mmol, 3.55 equiv) of 1, 32.9 mg (0.168 mmol) of ketal, 10.7 mg (0.065 mmol) of $(C_6H_5)_2CH_2$ standard, and 0.30 mL of CD_3CN, as described above for cyclohexanone dimethyl ketal. After 3 days, ^1H NMR analysis showed 1 to be consumed. GLC analysis showed starting ketal (58%), 1-cyclohexenyl allyl ether (42%), and $H_2C{=}CHCH_2OSi(CH_3)_3$ (48%).

Reaction of Trimethyl Orthoacetate with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 70 mg (0.261 mmol, 1.35 equiv) of 1, 23.2 mg (0.193 mmol) of orthoacetate, 14.0 mg (0.085 mmol) of $C_6H_5CH_2Si(CH_3)_3$, and 0.30 mL of CD_3CN as described above for cyclohexanone dimethyl ketal. After 1.5 h, ^1H NMR analysis showed 1 to be consumed and a trace of $(CO)_5MnCH_3$ (δ -0.15). GLC analysis indicated 30%, 60%, and 35% yields of $CH_3CO_2CH_3$, $CH_3OSi(CH_3)_3$, and starting material, respectively. An IR spectrum of an aliquot showed weak absorbances (2090, 2000, 1972 cm^{-1}) attributable to $(CO)_5MnCH_3$.[42]

Reaction of Triethyl Orthoacetate with 1. A reaction was conducted at 50 °C in a 5-mm NMR tube with 70 mg (0.261 mmol, 1.48 equiv) of 1, 28.4 mg (0.176 mmol) of orthoacetate, 9.6 mg (0.060 mmol) of $C_6H_5CH_2Si(CH_3)_3$, and 0.30 mL of CD_3CN as described above for trimethyl orthoacetate. After 1.5 h, ^1H NMR analysis showed 1 to be consumed. GLC analysis indicated 32%, 40%, and 8% yields of $CH_3CO_2CH_2CH_3$, $CH_3CH_2OSi(CH_3)_3$, and starting material, respectively.

Acknowledgment. We thank the National Science Foundation for support. FT NMR spectrometers utilized in this study wre provided by NSF Departmental instrumentation grants.

Registry No. 1, 26500-16-3; 2, 53119-71-4; (*Z*)-3, 53119-73-6; (*E*)-3, 53119-72-5; (*E*)-4, 82996-09-6; (*Z*)-4, 82996-10-9; 5, 14031-96-0; 6, 83024-95-7; 7, 82996-11-0; cyclohexanone dimethyl ketal, 933-40-4; 2-methylcyclohexanone dimethyl ketal, 38574-09-3; cyclopentanone dimethyl ketal, 931-94-2; 2-norbornanone dimethyl ketal, 10395-51-4; acetone dimethyl ketal, 77-76-9; cyclooctanone dimethyl ketal, 25632-03-5; 5-nonanone dimethyl ketal, 69470-13-9; acetophenone dimethyl ketal, 4316-35-2; cyclopropyl methyl ketone dimethyl ketal, 52829-97-7; 4-methyl-2-pentanone dimethyl ketal, 1112-78-3; 1-methoxycyclohexene, 931-57-7; 1-methoxy-2-methylcyclohexene, 1728-38-7; 1-methoxy-6-methylcyclohexene, 1728-37-6; 1-methoxycyclopentene, 1072-59-9; 2-methoxy-2-norbornene, 17190-90-8; 2-methoxypropene, 116-11-0; 1-methoxycyclooctene, 50438-51-2; (*E*)-5-methoxy-4-nonene, 82215-72-3; (*Z*)-5-methoxy-4-nonene, 82215-71-2; 1-(methoxyethenyl)benzene, 4747-13-1; 1-(methoxyethenyl)cyclopropane, 66031-87-6; 1,3,3-trimethoxybutane, 6607-66-5; 2,4-dimethoxybutene, 52128-62-8; 3,3-dimethoxy-1-butene, 72757-52-9; 2-methoxy-1,3-butadiene, 3588-30-5; 2-methoxytetrahydropyran, 6581-66-4; hydrocinnamaldehyde dimethyl acetal, 30076-98-3; cyclohexanone ethylene glycol ketal, 177-10-6; cyclohexanone diallyl ketal, 53608-84-7; 1-cyclohexenyl allyl ether, 79643-88-2; trimethyl orthoacetate, 1445-45-0; triethyl orthoacetate, 78-39-7; $(CO)_5MnCOCH(OCH_3)CH_2CH_2C_6H_5$, 83005-51-0.

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[42] Closson, R. D.; Kozikowski, J.; Coffield, T. H. *J. Org. Chem.* **1957**, *22*, 598.

Palladium-Catalyzed Formation of 1,4-Disilacyclohexa-2,5-dienes from 1-Silacyclopropenes

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Received June 3, 1982

When 3-(trimethylsilyl)-, 3-(ethyldimethylsilyl)-, 3-(*tert*-butyldimethylsilyl)-, or 3-(phenyldimethylsilyl)-1,1-dimethyl-2-phenyl-1-silacyclopropene was heated with a catalytic amount of dichlorobis(triethylphosphine)palladium(II) in a sealed glass tube at 120 °C, the respective 1,4-disilacyclohexa-2,5-diene was produced with high regioselectivity. Under identical conditions, 1-methyl-1,2-diphenyl-3-(trimethylsilyl)-1-silacyclopropene afforded *trans*-1,4-dimethyl-1,2,4,5-tetraphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (**10**) as the sole product. Similar reaction of 1,1,2-triphenyl-3-(trimethylsilyl)-1-silacyclopropene gave 1,1,2,4,4,5-hexaphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene. Treatment of 1,2-dimethyl-1-phenyl-3-(trimethylsilyl)-1-silacyclopropene with the same catalyst in hexane gave *trans*-1,2,4,5,-tetramethyl-1,4-diphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene. The crystal structure of **10** has been determined. Compound **10** crystallizes in the orthorhombic space group *Pbca* with cell dimensions $a = 20.771$ (4) Å, $b = 18.842$ (3) Å, $c = 9.201$ (1) Å; $V = 3600.7$ (1) Å^3; $D_{calcd} = 1.087$ ($Z = 4$) Mg m^{-3}.

Introduction

Although considerable attention has been devoted to investigations of silacyclopropenes,[2] much less interest has been shown in the reaction of these compounds with transition-metal complexes.[3-6] Recently, we have reported that the nickel-catalyzed reaction of the silacyclopropenes prepared by the photolysis of (phenylethynyl)disilanes in the presence of phenylsilylacetylenes affords 1-silacyclopenta-2,4-dienes arising from two-atom insertion of the acetylene into a silicon–carbon bond in the silacyclopropene ring in excellent yields.[7] However, the palladium-catalyzed reaction of the silacyclopropenes led to the

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[1] (a) Department of Synthetic Chemistry in Kyoto University. (b) Department of Chemistry in Osaka City University.

[2] Ishikawa, M.; Nishimura, K.; Sugisawa, H.; Kumada, M. *J. Organomet. Chem.* **1980**, *194*, 147 and references cited therein.

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[5] Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879.

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[7] Ishikawa, M.; Sugisawa, H.; Harata, O.; Kumada, M. *J. Organomet. Chem.* **1981**, *217*, 43.

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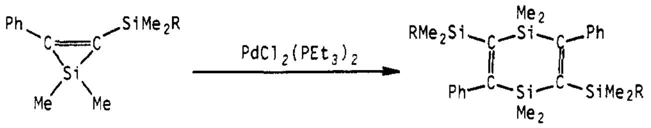
Scheme I



1, R = Me
3, R = Et
5, R = *tert*-Bu
7, R = Ph

2, R = Me
4, R = Et
6, R = *tert*-Bu
8, R = Ph

results different from those of the nickel catalyst. For examples, we[4] and Sakurai et al.[5] found independently that treatment of 1,1-dimethyl-2-phenyl-3-(trimethylsilyl)-1-silacyclopropene with a catalytic amount of a palladium(II) complex in the presence or absence of phenyl(trimethylsilyl)acetylene gave 1,1,4,4-tetramethyl-2,5-diphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene as the sole product. Seyferth and his co-workers[6] reported that the reaction of 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacyclopropene with methyl(trimethylsilyl)acetylene in the presence of a palladium(II) catalyst afforded 1,1,2,4,4,5-hexamethyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene, whereas with methylphenylacetylene two-atom insertion of this acetylene into a silicon–carbon bond in the silacyclopropene ring took place. Furthermore, Seyferth et al.[3,6] and Sakurai et al.[5] found that, with terminal acetylenes under the same conditions, the silacyclopropenes gave 3,4-disubstituted 1-silacyclopenta-2,4-dienes produced formally from two molecules of the terminal acetylene and a silylene molecule. It has been known that dimethylsilylene generated by the palladium-catalyzed reaction of 1,1,2,2-tetramethyldisilane reacts with phenylacetylene to give 1,1-dimethyl-3,4-diphenyl-1-silacyclopenta-2,4-diene.[8]

In this paper, we describe the reaction of photochemically generated 1-silacyclopropenes with a catalytic amount of dichlorobis(triethylphosphine)palladium(II).

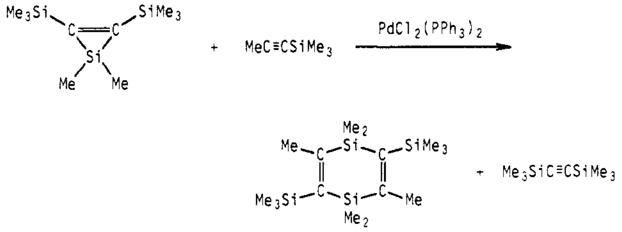
Results and Discussion

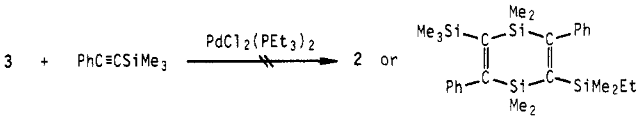
The silacyclopropenes used were synthesized by the photolysis of substituted ethynyldisilanes according to the method reported previously.[9a] All palladium-catalyzed reactions of the silacyclopropenes, excepting 1,2-dimethyl-1-phenyl-3-(trimethylsilyl)-1-silacyclopropene, were carried out at 120 °C in the absence of solvent in sealed glass tubes.

The most important result of our experiments is that the silacyclopropenes described here readily undergo dimerization with high regio and stereoselectivity. Thus, from 1,1-dimethyl-2-phenyl-3-(trimethylsilyl)-1-silacyclopropene (**1**), 1,1,4,4-tetramethyl-2,5-diphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene[4] (**2**) was produced in 70% yield (Scheme I). No other isomers such as 1,1,4,4,-tetramethyl-2,6-diphenyl-3,5-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene which was obtained in the thermolysis of **1**[9b] were detected spectroscopically. The palladium-catalyzed reaction of **1** in the presence of phenyl(trimethylsilyl)acetylene also gave **2** as the sole product, which is in marked contrast to the nickel-catalyzed reaction that produced 1,1-dimethyl-3,4-diphenyl-2,5-bis(trimethylsilyl)-1-silacyclopenta-2,4-diene in high yield.[7,10]

Similar treatment of 3-(ethyldimethylsilyl)-1,1-dimethyl-2-phenyl-1-silacyclopropene (**3**) with the same catalyst gave 1,4- disilacyclohexa-2,5-diene (**4**) in 64% yield, as a single product. The ^{1}H NMR spectrum of **4** showed two singlets at δ −0.25 and 0.11 due to Me$_2$SiEt and Me$_2$Si, and two multiplets at δ 0.20 and 0.75 attributed to CH$_2$Si and CH$_3$C, respectively, as well as a multiplet signal due to phenyl ring protons at 6.8–7.3 ppm. The mass spectrum of **4** was also consistent with the proposed structure.

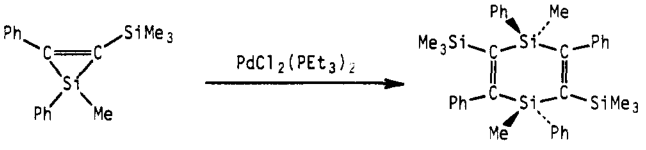
Since the palladium-catalyzed reaction of 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacyclopropene with methyl(trimethylsilyl)acetylene was reported to afford 1,1,2,4,4,5-hexamethyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene as the major product,[6] we checked this possibility in our reaction by treating silacyclopropene **3** with a 2-fold excess of phenyl(trimethylsilyl)acetylene in the presence of the palladium catalyst at 120 °C. VPC and ^{1}H NMR spectroscopic analysis of the reaction mixture showed the presence of dimer **4** (62% yield) as the sole product. Neither **2** nor 3-(ethyldimethylsilyl)-1,1,4,4-tetramethyl-2,5-diphenyl-6-(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene was detected, indicating that no replacement of phenyl(trimethylsilyl)acetylene took place.





The present palladium-catalyzed reaction appears to be a general reaction for the production of the 1,4-disilacyclohexa-2,5-diene. Those silacyclopropenes that did not afford 1,4-disilacyclohexa-2,5-dienes under thermolysis conditions also gave the silacyclohexa-2,5-dienes. Thus, 3-(*tert*-butyldimethylsilyl)-1,1-dimethyl-2-phenyl-1-silacyclopropene (**5**) led to 1,4-disilacyclohexa-2,5-diene (**6**) in 61% yield, while 1,1-dimethyl-2-phenyl-3-(phenyldimethylsilyl)-1-silacyclopropene (**7**) led to its dimerization product (**8**) in 40% yield as a single volatile product. Products **6** and **8** were identified by mass, IR, and ^{1}H NMR spectroscopic analysis (see Experimental Section).

The palladium-catalyzed dimerization of 1-methyl-1,2-diphenyl-3-(trimethylsilyl)-1-silacyclopropene (**9**) was of considerable interest, because the formation of cis and trans isomers would be possible. In fact, however, only *trans*-1,4-dimethyl-1,2,4,5-tetraphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (**10**) was obtained in 30% yield. The structure of **10** was verified by an X-ray diffraction study. The crystals obtained by recrystalliza-



9

10

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[8] Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1975**, *86*, C27.

[9] (a) Ishikawa, M.; Sugisawa, H.; Fuchikami, T.; Kumada, M.; Yamabe, T.; Kawakami, H.; Fukui, K.; Ueki, Y.; Shizuka, H. *J. Am. Chem. Soc.* **1982**, *104*, 2872. (b) Ishikawa, M.; Sugisawa, H.; Kumada, M.; Kawakami, H.; Yamabe, T., to be submitted for publication.

[10] The reaction of 1 with a nickel(II) catalyst in the absence of phenyl(trimethylsilyl)acetylene at 135 °C for 10 h gave 2 in 47% yield.

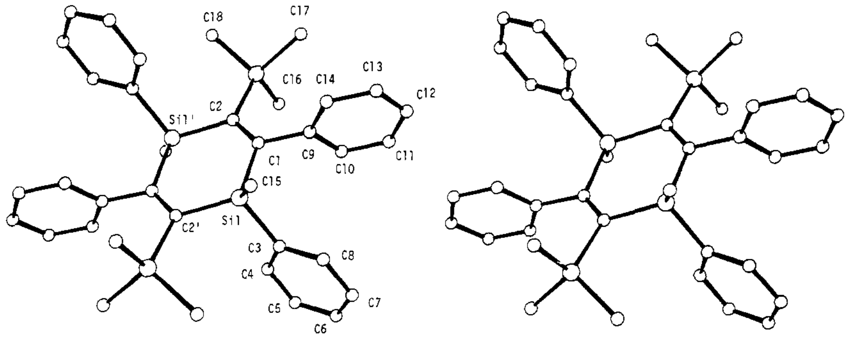

Figure 1. Stereoscopic view of *trans*-1,4-dimethyl-1,2,4,5-tetraphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (**10**).

Table I. Fractional Coordinates and Temperature Factors for Non-Hydrogen Atoms of 10[a]

atom	x	y	z	B_{eq},[b] Å	atom	x	y	z	B_{eq},[b] Å
Si1	0.04400 (4)	−0.04410 (5)	0.1282 (1)	3.04 (2)	C9	0.1414 (1)	0.0538 (2)	0.0619 (4)	3.3 (1)
Si2	0.07880 (5)	0.1449 (1)	−0.1977 (1)	3.93 (2)	C10	0.1915 (2)	0.0261 (2)	−0.0206 (4)	4.3 (1)
C1	0.0726 (1)	0.0363 (2)	0.0230 (3)	3.0 (1)	C11	0.2550 (2)	0.0420 (2)	0.0160 (5)	5.7 (1)
C2	0.0405 (1)	0.0717 (2)	−0.0828 (3)	3.1 (1)	C12	0.2680 (2)	0.0844 (2)	0.1317 (5)	6.8 (1)
C3	0.1011 (1)	−0.1165 (2)	0.0752 (4)	3.5 (1)	C13	0.2198 (2)	0.1105 (2)	0.2153 (5)	6.6 (1)
C4	0.0912 (2)	−0.1556 (2)	−0.0488 (4)	5.1 (1)	C14	0.1566 (2)	0.0949 (2)	0.1805 (4)	4.7 (1)
C5	0.1323 (2)	−0.2076 (2)	−0.0945 (6)	7.0 (2)	C15	0.0510 (2)	−0.0247 (2)	0.3267 (4)	5.3 (1)
C6	0.1858 (2)	−0.2229 (2)	−0.0149 (6)	7.0 (1)	C16	0.1188 (2)	0.1034 (2)	−0.3550 (4)	6.1 (1)
C7	0.1987 (2)	−0.1856 (2)	0.1070 (5)	6.6 (1)	C17	0.1368 (2)	0.2030 (2)	−0.1041 (5)	5.8 (1)
C8	0.1566 (2)	−0.1326 (2)	0.1538 (4)	5.0 (1)	C18	0.0152 (2)	0.2065 (2)	−0.2636 (6)	7.1 (2)

[a] Standard deviations of the least significant figures are given in parentheses. [b] B_{eq} is given by the express $(4/3)\Sigma_i\Sigma_j\beta_{ij}(a_ia_j)$.

Table II. Bond Distances (Å) of 10[a]

Si1-C1	1.893 (3)	C4-C5	1.366 (6)
Si1-C3	1.872 (3)	C5-C6	1.362 (6)
Si1-C15	1.868 (4)	C6-C7	1.350 (7)
Si1-C2′	1.878 (3)	C7-C8	1.395 (6)
Si2-C2	1.904 (3)	C9-C10	1.390 (5)
Si2-C16	1.850 (4)	C9-C14	1.375 (5)
Si2-C17	1.853 (4)	C10-C11	1.394 (5)
Si2-C18	1.848 (4)	C11-C12	1.358 (6)
C1-C2	1.355 (4)	C12-C13	1.355 (6)
C1-C9	1.510 (4)	C13-C14	1.383 (6)
C3-C4	1.374 (5)	C18-H1	0.92 (3)
C3-C8	1.394 (5)		

[a] The standard deviation of the least significant figure of each distance is given in parentheses.

tion from ethanol are orthorhombic of space group *Pbca* with cell dimensions a = 20.771 (4) Å, b = 18.842 (3) Å, c = 9.201 (1) Å; V = 3600.7 (1) Å^3; D_{calcd} = 1.087 (Z = 4) Mg m^{-3}. A total of 3098 independent reflections were collected.[11] The crystal structure was solved by direct methods,[12] and all hydrogen atoms were found in the difference Fourier map. By a least-squares procedure, for the 2074 reflections with $I > 2\sigma(I)$, R was reduced to 0.053. Final atomic parameters are given in Table I. Bond distances and angles are listed in Tables II and III. As can be seen in Figure 1, the molecule has a center of symmetry; therefore, the phenyl group on the silicon atom in the 1-position in the 1,4-disilacyclohexa-2,5-diene ring is trans with respect to the phenyl group in the 4-position. The ring is a chair form with smaller deviations from the best-fit plane (Si −0.013, C1, 0.017, C2, −0.016 Å) than those for 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexa-2,5-diene (Si, 0.024, C, 0.065 Å) reported by Vol' pin et al.[13] It is noteworthy that the endocyclic bond angle

Table III. Bond Angles (deg) of 10[a]

C1-Si1-C3	104.5 (1)	Si1-C3-C4	120.8 (2)
C1-Si1-C15	108.6 (2)	Si1-C3-C8	123.2 (3)
C1-Si1-C2′	113.7 (1)	C4-C3-C8	116.0 (3)
C3-Si1-C15	110.4 (2)	C3-C4-C5	123.2 (4)
C3-Si1-C2′	109.4 (1)	C4-C5-C6	119.8 (4)
C15-Si1-C2′	110.1 (2)	C5-C6-C7	119.9 (4)
C2-Si2-C16	108.4 (2)	C6-C7-C8	120.3 (4)
C2-Si2-C17	116.1 (2)	C3-C8-C7	120.9 (4)
C2-Si2-C18	110.4 (2)	C1-C9-C10	119.8 (3)
C16-Si2-C17	108.1 (2)	C1-C9-C14	121.9 (3)
C16-Si2-C18	109.4 (2)	C10-C9-C14	118.2 (3)
C17-Si2-C18	104.3 (2)	C9-C10-C11	119.7 (3)
Si1-C1-C2	127.3 (2)	C10-C11-C12	120.3 (4)
Si1-C1-C9	110.5 (2)	C11-C12-C13	120.8 (4)
C2-C1-C9	121.9 (3)	C12-C13-C14	119.5 (4)
Si2-C2-C1	123.6 (2)	C9-C14-C13	121.4 (3)
Si2-C2-Si1′	117.3 (2)		
C1-C2-Si1′	118.9 (2)		

[a] The standard deviation of the least significant figure of each angle is given in parentheses.

of C1 (127.3 (2)°) is significantly larger than that of C2 (118.9 (2)°).

Such stereoselective formation of *trans*-1,4-disilacyclohexa-2,5-diene is not restricted to dimerization of **9**. We have found that 1,2-dimethyl-1-phenyl-3-(trimethylsilyl)-1-silacyclopropene (**12**) readily undergoes dimerization with high stereoselectivity by the catalytic action of $PdCl_2(PEt_3)_2$. Unfortunately, silacyclopropene **12** was kinetically unstable; all attempts to isolate it in a pure form were unsuccessful. Therefore, we examined the behavior of **12** toward $PdCl_2(PEt_3)_2$ in solution. Thus, a hexane solution of **11** in the presence of a catalytic amount of $PdCl_2(PEt_3)_2$ was irradiated with a low-pressure mercury lamp for 3.4 h with ice cooling. In this photolysis, a colorless crystalline compound, 1,2,4,5-tetramethyl-1,4-diphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene

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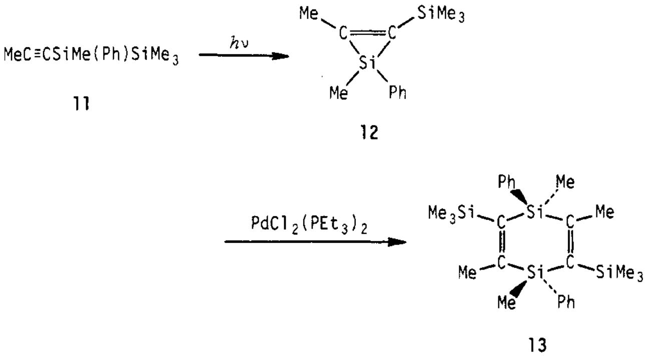
[11] The intensities of 3098 independent reflections (3.4 < 2θ < 50.0°) were measured by the ω scan technique on a Philips PW1100 automatic four-circle diffractometer with graphite-monochromatized Mo radiation.

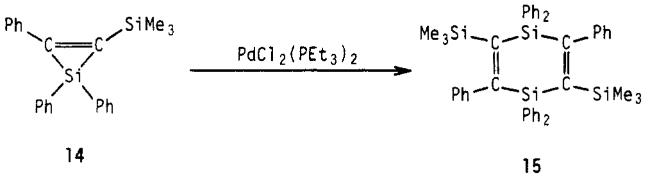
[12] Germain, G.; Woolfson, M. M. *Acta Crystallogr., Sect. B* **1968**, *β24*, 91.

[13] Vol'in, M. E.; Dulova, V. G.; Struchkov, Y. T.; Bokiy, N. K.; Kursanov, D. N. *J. Organomet. Chem.* **1967**, *8*, 87.

(**13**) was obtained in 11% yield, as a single product. The ^1H NMR spectrum of **13** showed three singlets at δ -0.08, 0.57, 1.92, attributed to Me_3Si, MeSi, and MeC protons, respectively, as well as a complex pattern due to the phenyl ring protons at 7.2–7.5 ppm. We have assigned this compound to trans isomer for steric reasons as indicated by examination of molecular models.



Introduction of the bulky groups onto the silicon atom in the silacyclopropene ring retards the formation of the 1,4-disilacyclohexa-2,5-diene. Thus, 1,1,2-triphenyl-3-(trimethylsilyl)-1-silacyclopropene (**14**) was converted to



1,1,2,4,4,5-hexaphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (**15**) in only 15% yield, while 1,1-dimesityl-2-phenyl-3-(trimethylsilyl)-1-silacyclopropene[2] was recovered unchanged.

Experimental Section

General Procedure. All reactions were carried out in a 10 cm × 0.8 cm degassed sealed glass tube at 120 °C. Yields were determined by VPC using an internal standard.

Infrared spectra were obtained with the use of Hitachi Model EPI-G3 Grating infrared spectrometer. ^1H NMR spectra were determined with a JEOL Model JNM-MH-100 spectrometer in carbon tetrachloride with the use of cyclohexane as an internal standard. Mass spectra were measured on a JEOL Model JMS-D300 equipped with a JMA-2000 data processing system.

Materials. Silacyclopropenes, **1**, **7**, **9**, and **14** were prepared as reported previously.[9]

Preparation of 2-Ethyl-1-(phenylethynyl)tetramethyldisilane. To 8.0 g (0.043 mol) of 1,2-dichlorotetramethyldisilane dissolved in 15 mL of THF was added 25 mL (0.048 mol) of 1.9 M ethylmagnesium bromide in diethyl ether with ice cooling. The mixture was stirred at room temperature for 1.5 h and then refluxed for 1.5 h. To this mixture was added a solution of (phenylethynyl)lithium prepared from 7.0 g (0.069 mol) of phenylacetylene and 38 mL (0.059 mol) of 1.55 M butyllithium in hexane at 10 °C. The reaction mixture was then refluxed for 1 h. The mixture was hydrolyzed with dilute hydrochloric acid. The organic layer was separated, washed with water, and dried over potassium carbonate. After evaporation of the solvent, the residue of the flask was distilled under reduced pressure to give 4.6 g (44% yield) of a colorless liquid: bp 87 °C (2 mm); mass spectrum, *m/e* 246; IR 2160 cm^{-1}; ^1H NMR δ 0.13 (6 H, s, Me_2Si), 0.27 (6 H, s, Me_2Si), 0.70 (2 H, m, CH_2Si), 1.05 (3 H, m, CH_3C), 7.1–7.5 (5 H, m, ring protons). Anal. Calcd for $C_{14}H_{22}Si_2$: C, 68.22; H, 9.00. Found: C, 68.09; H, 9.02.

Preparation of 1-*tert*-Butyl-2-phenyltetramethyldisilane. To 17 g (0.113 mol) of *tert*-butyldimethylchlorosilane dissolved in 100 mL of THF was added 100 mL (0.164 mol) of 1.64 M (phenyldimethylsilyl)lithium in THF at room temperature. The mixture was stirred for 10 h at room temperature and was hydrolyzed with water. The organic layer was separated, washed with water, and then dried over potassium carbonate. After evaporation of the solvent, the residue of the flask was distilled under reduced pressure to give 21.4 g (76% yield) of colorless liquid: bp 85 °C (2 mm); mass spectrum, *m/e* 250; ^1H NMR δ -0.02 (6 H, s, Me_2Si), 0.38 (6 H, s, Me_2Si), 0.85 (9 H, s, *t*-Bu), 7.15–7.50 (5 H, m, ring protons). Anal. Calcd for $C_{14}H_{26}Si_2$: C, 67.12; H, 10.46. Found: C, 67.21; H, 10.27.

Preparation of 1-*tert*-Butyl-2-chlorotetramethyldisilane. In a 200-mL three-necked flask was placed a mixture of 17.9 g (0.071 mol) of 1-*tert*-butyl-2-phenyltetramethyldisilane dissolved in 80 mL of dry benzene and 0.5 g of sublimed aluminum chloride. Dry hydrogen chloride was passed into the stirred solution over a period of 3 h at room temperature. After 5 mL of acetone was added to the mixture in order to deactivate the catalyst, the solvent was evaporated and the residue of the flask was distilled under reduced pressure to give 11.6 g (77% yield) of a colorless liquid: bp 70 °C (12 mm); mass spectrum, *m/e* 208; ^1H NMR δ 0.11 (6 H, s, Me_2Si), 0.50 (6 H, s, Me_2Si), 0.98 (9 H, s, *t*-Bu). Anal. Calcd for $C_8H_{21}ClSi_2$: C, 46.00; H, 10.13; Cl, 16.97. Found: C, 45.92; H, 10.07; Cl, 16.72.

Preparation of 2-*tert*-Butyl-1-(phenylethynyl)tetramethyldisilane. To 8.3 g (0.081 mol) of phenylacetylene in 40 mL of hexane was slowly added 42 mL (0.065 mol) of 1.55 M butyllithium in hexane at 0 °C over a period of 15 min. The mixture was stirred for 30 min at room temperature. To this mixture was added 8.9 g (0.043 mol) of 1-*tert*-butyl-2-chlorotetramethyldisilane dissolved in 40 mL of THF. The mixture was heated to reflux for 2 h, and it was hydrolyzed with water. The organic layer was washed with water and dried over potassium carbonate. Evaporation of the solvent followed by distillation of the residue under reduced pressure gave 10.4 g (89% yield) of a colorless liquid: bp 111 °C (2 mm); mass spectrum, *m/e* 274; IR 2160 cm^{-1}; ^1H NMR δ 0.11 (6 H, s, Me_2Si), 0.31 (6 H, s, Me_2Si), 1.01 (9 H, s, *t*-Bu), 7.15–7.45 (5 H, m, ring protons). Anal. Calcd for $C_{16}H_{26}Si_2$: C, 70.00; H, 9.55. Found: C, 70.21; H, 9.64.

Preparation of 3-(Ethyldimethylsilyl)-1,1,-dimethyl-2-phenyl-1-silacyclopropene (3). A solution of 0.2412 g (0.978 mmol) of 2-ethyl-1-(phenylethynyl)tetramethyldisilane in 25 mL of hexane was irradiated with a low-pressure mercury lamp bearing a Vycor filter for 50 min at room temperature. The solvent was evaporated under a nitrogen atmosphere, and the residue was distilled under reduced pressure to give 55.5 mg (23% yield) of **3**: ^1H NMR δ (in C_6D_6) 0.28 (6 H, s, Me_2Si), 0.33 (6 H, s, Me_2Si), 0.75 (2 H, m, CH_2Si), 1.05 (3 H, m, CH_3C), 6.9–7.7 (m, ring protons). Exact mass Calcd for $C_{14}H_{22}Si_2$: 246.1260. Found: 246.1264.

Preparation of 3-(*tert*-Butyldimethylsilyl)-1,1-dimethyl-2-phenyl-1-silacyclopropene (5). A solution of 0.2526 g (0.920 mmol) of 2-*tert*-butyl-1-(phenylethynyl)tetramethyldisilane in 25 mL of hexane was irradiated with a low-pressure mercury lamp for 55 min. After evaporation of the solvent, the residue of the flask was distilled under reduced pressure to give 53.0 mg (21% yield) of **5**: ^1H NMR δ (in C_6D_6) 0.28 (6 H, s, Me_2Si), 0.30 (6 H, s, Me_2Si), 1.09 (9 H, s, *t*-Bu), 6.6–7.7 (m, ring protons). Exact mass Calcd for $C_{16}H_{26}Si_2$: 274.1573. Found: 274.1576.

Dimerization of Silacyclopropene 1. A mixture of 0.1446 g (0.622 mmol) of **1**, 0.0397 g (0.175 mmol) of cetane as an internal standard, and 3.3 mg (8.0 × 10^{-3} mmol) of $PdCl_2(PEt_3)_2$ was heated at 120 °C for 10 h in a sealed glass tube. VPC analysis of the reaction mixture showed the presence of 1,4-disilacyclohexa-2,5-diene **2** (70% yield).[14] Ethanol (ca. 1 mL) was added to the mixture, and the resulting mixture was allowed to stand overnight to give 60.7 mg of crude crystals. Pure **2** was obtained by recrystallization from ethanol: mp 182–183 °C; ^1H NMR δ -0.25 (18 H, s, Me_3Si), 0.12 (12 H, s, Me_2Si), 6.8–7.3 (10 H, m, ring protons). Anal. Calcd for $C_{26}H_{40}Si_4$: C, 67.17; H, 8.67. Found: C, 66.95; H, 8.71.

Dimerization of Silacyclopropene 3. A mixture of 0.1299 g (0.527 mmol) of **3**, 0.0275 g (0.139 mmol) of tetradecane as an internal standard, and 3.5 mg (8.5 × 10^{-3} mmol) of $PdCl_2(PEt_3)_2$ was heated at 120 °C for 10 h. The yield of 1,4-disilacyclo-

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(14) The reaction of silacyclopropene 1 with a catalytic amount of tetrakis(triphenylphosphine)palladium(0) gave dimer 2 in 65% yield.

hexa-2,5-diene 4 was determined to be 64% by VPC analysis. The addition of ca. 1 mL of ethanol to the mixture gave 49.9 mg of crude crystals: mp 133–134 °C (recrystallization from ethanol); mass spectrum, *m/e* 492; ^{1}H NMR δ -0.25 (12 H, s, Me_2Si), 0.11 (12 H, s, Me_2Si), 0.20 (4 H, m, CH_2Si), 0.75 (6 H, m, CH_3C), 6.8–7.3 (10 H, m, ring protons). Anal. Calcd for $C_{28}H_{44}Si_4$: C, 68.22; H, 9.00. Found: C, 68.45; H, 9.27.

Reaction of 3 with $PdCl_2(PEt_3)_2$ in the Presence of Phenyl(trimethylsilyl)acetylene. A mixture of 0.1506 g (0.611 mmol) of **3**, 0.0274 g (0.138 mmol) of tetradecane, 0.1452 g (0.833 mmol) of phenyl(trimethylsilyl)acetylene, and 4.5 mg (1.1×10^{-2} mmol) of $PdCl_2(PEt_3)_2$ was heated in a sealed tube at 120 °C for 16 h. VPC analysis of the reaction mixture indicated the presence of **4** (62% yield). The mixture was allowed to stand at room temperature to give crystals (56.0 mg). All spectral data of the crystals were identical with those of an authentic sample.

Dimerization of Silacyclopropene 5. A mixture of 0.1625 g (0.592 mmol) of **5**, 0.0297 g (0.131 mmol) of cetane, and 3.9 mg (9.4×10^{-3} mmol) of $PdCl_2(PEt_3)_2$ was heated at 120 °C for 15 h in a sealed tube. The yield of **6** was determined to be 61% by VPC analysis: mp 168–169 °C (recrystallization from ethanol); mass spectrum, *m/e* 548; ^{1}H NMR δ -0.36 (12 H, s, Me_2Si), 0.10 (12 H, s, Me_2Si), 0.83 (18 H, s, *t*-Bu), 6.8–7.3 (10 H, m, ring protons). Anal. Calcd for $C_{32}H_{52}Si_4$: C, 70.00; H, 9.55. Found: C, 69.76; H, 9.54.

Dimerization of Silacyclopropene 7. A mixture of 0.1673 g (0.568 mmol) of **7**, 0.0392 g (0.173 mmol) of cetane as an internal standard, and 3.4 mg (8.2×10^{-3} mmol) of $PdCl_2(PEt_3)_2$ in a sealed tube was heated at 120 °C for 9 h. The mixture was analyzed by VPC as being 1,4-disilacyclohexa-2,5-diene **8** (40% yield). After recrystallization from ethanol, pure **8** (40.2 mg) was obtained as colorless crystals: mp 135 °C; mass spectrum, *m/e* 588; ^{1}H NMR δ -0.04 (24 H, s, Me_2Si), 6.7–7.3 (20 H, m, ring protons). Anal. Calcd for $C_{36}H_{44}Si_4$: C, 73.40; H, 7.53. Found: C, 73.64; H, 7.66.

Dimerization of Silacyclopropene 9. A mixture of 0.1493 g (0.507 mmol) of **9** contaminated with 0.096 mmol of phenyl(trimethylsilyl)acetylene, 0.0392 g (0.173 mmol) of cetane, and 2.0 mg (4.8×10^{-3} mmol) of $PdCl_2(PEt_3)_2$ was heated at 120 °C for 12 h in a sealed tube. The yield of **10** was determined to be 30% by VPC analysis. The mixture was allowed to stand at room temperature to give 26.9 mg of white crystals: mp 231–232 °C (recrystallization from ethanol); mass spectrum, *m/e* 588; ^{1}H NMR δ -0.52 (18 H, s, Me_3Si), 0.51 (6 H, s, MeSi), 5.9–6.1 and 6.8–7.4 (20 H, m, ring protons). Anal. Calcd for $C_{36}H_{44}Si_4$: C, 73.40; H, 7.53. Found: C, 73.19; H, 7.55.

Preparation of 1-Phenyl-1-propynyltetramethyldisilane (11). To 8.4 g (0.038 mol) of 1-ethynyl-1-phenyltetramethyldisilane[15] in 50 mL of hexane was added 40 mL (0.062 mol) of a 1.55 M BuLi–hexane solution at -78 °C over a period of 15 min. The mixture was stirred for 1 h at room temperature. To this solution was added 15.3 g (0.108 mol) of methyl iodide in 10 mL of hexane at room temperature, and it was stirred for 1 h. Then 20 mL of THF was added to the mixture and refluxed for 10 h. The mixture was hydrolyzed with water, and the organic layer was washed with water and dried over potassium carbonate. After evaporation of the solvent, the residue of the flask was distilled under reduced pressure to give 6.4 g (72% yield) of a colorless liquid: bp 72 °C (1 mm); mass spectrum, *m/e* 232; IR 2180 cm^{-1}; ^{1}H NMR δ 0.09 (9 H, s, Me_3Si), 0.40 (3 H, s, MeSi), 1.98 (3 H, s, MeC), 7.2–7.6 (5 H, m, ring protons). Anal. Calcd for $C_{13}H_{20}Si_2$: C, 67.17; H, 8.67. Found: C, 67.22; H, 8.84.

Photolysis of 11 in the Presence of $PdCl_2(PEt_3)_2$. A mixture of 0.2934 g (1.26 mmol) of **11**, 0.0269 g (0.146 mmol) of tridecane as an internal standard, and 4.7 mg (1.1×10^{-2} mmol) of $PdCl_2(PEt_3)_2$ in 25 mL of dry hexane was irradiated with a low-pressure mercury lamp for 3.4 h with ice cooling. VPC analysis of the mixture showed the presence of **13** (11% yield) and 5% of the starting **11**. The solvent was evaporated to give 19.0 mg of crude crystals. Recrystallization from ethanol gave pure **13**: mp 189–191 °C; mass spectrum, *m/e* 464; ^{1}H NMR δ -0.08 (18 H, s, Me_3Si), 0.57 (6 H, s, MeSi), 1.92 (6 H, s, MeC), 7.2–7.5 (10 H, m, ring protons). Anal. Calcd for $C_{26}H_{40}Si_4$: C, 67.17; H, 8.67. Found: C, 66.92; H, 8.81.

Dimerization of Silacyclopropene 14. A mixture of 0.1260 g (0.353 mmol) of **14**, 0.0239 g (0.085 mmol) of eicosane as an internal standard, and 2.0 mg (4.8×10^{-3} mmol) of $PdCl_2(PEt_3)_2$ was heated at 120 °C for 18 h. The reaction mixture was analyzed by VPC as being **15** (15% yield). The mixture was allowed to stand overnight to give 11.3 mg of crude crystals. Recrystallization from ethanol gave pure **15**: mp 295–297 °C; mass spectrum *m/e* 712; ^{1}H NMR δ -0.70 (18 H, s, Me_3Si), 6.2–6.4 and 6.8–7.7 (30 H, m, ring protons). Anal. Calcd for $C_{46}H_{48}Si_4$: C, 77.47; H, 6.78. Found: C, 77.05; H, 6.86.

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Supplementary Material Available: Tables of structure factors, anisotropic thermal parameters and H atom parameters, and deviations from the plane of the disilacyclohexadiene ring (5 pages). Ordering information is given on any current masthead page.

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