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Substitution Effects on the Thermal Extrusion of Silylenes from 1,1-Diarylsilacyclopropenes

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Thermal extrusion of silylenes from 1,1-dimesitylsilacyclopropenes and 1,1-bis(2,6-dimethoxyphenyl)silacyclopropene was studied. Heating 1,1-dimesityl-2-(trimethylsilyl)-3-phenyl-1-silacyclopropene at 250 °C led to the clean formation of dimesitylsilylene, which was readily trapped by methyldiphenylsilane, giving the insertion product. The rate of the silylene extrusion was affected by the substituents at the ring silicon and carbon atoms. Thus, replacement of the phenyl group on the carbon by a trimethylsilyl group, as well as substitution of the silicon by 2,6-dimethoxyphenyl groups in place of mesityls, clearly facilitate the silylene extrusion.

Introduction

Silicon-containing small-ring compounds are of importance in the field of organosilicon chemistry.[1] Of these, silacyclopropenes constitute one of the most strained classes of organosilacycles, and their chemical behavior has been extensively studied. Insertion reactions of unsaturated organic compounds into the silacyclopropene Si−C bond and head-to-tail dimerization of silacyclopropenes in the presence or absence of a transition-metal catalyst provide convenient methodologies leading to organosilacycles, such as siloles and disilacyclohexadienes.[2] They also undergo a variety of reactions, depending on the substituents on the ring. Sekiguchi et al. have reported the formation of 2,2-dilithiotrisilane from the cleavage of the inner-ring Si−C bonds of tetrasilylsilacyclopropene by interaction with lithium.[3] It has been reported by Kira et al. that facile silylene extrusion from 1,1-diamino-2,3-bis(trimethylsilyl)silacyclopropenes occurs exclusively under photochemical conditions,[4] in contrast to the fact that photochemical isomerization to 1-silapropadienes has been often noted for silyl-, alkyl-, and aryl-substituted silacyclopropenes.[6] Interesting isomerization leading to disilabenzvalene has been reported for bis(silacyclopropene) by Ando and co-workers.[5]

Recently, we have found that 1,1-dimesityl-3-phenyl-2-(trimethylsilyl)silacyclopropene (**1a**) may be an efficient silylene precursor and heating **1a** at 250 °C cleanly produces phenyl(trimethylsilyl)acetylene and dimesitylsilylene. Dimesitylsilylene thus produced can be readily trapped by methyldiphenylsilane, diphenylacetylene, and 1,4-bis(trimethylsilyl)butadiyne.[7] This is in contrast to similar thermal reactions of 1-(trimethylsilyl)-1-arylsilacyclopropenes, which afford complex mixtures arising from isomerization of the silacyclopropenes.[8] In this paper, we report the thermal reactions of 1,1-dimesityl- and 1,1-bis(2,6-dimethoxyphenyl)silacyclopropenes having trimethylsilyl or phenyl groups on the ring carbons. These reactions produced the corresponding silylenes cleanly, and the rate of silylene extrusion was considerably affected by the nature of the substituents on the ring silicon and carbon atoms. Crystal structures of the silacyclopropenes and reaction heats for the silylene extrusion were obtained from X-ray diffraction studies and molecular orbital (MO) calculations, respectively, to understand the substitution effects.

Results and Discussion

Synthesis of Silacyclopropenes. The starting silacyclopropenes were obtained as shown in Scheme 1. Thus, 2-(trimethylsilyl)silacyclopropenes (**1a**,[6a,9] **1b**,[6b] and **2a**) were readily prepared by the photochemical isomerization of ethynyldisilanes.[10] The precursors of

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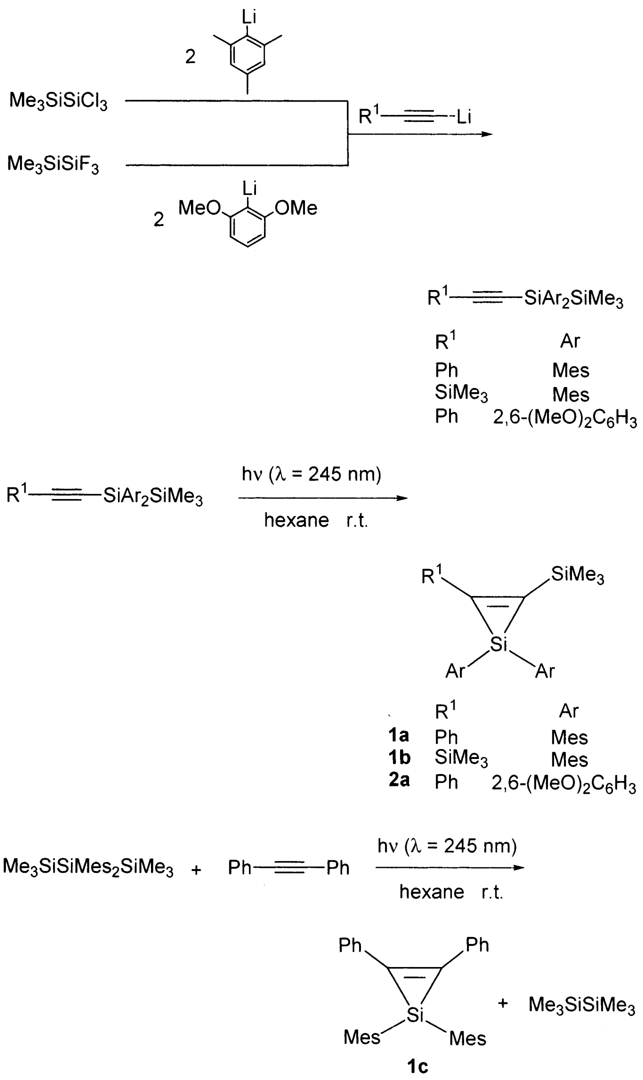
Scheme 1



1a and **1b** were obtained by successive treatment of 1,1,1-trichlorotrimethyldisilane with 2 equiv of mesityllithium and 1 equiv of the corresponding ethynyllithium. Since the reaction of 1,1,1-trichlorotrimethyldisilane with 2 equiv of (2,6-dimethoxyphenyl)lithium gave only the monosubstitution product, it was necessary to start with 1,1,1-trifluorotrimethyldisilane for the preparation of the precursor of **2a**. 1,1-Dimesityl-2,3-diphenylsilacyclopropene (**1c**) was obtained by the reaction of photochemically generated dimesitylsilylene with diphenylacetylene.[11] The present silacyclopropenes are stable in air and can be handled without special care.

Silylene Extrusion from 1,1-Dimesitylsilacyclopropenes 1a–c. When silacyclopropenes **1a**,**b** were heated in a degassed sealed glass tube in the presence of an excess of methyldiphenylsilane as the silylene trapping agent,[12] the trapped products were obtained, together with the corresponding acetylenes as shown in Scheme 2 and Table 1. The ^{1}H and ^{13}C NMR spectra of the reaction mixtures indicated that silylene extrusion had occurred in excellent yields based on the consumed silacyclopropenes, although some unidentified signals in low intensity were always observed in the spectra. Thus, heating silacyclopropene **1a** at 250 °C for 24 h resulted in a 90% yield of dimesityl-1-methyl-1,1-diphenyldisilane (**3**) together with phenyl(trimethylsilyl)acetylene. However, **1a** did not react at 190 °C and the starting **1a** was recovered unchanged. Similarly, when diphenylsilacyclopropene **1c** was heated at 250 °C in the presence of an excess of methyldiphenylsilane, no change was observed and the starting compound **1c** was recovered quantitatively. In contrast to this, bis(trimethylsilyl)silacyclopropene **1b** underwent silylene extrusion even at 180 °C to an extent, giving **3** in 67% yield, together with a 18% yield of **1b** recovered. These results indicate the clear dependence of the rate of silylene extrusion on the nature of the substituents attached to the ring carbons; i.e., the rate increased by replacing the phenyl group with a trimethylsilyl group, in the order **1c** < **1a** < **1b**.

Scheme 2

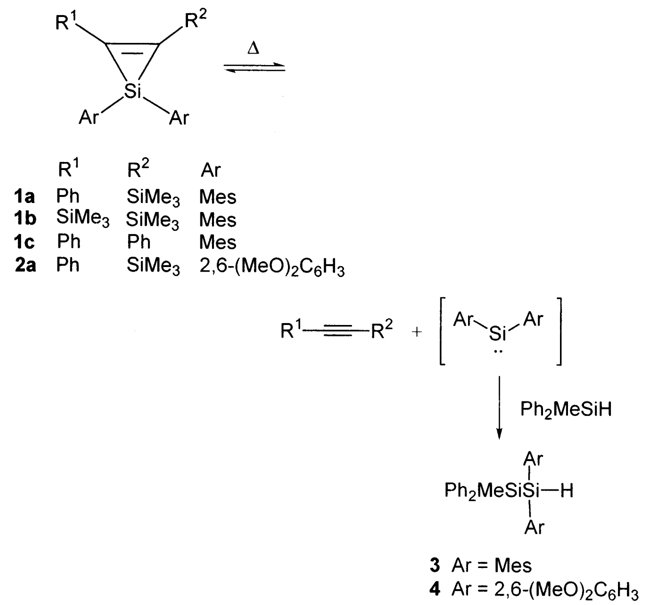


Table 1. Reactions of Silacyclopropenes in the Presence of Methyldiphenylsilane for 24 h

		product yield[a]/%		
compd	temp/°C	$Ph_2MeSiAr_2SiH$	$R^1C{\equiv}CR^2$	silacyclopropene[b]
1a	250	90	90	5
	220	16	16	75
	190	0	0	100
1b	220	85	80	2
	180	67	68	18
1c	250	0	0	100
2a	250	87	87	0
	220	55	56	32

[a] Determined by ^{1}H NMR spectrum of the reaction mixture. [b] Silacyclopropene recovered.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 1a−c and 2a with Their Esd's in Parentheses

compd	C=C	Si−C(Ph)	Si−C(SiMe)	compd	C=C	Si−C(Ph)
1a	1.349(3)	1.800(2)	1.839(2)	**1c**	1.347(3)	1.816(2), 1.818(2)
1b	1.363(7)		1.829(4)	**2a**	1.348(6)	1.782(4)

compd	Ph−C=C	Ph−C−Si	C=C(Ph)−Si	MeSi−C=C	MeSi−C−Si	C=C(SiMe)−Si
1a	137.1(2)	152.8(2)	69.8(1)	143.3(2)	149.6(1)	66.7(1)
1b			138.0(1)	153.2(2)	68.1(1)	
1c	137.5(2)	154.1(2)	68.3(1)			
	136.9(2)	154.0(2)	68.2(1)			
2a	136.6(4)	153.5(4)	69.7(3)	146.9(4)	146.6(3)	66.4(3)

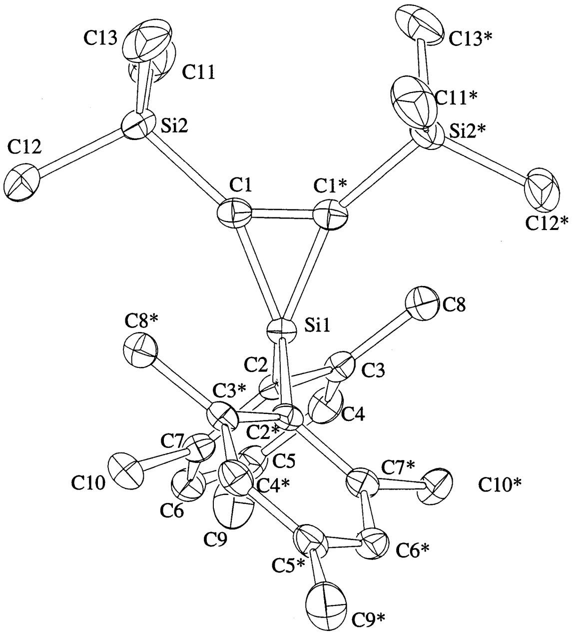

Figure 1. ORTEP view of compound **1b**. Protons are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

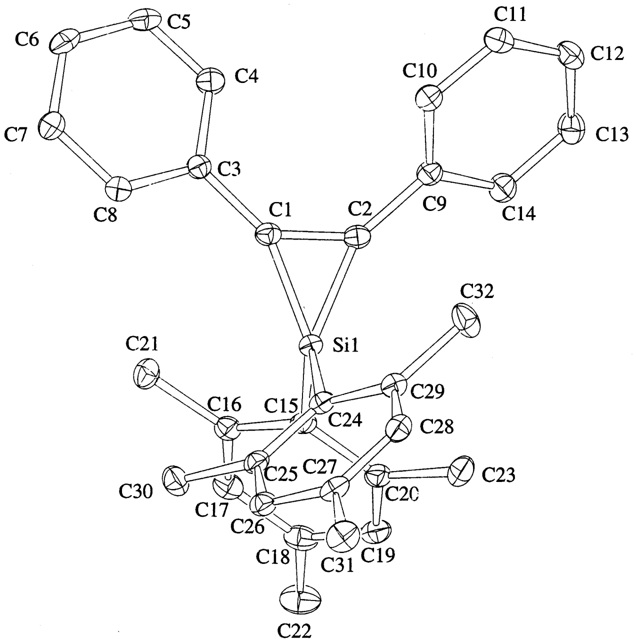

Figure 2. ORTEP view of compound **1c**. Protons are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Compounds **1b** and **1c** crystallized from ethanol, and the structures were determined by X-ray diffraction studies, as shown in Figures 1 and 2. Selected bond distances and angles are given in Table 2, together with those of **1a**, reported previously. As can be seen in Table 2, the inner-ring Si−C(SiMe) bond is considerably longer than the Si−C(Ph) bond in the structure of **1a**. Furthermore, the C=C(SiMe)−Si angle is smaller than the C=C(Ph)−Si angle, while the C=C−SiMe angle is larger than the C=C−Ph angle. These are indicative of higher p character of the Si−C(SiMe) bond, as compared with the Si−C(Ph) bond. A similar tendency is also observed when the structures of **1b** and **1c** are compared, although it is less evident than that in **1a**. This may be due to the steric repulsion of the relatively large trimethylsilyl group as compared with the phenyl group. Electron-donating properties of the trimethylsilyl group may be also responsible for the longer Si−C(SiMe) bonds, by elevating the σ-orbital level. The inner-ring C=C bonds are elongated from the standard values,[13] in the order **1c** < **1a** < **1b**, agreeing with the rate of silylene extrusion. It should be noted that the alkene unit in **1b** is slightly twisted, as indicated by the torsion angle for $Me_3Si{-}C{=}C{-}SiMe_3$ (15.5(9)°), while that of Ph−C=C−Ph in **1c** is only 5.9(5)°. The C=C bond length of **1b** (1.363 (7) Å) is extremely long and close to the values previously reported for twisted C=C bonds in tetrasilylethene (1.367−1.370 Å, torsion angle 22.6−52.7°).[14]

To know more about the substitution effects, we carried out molecular orbital (MO) calculations for silylene extrusion from silacyclopropenes **1a**−**c** at the level of B3LYP/6-31G(d,p).[15] For these calculations, the silylene was assumed to have the singlet ground state.[12]

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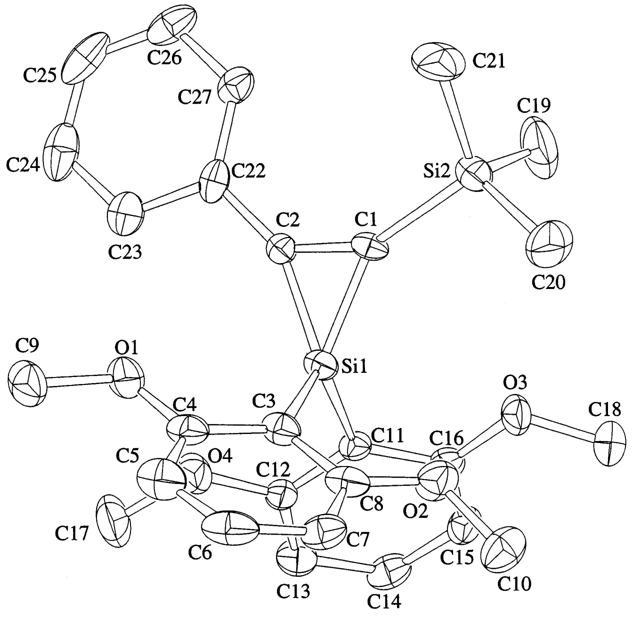


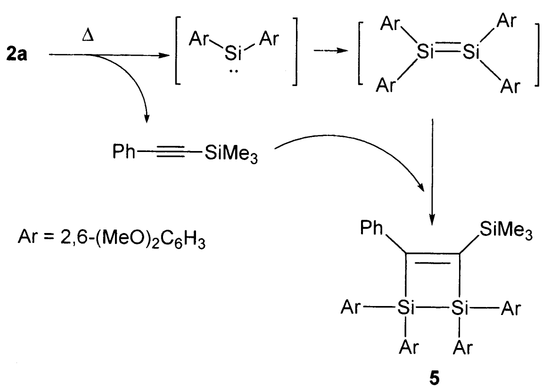
Figure 3. ORTEP view of compound **2a**. Protons are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

The optimized geometries of silacyclopropenes closely resemble those of the crystal structures, indicating the high reliability of the results of the MO calculations. The reactions were found to be highly endothermic, and the absolute values of the reaction heats decrease in the order **1c** (43.3 kcal/mol) > **1a** (39.4 kcal/mol) > **1b** (33.1 kcal/mol), in good agreement with the experimental results. Attempts to find out the transition states (TSs) of the reactions were unsuccessful, probably due to the rather flat energy surface around the TSs. However, the highly endothermic profiles of the reactions seem to indicate that the TSs are highly product-like and would permit us to estimate the relative order of the activation energies of the reactions by comparing the reaction heats.

Silylene Extrusion from 1,1-Bis(2,6-dimethoxyphenyl)silacyclopropene (2a). Introduction of the 2,6-dimethoxyphenyl groups in place of the mesityl groups on the ring silicon atom markedly accelerated the rate of thermolysis. Thus, heating **2a** at 220 °C led to a higher yield of trapped product, bis(2,6-dimethoxyphenyl)-1-methyl-1,1-diphenyldisilane (**4**), as compared with that from **1a** at the same temperature (Table 1).

Acceleration of the reaction by the dimethoxyphenyl group may be understood in terms of the coordination of the oxygen atoms of the dimethoxyphenyl groups to the silacyclopropene ring silicon through an n$-\sigma^*$ type interaction, which would destabilize the ring Si$-$C bonds. However, the ^{29}Si NMR spectrum of **2a** showed the signal of the ring silicon at -122.2 ppm, at slightly higher field than that of **1a** (-117.7 ppm), indicating that the coordination of the oxygen to the ring silicon is weak. Furthermore, the structural parameters of **2a** determined by an X-ray diffraction study indicated inner-ring Si$-$C bond distances rather shorter than those in **1a** (Table 1 and Figure 3), although the intramolecular contacts between the ring silicon and the oxygen atoms range from 3.08 to 2,80 Å, shorter than the sum of van der Waals radii (3.62 Å). We therefore assume that extracoodination of the oxygen atoms to the silylene center by n$-$p interaction[12] takes place in bis(2,6-dimethoxyphenyl)silylene to stabilize it, being primarily responsible for the accelerated silylene extrusion. Indeed, the MO calculations at the B3LYP/6-31G-(d,p) level led to a heat of formation of bis(2-methoxy-4,6-dimethylphenyl)silylene smaller by 6.9 kcal/mol than that obtained for bis(4-methoxy-2,6-dimethylphenyl)silylene, clearly indicating the stabilizing effect of the *o*-methoxy group on the silylene.[15]

Scheme 3



Interestingly, when **2a** was heated at 250 °C for 24 h with continuous removal of the resulting phenyl(trimethylsilyl)acetylene from the reaction mixture, 1,1,2,2-tetrakis(2,6-dimethoxyphenyl)-4-phenyl-3-(trimethylsilyl)-1,2-disilacyclobut-3-ene (**5**) was produced in 28% yield, together with a 53% yield of the starting **2a** recovered. Since simple heating of **2a** without removing the acetylene at the same temperature resulted in the quantitative recovery of **2a**, the silylene would not react with **2a**, probably due to the steric requirements. The formation of **5**, therefore, may be better explained by assuming a disilene intermediate formed from dimerization of bis(2,6-dimethoxyphenyl)silylene (Scheme 3), rather than by insertion of the silylene into an Si$-$C bond of **2a**, although we have no evidence to confirm the formation of the disilene.

In conclusion, we demonstrated that the silylene extrusion from silacyclopropenes under the thermal conditions was considerably influenced by the nature of substituents on both the ring silicon and carbon atoms. We also attempted to understand the substitution effects by the comparison of structural parameters of the silacyclopropenes and MO calculations. However, the origin of the effects has not yet been unambiguously explained and further studies to understand it seem to be necessary.

Experimental Section

General Considerations. THF and ether were dried over sodium$-$potassium alloy and distilled just before use. Hexane and benzene were distilled from lithium aluminum hydride and stored over activated molecular sieves 4A before use. Silacyclopropenes **1a**[6a,9] and **1b**,[6b] 2,2-dimesitylhexamethyltrisilane,[16] and 1,1,1-trifluorotrimethyldisilane[17] were obtained as reported in the literature.

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Preparation of 1,1-Dimesityl-2,3-diphenyl-1-silacyclopropene (1c). A mixture of 0.824 g (2.00 mmol) of 2,2-dimesitylhexamethyltrisilane and 1.78 g (10.0 mmol) of diphenylacetylene in 100 mL of hexane was irradiated for 1 h internally with a 6 W low-pressure mercury lamp bearing a Vycor filter. The solvent was evaporated, and the residue was chromatographed on a silica gel column with hexane as an eluent. The resulting crude solids were recrystallized from ethanol to give 0.49 g (55% yield) of **1c**: MS *m/z* 444 (M^+); ^{1}H NMR (δ in $CDCl_3$) 2.24 (s, 6H), 2.42 (s, 12H), 6.81 (s, 4H), 7.26−7.61 (m, 10H); ^{13}C NMR (δ in $CDCl_3$) 21.2, 24.0 (Me), 127.6, 128.2, 128.4, 128.7, 131.2, 134.9, 139.2, 144.1 (aromatic C), 152.4 (olefin C); ^{29}Si NMR (δ in $CDCl_3$) −111.0. Anal. Calcd for $C_{32}H_{32}Si$: C, 86.43; H, 7.25. Found: C, 86.13; H, 7.30.

Preparation of 1,1-Bis(2,6-dimethoxyphenyl)-1-(phenylethynyl)trimethyldisilane. In a 100 mL two-necked flask was placed 1.4 g (9.3 mmol) of 1,1,1-trifluorotrimethyldisilane in 10 mL of ether. To this was added a solution of (2,6-dimethoxyphenyl)lithium prepared from treating 2.60 g (18.6 mmol) of *m*-dimethoxybenzene with 11.6 mL of a butyllithium/hexane solution (1.6 M) in 15 mL of ether containing 0.05 mL of TMEDA at 0 °C.[18] The mixture was stirred for 1 h at room temperature. To the mixture was then added a solution of (phenylethynyl)lithium prepared from 0.9 g (8.8 mmol) of phenylacetylene and 5.5 mL of a butyllithium/hexane solution (1.6 M) in 13 mL of hexane/THF (3/1). The resulting mixture was stirred for 1 h at room temperature and hydrolyzed with dilute hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was chromatographed on a silica gel column with hexane/ethyl acetate (4/1) as an eluent, and the resulting crude solids were recrystallized from hexane to give 2.3 g (52% yield) of the title compound: MS *m/z* 476 (M^+); ^{1}H NMR (δ in C_6D_6) 0.53 (s, 9H), 3.38 (s, 12H), 6.35 (d, 4H, J = 8.0 Hz, *m*-$(MeO)_2C_6H_3$), 6.97−7.05 (m, 3H, *m*-Ph and *p*-Ph), 7.18 (t, 2H, J = 8.0 Hz, *p*-$(MeO)_2C_6H_3$), 7.57 (dd, 2H, J = 7.2 Hz, J = 2.0 Hz, *o*-Ph); ^{13}C NMR (δ in C_6D_6) −0.8, 55.2, 95.7, 104.2, 105.6, 113.2, 125.8, 127.6, 128.3, 131.0, 132.1, 165.3; IR $\nu_{C\equiv C}$ 2152 cm^{-1}. Anal. Calcd for $C_{27}H_{32}O_4Si_2$: C, 68.03; H, 6.77. Found: C, 68.04; H, 6.66.

Preparation of 1,1-Bis(2,6-dimethoxyphenyl)-3-phenyl-2-(trimethylsilyl)-1-silacyclopropene (2a). A solution of 0.941 g (1.98 mmol) of 1,1-bis(2,6-dimethoxyphenyl)-1-(phenylethynyl)trimethyldisilane in a solvent mixture of 90 mL of hexane and 50 mL of benzene was irradiated for 2 h internally with a 6 W low-pressure mercury lamp bearing a Vycor filter. At this stage almost all of the starting disilane was photolyzed. The solvent was evaporated, and the residue was recrystallized from hexane and then from ethanol to give 0.263 g of **2a** (28% yield): MS *m/z* 476 (M^+); ^{1}H NMR (δ in C_6D_6) 0.51 (s, 9H), 3.45 (s, 12H), 6.29 (d, 4H, J = 8.3 Hz, *m*-$(MeO)_2C_6H_3$), 7.12 (t, 2H, J = 8.3 Hz, *p*-$(MeO)_2C_6H_3$), 7.25 (t, 1H, J = 7.5 Hz, *p*-Ph), 7.45 (br t, 2H, J = 7.5 Hz, *m*-Ph), 8.21 (d, 2H, J = 7.5 Hz, *o*-Ph); ^{13}C NMR (δ in C_6D_6) 0.4 (MeSi), 55.1 (MeO), 103.7, 114.0, 130.5, 131.3, 137.3, 165.6 (aromatic C), 161.4, 177.5 (olefin C), two signals of aromatic carbons may overlap with those of the solvent C_6D_6; ^{29}Si NMR (δ in C_6D_6) −122.2 (ring Si), −13.2 (MeSi). Anal. Calcd for $C_{27}H_{32}O_4Si_2$: C, 68.03; H, 6.77. Found: C, 68.04; H, 6.71.

Table 3. Crystal Data, Experimental Conditions, and Summary of Structural Refinement Details for Silacyclopropenes

	1b	**1c**	**2a**
mol formula	$C_{26}H_{40}Si_3$	$C_{32}H_{32}Si$	$C_{27}H_{32}O_4Si_2$
mol wt	436.86	444.69	476.72
space group	*C*2/*c* (No. 15)	$P2_1/c$ (No. 14)	$P4_n/n$ (No. 86)
cell dimens			
a, Å	20.9888(3)	15.7858(6)	21.2906(5)
b, Å	10.0371(4)	10.0472(3)	
c, Å	16.5044(3)	17.5286(4)	11.7996(3)
β, deg	127.007(2)	114.196(2)	
V, Å^3	2776.5(1)	2535.9(1)	5348.6(2)
Z	4	4	8
D_{calcd}, Mg/m^3	1.045	1.165	1.184
F_{000}	952.00	952.00	2032.00
cryst size, mm^3	0.5 × 0.5 × 0.1	0.6 × 0.3 × 0.2	0.4 × 0.1 × 0.1
cryst color	colorless	colorless	colorless
μ, cm^{-1}	1.80	1.10	1.61
radiation	Mo Kα		
2θ max	55.0	54.9	55.0
no. of unique rflns	3169	5782	6143
no. of obsd rflns ($I \geq 3\sigma(I)$)	2070	4949	2486
ref/params	15.7	16.6	8.34
corrections	Lorentz−polarization absorption		
abs range	0.516−0.982	0.884−0.978	0.730−0.984
R	0.095	0.095	0.079
R_w[a]	0.162	0.228	0.088

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

Thermolysis of Silacyclopropenes in the Presence of Methyldiphenylsilane. An illustrative procedure is as follows. In a degassed, sealed glass tube was placed 20 mg (0.050 mmol) of **1a** and 50 mg (0.25 mmol) of dimethylphenylsilane, and the tube was heated at 250 °C for 24 h. The resulting mixture was dissolved in C_6D_6 and analyzed with respect to the ^{1}H NMR spectrum, using decane as an internal standard, as being **3** (90% yield), phenyl(trimethylsilyl)acetylene (90% yield), and the starting **1a** (5% yield). Products were separated from the mixture by preparative TLC. The ^{1}H and ^{13}C NMR spectra obtained for phenyl(trimethylsilyl)acetylene were identical with those of the authentic sample.[19] Data for **3**: MS *m/z* 485 (M^+ − Me); ^{1}H NMR (δ in $CDCl_3$) 0.79 (s, 3H), 2.09 (s, 12H), 2.24 (s, 6H), 5.36 (s, 1H, SiH), 6.74 (s, 4H, Mes), 7.22−7.40 (m, 10H, Ph); ^{13}C NMR (δ in C_6D_6) −3.2, 21.0, 24.0, 127.7, 128.4, 128.9, 129.5, 135.1, 137.1, 138.5, 144.7. Anal. Calcd for $C_{31}H_{36}Si_2$: C, 80.11; H, 7.81. Found: C, 80.10; H, 7.74. Thermolysis of **1b**,**c** and **2a** was carried out as above. Data for **4**: MS *m/z* 485 (M^+ − Me); ^{1}H NMR (δ in C_6D_6) 0.85 (s, 3H), 3.13 (s, 12H), 5.99 (s, 1H, SiH), 6.28 (d, 4H, J = 8.3 Hz, *m*-$(MeO)_2C_6H_3$), 7.13−7.17, 7.68−7.71 (m, 12H, ring H); ^{13}C NMR (δ in $CDCl_3$) −3.1, 54.8, 103.5, 111.3, 131.1, 135.3, 140.2, 165.3, two signals of phenyl meta and para carbons may overlap with those of the solvent C_6D_6. Anal. Calcd for $C_{29}H_{32}O_4Si_2$: C, 69.56; H, 6.44. Found: C, 69.56; H, 6.37.

Formation of 5. In one end of a sealed, V-shaped glass tube was placed 0.590 g (1.24 mmol) of **2a**, and the end was heated at 250 °C for 24 h while the other end was cooled by liquid nitrogen. Phenyl(trimethylsilyl)acetylene was collected at the cooled end as the colorless liquid. The products at both ends were combined and analyzed by ^{1}H NMR, using decane as an internal standard, as being phenyl(trimethylsilyl)acetylene (0.24 mmol, 40%) and **5** (0.16 mmol, 55%), together with a 53% yield of **2a** recovered. The mixture was subjected to preparative TLC with hexane/ethyl acetate (5/1) as an eluent, and the resulting crude solids were recrystallized from hexane to give 34 mg (7%) of **5**: MS *m/z* 778 (M^+); ^{1}H NMR (δ in C_6D_6) 0.19 (s, 9H), 3.06 (s, 12H), 3.23 (s, 12H), 6.21 (d, 4H, J = 8.3 Hz), 6.29 (d, 4H, J = 8.3 Hz), 7.10 (t, 2H, J = 8.1 Hz), 7.16 (t, 2H, J = 8.1 Hz), 7.31 (t, 2H, J = 7.6 Hz), 7.43 (dd, 2H, J = 8.3 Hz, 1.5 Hz), the phenyl para proton signal may overlap with that of the solvent C_6D_5H; ^{1}H NMR (δ in acetone-d_6) −0.29 (s, 9H), 3.17 (s, 12H), 3.33 (s, 12H), 6.25 (d, 4H, J = 8.1 Hz), 6.36 (d, 4H, J = 8.1 Hz), 7.00−7.21 (m, 9H); ^{13}C NMR (δ in acetone-d_6) 1.65, 54.6, 55.1, 103.0, 103.5, 116.1, 116.8, 124.5, 126.9, 128.0, 130.4, 130.7, 150.9, 165.3, 165.7, 174.2, 185.2; ^{29}Si NMR (δ in $CDCl_3$) −18.7, −11.1, −9.3. Anal. Calcd for $C_{43}H_{50}O_8Si_3$: C, 66.29; H, 6.47. Found: C, 66.35; H, 6.46.

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X-ray Crystallographic Analysis of Silacyclopropenes. Crystal data, experimental conditions, and a summary of structural refinement details for **1b**,**c** and **2a** are presented in Table 3. Data were collected on a Rigaku RAXIS imaging plate system at 100 K. The structure was solved by SIR92 direct methods.[20] The non-hydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber.[21] Anomalous dispersion effects were included in F_c;[22] the values for $\Delta f'$ and $\Delta f''$were those of Creagh and McAuley.[23] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[24] All calculations were performed using the teXsan[25] crystallographic software package of Molecular Structure Corp. No decay correction was applied.

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Supporting Information Available: Tables of positional and anisotropic displacement parameters and bond distances and angles for compounds **1b**,**c** and **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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