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Photolysis of Organopolysilanes. Thermal Behavior of 1-Silacyclopropenes

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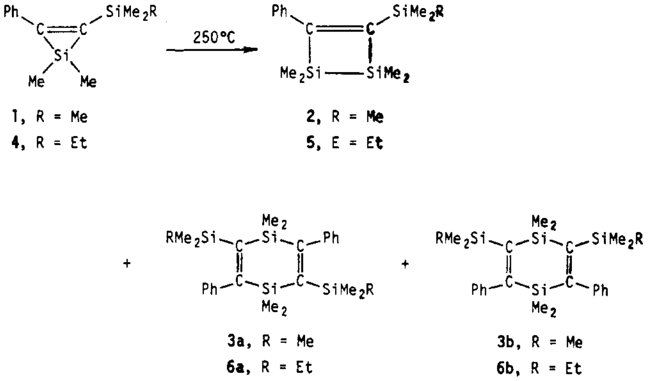
Thermolysis of 1,1-dimethyl-2-phenyl-3-(trimethylsilyl)-1-silacyclopropene and 3-(ethyldimethylsilyl)-1,1-dimethyl-2-phenyl-1-silacyclopropene in a sealed glass tube at 250 °C afforded the respective 1,4-disilacyclohexa-2,5-dienes consisting of two isomers in good yields. Under identical conditions 3-(*tert*-butyldimethylsilyl)-1,1-dimethyl-2-phenyl-1-silacyclopropene yielded 4-(*tert*-butyldimethylsilyl)-1,1,2,2-tetramethyl-3-phenyl-1,2-disilacyclobutene in high yield, while 1,1-dimethyl-2-phenyl-3-(phenyldimethylsilyl)-1-silacyclopropene gave two isomers of a 1-silacyclopenta-2,4-diene and 1,1,2,2-tetramethyl-3-phenyl-4-(phenyldimethylsilyl)-1,2-disilacyclobutene. From 1-methyl-1,2-diphenyl-3-(trimethylsilyl)-1-silacyclopropene, two isomers of the 1-silacyclopenta-2,4-diene and *trans*-1,4-dimethyl-1,2,4,5-tetraphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene were obtained. Similar thermolysis of 1,1,2-triphenyl-3-(trimethylsilyl)-1-silacyclopropene gave 1,1,3,4-tetraphenyl-2,5-bis(trimethylsilyl)-1-silacyclopenta-2,4-diene as a main product. A mechanism for dimerization of the silacyclopropenes is discussed on the basis of the molecular orbital calculations.

Introduction

The chemistry of silacyclopropenes constitutes one of the most active areas of current research and many papers that deal with the preparation and reactions of these compounds have been reported.[2-16] Most of the silacyclopropenes reported to date, with the two exceptions of 1,1-dimesityl-2-phenyl-3-(trimethylsilyl)- and 1,1-dimesityl-2,3-bis(trimethylsilyl)-1-silacyclopropene,[15] are extremely air-sensitive, and therefore only a few compounds have been isolated in a pure form.[3,4,6] For this reason, little study has been done on the thermolysis of the silacyclopropenes. To our knowledge, four different types of reactions for thermolysis of the silacyclopropenes have been reported: polymerization without forming volatile products,[2,15] silylene extrusion,[3,15] head-to-tail dimerization,[11] and isomerization to an alkyne.[15]

In an effort to learn more about the thermal behavior of the silacyclopropenes, we have examined the thermolysis of the silacyclopropenes prepared from photolysis of phenylethynyldisilanes.[16]

Scheme I



1, R = Me
4, R = Et

2, R = Me
5, E = Et

3a, R = Me
6a, R = Et

3b, R = Me
6b, R = Et

Results and Discussion

The thermolysis of 1-silacyclopropenes was carried out in a closed system at 250 °C. When 1,1-dimethyl-2-phenyl-3-(trimethylsilyl)-1-silacyclopropene (1) was heated for 6 h in a sealed glass tube, two products were obtained in 20 and 70% yield (Scheme I). A minor colorless product was identified to be 1,1,2,2-tetramethyl-3-phenyl-4-(trimethylsilyl)-1,2-disilacyclobutene (2) by spectroscopic method. All spectral data obtained for **2** were identical with those reported.[17] The major product was crystalline, the VPC analysis of which under various conditions showed a single peak whose retention time coincided with that of 1,1,4,4-tetramethyl-2,5-diphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (**3a**) obtained from the palladium-catalyzed dimerization of **1**.[8,18] However, the proton NMR spectrum of the product indicated it to be a mixture of **3a** whose chemical shifts were identical with those of an authentic sample and its isomer (**3b**) in the ratio of 3/1. In this thermolysis small amounts of two other products (less than 5% combined yield) were also detected. Gas chromatographic–mass spectrometric analysis of these compounds showed a parent peak at *m/e* 406, corresponding to the calculated value for bis(trimethylsilyl)diphenyl-1-silacyclopenta-2,4-diene.

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(1) (a) Department of Synthetic Chemistry. (b) Department of Hydrocarbon Chemistry.

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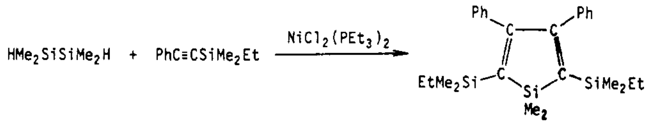
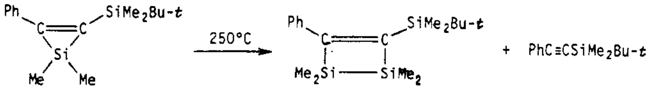
When similar thermolysis was carried out by using 3-(ethyldimethylsilyl)-1,1-dimethyl-2-phenyl-1-silacyclopropene (**4**), 4-(ethyldimethylsilyl)-1,1,2,2-tetramethyl-3-phenyl-1,2-disilacyclobutene (**5**) and a mixture of two isomers (**6a** and **6b**) of the 1,4-disilacyclohexa-2,5-diene were obtained in 42 and 38% yield, respectively, in addition to 2,5-bis(ethyldimethylsilyl)-1,1-dimethyl-3,4-diphenyl-1-silacyclopenta-2,4-diene (**7**) (12%) and its isomer (less than 4%). All attempts to separate **6a** from **6b** by VPC using various columns were unsuccessful. However, the ratio of two isomers were determined to be 3/1 by proton NMR spectroscopic analysis.

The structure of **5** which is extremely air-sensitive was established by mass and ^{1}H NMR spectroscopic method. The ^{1}H NMR spectrum of **5** showed three singlets at δ -0.14, 0.30, and 0.38, attributed to Me_2SiEt and two different kinds of Me_2Si in the four-membered ring, with equal intensities, and three multiplets at 0.25, 0.80, and 6.8–7.3 ppm due to CH_2Si, CH_3C, and phenyl ring protons, respectively. The proton chemical shifts of **6a** in the mixture isolated by preparative VPC were identical with those of 2,5-bis(ethyldimethylsilyl)-1,1,4,4-tetramethyl-3,6-diphenyl-1,4-disilacyclohexa-2,5-diene prepared by an independent synthesis.[18] Compound **6b** was identified unambiguously to have the proposed structure by its proton NMR spectrum which showed three singlets with relative intensities of 1/2/1, at δ -0.20, -0.15, and 0.41 ppm due to Me_2Si, Me_2SiEt, and Me_2Si, respectively. All spectral data of **7** were identical with those of an authentic sample obtained by the reaction of 1,2-dihydrotetramethyldisilane with phenyl(ethyldimethylsilyl)acetylene in the presence of a catalytic amount of dichlorobis(triethylphosphine)nickel(II) at 120 °C.[19]



7

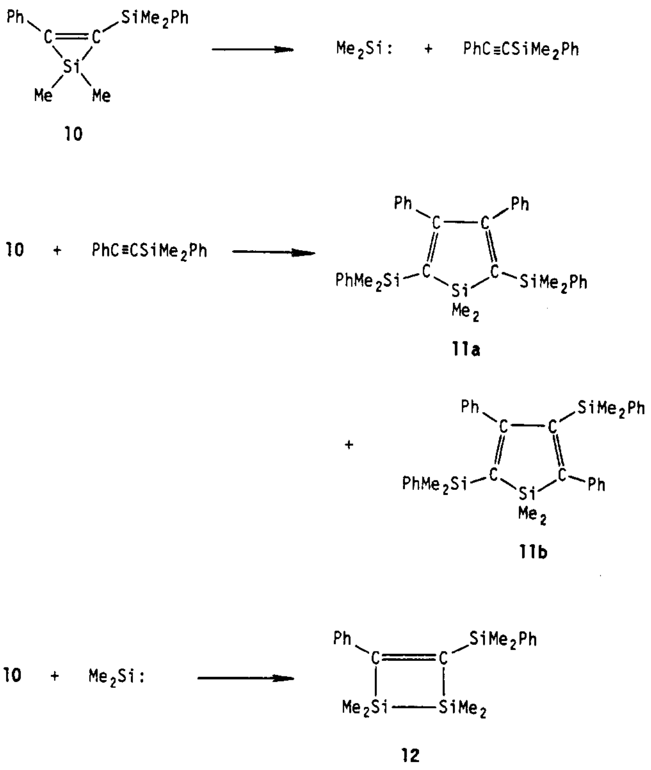
In contrast to **1** and **4**, the thermolysis of 3-(*tert*-butyldimethylsilyl)-1,1-dimethyl-2-phenyl-1-silacyclopropene (**8**) gave rise to 4-(*tert*-butyldimethylsilyl)-1,1,2,2-tetramethyl-3-phenyl-1,2-disilacyclobutene (**9**) in 75% yield. In this case, dimerization of silacyclopropene **8** was completely suppressed. Presumably the presence of a bulky *tert*-butyldimethylsilyl group on the carbon atom in the silacyclopropene ring prevents two molecules of **8** approaching each other for σ dimerization. Consequently, decomposition of some silacyclopropene **8** to phenyl(*tert*-butyldimethylsilyl)acetylene and dimethylsilylene may occur, with the latter inserting into a silicon–carbon bond in the three-membered ring of **8** to give thermally stable 1,2-disilacyclobutene **9**. Two-atom insertion of phenyl(*tert*-butyldimethylsilyl)acetylene into **8** is thought to be unfavored for steric reasons.



8 **9**

The structure of **9** was confirmed by spectroscopic method (see Experimental Section). Similarly, thermolysis of 1,1-dimethyl-2-phenyl-3-(phenyldimethylsilyl)-1-silacyclopropene (**10**) under identical conditions afforded 1,1-dimethyl-3,4-diphenyl-2,5-bis(phenyldimethylsilyl)-1-silacyclopenta-2,4-diene (**11a**) and 1,1-dimethyl-3,5-diphenyl-2,4-bis(phenyldimethylsilyl)-1-silacyclopenta-2,4-diene (**11b**) in 45 and 32% yield, respectively, in addition to 22% of 1,1,2,2-tetramethyl-3-phenyl-4-(phenyldimethylsilyl)-1,2-disilacyclobutene (**12**), as shown in Scheme II. Again, no dimerization product was detected by VPC and spectroscopic analyses. The formation of **11a** and **11b** can be explained by a two-atom insertion[10] of phenyl(phenyldimethylsilyl)acetylene, produced from thermal decomposition of some silacyclopropene **10**. Again, all attempts to separate **11a** and **11b** by VPC technique were unsuccessful. However, the chemical shifts of **11a** in the ^{1}H NMR spectrum of the mixture were identical with those of an authentic sample prepared by an independent route.[20] The exact mass of the mixture was also identical with the calculated molecular weight for $C_{34}H_{38}Si_3$. Three different resonances with equal intensities in the methylsilyl region for the proton NMR spectrum of **11b** are consistent with the proposed structure.

Scheme II



In order to learn more about the production of the 1,2-disilacyclobutene such as **2**, **5**, **9**, and **12**, we carried out the thermolysis of silacyclopropene **1** in the presence of anthracene. Heating **1** at 250 °C in the presence of anthracene gave **2** in 22% yield, together with 72% combined yield of **3a** and **3b**. No 2,3,5,6-dibenzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**13**) which might be expected to form from the reaction of tetramethyldisilene intermediate (A) (arising from dimerization of dimethylsilylene) with anthracene was detected (Scheme III).[21,22] This result clearly indicates that the 1,2-disilacyclobutene is produced from insertion of dimethylsilylene into a silicon–carbon bond in the silacyclopropene ring but not from tetramethyldisilene (A) and phenyl(silyl)-

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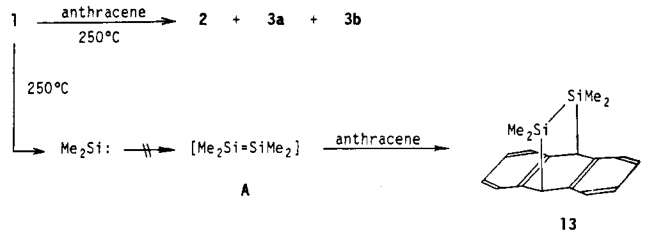
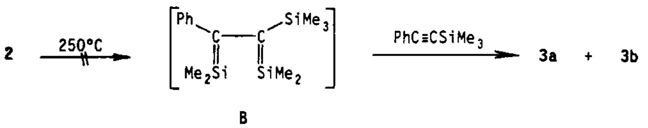
Scheme III



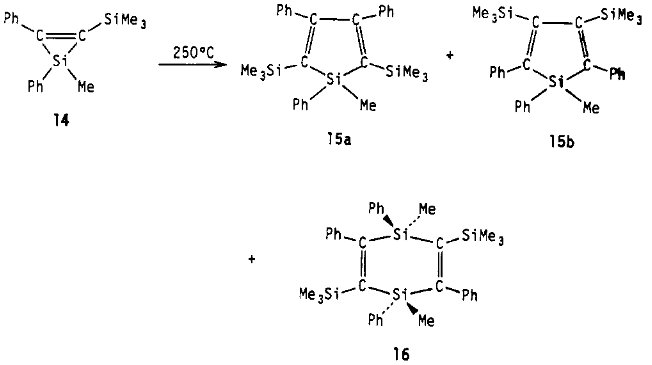
acetylene. Insertion of the silylene into the silacyclopropene has been reported by Seyferth et al.[7]

For the formation of 1,4-disilacyclohexa-2,5-dienes from the reaction of the silylenes with an acetylene, Barton and Kilgour proposed a mechanism involving the intermediacy of 1,4-disilabuta-1,3-diene (B) which undergoes the Diels–Alder addition to the acetylene.[23] In the present thermolyses, the 1,2-disilacyclobutene is formed; therefore, one might consider the possibility that the production of **3** and **6** involves the Diels–Alder addition of 1,4-disilabuta-1,3-diene B produced by thermal isomerization of the 1,2-disilacyclobutene to phenyl(silyl)acetylene. However, when **2** was heated at 250 °C in the presence of a 20-fold excess of phenyl(trimethylsilyl)acetylene for 18 h, both the starting substances were recovered quantitatively. After 18 h of heating at 310 °C, 90% of phenyl(trimethylsilyl)acetylene used was decomposed to give several unidentified products, but **2** itself remained unchanged. These results clearly indicate that the production of **3a** and **3b** does not involve the Diels–Alder reaction. Sakurai et al. also reported that the thermal reaction of 1,1,2,2-tetramethyl-3,4-diphenyl-1,2-disilacyclobutene with diphenylacetylene at 350 °C for 4 h in a sealed tube yielded 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexa-2,5-diene in only 1.2% yield.[17] In a previous communication, we proposed a mechanism involving a direct σ dimerization of the silacyclopropenes for the formation of the 1,4-disilacyclohexa-2,5-dienes.[11] The results obtained here are completely consistent with this mechanism.

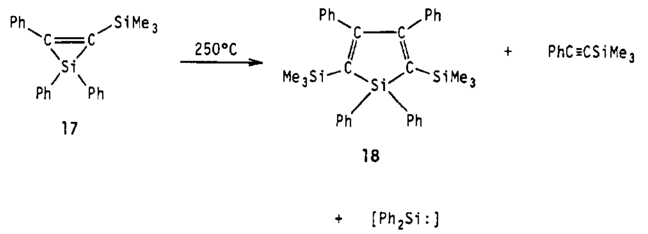


In an effort to obtain more information about the σ dimerization of the silacyclopropenes, we carried out the thermolysis of **1** in the presence of a radical trapping agent. Heating **1** in isopropylbenzene at 250 °C yielded again **2** and a mixture of **3a** and **3b** in 15 and 75% yield, respectively. No evidence for homolytic scission of the silicon–carbon bond in the silacyclopropene ring, followed by hydrogen abstraction was observed. Therefore, a mechanism involving a concerted pathway is attractive for the dimerization of the silacyclopropenes. In fact, the results from molecular orbital calculations described later are consistent with this mechanism.

We next investigated the thermolysis of the silacyclopropenes bearing a phenyl group on the ring silicon atom. When 1-methyl-1,2-diphenyl-3-(trimethylsilyl)-1-silacyclopropene (**14**) was heated at 250 °C for 6 h, 1-methyl-1,3,4-triphenyl-2,5-bis(trimethylsilyl)-1-silacyclopenta-2,4-diene (**15a**), 1-methyl-1,2,5-triphenyl-3,4-bis(trimethylsilyl)-1-silacyclopenta-2,4-diene (**15b**), and 1,4-dimethyl-1,2,4,5-tetraphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene (**16**) were produced in 42, 17, and 10% yield, along with 7% of phenyl(trimethylsilyl)acetylene. No 1,2-disilacyclobutene was detected in the reaction mixture by VPC or spectroscopic analyses. All spectral data of **15a** were identical with those of an authentic sample.[20] The proton NMR spectrum of **15b** showed two signals at δ −0.28 and 0.51 with relative intensities 6/1 attributed to trimethylsilyl protons and methylsilyl protons, respectively, as well as multiple signals at 6.7–7.6 ppm due to the phenyl ring protons. The mass spectrum showed a parent peak at m/e 468, corresponding to the correct molecular weight. All spectral data of dimer **16** were identical with those of *trans*-1,4-dimethyl-1,2,4,5-tetraphenyl-3,6-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene prepared by the palladium-catalyzed reaction of **14**.[18] Interestingly, in this thermolysis, no other isomers of 1,4-disilacyclohexa-2,5-diene, analogous to **3b**, or cis isomer were detected either by TLC or spectroscopic analysis. The fact that only trans isomer is produced in the thermolysis of **14** indicates that the steric approach control is important for dimerization.



Thermolysis of 1,1,2-triphenyl-3-(trimethylsilyl)-1-silacyclopropene (**17**) under similar conditions, however, gave only 1,1,3,4-tetraphenyl-2,5-bis(trimethylsilyl)-1-silacyclopenta-2,4-diene (**18**) in 38% yield, along with 17% yield of phenyl(trimethylsilyl)acetylene. Neither 1,2-disilacyclobutene nor 1,4-disilacyclohexa-2,5-diene was formed in this thermolysis.



The thermolyses of the silacyclopropenes reported here afforded no compounds derived from isomerization via a 1,2-silyl shift, which was observed in the thermolysis of 1-phenyl-1,2,3-tris(trimethylsilyl)-1-silacyclopropene[14] and 1,1-dimesityl-2,3-bis(trimethylsilyl)-1-silacyclopropene[15] and also in the thermal reaction of the silylene with alkynes.[24,25]

MO Calculations. The fact that dimerization of the silacyclopropenes involves no biradical intermediate as described above suggests that the 1,4-disilacyclohexa-2,5-dienes may be formed by a concerted pathway, [$2\sigma + 2\sigma$] mechanism, which is thought to be thermally forbidden. In order to confirm this possibility, we carried out ab initio SCF calculations of 2-silyl-1-silacyclopropene[16] (**19**) as a

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[23] Barton, T. J.; Kilgour, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 7746.

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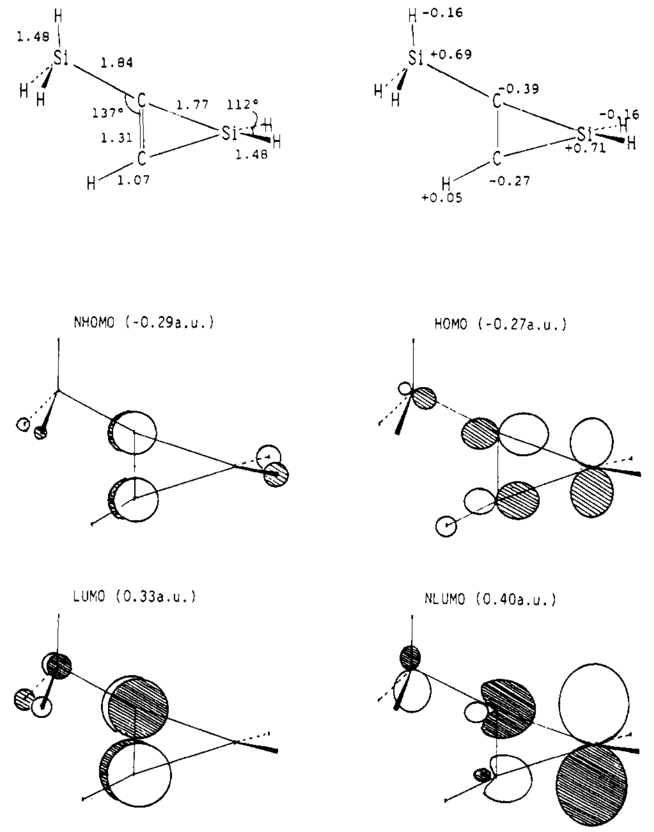

Figure 1. Geometry, atomic net charges, and total energies of NHOMO, HOMO, LUMO, and NLUMO of silacyclopropene (**19**).

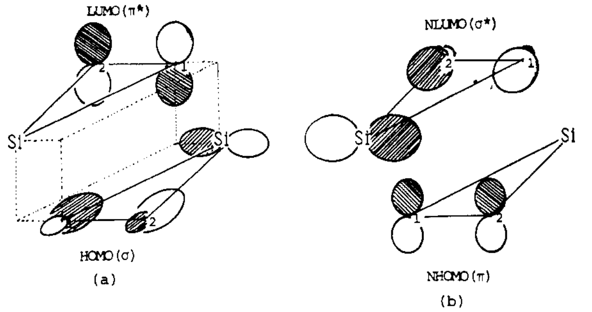

Figure 2. A schematic representation of the NHOMO–NLUMO and HOMO–LUMO interactions.

model compound using the Gaussian-76 program. The STO-3G basis set was employed for the calculations.

Figure 1 shows the results of charge distribution and the most important MO's (frontier orbitals) of **19**. As can be seen in this figure, the next HOMO (NHOMO) has π-bonding nature for a carbon–carbon bond in the ring, while the HOMO has σ-bonding nature for two silicon–carbon bonds in the ring. The LUMO and NLUMO are π antibonding for the carbon–carbon bond and σ antibonding for the silicon–carbon bond, respectively. The energy levels of the NHOMO and HOMO and of the LUMO and NLUMO lie in very close proximity to each other. Thus, these four MO's NHOMO(π), HOMO(σ), LUMO(π^*), and NLUMO(σ^*) play an important role for the present dimerization reactions.

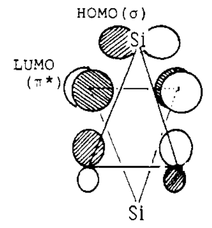

Figure 3. A schematic representation of the HOMO–LUMO interactions.

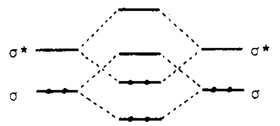

Figure 4. The energy level diagram of σ–σ and σ^*–σ^* interaction.

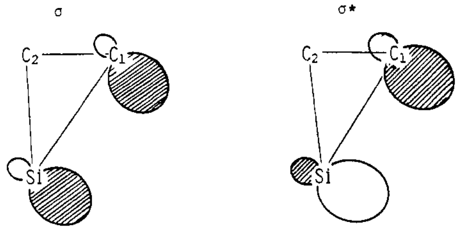

Figure 5. A schematic representation of spread lobes of C_1 and Si atoms after deformation of the molecule.

If we consider only HOMO–LUMO (σ–π^*) interactions, the effective overlap of the orbitals between two molecules of the silacyclopropenes leads to two geometrical configurations shown in Figures 2 and 3. The geometrical configuration in Figure 2 would be more favorable than that in Figure 3 if interactions of NHOMO–NLUMO (π–σ^*) are additionally considered, together with the HOMO–LUMO interactions, because of the large overlap between the 2p$_z$ atomic orbital of carbon and the 3p$_x$ one of silicon as shown in Figure 2b. Moreover, the symmetry-forbidden reaction involving [$2\sigma + 2\sigma$] mechanism may be allowed to proceed if the energy levels of σ and σ^* in a silacyclopropene molecule is brought so close together that the σ–σ^* excitation energy can be smaller than the stabilization energy arising from the σ–σ and σ^*–σ^* interaction between two excited molecules, as shown in Figure 4. This type of reaction is considered as a kind of "pseudoexcitation".[26]

In the present case, the electron transfer occurs between two molecules from π to σ^* and from σ to π^*, and hence silicon–carbon bonds (Si–C_1) in Figure 2 are weakened. By subsequent deformation, energy levels of σ and σ^* in the molecule come to close, and the lobes on C_1 and Si atoms in σ and σ^* spread out to the outer sphere from the Si–C_1 bond as shown in Figure 5, so that both σ–σ and σ^*–σ^* interactions between two molecules would be very strong.

Thus contributions of σ and σ^* can make the pseudoexcitation easy enough to facilitate the formation of the 1,4-disilacyclohexa-2,5-diene, while the orbital of π and π^* remains unchanged as it was.

The present discussion is based on the results of calculations for the silacyclopropene. Detailed quantitative investigations containing more sophisticated calculations for the system consisting of two molecules will be reported elsewhere.

In conclusion, the thermolysis of the silacyclopropenes prepared from phenylethynyldisilanes has been found to proceed simultaneously by two different routes, one of which involves the concerted [$2\sigma + 2\sigma$] dimerization, the other comprises the silylene extrusion. The former reaction is suppressed when a bulkier substituent is introduced onto the carbon atom in the silacyclopropene ring. Con-

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[26] Inagaki, S.; Fujimoto, H.; Fujui, K. *J. Am. Chem. Soc.* **1975**, *97*, 6108.

sequently, the silylene extrusion takes place predominantly, and 1,2-disilacyclobutenes are obtained. When substituents on the ring silicon atom are changed from methyl to phenyl no 1,2-disilacyclobutenes are produced, but silacyclopentadienes are formed as main products.

Experimental Section

General Procedure. All reactions were carried out in a 10 cm × 0.6 cm degassed sealed glass tube at 250 °C.

Infrared spectra were observed with the use of a Hitachi Model EPI-G3 grating infrared spectrometer. ^{1}H 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. The yields were determined by VPC using an internal standard on the basis of the starting silacyclopropenes.

Materials. Silacyclopropenes, 1,[16] 4,[18] 8,[18] 10,[16] 14,[16] and 17[16] were prepared as reported previously.

Thermolysis of Silacyclopropene 1. A mixture of 0.1738 g (0.75 mmol) of 1 and 0.0592 g (0.26 mmol) of cetane was placed in a carefully dried glass tube, previously flushed with argon. The glass tube was sealed under reduced pressure and then heated at 250 °C for 6 h. VPC analysis of the reaction product showed that disilacyclobutene 2 and 1,4-disilacyclohexa-2,5-dienes consisting of **3a** and **3b** in a ratio of 3/1 were formed in 20 and 70% yield, together with 10% yield of phenyl(trimethylsilyl)acetylene and two isomers of diphenylbis(trimethylsilyl)-1-silacyclopenta-2,4-diene (less than 5% yield). The mixture was distilled under reduced pressure to give 2 and 3 (~250 °C at 1 mm). Pure 2 and 3 were isolated by preparative VPC. For 2:[17] mp ca. 33 °C; ^{1}H NMR δ -0.11(s, 9 H, Me$_3$Si), 0.31 (s, 6 H, Me$_2$Si), 0.37 (s, 6 H, Me$_2$Si), 6.8–7.3 (m, 5 H, ring protons); exact mass 290.1351 (calcd 290.1342). For 3: ^{1}H NMR δ -0.25 (s, 18 H, Me$_3$Si of **3a**), -0.20 (s, 6 H, Me$_2$Si of **3b**), -0.18 (s, 18 H, Me$_3$Si of **3b**), 0.12 (s, 12 H, Me$_2$Si of **3a**), 0.42 (s, 6 H, Me$_2$Si of **3b**), 6.8–7.3 (m, ring protons); exact mass 464.2213 (calcd 464.2207). Anal. Calcd for $C_{26}H_{40}Si_4$: C, 67.17; H, 8.67. Found for a mixture of **3a** and **3b**: C, 67.13; H, 8.86.

Thermolysis of Silacyclopropene 4. A mixture of 0.1418 g (0.58 mmol) of 4 contaminated with phenyl(ethyldimethylsilyl)acetylene (0.09 mmol) and 0.0263 g (0.13 mmol) of tetradecane as an internal standard was heated at 250 °C for 7 h. The reaction mixture was analyzed by VPC as being 1,2-disilacyclobutene 5 (42% yield), 1,4-disilacyclohexa-2,5-dienes consisting of **6a** and **6b** (38% combined yield) in a ratio of 3/1, and 1-silacyclopenta-2,4-diene 7 (12% yield) and its isomer (less than 4%). For 5: ^{1}H NMR δ -0.14 (s, 6 H, Me$_2$Si), 0.25 (m, 2 H, CH$_2$Si), 0.30 (s, 6 H, Me$_2$Si), 0.38 (s, 6 H, Me$_2$Si), 0.80 (m, 3 H, CH$_3$C), 6.8–7.3 (m, 5 H, ring protons); exact mass 304.1493 (calcd 304.1499). For 6: -0.25 (s, 12 H, Me$_2$Si of **6a**), -0.20 (s, 6 H, Me$_2$Si of **6b**), -0.15 (s, 12 H, Me$_2$Si of **6b**), 0.11 (s, 12 H, Me$_2$Si of **6a**), 0.20 (m, 8 H, CH$_2$Si of **6a** and **6b**), 0.41 (s, 6 H, Me$_2$Si of **6b**), 0.75 (m, 12 H, CH$_3$C of **6a** and **6b**), 6.8–7.4 (m, ring protons); exact mass for a mixture of **6a** and **6b** 492.2519 (calcd 492.2520). The IR, mass, and ^{1}H NMR spectra of 7 were identical with those of an authentic sample.

Preparation of 1-Silacyclopenta-2,4-diene 7. A mixture of 0.3629 g (3.07 mmol) of 1,2-dihydrotetramethyldisilane, 1.1763 g (6.25 mmol) of phenyl(ethyldimethylsilyl)acetylene, and 4.7 mg (1.3×10^{-2} mmol) of dichlorobis(triethylphosphine)nickel(II) was heated at 120 °C for 14 h in a degassed sealed glass tube. VPC analysis of the mixture showed the presence of 7 in 19% yield. Pure 7 was isolated by distillation of the mixture (~230 °C at 1 mm), followed by recrystallization from ethanol: mp 103 °C; ^{1}H NMR δ -0.20 (s, 12 H, Me$_2$Si), 0.25 (m, 4 H, CH$_2$Si), 0.39 (s, 6 H, Me$_2$Si), 0.80 (m, 6 H, CH$_3$C), 6.7–7.1 (m, 10 H, ring protons); exact mass 434.2288 (calcd 434.2281). Anal. Calcd for $C_{26}H_{38}Si_3$: C, 71.82; H, 8.81. Found: C, 71.55; H, 8.98.

Thermolysis of Silacyclopropene 8. A mixture of 0.1387 g (0.51 mmol) of 1-silacyclopropene 8 and 0.0256 g (0.11 mmol) of cetane was heated at 250 °C for 7 h. The reaction mixture was analyzed by VPC as being 1,2-disilacyclobutene 9 (75% yield): ^{1}H NMR δ -0.18 (s, 6 H, Me$_2$Si), 0.28 (s, 6 H, Me$_2$Si), 0.40 (s, 6 H, Me$_2$Si), 0.76 (s, 9 H, *t*-BuSi), 6.8–7.3 (m, 5 H, ring protons); exact mass 332.1811 (calcd 332.1812).

Thermolysis of Silacyclopropene 10. A mixture of 0.1960 g (0.67 mmol) of 10 contaminated with phenyl(phenyldimethylsilyl)acetylene (0.19 mmol) and 0.0486 g (0.22 mmol) of cetane was heated for 6 h at 250 °C. The mixture was analyzed by VPC as 1-silacyclopenta-2,4-diene **11a** (45% yield) and **11b** (32% yield) and 1,2-disilacyclobutene 12 (22% yield). A mixture of **11a** and **11b** and compound 12 were separated by preparative VPC. The mass and ^{1}H NMR spectra and the retention time on VPC of **11a** were identical with those of an authentic sample.[20] For **11b**: ^{1}H NMR δ -0.40 (s, 6 H, Me$_2$Si), -0.04 (s, 6 H, Me$_2$Si), 0.11 (s, 6 H, Me$_2$Si), 6.6–7.4 (m, ring protons); exact mass 530.2268 (calcd 530.2281). For 12: ^{1}H NMR δ 0.11 (s, 6 H, Me$_2$Si), 0.21 (s, 6 H, Me$_2$Si), 0.32 (s, 6 H, Me$_2$Si), 6.7–7.4 (m, 10 H, ring protons); exact mass 352.1484 (calcd 352.1499).

Thermolysis of 1 in the Presence of Anthracene. A mixture of 0.1554 g (0.67 mmol) of 1 contaminated with phenyl(trimethylsilyl)acetylene (0.13 mmol), 0.1590 g (0.89 mmol) of anthracene, and 0.0253 g (0.14 mmol) of tridecane was heated in a sealed glass tube at 250 °C for 13 h. VPC analysis of the reaction mixture showed that disilacyclobutene 2 and 1,4-disilacyclohexa-2,5-dienes consisting of **3a** and **3b** in a ratio of 3/1 were produced in 22 and 72% yield, in addition to 1,1-dimethyl-3,4-diphenyl-2,5-bis(trimethylsilyl)-1-silacyclopenta-2,4-diene (3% yield) and its isomer (less than 2%). All spectral data for 2 and a mixture of **3a** and **3b** isolated by preparative VPC were identical with those of the authentic samples. The retention time on VPC of 1,1-dimethyl-3,4-diphenyl-2,5-bis(trimethylsilyl)-1-silacyclopenta-2,4-diene and its mass spectrum were identical with an authentic sample.[20]

Thermolysis of 1 in the Presence of Isopropylbenzene. A mixture of 0.1301 g (0.56 mmol) of 1 contaminated with phenyl(trimethylsilyl)acetylene (0.16 mmol), 0.1935 g (1.61 mmol) of isopropylbenzene, and 0.0301 g (0.16 mmol) of tridecane was heated in a sealed glass tube at 250 °C for 11 h. The mixture was analyzed by VPC as being 2 (15% yield), **3a** and **3b** (75% combined yield), and 1,1-dimethyl-3,4-diphenyl-2,5-bis(trimethylsilyl)-1-silacyclopenta-2,4-diene (3% yield) and its isomer (1% yield).

Thermolysis of 1,2-Disilacyclobutene 2 in the Presence of Phenyl(trimethylsilyl)acetylene. A mixture of 0.0041 g (0.01 mmol) of 2, 0.0490 g (0.28 mmol) of phenyl(trimethylsilyl)acetylene, and 0.0077 g (0.04 mmol) of tridecane as an internal standard in a sealed tube was heated at 250 °C for 18 h. VPC analysis of the mixture showed that 1,2-disilacyclobutene 2 was recovered, quantitatively. After an 18-h reaction at 310 °C, 2 was recovered unchanged, but 90% of phenyl(trimethylsilyl)acetylene was decomposed to give unidentified products.

Thermolysis of Silacyclopropene 14. A mixture of 0.1960 g (0.67 mmol) of 14 and 0.034 g (0.15 mmol) of cetane as an internal standard was heated at 250 °C for 6 h. The reaction products were analyzed by VPC as 1-silacyclopenta-2,4-dienes **15a** (42% yield), **15b** (17% yield), and 1,4-disilacyclohexa-2,5-diene 16 (10% yield), in addition to 7% yield of phenyl(trimethylsilyl)acetylene. Compounds **15a**, **15b**, and 16 were isolated by preparative VPC. The IR, mass, and ^{1}H NMR spectra of **15a**[20] and 16[18] (mp 231–232 °C) were identical with those of the authentic samples. For **15b**: ^{1}H NMR δ -0.28 (s, 18 H, Me$_3$Si), 0.51 (s, 3 H, MeSi), 6.7–7.6 (m, 15 H, ring protons); exact mass 468.2137 (calcd 468.2125). Anal. Calcd for $C_{29}H_{36}Si_3$: C, 74.29; H, 7.74. Found: C, 74.13; H, 7.80.

Thermolysis of Silacyclopropene 17. A mixture of 0.0418 g (0.12 mmol) of 17, 0.0037 g (0.02 mmol) of tetradecane, and 0.0585 g (0.21 mmol) of eicosane as internal standards was heated in a sealed tube at 250 °C for 18 h. VPC analysis of the mixture showed that 1-silacyclopenta-2,4-diene 18 was produced in 38% yield, in addition to 17% of phenyl(trimethylsilyl)acetylene. Compound 18 was isolated by preparative TLC (Silica gel 60 PF$_{254}$), mp 208 °C. The IR, mass, and ^{1}H NMR spectra of 18 were identical with those of an authentic sample.[20]

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Registry No. 1, 61851-11-4; 2, 69307-60-4; 3a, 63261-73-4; 3b, 65568-79-8; 4, 83077-05-8; 5, 85443-38-5; 6a, 83077-06-9; 6b, 85452-99-9; 7, 65568-82-3; 8, 83077-07-0; 9, 85443-39-6; 10, 79628-11-8; 11a, 79628-07-2; 11b, 85443-41-0; 12, 81142-39-4; 13, 22843-39-6; 14, 79628-12-9; 15a, 79628-08-3; 15b, 85443-42-1; 16, 83095-62-9; 17, 79628-13-0; 18, 79628-09-4; PhC≡CSiMe$_2$Bu-*t*, 85443-40-9; PhC≡CSiMe$_3$, 2170-06-1; HMe$_2$SiSiMe$_2$H, 814-98-2; PhC≡CSiMe$_2$Et, 4131-45-7; PhC≡CSiMe$_2$Ph, 79628-15-2.

Synthesis of Di-*tert*-butyl(cyclopropylmethyl)phosphine, *trans*-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})_2$, and $\overline{PtCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2})(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})$. The Intramolecular Activation of C–C and C–H Bonds of a Cyclopropyl Phosphine

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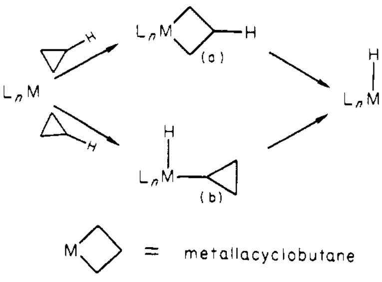
The synthesis of the cyclopropyl phosphine $(t\text{-}Bu)_2PCH_2\overline{CHCH_2CH_2}$ (1) is described. When this new phosphine is combined with dichlorobis(benzonitrile)platinum(II) in toluene, the resulting product is *trans*-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})_2$ (2). In refluxing 2-methoxyethanol, compound 2 undergoes an intramolecular cyclometalation reaction in which both a C–C and a C–H bond of one of the cyclopropane rings are cleaved to form the chelating σ-allyl complex $\overline{PtCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2})(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})$ (3). Complex 3 crystallizes in the monoclinic space group C^5_{2h}—$P2_1/c$, with four formula units in a cell of dimensions a = 11.847 (5) Å, b = 15.451 (7) Å, c = 16.802 (8) Å, β = 116.70 (2)°, and V = 2747 Å^3. The final agreement indices for 4630 reflections having $F_o^2 > 3\sigma(F_o^2)$ are $R(F)$ = 0.044 and $R_w(F)$ = 0.047 (253 variables). Bond lengths in the five-atom chelate ring $\overline{Pt—P—C{=}C—C}$ are Pt—P = 2.279 (2) Å, P—C = 1.824 (8) Å, C=C = 1.386 (11) Å, C—C = 1.432 (10) Å, and C—Pt = 2.018 (6) Å. Possible mechanims for the formation of 3 involve either initial C–H or C–C bond activation of the cyclopropane ring.

The activation of C–H and C–C bonds, especially in saturated systems, is of considerable interest.[1] Recent results have shown that alkane C–H bonds can be activated intermolecularly by selected metal complexes.[2-4] A more extensive literature clearly demonstrates that intramolecular C–H bond activation by a transition-metal complex occurs with relative ease, particularly when the C–H group is part of a phosphine.[5] This intramolecular C–H bond activation is very sensitive to the phosphine (bulky phosphines promote metalation) and the metal (group 8 metals are very reactive).[5a]

Intermolecular activation of C–C bonds has also been observed in strained ring compounds.[6] One example of C–C bond activation is the formation of metallacyclobutanes from the interaction of cyclopropanes with transition-metal complexes.[6b] The formation of allyl hydrides from the interaction of cyclopropanes with transition-metal complexes also occurs and may proceed through initial C–C bond activation (Scheme Ia), followed by hydride migration,[6c] or may arise from initial C–H bond activation with the intermediacy of a σ-bound cyclopropane complex (Scheme Ib).

Scheme I



Our general interest in C–H and C–C bond activation has led us to investigate the interaction with transition-

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