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# Reactivity of a Polar Silene toward Terminal Alkynes: Preference for C−H Insertion over Cycloaddition

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A variety of terminal alkynes were added to $Mes_2Si{=}CHCH_2t$-Bu, **4**, a naturally polarized silene. Three different modes of reactivity were observed: addition across the acetylenic C−H bond to give silylacetylenes **6a**−**i** and **12**, cycloaddition to give silacyclobutenes **7** and **9**, and ene-addition to give vinylsilane **8**. The reactivity of the naturally polarized silene **4** toward terminal alkynes is compared to that of nonpolar silenes.

## Introduction

Since the pioneering work of Gusel'nikov and Flowers in 1967,[1] silene ($R_2Si{=}CR_2$) chemistry has matured significantly;[2] much is now known regarding the properties and reactivity of these fundamentally important compounds, and applications of silene chemistry are now being developed. For example, silenes have been used as monomers in the synthesis of new inorganic polymers[3] and as reagents in organic synthesis.[4] To take full advantage of the chemistry of silenes, it is necessary to gain a better understanding of the scope and mechanisms of the reactions of silenes.

We have been interested in the addition of alkynes to Brook silenes, $(Me_3Si)_2Si{=}CR(OSiMe_3)$, a well-known regioselective reaction of these relatively nonpolar silenes that typically yields silacyclobutenes; however, when the alkyne or the silene contains an α-hydrogen, the formation of ene-adducts is also possible.[5,6] Both concerted[5b,c] and diradical[6e,g] pathways for silacyclobutene formation have been proposed. We have recently presented unambiguous evidence for the formation of a diradical intermediate during the addition of terminal alkynes to Brook silenes (Scheme 1).[7−9] Although these results provided evidence for the nature of the intermediate formed during the reaction and an understanding of the factors governing the regioselectivity of the reaction, Brook silenes are a special class of relatively nonpolar silenes, and thus, a generalization of the mechanism of addition of alkynes to all silenes cannot be made. Thus, we were interested in studying the mechanism of alkyne addition to naturally polarized silenes. After a thorough review of the literature, we realized that relatively little research has been reported on the addition of alkynes to polar silenes in comparison to the relatively large body of work reported on the addition of alkynes to the atypical, nonpolar Brook silenes.[2] The published work has focused on the addition of alkynes to three transient silenes: the highly reactive Wiberg silene $Me_2Si{=}C(SiMe_3)_2$, 1,1-dimethylsilene,

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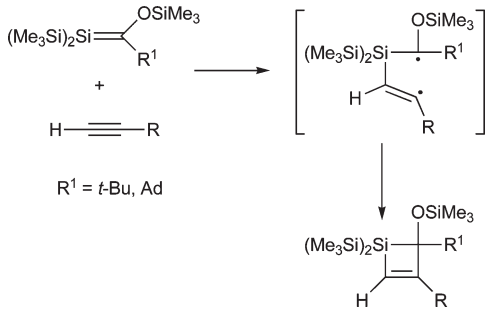
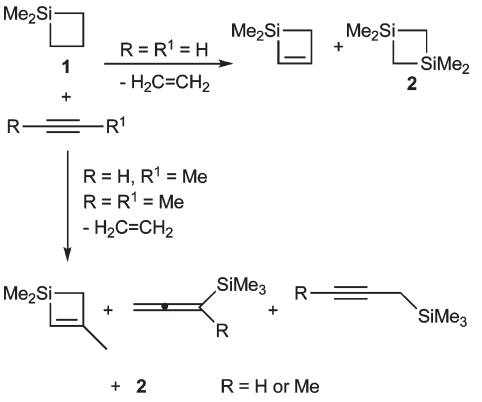
**Scheme 1. Addition of Alkynes to Brook Silenes**




**Scheme 2. Pyrolysis of 1,1-Dimethyl-1-silacyclobutane, 1, in the Presence of Acetylene, Propyne, or 2-Butyne**

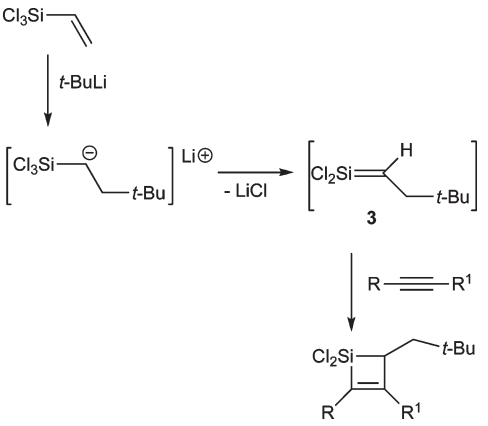



and 1,1-dichloroneopentylsilene, studied extensively by Auner and co-workers; as well as one sterically crowded stable silene. The work is briefly summarized here.

The Wiberg silene, $Me_2Si{=}C(SiMe_3)_2$, does not react with diphenylacetylene or bis(trimethylsilyl)acetylene;[10] the addition of terminal alkynes to $Me_2Si{=}C(SiMe_3)_2$ has not been examined. 1,1-Dimethyl-1-silacyclobutane, **1**, was pyrolyzed to afford 1,1-dimethylsilene and ethylene in the presence of acetylene, propyne, or 2-butyne (Scheme 2).[11] The reaction of 1,1-dimethylsilene with acetylene yielded 1,1-dimethyl-1-silacyclobutene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane, **2**, the product of silene dimerization. The reaction of the silene with propyne yielded the analogous silacyclobutene, silene dimer **2**, an allene (the product of formal ene-addition), and a propargylsilane, an isomerization product of the aforementioned allene. Pyrolysis of silacyclobutane **1** in the presence of 2-butyne formed the corresponding allene and propargylsilane; however, no silacyclobutene was observed. Evidently, internal alkynes do not readily cycloadd to this silene and, as a consequence, the ene-addition pathway becomes more dominant.

The addition of disubstituted alkynes to the putative 1,1-dichloroneopentylsilene, **3**, has been well studied by Auner and co-workers.[12] Silacyclobutenes are the major products formed; however, vinylsilanes, from a formal ene-addition, may also be obtained depending on the structure of the

**Scheme 3. Proposed Route to Silacyclobutene Formation from a Mixture of Trichlorovinylsilane, *t*-BuLi, and a Disubstituted Alkyne**




alkyne (Scheme 3). The structures of two silacyclobutenes, R = $SiMe_3$; $R^1$ = Ph and R = $SiMe_3$; $R^1$ = cyclohex-1-enyl, were determined by X-ray crystallography.[12a,d] The silene substrate was proposed to form by the addition of *t*-BuLi to trichlorovinylsilane, in the presence of the disubstituted alkyne, to form an α-silyl anion, which then eliminates LiCl. Formal [2+2] cycloaddition between the silene and the alkyne gives the silacyclobutene. Alternatively, the observed silacyclobutene may be formed by direct reaction of the α-silyl anion with the alkyne. It is difficult to determine unambiguously if the silene is an actual intermediate in these studies; however, the products obtained are readily explained by the intermediacy of a silene. Other related silenes with different substituents on the silicon or the α-carbon were also examined.[12b] The 1,1-dialkoxy-substituted analogue behaved in the same manner as 1,1-dichlorosilene **3**; however, no reaction was observed between disubstituted alkynes and 1,1-diorgano-substituted silenes.

The addition of acetylene to $Cl_3Si$-$CH_2Li$ has been examined by density functional theory.[13] Two possible reaction pathways for the addition were identified: pathway A, where the silene, $Cl_2Si{=}CH_2$, is formed prior to addition of acetylene to give 1,1-dichlorosilacyclobut-3-ene; and pathway B, where the α-silyl anion, $Cl_3Si$-$CH_2Li$, adds directly to acetylene followed by cyclization and elimination of LiCl to yield the same silacyclobutene (Scheme 4). Pathway B was calculated to be 29.9 kcal $mol^{-1}$ lower in energy than pathway A.[13] Thus, dichlorosilacyclobutene is likely formed by pathway B, bypassing the formation of the silene. Of course, the energetics of the addition reaction will be influenced by the reaction conditions (i.e., solvent, temperature) and the substituents on the silene. The pathway involving the deprotonation of acetylene by the lithio species was not considered, although presumably it is lower in energy than either pathway A or B.[13]

More recently, the reaction between a sterically crowded 1-hydrosilene (bearing a 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl and a xanthenyl substituent) and diphenylacetylene was reported to yield a silacyclobutene.[14]

In summary, there are few studies of the addition of alkynes to silenes, particularly where the intermediacy of the silene was proven unambiguously. The predominant reaction

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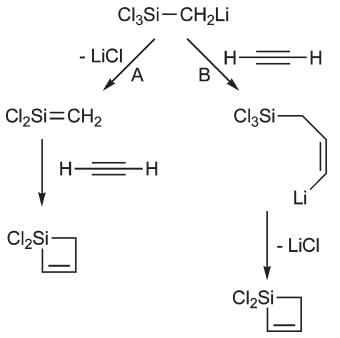
**Scheme 4. Theoretical Investigation of the Addition of Acetylene to an α-Silyl Anion**




pathway is regioselective cycloaddition of the alkyne to give a silacyclobutene; however, ene-addition also occurs. Silenes appear to be less reactive toward internal alkynes in comparison to terminal alkynes.

To explore the scope of the reactivity of naturally polarized silenes toward alkynes, we selected the stable 1,1-dimesitylneopentylsilene, $Mes_2Si{=}C(H)CH_2t\text{-}Bu$, **4**,[15] as a substrate that is relatively simple to prepare in near quantitative yield. The addition of a variety of terminal alkynes with varying electronic properties to silene **4** was examined.

## Results

Silene **4**[15] was prepared by the addition of *t*-BuLi to a pentane solution of fluorovinylsilane **5** at −78 °C followed by warming to room temperature. It was necessary to add $<1$ equivalent of *t*-BuLi to fluorosilane **5** when forming silene **4** to prevent polymerization of the silene.[3a] As such, silene **4** was always contaminated with residual fluorosilane **5**. After warming to room temperature, the pentane was removed and replaced with $C_6D_6$; the presence of **4** was confirmed by $^1$H NMR spectroscopy before addition of the alkyne.

When phenylacetylene was added to silene **4**, a mixture of silylacetylene **6a**, silacyclobutene **7**, and vinylsilane **8** (55:36:9) was produced as determined by $^1$H NMR spectroscopy (Scheme 5). In contrast, the addition of 1-ethynyl-4-(trifluoromethyl)benzene or 4-ethynylanisole to **4** produced only silylacetylenes **6b**,**c**, respectively (Scheme 5). The ratio of silacyclobutene **7** to silylacetylene **6a** was quite variable; the relative amount of **7** ranged from 0 to 30% of the product mixture. Vinylsilane **8** was consistently produced in minor amounts. No one compound could be isolated from the mixture of **5**, **6a**, **7**, and **8** by chromatography. In one experimental run, **6a** was obtained contaminated only by the fluorovinylsilane. Silylacetylene **6c** could be separated from unreacted fluorovinylsilane **5** by chromatography; however, **6a**,**b** could not. Although, after treatment of the mixtures (**6a**/**5** or **6b**/**5**) with aqueous NaOH in THF, silylacetylenes **6a**, **b** could both be separated from the corresponding vinylsilanol, presumably formed from hydrolysis of the fluorosilane.

Addition of ethoxyacetylene to **4** produced a mixture of silacyclobutene **9** and silylacetylene **6d** (48:52) as determined by $^1$H NMR spectroscopy (Scheme 6). Silene **4** gave only silylacetylenes **6e**,**f** when treated with other nonaromatic alkynes (*tert*-butylacetylene and trimethylsilylacetylene) (Scheme 6); silylacetylenes **6e**,**f** could be purified by chromatography. As with

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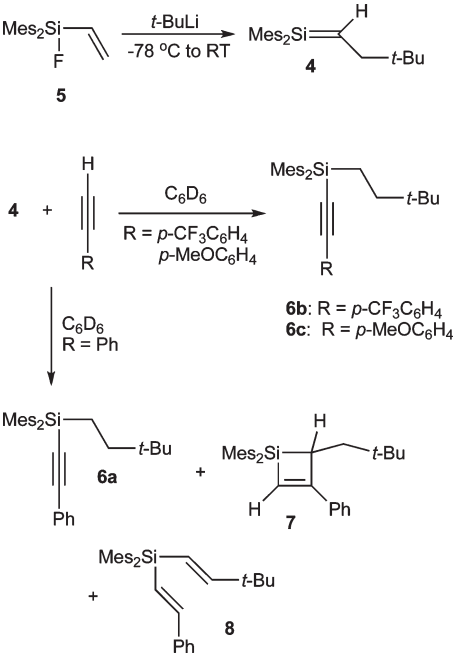
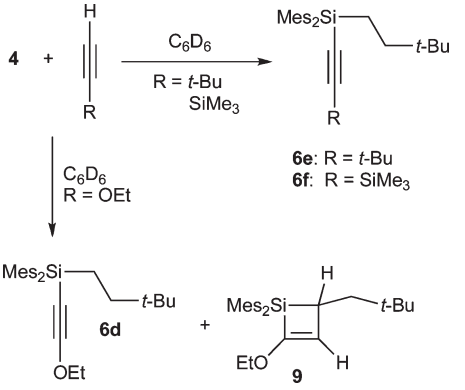
**Scheme 5. Addition of Aromatic Alkynes to 4**




**Scheme 6. Addition of Aliphatic Alkynes to 4**

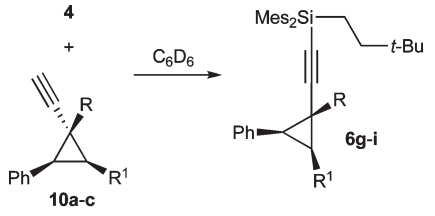



phenylacetylene, the ratio of silacyclobutene **9** to silylacetylene **6d** was quite variable; the relative amount of **9** ranged from 48 to 100% of the product mixture. Silylacetylene **6d** could not be separated from **9** or unreacted fluorovinylsilane **5** by chromatography; however, treatment of **9** contaminated only with **5** with aqueous NaOH in THF allowed for isolation of **9** from the corresponding vinylsilanol.

The addition of cyclopropyl alkynes **10a**−**c** to silene **4** produced silylacetylenes **6g**−**i** quickly and quantitatively (Scheme 7). Silylacetylene **6g** could not be separated from unreacted **5** by chromatography; however, treatment of the mixture with aqueous NaOH in THF allowed for isolation of **6g** from the corresponding vinylsilanol. Silylacetylenes **6h**,**i** were separated from unreacted fluorovinylsilane **5** by chromatography; however, **6i** remained contaminated with the starting alkyne, **10c**.

Silylacetylenes **6a**−**i**, silacyclobutenes **7** and **9**, and vinylsilane **8** were identified by IR, $^1$H, $^{13}$C, gCOSY, $^1$H−$^{13}$C gHSQC and gHMBC, $^1$H−$^{29}$Si gHMBC NMR spectroscopy, and mass spectrometry. The spectral features of **6a**−**i** are very similar, and thus, only the spectral data of silylacetylene **6g** will be discussed in detail. Two multiplets in the $^1$H NMR spectrum of

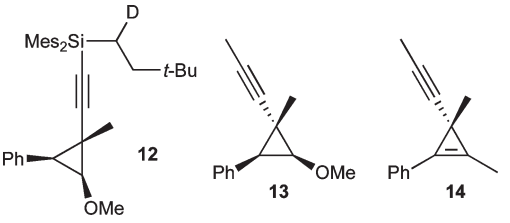
**Scheme 7. Addition of Alkynes 10a−c to Silene 4**




silylacetylene **6g** at 1.65−1.69 and 1.50−1.54 ppm were assigned to an AA′XX′ spin system attributable to an X−$CH_2CH_2$−Y moiety. The two substituents on the $CH_2CH_2$ moiety are (1) a *t*-Bu group, as seen by correlations between the multiplets assigned to the two $CH_2$ units in the $^1$H dimension and the signal assigned to the quaternary $^{13}$C of the *t*-Bu substituent in the $^{13}$C dimension of the $^1$H−$^{13}$C gHMBC NMR spectrum of **6g**, and (2) a $Mes_2RSi$ substituent, as revealed by correlations between the same multiplets in the $^1$H dimension and the $^{29}$Si signal at −29.6 ppm in the $^{29}$Si dimension of the $^1$H−$^{29}$Si gHMBC NMR spectrum of **6g**. The presence of an alkyne functional group was confirmed by the observation of two signals in the $^{13}$C NMR spectrum of **6g** at 110.94 and 82.65 ppm, which fall in the typical chemical shift range for alkynyl $^{13}$C's, and by the absorption observed in the IR spectrum of **6g** at 2161 $cm^{-1}$. On the basis of the $^1$H NMR spectrum of **6g** and the correlations observed in the $^1$H−$^{13}$C gHMBC NMR spectrum of **6g**, the cyclopropyl ring is still intact.

The NMR spectroscopic data of **7** and **9** are consistent with the proposed structures. A multiplet at 3.31 ppm (dt, $J$ = 9.6, 1.5 Hz) and a doublet at 6.88 ppm ($J$ = 1.2 Hz) or a multiplet at 2.66 ppm (dt, $J$ = 10, 1.8 Hz) and a doublet at 5.90 ppm ($J$ = 2.4 Hz) were observed in the $^1$H NMR spectra of **7** and **9**, respectively, assigned to the saturated C<u>H</u> in the ring and the vinylic hydrogen of each compound. The gCOSY NMR spectrum of **7** showed correlations between the multiplet at 3.31 ppm and signals at 1.73 and 1.84 ppm assigned to the C<u>H</u>$_2$*t*-Bu hydrogens as well as to the vinylic $^1$H signal at 6.88. Similar correlations were observed in the gCOSY NMR spectrum of **9**. The alkene functional group was confirmed by the presence of two signals in the $^{13}$C NMR spectra of **7** and **9** within the typical chemical shift range for alkenyl carbons. For **7**, the two signals resonated at 135.68 and 160.70 ppm, while in **9**, the adjacent OEt group influences the chemical shifts of the vinylic carbons: one carbon is shielded (119.55 ppm) and the other is deshielded (164.82 ppm). The $^{29}$Si gHMBC NMR spectrum of **7** revealed that the $^1$H signals at 3.31 and 6.88 ppm correlated to a signal at −13.0 ppm in the $^{29}$Si dimension. This $^{29}$Si resonance also showed correlations to $^1$H signals assigned to the Mes-<u>H</u> (6.72 and 6.73 ppm) and the C<u>H</u>$_2$*t*-Bu hydrogens. The $^{29}$Si signal at −3.5 ppm in the $^{29}$Si gHMBC NMR spectrum of **9** showed similar correlations. Thus, the signals at −13.0 and −3.5 ppm were assigned to the silacyclobutene silicon of **7** and **9**, respectively. The $^{29}$Si chemical shift data are consistent with the known data for other similar silacyclobutenes.[12] The $^1$H chemical shift of the signal assigned to the saturated C<u>H</u> in the ring and the correlations between the $^{29}$Si signal and both the saturated C<u>H</u> and vinylic signals in the $^1$H dimension of the $^{29}$Si gHMBC NMR spectrum of **7** and **9** provide strong evidence for silacyclobutenic structures. Determination of the regiochemistry of **7** and **9** will be presented below.

**Chart 1**




Since vinylsilane **8** was produced in only minor amounts and could not be separated from **6a** and **7**, it was difficult to identify all the signals corresponding to **8** in the 1D and 2D NMR spectra of the mixture. One pair of doublets observed in the $^1$H NMR spectrum of the mixture (6.22 and 6.32 ppm, $J$ = 18 Hz) was assigned to the vinylic hydrogens on the Si-CH=CH-*t*-Bu *trans*-oriented double bond. The chemical shifts and coupling constants of a second pair of doublets, obscured by the signals attributed to the phenyl substituent of **6a** or **7**, were estimated from the $^1$H−$^{29}$Si gHMBC spectrum of the mixture containing **6a**, **7**, and **8** (7.05 and 7.16 ppm, $J$ = 18 Hz). All the vinylic $^1$H signals assigned to **8** correlated to a $^{29}$Si resonance at −21.7 ppm.

Deuterated alkyne **11**, prepared by the treatment of the conjugate base of **10c** with $D_2O$, was added to a solution of silene **4** in $C_6D_6$; the only product obtained was the deuterated silylacetylene **12** (Chart 1). The $^1$H NMR chemical shifts of the deuterated silylacetylene **12** were essentially the same as those of **6i**; however, the splitting pattern and multiplicity of the signals attributable to the $CHDCH_2$ moiety reflected the incorporation of the deuterium. The $^2$H NMR spectrum of **12** revealed one broad signal at 1.47 ppm.

Alkyne **10c** was methylated by treatment with BuLi in the cold (THF) followed by the addition of MeI to give a mixture of alkyne **13** and cyclopropene **14**, contaminated with *trans, trans*-2-methoxy-1-methyl-3-phenylcyclopropylethene, **15**, in a ratio of 61:33:6, respectively, as determined by $^1$H NMR spectroscopy (Chart 1).[16] The desired alkyne **13** was readily separated from cyclopropene **14** by chromatography, yielding a mixture of alkyne **13** and alkene **15** in a ratio of 92:6, respectively, as determined by GC analysis.[16]

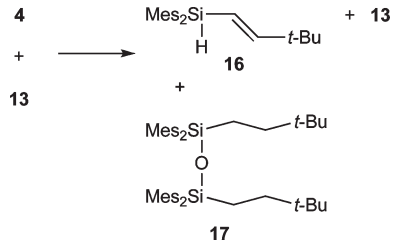
Alkyne **13** was added to a solution of silene **4** dissolved in $C_6D_6$ (Scheme 8). The disappearance of the signal assigned to the vinylic $^1$H of **4** was monitored by $^1$H NMR spectroscopy over the course of 6 days. New signals in the vinyl region of the $^1$H NMR spectrum of the reaction mixture were observed; however, the relative amount of alkyne **13** compared to residual fluorosilane **5** remained unchanged. Chromatographic separation of the crude product mixture yielded a mixture of vinylsilane **16** and disiloxane **17** (in a ratio of 83:17, respectively) as well as unreacted alkyne **13** and fluorosilane **5**, as determined by $^1$H NMR spectroscopy. Vinylsilane **16**[3a] and disiloxane **17**[15b] were identified by comparison of the $^1$H, $^{13}$C, and $^{29}$Si chemical shifts with the literature data.[17]

**Determination of the Regiochemistry of Silacyclobutenes.** Silacyclobutenes **7** and **9** were examined by $^1$H 1-D ROE

(16) The synthesis of (*trans,trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)ethyne, **10c**, produces (*trans,trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)ethene, **15**, as a byproduct. Alkyne **10c** is always contaminated with < 10% alkene **15**. See ref 9.

(17) A mixture of vinylsilane **16** and disiloxane **17** was isolated from the reaction mixture of alkyne **13** and silene **4**. Disiloxane **17**: high-resolution EI-MS for $C_{48}H_{69}OSi_2$ ($M^+ - H$) ($m/z$) calcd 717.4887, found 717.4907.

**Scheme 8. Reaction of Alkyne 13 and Silene 4**




spectroscopy to determine the regiochemistry of the addition. Irradiation of both mesityl *o*-C$\underline{H}_3$ signals (2.46 and 2.56 ppm) in **7** led to enhancement of the signal at 6.88, assigned to the vinylic $^1$H. Also, enhancement of the signal assigned to the *ortho* hydrogen of the phenyl substituent was observed after irradiation of the signals at 3.31 ppm (saturated ring SiC$\underline{H}$) and 1.84 ppm (one of the C$\underline{H}_2$*t*-Bu hydrogens); no enhancement of the vinylic $^1$H signal was observed in these cases. These results suggest that the vinylic $^1$H is attached to the unsaturated ring carbon adjacent to silicon.

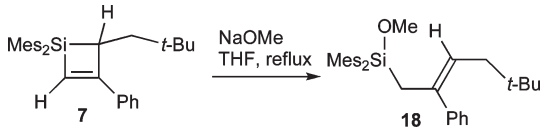
Upon examination of the $^1$H 1-D ROE spectroscopic data for ethoxy-substituted silacyclobutene **9**, some key differences were noted in comparison to **7**. Enhancement of the signal assigned to the vinylic $^1$H (5.90 ppm) was observed after irradiation of the signal at 2.66 ppm assigned to the saturated ring SiC$\underline{H}$ and the signal at 1.29 ppm assigned to one of the C$\underline{H}_2$*t*-Bu hydrogens. There was no enhancement of the vinylic $^1$H signal after irradiation at either of the signals assigned to the mesityl *o*-C$\underline{H}_3$ groups. Furthermore, irradiation of the signal at 1.07 ppm assigned to the OCH$_2$-C$\underline{H}_3$ group caused enhancement of the signals assigned to the mesityl *o*-C$\underline{H}_3$ hydrogens. These spectroscopic data lead to the conclusion that the regiochemistry of **9** is reversed from that of **7**; the vinyl $^1$H is bonded to the unsaturated ring carbon two bonds from silicon.

The $^1$H(vinylic)$-^{29}$Si coupling constants in **7** and **9** were also examined to support the assigned structures. The regiochemistry of silacyclobutenes can be assigned on the basis of the magnitude of the $^1$H(vinylic)$-^{29}$Si coupling constants; in general, the magnitude of the two-bond coupling constant (8−12 Hz) is significantly smaller than the magnitude of the *trans* three-bond coupling constant (17−30 Hz).[7] The magnitude of the $^1$H(vinylic)$-^{29}$Si coupling constant for **9** was obtained from the $^{29}$Si satellites of the vinylic $^1$H signal in the $^1$H NMR spectrum, while that for **7** was extracted from the $^1$H$-^{29}$Si gHMBC spectrum since the $^{29}$Si satellites of the vinylic signal in the $^1$H NMR spectrum were obscured. The values were found to be 6 Hz for **7** and 22 Hz for **9**, corresponding to a two-bond and a three-bond coupling, respectively, in agreement with the previously assigned regiochemistry.

Finally, the structures of **7** and **9** were implicated by chemical degradation. Compounds **7** and **9** were treated with NaOMe in refluxing THF (Scheme 9). Only silacyclobutene **7** was observed to react with NaOMe; the ethoxy-substituted ring **9** was unreactive toward NaOMe under these conditions.

The ring-opened product, **18**, was identified by $^1$H, $^{13}$C, gCOSY, $^1$H$-^{29}$Si gHMBC, $^1$H$-^{13}$C gHSQC, and gHMBC NMR spectroscopy and mass spectrometry. There are several features in the NMR spectral data of **18** that provide unambiguous evidence for the structure of the product. A triplet assigned to the vinylic $^1$H (5.35 ppm, 1 H, $J$ = 7.5 Hz), a

**Scheme 9. Chemical Degradation of Silacyclobutene 7**




doublet assigned to the C$\underline{H}_2$*t*-Bu (1.99 ppm, 2 H, $J$ = 7.2 Hz), and a singlet assigned to the SiC$\underline{H}_2$ (2.70 ppm, 2 H) were present in the $^1$H NMR spectrum of **18**. In the $^1$H$-^{29}$Si gHMBC NMR spectrum of **18**, a strong correlation was observed between the singlet at 2.70 ppm and the silicon signal at −1.6 ppm, which also correlated to the $^1$H signal assigned to the methoxy group of **18** (3.04 ppm, 3 H). There were no correlations between the silicon signal at −1.6 ppm and any of the $^1$H signals attributed to the phenyl substituent of **18**. On the basis of these correlations, the silicon signal at −1.6 ppm was assigned to the silicon in **18**. In addition, this silicon chemical shift is similar to that of Mes$_2$Si(O*t*-Bu)CH$_2$CH$_2$*t*-Bu (1.3 ppm), prepared from the addition of *t*BuOH to silene **4**.[15b] From the $^1$H and $^1$H$-^{29}$Si gHMBC NMR spectroscopic data, it is apparent that the structure contains the Mes$_2$Si(OMe)CH$_2$ moiety. The singlet at 2.70 ppm assigned to the SiC$\underline{H}_2$ also showed correlations to signals at 124.87, 137.70, and 143.34 ppm in the $^{13}$C dimension of the $^1$H$-^{13}$C gHMBC NMR spectrum, which correspond to the two vinylic carbons and the *ipso* carbon of the phenyl substituent, respectively. The two vinylic carbon signals (124.87, 137.70) also correlated to the doublet at 1.96 ppm in the $^1$H spectrum, assigned to the C$\underline{H}_2$*t*-Bu hydrogens. Thus, the SiC$\underline{H}_2$ must be connected to a C(Ph)=C(H)CH$_2$*t*-Bu moiety.

The structure assigned to **18**, where the phenyl substituent is attached to the carbon two bonds from silicon, is the only possibility that is consistent with the NMR spectroscopic data. Thus, the phenyl-substituted silacyclobutene **7** is derived from the terminal alkynyl carbon adding to the silicon of silene **4**. The original regiochemistry, with respect to alkyne addition to silene **4**, should be retained in the ring-opened product. The methoxide anion is presumed to selectively attack at the silicon, which leads to cleavage of the former silenic Si−C bond; similar behavior has been observed when other silacyclobutenes were treated with base.[18] Alternative ring-opened products derived from a silacyclobutene with the phenyl substituent adjacent to silicon were considered; however, none of these structures were consistent with the spectroscopic data obtained.

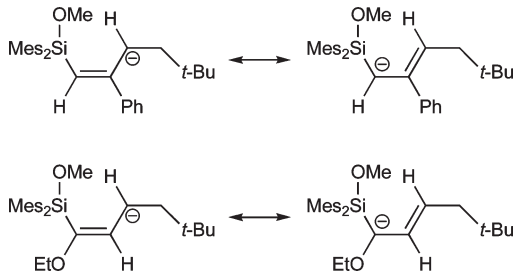
The reduced reactivity of **9** toward NaOMe in comparison to **7** is also consistent with the ethoxy substituent being located on the carbon adjacent to silicon. Presumably, the intermediate anion would be less stable; the added instability may be sufficient to make the addition of NaOMe unfavorable (Chart 2).

## Discussion

Silylacetylenes **6a**−**i** and **12** are derived from addition of the acetylenic C−H(D) bond across the Si=C of **4**. While addition of the deuterated alkyne **11** to silene **4** did not qualitatively reduce the rate of the reaction, the formation of deuterated silylacetylene **12** does provide evidence that the acetylenic hydrogen becomes bound to the former silenic

(18) Mohseni-Ala, J.; Auner, N. *Inorg. Chim. Acta* **2006**, *359*, 4677.

**Chart 2**




carbon in compounds **6a**−**i**. Insertion of a silene into the terminal CH bond of an alkyne has not previously been observed. The possibility that silylacetylenes **6a**−**i** and **12** were formed by reaction of the silene precursor, an α-silyl anion, with the alkynes was considered; however, the spectroscopic evidence clearly indicates that silene **4** is being formed *prior* to alkyne addition and, thus, rules out this possibility.

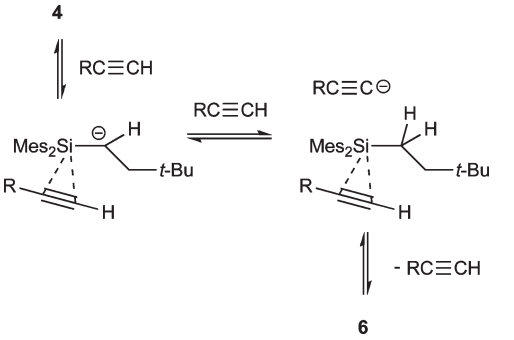
Analogous products have been isolated from the addition of phenylacetylene to a phosphasilene (Si=P).[19] The formation of the observed addition products to the phosphasilene was attributed to the highly polar nature of the double bond, i.e., $Si^{+}-P^{-}$. A C−H insertion product has also been observed in the reaction between an ylide-like silylene and terminal alkynes;[20] the preference for C−H insertion over cycloaddition with the C≡C bond has similarly been attributed to the polar nature of the compound.

On the basis of electronegativities, the Si=C bond of silene **4** is expected to be more polar than the Si=P of the phosphasilene, and thus, silylacetylenes **6a**−**i** may possibly be formed by silene **4** acting as a Brønsted base, abstracting the alkynyl proton. However, given an average p$K_a$ of 25 for alkynes, it is difficult to believe that the silene is a strong enough base to remove the weakly acidic proton of an alkyne. We have shown that silene **4** is a strong Lewis acid,[21] and thus, we propose that the alkyne first complexes to the silenic silicon, which would make the silenic carbon more basic. Abstraction of a proton from a second equivalent of alkyne (or, perhaps, from another complexed alkyne) followed by displacement of the complexed alkyne by the conjugate base (Scheme 10) would result in the formation of the silylacetylene. We have proposed a similar mechanism to account for the insertion of silene **4** into the CH bond of acetonitrile.[22] Yoshizawa and coworkers have examined the addition of methylacetylene to the Brook-type silene $(H_3Si)_2Si{=}C(OSiH_3)CH_3$ computationally. The triple bond of the alkyne complexes to the silenic silicon in the transition state; however in this case, the transfer of electron density is proposed to flow from the silene to the alkyne.[6e]

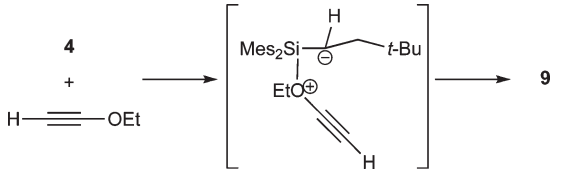
Interestingly, phenylacetylene and ethoxyacetylene were the only alkynes to give cycloadducts with silene **4**. The regiochemistry of silacyclobutene **7** is typical for the addition of terminal alkynes to silenes;[5,11,23] however, silacyclobutene **9** has the opposite regiochemistry.

Given that oxygen is a stronger nucleophile than the C≡C triple bond and the well-known oxaphilicity of silicon, it

**Scheme 10. Proposed Mechanism of the Addition of an Alkyne to Silene 4**




**Scheme 11. Proposed Mechanism of Ethoxyacetylene Cycloaddition**




seems probable that an initial oxonium complex could form, in addition to the complex with the triple bond, in the reaction between ethoxyacetylene and silene **4** (Scheme 11). The coordination of oxygen-containing donor molecules, such as ethers, to naturally polarized silenes has been studied extensively.[2] The THF complex of the polar silene $Me_2Si{=}C(SiMe_3)(SiMe\textit{t}\text{-}Bu_2)$ is quite stable and has been characterized by X-ray crystallography.[24] Oxonium complexes have long been proposed and since confirmed as intermediates in the addition of alcohols to silenes.[25] Evidence for the reversible formation of an acid−base complex between naturally polarized silenes and carbonyl compounds has been provided by Leigh and co-workers.[26,27] Interestingly, the lifetime of the Lewis acid−base complex formed in the reaction between silene **4** and *trans*-2-phenylcyclopropanecarbaldehyde was sufficient to allow ester formation via the Lewis acid-catalyzed aldehyde dimerization (Tishchenko reaction).[21] Hence, the initial formation of a complex in the addition of ethoxyacetylene to **4** is well precedented. After complexation to the ether oxygen, cyclization likely occurs via nucleophilic attack of the silenic carbon on the terminal alkynyl carbon of another ethoxyacetylene−silene complex, followed by attack of the substituted alkynyl carbon on silicon, forming silacyclobutene **9**, and thereby releasing the coordinated ethoxy group and an equivalent of silene **4**. Thus, the two products formed in the addition of ethoxyacetylene to silene **4** can be understood in terms of the formation of two competing Lewis acid−base complexes between the silene and the alkyne.

The addition of phenylacetylene to silene **4** also produces a silacyclobutene (**7**) in addition to silylacetylene **6a** and small

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(25) Morkin, T. L.; Leigh, W. J. *Acc. Chem. Res.* **2001**, *34*, 129.
(26) (a) Leigh, W. J.; Bradaric, C. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1993**, *115*, 5332. (b) Bradaric, C. J.; Leigh, W. J. *Organometallics* **1998**, *17*, 645.
(27) Owens, T. R.; Grinyer, J.; Leigh, W. J. *Organometallics* **2005**, *24*, 2307.

amounts of vinylsilane **8**. In contrast, the reaction of silene **4** with 1-ethynyl-4-(trifluoromethyl)benzene or 4-ethynylanisole resulted only in the formation of a silylacetylene. At this time, it is difficult to understand the differences in reactivity observed for the three aryl alkynes, particularly with regards to the formation (or lack thereof) of a cycloadduct. If a zwitterionic intermediate is formed, presumably the trifluoromethyl- or the alkoxy-substituted aryl alkyne (depending on the regiochemistry of the zwitterion) would (at least) equally favor cycloadduct formation. If a diradical intermediate was formed during the course of cycloaddition, as has been shown in the addition of alkynes to Brook silenes,[7,8] the three aryl alkynes are expected to be (at least) equally capable of stabilizing the intermediate. However, no cycloadduct was observed with the substituted aryl alkynes. Further studies are required to understand the reactivity differences.

We attempted to investigate the nature of a putative intermediate during the formation of a silacyclobutene by use of alkynes **10a**−**c** as mechanistic probes.[9] However, addition of these alkynes gave only the CH insertion products **6g**−**i**; no addition to the carbon−carbon triple bond was observed and, as a consequence, no mechanistic information regarding the cycloaddition could be deduced in these experiments.

The formation of vinylsilane **8** can be understood in terms of a formal ene-addition between phenylacetylene and silene **4** where the alkyne acts exclusively as the enophile. This type of behavior has previously been reported between **4** and aldehydes or ketones.[15b,21] Notably, the same relative regiochemistry is observed in **8** as in the phenyl-substituted silacyclobutene **7**. Phenylacetylene was the only alkyne that gave any ene-addition products upon reaction with silene **4**. Evidently, the other alkynes either are poorer enophiles (too electron rich) or are better substrates for C−H addition across the Si=C bond, which renders the ene-addition pathway less favorable.

The addition of alkyne **13** to silene **4** did not afford any products; evidently unpolarized internal alkynes do not add to this silene. This is consistent with previous work on the reactivity of disubstituted alkynes with 1,1-diorgano-substituted polar silenes.[10,11,12b] Although no addition occurred, in the presence of alkyne **13** silene **4** did slowly convert to vinylsilane **16** and disiloxane **17**. Vinylsilane **16** is likely formed by a hydrogen transfer in silene **4**. The formation of vinylsilane **16** from silene **4** has been observed previously,[3a] even though silene **4** has been reported to be stable in solution for extended periods of time (weeks).[15] Presumably disiloxane **17** is formed by the addition of adventitious water to silene **4**, the product of which then reacts with a second equivalent of **4**.[15b]

## Conclusions

We have examined the addition of cyclopropyl alkynes **10a**−**c**, **11**, and simple alkynes (RC≡CH; R = Ph, *p*-$CF_3C_6H_4$, *p*-$MeOC_6H_4$, OEt, *t*-Bu, $SiMe_3$) to $Mes_2Si{=}C(H)CH_2t$-Bu (**4**). The addition of an alkynyl CH bond across the Si=C bond of **4** is clearly favored over cycloaddition or an ene reaction. This is in stark contrast to the behavior of Brook-type silenes with alkynes, where cycloaddition is the preferred reaction pathway. Given the predominance of CH insertion in the studied reactions, it is surprising that CH insertion was not observed in the reaction between 1,2-dimethylsilene and acetylene or propyne.[11]

We believe the difference in reactivity between the naturally polarized silene **4** and Brook silenes is best understood in terms of the Lewis acidities of the two silenes: naturally polarized silenes are more Lewis acidic, and complexation with an alkyne increases the basicity of the silenic carbon (and the acidity of the alkynyl hydrogen), leading to CH insertion being favored over cycloaddition. With the nonpolar Brook silenes, cycloaddition via a diradical intermediate predominates.[7,8] This is a clear example of how the polarity of the Si=C bond of the silene can have a profound influence on the structure of the product formed in a given reaction. The formation of silacyclobutene **9** is best explained by proposing the formation of a complex with the ethereal oxygen rather than the triple bond.

At this time, the factors controlling the regioselectivity of the addition of phenylacetylene to silene **4** and the observed differences in reactivity between the various substituted aryl alkynes are not well understood. Studies using computational methods may allow us to gain further insights into the mechanistic details of alkyne additions to polar silenes and may help us to understand these important reactions more completely.

## Experimental Section

**General Experimental Details.** All reactions were performed in flame-dried Schlenk tubes, or NMR tubes sealed with a septum, under an inert atmosphere of argon. Benzene-$d_6$ was distilled from $LiAlH_4$, stored over 4 Å molecular sieves, and degassed prior to use. Pentane was purged with $N_2$ and passed through alumina prior to use. *t*-BuLi and BuLi were purchased from Aldrich Chemical Co., and methyl iodide was purchased from Fisher Chemical Inc. Phenylacetylene, 1-ethynyl-4-(trifluoromethyl)benzene, 4-ethynylanisole, ethoxyacetylene, trimethylsilylacetylene, and *tert*-butylacetylene were purchased from Aldrich Chemical Co. and stored over 4 Å molecular sieves. (*trans*-2-Phenylcyclopropyl)ethyne, **10a**,[9b] (*trans,trans*-2-methoxy-3-phenylcyclopropyl)ethyne, **10b**,[9b] (*trans,trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)ethyne, **10c**,[9b] and 1,1-dimesitylneopentylsilene, **4**,[15] were prepared according to the previously reported procedures. The NMR standards used are as follows: residual $C_6D_5H$ (7.15 ppm) for $^1H$ NMR spectra, $C_6D_6$ central transition (128.0 ppm) for $^{13}C$ NMR spectra, $Me_4Si$ as an external standard (0 ppm) for $^1H-^{29}Si$ gHMBC spectra, and $CF_3Ph$ as an external standard (−63.9 ppm against $CFCl_3$) for $^{19}F$ NMR spectra. IR spectra were recorded ($cm^{-1}$) from thin films on a Bruker Tensor 27 FT-IR spectrometer. Electron impact mass spectra were obtained using a MAT model 8400 mass spectrometer using an ionizing voltage of 70 eV. Mass spectral data are reported in mass-to-charge units, *m*/*z*.

**General Procedure for the Addition of Alkynes to 1,1-Dimesitylneopentylsilene, 4.** A pentane solution of fluorodimesitylvinylsilane, **5** (80 mg, 0.25 mmol), was converted to 1,1-dimesitylneopentylsilene, **4**. The pentane was removed in vacuo, yielding an orange residue. The residue was dissolved in $C_6D_6$ (0.7 mL) and then added to a septum-sealed NMR tube. The ratio of silene **4** to fluorosilane **5** was determined by $^1H$ NMR spectroscopy. Excess alkyne was added to the orange solution; the color faded to yellow upon addition of the alkyne. The ratio of products in the crude reaction mixture was determined by $^1H$ NMR spectroscopy; the mixture was usually contaminated with residual alkyne and fluorosilane **5**. The solvent was removed by rotary evaporation, yielding a pale yellow residue. The products were separated from fluorosilane **5** by chromatography or by treatment with aqueous NaOH followed by chromatography. Specific experimental details can be found in the Supporting Information.

**6a:** colorless, waxy solid; IR ($cm^{-1}$) 624 (s), 690 (s), 756 (s), 829 (s), 848 (m), 882 (m), 1026 (m), 1066 (m), 1158 (m), 1217 (m),

1236 (m), 1363 (m), 1410 (m), 1450 (m), 1488 (m), 1548 (w), 1605 (s), 2157 (s), 2865 (m), 2955 (s), 3024 (m); $^1$H NMR ($C_6D_6$) $\delta$ 0.89 (s, 9 H, C($CH_3$)$_3$), 1.56−1.59 (XX′ portion of an AA′XX′ spin system, 2 H, Si$CH_2$), 1.70−1.73 (AA′ portion of an AA′XX′ spin system, 2 H, $CH_2$*t*-Bu), 2.09 (s, 6 H, Mes *p*-$CH_3$), 2.62 (s, 12 H, Mes *o*-$CH_3$), 6.74 (s, 4 H, Mes-H), 6.86−6.90 (m, 3 H, Ph *m,p*-H), 7.37−7.38 (m, 2 H, Ph *o*-H); $^{13}$C NMR ($C_6D_6$) $\delta$ 15.94 (Si$CH_2$), 20.99 (Mes *p*-$CH_3$), 24.47 (Mes *o*-$CH_3$), 29.05 (C($CH_3$)$_3$), 31.24 (C($CH_3$)$_3$), 39.17 ($CH_2$*t*-Bu), 96.18 ($Me_2$Si-C≡C), 107.83 ($Me_2$Si−C≡C), 124.15 (Ph *i*-C), 128.47, 128.51 (Ph *m,p*-C), 129.94 (Mes *m*-C), 131.76 (Mes *i*-C), 131.87 (Ph *o*-C), 138.91 (Mes *p*-C), 144.12 (Mes *o*-C); $^{29}$Si NMR ($C_6D_6$) $\delta$ −28.6 ($Me_2$Si); high-resolution EI-MS for $C_{32}H_{40}Si$ ($M^+$) *m*/*z* calcd 452.2899, found 452.2888.

**6b:** colorless, waxy solid; IR (cm$^{-1}$) 625 (m), 654 (m), 705 (m), 806 (m), 843 (s), 884 (m), 1019 (m), 1069 (s), 1107 (m), 1133 (s), 1170 (s), 1236 (m), 1263 (m), 1325 (s), 1365 (m), 1408 (m), 1453 (m), 1608 (s), 2162 (m), 2867 (m), 2959 (s); $^1$H NMR ($C_6D_6$) $\delta$ 0.90 (s, 9 H, C($CH_3$)$_3$), 1.55−1.58 (XX′ portion of an AA′XX′ spin system, 2 H, Si$CH_2$), 1.67−1.70 (AA′ portion of an AA′XX′ spin system, 2 H, $CH_2$*t*-Bu), 2.09 (s, 6 H, Mes *p*-$CH_3$), 2.60 (s, 12 H, Mes *o*-$CH_3$), 6.75 (s, 4 H, Mes-H), 7.03−7.05 (m, 2 H, $C_6H_4CF_3$), 7.10−7.12 (m, 2 H, $C_6H_4CF_3$); $^{13}$C NMR ($C_6D_6$) $\delta$ 15.81 (Si$CH_2$), 20.98 (Mes *p*-$CH_3$), 24.44 (Mes *o*-$CH_3$), 29.02 (C($CH_3$)$_3$), 31.25 (C($CH_3$)$_3$), 39.18 ($CH_2$*t*-Bu), 99.28 ($Me_2$Si-C≡C), 105.99 ($Me_2$Si-C≡C), 124.6 (q, $CF_3$, $^1J_{CF}$ = 255 Hz),[28] 125.34 (q, Ar *m*-C, $^3J_{CF}$ = 3 Hz), 127.50 (Ar *i*-C), 130 (Ar *p*-C),[28] 130.01 (Mes *m*-C), 131.25 (Mes *i*-C), 131.99 (Ar *o*-C), 139.21 (Mes *p*-C), 144.06 (Mes *o*-C); $^{29}$Si NMR ($C_6D_6$) $\delta$ −28.3; $^{19}$F NMR ($C_6D_6$) $\delta$ −62.7; high-resolution EI-MS for $C_{33}H_{39}SiF_3$ ($M^+$) *m*/*z* calcd 520.2773, found 520.2780.

**6c:** colorless, waxy solid; IR (cm$^{-1}$) 623 (m), 764 (m), 831 (m), 847 (m), 882 (w), 1034 (m), 1171 (m), 1249 (s), 1292 (m), 1363 (w), 1410 (w), 1466 (m), 1507 (s), 1605 (s), 2154 (s), 2864 (m), 2955 (s); $^1$H NMR ($C_6D_6$) $\delta$ 0.91 (s, 9 H, C($CH_3$)$_3$), 1.58 − 1.61 (XX′ portion of an AA′XX′ spin system, 2 H, Si$CH_2$), 1.73−1.76 (AA′ portion of an AA′XX′ spin system, 2 H, $CH_2$*t*-Bu), 2.10 (s, 6 H, Mes *p*-$CH_3$), 2.65 (s, 12 H, Mes *o*-$CH_3$), 3.10 (s, 3 H, O$CH_3$), 6.49−6.51 (XX′ portion of an AA′XX′ spin system, 2 H, $C_6H_4$OMe), 6.75 (s, 4 H, Mes-H), 7.34 − 7.36 (AA′ portion of an AA′XX′ spin system, 2 H, $C_6H_4$OMe); $^{13}$C NMR ($C_6D_6$) $\delta$ 16.03 (Si$CH_2$), 20.99 (Mes *p*-$CH_3$), 24.49 (Mes *o*-$CH_3$), 29.07 (C($CH_3$)$_3$), 31.25 (C($CH_3$)$_3$), 39.20 ($CH_2$*t*-Bu), 54.63 (O$CH_3$), 94.39 ($Me_2$Si-C≡C), 108.07 ($Me_2$Si-C≡C), 114.23 (Ar *m*-C), 116.34 (Ar *i*-C), 129.92 (Mes *m*-C), 132.04 (Mes *i*-C), 133.43 (Ar *o*-C), 138.81 (Mes *p*-C), 144.13 (Mes *o*-C), 160.19 (Ar *p*-C); $^{29}$Si NMR ($C_6D_6$) $\delta$ −28.8; high-resolution EI-MS for $C_{33}H_{42}SiO$ ($M^+$) *m*/*z* calcd 482.3005, found 482.3013.

**6d:** contaminated with **9** (∼2:1 mixture of **9** to **6d**); $^1$H NMR ($C_6D_6$) $\delta$ 0.81 (t, 3 H, $OCH_2CH_3$, *J* = 7.2 Hz), 0.90 (s, 9 H, C($CH_3$)$_3$), 1.50−1.53 (XX′ portion of an AA′XX′ spin system, 2 H, Si$CH_2$), 1.64−1.67 (AA′ portion of an AA′XX′ spin system, 2 H, $CH_2$*t*-Bu), 2.09 (s, 6 H, Mes *p*-$CH_3$), 2.61 (s, 12 H, Mes *o*-$CH_3$), 3.49 (q, 2 H, $OCH_2CH_3$, *J* = 7.2 Hz), 6.74 (s, 4 H, Mes-H); $^{13}$C NMR ($C_6D_6$) $\delta$ 16.58 (Si$CH_2$), 20.98 (Mes *p*-$CH_3$), 24.47 (Mes *o*-$CH_3$), 29.09 (C($CH_3$)$_3$), 31.18 (C($CH_3$)$_3$), 39.21 ($CH_2$*t*-Bu), 111.6[29] ($Me_2$Si-C≡C), 129.82 (Mes *m*-C), 133.11 (Mes *i*-C), 138.44 (Mes *p*-C), 143.87 (Mes *o*-C) (not all signals from **6d** were visible); $^{29}$Si NMR ($C_6D_6$) $\delta$ −28.3 ($Me_2$Si); high-resolution EI-MS for $C_{28}H_{40}SiO$ ($M^+$) *m*/*z* calcd 420.2849, found 420.2845.

**6e:** colorless oil; IR (cm$^{-1}$) 622 (m), 768 (m), 847 (m), 1027 (m), 1064 (m), 1252 (m), 1362 (m), 1410 (m), 1454 (m), 1605 (m), 2153 (m), 2192 (w), 2865 (m), 2958 (s); $^1$H NMR ($C_6D_6$) $\delta$ 0.92 (br s, 9 H, $CH_2$C($CH_3$)$_3$), 1.12 (s, 9 H, SiC≡CC($CH_3$)$_3$), 1.46−1.49 (XX′ portion of an AA′XX′ spin system, 2 H, Si$CH_2$), 1.64−1.67 (AA′ portion of an AA′XX′ spin system, 2 H, $CH_2$*t*-Bu), 2.08 (s, 6 H, Mes *p*-$CH_3$), 2.57 (s, 12 H, Mes *o*-$CH_3$), 6.72 (s, 4 H, Mes-H); $^{13}$C NMR ($C_6D_6$) $\delta$ 16.07 (Si$CH_2$), 20.98 (Mes *p*-$CH_3$), 24.46 (Mes *o*-$CH_3$), 28.57 (C≡CC($CH_3$)$_3$), 29.12 ($CH_2$C($CH_3$)$_3$), 30.44 (C≡CC($CH_3$)$_3$), 31.21 ($CH_2$C($CH_3$)$_3$), 39.19 ($CH_2$*t*-Bu), 84.29 ($Me_2$Si-C≡C), 117.57 ($Me_2$Si-C≡C), 129.83 (Mes *m*-C), 132.31 (Mes *i*-C), 138.61 (Mes *p*-C), 144.04 (Mes *o*-C); $^{29}$Si NMR ($C_6D_6$) $\delta$ −29.5 ($Me_2$Si); high-resolution EI-MS for $C_{30}H_{44}Si$ ($M^+$) *m*/*z* calcd 432.3212, found 432.3199.

**6f:** colorless oil; IR (cm$^{-1}$) 623 (m), 768 (s), 846 (s), 1026 (w), 1065 (w), 1249 (m), 1363 (m), 1410 (m), 1451 (m), 1605 (m), 2865 (m), 2957 (s); $^1$H NMR ($C_6D_6$) $\delta$ 0.11 (s, 9 H, $SiMe_3$), 0.90 (s, 9 H, C($CH_3$)$_3$), 1.48−1.51 (XX′ portion of an AA′XX′ spin system, 2 H, Si$CH_2$), 1.66−1.69 (AA′ portion of an AA′XX′ spin system, 2 H, $CH_2$*t*-Bu), 2.06 (s, 6 H, Mes *p*-$CH_3$), 2.57 (s, 12 H, Mes *o*-$CH_3$), 6.70 (s, 4 H, Mes-H); $^{13}$C NMR ($C_6D_6$) $\delta$ −0.43 ($SiMe_3$), 15.83 (Si$CH_2$), 20.97 (Mes *p*-$CH_3$), 24.47 (Mes *o*-$CH_3$), 29.05 (C($CH_3$)$_3$), 31.20 (C($CH_3$)$_3$), 39.10 ($CH_2$*t*-Bu), 116.30 ($Me_2$Si-C≡C), 116.84 ($Me_2$Si-C≡C), 129.88 (Mes *m*-C), 131.53 (Mes *i*-C), 138.89 (Mes *p*-C), 144.10 (Mes *o*-C); $^{29}$Si NMR ($C_6D_6$) $\delta$ −19.3 ($Me_3$Si), −30.0 ($Me_2$Si); high-resolution EI-MS for $C_{29}H_{44}Si_2$ ($M^+$) *m*/*z* calcd 448.2982, found 448.2976.

**6g:** colorless solid; IR (cm$^{-1}$) 623 (m), 697 (m), 848 (m), 1028 (m), 1363 (m), 1410 (m), 1456 (m), 1605 (s), 2161 (s), 2864 (m), 2956 (s), 3028 (w); $^1$H NMR ($C_6D_6$) $\delta$ 0.85 (ddd, 1 H, $CH_2$, *J* = 4.6, 6.2, 8.6 Hz), 0.90 (s, 9 H, C($CH_3$)$_3$), 1.15 (ddd, 1 H, $CH_2$, *J* = 4.8, 5.6, 8.8 Hz), 1.38 (ddd, 1 H, SiC≡CCH, *J* = 4.4, 5.6, 8.8 Hz), 1.50−1.54 (XX′ portion of an AA′XX′ spin system, 2 H, Si$CH_2$), 1.65−1.69 (AA′ portion of an AA′XX′ spin system, 2 H, $CH_2$*t*-Bu), 2.09 (s, 6 H, Mes *p*-$CH_3$), 2.20 (ddd, 1 H, PhCH, *J* = 4.6, 6.2, 8.8 Hz), 2.60 (br s, 12 H, Mes *o*-$CH_3$), 6.65−6.69 (m, 2 H, Ph *o*-H), 6.74 (s, 4 H, Mes-H), 6.95−7.00 (m, 3 H, Ph *m,p*-H); $^{13}$C NMR ($C_6D_6$) $\delta$ 13.12 (SiC≡CCH), 16.04 (Si$CH_2$), 17.82 ($CH_2$), 20.99 (Mes *p*-$CH_3$), 24.48 (Mes *o*-$CH_3$), 26.49 (PhCH), 29.07 (C($CH_3$)$_3$), 31.22 (C($CH_3$)$_3$), 39.14 ($CH_2$*t*-Bu), 82.65 (Si-C≡C), 110.94 (Si-C≡C), 126.10 (Ph *o*-C), 126.30 (Ph *p*-C), 128.53 (Ph *m*-C), 129.89 (Mes *m*-C), 132.17 (Mes *i*-C), 138.74 (Mes *p*-C), 140.65 (Ph *i*-C), 144.00 (Mes *o*-C); $^{29}$Si NMR ($C_6D_6$) $\delta$ −29.6 ($Me_2$Si); high-resolution EI-MS for $C_{35}H_{44}Si$ ($M^+$) *m*/*z* calcd 492.3212, found 492.3198.

**6h:** colorless solid; IR (cm$^{-1}$) 625 (m), 700 (s), 849 (m), 1028 (m), 1118 (m), 1232 (m), 1409 (m), 1451 (s), 1605 (s), 2160 (s), 2864 (m), 2956 (s), 3026 (m); $^1$H NMR ($C_6D_6$) $\delta$ 0.90 (s, 9 H, C($CH_3$)$_3$), 1.50−1.53 (XX′ portion of an AA′XX′ spin system, 2 H, Si$CH_2$), 1.64−1.66 (AA′ portion of an AA′XX′ spin system, 2 H, $CH_2$*t*-Bu), 1.89 (dd, 1 H, SiC≡CCH, *J* = 3.3, 6.3 Hz), 2.09 (s, 6 H, Mes *p*-$CH_3$), 2.26 (t, 1 H, PhCH, *J* = 6.6 Hz), 2.58 (s, 12 H, Mes *o*-$CH_3$), 2.82 (s, 3 H, MeO), 3.47 (dd, 1 H, MeOCH, *J* = 3.3, 6.9 Hz), 6.74 (s, 4 H, Mes-H), 6.98−7.07 (m, 5 H, Ph-H); $^{13}$C NMR ($C_6D_6$) $\delta$ 16.03 (Si$CH_2$), 17.29 (SiC≡CCH), 20.99 (Mes *p*-$CH_3$), 24.49 (Mes *o*-$CH_3$), 29.07 (C($CH_3$)$_3$), 31.22 (C($CH_3$)$_3$), 33.34 (PhCH), 39.15 ($CH_2$*t*-Bu), 57.80 (MeO), 66.71 (MeOCH), 84.04 (Si-C≡C), 108.68 (Si-C≡C), 126.45 (Ph *p*-C), 128.1[29] (Ph *m*-C), 128.55 (Ph *o*-C), 129.90 (Mes *m*-C), 132.08 (Mes *i*-C), 135.75 (Ph *i*-C), 138.81 (Mes *p*-C), 144.00 (Mes *o*-C); $^{29}$Si NMR ($C_6D_6$) $\delta$ −29.6 ($Me_2$Si); high-resolution EI-MS for $C_{36}H_{46}OSi$ ($M^+$) *m*/*z* calcd 522.3318, found 522.3325.

**6i:** contaminated with alkyne **10c** (25%); $^1$H NMR ($C_6D_6$) $\delta$ 0.92 (s, 9 H, C($CH_3$)$_3$), 1.16 (s, 3 H, C≡C-C$CH_3$), 1.49−1.52 (XX′ portion of an AA′XX′ spin system, 2 H, Si$CH_2$), 1.66−1.69 (AA′ portion of an AA′XX′ spin system, 2 H, $CH_2$*t*-Bu), 2.09 (s, 6 H, Mes *p*-$CH_3$), 2.43 (d, 1 H, PhCH, *J* = 7.2 Hz), 2.59 (s, 6 H, Mes *o*-$CH_3$), 2.60 (s, 6 H, Mes *o*-$CH_3$), 2.99 (s, 3 H, MeO), 3.53 (d, 1 H, MeOCH, *J* = 7.2 Hz), 6.74 (s, 4 H, Mes-H), 7.01−7.03 (m, 1 H, Ph *p*-H), 7.10−7.12 (m, 2 H, Ph *m*-H), 7.35−7.36 (m, 2 H, Ph *o*-H); $^{13}$C NMR ($C_6D_6$) $\delta$ 12.32 (C≡C−C$CH_3$), 16.06 (Si$CH_2$), 18.02 (C≡C-C$CH_3$), 20.97 (Mes *p*-$CH_3$), 24.47 (Mes *o*-$CH_3$), 29.11 (C($CH_3$)$_3$), 31.22 (C($CH_3$)$_3$), 33.95 (PhCH), 39.25 ($CH_2$*t*-Bu), 58.46 (MeO), 68.35 (MeOCH), 82.16 (Si-C≡C),

(28) The chemical shift and *J* value were estimated from the $^1$H−$^{13}$C gHMBC spectrum.

(29) Chemical shift estimated from the $^1$H−$^{13}$C gHMBC spectrum.

114.91 (Si-C≡C), 126.60 (Ph *p*-C), 128.22 (Ph *m*-C), 129.90 (Mes *m*-C), 130.92 (Ph *o*-C), 132.21 (Mes *i*-C), 134.74 (Ph *i*-C), 138.76 (Mes *p*-C), 144.04 (Mes *o*-C); $^{29}$Si NMR ($C_6D_6$) $\delta$ −29.6 ($Mes_2\underline{Si}$); high-resolution EI-MS for $C_{37}H_{48}OSi$ ($M^+$) $m/z$ calcd 536.3474, found 536.3460.

**7:** as a mixture with **6a** and **8**; $^1$H NMR ($C_6D_6$) $\delta$ 0.90 (s, 9 H, $C(\underline{CH_3})_3$), 1.73 (dd, 1 H, $SiCHC\underline{H_2}$, $J$ = 14, 10 Hz), 1.84 (dd, 1 H, $SiCHC\underline{H_2}$, $J$ = 14, 1.0 Hz), 2.07 (s, 3 H, Mes *p*-$C\underline{H_3}$), 2.13 (s, 3 H, Mes *p*-$C\underline{H_3}$), 2.46 (s, 6 H, Mes *o*-$C\underline{H_3}$), 2.56 (s, 6 H, Mes *o*-$C\underline{H_3}$), 3.31 (dt, 1 H, SiC$\underline{H}$, $J$ = 10, 1.5), 6.72 (s, 2 H, Mes-$\underline{H}$), 6.73 (s, 2 H, Mes-$\underline{H}$), 6.88[30] (d, 1 H, SiC$\underline{H}$=CPh, $J$ = 1.2 Hz,[31] $J_{H-Si}$ = 6 Hz[32]), 7.10−7.12 (m, 1 H, Ph *p*-$\underline{H}$), 7.20−7.22 (m, 2 H, Ph *m*-$\underline{H}$), 7.58−7.60 (m, 2 H, Ph *o*-$\underline{H}$); $^{13}$C NMR ($C_6D_6$) $\delta$ 21.07 (Mes *p*-$\underline{C}H_3$), 24.11 (Mes *o*-$\underline{C}H_3$), 25.14 (Mes *o*-$\underline{C}H_3$), 29.89 ($C(\underline{C}H_3)_3$), 31.24 ($\underline{C}(CH_3)_3$), 33.93 ($SiCHC\underline{H_2}$), 43.76 ($SiCH\underline{C}H_2$), 126.39 (Ph *o*-$\underline{C}$), 128.26 (Ph *p*-$\underline{C}$), 128.63 (Ph *m*-$\underline{C}$), 129.21 (Mes *m*-$\underline{C}$), 129.65 (Mes *m*-$\underline{C}$), 130.56 (Mes *i*-$\underline{C}$), 134.67 (Mes *i*-$\underline{C}$), 135.68 (Si$\underline{C}$H=CPh), 137.35 (Ph *i*-$\underline{C}$), 138.56 (Mes *p*-$\underline{C}$), 139.43 (Mes *p*-$\underline{C}$), 142.92 (Mes *o*-$\underline{C}$), 144.76 (Mes *o*-$\underline{C}$), 160.70 (SiCH=$\underline{C}$Ph); $^{29}$Si NMR ($C_6D_6$) $\delta$ −13.0 ($\underline{Si}Mes_2$, $J_{H-Si}$ = 6).

**8:** as a mixture with **6a** and **7**; $^1$H NMR ($C_6D_6$) $\delta$ 0.95 (s, 9 H, $C(\underline{CH_3})_3$), 2.12 (s, 6 H, Mes *p*-$C\underline{H_3}$), 2.44 (s, 12 H, Mes *o*-$C\underline{H_3}$), 6.22 (d, 1 H, Si-CH=$\underline{C}$H-*t*-Bu, $J$ = 19 Hz), 6.32 (d, 1 H, Si-$\underline{C}$H=CH-*t*-Bu, $J$ = 18 Hz), 6.77 (s, 4 H, Mes-$\underline{H}$), 7.00−7.05 (m, 3 H, Ph-$\underline{H}$), 7.05 (d, 1 H, Si-CH=$\underline{C}$H-Ph, $J$ = 18 Hz),[33] 7.16 (d, 1 H, Si-$\underline{C}$H=CH-Ph, $J$ = 18 Hz),[33] 7.26−7.27 (m, 2 H, Ph-$\underline{H}$); $^{29}$Si NMR ($C_6D_6$) $\delta$ −21.7.

**9:** $^1$H NMR ($C_6D_6$) $\delta$ 0.97 (s, 9 H, $C(CH_3)_3$), 1.07 (t, 3 H, $OCH_2C\underline{H_3}$, $J$ = 6.9 Hz), 1.29 (dd, 1 H, $SiC\underline{H}CH_2$, $J$ = 14, 11 Hz), 1.68 (dd, 1 H, $SiCHC\underline{H_2}$, $J$ = 15, 2.1 Hz), 2.06 (s, 3 H, Mes *p*-$C\underline{H_3}$), 2.07 (s, 3 H, Mes *p*-$C\underline{H_3}$), 2.58 (s, 6 H, Mes *o*-$C\underline{H_3}$), 2.64 (s, 6 H, Mes *o*-$C\underline{H_3}$), 2.66 (dt, 1 H, $SiCHC\underline{H_2}$, $J$ = 10, 1.8 Hz), 3.55 (AB, 1 H, $OC\underline{H_2}CH_3$, $J_{AB}$ = 9.6, $J$ = 7.0), 3.58 (AB, 1 H, $OC\underline{H_2}CH_3$, $J_{AB}$ = 9.6, $J$ = 7.0 Hz), 5.90 (d, 1 H, SiC=C$\underline{H}$, $J$ = 2.4, $^3J_{H-Si}$ = 21), 6.69 (s, 2 H, Mes-$\underline{H}$), 6.73 (s, 2 H, Mes-$\underline{H}$); $^{13}$C NMR ($C_6D_6$) $\delta$ 14.52 ($OCH_2\underline{C}H_3$), 21.01 (Mes *p*-$\underline{C}H_3$), 23.70 (Mes *o*-$\underline{C}H_3$), 23.94 (Mes *o*-$\underline{C}H_3$), 25.17 ($SiCHCH_2$), 30.03 ($C(\underline{C}H_3)_3$), 32.28 ($\underline{C}(CH_3)_3$), 47.32 ($SiCHCH_2$), 63.94 ($O\underline{C}H_2$-$CH_3$), 119.55 (SiC=$\underline{C}$H), 129.15 (Mes *m*-$\underline{C}$), 129.27 (Mes *m*-$\underline{C}$), 131.20 (Mes *i*-$\underline{C}$), 132.36 (Mes *i*-$\underline{C}$), 139.05 (Mes *p*-$\underline{C}$), 139.20 (Mes *p*-$\underline{C}$), 143.84 (Mes *o*-$\underline{C}$), 144.11 (Mes *o*-$\underline{C}$), 164.82 (Si$\underline{C}$=CH); $^{29}$Si NMR ($C_6D_6$) $\delta$ −3.5 ($\underline{Si}Mes_2$, $^3J_{H-Si}$ = 21); high-resolution EI-MS for $C_{28}H_{40}SiO$ ($M^+$) $m/z$ calcd 420.2849, found 420.2853.

**Preparation of (*trans*,*trans*-2-Methoxy-1-methyl-3-phenylcyclopropyl)[$^2$H]ethyne, 11.** A colorless solution of alkyne **10c** (175 mg, 0.94 mmol) in THF (3.0 mL) was cooled to −78 °C, and BuLi (0.59 mL, 1.6 mmol) was added dropwise. Upon complete addition of the BuLi, the solution appeared clear and light yellow. Over the course of an hour, the color of the solution changed to green. The reaction mixture was then allowed to warm to RT, after which it appeared opaque and deep brown. $D_2O$ (2 mL) was added to the reaction mixture; the color faded instantly to pale yellow. The reaction mixture was then diluted with $Et_2O$, and the aqueous and organic layers were separated. The aqueous layer was extracted with $Et_2O$ (3 × 3 mL); the combined organic layers were dried over $MgSO_4$, and the solvent was removed by rotary evaporation, yielding a vibrant, yellow oil (151 mg, 85% yield). Deuterated alkyne **11** was contaminated with 5% alkene **15**.[16] **11**: $^2$H NMR ($C_6H_6$) $\delta$ 1.71 (s, C≡C$\underline{D}$).

(30) Due to overlap with the *m*,*p*-PhH signals of **6a**, the chemical shift was estimated from the gCOSY spectrum.

(31) Due to overlap with the *m*,*p*-PhH signals of **6a**, this $J$ value was estimated from the ROESY spectrum.

(32) Due to overlap with the *m*,*p*-PhH signals of **6a**, this $J$ value was estimated from the $^1$H−$^{29}$Si gHMBC spectrum.

(33) The chemical shift and $J$ value were estimated from the $^1$H−$^{29}$Si gHMBC spectrum.

**Addition of (*trans*,*trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)[$^2$H]ethyne, 11, to 1,1-Dimesitylneopentylsilene, 4.** Alkyne **11** was added to silene **4** as described in the general alkyne addition procedure. Specific experimental details can be found in the Supporting Information. **12**: $^2$H NMR ($C_6H_6$) $\delta$ 1.47 (br s, SiCH$\underline{D}$).

**Preparation of 1-(*trans*,*trans*-2-Methoxy-1-methyl-3-phenylcyclopropyl)-1-propyne, 13.** A solution of alkyne **10c** (200 mg, 1.07 mmol) in THF (3 mL) was cooled to −78 °C. BuLi (0.7 mL, 1.6 M in hexanes) was added dropwise to the cold solution. Upon completion of the addition, the reaction mixture was allowed to stir in the cold for 1 h, after which time, the reaction mixture appeared dark brown in color. The solution was allowed to warm to RT and then quenched with excess MeI. An aqueous solution of NaOH (15%) was added to the reaction mixture followed by the addition of $Et_2O$. The aqueous phase was extracted with $Et_2O$ (3 × 2 mL); the combined organic layers were dried over $MgSO_4$, the solids were removed by gravity filtration, and the solvent was removed by rotary evaporation, yielding a yellow oil (172 mg). $^1$H NMR spectroscopic analysis revealed that the residue contained alkyne **13**, cyclopropene **14**, and alkene **15** in a ratio of 61:33:6, respectively.[16] The mixture was separated by preparative thin-layer chromatography (silica gel, 3:1 hexanes:$CH_2Cl_2$), yielding alkyne **13** and alkene **15** as a colorless oil, in a ratio of 92:6, respectively, as determined by GC analysis (87 mg, 0.43 mmol, 41%).

**13:** IR ($cm^{-1}$) 700 (s), 996 (m), 1028 (s), 1080 (m), 1145 (s), 1205 (s), 1257 (w), 1450 (m), 1498 (m), 1603 (w), 2238 (w), 2827 (m), 2855 (m), 2938 (s), 3028 (w), 3059 (w); $^1$H NMR ($C_6D_6$) $\delta$ 1.24 (s, 3 H, C≡C-CC$\underline{H_3}$), 1.57 (s, 3 H, $C\underline{H_3}$-C≡C), 2.38 (d, 1 H, PhC$\underline{H}$, $J$ = 7.2 Hz), 3.08 (s, 3 H, MeO), 3.53 (d, 1 H, MeOC$\underline{H}$, $J$ = 7.2 Hz), 7.04 (t, 1 H, Ph *p*-$\underline{H}$, $J$ = 7.8 Hz), 7.14 (t, 2 H, Ph *m*-$\underline{H}$, $J$ = 7.8 Hz), 7.43 (d, 2 H, Ph *o*-$\underline{H}$, $J$ = 7.8 Hz); $^{13}$C NMR ($C_6D_6$) $\delta$ 3.48 ($\underline{C}H_3$-C≡C), 13.36 (C≡$\underline{C}$-$\underline{C}CH_3$), 16.88 (C≡C-$\underline{C}CH_3$), 33.81 (Ph$\underline{C}$H), 58.52 (MeO), 68.51 (MeO$\underline{C}$H), 71.94 ($\underline{C}H_3$-C≡C), 85.53 ($CH_3$-C≡$\underline{C}$), 126.46 (Ph *p*-$\underline{C}$), 128.21 (Ph *m*-$\underline{C}$), 130.95 (Ph *o*-$\underline{C}$), 135.43 (Ph *i*-$\underline{C}$); high-resolution EI-MS for $C_{14}H_{16}O$ ($M^+$) $m/z$ calcd 200.1201, found 200.1192.

**14:** IR ($cm^{-1}$) 802 (m), 1026 (m), 1075 (m), 1261 (m), 1451 (m), 1605 (m), 1651 (m), 2857 (m), 2923 (s), 2958 (s), 3025 (w); $^1$H NMR ($C_6D_6$) $\delta$ 1.58 (s, 3 H, $C\underline{H_3}$-C≡C), 1.64 (s, 3 H, C≡C-$C\underline{CH_3}$), 1.95 (s, 3 H, C=C-$C\underline{H_3}$), 7.01−7.03 (m, 1 H, Ph *p*-$\underline{H}$), 7.12−7.15 (m, 2 H, Ph *m*-$\underline{H}$), 7.50−7.51 (m, 2 H, Ph *o*-$\underline{H}$); $^{13}$C NMR ($C_6D_6$) $\delta$ 3.58 ($\underline{C}H_3$-C≡C), 9.21 (C=C-$\underline{C}H_3$), 15.04 (C≡C-$\underline{C}CH_3$), 24.65 (C≡C-$\underline{C}CH_3$), 70.13 ($CH_3$-$\underline{C}$≡C), 86.12 ($CH_3$-$\underline{C}$≡C), 117.05 (Ph$\underline{C}$=CMe), 117.90 (PhC=$\underline{C}$Me), 128.1[29] (Ph *p*-$\underline{C}$), 128.84 (Ph *i*-$\underline{C}$), 128.88 (Ph *m*-$\underline{C}$), 129.11 (Ph *o*-$\underline{C}$); high-resolution EI-MS for $C_{14}H_{14}$ ($M^+$) $m/z$ calcd 182.1096, found 182.1092.

**Reaction of 1-(*trans*,*trans*-2-Methoxy-1-methyl-3-phenylcyclopropyl)-1-propyne, 13, and 1,1-Dimesitylneopentylsilene, 4.** A solution containing 1,1-dimesitylneopentylsilene, **4**, and fluorosilane **5** in a ratio of 85:15, respectively, dissolved in $C_6D_6$ (0.5 mL) was prepared from fluorosilane **5** (53 mg, 0.17 mmol). To this solution, alkyne **13** (70 mg, 0.35 mmol) in $C_6D_6$ (0.5 mL) was added. The progress of the reaction was monitored over 6 days, after which time no silene remained in the reaction mixture. The relative ratio of alkyne **13** to residual fluorosilane **5** remained unchanged, as determined by $^1$H NMR spectroscopy. The solvent was removed by rotary evaporation, yielding a pale yellow residue (138 mg). The crude mixture was separated by preparative chromatography (silica gel, 3:1 hexanes:$CH_2Cl_2$), yielding a mixture of vinylsilane **16**[3a] and disiloxane **17**[15b] (83:17, 15 mg), fluorosilane **5**, and a mixture of alkyne **13** and alkene **15**.[16]

**Reaction of Silacyclobutene 7 with Sodium Methoxide.** Excess sodium methoxide (30 mg) was added to a mixture of silylacetylene **6a**, silacyclobutene **7**, vinylsilane **8**, and fluorovinylsilane **5** (38 mg) dissolved in THF (2 mL). The solution was refluxed for 18 h. The reaction mixture was then cooled and added to water (2 mL). The mixture was extracted with $Et_2O$,

then brine, and the solvents were removed under vacuum to yield a light yellow oil (35 mg). The oil was purified by preparative thin-layer chromatography (1:1 hexanes:$CH_2Cl_2$) to give ring-opened product **18** as a mixture with silylacetylene **6a** and vinylsilane **8** in a ratio of 24:70:6, respectively (21 mg).[34]

**18:** $^1$H NMR ($C_6D_6$) $\delta$ 0.79 (s, 9 H, C($CH_3$)$_3$), 1.99 (d, 2 H, $CH_2$*t*-Bu, $J$ = 7.2 Hz), 2.10 (s, 6 H, Mes *p*-$CH_3$), 2.40 (s, 12 H, Mes *o*-$CH_3$), 2.70 (s, 2 H, Si$CH_2$), 3.04 (s, 3 H, MeO), 5.35 (t, 1 H, CH=CPh, $J$ = 7.5 Hz), 6.67 (s, 4 H, Mes-H), 7.09 − 7.10 (Ph-H); $^{13}$C NMR ($C_6D_6$) $\delta$ 20.98 (Mes *p*-$CH_3$), 23.90 (Mes *o*-$CH_3$), 29.38 (C($CH_3$)$_3$), 31.16 (C($CH_3$)$_3$), 31.46 (Si$CH_2$), 43.41 ($CH_2$*t*-Bu), 49.48 (MeO), 124.87 (Ph-C=C(H)$CH_2$), 128.42−128.53 (Ph *o*,*m*,*p*-C), 129.65 (Mes *m*-C), 132.18 (Mes *i*-C), 137.70 (Ph-C=C(H)$CH_2$), 139.01 (Mes *p*-C), 143.34 (Ph *i*-C), 144.23 (Mes *o*-C); $^{29}$Si NMR ($C_6D_6$) $\delta$ −1.6; high-resolution EI-MS for $C_{33}H_{44}SiO$ ($M^+$) $m/z$ calcd 484.3161, found 484.3146.

(34) The mixture was also contaminated with the product formed from the reaction of vinylsilane **5** and sodium methoxide.

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**Supporting Information Available:** Experimental details concerning the addition of all alkynes to **4** and $^1$H NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.