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Silicon−Carbon Unsaturated Compounds. 69. Reactions of Silenes Produced Thermally from Pivaloyl- and Adamantoyltris(trimethylsilyl)silane with Silyl-Substituted Butadiynes and Enynes

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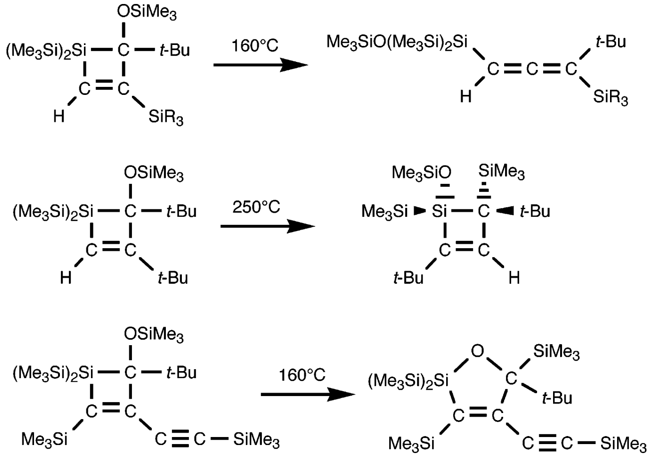
The thermolysis of pivaloyl- and adamantoyltris(trimethylsilyl)silane (**1a** and **1b**) with bis(trimethylsilyl)butadiyne and bis(dimethylphenylsilyl)butadiyne at 120 °C gave regiospecifically 2-trimethylsiloxy-3-silylethynyl-1-silacyclobut-3-ene derivatives (**2a**, **2b** and **3a**, **3b**), arising from the reaction of silenes generated thermally from **1a** and **1b** with the butadiynes. Similar treatment of **1a** and **1b** in the presence of bis(trimethylsilyl)butadiyne and bis(dimethylphenylsilyl)butadiyne at 160 °C gave 2,5-dihydro-1,2-oxasilole derivatives (**4a**, **4b** and **5a**, **5b**). When **2a** and **2b** were heated in the presence of methanol at 160 °C, methanol adducts **6a** and **6b** were obtained, respectively, as the sole product. The ring-opening processes of **2a** and the regiochemistry of [2 + 2] cycloaddition of the silene with bis(silyl)butadiyne and bis(silyl)but-1-en-3-yne are discussed on the basis of theoretical treatment. The thermolysis of **1a** and **1b** with bis(*tert*-butyldimethylsilyl)butadiyne at 160 °C produced [2 + 2] cycloadducts (**7a** and **7b**). With bis(*tert*-butyldimethylsilyl)butadiyne at 220 °C, **1a** and **1b** gave 2,5-dihydro-1,2-oxasilole derivatives (**8a** and **8b**). The reaction of **1a** and **1b** with (*E*)-1,4-bis(dimethylphenylsilyl)but-1-en-3-yne and (*E*)-1,4-bis(pentamethyldisilanyl)but-1-en-3-yne at 120 °C produced regiospecifically 2-trimethylsiloxy-3-[*trans*-(silyl)ethenyl]-1-silacyclobut-3-ene derivatives (**9a**, **9b** and **10a**, **10b**). At 200 °C, similar treatment of **1a** and **1b** with silyl-substituted but-1-en-3-ynes afforded 2,5-dihydro-1,2-oxasilole derivatives (**11a**, **11b** and **12a**, **12b**, respectively). UV−vis absorption and fluorescence spectra have been reported.

Introduction

Numerous examples of the reactions of silenes, which are produced by the photolysis and Peterson-type reaction of acylpolysilanes, have been reported to date.[1−7] We have found that the thermolysis of acylpolysilanes offers a convenient route to the preparation of many types of silenes, and the silenes thus formed react with various substrates, such as olefins,[8] dienes,[8] alkynes,[9] and carbonyl compounds[10] to give the respective adducts.

Recently, we have demonstrated that the thermolysis of pivaloyl- and adamantoyltris(trimethylsilyl)silane with monosubstituted acetylenes undergoes formal [2 + 2] cycloaddition to give adducts, which isomerize cleanly to afford various products at higher tempera-



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ture. The structures of the isomerization products depend highly on the substituents on the sp^2-hybridized carbon atoms in the silacyclobutenyl ring. For example, 2-*tert*-butyl-3-(silyl)-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-enes formed by the cothermolysis of pivaloyltris(trimethylsilyl)silane with monosilyl-substituted acetylenes at 120 °C isomerize cleanly to give the ring-opened allene derivatives at 160 °C,[9b] while 2,3-di(*tert*-butyl)-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene prepared by the reaction of pivaloyltris(trimethylsilyl)silane and *tert*-butylacetylene at 140 °C undergoes isomerization at 250 °C to give *trans*-2,4-di(*tert*-butyl)-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclobut-3-ene in almost quantitative yield.[11] On the other hand, when a silacyclobut-3-ene derivative formed by the thermal reaction of pivaloyltris(trimethylsilyl)silane with bis(trimethylsilyl)butadiyne is heated at 160 °C, 5-*tert*-butyl-2,5-dihydro-2,2,3,5-tetrakis(trimethylsilyl)-4-[2-(trimethylsilyl)ethynyl]-1,2-oxasilole is produced in high yield.[12]

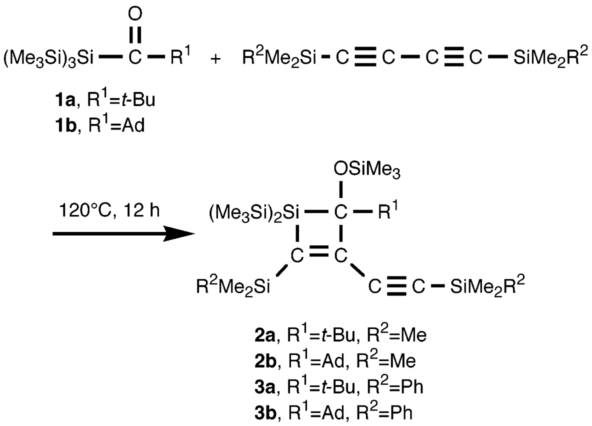
To learn more about thermal isomerization of the silacyclobut-3-ene system, we have initiated the investigation of the thermolysis of silacyclobut-3-ene derivatives bearing various substituents on the sp^2 carbons in the silacyclobutenyl ring. In this paper we report the cothermolysis of pivaloyl- and adamantoyltris(trimethylsilyl)silane with silyl-substituted butadiynes and enynes at various temperatures, the results of theoretical calculations for the thermal ring opening of the silacyclobut-3-ene derivatives to the 1-silabut-1,3-dienes, and the regiochemistry of [2 + 2] cycloaddition of silenes to the silyl-substituted butadiyne and but-1-en-3-yne derivatives. We also report UV−vis absorption and fluorescence spectra of the resulting products.

Results and Discussion

Reactions with Bis(silyl)butadiynes. When a mixture of pivaloyltris(trimethylsilyl)silane (**1a**) and bis(trimethylsilyl)butadiyne was heated in a sealed glass tube at 120 °C for 12 h, 2-*tert*-butyl-2-trimethylsiloxy-1,1,4-tris(trimethylsilyl)-3-[2-(trimethylsilyl)ethynyl]-1-silacyclobut-3-ene (**2a**) was obtained in 85% yield, along with 10% of the unchanged starting compound **1a** as reported previously.[12] A similar reaction of adamantoyltris(trimethylsilyl)silane (**1b**) with bis(trimethylsilyl)butadiyne proceeded to give the product analogous to **2a**, 2-adamantyl-2-trimethylsiloxy-1,1,4-tris(trimethylsilyl)-3-[2-(trimethylsilyl)ethynyl]-1-silacyclobut-3-ene (**2b**), in 97% yield (Scheme 1).[12] In both reactions, neither regioisomers nor byproducts were detected in the reaction mixture.

Phenyl-substituted bis(silyl)butadiyne also reacted with the silenes formed thermally from **1a** and **1b** to give the respective adducts. Thus, the reaction of **1a** with bis(dimethylphenylsilyl)butadiyne at 120 °C for 12 h afforded 2-*tert*-butyl-4-dimethylphenylsilyl-3-[(2-dimethylphenylsilyl)ethynyl]-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**3a**) in 82% yield, together with 10% of the starting compound **1a**. Similar reaction of **1b** with bis(dimethylphenylsilyl)butadiyne gave 2-adamantyl-4-dimethylphenylsilyl-3-[2-(dimethylphenylsilyl)ethynyl]-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**3b**) in 85% yield, in addition to 10% of the unchanged starting compound **1b**. The structures of products **3a** and **3b** were confirmed by mass, IR, and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis, as well as by elemental analysis.

Scheme 1



The formation of products **2a**, **2b**, **3a**, and **3b** can be best understood in terms of formal [2 + 2] cycloaddition of the silenes produced thermally from the acylpolysilanes **1a** and **1b** with bis(silyl)butadiynes. All reactions shown here proceeded with high regiospecificity to give the adducts. No trace amount of the regioisomers was detected in the reaction mixture. (For the regiochemistry of the [2 + 2] cycloaddition reactions of the silenes to bis(silyl)butadiynes and bis(silyl)but-1-en-3-ynes, see the Theoretical Calculations and Regiochemistry sections below.)

Next, we carried out the reaction of **1a** with bis(trimethylsilyl)butadiyne at high temperature. To our surprise, treatment of **1a** with bis(trimethylsilyl)butadiyne in a sealed glass tube at 160 °C for 24 h gave 5-*tert*-butyl-2,5-dihydro-2,2,3,5-tetrakis(trimethylsilyl)-4-[2-(trimethylsilyl)ethynyl]-1,2-oxasilole (**4a**) in 93% yield as the sole product.[12] The reaction of **1b** with bis(trimethylsilyl)butadiyne under the same conditions afforded 5-adamantyl-2,5-dihydro-2,2,3,5-tetrakis(trimethylsilyl)-4-[2-(trimethylsilyl)ethynyl]-1,2-oxasilole (**4b**) in 92% yield.[12] In both cases, no 1-silacyclobut-3-ene derivatives, **2a** and **2b**, were detected in the reaction mixtures.

Similarly, the thermolysis of **1a** and **1b** with bis(dimethylphenylsilyl)butadiyne at 160 °C proceeded cleanly to give the respective 2,5-dihydro-1,2-oxasilole derivatives. Thus, treatment of **1a** with bis(dimethylphenylsilyl)butadiyne at 160 °C for 12 h afforded 5-*tert*-butyl-2,5-dihydro-3-(dimethylphenylsilyl)-4-[2-(dimethylphenylsilyl)ethynyl]-2,2,5-tris(trimethylsilyl)-1,2-oxasilole (**5a**) in 80% yield, while **1b** with bis(trimethylsilyl)butadiyne produced 5-adamantyl-2,5-dihydro-3-(dimethylphenylsilyl)-4-[2-(dimethylphenylsilyl)ethynyl]-2,2,5-tris(trimethylsilyl)-1,2-oxasilole (**5b**) in 81% yield. No other volatile products were detected

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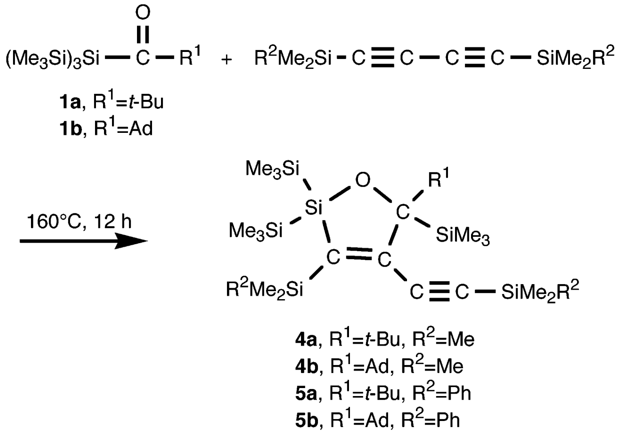
Scheme 2



1a, R^1=*t*-Bu
1b, R^1=Ad

4a, R^1=*t*-Bu, R^2=Me
4b, R^1=Ad, R^2=Me
5a, R^1=*t*-Bu, R^2=Ph
5b, R^1=Ad, R^2=Ph

in the reaction mixture. Compounds **5a** and **5b** were verified to have the 2,5-dihydro-1,2-oxasilole structures by spectrometric analysis.

Isomerization of Silacyclobutenes. To learn more about the formation of the products **4a**, **4b**, **5a**, and **5b**, we investigated the thermolyses of the 1-silacyclobut-3-enes **2a**, **2b**, **3a**, and **3b** at 160 °C. In marked contrast to the thermal isomerization of 2,3-di(*tert*-butyl)-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene,[11] which produces *trans*-2,4-di(*tert*-butyl)-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclobut-3-ene in high yield, via 1,2-di(*tert*-butyl)-3-[(trimethylsiloxy)bis(trimethylsilyl)silyl]cycloprop-2-ene, the present isomerization involves expansion of the silacyclobutene ring to give the oxygen-containing five-membered ring. In fact, when **2a** was heated in a sealed glass tube at 160 °C for 12 h, **4a** was obtained in almost quantitative yield. The thermolyses of **2b**, **3a**, and **3b** under the same conditions again afforded the respective 2,5-dihydro-1,2-oxasilole derivatives **4b**, **5a**, and **5b** in 97%, 84%, and 82% yields, respectively. In an effort to trap the intermediate, which might be involved in the present isomerization, we carried out the thermal reaction of the silacyclobutenes **2a** and **2b** in the presence of methanol. Thus, the reaction of **2a** with a slight excess of methanol in a sealed glass tube at 160 °C for 24 h afforded (*E*)-1-*tert*-butyl-2-{[methoxybis(trimethylsilyl)silyl](trimethylsilyl)}methyl-1-(trimethylsiloxy)-4-(trimethylsilyl)but-1-en-3-yne (**6a**) in 83% isolated yield, as the sole product (Scheme 3). No other stereoisomers were detected in the reaction mixture by spectrometric analysis. The formation of **6a** can be best explained in terms of the reaction of 4-*tert*-butyl-4-trimethylsiloxy-1,1,2-tris(trimethylsilyl)-3-[2-(trimethylsilyl)ethynyl]]-1-sila-1,3-butadiene (**A**, R = *t*-Bu) with methanol.

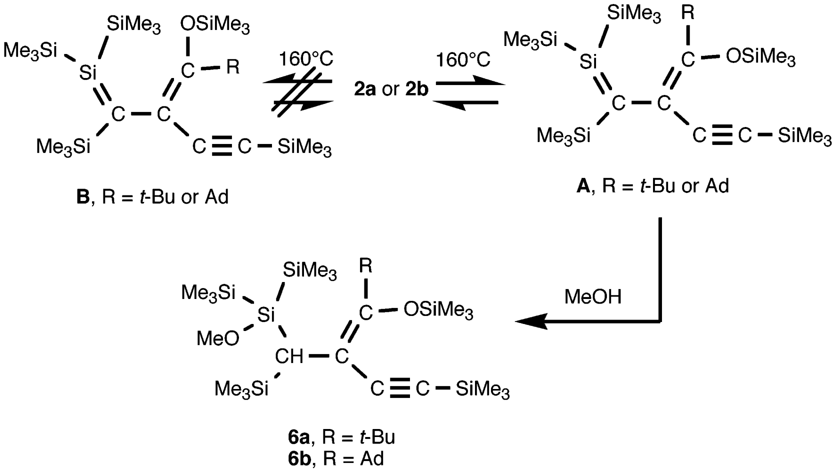
Similar reaction of **2b** with methanol again gave a product analogous to **6a**, (*E*)-1-adamantyl-2-{[methoxybis(trimethylsilyl)silyl](trimethylsilyl)}methyl-1-(trimethylsiloxy)-4-(trimethylsilyl)but-1-en-3-yne (**6b**) in 84% isolated yield. No geometrical isomer of **6b**, potentially derived from the reaction of the intermediate (**B**, R = Ad) with methanol, was detected in the reaction mixture. Therefore, it seems reasonable to assume that the thermal isomerization products **4a**,**b** and also **5a**,**b** may be formed via the intermediates such as **A**, but not **B**.

The formation of **4a**,**b** and also **5a**,**b** via the 1-silabut-1,3-diene intermediates presumably involves isomerization of the silabutadiene to a bicyclic intermediate (**C**), as described in Scheme 4 by using the intermediate **A** as an example. We have proposed the bicyclic intermediate such as **C** in the thermal isomerization of 2,3-di-*tert*-butyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene.[11]

Heating **1a** and **1b** with bis(silyl)butadiyne bearing a bulky substituent on the silicon atom, such as bis(*tert*-butyldimethylsilyl)butadiyne, at 120 °C for 12 h afforded no adducts, but the starting compounds **1a** and **1b** were recovered unchanged. However, at higher temperature, the reaction proceeded cleanly to give the adducts. When a mixture of **1a** with bis(*tert*-butyldimethylsilyl)butadiyne in a sealed glass tube was heated at 160 °C for 12 h, 2-*tert*-butyl-4-(*tert*-butyldimethylsilyl)-3-[2-(*tert*-butyldimethylsilyl)ethynyl]-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**7a**) was obtained in 95% yield (Scheme 5). Similar treatment of **1b** with bis(*tert*-butyldimethylsilyl)butadiyne at 160 °C for 12 h gave 2-adamantyl-4-(*tert*-butyldimethylsilyl)-3-[2-(*tert*-butyldimethylsilyl)ethynyl]-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**7b**) in 90% yield. The structures of **7a** and **7b** were verified by spectrometric analysis, as well as by elemental analysis (Scheme 5).

Next, we carried out the reactions of **1a** and **1b** with the butadiyne at higher temperature. Thus, treatment

Scheme 3

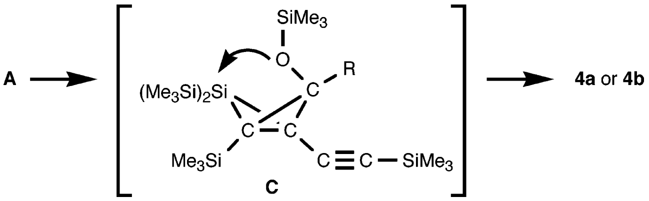


B, R = *t*-Bu or Ad

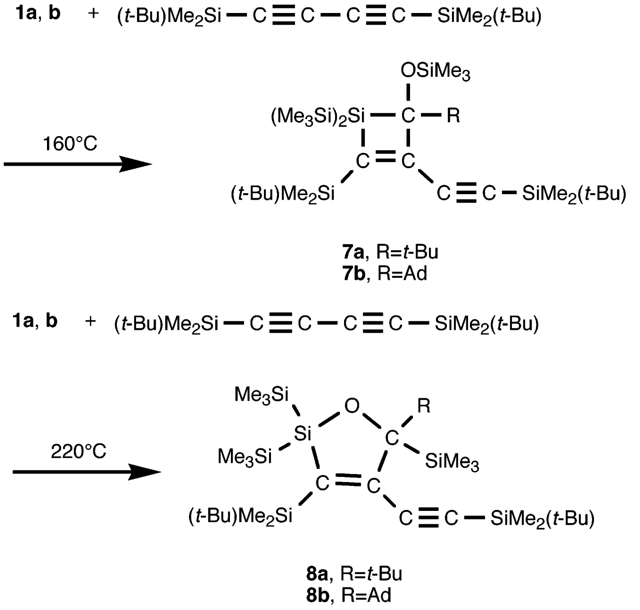
A, R = *t*-Bu or Ad

6a, R = *t*-Bu
6b, R = Ad

Scheme 4



Scheme 5



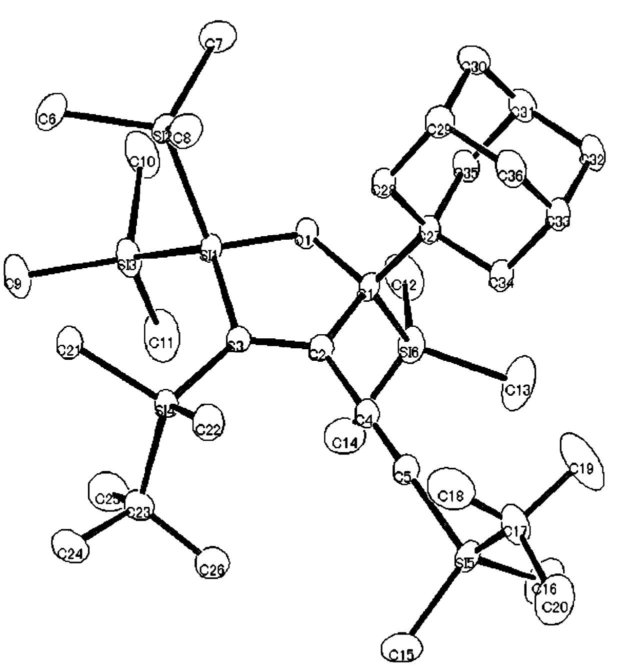
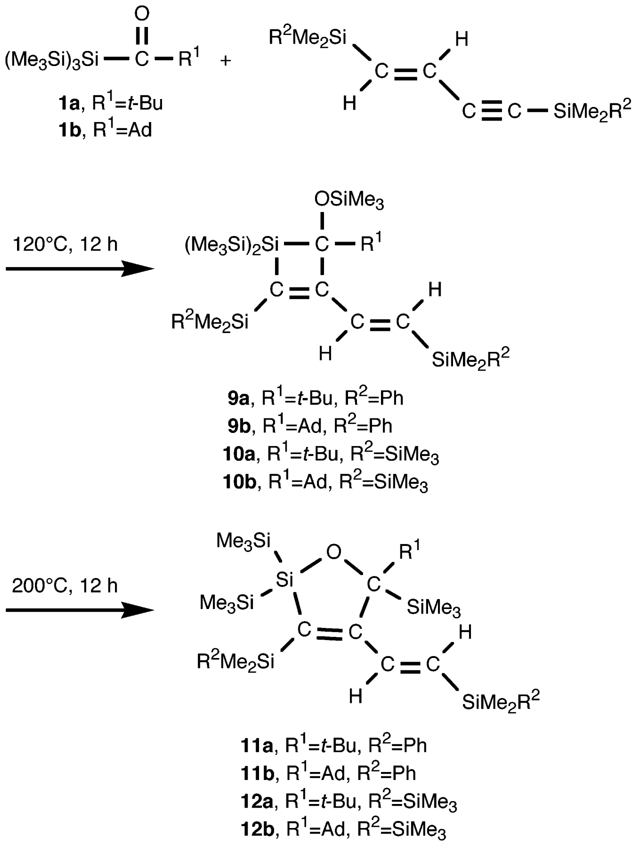


Figure 1. ORTEP diagram for **8b** showing thermal ellipsoids at the 50% level; hydrogen atoms were omitted for clarity.

Scheme 6



of **1a** with bis(*tert*-butyldimethylsilyl)butadiyne at 220 °C for 12 h gave 5-*tert*-butyl-3-(*tert*-butyldimethylsilyl)-4-[2-(*tert*-butyldimethylsilyl)ethynyl]-2,5-dihydro-2,2-bis(trimethylsilyl)-1,2-oxasilole (**8a**) in 90% yield. The product **8a** could readily be isolated by column chromatography. Treatment of **1b** with bis(*tert*-butyldimethylsilyl)butadiyne under the same conditions afforded 5-adamantyl-3-(*tert*-butyldimethylsilyl)-4-[2-(*tert*-butyldimethylsilyl)ethynyl]-2,5-dihydro-2,2-bis(trimethylsilyl)-1,2-oxasilole (**8b**), analogous to **8a** in 90% yield. The structures of **8a** and **8b** were confirmed by spectrometric analysis and also by elemental analysis. The fact that **8b** has the 2,5-dihydro-1,2-oxasilole structure was verified by X-ray crystallographic analysis. An ORTEP representation of the molecular structure for **8b** is shown in Figure 1.

All bond distances and angles agree well with generally accepted values. The five-membered ring (Si1, O1, C1, C2, and C3) is in a twist conformation. The length of Si6–C1 is slightly longer (1.949(4) Å) than those of usual silicon–carbon bonds due to the C13- - -C34 contact (3.424(5) Å). There are no intermolecular contacts less than 3.6 Å.

Reactions with Bis(silyl)but-1-en-3-ynes. To confirm whether the presence of an ethynyl group on the sp^2-hybridized carbon atom at the 3-position in the silacyclobutenyl ring plays an important role for the production of the 2,5-dihydro-1,2-oxasilole structure, we investigated the similar reaction of **1a** and **1b** using silyl-substituted but-1-en-3-ynes. Thus, the reaction of **1a** with (*E*)-1,4-bis(dimethylphenylsilyl)but-1-en-3-yne at 120 °C for 12 h proceeded with high regiospecificity to give 2-*tert*-butyl-4-dimethylphenylsilyl-3-[(*E*)-2-(dimethylphenylsilyl)ethenyl]-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**9a**) in 70% yield, along with 23% of the unchanged starting compound **1a** (Scheme 6). No 3-(dimethylphenylsilyl)ethynyl-1-silacyclobutane, a regioisomer of **9a**, was detected in the reaction mixture. The ^{1}H NMR spectrum of **9a** shows the presence of three kinds of trimethylsilyl protons at

0.13, 0.16, and 0.20 ppm, four kinds of methylsilyl protons at 0.28, 0.29, 0.35, and 0.36 ppm, and a single resonance due to *tert*-butyl protons at 0.97 ppm, in addition to olefinic protons and phenyl ring protons. Its ^{13}C NMR spectrum shows no signals due to the ethynyl carbon atoms, indicating that the silene adds to a carbon−carbon triple bond, but not a carbon−carbon double bond. The ^{29}Si NMR spectrum reveals six resonances at −17.0, −16.9, −14.5, −10.8, −10.7, and 6.0 ppm. The reaction of **1b** with (*E*)-1,4-bis(dimethylphenylsilyl)but-1-en-3-yne also afforded 2-adamantyl-4-dimethylphenylsilyl-3-[(*E*)-2-(dimethylphenylsilyl)ethenyl]-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**9b**), whose structure was verified by spectrometric analysis, in 88% yield.

When **1a** was heated with (*E*)-1,4-bis(pentamethyldisilanyl)but-1-en-3-yne at 120 °C for 12 h, 2-*tert*-butyl-4-pentamethyldisilanyl-3-[(*E*)-2-(pentamethyldisilanyl)ethenyl]-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**10a**) was obtained in 60% yield as the sole product, along with 28% of the unchanged starting compound **1a**. The similar reaction of **1b** with (*E*)-1,4-bis(pentamethyldisilanyl)but-1-en-3-yne again proceeded regiospecifically to afford the [2 + 2] cycloadduct, 2-adamantyl-4-pentamethyldisilanyl-3-[(*E*)-2-(pentamethyldisilanyl)ethenyl]-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**10b**), which was readily isolated by column chromatography.

In analogy with the reactions with bis(silyl)butadiynes, the thermolysis of **1a** and **1b** with bis(silyl)but-1-en-3-ynes at high temperature produced the 2,5-dihydro-1,2-oxasilole derivatives arising from isomerization of the silacyclobut-3-enes. Interestingly, these reactions proceeded with high regio- and stereospecificity to give the adducts. Thus, treatment of **1a** with (*E*)-1,4-bis(dimethylphenylsilyl)but-1-en-3-yne at 200 °C for 12 h gave 5-*tert*-butyl-2,5-dihydro-3-(dimethylphenylsilyl)-4-[(*E*)-2-(dimethylphenylsilyl)ethenyl]-2,2,5-tris(trimethylsilyl)-1,2-oxasilole (**11a**) in 92% yield, while **1b** with (*E*)-1,4-bis(dimethylphenylsilyl)but-1-en-3-yne produced 5-adamantyl-2,5-dihydro-3-(dimethylphenylsilyl)-4-[(*E*)-2-(dimethylphenylsilyl)ethynyl]-2,2,5-tris(trimethylsilyl)-1,2-oxasilole (**11b**) in 91% yield.

The structures of **11a** and **11b** were verified by spectrometric analysis. For example, the ^{1}H NMR spectrum of **11b** shows the presence of three kinds of trimethylsilyl protons at 0.10, 0.20, and 0.24 ppm and four kinds of methylsilyl protons at 0.17, 0.19, 0.34, and 0.38, as well as resonances due to adamantyl, olefinic, and phenyl ring protons. The ^{29}Si NMR spectrum of **11b** reveals six resonances at −20.4, −18.7, −15.8, −10.8, 0.7, and 38.5 ppm. These results are wholly consistent with the structure proposed for **11b**.

When a mixture of **1a** and (*E*)-1,4-bis(pentamethyldisilanyl)but-1-en-3-yne was heated in a sealed glass tube under the same conditions, 5-*tert*-butyl-2,5-dihydro-3-(pentamethyldisilanyl)-4-[(*E*)-2-(pentamethyldisilanyl)ethenyl]-2,2,5-tris(trimethylsilyl)-1,2-oxasilole (**12a**) was obtained in 86% yield. Similarly, **1b** reacted with (*E*)-1,4-bis(pentamethyldisilanyl)but-1-en-3-yne regio- and stereospecifically to give 5-adamantyl-2,5-dihydro-3-(pentamethyldisilanyl)-4-[(*E*)-2-(pentamethyldisilanyl)ethenyl]-2,2,5-tris(trimethylsilyl)-1,2-oxasilole (**12b**) in 84% yield.

In these reactions, the silacyclobutenes and the intermediates analogous to 1-sila-1,3-butadiene **A** and bicyclic compound **C** are probably involved in the formation of **11a**,**b** and **12a**,**b**. For the formation of the 2,5-dihydro-1,2-oxasilole structure, the presence of the unsaturated group at the 3-position of the silacyclobutenyl ring seems to be important.

Theoretical Calculations. We considered how the thermal ring opening of **2a** and **2b** occurs using the B3LYP density functional theory method[13,14] combined with the 6-31G* basis set[15] available in the Gaussian 98 program.[16] There are four possible reaction pathways for the ring opening in principle. Taking the Woodward−Hoffmann rule[17] for concerted reactions into account, we can reasonably rule out the disrotatory processes, in which the Si−C and C−C bonds of the four-membered ring rotate in opposite directions. We thus calculated the two conrotatory processes that convert **2a** to **A** and **B** via $\mathbf{TS1_A}$ and $\mathbf{TS1_B}$, respectively, as shown in Figure 2. The activation energies for the two processes were computed to be 24.9 and 35.5 kcal/mol in **A** and **B**, respectively. The results obtained here can reasonably explain our prediction from the experiments that the formation of **A** is dominant in the ring opening of **2a** and **2b**. Since the two processes are symmetry-allowed in terms of orbital interactions, these DFT calculations suggest that this energy difference should come from steric effects of the substituents. The repulsive interaction between the $SiMe_3$ and *t*-Bu groups in $\mathbf{TS1_A}$ is smaller than that between the $SiMe_3$ and *t*-Bu groups in $\mathbf{TS1_B}$. Calculated atomic charges in the reactions from **2a** to **A** and **B** are summarized in Table 2. Since no significant difference is observed in these atomic charge distributions, the steric effects of bulky groups are likely to control the branching ratio of **A** and **B**.

We performed additional calculations to analyze the formation of the methanol adducts. Insertion of methanol into **A** (**B**) is a downhill process with an exothermal energy of 53.7 (44.4) kcal/mol, the activation energy for the methanol insertion being 5.0 (6.0) kcal/mol in **A** (**B**). These values are in good agreement with the activation energy of less than 6 kcal/mol in the reaction of alcohol insertion into an Si═C bond.[18] Therefore, if **A** and **B** are formed, they can easily react with methanol at 160 °C. However, we could not experimentally observe the

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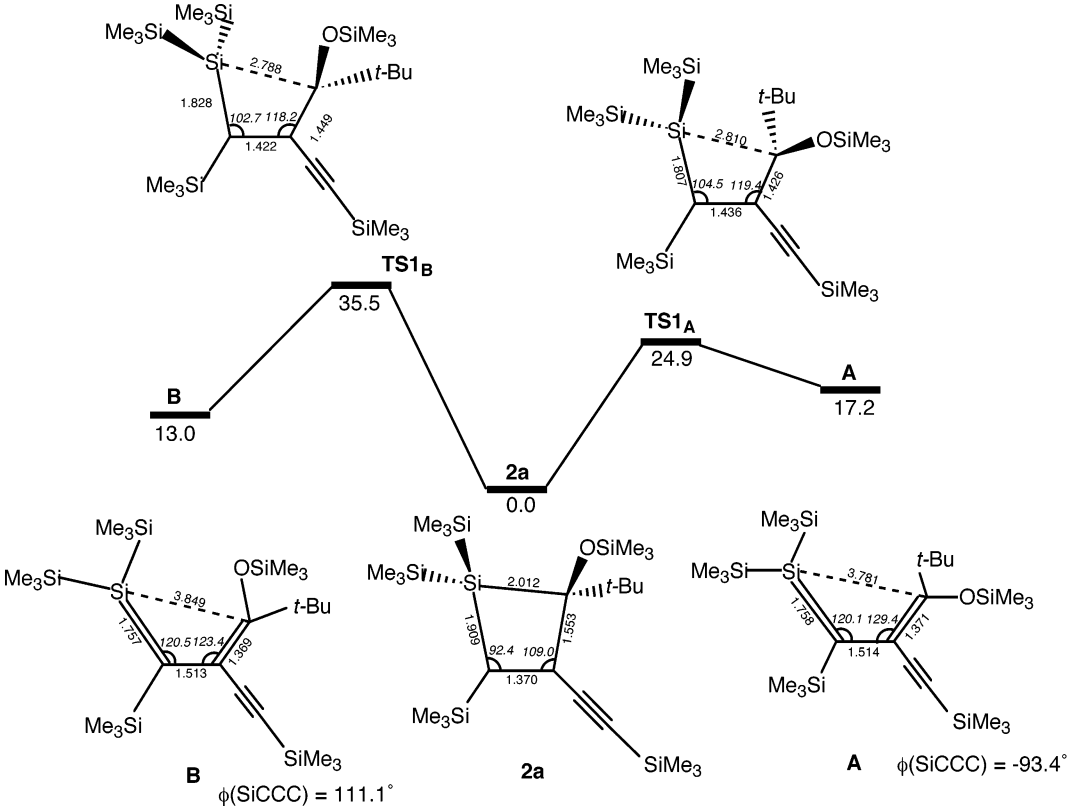
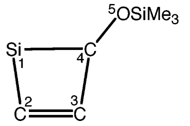


Figure 2. Computed energy diagram at the B3LYP/6-31G* level of theory for the ring-opening processes that convert **2a** into **A** and **B**. Units are in kcal/mol. *ϕ* is the dihedral angle.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 8b

Si(1)−Si(2)	2.392(1)	Si(1)−Si(3)	2.372(1)
Si(1)−O(1)	1.673(2)	Si(1)−C(3)	1.876(4)
Si(4)−C(3)	1.887(3)	Si(6)−C(1)	1.949(3)
O(1)−C(1)	1.466(3)	C(1)−C(2)	1.546(4)
C(2)−C(3)	1.359(4)	C(2)−C(4)	1.448(4)
O(1)−Si(1)−C(3)	94.2(1)	Si(1)−O(1)−C(1)	115.4(2)
O(1)−C(1)−C(2)	105.3(2)	C(1)−C(2)−C(3)	119.1(3)
Si(1)−C(3)−C(2)	105.7(2)		

Table 2. Calculated Atomic Charges from the Mulliken Population Analysis



entry	Si(1)	C(2)	C(3)	C(4)	O(5)
2a	0.25	−0.20	0.08	0.12	−0.63
TS1$_A$	−0.01	−0.32	−0.10	0.29	−0.63
TS1$_B$	0.02	−0.21	0.07	0.26	−0.59
A	0.02	−0.36	−0.11	0.36	−0.63
B	0.03	−0.40	−0.13	0.37	−0.62

product that derives from **B**. To estimate the branching ratio of the formation of **A** and **B** from **2a**, we calculated the relative rate constant ($k_{\mathbf{A}}/k_{\mathbf{B}}$) for the ring-opening processes using transition-state theory[19] with eq 1.

$$\frac{k_{\mathbf{A}}}{k_{\mathbf{B}}} = \frac{(I_x^{\mathbf{A}} I_y^{\mathbf{A}} I_z^{\mathbf{A}})^{1/2}}{(I_x^{\mathbf{B}} I_y^{\mathbf{B}} I_z^{\mathbf{B}})^{1/2}} \frac{q_v^{\mathbf{A}}}{q_v^{\mathbf{B}}} \exp\left(\frac{E^{\#}_{\mathbf{A}} - E^{\#}_{\mathbf{B}}}{RT}\right) \qquad (1)$$

Here *I* and *q* are the moment of inertia and the vibrational partition function of the transition state, respectively. $E^{\#}$ is the activation energy that includes zero-point energies and thermal corrections. The last exponential term is dominant in eq 1 because the other terms can be almost all canceled between the denominators and numerators. Since the $k_{\mathbf{A}}/k_{\mathbf{B}}$ value thus calculated is 8.44×10^4 at 160 °C, the formation of **B** is negligible from the viewpoint of theoretical consideration. This is fully consistent with the experimental result that the thermal reaction gives **6a** alone as the product in the presence of methanol. Our calculations successfully reproduce the complicated chemical processes between silacylobutene and methanol.

Let us next consider the regiochemistry of [2 + 2] cycloaddition of silene with bis(silyl)butadiyne or bis(silyl)but-1-en-3-yne. Since these reactions are symmetry-forbidden according to the Woodward−Hoffmann rule,[17] they are predicted to take place in a stepwise manner via a radical intermediate. To find a reasonable reaction mechanism, we carried out DFT calculations with respect to possible radical intermediates using simplified models at the B3LYP/6-31G* level of theory. In the reaction between silene and butadiyne, two kinds of radical intermediates, **IntA** and **IntB**, can be formed, as shown in Scheme 7, in which their relative energies are indicated. On the basis of the energetics, **IntA** is predicted to play a role in this reaction. **IntC** is also predicted to occur in the reaction between silene and but-1-en-3-yne. The more stable radical intermediates, **IntA** and **IntC**, undergo a coupling reaction to form a four-membered ring in the subsequent step. These calculational results are fully consistent with our ex-

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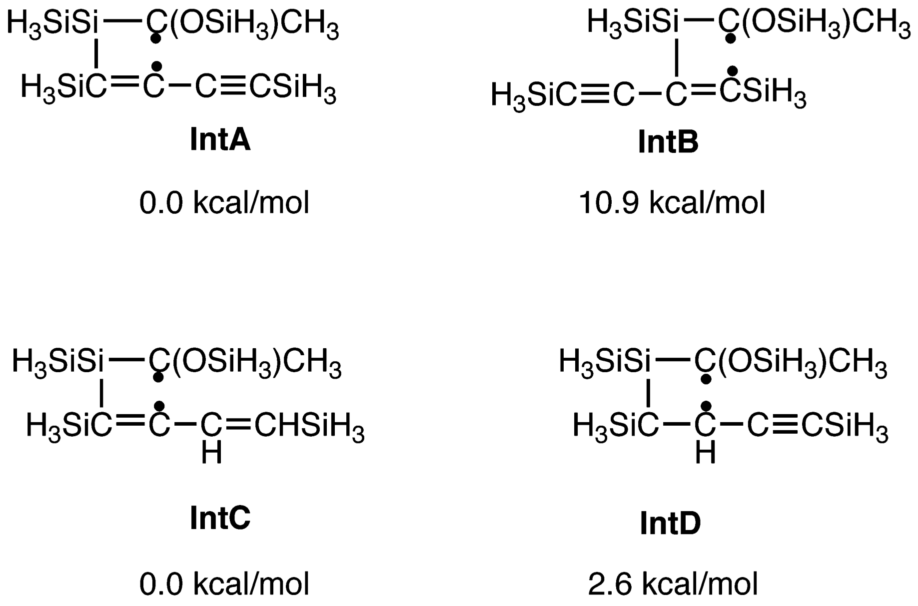
Scheme 7



perimental observations about the regiochemistry of the [2 + 2] cycloaddition reactions.

Regiochemistry. As mentioned above, the results of the theoretical calculations for the regiochemistry in the reactions of 2-methyl-2-siloxy-1,1-bis(silyl)silene with bis(silyl)butadiyne and bis(silyl)but-1-en-3-yne and the crystallographic analysis for **8b** were consistent with the structures proposed for the cycloadducts **2a**,**b**−**5a**,**b** and **7a**,**b**−**12a**,**b**. We also confirmed the regiochemistry of the cycloadducts by NMR spectrometric analysis including NOE-FID difference experiments at 300 MHz, using compounds **7b**, **10b**, and **11b**.

The ^{1}H NMR spectrum for **7b** shows the signals at 0.08, 0.12, 0.13, and 0.19 ppm, due to four nonequivalent MeSi protons in two *t*-BuMe$_2$Si groups, the signals at 0.23, 0.26, and 0.28 ppm, attributed to the Me$_3$SiO protons and two Me$_3$Si protons, and the signals at 0.95 and 0.96 ppm, due to two kinds of *t*-Bu protons, as well as the proton signals of the adamantyl group at 1.66−1.98 ppm. Irradiation of the *t*-Bu protons at 0.96 ppm resulted in a positive NOE of the signals at 0.12 and 0.13 ppm, due to two nonequivalent MeSi protons attached to the *t*-Bu group being irradiated. No enhancement was observed for other protons. These results indicate that this *t*-BuMe$_2$Si group must be situated on the terminal sp-hybridized carbon of **7b**. Similar irradiation of the *t*-Bu protons at 0.95 ppm led to a strong enhancement of the signals at 0.26 and 0.28 ppm, attributed to two Me$_3$Si protons on the ring silicon atom, together with enhancement of the signals appearing at 0.08 and 0.19 ppm, attributed to two nonequivalent MeSi protons attached to the *t*-Bu group. These results are wholly consistent with the structure proposed for **7b**.

The ^{13}C NMR spectrum for **10b** shows no signals due to ethynyl carbons, but reveals the presence of four olefinic carbons, indicating that the silene adds only to the triple bond, but not to the double bond in the but-1-en-3-yne moiety. In its ^{1}H NMR spectrum, the coupling constant ($J = 19$ Hz) of the olefinic protons at 6.18 and 6.48 ppm clearly indicates that **10b** must have an *E*-configuration. Furthermore, irradiation of an olefinic proton at 6.18 ppm resulted in enhancement of the signals at 0.10 and 0.141 ppm attributable to the Me$_3$Si protons and Me$_2$Si protons, as well as the signals due to the adamantyl protons. As expected, no enhancement is observed for the olefinic proton at 6.48 ppm. Irradiation of the proton at 6.48 ppm caused a positive NOE of the signal at 0.141 ppm, due to the Me$_2$Si protons. Again, the results are consistent with the structure proposed for **10b**.

We also carried out the NOE-FID difference experiments for the oxasilole **11b**. In the ^{1}H NMR spectrum for **11b**, the coupling constant ($J = 19$ Hz) of the olefinic protons shows that this compound must have the *E*-configuration. The NOE-FID difference experiments also indicate the *E*-configuration for this compound. Thus, irradiation of the olefinic proton at 6.34 ppm resulted in a strong enhancement of the signals at 0.10, 0.17, and 0.19 ppm, due to the Me$_3$Si protons and two nonequivalent Me$_2$Si protons, respectively, together with enhancement of the signals appearing at the phenyl region. Saturation of the olefinic proton at 5.94 ppm caused a positive NOE of the signals at 0.17 and 0.19 ppm, attributed to nonequivalent Me$_2$Si protons, as well as signals appearing at the adamantyl and phenyl region. Irradiation of the Me$_3$Si protons at 0.10 ppm led to a strong enhancement of the signals at 0.20, 1.53−1.90, and 6.34 ppm, due to the Me$_3$Si protons, adamantyl protons, and olefinic proton, respectively, in agreement with the structure proposed for **11b**. The results of the NOE-FID difference experiments for **7b**, **10b**, and **11b** are wholly consistent with those obtained from X-ray crystallographic analysis of **8b**.

Photophysical Properties of Silacyclobutenes and 1,2-Oxasiloles. UV−vis absorption spectra and fluorescence spectra of silacyclobutenes and oxasiloles are measured, and their data are summarized in Table 3. All of the silacyclobutenes obtained in the present study show almost the same absorption maxima at around 300 nm with almost the same molar absorption coefficients. On the other hand, the absorption maxima

Table 3. UV−Vis and Fluorescence Spectral Data for for 2−11 in Cyclohexane

	UV−vis	FL		
compound	$\lambda_{max,Abs}$/nm	ϵ	λ_{em}/nm[a]	Φ_f[b]
silacyclobutenes				
2a	296	7900	446.5	0.0012
2b	298	7000	441.0	0.0009
3a	301	7200	450.5	0.0034
3b	303	7700	453.5	0.0033
7a	301	8000	441.0	0.0042
7b	300	6900	446.5	0.0055
9a	296	8300	469.5	0.0120
9b	297	7000	470.0	0.0103
10a	304	8000	455.5	0.0095
10b	306	6900	454.0	0.0089
1,2-oxasilole				
4a	329	5100	438.5	0.2003
4b	328	6200	442.5	0.2289
5a	331	6600	449.5	0.2109
5b	332	7000	450.0	0.2103
8a	329	6800	449.5	0.2263
8b	332	5200	440.0	0.2019
11a	318	6200	468.0	0.2389
11b	320	5500	469.5	0.2394
12a	332	5900	454.5	0.2111
12b	329	6000	455.0	0.2191

[a] Maximum wavelength in emission spectra. [b] Based on 9,10-diphenylanthracene ($\Phi_{331} = 0.90$) as a standard.

for 2,5-dihydro-1,2-oxasiloles appear at about 20−30 nm longer wavelength than those of silacyclobutenes. These results suggest that some differences in the electronic structure exist between silacyclobutenes and oxasilacyclopentenes. In fluorescence spectra, the emission maxima appear at similar wavelength for the silacyclobutenes and 2,5-dihydro-1,2-oxasiloles, but the quantum yields are very different from each other. The quantum yields of the 1,2-oxasiloles are much higher than those of the silacyclobutenes.

In conclusion, the thermolysis of acylpolysilanes **1a** and **1b** with bis(trimethylsilyl)- and bis(dimethylphenylsilyl)butadiyne at 120 °C proceeded regiospecifically to give the [2 + 2] cycloadducts formed by addition of the silenes generated thermally from acylpolysilanes to bis(silyl)butadiynes. At 160 °C, however, **1a** and **1b** reacted with bis(trimethylsilyl)- and bis(dimethylphenylsilyl)butadiyne to give the 2,5-dihydro-1,2-oxasilole derivatives, arising from isomerization of the 1-silabut-1,3-dienes formed by the ring opening of the silacyclobutenes. The reaction of **1a** and **1b** with bis(dimethylphenylsilyl)but-1-en-3-yne and bis(pentamethyldisilanyl)but-1-en-3-yne at 120 °C gave regio- and stereospecifically the respective 2-trimethylsiloxy-3-silylethenyl-1-silacyclobut-2-ene derivatives. Treatment of **1a** and **1b** with silyl-substituted but-1-en-3-ynes at 200 °C, however, afforded the 1,2-oxasilole derivatives. Theoretical treatment of **2a** for the ring-opening reaction indicated the formation of the silabutadiene **A**, which was consistent with the experimental result. The results of the theoretical calculations for the regiochemistry of [2 + 2] cycloaddition were also consistent with experimental observations. Absorption maxima for the 1,2-oxasilole derivatives appear at about 20−30 nm longer wavelengths than those of the silacyclobutene derivatives. The quantum yields of the 1,2-oxasiloles are much higher than those of the silacyclobutenes.

Experimental Section

General Procedures. All reactions were carried out in a degassed sealed tube (1.0 cm i.d. × 15 cm). Yields of the products were calculated on the basis of the isolated products. NMR spectra were recorded on JNM-LA300 and JNM-LA500 spectrometers. Infrared spectra were recorded on a JEOL model JIR-DIAMOND 20 infrared spectrophotometer. Mass spectra were measured on a JEOL model JMS-700 instrument. UV−visible absorption spectra were measured with a JASCO V-560 spectrometer in spectral grade cyclohexane. Fluorescence spectra were measured with a JASCO FP-777 spectrometer in degassed spectral grade cyclohexane. Melting points were measured with a Yanaco-MP-S3 apparatus. Column chromatography was performed by using Wakogel C-300 (WAKO). Acylpolysilanes **1a** and **1b** were prepared according to the method reported by Brook et al.[20,21] The syntheses of silyl-substituted but-1-en-3-ynes are described in ref 22.

Thermolysis of 1a with Bis(dimethylphenylsilyl)butadiyne at 120 °C. A mixture of 0.1457 g (0.438 mmol) of **1a** and 0.1396 g (0.439 mmol) of bis(dimethylphenylsilyl)-butadiyne was heated in a sealed glass tube at 120 °C for 12 h. Product **3a** (0.2338 g, 82% isolated yield) and the starting compound **1a** (0.0146 g, 10% isolated yield) were isolated by column chromatography. Data for **3a**: Anal. Calcd for $C_{34}H_{58}OSi_6$: C, 62.70; H, 8.98. Found: C, 62.77; H, 9.12. MS *m/z* 650 (M^+); IR 3070, 3048, 2954, 2869, 2127, 1429, 1247, 1112, 1043, 836, 813, 779, 730, 698 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.02 (s, 9H, Me_3Si), 0.21 (s, 9H, Me_3Si), 0.22 (s, 9H, Me_3Si), 0.44 (s, 3H, MeSi), 0.45 (s, 6H, Me_2Si), 0.48 (s, 3H, MeSi), 1.03 (s, 9H, *t*-Bu), 7.28−7.41 (m, 6H, phenyl ring protons), 7.55−7.64 (m, 4H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −2.25, −2.04, −1.36, −1.28 (MeSi), 1.35, 1.52, 4.21 (Me_3Si), 27.85 (Me_3C), 36.40 (CMe_3), 94.49 (CO), 96.53, 106.28 (sp carbons), 127.69, 127.80, 128.95, 129.37, 133.78, 134.07, 136.56, 138.66 (phenyl ring carbons), 153.88, 166.94 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −22.0, −15.6, −15.4 (2Si), −3.7, 9.0.

Thermolysis of 1b with Bis(dimethylphenylsilyl)butadiyne at 120 °C. A mixture of 0.0850 g (0.207 mmol) of **1b** and 0.0865 g (0.272 mmol) of bis(dimethylphenylsilyl)-butadiyne was heated at 120 °C for 12 h. Product **3b** (0.1281 g, 85% isolated yield) and the starting compound **1b** (0.0085 g, 10% isolated yield) were isolated by column chromatography. Data for **3b**: Anal. Calcd for $C_{40}H_{64}OSi_6$: C, 65.86; H, 8.84. Found: C, 65.70; H, 8.80. MS *m/z* 728 (M^+); IR 3070, 2954, 2904, 2848, 2127, 1429, 1247, 1114, 1052, 835, 730, 698 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.03 (s, 9H, Me_3Si), 0.20 (s, 9H, Me_3Si), 0.23 (s, 9H, Me_3Si), 0.457 (s, 3H, MeSi), 0.464 (s, 6H, Me_2Si), 0.49 (s, 3H, MeSi), 1.53−1.98 (m, 15H, Ad), 7.30−7.40 (m, 6H, phenyl ring protons), 7.56−7.70 (m, 4H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −2.16, −2.09, −1.42, −1.28 (MeSi), 1.45, 1.59, 4.23 (Me_3Si), 28.65, 37.22, 38.92, 41.65 (Ad), 95.84 (CO), 96.46, 106.71 (sp carbons), 127.69, 127.79, 128.95, 129.38, 133.77, 134.11, 136.57, 138.73 (phenyl ring carbons), 153.43, 167.75 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −22.0, −15.8, −15.6, −15.0, −4.1, 9.6.

Thermolysis of 1a with Bis(dimethylphenylsilyl)butadiyne at 160 °C. A mixture of 0.1002 g (0.302 mmol) of **1a** and 0.1248 g (0.392 mmol) of bis(dimethylphenylsilyl)-butadiyne was heated at 160 °C for 12 h. Product **5a** (0.1573 g, 80% isolated yield) was isolated by column chromatography: Anal. Calcd for $C_{34}H_{58}OSi_6$: C, 62.70; H, 8.98. Found: C, 62.77; H, 8.60. MS *m/z* 650 (M^+); IR 3070, 2954, 2898, 2138, 1479, 1427, 1245, 1114, 1054, 960, 836, 781, 728, 698 cm^{-1};

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^{1}H NMR δ (CDCl$_3$) 0.13 (s, 9H, Me$_3$Si), 0.14 (s, 9H, Me$_3$Si), 0.16 (s, 9H, Me$_3$Si), 0.26 (s, 6H, Me$_2$Si), 0.42 (s, 6H, Me$_2$Si), 1.07 (s, 9H, *t*-Bu), 7.28−7.44 (m, 6H, phenyl ring protons), 7.56−7.67 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −1.73, −1.69, −1.42, −0.89 (MeSi), 0.70, 0.95, 1.41 (Me$_3$Si), 28.38 (Me$_3$C), 41.17 (CMe$_3$), 99.32 (CO), 102.55, 106.77 (sp carbons), 127.49, 127.71, 128.67, 129.27, 133.70, 134.16, 136.36, 138.94 (phenyl ring carbons), 148.82, 153.24 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −22.3, −19.3, −18.7, −14.4, 2.0, 38.4.

Thermolysis of 1b with Bis(dimethylphenylsilyl)butadiyne at 160 °C. A mixture of 0.0901 g (0.220 mmol) of **1b** and 0.0865 g (0.272 mmol) of bis(dimethylphenylsilyl)butadiyne was heated at 160 °C for 12 h. Product **5b** (0.1298 g, 81% isolated yield) was isolated by column chromatography: Anal. Calcd for C$_{40}$H$_{64}$OSi$_6$: C, 65.86; H, 8.84. Found: C, 65.52; H, 8.85. MS *m/z* 728 (M$^+$); IR 2952, 2904, 2848, 2132, 1481, 1427, 1245, 1112, 1051, 836, 781, 728, 698 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.14 (s, 9H, Me$_3$Si), 0.158 (s, 9H, Me$_3$Si), 0.160 (s, 9H, Me$_3$Si), 0.26 (s, 3H, MeSi), 0.28 (s, 3H, MeSi), 0.44 (s, 3H, MeSi), 0.45 (s, 3H, MeSi), 1.61−1.96 (m, 15H, Ad), 7.27−7.45 (m, 6H, phenyl ring protons), 7.59−7.69 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −1.72, −1.65, −1.37, −0.83 (MeSi), 0.57, 0.96, 1.60 (Me$_3$Si), 28.81, 37.21, 38.91, 43.74 (Ad), 99.79 (CO), 102.80, 106.97 (sp carbons), 127.46, 127.70, 128.67, 129.27, 133.69, 134.20, 136.46, 139.01 (phenyl ring carbons), 149.12, 152.28 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −22.2, −19.8, −18.6, −14.4, 1.5, 38.7.

Thermolysis of 3a at 160 °C. Compound **3a** (0.1111 g, 1.71 mmol) was heated at 160 °C for 12 h. Product **5a** (0.0933 g, 84% isolated yield) was isolated by column chromatography: All spectral data for **5a** were identical with those of the authentic sample obtained from the above reaction.

Thermolysis of 3b at 160 °C. Compound **3b** (0.0655 g, 0.0898 mmol) was heated at 160 °C for 12 h. Product **5b** (0.0537 g, 82% isolated yield) was isolated by column chromatography: All spectral data for **5b** were identical with those of the authentic sample.

Thermolysis of 2a with Methanol. A mixture of 0.1320 g (0.237 mmol) of **2a** and 0.0155 g (0.484 mmol) of methanol was heated in a sealed tube at 160 °C for 24 h. Product **6a** (0.1165 g, 83% isolated yield) was isolated by column chromatography: Anal. Calcd for C$_{25}$H$_{58}$O$_2$Si$_6$: C, 53.69; H, 10.45. Found: C, 53.49; H, 10.71. MS *m/z* 558 (M$^+$); IR 2956, 2898, 2825, 2138, 1556, 1396, 1274, 1174, 1199, 1157, 1091, 971, 887, 842, 759, 713 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.16 (s, 9H, Me$_3$Si), 0.17 (s,9H, Me$_3$Si), 0.19 (s, 9H, Me$_3$Si), 0.24 (s, 9H, Me$_3$Si), 0.30 (s, 9H, Me$_3$Si), 1.16 (s, 9H, t-Bu), 2.20 (s, 1H, CH), 3.47 (s, 3H, MeO); ^{13}C NMR δ (CDCl$_3$) 0.14, 0.90, 1.53, 1.63, 2.45 (Me$_3$Si), 23.49 (CH), 30.67 (Me$_3$C), 38.25 (CMe$_3$), 54.05 (MeO), 96.87, 104.15 (sp carbons), 111.04, 159.25 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −20.0, −19.2, −18.6, 3.2, 14.5, 16.1.

Thermolysis of 2b with Methanol. A mixture of 0.1804 g (0.237 mmol) of **2b** and 0.0160 g (0.499 mmol) of methanol was heated in a sealed tube at 160 °C for 24 h. Product **6b** (0.1595 g, 84% isolated yield) was isolated by column chromatography: Anal. Calcd for C$_{31}$H$_{64}$O$_2$Si$_6$: C, 58.42; H, 10.12. Found: C, 58.36; H, 10.41. MS *m/z* 636 (M$^+$); IR 2950, 2906, 2850, 2825, 2129, 1552, 1452, 1243, 1186, 1153, 1085, 887, 838, 757 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.16 (s, 9H, Me$_3$Si), 0.17 (s, 9H, Me$_3$Si), 0.20 (s, 9H, Me$_3$Si), 0.24 (s, 9H, Me3Si), 0.30 (s, 9H, Me$_3$Si), 1.66−1.98 (m, 15H, Ad), 2.35 (s, 1H, CH), 34.47 (s, 3H, MeO); ^{13}C NMR δ (CDCl$_3$) 0.15, 0.80, 1.48, 1.65, 2.63 (Me$_3$Si), 23.16 (CH), 28.63, 36.75, 41.01 (2 carbons) (Ad), 54.08 (MeO), 96.76, 104.56 (sp carbons), 111.38, 158.99 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −20.0, −19.6, −18.6, 3.2, 14.2, 15.9.

Thermolysis of 1a with Bis(*tert*-butyldimethysilyl)butadiyne at 160 °C. A mixture of 0.0782 g (0.235 mmol) of **1a** and 0.0689 g (0.247 mmol) of bis(*tert*-butyldimethylsilyl)butadiyne was heated in a sealed glass tube at 160 °C for 12 h. Product **7a** (0.1364 g, 95% isolated yield) was isolated by column chromatography: Anal. Calcd for C$_{30}$H$_{66}$OSi$_6$: C, 58.94; H, 10.88. Found: C, 58.74; H, 11.15. MS *m/z* 610 (M$^+$); IR 2954, 2929, 2898, 2858, 2125, 1471, 1361, 1247, 1041, 835, 808 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.06 (s, 3H, MeSi), 0.12 (s, 3H, MeSi), 0.13 (s, 3H, MeSi), 0.20 (s, 3H, MeSi), 0.23 (s, 9H, Me$_3$Si), 0.238 (s, 9H, Me$_3$Si), 0.240 (s, 9H, Me$_3$Si), 0.936 (s, 9H, *t*-Bu), 0.943 (s, 9H, *t*-Bu), 1.05 (s, 9H, *t*-Bu); ^{13}C NMR δ (CDCl$_3$) −5.46, −4.77, −4.73, −3.63 (MeSi), 1.23, 2.16, 4.62 (Me$_3$Si), 16.89, 18.71 (CMe$_3$), 26.29, 27.50, 28.25 (Me$_3$C), 36.30 (CMe$_3$), 94.88 (CO), 96.75, 106.36 (sp carbons), 154.81, 164.22 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −16.7, −15.0, −8.6, −4.2, −3.2, 7.7.

Thermolysis of 1b with Bis(*tert*-butyldimethylsilyl)butadiyne at 160 °C. A mixture of 0.0982 g (0.239 mmol) of **1b** and 0.0770 g (0.276 mmol) of bis(*tert*-butyldimethylsilyl)butadiyne was heated at 160 °C for 12 h. Product **7b** (0.1483 g, 90% yield) was isolated by column chromatography: Anal. Calcd for C$_{36}$H$_{72}$OSi$_6$: C, 62.71; H, 10.53. Found: C, 62.70; H, 10.80. MS *m/z* 688 (M$^+$); IR 2952, 2927, 2904, 2854, 2125 1469, 1461, 1247, 1056, 1008, 908, 836, 806, 736 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.08 (s, 3H, MeSi), 0.12 (s, 3H, Me$_2$Si), 0.13 (s, 3H, MeSi), 0.19 (s, 3H, MeSi), 0.23 (s, 9H, Me$_3$Si), 0.26 (s, 9H, Me$_3$Si), 0.28 (s, 9H, Me$_3$Si), 0.95 (s, 9H, *t*-Bu), 0.96 (s, 9H, *t*-Bu), 1.66−1.98 (m, 15H, Ad); ^{13}C NMR δ (CDCl$_3$) −5.20, −4.79, −4.76, −3.65 (MeSi), 1.49, 2.44, 4.72 (Me$_3$Si), 16.87, 18.58 (Me$_3$C), 26.29, 27.62 (CMe$_3$), 28.74, 37.25, 37.95, 38.96 (Ad), 96.77 (CO), 96.86, 106.97 (sp carbons), 154.57, 165.03 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −16.0, −15.2, −8.5, −4.0, −3.1, 8.3.

Thermolysis of 1a with Bis(*tert*-butyldimethylsilyl)butadiyne at 220 °C. A mixture of 0.0888 g (0.267 mmol) of **1a** and 0.0700 g (0.287 mmol) of bis(*tert*-butyldimethylsilyl)butadiyne was heated at 220 °C for 12 h. Product **8a** (0.1468 g, 90% yield) was isolated by column chromatography: Anal. Calcd for C$_{30}$H$_{66}$OSi$_6$: C, 58.94; H, 10.88. Found: C, 59.14; H, 10.55. MS *m/z* 610 (M$^+$); IR 2954, 2929, 2869, 2858, 2132, 1471, 1392, 1363, 1245, 1155, 1051, 960, 838, 809, 775 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.12 (s, 3H, MeSi), 0.13 (s, 3H, MeSi), 0.16 (s, 3H, MeSi), 0.190 (s, 9H, Me$_3$Si), 0.194 (s, 9H, Me$_3$Si), 0.20 (s, 9H, Me$_3$Si), 0.21 (s, 3H, MeSi), 0.94 (s, 9H, *t*-Bu), 0.99 (s, 9H, *t*-Bu), 1.08 (s, 9H, *t*-Bu); ^{13}C NMR δ (CDCl$_3$) −4.82, −4.70, −3.73, −3.44 (MeSi), 0.94, 1.03, 1.65 (Me$_3$Si), 16.95, 20.04 (CMe$_3$), 26.38, 28.13, 28.63 (Me$_3$C), 41.09 (CMe$_3$), 99.38 (CO), 101.87, 107.67 (sp carbons), 147.95, 152.75 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −19.6, −19.1, −8.9, −2.9, 1.7, 39.1.

Thermolysis of 1b with Bis(*tert*-butyldimethylsilyl)butadiyne at 220 °C. A mixture of 0.0573 g (0.139 mmol) of **1b** and 0.0410 g (0.147 mmol) of bis(*tert*-butyldimethylsilyl)butadiyne was heated at 220 °C for 12 h. Product **8b** (0.0865 g, 90% yield) was isolated by column chromatography: Anal. Calcd for C$_{36}$H$_{72}$OSi$_6$: C, 62.71; H, 10.53. Found: C, 62.55; H, 10.50. Mp 162−163 °C; MS *m/z* 688 (M$^+$); IR 2954, 2927, 2904, 2854, 2129, 1654, 1471, 1243, 1047, 836, 809 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.12 (s, 3H, MeSi), 0.13 (s, 3H, Me$_2$Si), 0.14 (s, 3H, MeSi), 0.19 (s, 18H, Me$_3$Si), 0.21 (s, 9H, Me$_3$Si), 0.24 (s, 3H, MeSi), 0.94 (s, 9H, *t*-Bu), 0.99 (s, 9H, *t*-Bu), 1.61−1.94 (m, 15H, Ad); ^{13}C NMR δ (CDCl$_3$) −4.87, −4.73, −3.87, −3.13 (MeSi), 0.86, 0.94, 1.88 (Me$_3$Si), 16.95, 20.07 (Me$_3$C), 26.31, 28.14 (CMe$_3$), 28.85, 37.23, 38.95, 43.65 (Ad), 99.97 (CO), 102.24, 107.81 (sp carbons), 148.28, 151.80 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −20.2, −19.1, −9.0, −3.0, 1.3, 39.6.

Thermolysis of 1a with Bis(dimethylphenylsilyl)but-1-en-3-yne at 120 °C. A mixture of 0.0942 g (0.283 mmol) of **1a** and 0.0997 g (0.310 mmol) of bis(dimethylphenylsilyl)but-1-en-3-yne was heated in a sealed glass tube at 120 °C for 12 h. Product **9a** (0.1294 g, 70% isolated yield) and the starting compound **1a** (0.0216 g, 23% isolated yield) were isolated by column chromatography. Data for **9a**: Anal. Calcd for C$_{34}$H$_{60}$OSi$_6$: C, 62.50; H, 9.26. Found: C, 62.71; H, 9.22. MS *m/z* 652 (M$^+$); IR 3068, 2952, 2896, 1427, 1249, 1112, 1066, 1037, 835, 728, 698 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.13 (s, 9H, Me$_3$Si), 0.16 (s, 9H, Me$_3$Si), 0.20 (s, 9H, Me$_3$Si), 0.28 (s, 3H, MeSi), 0.29 (s, 3H, MeSi), 0.35 (s, 3H, MeSi), 0.36 (s, 3H, MeSi), 0.97 (s, 9H, *t*-Bu), 6.09 (d, 1H, HC═C, $J = 19$ Hz), 6.52 (d, 1H, HC═C, $J = 19$ Hz), 7.29−7.37 (m, 6H, phenyl ring protons), 7.42−7.46 (m, 2H, phenyl ring protons), 7.48−7.50 (m, 2H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −2.75, −2.72, −1.05, −0.23 (MeSi), 1.37, 1.85, 3.98 (Me_3Si), 28.81 (Me_3C), 36.86 (CMe_3), 93.39 (CO), 127.69, 127.73, 128.69, 128.95, 132.64, 133.87, 134.05, 138.11, 139.71, 144.86, 149.14, 174.06 (phenyl ring and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −17.0, −16.9, −14.5, −10.8, −10.7, 6.0.

Thermolysis of 1b with Bis(dimethylphenylsilyl)but-1-en-3-yne at 120 °C. A mixture of 0.0951 g (0.231 mmol) of **1b** and 0.0897 g (0.279 mmol) of bis(dimethylphenylsilyl)but-1-en-3-yne was heated at 120 °C for 12 h. Product **9b** (0.1490 g, 88% isolated yield) was isolated by column chromatography: Anal. Calcd for $C_{40}H_{66}OSi_6$: C, 65.68; H, 9.09. Found: C, 65.79; H, 8.83. MS *m*/*z* 730 (M^+); IR 3068, 2950, 2902, 2848, 1427, 1247, 1112, 1052, 835, 828, 698 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.11 (s, 9H, Me_3Si), 0.16 (s, 9H, Me_3Si), 0.17 (s, 9H, Me_3Si), 0.28 (s, 3H, MeSi), 0.29 (s, 3H, MeSi), 0.33 (s, 3H, MeSi), 0.35 (s, 3H, MeSi), 1.44−1.93 (m, 15H, Ad), 5.99 (d, 1H, HC═C, $J = 19$ Hz), 6.50 (d, 1H, HC═C, $J = 19$ Hz), 7.27−7.36 (m, 6H, phenyl ring protons), 7.43−7.49 (m, 4H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −2.79, −2.64, −0.97, −0.29 (MeSi), 1.53, 2.04, 4.13 (Me_3Si), 28.76, 37.12, 38.39, 39.50 (Ad), 95.22 (CO), 127.67, 127.74, 128.68, 128.98, 132.00, 133.89, 134.15, 138.14, 139.72, 145.63, 149.99, 174.17 (phenyl ring and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −17.0, −16.1, −15.1, −10.6, −10.4, 6.6.

Thermolysis of 1a with Bis(pentamethyldisilanyl)but-1-en-3-yne at 120 °C. A mixture of 0.0816 g (0.245 mmol) of **1a** and 0.0997 g (0.286 mmol) of bis(pentamethyldisilanyl)-but-1-en-3-yne was heated in a sealed glass tube at 120 °C for 12 h. Product **10a** (0.0950 g, 60% isolated yield) and the starting compound **1a** (0.0228 g, 28% isolated yield) were isolated by column chromatography. Data for **10a**: Anal. Calcd for $C_{28}H_{68}OSi_8$: C, 52.10; H, 10.62. Found: C, 52.00; H, 10.22. MS *m*/*z* 644 (M^+); IR 2950, 2894, 1571, 1390, 1361, 1243, 1091, 1066, 1037, 908, 833, 794, 736, 686 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.06 (s, 9H, Me_3Si), 0.10 (s, 9H, Me_3Si), 0.14 (s, 3H, MeSi), 0.15 (s, 6H, Me_2Si), 0.16 (s, 3H, MeSi), 0.19 (s, 9H, Me_3Si), 0.22 (s, 9H, Me_3Si), 0.23 (s, 9H, Me_3Si), 0.99 (s, 9H, *t*-Bu), 6.14 (d, 1H, HC═C, $J = 19$ Hz), 6.48 (d, 1H, HC═C, $J = 19$ Hz); ^{13}C NMR δ ($CDCl_3$) −4.52, −4.30, −3.09 (MeSi), −2.15, −0.72 (Me_3Si), −0.53 (MeSi), 1.39, 2.06, 4.11 (Me_3Si), 29.18 (Me_3C), 36.95 (CMe_3), 93.07 (CO), 132.76, 142.63, 149.34, 171.51 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −32.1, −24.5, −19.0, −18.0, −17.7, −13.9, −13.0, 5.4.

Thermolysis of 1b with Bis(pentamethyldisilanyl)but-1-en-3-yne at 120 °C. A mixture of 0.0505 g (0.123 mmol) of **1b** and 0.0444 g (0.142 mmol) of bis(pentamethyldisilanyl)-but-1-en-3-yne was heated at 120 °C for 12 h. Product **10b** (0.0605 g, 68% isolated yield) and the starting compound **1b** (0.0128 g, 25% isolated yield) were isolated by column chromatography. Data for **10b**: Anal. Calcd for $C_{34}H_{74}OSi_8$: C, 56.43; H, 10.31. Found: C, 56.33; H, 9.99. MS *m*/*z* 722 (M^+); IR 2950, 2904, 2848, 1243, 1081, 1052, 835, 796, 686 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.06 (s, 9H, Me_3Si), 0.10 (s, 9H, Me_3Si), 0.141 (s, 6H, Me_2Si), 0.144 (s, 3H, MeSi), 0.18 (s, 3H, MeSi), 0.20 (s, 9H, Me_3Si), 0.21 (s, 9H, Me_3Si), 0.26 (s, 9H, Me_3Si), 1.54−1.98 (m, 15H, Ad), 6.18 (d, 1H, HC═C, $J = 19$ Hz), 6.48 (d, 1H, HC═C, $J = 19$ Hz); ^{13}C NMR δ ($CDCl_3$) −4.42 (Me_2Si), −2.94 (MeSi), −2.20, −0.81 (Me_3Si), −0.62 (MeSi), 1.63, 2.16, 4.20 (Me_3Si), 28.94, 37.06, 38.74, 39.98 (Ad), 95.21 (CO), 132.46, 143.25, 149.61, 170.67 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −32.4, −24.7, −19.1, −18.0, −17.4, −14.8, −13.0, 5.6.

Thermolysis of 1a with Bis(dimethylphenylsilyl)but-1-en-3-yne at 200 °C. A mixture of 0.0502 g (0.151 mmol) of **1a** and 0.0965 g (0.301 mmol) of bis(dimethylphenylsilyl)but-1-en-3-yne was heated at 200 °C for 12 h. Product **11a** (0.0907 g, 92% isolated yield) was isolated by column chromatography: Anal. Calcd for $C_{34}H_{60}OSi_6$: C, 62.50; H, 9.26. Found: C, 62.47; H, 9.60. MS *m*/*z* 652 (M^+); IR 3068, 3050, 2954, 2898, 1500, 1427, 1245, 1114, 1041, 989, 958, 833, 732 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.08 (s, 9H, Me_3Si), 0.16 (s, 9H, Me_3Si), 0.21 (s, 9H, Me_3Si), 0.22 (s, 6H, Me_2Si), 0.33 (s, 3H, MeSi), 0.34 (s, 3H, MeSi), 0.97 (s, 9H, *t*-Bu), 5.92 (d, 1H, HC═C, $J = 19$ Hz), 6.35 (d, 1H, HC═C, $J = 19$ Hz), 7.29−7.33 (m, 8H, phenyl ring protons), 7.47−7.49 (m, 2H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −3.16 (Me_2Si), 0.00 (MeSi), 1.09, 1.20 (Me_3Si), 1.88 (Me_3Si and MeSi), 28.69 (Me_3C), 40.67 (CMe_3), 99.01 (CO), 127.68, 127.69, 128.48, 128.95, 132.05, 133.69, 133.81, 133.88, 137.54, 141.11, 147.02, 174.38 (phenyl ring and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −19.7, −18.8, −15.7, −10.9, 1.1, 38.0.

Thermolysis of 1b with Bis(dimethylphenylsilyl)but-1-ene-3-yne at 200 °C. A mixture of 0.1231 g (0.300 mmol) of **1b** and 0.1166 g (0.364 mmol) of bis(dimethylphenylsilyl)but-1-en-3-yne was heated at 200 °C for 12 h. Product **11b** (0.1995 g, 91% isolated yield) was isolated by column chromatography: Anal. Calcd for $C_{40}H_{66}OSi_6$: C, 65.68; H, 9.09. Found: C, 65.66; H, 9.00. MS *m*/*z* 730 (M^+); IR 3068, 3050, 2950, 2904, 2848, 1589, 1500, 1427, 1309, 1245, 1114, 1047, 910, 835, 732, 700 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.10 (s, 9H, Me_3Si), 0.17 (s, 3H, MeSi), 0.19 (s, 3H, MeSi), 0.20 (s, 9H, Me_3Si), 0.24 (s, 9H, Me_3Si), 0.34 (s, 3H, MeSi), 0.38 (s, 3H, MeSi), 1.53−1.90 (m, 15H, Ad), 5.94 (d, 1H, HC═C, $J = 19$ Hz), 6.34 (d, 1H, HC═C, $J = 19$ Hz), 7.28−7.35 (m, 8H, phenyl ring protons), 7.49−7.51 (m, 2H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −3.24 (Me_2Si), 0.31 (MeSi), 0.96, 1.22 (Me_3Si), 1.93 (MeSi), 2.14 (Me_3Si), 28.82, 37.15, 38.81, 43.31 (Ad), 99.37 (CO), 127.67 (two carbons), 128.49, 128.95, 131.88, 133.77, 133.93, 134.00, 137.61, 140.93, 147.28, 173.40 (phenyl ring and olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −20.4, −18.7, −15.8, −10.8, 0.7, 38.5.

Thermolysis of 1a with Bis(pentamethyldisilanyl)but-1-en-3-yne at 200 °C. A mixture of 0.0822 g (0.247 mmol) of **1a** and 0.1111 g (0.355 mmol) of bis(pentamethyldisilanyl)-but-1-en-3-yne was heated at 200 °C for 12 h. Product **12a** (0.1371 g, 86% isolated yield) was isolated by column chromatography: Anal. Calcd for $C_{28}H_{68}OSi_8$: C, 52.10; H, 10.62. Found: C, 52.13; H, 10.60. MS *m*/*z* 644 (M^+); IR 2952, 2894, 1498, 1390, 1245, 1050, 908, 836, 798, 736, 688 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) −0.01 (s, 9H, Me_3Si), 0.02 (s, 9H, Me_3Si), 0.07 (s, 9H, Me_3Si), 0.08 (s, 3H, MeSi), 0.09 (s, 6H, Me_2Si), 0.11 (s, 18H, Me_3Si), 0.13 (s, 3H, MeSi), 0.89 (s, 9H, *t*-Bu), 5.96 (d, 1H, HC═C, $J = 19$ Hz), 6.44 (d, 1H, HC═C, $J = 19$ Hz); ^{13}C NMR δ ($CDCl_3$) −4.43, −3.89 (MeSi), −1.90 (Me_3Si), −1.40 (MeSi), −0.23, 1.09, 1.23 (Me_3Si), 1.37 (MeSi), 2.11 (Me_3Si), 28.70 (Me_3C), 40.91 (CMe_3), 99.06 (CO), 132.33, 135.92, 144.95, 170.74 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −30.9, −24.4, −19.8, −19.0, −18.9, −17.5, 0.4, 37.3.

Thermolysis of 1b with Bis(pentamethyldisilanyl)but-1-ene-3-yne at 200 °C. A mixture of 0.0797 g (0.194 mmol) of **1b** and 0.0987 g (0.315 mmol) of bis(pentamethyldisilanyl)-but-1-en-3-yne was heated at 200 °C for 12 h. Product **12b** (0.1179 g, 84% isolated yield) was isolated by column chromatography: Anal. Calcd for $C_{34}H_{74}OSi_8$: C, 56.43; H, 10.31. Found: C, 56.66; H, 10.00. MS *m*/*z* 722 (M^+); IR 2950, 2904, 2848, 1243, 1043, 835, 796, 736, 686 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.08 (s, 9H, Me_3Si), 0.12 (s, 9H, Me_3Si), 0.17 (s, 9H, Me_3Si), 0.18 (s, 3H, MeSi), 0.19 (br s, 15H, Me_3Si, Me_2Si), 0.21 (s, 9H, Me_3Si), 0.22 (s, 3H, MeSi), 1.57−1.98 (m, 15H, Ad), 6.04 (d, 1H, HC═C, $J = 19$ Hz), 6.52 (d, 1H, HC═C, $J = 19$ Hz); ^{13}C NMR δ ($CDCl_3$) −4.42, −4.06 (MeSi), −2.06 (Me_3Si), −1.84 (MeSi), −0.27, 0.91, 1.19 (Me_3Si), 1.32 (MeSi), 2.26 (Me_3Si), 28.82, 37.17, 38.82, 43.51 (Ad), 99.60 (CO), 131.86, 136.96, 144.76, 168.73 (olefinic carbons); ^{29}Si NMR δ ($CDCl_3$) −30.9, −24.2, −20.2, −18.9, −18.7, −17.7, 0.1, 37.6.

X-ray Structure Determination of 8b. Crystal data for $C_{37}H_{72}OSi_6$: colorless block, monoclinic, space group $P2_1/n$ (no.14), $a = 16.638(8)$ Å, $b = 10.989(5)$ Å, $c = 24.76(1)$ Å, $\beta = 109.361(4)°$, $V = 4270(3)$ Å^3, $F(000) = 1548.00$, $Z = 4$, $D_c =$

1.093 g cm^{-3}, μ(Mo Kα) = 2.21 cm^{-1}. Crystal dimensions: 0.3 × 0.2 × 0.2 mm. A total of 32 180 reflections were collected, 9479 unique ($R_{int} = 0.042$). The structure was solved by direct methods (SIR92) and developed through subsequent cycles of least-squares refinement and difference Fourier synthesis, final R1 = 0.060, $R_w = 0.185$ for 6781 ($I > 2\sigma(I)$) with a GOF of 0.89. Data were measured on a Rigaku/MSC mercury CCD diffractometer with graphite-monochoromatized Mo Kα at 150 K.

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Supporting Information Available: An X-ray crystallographic file in CIF format is available free of charge via the Internet at http://pubs.acs.org.

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