

## Addition of Cyclopropyl Alkynes to a Brook Silene: Definitive Evidence for a Biradical Intermediate

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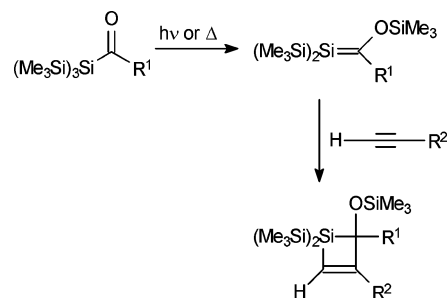
**Abstract:** The addition of three newly developed mechanistic probes, (*trans*-2-phenylcyclopropyl)ethyne, (*trans,trans*-2-methoxy-3-phenylcyclopropyl)ethyne, and (*trans,trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)ethyne, **1a–c**, to a Brook silene, 2-*tert*-butyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silene, **10**, was examined. When alkyne **1a** was added to silene **10** products derived from a formal ene reaction were obtained. When alkynes **1b–c** were added to silene **10**, in addition to the typical silacyclobutenes, a variety of silacycloheptenes were obtained in which the cyclopropyl ring had clearly opened. Formal ene-addition products were also produced from the addition of **1b** to **10**. Based on the relative positions of the phenyl and methoxy substituents within the seven-membered ring of the silacycloheptenes and the known behavior of the alkyne probes under both radical and ionic conditions, it was concluded that a biradical intermediate was formed during the addition of alkynes **1b–c** to silene **10**. In the addition of alkynes **1a–b** to silene **10**, the ene products are most likely formed by a competitive pericyclic reaction. We also present a straightforward method for the unambiguous determination of the regiochemistry of silacyclobutenes derived from the cycloaddition of terminal alkynes to silenes.

### Introduction

Since the definitive experiments by Gusel'nikov and Flowers in the 1960s, in which a silacyclobutane derivative was pyrolyzed to form a transient silene,<sup>1</sup> the synthesis and reactivity of multiply bonded silicon compounds have been a major focus of research. One of the most significant advances in this area was the preparation of stable silenes of the general formula  $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{R})(\text{OSiMe}_3)$  by the thermolysis or photolysis of the corresponding acylsilane by Brook and co-workers in 1979 (Scheme 1).<sup>2</sup> The stability of silenes of this type (referred to as Brook silenes herein) is attributed, at least in part, to the reduced polarity of the  $\pi$  bond which is a consequence of the bis(trimethylsilyl) substituents at the silenic silicon and the trimethylsiloxy substituent at the silenic carbon.<sup>2b,3</sup> The greater polarity of the  $\pi$  bond in simple silenes (those without strongly polarizing substituents) leads to enhanced reactivity; however, both types of silenes most often exhibit the same reactivity patterns.<sup>4</sup>

The cycloaddition of alkynes to silenes to give silacyclobutenes is a well-known reaction (Scheme 1).<sup>4</sup> The reaction generally occurs cleanly and in high yield, and as a consequence, alkynes have been widely utilized as reliable trapping reagents; the isolation of a silacyclobutene is taken as convincing evidence for the formation of a transient silene. The cycloaddition is

**Scheme 1.** Formation of Brook Silenes and Addition of an Alkyne



highly regioselective although unambiguous determination of the regiochemistry of the adduct has proven to be problematic. The regiochemistry of only a few silacyclobutenes derived from the addition of alkynes to Brook silenes has been unambiguously determined by X-ray crystallography. Examples include the phenylacetylene and the trimethylsilylacetylene adducts of  $(\text{Me}_3\text{Si})(\text{Mes})\text{Si}=\text{C}(1\text{-Ad})(\text{OSiMe}_3)$  and the 1-phenylpropyne adduct of  $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(t\text{-Bu})(\text{OSiMe}_3)$ .<sup>5a</sup> In the latter example, the original assignment of the structure, based on the mass

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(2) (a) Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83. (b) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

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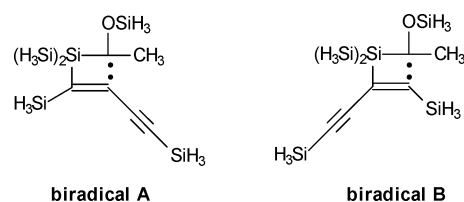
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spectrometric fragmentation pattern, was erroneous;<sup>2a</sup> the correct structure was later assigned using X-ray crystallography.<sup>5a</sup>

Only a few studies have been directed at elucidating the factors which influence the regioselectivity of this reaction. The stereoselectivity of the reaction was examined by studying the addition of phenylacetylene and trimethylsilylacetylene to an *E/Z* mixture of the silenes (Me<sub>3</sub>Si)(R)Si=C(1-Ad)(OSiMe<sub>3</sub>), R = Mes (2,4,6-trimethylphenyl) or Tip (2,4,6-triisopropylphenyl), where the ratio of the silene isomers was known but not assigned.<sup>5</sup> In each case, the ratio of the two isomeric silacyclobutenes produced was found to be identical to the *E/Z* ratio of the starting silene mixture. The stereochemistry of the silacyclobutene isomer formed in greater yield from the addition of either phenyl- or trimethylsilylacetylene to the *E/Z* mixture of silenes (R = Mes) was determined by X-ray crystallography. Since the relative stereochemistry of the major silacyclobutene isomer was the same as what would reasonably be expected for the major geometric isomer of the silene, the results were taken as evidence for a concerted, suprafacial addition of the alkyne to the silene. It was assumed that bond rotation in a zwitterionic or biradical intermediate would likely result in a variation in the ratio of the diastereomeric silacyclobutenes isolated compared to the isomeric silenes. However, since the rate constants for both the cyclization of and bond rotation in a putative intermediate are unknown, the conclusions from this study are tentative.

Ishikawa and co-workers have also extensively studied the addition of alkynes to Brook silenes.<sup>6,7</sup> In these studies, the silene was generated typically by thermolysis of the acylsilane in the presence of the alkyne. When a hydrogen is present  $\alpha$  to the silenic carbon, disproportionation products were obtained. The authors attribute the formation of such products to the intermediacy of a biradical;<sup>6g</sup> however, the same product may also reasonably be formed via a concerted six-membered cyclic transition state. In the absence of an  $\alpha$ -hydrogen, the typical [2 + 2] cycloadducts are obtained when the thermolysis temperature is kept below 140 °C.<sup>6,7</sup> At higher temperatures (>160 °C), the silacyclobutenes were found to rearrange yielding various products depending on the substituents present on the alkyne. When the substituents were nonaromatic (i.e., *t*-Bu, SiR<sub>3</sub>), 1:1 adducts of the silene and the alkyne were formed in most cases.<sup>6b–g</sup> However, when mesitylacetylene was added to the silene, 1:3 and 1:4 adducts (silene/mesitylacetylene) were isolated.<sup>6a</sup> The mechanism for the formation of these products is believed to involve biradicals, although the experimental evidence for such intermediates was weak. The regiochemistry of the silacyclobutenes was most often determined by NOE spectroscopy; however, ambiguity in the NOE spectroscopic data has led to the report of erroneous structures.<sup>6e,g</sup> Thus, there is no straightforward, simple method to determine the regiochem-

**Scheme 2.** Two Possible Biradical Intermediates



istry of silacyclobutene adducts apart from obtaining an X-ray crystal structure, which depends on the successful formation of a suitable crystal.

Ishikawa and co-workers also examined the addition of propyne to the parent Brook silene, (H<sub>3</sub>Si)<sub>2</sub>Si=C(CH<sub>3</sub>)(OSiH<sub>3</sub>), theoretically using density functional theory at the B3LYP/6-31G\* level.<sup>7</sup> The calculations revealed that the bond between the silenic silicon and the terminal end of the alkyne forms earlier than the bond between the silenic carbon and the substituted carbon of the alkyne. The authors describe the cycloaddition as a “concerted but nonsynchronous process, this is more likely to be viewed as a stepwise reaction with a diradical character”.<sup>7</sup> They also describe a strong interaction between the silenic silicon and the more substituted carbon of the acetylene which exists in the initial stages of the reaction. It was proposed that this diagonal interaction is the reason the concerted [2 + 2] cycloaddition is thermally allowed. It is not clear that the theoretical methods used for this study would reliably be able to distinguish between biradical or zwitterionic intermediates. Ishikawa later determined the relative energies of two of four possible biradical intermediates possibly formed during the addition of bis(silyl)butadiyne to (H<sub>3</sub>Si)<sub>2</sub>Si=C(CH<sub>3</sub>)(OSiH<sub>3</sub>) using density functional theory at the B3LYP/6-31G\* level (Scheme 2).<sup>6b</sup> It was determined that biradical A is 10.9 kcal/mol lower in energy than biradical B; however, the relative energies of the biradicals with the radical centered on the silicon atom of the former silene were not considered, nor were the relative energies of possible zwitterionic intermediates.

In summary, no conclusive evidence for the formation of an intermediate (or lack thereof) during the addition of alkynes to Brook silenes has been provided to date. Given the importance of this reaction in silene chemistry, we decided to undertake an experimental study of the mechanism of the cycloaddition of alkynes to Brook silenes. Our approach utilizes a series of cyclopropyl alkynes (*trans*-2-phenylcyclopropyl)ethyne, **1a**, (*trans,trans*-2-methoxy-3-phenylcyclopropyl)ethyne, **1b**, and (*trans,trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)ethyne, **1c**, which we have developed as mechanistic probes. These probes were designed to discriminate between vinyl radical and ionic intermediates based on regiochemically distinct radical, cationic, and anionic reaction modes.<sup>8</sup> Thus, the  $\alpha$ -cyclopropylvinyl radical **2**, derived from alkyne **1b** or **c**, opens rapidly and regioselectively toward the phenyl substituent yielding a benzyl radical. In contrast, the  $\alpha$ -cyclopropylvinyl cation **3** rearranges selectively toward the methoxy substituent (Scheme 3), and the analogous anion (as modeled by the lithium derivative of **1a**) is stable toward ring opening.<sup>8a</sup>

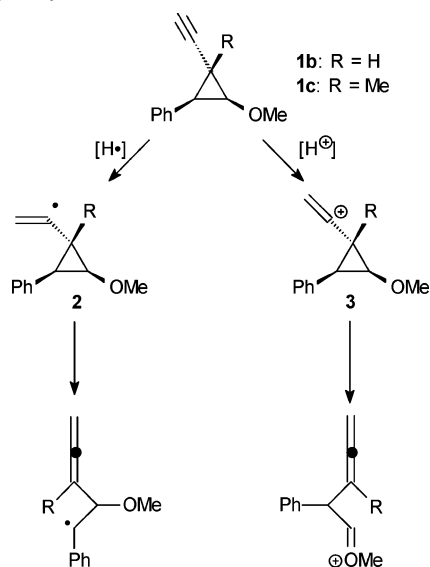
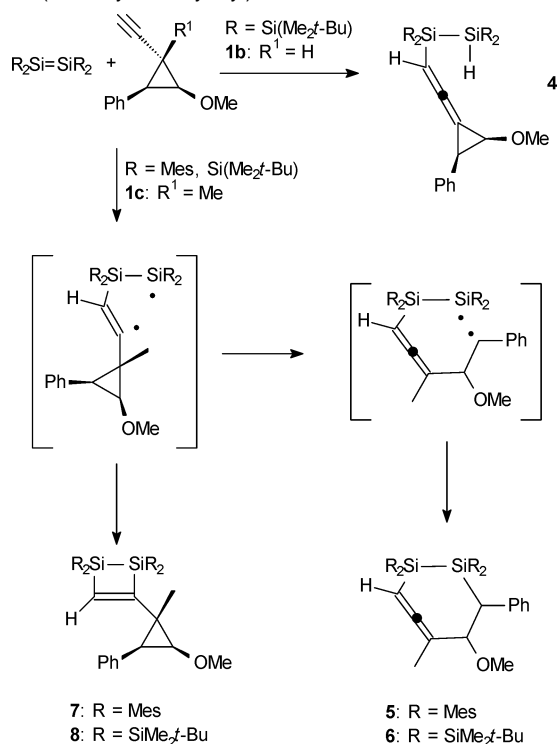
Mechanistic probes **1b–c** have recently been used to investigate the mechanism of alkyne addition to both tetramesityl-<sup>9</sup>

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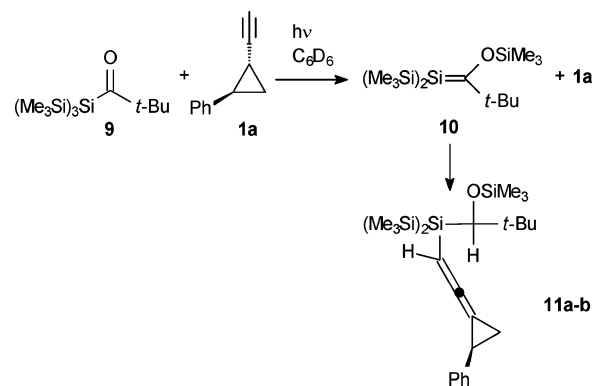
(6) (a) Naka, A.; Ohnishi, H.; Ohshita, J.; Ikadai, J.; Kunai, A.; Ishikawa, M. *Organometallics* **2005**, *24*, 5356. (b) Naka, A.; Ohnishi, H.; Miyahara, I.; Hirotsu, K.; Shiota, Y.; Yoshizawa, K.; Ishikawa, M. *Organometallics* **2004**, *23*, 4277. (c) Naka, A.; Ishikawa, M. *Chem. Lett.* **2002**, *3*, 364. (d) Naka, A.; Ikadai, J.; Shingo, M.; Yoshizawa, K.; Kondo, Y.; Kang, S.-Y.; Ishikawa, M. *Organometallics*, **2002**, *21*, 2033. (e) Naka, A.; Ishikawa, M. *J. Organomet. Chem.* **2000**, *611*, 248. (f) Naka, A.; Ishikawa, M. *Organometallics* **2000**, *19*, 4921. (g) Naka, A.; Ishikawa, M.; Matsui, S.; Ohshita, J.; Kunai, A. *Organometallics* **1996**, *15*, 5759.

(7) Yoshizawa, K.; Kondo, Y.; Kang, S.-Y.; Naka, A.; Ishikawa, M. *Organometallics* **2002**, *21*, 3271.

(8) (a) Gottschling, S. E.; Grant, T. N.; Milnes, K. K.; Jennings, M. C.; Baines, K. M. *J. Org. Chem.* **2005**, *70*, 2686. (b) Milnes, K. K.; Gottschling, S. E.; Baines, K. M. *Org. Biomol. Chem.* **2004**, *2*, 3530.

**Scheme 3.** Reactivity of Vinylic Intermediates Derived from Cyclopropyl Alkynes **1b–c****Scheme 4.** Addition of Alkynes **1b–c** to Tetramesityl- and Tetrakis(*tert*-butyldimethylsilyl)disilene

and tetrakis(*tert*-butyldimethylsilyl)disilene.<sup>10</sup> When alkyne **1b** was added to tetrakis(*tert*-butyldimethylsilyl)disilene, allene **4**, the product of a formal ene-addition, was produced where the cyclopropyl ring was still intact (Scheme 4). However, when alkyne **1c** was added to either tetramesityl disilene or tetrakis(*tert*-butyldimethylsilyl)disilene, three diastereomers of a disilacyclohepta-1,2-diene (**5** or **6**, respectively) and a disilacyclobutene (**7** or **8**, respectively) were produced. Clearly, the cyclopropyl ring has opened during the formation of disilacy-

**Scheme 5.** Reaction of Alkyne **1a** with Silene **10**

clohepta-1,2-dienes **5** and **6**. Using a variety of spectroscopic techniques, the placement of the phenyl substituent was found to be  $\alpha$  to the former disilenic silicon and the methoxy group was found to be  $\beta$  in all compounds. The regiochemistry of the substituents in the seven-membered rings of **5** and **6** provides decisive evidence for the formation of a vinyl radical during the addition of alkyne **1c** to the disilenes, since ring opening has occurred toward the phenyl substituent (Scheme 4). Cyclization of the initially formed 1,4-biradical to give disilacyclobutenes **7** and **8** apparently competes with rearrangement to give the 1,7-biradical.

In this paper, we now report on the addition of cyclopropyl alkynes **1b–c** to the Brook silene (Me<sub>3</sub>Si)<sub>2</sub>Si=C(*t*-Bu)(OSiMe<sub>3</sub>). For comparison purposes, the addition of alkyne **1a** to the same silene was also examined. During the course of this work, we developed a simple NMR spectroscopic method for the determination of the regiochemistry of silacyclobutenes derived from the [2 + 2] cycloaddition of a terminal alkyne to a silene; this method is also described herein.

## Results and Discussion

Irradiation of pivaloyltris(trimethylsilyl)silane, **9**, in the presence of alkyne **1a** produces a diastereomeric mixture of allenes **11a–b** (59:41) as the major products as revealed by <sup>1</sup>H NMR spectroscopy (Scheme 5). Allenes **11a–b** were identified by IR, <sup>1</sup>H, <sup>13</sup>C, gCOSY, <sup>1</sup>H–<sup>13</sup>C gHSQC and gHMBC and <sup>1</sup>H–<sup>29</sup>Si gHMBC NMR spectroscopy, and mass spectrometry.<sup>11</sup> When alkyne **1a** is added to a solution of the preformed silene **10** in the dark, the same product mixture was obtained in a similar ratio.

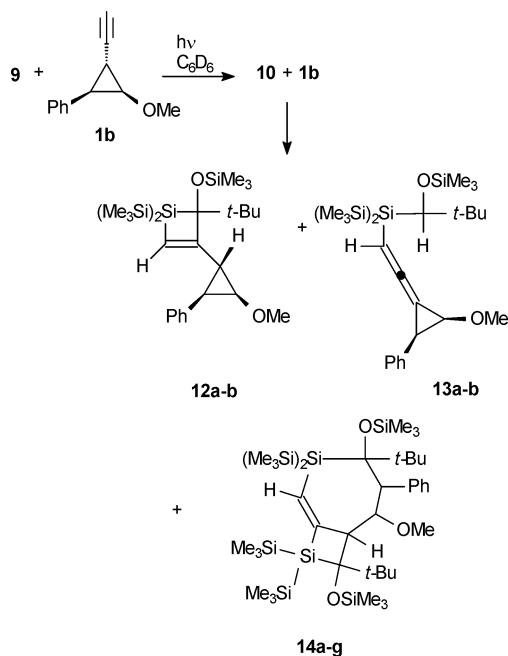
Irradiation of acylsilane **9** in the presence of alkyne **1b** produces a mixture of silacyclobutenes **12a–b**, allenes **13a–b**, and silacycloheptenes **14a–g** (in a ratio of 17:48:35/12:13:14) as revealed by <sup>1</sup>H NMR spectroscopy (Scheme 6). Chromatographic separation of the crude product mixture yields a mixture of **12a–b** and **13a–b** (in a ratio of 15:10:51:24) and a mixture of **14a–g**.<sup>12</sup> The mixture of **12a–b** and **13a–b** could not be completely separated, since **12a–b** is prone to decomposition upon chromatography. Separation of **14a–g** by chromatography yielded **14a–b** (89:11), **14c–d** (86:14), **14e–f** (76:24), and **14g**. Compounds **12a–b**, **13a–b**, and **14a–g** were identified by IR, <sup>1</sup>H, <sup>13</sup>C, gCOSY, <sup>1</sup>H–<sup>13</sup>C gHSQC and gHMBC

(9) Gottschling, S. E.; Milnes, K. K.; Jennings, M. C.; Baines, K. M. *Organometallics* **2005**, *24*, 3811.

(10) Gottschling, S. E.; Jennings, M. C.; Baines, K. M. *Can. J. Chem.* **2005**, *83*, 1568.

(11) A more detailed discussion of the NMR spectral data for an example of this type of molecule can be found in the structure elucidation section in the Supporting Information.

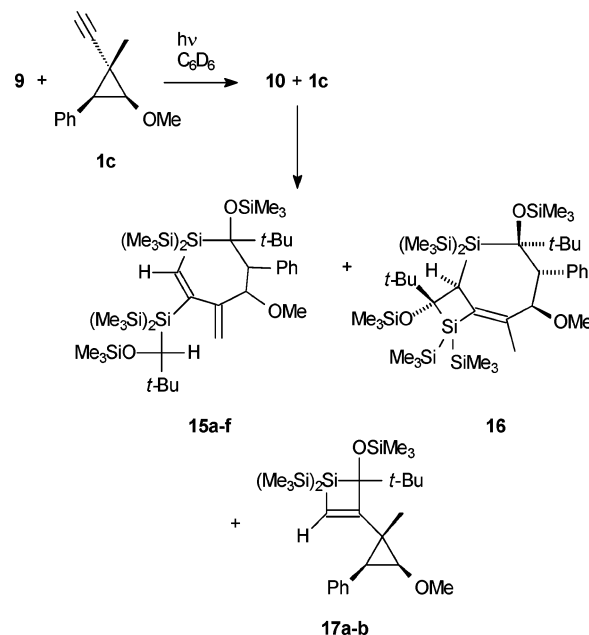
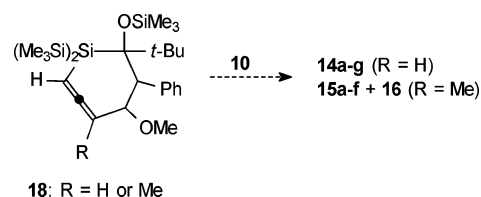
(12) The ratio of silacycloheptenes **14a–g** could not be obtained due to overlap of the signals in the <sup>1</sup>H NMR spectrum of the mixture.

**Scheme 6.** Reaction of Alkyne **1b** with Silene **10**

and  $^1\text{H}$ - $^{29}\text{Si}$  gHMBC NMR spectroscopy, and mass spectrometry, and in the case of **14a** or **14e**, the structure was unambiguously confirmed by X-ray crystallography.<sup>11,13</sup> Other addition products, present in minor amounts, were observed in the  $^1\text{H}$  NMR spectrum of the crude reaction mixture. These compounds appeared to have similar  $^1\text{H}$  NMR spectroscopic characteristics as **14a-g**; however, sufficient amounts could not be isolated for identification. We are confident, however, that the majority of the products are accounted for in compounds **12a-b**, **13a-b**, and **14a-g**. When alkyne **1b** is added to a solution of the preformed silene **10** in the dark, the same product mixture was obtained in similar ratios.

Irradiation of acylsilane **9** in the presence of alkyne **1c** produced a mixture of six diastereomers of silacycloheptene **15a-f**, **16**, and two diastereomers of silacyclobutene **17a-b** (in a ratio of 16:10:16:5:17:4:11:11:10, respectively) as revealed by  $^1\text{H}$  NMR spectroscopy (Scheme 7). When alkyne **1c** is added to a solution of the preformed silene **10** in the dark, the same product mixture was obtained in a similar ratio. Chromatographic separation of the products yielded a mixture of **15a-b** (64:36), a mixture of **15a-f** and **16** (6:3:27:6:32:6:20), and a mixture of **17a-b** and recovered **9** (41:44:15). The mixture of **15a-f** and **16** could be further separated by careful chromatography yielding a mixture of **15c-d** and **16** (60:17:23) and a mixture of **15e-f** (89:11). Despite many attempts, no one compound could be isolated from the mixtures.

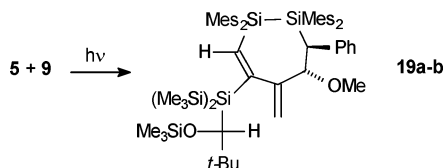
Silacyclobutenes **17a-b** and silacycloheptenes **15a-f** were identified by  $^1\text{H}$ ,  $^{13}\text{C}$ , gCOSY,  $^1\text{H}$ - $^{13}\text{C}$  gHSQC and gHMBC and  $^1\text{H}$ - $^{29}\text{Si}$  gHMBC NMR spectroscopy, and mass spectrometry, and in the case of **15a** or **15b**, **15c-d**, and **16**, the structures were unambiguously confirmed by X-ray crystallography.<sup>11,13</sup>

**Scheme 7.** Reaction of Alkyne **1c** with Silene **10****Scheme 8.** Possible Route for the Formation of **14a-g**, **15a-f**, and **16**

Allenes **11a-b** and **13a-b** are the products of formal ene-addition between silene **10** and alkynes **1a** or **1b**, respectively. Products of this type have previously been observed in the addition of alkyne **1b** to tetrakis(*tert*-butyldimethylsilyl)disilene (Scheme 4).<sup>10</sup> Silacyclobutenes **12a-b** and **17a-b** are the typical products derived from the addition of alkynes to silenes; the mechanism for the formation of these products will be discussed later. The formation of silacycloheptenes **14a-g**, **15a-f**, and **16** was somewhat surprising. All silacycloheptenes are derived from 2 equiv of silene **10** and 1 equiv of the alkyne. The possibility that **14a-g**, **15a-f**, and **16** are secondary products derived from subsequent reaction of the silacyclobutenes with silene **10** was investigated. Thus, a mixture of acylsilane **9** and silacyclobutenes **17a-b** was irradiated in the presence of an internal standard. The progress of the reaction was monitored by  $^1\text{H}$  NMR spectroscopy; other than silene **10**, no new products were observed. The ratio of **17a-b** to the standard did not change, even over the course of several days. Over time, in the absence of light, silene **10** slowly converted back to acylsilane **9**.<sup>2a</sup> Based on these results, this pathway to silacycloheptenes **14a-g**, **15a-f**, and **16** was excluded.

Deconstruction of **14a-g**, **15a-f**, and **16** reveals that a former silenic silicon center is bonded to the same carbon atom of the seven-membered ring framework in all of the silacycloheptenes. Silacycloheptenes **14a-g**, **15a-f**, and **16** could reasonably be formed by addition of silene **10** to silacyclohepta-1,2-diene **18** (Scheme 8). We have recently reported the formation of the stable disilacyclohepta-1,2-diene **5** derived from the addition of alkyne **1c** to tetramesityldisilene.<sup>9</sup> Thus, it seems reasonable to propose the formation of silacyclohepta-1,2-diene **18** from

(13) CCDC-286996 (**14a** or **14e**), CCDC-286997 (**15a** or **15b**), CCDC-286998 (**15c** and **15d**), CCDC-286999 (**16**), and CCDC-287000 (**19a** or **19b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

**Scheme 9.** Irradiation of Disilacyclohepta-1,2-diene **5** and Acylsilane **9**

the addition of the same alkyne to a silene. However, in this case, the allene moiety of silacyclohepta-1,2-diene **18** appears to readily undergo reaction with a second equivalent of silene **10**. When R = Me, the cycloadduct is only formed in low yield (**16**), presumably due to steric effects; however, when R = H, the cycloadduct is formed in significant quantities (**14a–g**). When R = Me, the major product formed from the addition of a second equivalent of silene **10** to silacyclohepta-1,2-diene **18** appears to be derived from a formal ene reaction (**15a–f**) as evidenced by the hydrogen present on the former silenic carbon and the transformation of the methyl group to a methylene on the seven-membered ring. Attempts were made to detect the formation of intermediates during the reaction of alkynes **1b–c** with silene **10** by  $^1\text{H}$  NMR spectroscopy; no intermediate species were observed. Thus, the relative reactivity of silacyclohepta-1,2-diene **18** compared to alkynes **1b–c** toward silene **10** is at least 20:1. To test the hypothesis that silacyclohepta-1,2-diene **18** (R = Me) reacts with silene **10** to give **15a–f** and **16**, an analogous reaction was performed on the isolable and structurally related allene **5**.<sup>9</sup>

A mixture of acylsilane **9** and allene **5** was irradiated, and the progress of the reaction was monitored by  $^1\text{H}$  NMR spectroscopy over several days; a diastereomeric mixture of disilacycloheptenes **19a–b** was formed (Scheme 9).<sup>11,13</sup> Due to the similarity in the structures of proposed allene **18** and allene **5**, we believe these results provide reasonable evidence for the formation of **15a–f** and **16** via silacyclohepta-1,2-diene **18** (R = Me) and, by analogy, the formation of compound **14a–g** via **18** (R = H).

The structures of several of the silacycloheptene compounds were confirmed by X-ray crystallography including **14a** or **14e**, **15a** or **15b**, **15c–d**, **16**, and **19a** or **19b**.<sup>13</sup> All the crystallographic data are presented in the Supporting Information. Within the seven-membered rings, some of the bonds were found to be slightly elongated; however, the bond angles about the ring were within the expected range as compared to cycloheptene.<sup>14</sup>

In summary, when alkyne **1a** is added to silene **10** the only products formed are allenes **11a–b** (R<sup>1</sup> = H) (Scheme 10); however, when alkynes **1b–c** are added to silene **10**, allenes **13a–b** (R<sup>1</sup> = OMe), silacyclobutenes **12a–b** (R = H) or **17a–b** (R = Me), and silacyclohepta-1,2-diene **18** (R = H or OMe) are formed. Silacyclohepta-1,2-diene **18** is not observed, since it apparently undergoes further reaction with silene **10** yielding **14a–g** (R = H) or **15a–f** and **16** (R = Me).

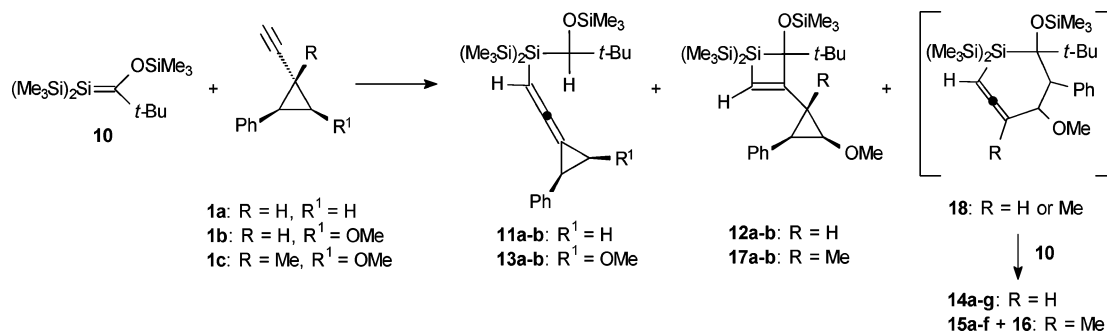
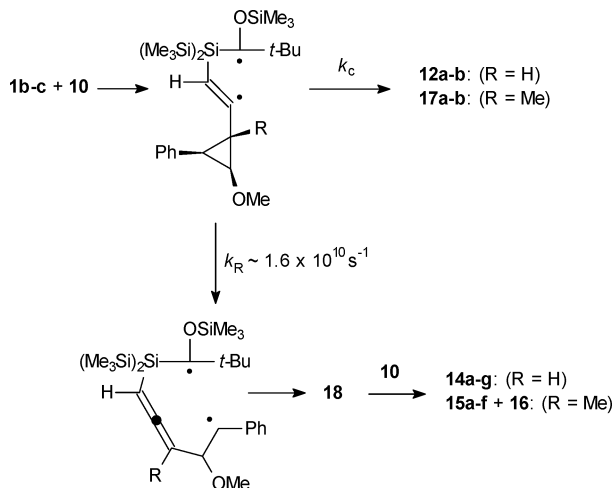
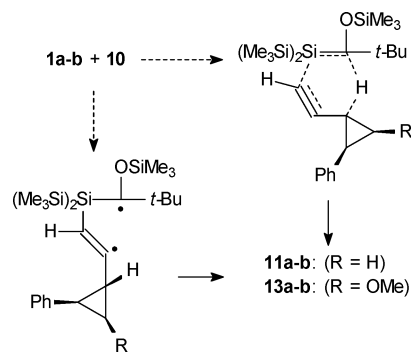
From the NMR and X-ray spectral data of the products derived from the addition of alkynes **1b–c** to silene **10**, it is evident that in silacycloheptenes **14a–g**, **15a–f**, and **16** the cyclopropyl ring is no longer intact. The ring opening rear-

angement of the cyclopropyl moiety implies the formation of an  $\alpha$ -cyclopropylvinyl intermediate during the course of the addition of alkynes **1b–c** to silene **10**. The regiochemistry of the phenyl and methoxy substituents in the seven-membered ring of silacycloheptenes **14a–g**, **15a–f**, and **16** implies that the cyclopropyl ring has opened toward the phenyl substituent providing convincing evidence for the formation of a biradical intermediate during the addition of alkynes to silene **10**. Thus, alkynes **1b–c** add to silene **10** forming a 1,4-biradical intermediate which can cyclize to form silacyclobutenes **12a–b** and **17a–b** or rearrange to yield a 1,7-biradical (Scheme 11). Cyclization of the 1,7-biradical gives the seven-membered ring allene **18** which is susceptible to further reaction with silene **10** yielding the observed products **14a–g**, **15a–f**, and **16**. The results are only consistent with the formation of a biradical, since it has been shown that if an  $\alpha$ -cyclopropylvinyl cation was formed, rearrangement would occur toward the methoxy substituent and if an  $\alpha$ -cyclopropylvinyl anion was formed, no rearrangement would take place. The fact that silacyclobutenes **12a–b** and **17a–b** are observed implies that ring closure of the 1,4-biradical intermediate ( $k_C$ , Scheme 11) competes with the ring-opening rearrangement ( $k_R$ , Scheme 11). In the case of the addition of alkyne **1c** to silene **10**, the only products formed are those derived from either ring closure of the 1,4-biradical intermediate (**17a–b**) or rearrangement of the 1,4-biradical intermediate (**15a–f** and **16**). Since the rate constant for ring opening of a phenyl-substituted  $\alpha$ -cyclopropylvinyl radical has been determined,  $k_R = 1.6 \times 10^{10} \text{ s}^{-1}$ ,<sup>8b</sup> the rate constant for ring closure of the 1,4-biradical may be estimated using the following equation:  $k_C = k_R([\mathbf{17}]/[\mathbf{15} + \mathbf{16}])$ . The ratio of (**15** + **16**):**17** is 79:21, and thus, the value of  $k_C$  is  $\sim 4 \times 10^9 \text{ s}^{-1}$ . A similar competition occurred during the addition of alkyne **1c** to tetrakis(*tert*-butyldimethylsilyl)disilene yielding disilacyclohepta-1,2-diene **6** and disilacyclobutene **8** (Scheme 6).<sup>10</sup> The rate constant of ring closure of the 1,4-biradical intermediate, in that case, could also be estimated and was found to be  $\sim 6 \times 10^9 \text{ s}^{-1}$ .<sup>10</sup> The two values obtained for the rate constant of ring closure to form either a silacyclobutene or a disilacyclobutene are essentially equal.

The regiochemistry of the addition of the second equivalent of silene **10** to the seven-membered ring allene **18** to form **14a–g**, **15a–f**, and **16** is also noteworthy; in all cases, the silenic silicon apparently adds to the central carbon of allene **18**. Based on the results herein, it is reasonable to expect that the addition of a silene to an alkene will proceed by way of a biradical intermediate. Thus, the regioselectivity in these additions is governed by preferential formation of an allyl versus a vinyl radical.

The mechanism by which allenes **11a–b** and **13a–b** are formed is more ambiguous. These allenes could form by disproportionation of a 1,4-biradical intermediate or by a concerted ene-addition (Scheme 12). Given the magnitude of the rate constant for ring opening of a phenyl-substituted  $\alpha$ -cyclopropylvinyl radical,  $1.6 \times 10^{10} \text{ s}^{-1}$ ,<sup>8b</sup> the ring-opening rearrangement should effectively compete with disproportionation if indeed a biradical is an intermediate. It has been shown, in the phenyl-substituted cyclopropylcarbinyl radical system, that incorporation of an alkoxy group on the cyclopropyl ring does not significantly influence the rate constant for ring opening of the radical.<sup>15</sup> As such, it was presumed that the rate constants

(14) (a) Leong, M. K.; Mastryukov, V. S.; Boggs, J. E. *J. Mol. Struct.* **1998**, *445*, 149. (b) Ermolaeva, L. I.; Mastryukov, V. S.; Allinger, N. L.; Almenningen, A. *J. Mol. Struct.* **1989**, *196*, 151.

**Scheme 10.** Summary of the Addition of Alkynes **1a–c** to Silene **10****Scheme 11.** Mechanism of Alkyne Addition to Silene **10****Scheme 12.** Possible Routes Forming Allenes **11a–b** and **13a–b**

for ring opening for the cyclopropylvinyl radicals derived from alkyne **1a** (no methoxy substituent) and alkynes **1b–c** (with methoxy substituent) would not vary dramatically. Thus, it seems unlikely, in the case of the addition of alkyne **1a** to silene **10** where allenes **11a–b** are the only products formed, that a 1,4-biradical was formed during this reaction. We believe the most likely mechanism for the formation of allenes **11a–b** from the addition of alkyne **1a** to silene **10** is via a concerted pericyclic ene reaction. In the addition of alkyne **1b** to silene **10**, apparently competition between the ene pathway and one involving the formation of a biradical occurs, since products derived from both pathways are observed. However, disproportionation of the biradical cannot be ruled out. It is intriguing that only ene-addition products are formed in the addition of alkyne **1a** to silene **10**, whereas products derived from both ene-

addition and cycloaddition are formed in the addition of alkyne **1b** to silene **10**. Alkynes **1a** and **1b** only differ by a methoxy substituent, which clearly has a profound influence; however, the nature of this effect is not known. Finally, in the addition of alkyne **1c** to silene **10**, disproportionation via a six-membered cyclic transition state is not possible, and as a consequence, only products derived from a biradical intermediate are observed.

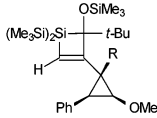
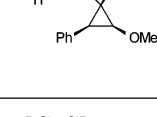
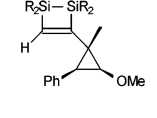
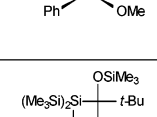
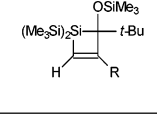
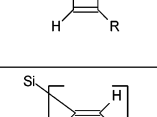
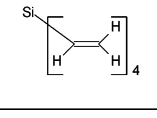
### Determination of Silacyclobutene Regiochemistry

Given the problems associated with the determination of the regiochemistry of silacyclobutenes by NOE spectroscopy or mass spectrometry and the difficulty in routinely obtaining suitable crystals for an X-ray study,<sup>2a,6d,e,g</sup> it was necessary to find a simple and reliable method for ascertaining the regiochemistry of these compounds. Initially, the <sup>1</sup>H 1D-ROE spectroscopic data of silacyclobutene **17a** was examined. Irradiation of the signal at 1.20 ppm of **17a**, assigned to the *t*-Bu <sup>1</sup>H's, caused enhancement of the signal at 1.48 ppm, assigned to the methyl group on the cyclopropyl ring. No enhancement of the signal at 5.97 ppm, assigned to the vinylic <sup>1</sup>H, was observed. The signal at 5.97 ppm (vinylic <sup>1</sup>H) was also irradiated; however, no enhancements were observed in the <sup>1</sup>H 1D-ROE spectroscopic data of **17a**. These spectroscopic data lead to the conclusion that the *t*-Bu and cyclopropyl groups are on adjacent ring atoms. Although ROE spectroscopic data can be used to assign the regiochemistry of such a compound, we found the results to often be ambiguous due to a lack of enhancements. Therefore, an alternative and more reliable method for the determination of the regiochemistry of silacyclobutenes was necessary. The <sup>29</sup>Si satellites of the signals assigned to the vinylic <sup>1</sup>H's in the <sup>1</sup>H NMR spectra of several (di)silacyclobutenes are listed in Table 1. The <sup>1</sup>H (vinylic)–<sup>29</sup>Si coupling constants of silacyclobutenes **17a** and **17b** were found to be 9.6 Hz (entry 2, Table 1). The ROE spectroscopic data for **17a** suggest this *J* value corresponds to the geminal coupling constant. Indeed, this value is comparable to the <sup>2</sup>J<sub>H–Si</sub> geminal coupling constant of tetravinylsilane (6 Hz) rather than the <sup>3</sup>J<sub>H–Si<sub>vins</sub></sub> (17 Hz).<sup>16</sup> In a related compound, 1,1,2,2-tetramesityl-3-(2-methoxy-1-methyl-3-phenylcyclopropyl)disilacyclobut-3-ene, **7** (entry 3, Table 1),<sup>9</sup> the vinylic <sup>1</sup>H couples to the two ring <sup>29</sup>Si's with *J* = 7 and 30 Hz. Again, these *J* values were extracted from the <sup>29</sup>Si satellites of the vinylic <sup>1</sup>H signal in the <sup>1</sup>H NMR spectrum of **7**. Disilacyclobutene **7** was also analyzed by <sup>1</sup>H 1D-ROE spectroscopy. Irradiation of the signal assigned to the methyl group on the cyclopropyl ring caused an enhancement of two of the four signals assigned to

(15) Le Tadic-Biadatti, M.-H.; Newcomb, M. J. *Chem. Soc., Perkin Trans.* **1996**, 1467.

(16) Krebs, P.; Dreeskamp, H. *Spectrochim. Acta* **1968**, *25A*, 1399.

**Table 1.** Coupling Constants between Vinyl  $^1\text{H}$  and  $^{29}\text{Si}$  for (di)silacyclobutenes

Entry	(di)silacyclobutene	$^2J_{\text{H-Si}}$ , Hz	$^3J_{\text{H-Si}}$ , Hz	Reference	
1	12a-b: R = H		8.4 (12a)	This work	
		8.4 (12b)			
2	17a-b: R = Me		9.6 (17a)	This work	
		9.6 (17b)			
3	7: R = Mes		7	30 ( <i>trans</i> )	9
4	8: R = SiMe <sub>2</sub> <i>t</i> -Bu		9	23 ( <i>trans</i> )	10
5	20: R = <i>t</i> -Bu		9.6		6d
6	21: R = SiMe <sub>3</sub>		11.6	5.6 ( <i>cis</i> )	6e,g
7	Tetravinylsilane		6	9 ( <i>cis</i> ) 17 ( <i>trans</i> )	16

the *o*-CH<sub>3</sub>'s of the mesityl substituents. Thus, these signals were assigned to the mesityl groups on the Si atom attached to the substituted end of the C=C of the four-membered ring. By  $^1\text{H}$ - $^{29}\text{Si}$  gHMBC the same *o*-CH<sub>3</sub>  $^1\text{H}$  signals correlated to the  $^{29}\text{Si}$  signal at  $-15$  ppm in the  $^{29}\text{Si}$  dimension and this signal correlated to the vinylic  $^1\text{H}$  with a  $J$  value of 30 Hz, as evidenced by a doublet in the  $^1\text{H}$  dimension in the  $^1\text{H}$ - $^{29}\text{Si}$  gHMBC spectrum of **7**. Therefore, the  $^1\text{H}$ - $^{29}\text{Si}$  coupling constant of 30 Hz was assigned to  $^3J_{\text{H-Si}}$ . Consequently, the  $J$  value of 7 Hz must be assigned to  $^2J_{\text{H-Si}}$ , the two-bond coupling constant between the vinylic  $^1\text{H}$  and the ring  $^{29}\text{Si}$ ; this value is consistent with the observed coupling constant between the vinylic  $^1\text{H}$  and the ring  $^{29}\text{Si}$  of silacyclobutenes **17a-b**. The  $^1\text{H}$ - $^{29}\text{Si}$  coupling constants were also extracted from the  $^{29}\text{Si}$  satellites of the vinylic  $^1\text{H}$  signal in the  $^1\text{H}$  NMR spectrum of a second disilacyclobutene, **8**, (entry 4, Table 1);<sup>10</sup> the values of  $J$  are comparable to those of disilacyclobutene **7**. To provide additional examples, the  $^1\text{H}$ - $^{29}\text{Si}$  coupling constants of silacyclobutenes **20**<sup>6d</sup> and **21**<sup>6e,g</sup> were determined (entries 5 and 6, Table 1). The  $^1\text{H}$ - $^{29}\text{Si}$  coupling constant of the vinylic  $^1\text{H}$  and the ring  $^{29}\text{Si}$  of silacyclobutene **20** was found to be 9.6 Hz. The assignment of the  $^1\text{H}$ - $^{29}\text{Si}$  coupling constants in silacyclobutene **21** was slightly more complex due to the presence of the vinylic trimethylsilyl group. In the  $^1\text{H}$ - $^{29}\text{Si}$  gHMBC NMR spectrum of **21**, the  $^{29}\text{Si}$  signal that correlated to two types of SiMe<sub>3</sub>  $^1\text{H}$  signals in the  $^1\text{H}$  dimension was assigned to the endocyclic  $^{29}\text{Si}$ . The ring  $^{29}\text{Si}$  signal coupled to the vinylic  $^1\text{H}$  with a  $J$  value of 11.6 Hz, as evidenced by a doublet in the  $^1\text{H}$  dimension of the  $^1\text{H}$ - $^{29}\text{Si}$  gHMBC NMR spectrum of **21**; the  $^{29}\text{Si}$  signal attributable to the vinylic SiMe<sub>3</sub> was found to correlate to the vinylic  $^1\text{H}$  with a  $J$  value of 5.6 Hz. Based on the value of the coupling constants between the vinylic  $^1\text{H}$  and  $^{29}\text{Si}$  in silacyclobutenes **20** and **21**, the  $J$  value of 9.6 Hz (**20**) and the  $J$  value of 11.6 Hz (**21**) are assigned to the geminal  $^2J_{\text{H-Si}}$ .

From the data listed in Table 1, the magnitude of  $^2J_{\text{H-Si}}$  varies from  $\sim 8$ –12 Hz, whereas the magnitude of  $^3J_{\text{H-Si}}$  is considerably larger and has a broader range ( $\sim 17$ –30 Hz). The data suggest that the regiochemistry of adducts between terminal

alkynes and silenes can be assigned based on the magnitude of the  $^1\text{H}$ - $^{29}\text{Si}$  coupling constants. Since it is now routinely possible to observe  $^{29}\text{Si}$  satellites in  $^1\text{H}$  NMR spectra due to the high sensitivity of modern NMR spectrometers, the coupling constants provide a simple and straightforward means for the routine assessment of the regiochemistry of silacyclobutenes derived from the cycloaddition of terminal alkynes to Brook silenes. Now we have established the range of geminal  $^1\text{H}$ -C(sp<sup>2</sup>)- $^{29}\text{Si}$  coupling constants, we believe they can be utilized more generally in the elucidation of the structures of organo-silicon compounds by NMR spectroscopy.

## Conclusions

We have found, by examination of the addition of cyclopropyl alkyne probes **1a-c** to silene **10**, that two mechanistic pathways for the addition of alkynes to Brook silenes are operative. In the absence of an  $\alpha$ -hydrogen, the reaction proceeds via the formation of a biradical as evidenced by the regioselective ring-opening of the cyclopropyl group toward the phenyl substituent. On the other hand, the exclusive formation of allenes **11a-b**, observed in the addition of **1a** to silene **10**, is convincing evidence for the absence of an intermediate  $\alpha$ -cyclopropylvinyl radical or cation during this addition, since ring opening was not observed. Either the formation of an intermediate  $\alpha$ -cyclopropylvinyl anion or the absence of any intermediate is a plausible explanation for this observation; however, further experiments will be required to make any substantive conclusions. Given our previous experience with the difficulties associated with the formation of  $\alpha$ -(2-phenyl-3-methoxycyclopropyl)vinyl lithium,<sup>8a</sup> we favor a pericyclic ene mechanism. No evidence for any product derived from the formation of a 1,4-biradical with a radical centered on silicon was observed. Clearly the formation of a biradical with the radical centered on the silenic carbon is favored. We continue to probe the generality of these findings with other Brook silenes. The reactivity of normally polarized silenes with alkynes **1a-c** is also under investigation.

We have determined the magnitude of a number of two-bond  $^1\text{H}-\text{C}(\text{sp}^2)-^{29}\text{Si}$  and three-bond  $^1\text{H}-\text{C}(\text{sp}^2)-\text{C}(\text{sp}^2)-^{29}\text{Si}$  coupling constants in (di)silacyclobutene rings. The values for  $^2J$  range from 8 to 12 Hz, whereas the values for  $^3J_{\text{H}-\text{Si}_{\text{trans}}}$  range from 17 to 30 Hz. The magnitude of the corresponding  $^3J_{\text{H}-\text{Si}_{\text{cis}}}$  coupling constant is significantly smaller. We believe that the magnitude of these coupling constants is a reliable diagnostic tool for the determination of the regiochemistry in these and related compounds.

## Experimental Section

**General Experimental Details.** All reactions were performed in flame-dried NMR tubes sealed with a septum under an inert atmosphere of argon. Irradiations were carried out using three 100 W mercury spot lamps (Blak-Ray B-100AP series;  $\lambda > 350$  nm); the NMR tubes were cooled in a cold water jacket ( $\sim 6$  °C). Benzene- $d_6$  was distilled from LAH prior to use and stored over 4 Å molecular sieves. Mesitylene, *tert*-butylacetylene, and trimethylsilylacetylene were purchased from Aldrich Chemical Co. Pivaloyltris(trimethylsilyl)silane, **9**, *2-tert*-butyl-2-trimethylsilyloxy-1,1-bis(trimethylsilyl)-1-silene, **10**,<sup>2</sup> 1,1,2,2-tetramesityl-6-methoxy-5-methyl-7-phenyl-1,2-disilacyclohepta-3,4-diene, **5**,<sup>9</sup> (*trans*-2-phenylcyclopropyl)ethyne, **1a**,<sup>17</sup> (*trans,trans*-2-methoxy-3-phenylcyclopropyl)ethyne, **1b**,<sup>8a</sup> and (*trans,trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)ethyne, **1c**,<sup>8a</sup> were prepared according to the previously reported procedures.

The NMR standards used are as follows: residual  $\text{C}_6\text{D}_5\text{H}$  (7.15 ppm) for  $^1\text{H}$  NMR spectra and  $\text{C}_6\text{D}_6$  central transition (128.0 ppm) for  $^{13}\text{C}$  NMR spectra;  $\text{Me}_4\text{Si}$  as an external standard, 0 ppm, for  $^1\text{H}-^{29}\text{Si}$  gHMBC spectra. Mass spectral data are reported in mass-to-charge units,  $m/z$ , with ion identity in parentheses. IR spectra were recorded ( $\text{cm}^{-1}$ ) from thin films.

**Irradiation of Pivaloyltris(trimethylsilyl)silane (9) with *tert*-Butylacetylene or Trimethylsilylacetylene.** A solution of pivaloyltris(trimethylsilyl)silane, **9**, ( $\sim 100$  mg, 0.3 mmol) and an excess of either *tert*-butylacetylene or trimethylsilylacetylene in  $\text{C}_6\text{D}_6$  (1.5 mL) was irradiated for 16 h. The progress of the irradiation was monitored by  $^1\text{H}$  NMR spectroscopy. Upon completion of the reaction, the solvent was removed by rotary evaporation and excess *tert*-butyl or trimethylsilylacetylene was removed under high vacuum yielding silacyclobutenes **20** and **21**, respectively, as colorless oils.<sup>6d,e,g</sup>

**Irradiation of Pivaloyltris(trimethylsilyl)silane (9) and (*trans*-2-Phenylcyclopropyl)ethyne (1a).** A solution of pivaloyltris(trimethylsilyl)silane, **9**, (93 mg, 0.28 mmol) and alkyne **1a** (50 mg, 0.35 mmol) in  $\text{C}_6\text{D}_6$  (1.5 mL) was irradiated for 2 h.  $^1\text{H}$  NMR spectroscopic analysis of the crude product revealed a mixture of two diastereomers of **11a-b** contaminated with small amounts of impurities and alkyne **1a**. The crude product was purified by preparative thin-layer chromatography (silica gel, 70:30 hexanes/ $\text{CH}_2\text{Cl}_2$ ) yielding **11a-b** (59:41, 65 mg) as a colorless oil (50% yield). **11a-b**: IR ( $\text{cm}^{-1}$ ) 2955 (s), 2894 (m), 1982 (s), 1609 (w), 1240 (s), 1056 (s), 835 (s), 743 (m), 687 (m). **11a**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  6.9–7.4 (m, PhH), 5.59 (q, 1H,  $\text{HC}=\text{C}=\text{C}$ ,  $J = 4.8$  Hz), 3.76 (s, 1H,  $\text{Me}_3\text{SiOCH}$ ), 2.78 (ddd, 1H, PhCH,  $J = 4.8, 4.8, 7.7$  Hz), 1.85 (ddd, 1H,  $\text{CH}_2$ ,  $J = 5.3, 6.5, 7.0$  Hz), 1.68 (dt, 1H,  $\text{CH}_2$ ,  $J = 5.2, 6.5$  Hz), 1.02 (s, 9H, *t*-Bu), 0.33 (s, 9H, SiMe<sub>3</sub>), 0.31 (s, 9H, SiMe<sub>3</sub>), 0.09 (s, 9H, OSiMe<sub>3</sub>);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  196.87 (C=C=C), 141.50 (*i*-PhC), 128.51 (*m*-PhC), 126.84 (*o*-PhC), 126.45 (*p*-PhC), 83.66 (HC=C=C), 82.84 ( $\text{Me}_3\text{OSiCH}$ ), 76.11 (HC=C=C), 36.14 (C(CH<sub>3</sub>)), 28.67 (C(CH<sub>3</sub>)), 26.12 (PhCH), 18.10 (CH<sub>2</sub>), 1.28 (SiMe<sub>3</sub>), 1.22 (OSiMe<sub>3</sub>), 0.69 (SiMe<sub>3</sub>);  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  14.5 (OSiMe<sub>3</sub>), -15.1 (2 × SiMe<sub>3</sub>), -46.8 (Si(SiMe<sub>3</sub>)<sub>2</sub>). **11b**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  6.9–7.4 (m, PhH), 5.51 (q, 1H,  $\text{HC}=\text{C}=\text{C}$ ,  $J = 4.9$  Hz), 3.96 (s, 1H,  $\text{Me}_3\text{SiOCH}$ ), 2.82 (ddd, 1H, PhCH,  $J = 4.9, 4.9, 8.0$  Hz), 1.87 (ddd, 1H,  $\text{CH}_2$ ,  $J = 5.4, 6.6, 7.8$  Hz), 1.80 (dt, 1H,  $\text{CH}_2$ ,  $J = 6.5, 5.2$  Hz), 1.03 (s, 9H, *t*-Bu), 0.30 (s,

9H, SiMe<sub>3</sub>), 0.27 (s, 9H, OSiMe<sub>3</sub>), 0.15 (s, 9H, SiMe<sub>3</sub>);  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  196.30 (C=C=C), 140.86 (*i*-PhC), 128.51 (*m*-PhC), 127.00 (*o*-PhC), 126.45 (*p*-PhC), 83.56 (HC=C=C), 80.40 ( $\text{Me}_3\text{OSiCH}$ ), 76.04 (HC=C=C), 36.11 (C(CH<sub>3</sub>)), 28.76 (C(CH<sub>3</sub>)), 26.03 (PhCH), 17.46 (CH<sub>2</sub>), 1.48 (OSiMe<sub>3</sub>), 1.24 (SiMe<sub>3</sub>), 0.29 (SiMe<sub>3</sub>);  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  14.3 (OSiMe<sub>3</sub>), -15.4 (SiMe<sub>3</sub>), -15.8 (SiMe<sub>3</sub>), -46.3 (Si(SiMe<sub>3</sub>)<sub>2</sub>). **11a-b**: High-resolution ESI-MS for  $\text{C}_{25}\text{H}_{47}\text{OSi}_4$  ( $M + \text{H}^+$ ) ( $m/z$ ) calcd 475.2704, found 475.2727.

**Irradiation of Pivaloyltris(trimethylsilyl)silane (9) and (*trans,trans*-2-Methoxy-3-phenylcyclopropyl)ethyne (1b).** Three solutions of pivaloyltris(trimethylsilyl)silane, **9**, (196 mg, 0.59 mmol; 196 mg, 0.59 mmol; 195 mg, 0.58 mmol) and alkyne **1b** (137 mg, 0.80 mmol; 134 mg, 0.78 mmol; 142 mg, 0.82 mmol) in  $\text{C}_6\text{D}_6$  (1.5 mL each) were simultaneously irradiated. The progress of the reactions was monitored by  $^1\text{H}$  NMR spectroscopy. After 10 h of irradiation, the three reaction mixtures were combined (916 mg) and a mixture of **12a-b**, **13a-b**, and **14a-g** was obtained (in a ratio of 17:48:35 **12:13:14**) as revealed by  $^1\text{H}$  NMR spectroscopy. The crude product mixture was separated by column chromatography (silica gel, 5:1 hexanes/ $\text{CH}_2\text{Cl}_2$ ) yielding a mixture of **12a-b** and **13a-b** (15:10:51:24, 168 mg, 0.33 mmol) and a mixture of **14a-g** (255 mg, 0.30 mmol). Compounds **14a-g** were further separated by preparative thin-layer chromatography (silica gel, 10:1 hexanes/ $\text{CH}_2\text{Cl}_2$ ) yielding **14a-b** (40.4 mg), **14c-d** (46.1 mg), **14e-f** (42.9 mg), and **14g** (29.9 mg) contaminated with minor impurities. Compounds **14** were purified by precipitation from acetone yielding **14a-b** (89:11, 15.7 mg, 0.02 mmol), **14c-d** (86:14, 22.6 mg, 0.03 mmol), **14e-f** (76:24, 20.7 mg, 0.02 mmol), and **14g** (9.9 mg, 0.01 mmol). Further attempts at separation of compounds **12** and **13** were unsuccessful; they could not be isolated from each other, and thus, they were characterized as a mixture with minor impurities present. **12a-b** and **13a-b**: IR ( $\text{cm}^{-1}$ ) 2953 (s), 2898 (m), 2825 (w), 1982 (s), 1248 (s), 1153 (m), 1053 (s), 839 (s), 746 (w), 695 (m). **12a**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.00–7.45 (PhH), 5.83 (s, 1H, SiC(H)=C,  $^2J_{\text{H}-\text{Si}} = 8.4$  Hz), 3.26 (dd, 1H, MeOCH,  $J = 3.6, 6.4$  Hz), 2.94 (s, 3H, MeO), 2.33 (dd, 1H, C=C(C)H,  $J = 3.2, 6.4$  Hz), 2.24 (t, 1H, PhCH,  $J = 6.4$  Hz), 1.24 (s, 9H, *t*-Bu), 0.32 (s, 9H, SiMe<sub>3</sub>), 0.27 (s, 9H, SiMe<sub>3</sub>), 0.20 (s, 9H, OSiMe<sub>3</sub>);  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.6 (OSiMe<sub>3</sub>), -16.6 (SiMe<sub>3</sub>).<sup>18</sup> **12b**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.00–7.45 (PhH), 5.79 (s, 1H, SiC(H)=C,  $^2J_{\text{H}-\text{Si}} = 8.4$  Hz), 3.54 (dd, 1H, MeOCH,  $J = 3.6, 6.4$  Hz), 2.98 (s, 3H, MeO), 2.36 (dd, 1H, C=C(C)H,  $J = 3.6, 6.4$  Hz), 1.99 (t, 1H, PhCH,  $J = 6.4$  Hz), 1.07 (s, 9H, *t*-Bu), 0.40 (s, 9H, OSiMe<sub>3</sub>), 0.35 (s, 9H, SiMe<sub>3</sub>), 0.25 (s, 9H, SiMe<sub>3</sub>);  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.4 (OSiMe<sub>3</sub>).<sup>18</sup> **13a**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.00–7.45 (PhH), 5.58 (dd, 1H, HC=C=C,  $J = 3.2, 5.6$  Hz), 3.87 (s, 1H,  $\text{Me}_3\text{SiOCH}$ ), 3.83 (dd, 1H, MeOCH,  $J = 3.6, 6.0$  Hz), 2.88 (s, 3H, MeO), 2.87 (t, 1H, PhCH,  $J = 5.6$  Hz), 1.04 (s, 9H, *t*-Bu), 0.41 (s, 9H, SiMe<sub>3</sub>), 0.33 (s, 9H, SiMe<sub>3</sub>), 0.04 (s, 9H, OSiMe<sub>3</sub>);  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  14.5 (OSiMe<sub>3</sub>), -14.9, -15.5 (SiMe<sub>3</sub>), -45.6 (Si(SiMe<sub>3</sub>)<sub>2</sub>). **13b**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.00–7.45 (PhH), 5.48 (dd, 1H, HC=C=C,  $J = 3.6, 5.6$  Hz), 4.02 (s, 1H,  $\text{Me}_3\text{SiOCH}$ ), 3.86 (dd, 1H, MeOCH,  $J = 3.6, 6.0$  Hz), 2.91 (s, 3H, MeO), 2.87 (t, 1H, PhCH,  $J = 5.6$  Hz), 1.05 (s, 9H, *t*-Bu), 0.34 (s, 9H, SiMe<sub>3</sub>), 0.28 (s, 9H, OSiMe<sub>3</sub>), 0.21 (s, 9H, SiMe<sub>3</sub>);  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  14.6 (OSiMe<sub>3</sub>), -15.1, -15.6 (SiMe<sub>3</sub>), -45.9 (Si(SiMe<sub>3</sub>)<sub>2</sub>). **12a-b** and **13a-b**:  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  197.26 (HC=C=C, **13a**), 197.10 (HC=C=C, **13b**), 167.67 (SiC(H)=C, **12a**), 167.21 (SiC(H)=C, **12b**), 137.61, 137.29, 137.06 (*i*-PhC, **13a**), 136.71 (*i*-PhC, **13b**), 129.28 (*o*-PhC, **13b**), 129.11 (*o*-PhC, **13a**), 128.6 (*m*-PhC, **13b**),<sup>19</sup> 128.0 (*m*-PhC, **13a**),<sup>19</sup> 126.66, 126.45 (*p*-PhC, **13a**), 126.42 (*m*-PhC, **13b**), 126.18, 126.11, 125.38, 94.01 ( $\text{Me}_3\text{SiOC}$ , **12a**), 93.86 ( $\text{Me}_3\text{SiOC}$ , **12b**), 83.21 ( $\text{Me}_3\text{SiOC}$ , **13a**), 82.82 (HC=C=C, **13a**), 82.48 (HC=C=C, **13b**), 80.63 ( $\text{Me}_3\text{SiOC}$ , **13b**), 76.35 (HC=C=C, **13a**), 76.29 (HC=C=C, **13b**), 70.82 (MeOCH, **12a**), 67.73 (MeOCH, **12b**), 63.13 (MeOCH, **13a**), 63.10 (MeOCH, **13b**), 57.93 (MeO, **12a**), 57.90 (MeO, **12b**), 57.74 (MeO, **13a**), 57.65

(18) It was difficult to assign all  $^{29}\text{Si}$  signals due to extensive overlap of the signals.

(19) Chemical shift estimated from the  $^1\text{H}-^{13}\text{C}$  gHMBC spectrum.

(17) Charette, A. B.; Giroux, A. *J. Org. Chem.* **1996**, *61*, 8718.



(MeO, **13b**), 37.77 (PhCH, **12a**), 37.23 ( $C(CH_3)_3$ , **12a**), 37.15 ( $C(CH_3)_3$ , **12b**), 36.81, 36.22 ( $C(CH_3)_3$ , **13a** and **13b**), 33.21 (PhCH, **13a** and **13b**), 31.03 ( $C=C(C)H$ , **12a**), 30.40 ( $C=C(C)H$ , **12b**), 29.10 ( $C(CH_3)_3$ , **12a**), 29.01 ( $C(CH_3)_3$ , **12b**), 28.83 ( $C(CH_3)_3$ , **13b**), 28.76 ( $C(CH_3)_3$ , **13a**), 3.89, 3.78, 1.78, 1.57, 1.35, 1.26, 0.85, 0.53. High-resolution CI-MS for  $C_{26}H_{49}O_2Si_4$  ( $M + H^+$ ) ( $m/z$ ) calcd 505.2810, found 505.2790. **14a–b**: IR ( $cm^{-1}$ ) 2951 (s), 1249 (s), 1079 (s), 1053 (s), 839 (s), 751 (w), 716 (w), 670 (w). **14a**:  $^1H$  NMR ( $C_6D_6$ )  $\delta$  7.72 (d, 1H, *o*-PhH,  $J = 7.2$  Hz), 7.36 (t, 1H, *m*-PhH,  $J = 8.0$  Hz), 7.12 (t, 1H, *m*-PhH,  $J = 7.2$  Hz), 7.07 (t, 1H, *p*-PhH,  $J = 7.2$  Hz), 6.95 (d, 1H, *o*-PhH,  $J = 6.6$  Hz), 6.28 (d, 1H,  $HC=C$ ,  $J = 3.6$  Hz), 4.40 (br s, 1H, CH), 3.80 (d, 1H, PhCH,  $J = 3.6$  Hz), 3.40 (br d, 1H, MeOCH,  $J = 3$  Hz), 3.30 (s, 3H, MeO), 1.48 (s, 3H, one Me of *t*-Bu<sub>cyclobutane</sub>), 1.17 (s, 9H, *t*-Bu<sub>cycloheptene</sub>), 1.13, 1.03 (each s, 3H, one Me of *t*-Bu<sub>cyclobutane</sub>), 0.51 (s, 9H, SiMe<sub>3</sub><sub>cyclobutane</sub>), 0.48, 0.42 (each s, 9H, SiMe<sub>3</sub><sub>cycloheptene</sub>), 0.39 (s, 9H, SiMe<sub>3</sub><sub>cyclobutane</sub>), 0.03, -0.07 (each s, 9H, OSiMe<sub>3</sub>);  $^{13}C$  NMR ( $C_6D_6$ )  $\delta$  157.92 ( $HC=C$ ), 142.67 (*i*-PhC), 134.94 (*o*-PhC), 132.88 (*o*-PhC), 132.33 ( $HC=C$ ), 129.39 (*m*-PhC), 129.06 (*m*-PhC), 126.67 (*p*-PhC), 98.73 (Me<sub>3</sub>SiOC<sub>cyclobutane</sub>), 96.50 (Me<sub>3</sub>SiOC<sub>cycloheptene</sub>), 90.73 (MeOCH), 67.57 (CH), 60.34 (MeO), 58.10 (PhCH), 42.19 ( $C(CH_3)_3$ <sub>cycloheptene</sub>), 38.69 ( $C(CH_3)_3$ <sub>cyclobutane</sub>), 33.89 (one of  $C(CH_3)_3$ <sub>cyclobutane</sub>), 30.53 (br s,  $C(CH_3)_3$ <sub>cycloheptene</sub>), 27.05, 26.43 (one of  $C(CH_3)_3$ <sub>cyclobutane</sub> each), 6.37 (OSiMe<sub>3</sub>), 4.02 (SiMe<sub>3</sub><sub>cycloheptene</sub>), 3.85 (OSiMe<sub>3</sub>), 3.53 (SiMe<sub>3</sub><sub>cycloheptene</sub>), 2.05 (SiMe<sub>3</sub><sub>cyclobutane</sub>), 1.52 (SiMe<sub>3</sub><sub>cyclobutane</sub>);  $^{29}Si$  NMR ( $C_6D_6$ )  $\delta$  2.6, 2.0 (OSiMe<sub>3</sub>), -12.5, -13.0 (SiMe<sub>3</sub><sub>cycloheptene</sub>), -13.2, -14.8 (SiMe<sub>3</sub><sub>cyclobutane</sub>), -20.5 (Si(SiMe<sub>3</sub>)<sub>2</sub><sub>cyclobutane</sub>), -30.0 (Si(SiMe<sub>3</sub>)<sub>2</sub><sub>cycloheptene</sub>). High-resolution CI-MS for  $C_{37}H_{75}O_3Si_7$  ( $M^+ - SiMe_3$ ) ( $m/z$ ) calcd 763.4101, found 763.4077. **14b**:  $^1H$  NMR ( $C_6D_6$ )  $\delta$  7.69–7.71 (m, 1H, PhH), 7.20–7.23 (m, PhH), 7.00–7.04 (m, PhH), 6.80 (d, 1H,  $J = 3.0$  Hz), 4.44 (dd, 1H,  $J = 3.0, 10.2$  Hz), 3.95 (br s, 1H), 3.77 (d, 1H,  $J = 10.2$  Hz), 3.34 (s, 3H, MeO), 0.61, 0.56, 0.38, 0.37, 0.22, 0.19 (each s, 9H, SiMe<sub>3</sub>). **14c–d**: IR ( $cm^{-1}$ ) 2953 (s), 2899 (m), 1454 (w), 1397 (w), 1250 (s), 1199 (w), 1081 (s), 837 (s), 749 (w). **14c**:  $^1H$  NMR ( $C_6D_6$ )  $\delta$  8.09 (d, 1H, *o*-PhH,  $J = 7.8$  Hz), 7.55 (d, 1H, *o*-PhH,  $J = 7.2$  Hz), 7.19 (m, 1H, *m*-PhH), 7.13–7.16 (m, PhH), 7.11 (t, 1H, *p*-PhH,  $J = 7.2$  Hz), 6.29 (d, 1H,  $HC=C$ ,  $J = 3.6$  Hz), 4.73 (dd, 1H, CH,  $J = 3.6, 7.2$  Hz), 4.54 (dd, 1H, MeOCH,  $J = 3.6, 7.2$  Hz), 4.48 (d, 1H, PhCH,  $J = 3$  Hz), 3.54 (s, 3H, MeO), 1.25 (s, 9H, *t*-Bu<sub>cycloheptene</sub>), 0.95 (s, 3H, one Me of *t*-Bu<sub>cyclobutane</sub>), 0.455 (s, 9H, SiMe<sub>3</sub><sub>cycloheptene</sub>), 0.448 (s, 9H, SiMe<sub>3</sub><sub>cycloheptene</sub>), 0.44 (s, 9H, SiMe<sub>3</sub><sub>cyclobutane</sub>), 0.34 (s, 9H, SiMe<sub>3</sub><sub>cyclobutane</sub>), 0.21, 0.17 (s, 9H, OSiMe<sub>3</sub>);  $^{13}C$  NMR ( $C_6D_6$ )  $\delta$  165.29 ( $HC=C$ ), 138.37 (*o*-PhC), 138.09 (*i*-PhC), 137.54 (*o*-PhC), 130.24 ( $HC=C$ ), 126.81, 126.71, 126.04 (*m,p*-PhC), 103.30 (Me<sub>3</sub>SiOC<sub>cycloheptene</sub>), 99.86 (Me<sub>3</sub>SiOC<sub>cyclobutane</sub>), 81.82 (MeOCH), 70.98 (CH), 59.39 (PhCH), 56.34 (MeO), 40.67 ( $C(CH_3)_3$ <sub>cycloheptene</sub>), 38.29 ( $C(CH_3)_3$ <sub>cyclobutane</sub>), 30.20 (br s,  $C(CH_3)_3$ ), 30.03 ( $C(CH_3)_3$ ), 6.69 (OSiMe<sub>3</sub>), 4.49 (SiMe<sub>3</sub>), 3.82 (OSiMe<sub>3</sub>), 2.80 (SiMe<sub>3</sub>), 2.18 (SiMe<sub>3</sub>), 1.71 (SiMe<sub>3</sub>);  $^{29}Si$  NMR ( $C_6D_6$ )  $\delta$  2.9, 1.6 (OSiMe<sub>3</sub>), -13.1 to -14.4 (3  $\times$  SiMe<sub>3</sub>), -14.5 (SiMe<sub>3</sub>), -20.6 (Si(SiMe<sub>3</sub>)<sub>2</sub><sub>cyclobutane</sub>), -32.2 (Si(SiMe<sub>3</sub>)<sub>2</sub><sub>cycloheptene</sub>). **14d**:  $^1H$  NMR ( $C_6D_6$ )  $\delta$  7.58 (d, 1H, *o*-PhH,  $J = 7.8$  Hz), 7.31 (dt, 1H, *m*-PhH,  $J = 2.4, 7.8$  Hz), 7.03–7.13 (m, PhH), 6.23 (d, 1H,  $HC=C$ ,  $J = 3.6$  Hz), 4.33 (dd, 1H, MeOCH,  $J = 1.8, 9.3$  Hz), 3.89 (d, 1H, PhCH,  $J = 1.8$  Hz), 3.70 (dd, 1H, CH,  $J = 3.2, 9.3$  Hz), 3.41 (s, 3H, MeO), 0.90 (s, 9H, *t*-Bu<sub>cycloheptene</sub>), 0.55 (s, 9H, OSiMe<sub>3</sub>), 0.47 (s, 9H, SiMe<sub>3</sub><sub>cycloheptene</sub>), 0.46 (s, 9H, OSiMe<sub>3</sub>), 0.42 (s, 9H, SiMe<sub>3</sub><sub>cyclobutane</sub>), 0.41 (s, 9H, SiMe<sub>3</sub><sub>cycloheptene</sub>), 0.37 (s, 9H, SiMe<sub>3</sub><sub>cyclobutane</sub>);  $^{13}C$  NMR ( $C_6D_6$ )  $\delta$  162.87 ( $HC=C$ ), 139.86 (*i*-PhC), 133.53 ( $HC=C$ ), 133.00 (*o*-PhC), 131.70 (*o*-PhC), 126.54 (*m*-PhC), 99.8 (Me<sub>3</sub>SiOC<sub>cyclobutane</sub>), 94.13 (Me<sub>3</sub>SiOC<sub>cycloheptene</sub>), 79.30 (MeOCH), 64.15 (CH), 61.01 (PhCH), 56.57 (MeO), 41.73 ( $C(CH_3)_3$ <sub>cycloheptene</sub>), 38.04 ( $C(CH_3)_3$ <sub>cyclobutane</sub>), 30.20 (br s,  $C(CH_3)_3$ ), 7.21 (OSiMe<sub>3</sub>), 5.92 (SiMe<sub>3</sub>), 3.67 (SiMe<sub>3</sub>), 3.53 (SiMe<sub>3</sub>), 2.32 (SiMe<sub>3</sub>), 1.36 (SiMe<sub>3</sub>);  $^{29}Si$  NMR ( $C_6D_6$ )  $\delta$  2.6, 2.0 (OSiMe<sub>3</sub>), -12.9, -13.4, -15.0, -15.6 (each SiMe<sub>3</sub>), -24.2 (Si(SiMe<sub>3</sub>)<sub>2</sub><sub>cyclobutane</sub>), -32.8 (Si(SiMe<sub>3</sub>)<sub>2</sub><sub>cycloheptene</sub>). **14c–**

(20) **14b** was present in small quantities, and thus, only the  $^1H$  NMR data are listed.

**d**: High-resolution CI-MS for  $C_{37}H_{75}O_3Si_7$  ( $M^+ - SiMe_3$ ) ( $m/z$ ) calcd 763.4101, found 763.4123. **14e–f**: IR ( $cm^{-1}$ ) 2952 (s), 1458 (w), 1395 (w), 1245 (s), 1095 (s), 1063 (s), 831 (s), 746 (w). **14e**:  $^1H$  NMR ( $C_6D_6$ )  $\delta$  8.09 (d, 1H, *o*-PhH,  $J = 8.4$  Hz), 7.31 (d, 1H, *o*-PhH,  $J = 7.8$  Hz), 7.20 (t, 1H, *m*-PhH,  $J = 7.2$  Hz), 7.14 (t, 1H, *m*-PhH,  $J = 7.8$  Hz), 7.09 (t, 1H, *p*-PhH,  $J = 7.2$  Hz), 6.14 (d, 1H,  $HC=C$ ,  $J = 3.6$  Hz), 5.18–5.21 (m, 1H, MeOCH, obscured by MeOCH signal of **14f**), 4.15 (dd, 1H, CH,  $J = 3.0, 10.8$  Hz), 3.69 (d, 1H, PhCH,  $J = 1.8$  Hz), 2.79 (s, 3H, MeO), 1.36 (br s, 9H, *t*-Bu<sub>cyclobutane</sub>), 1.24, 1.00, 0.99 (each s, 3H, one Me of *t*-Bu<sub>cycloheptene</sub>), 0.57 (s, 9H, OSiMe<sub>3</sub>), 0.48 (s, 9H, SiMe<sub>3</sub><sub>cyclobutane</sub>), 0.43 (s, 9H, SiMe<sub>3</sub><sub>cycloheptene</sub>), 0.41 (s, 9H, SiMe<sub>3</sub><sub>cycloheptene</sub>), 0.37 (s, 9H, SiMe<sub>3</sub><sub>cyclobutane</sub>), 0.13 (s, 9H, OSiMe<sub>3</sub>);  $^{13}C$  NMR ( $C_6D_6$ )  $\delta$  161.50 ( $HC=C$ ), 140.68 (*i*-PhC), 135.15 (*o*-PhC), 134.03 (*o*-PhC), 130.96 ( $HC=C$ ), 127.43, 126.85, 126.56 (*m,p*-PhC), 95.67 (Me<sub>3</sub>SiOC<sub>cycloheptene</sub>), 93.10 (Me<sub>3</sub>SiOC<sub>cyclobutane</sub>), 78.78 (MeOCH), 71.19 (CH), 64.47 (PhCH), 54.46 (MeO), 41.02 ( $C(CH_3)_3$ <sub>cycloheptene</sub>), 40.56 ( $C(CH_3)_3$ <sub>cyclobutane</sub>), 35.03 (one Me of  $C(CH_3)_3$ <sub>cycloheptene</sub>), 30.18 ( $C(CH_3)_3$ <sub>cyclobutane</sub>), 28.74, 28.09 (one of  $C(CH_3)_3$ <sub>cycloheptene</sub>), 5.42 (OSiMe<sub>3</sub>), 3.15 (SiMe<sub>3</sub><sub>cycloheptene</sub>), 3.09 (OSiMe<sub>3</sub>), 2.62 (SiMe<sub>3</sub><sub>cycloheptene</sub>), 2.20 (SiMe<sub>3</sub><sub>cyclobutane</sub>), 1.86 (SiMe<sub>3</sub><sub>cyclobutane</sub>);  $^{29}Si$  NMR ( $C_6D_6$ )  $\delta$  5.2, 3.0 (OSiMe<sub>3</sub>), -12.2 (SiMe<sub>3</sub><sub>cycloheptene</sub>), -13.9, -14.6 (each SiMe<sub>3</sub><sub>cyclobutane</sub>), -14.8 (SiMe<sub>3</sub><sub>cycloheptene</sub>), -21.5 (Si(SiMe<sub>3</sub>)<sub>2</sub><sub>cyclobutane</sub>), -34.0 (Si(SiMe<sub>3</sub>)<sub>2</sub><sub>cycloheptene</sub>). **14f**:  $^1H$  NMR ( $C_6D_6$ )  $\delta$  7.86 (d, 1H, *o*-PhH,  $J = 7.8$  Hz), 7.24–7.28 (m, 2H, PhH), 7.00–7.06 (m, 1H, PhH), 6.26 (d, 1H,  $HC=C$ ,  $J = 3.0$  Hz), 5.18–5.20 (m, 1H, MeOCH, obscured by MeOCH signal of **14e**), 4.10 (dd, 1H, CH,  $J = 3.6, 10.2$  Hz), 4.04 (br s, 1H, PhCH), 3.25 (s, 3H, MeO), 1.50 (s, 9H, *t*-Bu), 0.64 (s, 9H, OSiMe<sub>3</sub>), 0.42 (s, 9H, SiMe<sub>3</sub><sub>cycloheptene</sub>), 0.39 (s, 9H, SiMe<sub>3</sub><sub>cyclobutane</sub>), 0.38 (s, 9H, SiMe<sub>3</sub><sub>cyclobutane</sub>), 0.37 (s, 9H, SiMe<sub>3</sub><sub>cycloheptene</sub>), 0.11 (s, 9H, OSiMe<sub>3</sub>);  $^{13}C$  NMR ( $C_6D_6$ )  $\delta$  163.52 ( $HC=C$ ), 140.5 (*i*-PhC), 134.51 (*o*-PhC), 131.21 ( $HC=C$ ), 130.82 (*o*-PhC), 129.39, 128.40, 126.74 (*m,p*-PhC), 95.0 (Me<sub>3</sub>SiOC<sub>cycloheptene</sub>), 92.5 (Me<sub>3</sub>SiOC<sub>cyclobutane</sub>), 76.55 (MeOCH), 66.79 (CH), 65.30 (PhCH), 53.31 (MeO), 41.70 ( $C(CH_3)_3$ <sub>cycloheptene</sub>), 40.6 ( $C(CH_3)_3$ <sub>cyclobutane</sub>), 5.53 (OSiMe<sub>3</sub>), 3.65 (SiMe<sub>3</sub>), 3.43 (SiMe<sub>3</sub>), 1.95 (SiMe<sub>3</sub>), 1.35 (SiMe<sub>3</sub>);  $^{29}Si$  NMR ( $C_6D_6$ )  $\delta$  6.1, 4.7 (OSiMe<sub>3</sub>), -12 to -16 (SiMe<sub>3</sub>), -21.8 (Si(SiMe<sub>3</sub>)<sub>2</sub><sub>cyclobutane</sub>), -35.0 (Si(SiMe<sub>3</sub>)<sub>2</sub><sub>cycloheptene</sub>). **14e–f**: High-resolution CI-MS for  $C_{37}H_{75}O_3Si_7$  ( $M^+ - SiMe_3$ ) ( $m/z$ ) calcd 763.4101, found 763.4108. **14g**: IR ( $cm^{-1}$ ) 2954 (s), 1249 (s), 1102 (s), 1044 (s), 837 (s);  $^1H$  NMR ( $C_6D_6$ )  $\delta$  8.07 (d, 1H, *o*-PhH,  $J = 7.8$  Hz), 7.49 (br s, 1H, PhH), 7.11–7.16 (m, *m*-PhH), 7.07 (t, 1H, *p*-PhH,  $J = 7.2$  Hz), 6.26 (br s, 1H,  $HC=C$ ), 4.74 (br s, 1H, MeOCH), 4.13 (d, 1H, CH,  $J = 7.8$  Hz), 3.93 (d, 1H, PhCH,  $J = 1.8$  Hz), 2.74 (br s, 3H, MeO), 1.37 (br s, 9H, *t*-Bu<sub>cycloheptene</sub>), 1.23 (br s, 9H, *t*-Bu<sub>cyclobutane</sub>), 0.51 (s, 9H, SiMe<sub>3</sub><sub>cyclobutane</sub>), 0.45 (s, 9H, SiMe<sub>3</sub><sub>cycloheptene</sub>), 0.42 (br s, 9H, SiMe<sub>3</sub><sub>cycloheptene</sub>), 0.34 (s, 9H, SiMe<sub>3</sub><sub>cyclobutane</sub>), 0.15 (br s, 9H, OSiMe<sub>3</sub>), 0.09 (br s, 9H, OSiMe<sub>3</sub>);  $^{13}C$  NMR ( $C_6D_6$ )  $\delta$  162.88 ( $HC=C$ ), 139.2 (*i*-PhC), 136.41, 136.01 (each br s, *o*-PhC), 127.47, 127.41 (*m,p*-PhC), 98.1 (Me<sub>3</sub>SiOC<sub>cycloheptene</sub>), 94.1 (Me<sub>3</sub>SiOC<sub>cyclobutane</sub>), 78.8 (MeOCH), 73.41 (CH), 55.56 (MeO), 39.99 ( $C(CH_3)_3$ <sub>cycloheptene</sub>), 39.76 ( $C(CH_3)_3$ <sub>cyclobutane</sub>), 30.18 ( $C(CH_3)_3$ <sub>cycloheptene</sub>), 5.64 (OSiMe<sub>3</sub>), 3.85 (SiMe<sub>3</sub><sub>cycloheptene</sub>), 3.19 (OSiMe<sub>3</sub>), 2.32 (SiMe<sub>3</sub><sub>cyclobutane</sub>), 2.09 (SiMe<sub>3</sub><sub>cycloheptene</sub>), 1.93 (SiMe<sub>3</sub><sub>cyclobutane</sub>);  $^{29}Si$  NMR ( $C_6D_6$ )  $\delta$  4.6, 3.6 (OSiMe<sub>3</sub>), -13.9, -14.1 (SiMe<sub>3</sub><sub>cycloheptene</sub>), -14.2, -14.6 (SiMe<sub>3</sub><sub>cyclobutane</sub>), -20.5 (Si(SiMe<sub>3</sub>)<sub>2</sub><sub>cyclobutane</sub>), -29.1 (Si(SiMe<sub>3</sub>)<sub>2</sub><sub>cycloheptene</sub>); High-resolution CI-MS for  $C_{40}H_{85}O_3Si_8$  ( $M + H^+$ ) ( $m/z$ ) calcd 837.4653, found 837.4596.

**Irradiation of Pivaloyltris(trimethylsilyl)silane (9) and (trans,trans-2-Methoxy-1-methyl-3-phenylcyclopropyl)ethyne (1c)**. Three solutions of pivaloyltris(trimethylsilyl)silane, **9**, (200 mg, 0.60 mmol; 205 mg, 0.62 mmol; 206 mg, 0.62 mmol) and alkyne **1c** (147 mg, 0.79 mmol; 149 mg, 0.80 mmol; 143 mg, 0.77 mmol) in  $C_6D_6$  (1.5 mL each) were simultaneously irradiated. The progress of the

(21) Some signals of **14f** were obscured by overlap with the signals assigned to **14e**.

(22) Several signals were not observed in either the  $^{13}C$  NMR spectrum or in the  $^1H$ - $^{13}C$  gHMBC and gHSQC spectra.

reactions was monitored by  $^1\text{H}$  NMR spectroscopy. After 14 h of irradiation, the three reaction mixtures were combined and the solvent was removed by rotary evaporation (1.05 g); a mixture of **15a–f**, **16**, and **17a–b**, in a ratio of 16:10:16.5:17.4:11:11:10, respectively, was obtained, as determined by  $^1\text{H}$  NMR spectroscopy. The ratio of the combined products was reflective of the ratio of the individual reaction mixtures. Chromatographic separation of the crude mixture (silica gel, 7:3 hexanes/ $\text{CH}_2\text{Cl}_2$ ) yielded a mixture of **15a–b** (64:36, 240 mg, 0.287 mmol), a mixture of **15a–f** and **16** (6:3:27:6:32:6:20, 333 mg, 0.39 mmol), and a mixture of **17a–b** and recovered **9** (41:44:15, 34 mg). The mixture of **15a–f** and **16** was further separated by extensive chromatography (one column and two preparative plates, silica gel, all 5:1 hexanes/ $\text{CH}_2\text{Cl}_2$ ) yielding a mixture of **15c–d** and **16** (60:17:23, 40 mg, 0.05 mmol) and a mixture of **15e–f** (89:11, 19 mg, 0.02 mmol). In general, no one compound could be separated from the mixture, and thus, the compounds were characterized as mixtures. On one occasion only, **15c–d** was separated from **16** by chromatography to give approximately 4 mg of each. These samples were utilized for the molecular structure determinations by X-ray crystallography. **15a–b** (colorless crystals): IR ( $\text{cm}^{-1}$ ) 2955 (s), 2899 (m), 1263 (s), 1252 (s), 1111 (s), 838 (s). **15a**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.97 (br s), 7.39 (br s), 7.05–7.30 (br m) (all PhH), 6.72 (s, 1H,  $\text{SiC}(\text{H})=\text{CSi}$ ), 5.47 (br s, 1H,  $\text{C}=\text{CH}_2$ ), 5.06 (br s, 1H,  $\text{C}=\text{CH}_2$ ), 4.48 (br s, 1H,  $\text{MeOCH}$ ), 4.34 (s, 1H,  $\text{Me}_3\text{SiOCH}$ ), 3.82 (d, 1H, PhCH,  $J = 2$  Hz), 3.09 (s, 3H, MeO), 1.38 (br s, 9H,  $t\text{-Bu}_{\text{cyclic}}$ ), 1.10 (s, 9H,  $t\text{-Bu}_{\text{linear}}$ ), 0.54 (s, 9H,  $\text{SiMe}_{3\text{linear}}$ ), 0.49 (s, 9H,  $\text{SiMe}_{3\text{cyclic}}$ ), 0.47 (s, 9H,  $\text{SiMe}_{3\text{linear}}$ ), 0.43 (s, 9H,  $\text{SiMe}_{3\text{cyclic}}$ ), 0.21 (s, 9H,  $\text{OSiMe}_{3\text{linear}}$ ), 0.04 (s, 9H,  $\text{OSiMe}_{3\text{cyclic}}$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  159.46 ( $\text{SiC}(\text{H})\text{C}=\text{CSi}$ ), 151.27 ( $\text{C}=\text{CH}_2$ ), 142.97 ( $\text{SiC}(\text{H})\text{C}=\text{CSi}$ ), 137.00 ( $i\text{-PhC}$ ), 127.45, 126.6 (br s, PhC), 116.01 ( $\text{C}=\text{CH}_2$ ), 100.18 ( $\text{Me}_3\text{SiOC}_{\text{cyclic}}$ ), 80.76 ( $\text{MeOCH}$ ), 79.33 ( $\text{Me}_3\text{SiOCH}$ ), 65.51 (PhCH), 56.05 (MeO), 40.09 ( $\text{C}(\text{CH}_3)_{3\text{cyclic}}$ ), 38.23 ( $\text{C}(\text{CH}_3)_{3\text{linear}}$ ), 29.53 ( $\text{C}(\text{CH}_3)_{3\text{linear}}$ ), 5.33 ( $\text{OSiMe}_{3\text{cyclic}}$ ), 4.06 ( $\text{SiMe}_3$ ), 3.33 ( $\text{SiMe}_3$ ), 3.15 ( $\text{SiMe}_3$ ), 2.39 ( $\text{SiMe}_3$ ), 2.24 ( $\text{OSiMe}_{3\text{linear}}$ );  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  13.6 ( $\text{OSiMe}_{3\text{linear}}$ ), 5.5 ( $\text{OSiMe}_{3\text{cyclic}}$ ),  $-13.4$  ( $\text{SiMe}_{3\text{cyclic}}$ ),  $-14.9$  ( $\text{SiMe}_{3\text{cyclic}}$ ),  $-16.8$  ( $\text{SiMe}_{3\text{linear}}$ ),  $-17.0$  ( $\text{SiMe}_{3\text{linear}}$ ),  $-20.8$  ( $\text{Si}(\text{SiMe}_3)_{2\text{cyclic}}$ ),  $-30.3$  ( $\text{Si}(\text{SiMe}_3)_{2\text{linear}}$ ). **15b**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.97 (br s), 7.39 (br s), 7.05–7.30 (br m) (all PhH), 6.79 (s, 1H,  $\text{SiC}(\text{H})=\text{CSi}$ ), 5.41 (br s, 1H,  $\text{C}=\text{CH}_2$ ), 4.98 (br s, 1H,  $\text{C}=\text{CH}_2$ ), 4.54 (br s, 1H,  $\text{MeOCH}$ ), 4.39 (s, 1H,  $\text{Me}_3\text{SiOCH}$ ), 3.77 (d, 1H, PhCH,  $J = 2$  Hz), 3.12 (s, 3H, MeO), 1.38 (br s, 9H,  $t\text{-Bu}_{\text{cyclic}}$ ), 1.24 (s, 9H,  $t\text{-Bu}_{\text{linear}}$ ), 0.58 (s, 9H,  $\text{SiMe}_{3\text{linear}}$ ), 0.49 (s, 9H,  $\text{SiMe}_{3\text{cyclic}}$ ), 0.43 (s, 9H,  $\text{SiMe}_{3\text{cyclic}}$ ), 0.34 (s, 9H,  $\text{SiMe}_{3\text{linear}}$ ), 0.22 (s, 9H,  $\text{OSiMe}_{3\text{linear}}$ ), 0.01 (s, 9H,  $\text{OSiMe}_{3\text{cyclic}}$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  159.93 ( $\text{SiC}(\text{H})\text{C}=\text{CSi}$ ), 150.98 ( $\text{C}=\text{CH}_2$ ), 143.88 ( $\text{SiC}(\text{H})\text{C}=\text{CSi}$ ), 135.82 ( $i\text{-PhC}$ ), 127.38, 126.02 (br s, PhC), 115.65 ( $\text{C}=\text{CH}_2$ ), 100.82 ( $\text{Me}_3\text{SiOC}_{\text{cyclic}}$ ), 80.76 ( $\text{Me}_3\text{SiOCH}$ ), 80.60 ( $\text{MeOCH}$ ), 65.02 (PhCH), 56.12 (MeO), 40.09 ( $\text{C}(\text{CH}_3)_{3\text{cyclic}}$ ), 38.21 ( $\text{C}(\text{CH}_3)_{3\text{linear}}$ ), 29.76 ( $\text{C}(\text{CH}_3)_{3\text{linear}}$ ), 5.33 ( $\text{OSiMe}_{3\text{cyclic}}$ ), 4.11 ( $\text{SiMe}_3$ ), 3.50 ( $\text{SiMe}_3$ ), 3.27 ( $\text{SiMe}_3$ ), 2.26 ( $\text{OSiMe}_{3\text{linear}}$ ), 2.09 ( $\text{SiMe}_3$ );  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  13.6 ( $\text{OSiMe}_{3\text{linear}}$ ), 5.5 ( $\text{OSiMe}_{3\text{cyclic}}$ ),  $-13.4$  ( $\text{SiMe}_{3\text{cyclic}}$ ),  $-14.9$  ( $\text{SiMe}_{3\text{cyclic}}$ ),  $-16.4$  ( $\text{SiMe}_{3\text{linear}}$ ),  $-17.1$  ( $\text{SiMe}_{3\text{linear}}$ ),  $-21.4$  ( $\text{Si}(\text{SiMe}_3)_{2\text{cyclic}}$ ),  $-29.7$  ( $\text{Si}(\text{SiMe}_3)_{2\text{linear}}$ ). **15a–b**: High-resolution ESI-MS for  $\text{C}_{41}\text{H}_{86}\text{O}_3\text{Si}_8\text{Na}$  ( $\text{M} + \text{Na}^+$ ) ( $m/z$ ) calcd 873.4629, found 873.4669. **15c–d/16**: IR ( $\text{cm}^{-1}$ ) 2955 (m), 2900 (m), 1395 (w), 1363 (w), 1264 (s), 1252 (s), 1100 (m), 1051 (s), 838 (s). **15c**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.02–7.29 (m, PhH), 6.51 (s, 1H,  $\text{SiC}(\text{H})=\text{CSi}$ ), 5.19 (d, 1H,  $\text{C}=\text{CH}_2$ ,  $J = 1.6$  Hz), 4.72 (br s, 1H,  $\text{MeOCH}$ ), 4.70 (br s, 1H,  $\text{C}=\text{CH}_2$ ), 4.40 (s, 1H,  $\text{Me}_3\text{SiOCH}$ ), 4.02 (br s, 1H, PhCH), 3.28 (s, 3H, MeO), 1.18 (br s, 9H,  $t\text{-Bu}_{\text{linear}}$ ), 0.91 (s, 9H,  $t\text{-Bu}_{\text{cyclic}}$ ), 0.57 (s, 9H,  $\text{OSiMe}_{3\text{cyclic}}$ ), 0.50 (s, 9H,  $\text{SiMe}_{3\text{cyclic}}$ ), 0.448 (s, 9H,  $\text{SiMe}_{3\text{linear}}$ ), 0.447 (s, 9H,  $\text{SiMe}_{3\text{cyclic}}$ ), 0.44 (s, 9H,  $\text{SiMe}_{3\text{cyclic}}$ ), 0.25 (s, 9H,  $\text{OSiMe}_{3\text{linear}}$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  162.74 ( $\text{SiC}(\text{H})\text{C}=\text{CSi}$ ), 150.55 ( $\text{C}=\text{CH}_2$ ), 141.16 ( $\text{SiC}(\text{H})\text{C}=\text{CSi}$ ), 139.06 ( $i\text{-PhC}$ ), 133.20, 132.67, 126.88, 126.48, 127.7<sup>19</sup> (all PhC), 120.53 ( $\text{C}=\text{CH}_2$ ), 93.39 ( $\text{Me}_3\text{SiOC}_{\text{cyclic}}$ ), 84.07 ( $\text{MeOCH}$ ), 81.52 ( $\text{Me}_3\text{SiOCH}$ ), 65.85 (PhCH), 56.42 (MeO), 41.25 ( $\text{C}(\text{CH}_3)_{3\text{cyclic}}$ ), 38.23 ( $\text{C}(\text{CH}_3)_{3\text{linear}}$ ), 30.24 ( $\text{C}(\text{CH}_3)_{3\text{linear}}$ ), 5.35 ( $\text{OSiMe}_{3\text{cyclic}}$ ), 4.41 ( $\text{SiMe}_{3\text{cyclic}}$ ), 4.24 ( $\text{SiMe}_3$ ), 3.15 ( $\text{SiMe}_{3\text{linear}}$ ), 2.35 ( $\text{SiMe}_{3\text{linear}}$ ), 1.99 ( $\text{OSiMe}_{3\text{linear}}$ );  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  13.5 ( $\text{OSiMe}_{3\text{linear}}$ ), 5.9 ( $\text{SiMe}_{3\text{cyclic}}$ ),  $-13.3$  ( $\text{SiMe}_3$ ),  $-13.5$  ( $\text{SiMe}_{3\text{cyclic}}$ ),  $-16.8$  ( $\text{SiMe}_3$ ),  $-17.2$  ( $\text{SiMe}_{3\text{linear}}$ ),  $-28.4$  ( $\text{Si}(\text{SiMe}_3)_{2\text{cyclic}}$ ),  $-28.7$  ( $\text{Si}(\text{SiMe}_3)_{2\text{linear}}$ ). **15d**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  6.45 (s, 1H,  $\text{SiC}(\text{H})=\text{CSi}$ ), 5.40 (d, 1H,  $\text{C}=\text{CH}_2$ ,  $J = 1.6$  Hz), 4.86 (br s, 1H,  $\text{C}=\text{CH}_2$ ), 4.66 (br s, 1H,  $\text{MeOCH}$ ), 4.43 (s, 1H,  $\text{Me}_3\text{SiOCH}$ ), 4.00 (br s, 1H, PhCH), 3.29 (s, 3H, MeO), 1.14 (br s, 9H,  $t\text{-Bu}_{\text{linear}}$ ), 0.91 (s, 9H,  $t\text{-Bu}_{\text{cyclic}}$ ), 0.56 (s, 9H,  $\text{OSiMe}_{3\text{cyclic}}$ ), 0.53 (s, 9H,  $\text{SiMe}_{3\text{cyclic}}$ ), 0.48 (s, 9H,  $\text{SiMe}_{3\text{linear}}$ ), 0.44 (s, 9H,  $\text{SiMe}_{3\text{cyclic}}$ ), 0.41 (s, 9H,  $\text{SiMe}_{3\text{linear}}$ ), 0.21 (s, 9H,  $\text{OSiMe}_{3\text{linear}}$ );  $^{24}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  161.8 ( $\text{SiC}(\text{H})\text{C}=\text{CSi}$ ),<sup>19</sup> 149.07 ( $\text{C}=\text{CH}_2$ ), 139.4 ( $\text{SiC}(\text{H})\text{C}=\text{CSi}$ ),<sup>19</sup> 139.22 ( $i\text{-PhC}$ ), 132.62, 126.61, 126.24 (all PhC), 121.16 ( $\text{C}=\text{CH}_2$ ), 93.49 ( $\text{Me}_3\text{SiOC}_{\text{cyclic}}$ ), 84.56 ( $\text{MeOCH}$ ), 78.58 ( $\text{Me}_3\text{SiOCH}$ ), 66.02 (PhCH), 56.34 (MeO), 39.95 ( $\text{C}(\text{CH}_3)_{3\text{cyclic}}$ ), 37.73 ( $\text{C}(\text{CH}_3)_{3\text{linear}}$ ), 29.71 ( $\text{C}(\text{CH}_3)_{3\text{linear}}$ ), 5.39 ( $\text{OSiMe}_{3\text{cyclic}}$ ), 4.20 ( $\text{SiMe}_3$ ), 4.18 ( $\text{SiMe}_3$ ), 2.93 ( $\text{SiMe}_3$ ), 2.28 ( $\text{SiMe}_3$ ), 2.06 ( $\text{OSiMe}_{3\text{linear}}$ );  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  13.5 ( $\text{OSiMe}_{3\text{linear}}$ ), 5.9 ( $\text{SiMe}_3$ ),  $-17.6$  ( $\text{SiMe}_{3\text{linear}}$ ),  $-25.8$  ( $\text{Si}(\text{SiMe}_3)_{2\text{cyclic}}$ ),  $-29.4$  ( $\text{Si}(\text{SiMe}_3)_{2\text{linear}}$ ).<sup>18</sup> **16**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.91 (d, 1H,  $o\text{-PhH}$ ,  $J = 8$  Hz), 4.81 (br m, 1H,  $\text{MeOCH}$ ), 4.75 (d, 1H, PhCH,  $J = 2$  Hz), 3.91 (1H, quint, ( $\text{Me}_3\text{Si}$ )<sub>2</sub>SiCH,  $J = 3.2$  Hz), 3.10 (s, 3H, MeO), 1.59 (br s, 3H, one methyl of  $t\text{-Bu}$ ), 1.52 (d, 3H, Me,  $J = 3.2$  Hz), 1.31 (br s, 9H,  $t\text{-Bu}$ ), 0.59 (br s, 9H,  $\text{SiMe}_3$ ), 0.51 (s, 9H,  $\text{SiMe}_3$ ), 0.42 (s, 9H,  $\text{SiMe}_3$ ), 0.37 (s, 9H,  $\text{SiMe}_3$ ), 0.36 (s, 9H,  $\text{OSiMe}_3$ ), 0.05 (s, 9H,  $\text{OSiMe}_3$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  144.86 ( $\text{C}=\text{C}$ ), 139.01 ( $i\text{-PhC}$ ), 137.00 ( $o\text{-PhC}$ ), 135.24 ( $\text{C}=\text{C}$ ), 134.90 ( $o\text{-PhC}$ ), 127.49 (PhC), 127.11 (PhC), 111.01 ( $\text{Me}_3\text{SiOC}_{\text{cycloheptene}}$ ), 97.92 ( $\text{Me}_3\text{SiOC}_{\text{cyclobutane}}$ ), 79.55 ( $\text{MeOCH}$ ), 65.43 (PhCH), 57.06 (MeO), 56.88 (( $\text{Me}_3\text{Si}$ )<sub>2</sub>SiCH), 40.92 ( $\text{C}(\text{CH}_3)_{3\text{cycloheptene}}$ ), 39.94 ( $\text{C}(\text{CH}_3)_{3\text{cyclobutane}}$ ), 33.79 ( $\text{C}(\text{CH}_3)_3$ ), 28.79 ( $\text{C}(\text{CH}_3)_3$ ), 27.62 ( $\text{C}(\text{CH}_3)_3$ ), 21.88 (Me), 6.23 ( $\text{SiMe}_3$ ), 5.79 ( $\text{OSiMe}_3$ ), 3.60 ( $\text{SiMe}_3$ ), 3.46 ( $\text{SiMe}_3$ ), 2.49 ( $\text{SiMe}_3$ ), 2.16 ( $\text{SiMe}_3$ );  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  5.8, 4.8 ( $\text{OSiMe}_3$ ),  $-11.5$ ,  $-11.7$  ( $\text{SiMe}_{3\text{cycloheptene}}$ ),  $-17.1$  ( $\text{SiMe}_{3\text{cyclobutane}}$ ),  $-18.9$  ( $\text{Si}(\text{SiMe}_3)_{2\text{cycloheptene}}$ ),  $-19.7$  ( $\text{Si}(\text{SiMe}_3)_{2\text{cyclobutane}}$ ). **15c–d/16**: High-resolution ESI-MS for  $\text{C}_{41}\text{H}_{86}\text{O}_3\text{Si}_8\text{Na}$  ( $\text{M} + \text{Na}^+$ ) ( $m/z$ ) calcd 873.4629, found 873.4600. **15e–f**: IR ( $\text{cm}^{-1}$ ) 2955 (s), 2899 (m), 1263 (s), 1252 (s), 1108 (s), 1050 (s), 1024 (s), 836 (s), 750 (m), 683 (m). **15e**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.93 (d, 1H,  $o\text{-PhH}$ ,  $J = 7.6$  Hz), 7.30–7.34 (m, 1H,  $p\text{-PhH}$ ), 7.11–7.20 (m,  $m\text{-PhH}$ ), 6.74 (s, 1H,  $\text{SiC}(\text{H})=\text{CSi}$ ), 5.49 (br s, 1H,  $\text{C}=\text{CH}_2$ ), 5.46 (br s, 1H,  $\text{C}=\text{CH}_2$ ), 4.88 (d, 1H,  $\text{MeOCH}$ ,  $J = 6$  Hz), 4.41 (s, 1H,  $\text{Me}_3\text{SiOCH}$ ), 3.52 (d, 1H, PhCH,  $J = 6$  Hz), 3.11 (s, 3H, MeO), 1.13 (s,  $t\text{-Bu}_{\text{linear}}$ ), 0.70–1.20 (br s,  $t\text{-Bu}_{\text{cyclic}}$ ) (18H total), 0.56 (s, 9H,  $\text{SiMe}_{3\text{cyclic}}$ ), 0.53 (s, 9H,  $\text{SiMe}_{3\text{linear}}$ ), 0.48 (s, 9H,  $\text{SiMe}_{3\text{cyclic}}$ ), 0.37 (s, 9H,  $\text{SiMe}_{3\text{linear}}$ ), 0.25 (s, 9H,  $\text{OSiMe}_{3\text{linear}}$ ), 0.24 (s, 9H,  $\text{OSiMe}_{3\text{cyclic}}$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  161.64 ( $\text{SiC}(\text{H})\text{C}=\text{CSi}$ ), 156.12 ( $\text{C}=\text{CH}_2$ ), 144.79 ( $\text{SiC}(\text{H})\text{C}=\text{CSi}$ ), 140.28 ( $i\text{-PhC}$ ), 134.62 ( $o\text{-PhC}$ ), 133.53 ( $m\text{-PhC}$ ), 127.04, 126.59, 126.16 (PhC), 116.34 ( $\text{C}=\text{CH}_2$ ), 96.67 ( $\text{Me}_3\text{SiOC}_{\text{cyclic}}$ ), 82.38 ( $\text{MeOCH}$ ), 81.25 ( $\text{Me}_3\text{SiOCH}$ ), 62.19 (PhCH), 56.63 (MeO), 41.32 ( $\text{C}(\text{CH}_3)_{3\text{cyclic}}$ ), 37.97 ( $\text{C}(\text{CH}_3)_{3\text{linear}}$ ), 29.65 ( $\text{C}(\text{CH}_3)_{3\text{linear}}$ ), 5.54 ( $\text{OSiMe}_{3\text{cyclic}}$ ), 4.12 ( $\text{SiMe}_{3\text{cyclic}}$ ), 3.44 ( $\text{SiMe}_{3\text{cyclic}}$ ), 3.02 ( $\text{SiMe}_{3\text{linear}}$ ), 2.30 ( $\text{OSiMe}_{3\text{linear}}$ ), 2.06 ( $\text{SiMe}_{3\text{linear}}$ );  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  13.8 ( $\text{OSiMe}_{3\text{linear}}$ ), 2.9 ( $\text{OSiMe}_{3\text{cyclic}}$ ),  $-12.1$  ( $\text{SiMe}_{3\text{cyclic}}$ ),  $-14.0$  ( $\text{SiMe}_{3\text{cyclic}}$ ),  $-16.0$  ( $\text{SiMe}_{3\text{linear}}$ ),  $-17.1$  ( $\text{SiMe}_{3\text{linear}}$ ),  $-30.5$  ( $\text{Si}(\text{SiMe}_3)_{2\text{linear}}$ ),  $-31.1$  ( $\text{Si}(\text{SiMe}_3)_{2\text{cyclic}}$ ). **15f**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.89, 7.59 (d, 1H,  $o\text{-PhH}$ ,  $J = 8.0$  Hz), 6.65 (s, 1H,  $\text{SiC}(\text{H})=\text{CSi}$ ), 5.70 (br s, 1H,  $\text{C}=\text{CH}_2$ ), 5.64 (br s, 1H,  $\text{C}=\text{CH}_2$ ), 4.78 (d, 1H,  $\text{MeOCH}$ ,  $J = 7$  Hz), 4.40 (s, 1H,  $\text{Me}_3\text{SiOCH}$ ), 3.61 (d, 1H, PhCH,  $J = 7$  Hz), 3.09 (s, 3H, MeO), 1.08 (s,  $t\text{-Bu}_{\text{linear}}$ ), 0.42 (s, 9H,  $\text{SiMe}_3$ ), 0.18 (s, 9H,  $\text{OSiMe}_3$ ).<sup>25</sup> **15e–f**: High-resolution ESI-MS for  $\text{C}_{41}\text{H}_{86}\text{O}_3\text{Si}_8\text{Na}$  ( $\text{M} + \text{Na}^+$ ) ( $m/z$ ) calcd 873.4629, found 873.4615. **17a**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.62 (d, 2H,  $o\text{-PhH}$ ,  $J = 7.2$  Hz), 7.19–7.25 (m, 2H,  $m\text{-PhH}$ ), 7.05–7.10 (m, 1H,  $p\text{-PhH}$ ), 5.97 (s, 1H,  $\text{SiC}(\text{H})=\text{C}$ ,  $^2J_{\text{H-Si}} = 9.6$  Hz), 3.95 (d, 1H,  $\text{MeOCH}$ ,  $J = 6.8$  Hz),

65.85 (PhCH), 56.42 (MeO), 41.25 ( $\text{C}(\text{CH}_3)_{3\text{cyclic}}$ ), 38.23 ( $\text{C}(\text{CH}_3)_{3\text{linear}}$ ), 30.24 ( $\text{C}(\text{CH}_3)_{3\text{linear}}$ ), 5.35 ( $\text{OSiMe}_{3\text{cyclic}}$ ), 4.41 ( $\text{SiMe}_{3\text{cyclic}}$ ), 4.24 ( $\text{SiMe}_3$ ), 3.15 ( $\text{SiMe}_{3\text{linear}}$ ), 2.35 ( $\text{SiMe}_{3\text{linear}}$ ), 1.99 ( $\text{OSiMe}_{3\text{linear}}$ );  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  13.5 ( $\text{OSiMe}_{3\text{linear}}$ ), 5.9 ( $\text{SiMe}_{3\text{cyclic}}$ ),  $-13.3$  ( $\text{SiMe}_3$ ),  $-13.5$  ( $\text{SiMe}_{3\text{cyclic}}$ ),  $-16.8$  ( $\text{SiMe}_3$ ),  $-17.2$  ( $\text{SiMe}_{3\text{linear}}$ ),  $-28.4$  ( $\text{Si}(\text{SiMe}_3)_{2\text{cyclic}}$ ),  $-28.7$  ( $\text{Si}(\text{SiMe}_3)_{2\text{linear}}$ ). **15d**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  6.45 (s, 1H,  $\text{SiC}(\text{H})=\text{CSi}$ ), 5.40 (d, 1H,  $\text{C}=\text{CH}_2$ ,  $J = 1.6$  Hz), 4.86 (br s, 1H,  $\text{C}=\text{CH}_2$ ), 4.66 (br s, 1H,  $\text{MeOCH}$ ), 4.43 (s, 1H,  $\text{Me}_3\text{SiOCH}$ ), 4.00 (br s, 1H, PhCH), 3.29 (s, 3H, MeO), 1.14 (br s, 9H,  $t\text{-Bu}_{\text{linear}}$ ), 0.91 (s, 9H,  $t\text{-Bu}_{\text{cyclic}}$ ), 0.56 (s, 9H,  $\text{OSiMe}_{3\text{cyclic}}$ ), 0.53 (s, 9H,  $\text{SiMe}_{3\text{cyclic}}$ ), 0.48 (s, 9H,  $\text{SiMe}_{3\text{linear}}$ ), 0.44 (s, 9H,  $\text{SiMe}_{3\text{cyclic}}$ ), 0.41 (s, 9H,  $\text{SiMe}_{3\text{linear}}$ ), 0.21 (s, 9H,  $\text{OSiMe}_{3\text{linear}}$ );  $^{24}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  161.8 ( $\text{SiC}(\text{H})\text{C}=\text{CSi}$ ),<sup>19</sup> 149.07 ( $\text{C}=\text{CH}_2$ ), 139.4 ( $\text{SiC}(\text{H})\text{C}=\text{CSi}$ ),<sup>19</sup> 139.22 ( $i\text{-PhC}$ ), 132.62, 126.61, 126.24 (all PhC), 121.16 ( $\text{C}=\text{CH}_2$ ), 93.49 ( $\text{Me}_3\text{SiOC}_{\text{cyclic}}$ ), 84.56 ( $\text{MeOCH}$ ), 78.58 ( $\text{Me}_3\text{SiOCH}$ ), 66.02 (PhCH), 56.34 (MeO), 39.95 ( $\text{C}(\text{CH}_3)_{3\text{cyclic}}$ ), 37.73 ( $\text{C}(\text{CH}_3)_{3\text{linear}}$ ), 29.71 ( $\text{C}(\text{CH}_3)_{3\text{linear}}$ ), 5.39 ( $\text{OSiMe}_{3\text{cyclic}}$ ), 4.20 ( $\text{SiMe}_3$ ), 4.18 ( $\text{SiMe}_3$ ), 2.93 ( $\text{SiMe}_3$ ), 2.28 ( $\text{SiMe}_3$ ), 2.06 ( $\text{OSiMe}_{3\text{linear}}$ );  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  13.5 ( $\text{OSiMe}_{3\text{linear}}$ ), 5.9 ( $\text{SiMe}_3$ ),  $-17.6$  ( $\text{SiMe}_{3\text{linear}}$ ),  $-25.8$  ( $\text{Si}(\text{SiMe}_3)_{2\text{cyclic}}$ ),  $-29.4$  ( $\text{Si}(\text{SiMe}_3)_{2\text{linear}}$ ).<sup>18</sup> **16**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  7.91 (d, 1H,  $o\text{-PhH}$ ,  $J = 8$  Hz), 4.81 (br m, 1H,  $\text{MeOCH}$ ), 4.75 (d, 1H, PhCH,  $J = 2$  Hz), 3.91 (1H, quint, ( $\text{Me}_3\text{Si}$ )<sub>2</sub>SiCH,  $J = 3.2$  Hz), 3.10 (s, 3H, MeO), 1.59 (br s, 3H, one methyl of  $t\text{-Bu}$ ), 1.52 (d, 3H, Me,  $J = 3.2$  Hz), 1.31 (br s, 9H,  $t\text{-Bu}$ ), 0.59 (br s, 9H,  $\text{SiMe}_3$ ), 0.51 (s, 9H,  $\text{SiMe}_3$ ), 0.42 (s, 9H,  $\text{SiMe}_3$ ), 0.37 (s, 9H,  $\text{SiMe}_3$ ), 0.36 (s, 9H,  $\text{OSiMe}_3$ ), 0.05 (s, 9H,  $\text{OSiMe}_3$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  144.86 ( $\text{C}=\text{C}$ ), 139.01 ( $i\text{-PhC}$ ), 137.00 ( $o\text{-PhC}$ ), 135.24 ( $\text{C}=\text{C}$ ), 134.90 ( $o\text{-PhC}$ ), 127.49 (PhC), 127.11 (PhC), 111.01 ( $\text{Me}_3\text{SiOC}_{\text{cycloheptene}}$ ), 97.92 ( $\text{Me}_3\text{SiOC}_{\text{cyclobutane}}$ ), 79.55 ( $\text{MeOCH}$ ), 65.43 (PhCH), 57.06 (MeO), 56.88 (( $\text{Me}_3\text{Si}$ )<sub>2</sub>SiCH), 40.92 ( $\text{C}(\text{CH}_3)_{3\text{cycloheptene}}$ ), 39.94 ( $\text{C}(\text{CH}_3)_{3\text{cyclobutane}}$ ), 33.79 ( $\text{C}(\text{CH}_3)_3$ ), 28.79 ( $\text{C}(\text{CH}_3)_3$ ), 27.62 ( $\text{C}(\text{CH}_3)_3$ ), 21.88 (Me), 6.23 ( $\text{SiMe}_3$ ), 5.79 ( $\text{OSiMe}_3$ ), 3.60 ( $\text{SiMe}_3$ ), 3.46 ( $\text{SiMe}_3$ ), 2.49 ( $\text{SiMe}_3$ ), 2.16 ( $\text{SiMe}_3$ );  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  5.8, 4.8 ( $\text{OSiMe}_3$ ),  $-11.5$ ,  $-11.7$  ( $\text{SiMe}_{3\text{cycloheptene}}$ ),  $-17.1$  ( $\text{SiMe}_{3\text{cyclobutane}}$ ),  $-18.9$  ( $\text{Si}(\text{SiMe}_3)_{2\text{cycloheptene}}$ ),  $-19.7$  ( $\text{Si}(\text{SiMe}_3)_{2\text{cyclobutane}}$ ). **15c–d/16**: High-resolution ESI-MS for  $\$

3.24 (s, 3H, MeO), 2.20 (d, 1H, PhCH,  $J = 6.8$  Hz), 1.48 (s, 3H, Me), 1.20 (s, 9H, *t*-Bu), 0.34 (s, 9H, SiMe<sub>3</sub>), 0.27 (s, 9H, SiMe<sub>3</sub>), 0.25 (s, 9H, OSiMe<sub>3</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 169.77 (SiC(H)=C), 137.34 (*i*-PhC), 130.67 (*o*-PhC), 128.2 (*m*-PhC),<sup>19</sup> 126.08 (*p*-PhC), 126.06 (SiC(H)=C), <sup>1</sup>J<sub>H-C</sub> = 165 Hz), 95.6 (Me<sub>3</sub>SiOC, <sup>3</sup>J<sub>Hvinyl-C</sub> = 21 Hz),<sup>19</sup> 67.96 (MeOCH), 58.48 (MeO), 38.27 (C(CH<sub>3</sub>)<sub>3</sub>), 37.72 (PhCH), 30.41 (CMe), 30.22 (C(CH<sub>3</sub>)<sub>3</sub>), 11.25 (Me), 3.12 (OSiMe<sub>3</sub>), 1.78 (SiMe<sub>3</sub>),<sup>26</sup> 1.31 (SiMe<sub>3</sub>); <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>) δ 6.6 (OSiMe<sub>3</sub>), -12.5 (SiMe<sub>3</sub>), -18.6 (SiMe<sub>3</sub>), -24.0 (Si(SiMe<sub>3</sub>)<sub>2</sub>). **17b**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 7.59 (d, 2H, *o*-PhH,  $J = 7.6$  Hz), 7.19–7.25 (m, 2H, *m*-PhH), 7.05–7.10 (m, 1H, *p*-PhH), 6.07 (s, 1H, SiC(H)=C, <sup>2</sup>J<sub>H-Si</sub> = 9.6 Hz), 3.38 (d, 1H, MeOCH,  $J = 7.0$  Hz), 3.26 (s, 3H, MeO), 2.75 (d, 1H, PhCH,  $J = 7.0$  Hz), 1.44 (s, 3H, Me), 1.23 (s, 9H, *t*-Bu), 0.34 (s, 9H, SiMe<sub>3</sub>), 0.27 (s, 9H, SiMe<sub>3</sub>), 0.26 (s, 9H, OSiMe<sub>3</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 169.07 (SiC(H)=C), 137.20 (*i*-PhC), 131.03 (*o*-PhC), 128.2 (*m*-PhC),<sup>19</sup> 125.84 (*p*-PhC), 125.81 (SiC(H)=C), 95.3 (Me<sub>3</sub>SiOC, <sup>3</sup>J<sub>Hvinyl-C</sub> = 20 Hz),<sup>19</sup> 70.79 (MeOCH), 58.69 (MeO), 38.12 (C(CH<sub>3</sub>)<sub>3</sub>), 31.20 (PhCH), 31.12 (CMe), 30.30 (C(CH<sub>3</sub>)<sub>3</sub>), 12.91 (Me), 3.13 (OSiMe<sub>3</sub>), 1.50 (SiMe<sub>3</sub>),<sup>26</sup> 1.31 (SiMe<sub>3</sub>); <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>) δ 6.6 (OSiMe<sub>3</sub>), -13.1 (SiMe<sub>3</sub>), -18.6 (SiMe<sub>3</sub>), -25.1 (Si(SiMe<sub>3</sub>)<sub>2</sub>). **17a–b**: High-Resolution ESI-MS for C<sub>27</sub>H<sub>50</sub>O<sub>2</sub>Si<sub>4</sub>Na (M+Na<sup>+</sup>) ( $m/z$ ) calcd 541.2786, found 541.2769.

**Reaction of Silacyclobutenes 17a–b with Silene 10.** A mixture of **17a–b** and **9** (25 mg, 1:2.5) and a small amount of mesitylene (internal standard) in C<sub>6</sub>D<sub>6</sub> (0.5 mL) were added to a septum sealed NMR tube. The solution was irradiated for 2 h and monitored by <sup>1</sup>H NMR spectroscopy. No new peaks were observed in the <sup>1</sup>H NMR spectrum of the reaction mixture. Over the course of a week silene **10** slowly converted back to acylsilane **9**, and the silene could then be regenerated by further irradiation; no new products were ever observed by <sup>1</sup>H NMR spectroscopy.

**Reaction of Silene 10 and Disilaheptadiene 5.** A mixture of disilacyclohepta-1,2-diene, **5**, (22 mg, 0.03 mmol, containing 8% disilacyclobutene **7**) and acylsilane **9** (16 mg, 0.05 mmol) dissolved in C<sub>6</sub>D<sub>6</sub> (1 mL) was added to a septum sealed NMR tube and irradiated for 2 h.<sup>27</sup> The reaction was monitored by <sup>1</sup>H NMR spectroscopy over the course of 4 days. The crude product mixture consisted of **19a–b**, **7**, acylsilane **9**, and a minor amount of a compound tentatively identified as *tert*-butyltrimethylsilyloxymethylbis(trimethylsilyl)silanol as revealed by <sup>1</sup>H NMR spectroscopy (in a ratio of 35:25:2:28:10). The mixture was separated by preparative thin-layer chromatography (silica gel, 1:1 CH<sub>2</sub>Cl<sub>2</sub>/hexanes) yielding a mixture of **19a–b** and **9** (41:31:28). Disilacycloheptenes **19a–b** were precipitated from CH<sub>3</sub>CN as a white solid (13.5 mg, 0.013 mmol, 43%). <sup>1</sup>H NMR spectroscopic analysis of the solid revealed a mixture of **19a–b** contaminated with a minor amount of acylsilane **9** (in a ratio of 58:40:2, respectively). **19a–b**: IR (cm<sup>-1</sup>) 2962 (s), 1507 (w), 1101 (s), 1023 (s), 801 (s); <sup>1</sup>H NMR

(C<sub>6</sub>D<sub>6</sub>) δ 7.37 (s, 1H, Me<sub>3</sub>SiC(H)=C, **19b**), 7.32 (s, 1H, Me<sub>3</sub>SiC(H)=C, **19a**), 6.95, 6.94, 6.91, 6.89, 6.87, 6.85, 6.81, 6.78, 6.75, 6.73, 6.68, 6.66, 6.65, 6.46, 6.45, 6.29, 6.23, 5.69, 5.52 (broad signals), 7.96, 6.28, 6.02, 5.64 (very broad signals) (30H, *m*-MesH, *o,m,p*-PhH, C=CH<sub>2</sub>, **19a** and **19b**), 5.47 (d, 1H, MeOCH,  $J = 2$  Hz, **19b**), 5.44 (d, 1H, MeOCH,  $J = 2$  Hz, **19a**), 4.30 (s, 1H, Me<sub>3</sub>SiOCH, **19b**), 4.24 (s, 1H, Me<sub>3</sub>SiOCH, **19a**), 3.30 (s, 6H, MeO, **19a** and **19b**), 3.23 (d, 1H, PhCH,  $J = 2$  Hz, **19a**), 3.08 (d, 1H, PhCH,  $J = 2$  Hz, **19b**), 2.94 (s, 3H, Mes-CH<sub>3</sub>, **19b**), 2.92 (s, 3H, Mes-CH<sub>3</sub>, **19a**), 2.84 (s, 3H, Mes-CH<sub>3</sub>, **19b**), 2.82 (s, 9H, Mes-CH<sub>3</sub>, 2 × **19a** and **19b**), 2.44 (s, 3H, Mes-CH<sub>3</sub>, **19a**), 2.41 (s, 3H, Mes-CH<sub>3</sub>, **19b**), 2.26 (s, 3H, Mes-CH<sub>3</sub>, **19a**), 2.25 (s, 3H, Mes-CH<sub>3</sub>, **19b**), 2.23 (s, 3H, Mes-CH<sub>3</sub>, **19a**), 2.18 (s, 3H, Mes-CH<sub>3</sub>, **19b**), 2.13 (s, 3H, Mes-CH<sub>3</sub>, **19b**), 2.12 (s, 3H, Mes-CH<sub>3</sub>, **19a**), 2.107 (**19a**), 2.103 (**19b**) (s, both 6H, Mes-CH<sub>3</sub>), 2.095 (s, 9H, Mes-CH<sub>3</sub>, **19a** and 2 × **19b**), 2.08 (s, 3H, Mes-CH<sub>3</sub>, **19a**), 1.56 (s, 3H, Mes-CH<sub>3</sub>, **19a**), 1.55 (s, 3H, Mes-CH<sub>3</sub>, **19b**), 1.27 (s, 3H, Mes-CH<sub>3</sub>, **19a**), 1.25 (s, 3H, Mes-CH<sub>3</sub>, **19b**), 1.13 (s, 9H, *t*-Bu, **19a**), 1.11 (s, 9H, *t*-Bu, **19b**), 0.42 (s, 9H, SiMe<sub>3</sub>, **19a**), 0.41 (s, 9H, SiMe<sub>3</sub>, **19b**), 0.35 (s, 9H, SiMe<sub>3</sub>, **19b**), 0.29 (s, 9H, SiMe<sub>3</sub>, **19a**), 0.24 (s, 9H, OSiMe<sub>3</sub>, **19b**), 0.23 (s, 9H, OSiMe<sub>3</sub>, **19a**); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 161.57 (SiC(H)=C, **19b**), 161.23 (SiC(H)=C, **19a**), 153.08 (SiC(H)=C, **19b**), 152.54 (SiC(H)=C, **19a**), 148.12, 148.04, 146.29, 146.16, 146.13, 146.02, 145.38, 145.29, 144.72, 144.49, 144.34, 144.21, 144.13, 143.31, 143.18, 142.39, 142.19, 138.74, 138.57, 138.40, 138.09, 138.01, 137.96, 137.78, 136.98, 136.75, 136.71, 136.62, 134.54, 133.78, 133.65, 133.42, 130.98, 130.76, 129.93, 129.84, 129.82, 129.73, 129.64, 129.47, 129.34, 129.29, 128.67, 128.63, 126.96, 126.79, 125.26 (*i,o,m,p*-MesC and *i,o,m,p*-PhC, C=CH<sub>2</sub>), 82.01 (Me<sub>3</sub>SiOCH, **19b**), 81.50 (Me<sub>3</sub>SiOCH, **19a**), 77.61 (MeOCH, **19a** and **19b**), 55.83 (MeO, **19b**), 55.78 (MeO, **19a**), 47.95 (PhCH, **19a**), 47.71 (PhCH, **19b**), 37.98 (C(CH<sub>3</sub>)<sub>3</sub>, **19b**), 37.90 (C(CH<sub>3</sub>)<sub>3</sub>, **19a**), 30.58 (C(CH<sub>3</sub>)<sub>3</sub>, **19a**), 29.78 (C(CH<sub>3</sub>)<sub>3</sub>, **19a**), 30.67, 30.50, 30.17, 26.80, 26.32, 26.05, 25.90, 25.43, 24.46, 24.14, 23.99, 23.86, 21.00, 20.96, 20.86, 20.83, 20.79 (Mes-CH<sub>3</sub>, **19a** and **19b**), 3.29 (SiMe<sub>3</sub>, **19a**), 3.07 (SiMe<sub>3</sub>, **19b**), 2.75 (SiMe<sub>3</sub>, **19a**), 2.69 (OSiMe<sub>3</sub>, **19b**), 2.53 (OSiMe<sub>3</sub>, **19a**), 2.47 (SiMe<sub>3</sub>, **19b**); <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>) δ 13.8 (OSiMe<sub>3</sub>, **19a**), 13.1 (OSiMe<sub>3</sub>, **19b**), -8.3, -8.4 (Mes<sub>2</sub>Si, **19b**), -8.8, -8.9 (Mes<sub>2</sub>Si, **19a**), -13.6 (SiMe<sub>3</sub>, **19b**), -15.2, -15.4 (SiMe<sub>3</sub>, **19a**), -15.9 (SiMe<sub>3</sub>, **19b**), -22.4 (Si(SiMe<sub>3</sub>)<sub>2</sub>, **19a** and **19b**); High-resolution ESI-MS for C<sub>63</sub>H<sub>94</sub>O<sub>2</sub>Si<sub>6</sub>Na (M + Na<sup>+</sup>) ( $m/z$ ) calcd 1073.5767, found 1073.5734.

**Acknowledgment.** We thank the NSERC (Canada), the University of Western Ontario, and the Ontario Photonics Consortium for financial support.

**Supporting Information Available:** Structure elucidation section and <sup>1</sup>H and <sup>13</sup>C NMR spectra for all new compounds. Experimental details for X-ray crystal structure analysis and crystallographic information files are provided for **14a** or **14e**, **15a** or **15b**, **15c–d**, **16**, and **19a** or **19b**. This material is available free of charge at <http://pubs.acs.org>.

JA057596G

(26) It was difficult to determine which isomer of **17a–b** the chemical shifts at 1.78 and 1.50 ppm correspond to. Thus, the assignment of these chemical shifts may possibly be reversed.

(27) The stability of the disilacyclohepta-1,2-diene, **5**, to the reaction conditions was tested by irradiating a small sample of **5** in C<sub>6</sub>D<sub>6</sub>. After 1 h of irradiation, no change was observed in the <sup>1</sup>H NMR spectrum of the test sample.