A mechanistic study of the addition of alkynes to Brook silenes[1]

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Abstract: The addition of the alkyne-containing mechanistic probes (*trans*-2-phenylcyclopropyl)ethyne, (*trans,trans*-2-methoxy-3-phenylcyclopropyl)ethyne, and (*trans,trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)ethyne (**1a**–**1c**) to a Brook silene 2-(1-adamantyl)-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silene (**14**) was examined. When alkyne **1a** was added to the silene, an ene adduct was observed; however, addition of alkyne **1c** to **14** gave a mixture of silacyclobutenes and silacycloheptenes. The regiochemistry of the phenyl and methoxy substituents on the seven-membered ring of the silacycloheptenes provides convincing evidence for the formation of a biradical intermediate along the reaction pathway.

Key words: Brook silene, alkyne, cycloaddition, reaction mechanism, mechanistic probe.

Résumé : On a étudié l'addition d'alcynes contenant des sondes mécanistiques, le (*trans*-2-phénylcyclopropyl)éthyne, le (*trans,trans*-2-méthoxy-3-phénylcyclopropyl)éthyne et le (*trans,trans*-2-méthoxy-1-méthyl-3-phénylcyclopropyl)éthyne (**1a**–**1c**) à un silène de Brook, le 2-(1-adamantyl)-2-triméthylsiloxy-1,1-bis(triméthylsilyl)-1-silène (**14**). Lorsque l'alcyne **1a** est additionné au silène, on observe la formation d'un adduit ène; toutefois, l'addition de l'alcyne **1c** au silène **14** conduit à la formation d'un mélange de silacyclobutènes et de silacycloheptènes. La régiochimie des substituants phényle et méthoxy sur le cycle à sept chaînons des silacycloheptènes fournit des données convaincantes de la formation d'un intermédiaire biradicalaire au cours de la voie réactionnelle.

Mots-clés : silène de Brook, alcyne, cycloaddition, mécanisme réactionnel, sonde mécanistique.

[Traduit par la Rédaction]

Introduction

There has been recent interest in the use of silenes as reagents in organic synthesis because of their highly regioselective cycloaddition reactions and the variety of transformations that the silicon can subsequently facilitate (1). In addition to their potential use in organic synthesis, the cycloaddition reactions of silenes have been critical for the synthesis of many new silacycles that have not been readily available by any other route (2). Furthermore, the cycloaddition reactions of silenes have played a central role in the development of silene chemistry, as they usually occur cleanly and in high yield, and thus these reactions have been used to provide indirect evidence for transient silenes (2). To fully exploit these important transformations, it is necessary to increase our understanding of their mechanisms.

In this work, we investigate the mechanism of the cycloaddition of alkynes to Brook silenes $(Me_3Si)_2Si{=}C(R)(OSiMe_3)$ (Scheme 1) (2). Brook silenes are a special class of relatively nonpolar silenes, which are important since they are one of the few stable silenes that can be easily synthesized (2). The products derived from the reactions of Brook silenes are, in general, the same as those derived from polar silenes; however, the rate constants for the reactions of Brook silenes appear to be less (2*c*). As with polarized silenes, the products formed from the addition of alkynes to Brook silenes are silacyclobutenes or, possibly, ene adducts if the silene or the alkyne contain an α-hydrogen (2). In an attempt to probe the mechanism of alkyne addition to silenes, Brook and co-workers (3) examined the addition of phenylacetylene and trimethylsilylacetylene to a mixture of the *E*- and *Z*-isomers of $(Me_3Si)(R)Si{=}C(1\text{-}Ad)(OSiMe_3)$, R = Mes (2,4,6-trimethylphenyl) or Tip (2,4,6-triisopropylphenyl); the E/Z ratio of the silene isomers was known but not assigned. In all cases, the ratio of the two isomeric silacyclobutenes produced was found to be identical to the E/Z ratio of the starting silene mixture. It was concluded that these results were, therefore, only consistent with a concerted mechanism of addition of the alkyne to the silene. Ishikawa and co-workers (4) have also examined the addition of alkynes to Brook silenes, both experimentally and theoretically, and in several cases implicate the involvement of biradical intermediates; however, unambiguous evidence for the intermediacy of biradicals was never obtained.

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This paper is dedicated to Professor Richard Puddephatt for his many valued contributions in to Canadian science.

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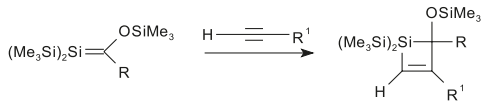
Scheme 1.

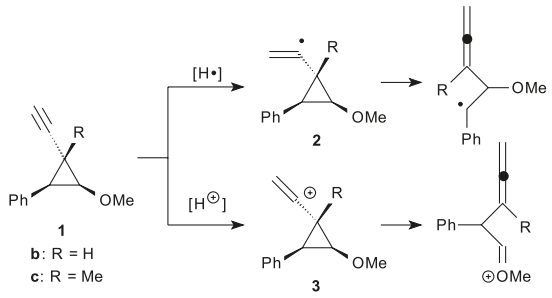


In the past few years, our group has investigated the use of molecular probes as a means of examining the mechanism of alkyne addition to group 14 (di)metallenes (5). We have developed alkynes **1b** and **1c** as mechanistic probes designed to undergo regiochemically distinct rearrangements to differentiate between the formation of α-cyclopropylvinyl radical and ionic intermediates (6). To exemplify, the α-cyclopropylvinyl radical (**2**), derived from alkyne **1b** or **1c**, rapidly ring opens toward the phenyl substituent yielding a benzyl radical. In contrast, the corresponding α-cyclopropylvinyl cation (**3**) undergoes ring-opening rearrangement selectively toward the methoxy substituent (Scheme 2). The analogous anion, as modeled by α-(*trans*-2-phenylcyclopropyl)vinyllithium (**4**) is stable towards ring opening (6*a*). Thus, an efficient method for distinguishing between the formation of all plausible intermediates has been established. (*trans*-2-Phenylcyclopropyl)ethyne **1a**, which does not contain a methoxy substituent on the cyclopropyl ring, undergoes ring-opening rearrangement toward the phenyl substituent when either a radical or a cation is generated at the α-cyclopropylvinyl position (6). Thus, alkyne **1a** is able to detect the formation of a reactive intermediate; however, there will be no structural differentiation observed in the products that are formed.

To examine the mechanism of the addition of alkynes to Brook silenes, we added cyclopropyl alkynes **1a**–**1c** to the Brook silene $(Me_3Si)_2Si{=}C(t\text{-}Bu)(OSiMe_3)$ (**5**) (7). When alkyne **1a** is added to silene **5**, the only products formed are two diastereomers of allene **6** (R^1 = H) (Scheme 3); however, when alkynes **1b** and **1c** are added to silene **5**, either allene **7** (R^1 = OMe), silacyclobutene **8** (R = H), and silacycloheptene **10**, or silacyclobutene **9** (R = Me) and silacycloheptenes **11** and **12** are formed, respectively. The products **6**–**12** have at least two stereocentres, and thus, two or more diastereomers of the products are typically observed, as indicated by the lower case letters following the compound numbers. Presumably, silacycloheptenes **10**, **11**, and **12** are formed by the reaction of intermediate silacyclohepta-1,2-dienes **13a** and **13b** (R = H or Me) with silene **5**.

In silacycloheptenes **10**, **11**, and **12**, the cyclopropyl ring has clearly undergone ring expansion. Using a variety of spectroscopic techniques, the phenyl substituent was found to be α and the methoxy group was found to be β to the former silenic carbon in all the silacycloheptenes. Because of the placement of the phenyl substituents on the 7-membered ring of silacycloheptenes **10**, **11**, and **12**, it was concluded that alkynes **1b** and **1c** must add to silene **5** to give an initial 1,4-biradical. The 1,4-biradical intermediate can then cyclize, forming silacyclobutenes **8** and **9** or undergo ring-opening rearrangement toward the phenyl substituent forming a 1,7-biradical intermediate. Cyclization of the 1,7-biradical intermediate yields silacyclohepta-1,2-diene (**13**). The addition of a second equivalent of silene **5** to **13** produces silacycloheptenes **10**, **11**, and **12**. Although these results provide evidence for the nature of the intermediate formed during the addition of alkynes to Brook silenes, it is important to remember that 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 based on these results. Nonetheless, we wished to explore the generality of these observations, and we now report on the addition of cyclopropyl alkynes **1a**–**1c** to a second example of a Brook silene, $(Me_3Si)_2Si{=}C(1\text{-}Ad)(OSiMe_3)$ (**14**) (8).

Scheme 2.



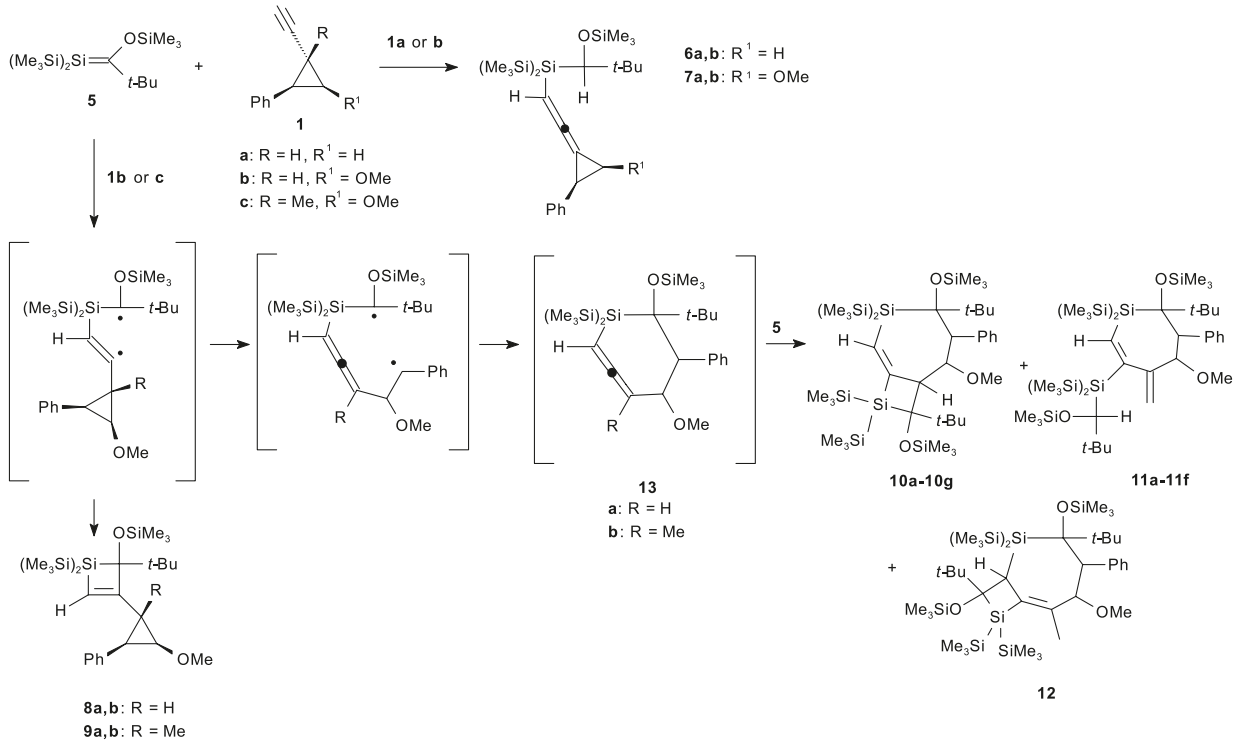
Results and discussion

Irradiation of 1-adamantanecarbonyltris(trimethylsilyl)-silane (**15**) in the presence of (*trans*-2-phenylcyclopropyl)-ethyne **1a** produces a diastereomeric mixture of allenes **16a** and **16b** (53:47), as revealed by ^{1}H NMR spectroscopy (Scheme 4). When alkyne **1a** is added to a solution of preformed silene **14** in the dark, the same product mixture was obtained in a similar ratio.

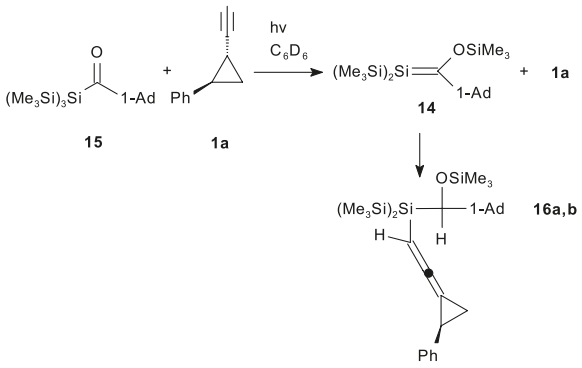
Irradiation of acylsilane **15** in the presence of alkyne **1c** produced a mixture of six diastereomers of silacycloheptene **17a**–**17f** and two diastereomers of silacyclobutene **18a** and **18b** (in ratios of 12:13:32:5:17:2:9:10) as revealed by ^{1}H NMR spectroscopy (Scheme 5). When alkyne **1c** is added to a solution of the preformed silene in the dark, the same product mixture was obtained in a similar ratio. Chromatographic separation of the crude product mixture yielded a mixture of silacycloheptenes **17a**–**17f** (14:17:34:8:24:3) and a mixture of silacyclobutenes **18a** and **18b** (56:44). Further chromatographic separation of the silacycloheptenes **17a**–**17f** yielded silacycloheptenes **17a** and **17b** (58:42) and silacycloheptenes **17c**–**17f** (65:14:19:2). Despite several attempts, no one compound could be isolated from the mixtures.

Allenes **16a** and **16b**, silacycloheptenes **17a**–**17f**, and silacyclobutenes **18a** and **18b** were identified by ^{1}H, ^{13}C, gCOSY, ^{1}H-^{13}C gHSQC and gHMBC, and ^{1}H-^{29}Si gHMBC NMR spectroscopy and mass spectrometry. The spectroscopic features that allowed for the elucidation of the structures of compounds **16a**, **16b**, **17a**–**17f**, **18a**, and **18b** are very similar to those seen for the products derived from the addition of alkynes **1a**–**1c** to silene **5** (7). For **17a**–**17e**, the phenyl substituent was found to be α and the methoxy substituent was found to be β to the former silenic carbon. Silacycloheptene **17f** was only present in a small amount, and as a consequence, not all the diagnostic correlations were evident in the NMR spectral data; however, the ^{1}H NMR spectral data for **17f** is very similar to that of the other

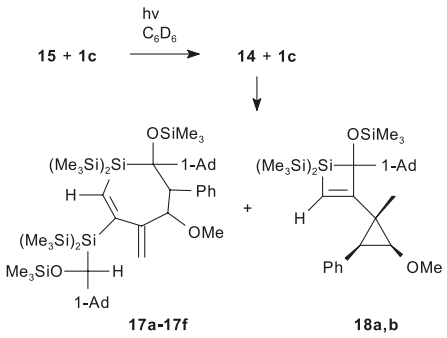
Scheme 3.



Scheme 4.



Scheme 5.



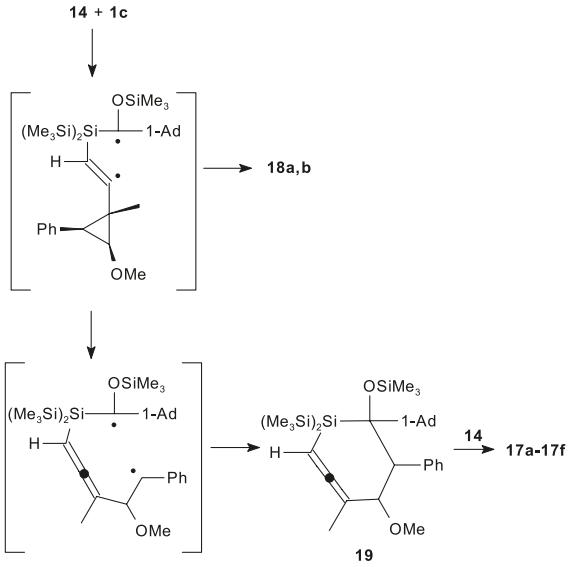
diastereomers of **17**, and therefore, its regiochemistry was assumed to be the same as **17a**–**17e**.

The formation of allenes **16a** and **16b** from the addition of alkyne **1a** to silene **14** is best described as a pericyclic ene-addition, as previously reported for the formation of allenes **6** and **7** (Scheme 3, R^1 = H or OMe) from the addition of alkynes **1a** and **1b** to silene **5** (7).

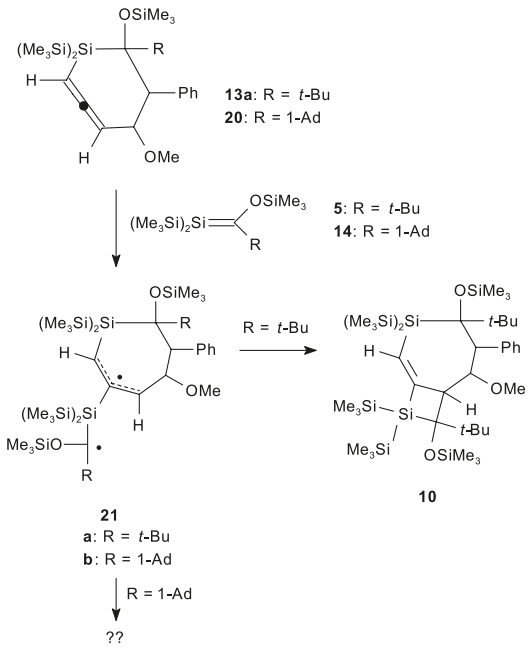
From the structure of silacycloheptenes **17a**–**17f**, it is evident that the cyclopropyl ring has undergone ring expansion. The location of the phenyl substituent on the carbon next to the former silenic carbon is *only* consistent with a mechanism that involves the formation of an α-cyclopropylvinyl *radical* intermediate during the course of the addition of alkyne **1c** to silene **14**: alkyne **1c** must add to the silene to give a 1,4-biradical intermediate that can cyclize forming silacyclobutenes **18a** and **18b** or ring open towards the phenyl substituent to yield a 1,7-biradical intermediate (Scheme 6). Ring closure of the 1,7-biradical intermediate yields silacyclohepta-1,2-diene (**19**), which apparently reacts with a second equivalent of silene via an ene addition to give the observed products **17a**–**17f**. The ene adduct is also likely derived from a biradical intermediate. The addition of alkyne **1c** to silene **14** did not afford a product analogous to **12** (Scheme 3), presumably because of steric effects.

The addition of alkyne **1b** to silene **14** was attempted several times, both by co-irradiation of the alkyne and acylsilane **15** and by addition of the alkyne to the preformed silene; however, a complex mixture of products was formed each time. The addition of alkyne **1b** to the related silene $(Me_3Si)_2Si{=}C(t\text{-Bu})(OSiMe_3)$ **5** yielded the bicycle **10**, where a second equivalent of silene **5** adds to the allene moiety of **13a**, presumably via the biradical intermediate **21a** (Scheme 7) (7). Only one regioisomer of **10** is formed, likely because of steric factors. The addition of silene **14** to the transient silacyclohepta-1,2-diene (**20**) may also form a biradical **21b** (R = 1-Ad) (Scheme 7). Biradical **21b** has no viable reaction pathways; it cannot disproportionate, and the

Scheme 6.



Scheme 7.

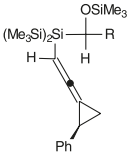
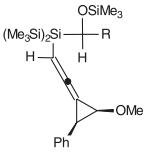
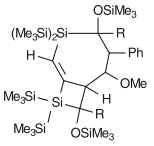
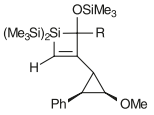
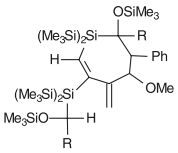
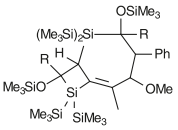
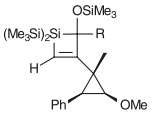


bulk of the adamantyl group apparently impedes cyclization to give a fused ring system. Thus, a complicated mixture of products is obtained when alkyne **1b** was added to silene **14**. The separation and characterization of the many products formed was not pursued.

Conclusions

The structure of silacycloheptenes **17a**–**17f**, resulting from the addition of alkyne **1c** to silene **14**, clearly indicates that the cyclopropyl ring has undergone a ring-opening rearrangement. Based on the location of the phenyl and methoxy substituents on the 7-membered ring in silacycloheptenes **17a**–**17f**, it can be concluded that the intermediate formed is an α-cyclopropylvinyl radical.

Table 1. Comparison of the product ratios obtained by the addition of alkynes **1a**–**1c** to $(Me_3Si)_2Si{=}C(R)(OSiMe_3)$.

		Silene	
Reaction	**Product**	**R= 1-Ad**	**R= t-Bu** (7)
Silene + 1a		100	100
Silene + 1b		0	48
		0	35
		0	17
Silene + 1c		81	68
		0	11
		19	21

The results presented in this report are very similar to those obtained previously (7); a summary of the product ratios obtained in the addition of alkynes **1a**–**1c** to the two silenes is presented in Table 1. The most significant difference is seen in the reactivity of silenes **5** and **14** toward alkyne **1b**. The *t*-butyl silene **5** reacts cleanly with the alkyne to form allenes **7a** and **7b**, silacyclobutenes **8a** and **8b**, and silacycloheptenes **10a**–**10g**. In contrast, the adamantyl silene **14** does not react cleanly with alkyne **1b**, and no products were isolated. Both silenes react with alkyne **1a** to give stereoisomers of an allenic silane (i.e., **6a** and **6b** from **5** or **16a** and **16b** from **14**) as the only products. With alkyne **1c**, a silacyclobutene (i.e., **9a** and **9b** from **5** or **18a** and **18b** from **14**) is formed in approximately the same relative amount. The remaining material is converted to the ring-opened silacyclohepta-1,2-diene (i.e., **13a** or **20**), which adds a second equivalent of the silene, most likely via a biradical that can disproportionate to give a silacycloheptene with an exocyclic methylene group (i.e., **11a**–**11f** from **5** or **17a**–**17f** from **14**) or undergo ring closure in the case of silene **5** (i.e.,

10a–**10g**). Interestingly, the additional steric bulk of the adamantyl group does not influence the reactivity of the initially formed 1,4-biradical; the ratio of silacyclobutene to silacycloheptene products remains the same, ~ 20:80. However, the bulky adamantyl group does influence the course of the reaction of the silacyclohepta-1,2-diene with an additional equivalent of silene: no fused ring products are obtained, presumably because of steric effects; only disproportioned products are observed.

Given that the addition of alkynes **1a**–**1c** to Brook silene **5** gave similar results, we are increasingly confident that the addition of the triple bond of alkynes to Brook silenes involves a biradical intermediate. Not surprisingly, the bulk of the alkyl substituent on the carbon of the silene does not alter the mechanism of the reaction. However, if the alkyne has an α-hydrogen, as in the case of alkyne **1a**, allenes such as **16a** and **16b** may be formed. It is likely that these products are formed by a concerted pericyclic ene-addition (7).

Experimental

General details

All reactions were performed in flame-dried Schlenk tubes, or 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; λ > 350 nm); the NMR tubes were cooled in a cold water jacket (~6 °C). Benzene-d_6 was distilled from LAH prior to use and stored over 4 Å molecular sieves. Acylsilane **15** (8), silene **14** (8), and alkynes **1a**–**1c** (6*a*) were prepared according to the previously reported procedures.

The NMR standards used are as follows: residual C_6D_5H (7.15 ppm) for ^{1}H NMR spectra and C_6D_6 central transition (128.0 ppm) for ^{13}C NMR spectra; Me_4Si as an external standard, 0 ppm, for ^{1}H-^{29}Si gHMBC spectra. IR spectra were recorded (cm^{-1}) from thin films. Mass spectra were obtained using an ionizing voltage of 70 eV, and the data are reported in mass-to-charge units *m*/*z*.

Irradiation of acylsilane 15 and alkyne 1a

A solution of acylsilane **15** (91 mg, 0.22 mmol) and alkyne **1a** (35 mg, 0.24 mmol) dissolved in C_6D_6 (1.5 mL) was irradiated for 3.5 h. ^{1}H NMR spectroscopic analysis of the crude product revealed a mixture of diastereomeric allenes **16a** and **16b** contaminated with small amounts of impurities and unreacted alkyne **1a**. The crude product was purified by preparative thin layer chromatography (silica gel, hexanes) yielding allenes **16a** and **16b** (53:47, 54 mg) as a pale yellow oil (44% yield). **16a** and **16b**: IR (cm^{-1}) 2945 (s), 2904 (s), 2848 (m), 1987 (s), 1603 (w), 1445 (m), 1240 (s), 1045 (s), 835 (s), 692 (m). **16a**: ^{1}H NMR (C_6D_6) δ: 7.16–7.19 (m, Ph*H*), 7.02–7.07 (m, Ph*H*), 5.60 (q, 1H, *H*C=C=C, *J* = 4.9 Hz), 3.70 (s, 1H, Me_3SiOCH), 2.78 (dt, 1H, PhC*H*, *J* = 8.1, 4.7 Hz), 1.99 (br s, 3H, Ad-C*H*), 1.79–1.90 (m, 1H, CH_2), 1.67–1.69 (br m, 12H, Ad-CH_2), 1.67–1.69 (m, 1H, CH_2) (9), 0.35 (s, 9H, $SiMe_3$), 0.34 (s, 9H, $SiMe_3$), 0.11 (s, 9H, $OSiMe_3$); ^{13}C NMR (C_6D_6) δ: 196.82 (C=*C*=C), 141.54 (*i*-Ph*C*), 128.54 (*m*-Ph*C*), 126.91 (*o*-Ph*C*), 126.44 (*p*-Ph*C*), 84.00 (Me_3OSiCH), 83.83 (H*C*=C=C), 76.06 (HC=C=*C*) (10), 41.24 (Ad-CH_2), 38.07 (4° Ad-*C*), 37.42 (Ad-CH_2), 29.05 (Ad-*C*H), 26.11 (Ph*C*H), 18.12 (CH_2), 1.38 ($OSiMe_3$), 1.30 (2 × $SiMe_3$); ^{29}Si NMR (C_6D_6) δ: 14.5 ($OSiMe_3$), –15.0 (2 × $SiMe_3$), –48.1 ($Si(SiMe_3)_2$). **16b**: ^{1}H NMR (C_6D_6) δ: 7.16–7.19 (m, Ph*H*), 7.02–7.07 (m, Ph*H*), 5.52 (q, 1H, *H*C=C=C, *J* = 4.9 Hz), 3.90 (s, 1H, Me_3SiOCH), 2.82 (dt, 1H, PhC*H*, *J* = 7.6, 4.9 Hz), 1.99 (br s, 3H, Ad-C*H*), 1.79–1.90 (m, 2H, CH_2), 1.67–1.69 (br m, 12H, Ad-CH_2), 0.32 (s, 9H, $SiMe_3$), 0.29 (s, 9H, $OSiMe_3$), 0.18 (s, 9H, $SiMe_3$); ^{13}C NMR (C_6D_6) δ: 196.25 (C=*C*=C), 140.93 (*i*-Ph*C*), 128.53 (*m*-Ph*C*), 127.06 (*o*-Ph*C*), 126.44 (*p*-Ph*C*), 83.77 (H*C*=C=C), 81.76 (Me_3OSiCH), 76.10 (HC=C=*C*) (10), 41.36 (Ad-CH_2), 38.01 (4° Ad-*C*), 37.39 (Ad-CH_2), 29.05 (Ad-*C*H), 26.02 (Ph*C*H), 17.42 (CH_2), 1.59 ($OSiMe_3$), 0.84 ($SiMe_3$), 0.44 ($SiMe_3$); ^{29}Si NMR (C_6D_6) δ 14.2 ($OSiMe_3$), –15.3 ($SiMe_3$), –15.7 ($SiMe_3$), –47.7 ($Si(SiMe_3)_2$). **16a** and **16b**: HR EI-MS for $C_{31}H_{52}OSi_4$ (M^+) (*m*/*z*): calcd. 552.3095; found 552.3102.

Irradiation of acylsilane 15 and alkyne 1c

Two solutions of acylsilane **15** (201 mg, 0.49 mmol; 200 mg, 0.49 mmol) and alkyne **1c** (148 mg, 0.80 mmol; 147 mg, 0.79 mmol) dissolved in C_6D_6 (1.5 mL for each) were simultaneously irradiated. The progress of the reactions was monitored by ^{1}H NMR spectroscopy. After 24 h of irradiation, the two reaction mixtures were combined and the solvent was removed by rotary evaporation (649 mg); a mixture of silacycloheptenes **17a**–**17f** and silacyclobutenes **18a** and **18b** in a ratio of 12:13:32:5:17:2:9:10, respectively, was obtained, as determined by ^{1}H NMR spectroscopy. The ratio of the combined products was the same as the ratio of the individual reaction mixtures. Chromatographic separation of the crude mixture (silica gel, hexanes/CH_2Cl_2 7:3) yielded a mixture of silacycloheptenes **17a**–**17f** (14:17:34:8:24:3, 327 mg, 0.32 mmol) and a mixture of silacyclobutenes **18a** and **18b** (56:44, 41 mg, 0.07 mmol). A portion of the mixture of silacycloheptenes **17a**–**17f** (206 mg, 0.20 mmol) was further separated by chromatography (two preparative plates, silica gel, hexanes/CH_2Cl_2 5:1, hexanes/CH_2Cl_2 9:1) yielding a mixture of silacycloheptenes **17a** and **17b** (58:42, 32 mg, 0.03 mmol), and silacycloheptenes **17c**–**17f** (65:14:19:2, 31 mg, 0.03 mmol). Further separation of silacycloheptenes **17c**–**17f** was attempted with little success. In general, no one compound could be separated from the mixture, and thus the compounds were characterized as mixtures. **17a** and **17b** (colourless crystals): IR (cm^{-1}) 2906 (s), 2850 (m), 1452 (w), 1247 (s), 1109 (w), 1043 (s), 837 (s), 745 (m), 684 (w); **17a**: ^{1}H NMR (C_6D_6) δ: 8.21 (br s), 7.07–7.28 (br m) (all Ph*H*), 6.64 (s, 1H, SiC(*H*) = CSi), 5.39 (s, 1H, C=CH_2), 5.02 (br s, 1H, C=CH_2), 4.48 (br s, 1H, MeOC*H*), 4.36 (s, 1H, Me_3SiOCH), 3.77 (d, 1H, PhC*H*, *J* = 2.4 Hz), 3.15 (s, 3H, MeO), 1.65–2.40 (br m, all Ad-C*H*), 0.62 (s, 9H, $SiMe_{3linear}$), 0.51 (s, 18H, 2 × $SiMe_3$), 0.49 (s, 9H, $SiMe_3$), 0.25 (s, 9H, $OSiMe_{3linear}$), 0.06 (s, 9H, $OSiMe_{3cyclic}$); ^{13}C NMR (C_6D_6) δ: 158.87 (SiC(H) = *C*Si), 151.61 (*C*=CH_2), 142.24 (Si*C*(H) = CSi), 137.11 (br s, *i,o*-Ph*C*), 127.50, 127.43, 126.48 (all Ph*C*), 115.07 (C=*C*H_2), 103.1 (Me_3SiOC_{cyclic}) (11), 81.22 (MeO*C*H), 80.66 (Me_3SiOCH), 66.13 (Ph*C*H), 56.11 (MeO), 42.19 (4° Ad-C_{cyclic}), 41.17, 40.93, 40.15, 37.30, 37.18, 29.22 (all Ad-*C*) (12), 5.53 ($OSiMe_{3cyclic}$), 4.17 ($SiMe_3$), 3.31 ($SiMe_3$), 2.99 ($SiMe_3$), 2.45 ($SiMe_3$), 2.40 ($SiMe_3$) (13); ^{29}Si NMR (C_6D_6) δ: 13.5 ($OSiMe_{3linear}$), 6.2 ($OSiMe_{3cyclic}$), –15.3, –17.0 (2 ×

SiMe_3), –12 to –20 (2 × *Si*Me_3) (1), –20.7 (*Si*($SiMe_3$)$_{2cyclic}$), –33.3 (*Si*($SiMe_3$)$_{2linear}$); **17b**: ^{1}H NMR (C_6D_6) δ: 7.37 (br s), 7.07–7.28 (br m) (all Ph*H*), 6.71 (s, 1H, SiC(*H*) = CSi), 5.50 (br s, 1H, C=CH_2), 5.00 (br s, 1H, C=CH_2), 4.53 (br s, 1H, MeOC*H*), 4.28 (br s, 1H, Me_3SiOC*H*), 3.85 (d, 1H, PhC*H*, *J* = 1.8 Hz), 3.16 (s, 3H, MeO), 1.65–2.40 (br m, all Ad-C*H*), 0.60 (s, 9H, $SiMe_3$), 0.50 (s, 9H, $SiMe_3$), 0.49 (s, 9H, $SiMe_3$), 0.38 (s, 9H, $SiMe_3$), 0.28 (s, 9H, OSi$Me_{3linear}$), 0.03 (s, 9H, OSi$Me_{3cyclic}$); ^{13}C NMR (C_6D_6) δ: 159.46 (SiC(H) = *C*Si), 150.47 (*C*=CH_2), 143.24 (Si*C*(H) = CSi), 137.11 (br s, *i,o*-Ph*C*), 127.50, 127.43, 126.48 (all Ph*C*), 115.07 (C=*C*H_2), 103.8 (Me_3SiOC_{cyclic}) (11), 82.48 (Me_3SiO*C*H), 81.22 (MeO*C*H), 65.83 (Ph*C*H), 56.26 (MeO), 42.19 (4° Ad-C_{cyclic}), 41.17, 40.93, 40.15, 37.30, 37.18, 29.22 (all Ad-*C*) (12), 5.53 (OSi$Me_{3cyclic}$), 4.21 ($SiMe_3$), 3.56 ($SiMe_3$), 3.02 ($SiMe_3$), 2.62 (OSi$Me_{3linear}$), 2.26 ($SiMe_3$) (13); ^{29}Si NMR (C_6D_6) δ 13.5 (OS*i*$Me_{3linear}$), 5.8 (OS*i*$Me_{3cyclic}$), –15.3, –16.8 (2 × *Si*Me_3), –12 to –20 (2 × *Si*Me_3) (14), –21.1 (*Si*($SiMe_3$)$_{2cyclic}$), –33.3 (*Si*($SiMe_3$)$_2$) (14). **17a** and **17b**: HR EI-MS for $C_{53}H_{98}O_3Si_8$ (M^+) (*m*/*z*): calcd. 1006.5670, found 1006.5639. **17c**–**17f** (colourless crystals): IR (cm^{-1}) 2905 (s), 2852 (m), 1452 (m), 1248 (s), 1102 (m), 1039 (s), 1000 (w), 837 (s), 746 (w), 683 (w); ^{1}H NMR (C_6D_6) δ: 7.92–7.96, 7.06–7.33 (br m, all Ph*H*, **17c**–**17f**), 6.72 (s, 1H, SiC(*H*) = CSi, **17c**), 6.58 (s, 1H, SiC(*H*) = CSi, **17d**), 6.53 (s, 1H, SiC(*H*) = CSi, **17e**), 6.42 (s, 1H, SiC(*H*) = CSi, **17f**), 5.66 (s, 1H, C=CH_2, **17d**), 5.60 (s, 1H, C=CH_2, **17d**), 5.50 (s, 1H, C=CH_2, **17c**), 5.43 (s, 1H, C=CH_2, **17c**), 5.40 (s, 1H, C=CH_2, **17f**), 5.30 (s, 1H, C=CH_2, **17e**), 4.87 (d, 1H, MeOC*H*, *J* = 6.0 Hz, **17c**), 4.81 (s, 1H, C=CH_2, **17f**) (15), 4.78 (d, 1H, MeOC*H*, *J* = 7.2 Hz, **17d**), 4.75 (br s, 1H, MeOC*H*, **17e**), 4.72 (br s, 1H, C=CH_2, **17e**), 4.68 (s, 1H, MeOC*H*, **17f**) (15), 4.38 (s, 1H, Me_3SiOC*H*, **17f**), 4.35 (s, 1H, Me_3SiOC*H*, **17e**), 4.34 (s, 1H, Me_3SiOC*H*, **17d**), 4.33 (s, 1H, Me_3SiOC*H*, **17c**), 4.11 (s, 1H, PhC*H*, **17e**), 4.10 (s, 1H, PhC*H*, **17f**), 3.75 (d, 1H, PhC*H*, *J* = 6.6 Hz, **17d**), 3.65 (d, 1H, PhC*H*, *J* = 6.0 Hz, **17c**), 3.36 (s, 3H, MeO, **17f**), 3.30 (s, 3H, MeO, **17e**), 3.14 (s, 3H, MeO, **17c**), 3.11 (s, 3H, MeO, **17d**), 1.46–2.13 (br m, all Ad-C*H*, **17c**–**17f**), 0.63, 0.59, 0.58, 0.564, 0.56, 0.55, 0.543, 0.535, 0.52, 0.42, 0.38, 0.33, 0.28, 0.27, 0.268, 0.266, 0.26 (s, all $SiMe_3$ and OSiMe_3, **17c**–**17f**); ^{13}C NMR (C_6D_6) δ: 162.0 (SiC(H) = *C*Si, **17e**) (11), 161.57 (SiC(H) = *C*Si, **17c** and **17d**), 155.9 (*C*=CH_2, **17d**) (11), 155.09 (*C*=CH_2, **17c**), 150.6 (*C*=CH_2, **17e**) (11), 144.80 (Si*C*(H) = CSi, **17c**), 143.23 (Si*C*(H) = CSi, **17d**), 142.75 (Si*C*(H) = CSi, **17e**), 141.23 (*i*-Ph*C*, **17d**), 141.02 (*i*-Ph*C*, **17c**), 139.41 (*i*-Ph*C*, **17e**), 134.46, 134.32 (**17c**), 134.07 (**17d**), 133.32 (**17c**), 133.02, 132.81 (**17e**), 127.23, 127.17 (**17c**), 126.96, 126.73, 126.56, 126.47, 126.24 (**17c**), 126.06 (all Ph*C*, **17c**–**17f**), 120.33 (C=*C*H_2, **17e**), 116.91 (C=*C*H_2, **17d**), 116.30 (C=*C*H_2, **17c**), 99.81 (Me_3SiOC_{cyclic}, **17c**), 97.93 (Me_3SiOC_{cyclic}, **17d**), 94.72 (Me_3SiOC_{cyclic}, **17e**), 84.03 (MeO*C*H, **17e**), 83.07 (MeO*C*H, **17d**), 82.76 (Me_3SiO*C*H, **17e**), 82.67 (MeO*C*H, **17c**), 82.37 (Me_3SiO*C*H, **17c**), 80.17 (Me_3SiO*C*H, **17d**), 64.53 (Ph*C*H, **17e**), 62.55 (Ph*C*H, **17d**), 61.05 (Ph*C*H, **17c**), 57.12 (MeO, **17d**), 56.66 (MeO, **17c**), 56.20 (MeO, **17e**), 43.9 (4° Ad-*C*, **17d**) (11), 43.64 (4° Ad-*C*, **17e**), 43.48 (4° Ad-*C*, **17c**), 41.11, 40.97, 40.75, 40.23, 39.89, 37.18, 37.10, 37.04, 36.90, 32.30, 30.16, 30.10, 29.79, 29.37, 29.29, 29.05 (all Ad-*C*, **17c**–**17f**), 6.27, 6.19, 5.90, 5.08, 4.61, 4.20, 4.16, 4.09, 3.96, 3.45, 3.32, 3.13, 2.62, 2.59, 2.48, 2.35, 2.29, 2.16, 1.36 (all $SiMe_3$ and OSiMe_3, **17c**–**17f**); ^{29}Si NMR (C_6D_6) δ: 13.6 (OS*i*$Me_{3linear}$, **17c**), 13.5–13.7 (OS*i*$Me_{3linear}$, **17d**–**17f**) (14), 6.0 (OS*i*$Me_{3cyclic}$, **17e**), 2.1–2.3 (OS*i*$Me_{3cyclic}$, **17d**, **17f**) (14), 2.2 (OS*i*$Me_{3cyclic}$, **17c**), –11.0, –13.4 (2 × $SiMe_{3cyclic}$, **17c**), –16.0, –17.0 (2 × *Si*Me_3, **17c**), –13 to –18 ($SiMe_3$, **17d**–**17f**) (14), –29.1 (*Si*($SiMe_3$)$_2$, **17e**), –31.5, –31.9 (2 × *Si*($SiMe_3$)$_2$, **17c**), –33.9 (*Si*($SiMe_3$)$_2$, **17d**) (16). **17c**–**17f**: HR EI-MS for $C_{53}H_{98}O_3Si_8$ (M^+) (*m*/*z*): calcd. 1006.5670, found 1006.5631. **18a** and **18b** (white solid): IR (cm^{-1}) 2906 (m), 2851 (w), 1650 (m), 1499 (w), 1451 (w), 1250 (m), 1093 (m), 1035 (m), 836 (s), 752 (w), 698 (w); **18a**: ^{1}H NMR (C_6D_6) δ: 7.59–7.61 (m, 2H, *o*-Ph*H*), 7.21–7.26 (m, 2H, *m*-Ph*H*), 7.06–7.11 (m, 1H, *p*-Ph*H*), 6.04 (s, 1H, SiC(*H*) = C, $^2J_{H\text{-}Si}$ = 8.8 Hz), 3.35 (d, 1H, MeOC*H*, *J* = 7.2 Hz), 3.29 (s, 3H, MeO), 2.68 (d, 1H, PhC*H*, *J* = 7.2 Hz), 1.97–2.10, 1.79–1.85, 1.67–1.74 (m, Ad-C*H*), 1.47 (s, 3H, Me), 0.37 (s, 9H, $SiMe_3$), 0.33 (s, 9H, $SiMe_3$) (17), 0.297 (s, 9H, OSiMe_3); ^{13}C NMR (C_6D_6) δ: 167.81 (SiC(H) = *C*), 137.25 (*i*-Ph*C*), 131.06 (*o*-Ph*C*), 128.2 (*m*-Ph*C*) (11), 126.78 (Si*C*(H) = C), 126.09 (*p*-Ph*C*), 97.64 (Me_3SiO*C*), 70.88 (MeOC*H*), 58.76 (MeO), 42.9 (4° Ad-*C*) (11), 40.30 (Ad-*C*), 37.21 (Ad-*C*), 31.65 (*C*Me), 31.53 (Ph*C*H), 29.55 (Ad-*C*), 13.01 (Me), 3.51 (OSiMe_3), 1.93 ($SiMe_3$), 1.53 ($SiMe_3$); ^{29}Si NMR (C_6D_6) δ: 6.5 (OS*i*Me_3), –12 to –13 (2 × *Si*Me_3) (14), –27.0 (*Si*($SiMe_3$)$_2$); **18b**: ^{1}H NMR (C_6D_6) δ: 7.65–7.66 (m, 2H, *o*-Ph*H*), 7.21–7.26 (m, 2H, *m*-Ph*H*), 7.06–7.11 (m, 1H, *p*-Ph*H*), 5.96 (s, 1H, SiC(*H*) = C, $^2J_{H\text{-}Si}$ = 9.2 Hz), 3.93 (d, 1H, MeOC*H*, *J* = 7.2 Hz), 3.25 (s, 3H, MeO), 2.20 (d, 1H, PhC*H*, *J* = 7.2 Hz), 1.97–2.10, 1.79–1.85, 1.67–1.74 (m, Ad-C*H*), 1.51 (s, 3H, Me), 0.36 (s, 9H, $SiMe_3$), 0.32 (s, 9H, $SiMe_3$) (17), 0.303 (s, 9H, OSiMe_3); ^{13}C NMR (C_6D_6) δ: 168.73 (SiC(H) = *C*), 137.25 (*i*-Ph*C*), 130.72 (*o*-Ph*C*), 128.2 (*m*-Ph*C*) (11), 126.09 (*p*-Ph*C*), 125.35 (Si*C*(H) = C), 98.06 (Me_3SiO*C*), 68.39 (MeOC*H*), 58.47 (MeO), 42.0 (4° Ad-*C*) (11), 40.30 (Ad-*C*), 38.17 (Ph*C*H), 37.21 (Ad-*C*), 30.83 (*C*Me), 29.55 (Ad-*C*), 11.27 (Me), 3.51 (OSiMe_3), 1.93 ($SiMe_3$), 1.53 ($SiMe_3$); ^{29}Si NMR (C_6D_6) δ: 6.5 (OS*i*Me_3), –12 to –13 (2 × *Si*Me_3), –25.8 (*Si*($SiMe_3$)$_2$); **18a**, **18b**: HR EI-MS for $C_{33}H_{56}O_2Si_4$ (M^+) (*m*/*z*): calcd. 596.3357, found 596.3370.

General procedure for the addition of alkynes to silene 14

Excess alkyne **1a** or **1c** (1.5–4 equiv.) dissolved in hexanes or ether was added to silene **14** dissolved in the same solvent (8). The reaction mixture was left to stir overnight. The solvent was removed and the residue was placed under high vacuum to remove the excess alkyne. The residue was analyzed by ^{1}H NMR spectroscopy.

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9. This signal is completely obscured by the signals assigned to the adamantyl ^{1}H's.
10. It was difficult to assign the ^{13}C signals at 76.06 and 76.10 ppm to a specific isomer, and thus the assignments may be reversed.
11. Chemical shift estimated from the ^{1}H-^{13}C gHMBC spectrum.
12. The adamantyl carbon signals were difficult to assign to a specific isomer, and thus the assignments may be reversed.
13. It was difficult to assign the $SiMe_3$ ^{13}C signals to a specific isomer, and thus the assignments may be reversed.
14. It was difficult to assign all ^{29}Si signals because of the extensive overlap of the signals.
15. The ^{1}H signals at 4.81 and 4.68 ppm were difficult to assign specifically to C=CH_2 or MeOC*H* for **17f**, and thus their assignment may be reversed.
16. Not all the expected ^{29}Si correlations could be observed because of the low percentage of some of the isomers of silacycloheptenes **17c**–**17f**.
17. The ^{1}H signals at 0.33 and 0.32 ppm were difficult to assign to a specific isomer, and thus their assignment may be reversed.