{66}Si_{10}$, 682.2857; found, 682.2842. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.360 (s, 18H), 0.362 (s, 12H), 0.38 (s, 6H), 0.39 (s, 6H), 0.40 (s, 6H), 0.43 (s, 6H), 0.46 (s, 6H), 0.47 (s, 6H). ^{13}C NMR (C_6D_6, 75 MHz): δ −6.3 (q), −6.2 (q), −6.0 (q), −2.0 (q), −1.7 (q), −1.2 (q), −0.01 (q), 1.5 (2 × q), 75.1 (s), 75.3 (s), 78.82 (s), 78.84 (s), 204.7 (s), 207.5 (s). ^{29}Si NMR (C_6D_6, 60 MHz): δ −48.1, −48.0, −46.5, −21.3, −21.2, −14.5, −4.0. IR (KBr): 1879 (C═C═C) cm^{-1}.

Crystallographic Analysis. Colorless crystals (0.20 × 0.20 × 0.30 mm for **2** and 0.20 × 0.20 × 0.20 mm for **10**), obtained from hexane solution at 25 °C, were used for X-ray analyses. Diffraction measurements were made on an Enraf-Nonius CAD4 computer-controlled diffractometer by using graphite-monochromatized Mo Kα radiation. The unit cell was determined and refined from 25 randomly selected reflections obtained using the CAD4 automatic search, center, index, and least-squares routines. Crystal data and data collection parameters and results of the analyses are listed in Table 1. All data processing was performed on a Micro VAX 3100 computer using the SDP and MOLEN structure-solving program obtained from Enraf-Nonius Corp., Delft, The Netherlands. The $\omega-\theta$ scan technique was adopted by varying the ω scan width. All intensities were corrected for Lorentz and polarization factors as well as decay. An empirical absorption correction based on a series of ψ-scans was also applied to the data. Neutral-atom scattering factors were calculated by the standard procedures.[9a] An anomalous dispersion correction was applied to all non-hydrogen atoms.[9b] Full-matrix least-squares refinements minimized the function $\sum w(|F_o| - |F_c|)^2$, $w = 1$. Compound **2** crystallized in the monoclinic crystal system. From the systematic absences of $h0l$, $l = 2n$, and $0k0$, $k = 2n$, and from subsequent least-squares refinement, the space group was determined to be $P2_1/c$. The structure was solved by a combination of direct methods (MULTAN) and difference Fourier syntheses. Hydrogen atoms were not included in the calculations.

Compound **10** crystallized in the triclinic crystal system. There was no systematic absences; the space group was determined to be $P\bar{1}$ bar. The structure was solved by a combination of direct methods (SIR) and difference Fourier syntheses. Hydrogen atoms were not included in the calculations.

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Supporting Information Available: Text describing X-ray procedures, tables of atom coordinates, thermal parameters, and bond distances and angles, and ORTEP diagrams (57 pages). Ordering information is given on any current masthead page.

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