Silver-Catalyzed Silacyclopropenation of 1-Heteroatom-Substituted Alkynes and Subsequent Rearrangement Reactions

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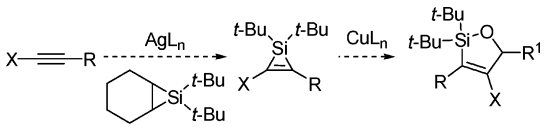
Silver phosphate-catalyzed silylene transfer from silacyclopropane **1** to 1-heteroatom-substituted alkynes resulted in alkoxy-, amino-, and alkylthiolate-substituted silacyclopropenes. Silver-catalyzed silylene transfer to 1-halo- and 1-sulfonyl-substituted alkynes led to insertion of silylene into the carbon−heteroatom bond. Attempts at copper-catalyzed insertion of carbonyl compounds into heteroatom-substituted silacyclopropenes led to rearrangement into silicon-substituted alkynes with a net silylene insertion into the carbon−heteroatom bond. Mechanistic studies were conducted utilizing crossover experiments. A mechanism involving transmetalation/elimination was supported by the observation of crossovers in double-labeling experiments for alkynyl sulfides, halides, and sulfones.

Introduction

The unusual ring strain and reactivity of silacyclopropanes and silacyclopropenes[1−7] has led to the development of C−C bond forming reactions utilizing these compounds.[8−14] For example, the ring expansion of silacyclopropenes by the insertion of carbonyl compounds provides oxasilacyclopentenes (Scheme 1).[12,15] These intermediates were shown to be synthetically valuable because they possess a reactive cyclic vinylsilane, which acts as a synthetic handle, leading to structurally diverse 1,3-diol products upon C−Si bond oxidation.[16]

The synthetic utility of oxasilacyclopentenes is dictated by the functional group tolerance of silylene transfer to alkynes. Generally, protocols for silacyclopropene formation require forcing reaction conditions, such as reducing metals and elevated temperatures,[5−7,17] but the functional group tolerance of these transformations was generally limited. Our group has recently communicated the formation of di-*tert*-butylsilacyclopropenes by silver-catalyzed silylene transfer to several functionalized alkynes, including conjugated enynes and propargylamines and ethers.[15] Application of the silver-catalyzed silylene transfer conditions to 1-heteroatom-substituted alkynes was desired to determine the generality of silylene transfer to alkynes and to enhance the reactivity of the resulting masked allylic alcohol synthons. We herein report the synthesis of silacyclopropenes resulting from silylene transfer to 1-alkoxy-, 1-amino-, 1-alkylthiolate-, and 1-boryl-substituted alkynes. In several cases, formation of alkynylsilanes by the net insertion of silylene into the carbon−heteroatom bond of the alkyne was observed and the mechanisms of these transformations were examined and found to proceed through elimination of the heteroatom substituent, followed by recombination with the alkynylsilane.

Scheme 1. Formation of Silacyclopropenes and Oxasilacyclopentenes



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Results and Discussion

Silver-Catalyzed Silylene Transfer to 1-Heteroatom-Substituted Alkynes. Silver phosphate-cata-

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(1) Gordon, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7419−7422.
(2) Goller, A.; Heydt, H.; Clark, T. *J. Org. Chem.* **1996**, *61*, 5840−5846.
(3) Naruse, Y.; Ma, J.; Inagaki, S. *J. Phys. Chem. A* **2003**, *107*, 2860−2864.
(4) Gordon, M. S.; Boatz, J. A.; Walsh R. *J. Phys. Chem.* **1989**, *93*, 1584−1585.
(5) Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 3715−3716.
(6) Seyferth, D.; Annarelli, D. C.; Vick, S. C. *J. Am. Chem. Soc.* **1976**, *98*, 6382−6384.
(7) Seyferth, D.; Annarelli, D. C.; Vick, S. C. *J. Organomet. Chem.* **1984**, *272*, 123−139.
(8) Franz, A. K.; Woerpel, K. A. *J. Am. Chem. Soc.* **1999**, *121*, 949−957.
(9) Franz, A. K.; Woerpel, K. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 4295−4299.
(10) Franz, A. K.; Woerpel, K. A. *Acc. Chem. Res.* **2000**, *33*, 813−820 and references therein.
(11) Seyferth, D.; Duncan, D. P.; Shannon, M. L. *Organometallics* **1984**, *3*, 579−583.
(12) Seyferth, D.; Vick, S. C.; Shannon, M. L. *Organometallics* **1984**, *3*, 1897−1905.
(13) Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355−1356.
(14) Kroke, E.; Willms, S.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Tetrahedron Lett.* **1996**, *37*, 3675−3678.
(15) Clark, T. B.; Woerpel, K. A. *J. Am. Chem. Soc.* **2004**, *126*, 9522−9523.
(16) For reviews of C−Si bond oxidation, see: (a) Tamao, K. In *Advances in Silicon Chemistry*; Larson, G. L., Ed.; JAI: Greenwich, CT, 1996; Vol. 3, pp 1−62. (b) Fleming, I. *Chemtracts-Org. Chem.* **1996**, *9*, 1−64. (c) Jones, G. R.; Landais, Y. *Tetrahedron* **1996**, *52*, 7599−7662.
(17) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 4824−4827.

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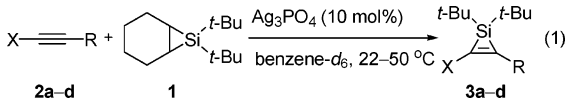
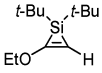
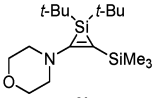
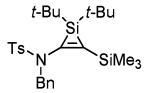
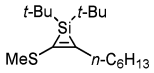


Table 1. Silacyclopropenation of 1-Heteroatom-Substituted Alkynes (Eq 1)

Entry	Product	% Yield[a]	^{29}Si (δ)[b]
1	 **3a**	89 (48)	–48.7
2	 **3b**	96 (74)	–63.6
3	 **3c**	95	–61.8
4	 **3d**	90 (71)	–58.9

[a] As determined by ^{1}H NMR spectroscopic analysis of the product relative to an internal standard ($PhSiMe_3$). Yields in parentheses are based on material isolated by distillation. [b] Chemical shift of the ring-bearing Si atom (99.3 MHz in C_6D_6).

lyzed silylene transfer to 1-heteroatom-substituted alkynes provided functionalized silacyclopropenes **3a**–**d** in good yields. Although Ag_3PO_4 provided attenuated reactivity as compared to more soluble silver salts such as silver triflate and silver trifluoroacetate, an increased functional group compatibility was observed.[15,18] The formation of alkoxy-, amino-, amido-, and thiolate-substituted silacyclopropenes was achieved in 89–96% yield, as determined by NMR spectroscopy (eq 1, Table 1). Full characterization of these air- and moisture-sensitive silacyclopropenes was obtained upon isolation and purification of these products on a preparative scale.[19] The ^{29}Si NMR spectrum of silacyclopropenes **3a**–**d** was characteristic of these substrates, with the silicon shift approximately 5–20 ppm downfield from those of typical di-*tert*-butylsilacyclopropenes (–65 to –70 ppm).[13,17] Previous reports of increased shielding of the ring-bearing silicon atom in the ^{29}Si NMR spectrum with $SiMe_3$ substituents corresponds well with the observed chemical shifts observed for **3a**–**d**. Downfield shifts are consistent with the electronegativity of the heteroatoms decreasing shielding of the silicon atom.[13,17]

Silylene Insertion into 1-Halo- and 1-Sulfonyl-Substituted Alkynes. Silver-catalyzed silylene transfer to alkynes with weakly basic substituents afforded rearranged alkynes without the formation of the corresponding silacyclopropenes. Silylene transfer from silacyclopropane **1** to 1-bromo-1-hexyne **4** led to silylene insertion into the carbon–bromine bond to form bromosilane **5** (Figure 1; eq 2). Attempted silacyclopropenation of ethynyl *p*-tolyl sulfone (**6**) resulted in the formation of the unexpected rearrangement product **7** (Figure 1; eq 3).[20]

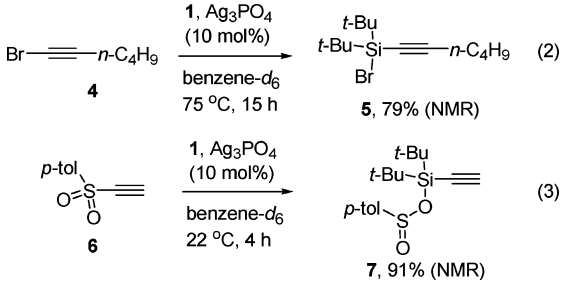


Figure 1. Silver-catalyzed silylene transfer to alkynes **4** and **6**.

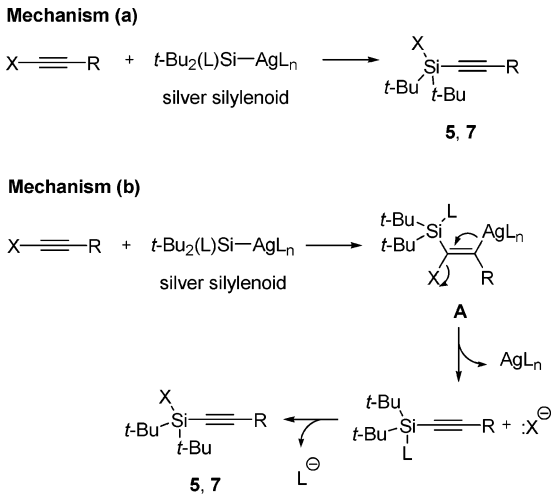
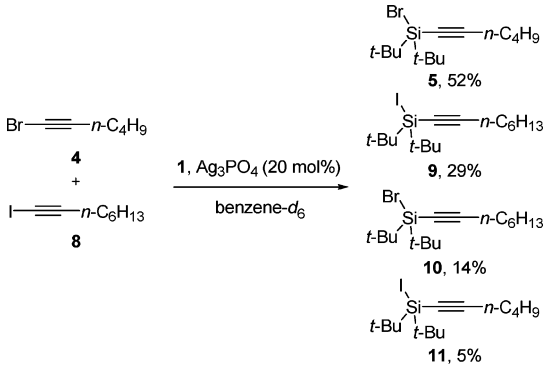


Figure 2. Possible mechanisms for the silver-catalyzed rearrangement of alkynes **4** and **6**.

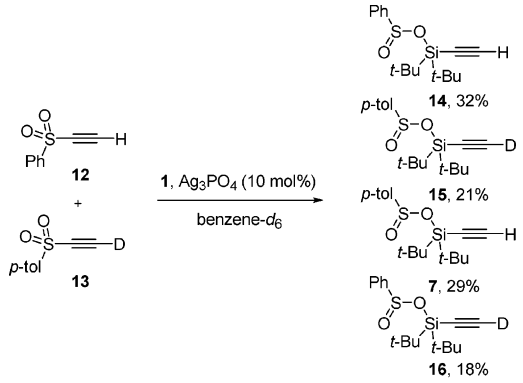
Several mechanisms for the formation of **5** and **7** could be postulated. Two possible mechanisms are supported by literature precedent. Mechanism (a) would involve the formation of a silver silylenoid,[21] followed by direct silylene insertion (Figure 2). This pathway is known for other examples of σ-bond insertions by free silylenes, including those into carbon–heteroatom bonds,[22–25] but formation of the sulfinate would require a subsequent rearrangement to provide **7**. Alternatively, mechanism (b) would entail insertion of the alkyne into the Ag–Si bond of the silver silylenoid. Subsequent β-elimination of the halide or sulfinate and recombination would provide the rearranged alkynes **5** and **7**. This second mechanistic pathway involves silver complex **A**, also postulated in the catalytic cycle for the silver-mediated formation of silacyclopropanes and silacyclopropenes.[21] Vinyl–metal complexes containing a β leaving group

(18) Ćiraković J.; Driver T. G.; Woerpel, K. A. *J. Org. Chem.* **2004**, *69*, 4007–4012.
(19) See the Experimental Section for details.
(20) The structure of **7** was determined by X-ray crystallography (see the Supporting Information for details).
(21) Driver, T. G.; Woerpel, K. A. *J. Am. Chem. Soc.* **2004**, *126*, 9993–10002.
(22) Steele, K. P.; Weber, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6095–6097.
(23) Steele, K. P.; Weber, W. P. *Inorg. Chem.* **1981**, *20*, 1302–1304.
(24) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **2002**, *124*, 3830–3831.
(25) Gehrhus, B.; Lappert, M. F. *J. Organomet. Chem.* **2001**, *617-618*, 209–223.

Scheme 2. Crossover Experiments with 1-Haloalkynes 4 and 8



Scheme 3. Crossover Experiments with Aryl Ethynyl Sulfones 12 and 13



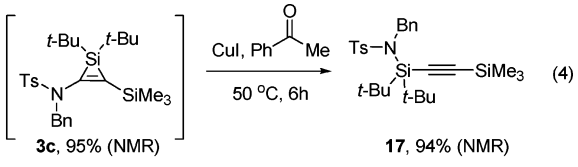
have been shown to undergo elimination mechanisms to provide alkynes.[26−31]

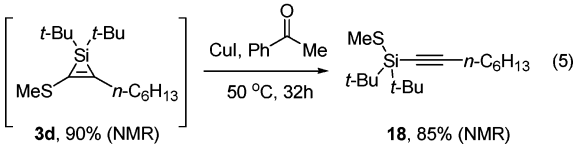
Mechanistic Study of Silylene Insertion. To distinguish between direct silylene insertion (mechanism (a), Figure 2) and the stepwise insertion of silylene (mechanism (b)), double-labeling experiments were performed. Silver phosphate-catalyzed silylene transfer to a mixture of bromoalkyne **4** and iodoalkyne **8** was analyzed to determine if the halide was separated from the alkyne during the course of the reaction (Scheme 2). GCMS analysis of the resulting mixture revealed all four possible products (**5** and **9**−**11**).[32] Formation of the crossover products **10** and **11** suggested that the halide and the alkyne were dissociated during the course of the reaction, providing evidence for the elimination/recombination mechanism (b) rather than the direct silylene insertion mechanism (a). Crossover products **10** and **11** are not believed to be the result of halide exchange between the alkynes **5** and **9**, which was established by a control experiment using an analogous substrate (vide infra).

Examination of ethynyl sulfones **12** and **13** under the double-labeling conditions resulted in crossover of the sulfinate anions. Alkynes **12** and **13** (95% deuterium incorporation) were treated with silacyclopropane **1** and Ag_3PO_4. The GCMS isotope analysis of the unpurified reaction mixture revealed nearly statistical crossover, providing the four alkyne products (Scheme 3).[33] The presence of crossover products **7** and **16** supports the proposal that silver-catalyzed rearrangement of ethynyl sulfones proceeded through mechanism (b).

The positive crossover observed for halogen- and sulfonyl-substituted alkynes under the silver-catalyzed silylene transfer conditions supports the assignment of mechanism (b) for the silylene insertion into alkynes **4** and **6**. Elimination of the halide and sulfinate is believed to occur through intermediate **A** (Figure 2). The dissimilar reactivity of alkynes **4** and **6** from alkynes **2a**−**d** is attributed to the strong leaving group ability of bromide and sulfinate anions.[34]

Copper-Catalyzed Rearrangement of Silacyclopropenes 3c,d. Examining silacyclopropene intermediates **3a**−**d** under metal-catalyzed carbonyl insertion conditions provided further insight into the mechanism of the rearrangement. In the presence of a copper catalyst and acetophenone, sulfonamidosilacyclopropene **3c** and thiolatosilacyclopropene **3d** rearranged to afford alkynylsilanes **17**[35] and **18** (eqs 4 and 5),[36] analogous





to the observations with alkynyl halides and sulfones (Figure 1, eqs 2 and 3). Treatment of ethoxysilacyclopropene **3a** with acetophenone and CuI afforded an unidentifiable mixture, and aminosilacyclopropene **3b** remained unreacted even at elevated temperatures.

The postulated mechanisms by which rearrangement products **17** and **18** form are similar to those proposed for the silver-catalyzed rearrangement (mechanisms (a) and (b), Figure 1). Formation of alkynes **17** and **18** could occur either by copper-catalyzed silylene extrusion to form a copper silylenoid,[37] followed by direct insertion

(26) Averbuj, C.; Kaftanov, J.; Marek, I. *Synlett* **1999**, 1939−1941.
(27) Morlender-Vais, N.; Kaftanov, J.; Marek, I. *Synthesis* **2000**, 917−920.
(28) Takahashi, T.; Kotora, M.; Fischer, R.; Nishihara, Y.; Nakajima, K. *J. Am. Chem. Soc.* **1995**, *117*, 11039−11040.
(29) Nakagawa, T.; Kasatkin, A.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 3207−3210.
(30) Kartashov, V. R.; Povelikina, L. N.; Skorobogatova, E. V. *J. Org. Chem. USSR* **1979**, *15*, 1829−1832.
(31) O'Connor, J. M.; Bunker, K. D.; Rheingold, A. L.; Zakharov, L. *J. Am. Chem. Soc.* **2005**, *127*, 4180−4181.
(32) The nonstatistical crossover is likely due to the different reaction rates of the two alkynes, and formation of insoluble silver halide salts could explain this discrepancy.
(33) Alkynes **12** and **13** were combined under the reaction conditions, in the absence of silacyclopropane **1** and were shown to provide no deuterium scrambling.
(34) For the reported pK_a values of HI (−10)[34a] and $PhSO_2H$ (1.8),[34b] see: (a) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure,* 4th ed.; Wiley-Interscience: New York, 1992; p 250. (b) Burkhard, R. K.; Sellers, D. E.; DeCou, F.; Lambert, J. L. *J. Org. Chem.* **1959**, *24*, 767−769.
(35) The structure of **17** was determined by X-ray crystallography (see the Supporting Information for details).
(36) The isolated silacyclopropene **3d** was also subjected to a catalytic amount of CuI under analogous reaction conditions and was also found to provide rearranged alkyne **18**.
(37) For examples of analogous metal silylenoids with silver and gold, see: (a) Reference 21. (b) Theil, M.; Jutzi, P.; Neumann, B.; Stammler, A.; Stammler, H.-G. *J. Organomet. Chem.* **2002**, *662*, 34−42.

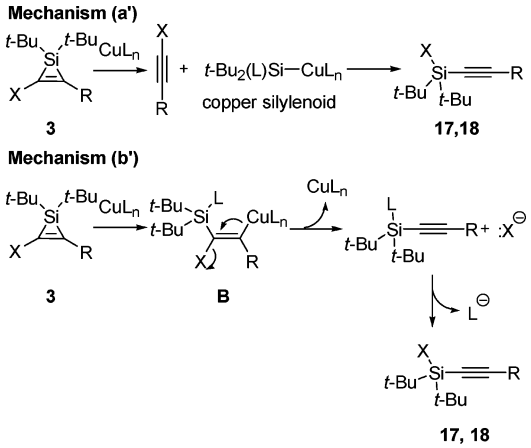
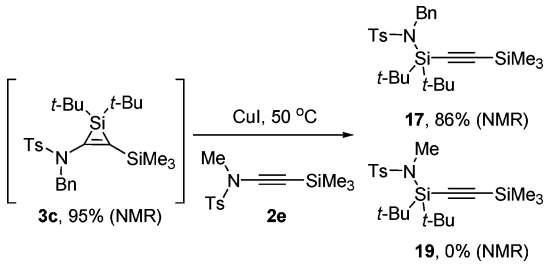


Figure 3. Possible mechanism for the copper-catalyzed rearrangement of **3**.

Scheme 4. Crossover Experiment of Silacyclopropene 3c with Alkyne 2e

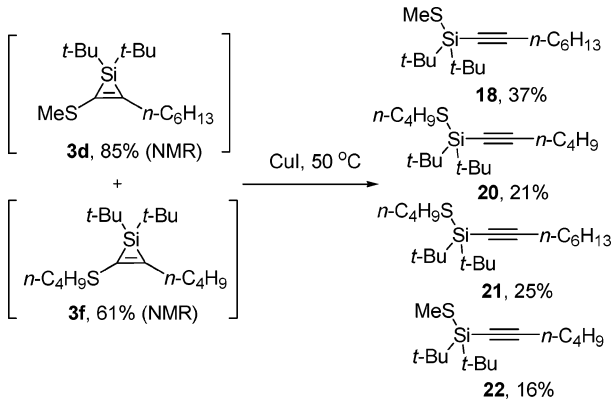


into the C−X bond (mechanism (a′)), Figure 3), or by elimination from the vinyl copper species **B** (mechanism (b′)). The copper-catalyzed insertion of carbonyl compounds into silacyclopropenes[8] is postulated to proceed via intermediate **B** and is analogous to intermediate **A** of mechanism (b) proposed for the formation of alkynylsilanes **5** and **7** (Figure 1, eqs 2 and 3). The vinyl copper intermediate **B** would undergo β-elimination, followed by recombination of the amido or sulfido substituent, resulting in the observed alkynes **17** and **18**.[26−31]

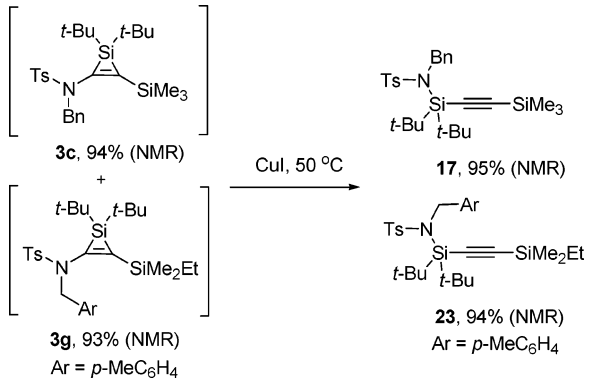
Mechanistic Study of the Copper-Catalyzed Rearrangement of Silacyclopropenes. A crossover experiment was conducted to determine if a copper silylenoid intermediate was involved in the mechanism of the copper-catalyzed rearrangement (mechanism (a′), Figure 3). Silacyclopropene **3c** was constructed under typical conditions (in an NMR tube fitted with an airtight seal), followed by the addition of a second alkynamide **2e** and a catalytic quantity of CuI. The mixture was heated to 50 °C (Scheme 4). Silacyclopropene **3c** rearranged to **17** without the formation of crossover product **19** (as determined by ^{1}H NMR spectroscopy and GCMS). The reverse crossover experiment, formation of the silacyclopropene derived from **2e** and addition of **2c** in the presence of CuI, also did not result in crossover. These experiments indicate that the rearranged alkynes were not formed through copper-catalyzed silylene extrusion and subsequent insertion of a copper-silylenoid species and, therefore, do not support mechanism (a′) for the rearrangement of **3c**,**d** to **17** and **18**, respectively.

After eliminating mechanism (a′) as a possible pathway for the copper-catalyzed rearrangement of silacyclopropenes **3c**,**d**, a second crossover experiment was

Scheme 5. Crossover Experiment with Silacyclopropenes 3d,f



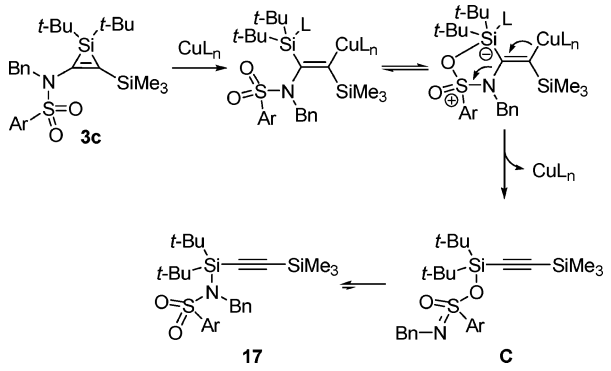
Scheme 6. Crossover Experiment with Silacyclopropenes 3c,g



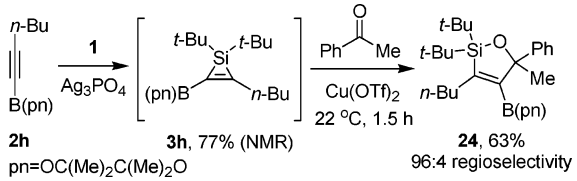
designed to examine if mechanism (b′) was viable for the rearrangement of silacyclopropene **3d** to alkyne **18**. Silacyclopropenes **3d**,**f** were generated in one NMR tube and were treated with CuI to determine if crossover occurred during the rearrangement. In addition to the standard products **18** and **20**, crossover products **21** and **22** were also observed (Scheme 5) by GCMS analysis of the unpurified reaction mixture. This result indicates that elimination of the thiolate substituent occurred, supporting the intermediates proposed in mechanism (b′). Alternatively, exchange of the thiolate substituents could have occurred after formation of alkynes **18** and **20**. To exclude this pathway, a mixture of isolated alkynylsilanes **18** and **20** were resubjected to the reaction conditions, and crossover products **21** or **22** were not formed.

To determine if mechanism (b′) could also be applied to the formation of alkynylsilane **17**, an analogous crossover experiment using sulfonamidosilacyclopropenes **3c**,**g** was examined (Scheme 6). Silacyclopropenes **3c**,**g** were generated in an NMR tube from the corresponding alkynes and treated with CuI at 50 °C to provide only two rearranged alkynes (**17** and **23**), as revealed by ^{1}H NMR spectroscopy and GCMS. Although no crossover was observed for silacyclopropenes **3c**,**g**, mechanism (b′) could not be discounted. It is proposed that the *N*-tosyl substituent interacts with the silicon of the silacyclopropene[38] after transmetalation with CuI (Scheme 7). Upon elimination of the amido substituent, the tosyl group could remain covalently bound to silicon. Rearrangement of intermediate **C** to **17** would be

Scheme 7. Proposed Rearrangement of Silacyclopropenes 3c,g



Scheme 8. In Situ Formation of Oxasilacyclopentene 24



favored thermodynamically.[39] Other thermal and Lewis acid catalyzed rearrangements of O-substituted sulfonimidates to the more stable sulfonamides with alkyl substituents have been reported.[40] We conclude that the silver- and copper-catalyzed formation of alkynylsilanes **5**, **7**, **17**, and **18** proceeds through similar mechanisms (b) and (b′), by β-elimination of the metal−alkene intermediates **A** and **B** (Figures 2 and 3).

Insertion of Acetophenone into a Boryl-Substituted Silacyclopropene. The elimination of halides, sulfinates, alkylthiolates, and sulfonamides in the proposed mechanisms (b) and (b′) require a moderate leaving group to facilitate the elimination of the substituent. Consequently, other silacyclopropenes were envisioned to provide the desired oxasilacyclopentenes upon copper-catalyzed insertion of carbonyl compounds if the silacyclopropene substituent was a poor leaving group.

The reactivity of a 1-alkynylborane was examined and found to provide both the desired silacyclopropene and oxasilacyclopentene. 1-Hexynylpinacolatoborane (**2h**) was treated with a catalytic quantity of Ag_3PO_4 in the presence of **1** to provide silacyclopropene **3h** in good yield (Scheme 8). The chemical shift observed in the ^{29}Si NMR (−68.2 ppm) is consistent with the assigned structure (vide supra). In situ treatment of **3h** with acetophenone and $Cu(OTf)_2$ resulted in regioselective formation of oxasilacyclopentene **24**. The selective formation of **24** suggests that oxasilacyclopentenes could be obtained, provided the substituent on the alkyne was chosen carefully.

Conclusions

Silver-catalyzed silylene transfer from **1** to 1-heteroatom-substituted alkynes **2a**−**d** revealed the mild nature of this method for the formation of heteroatom-functionalized silacyclopropenes. Crossover products observed in double-labeling experiments indicate that 1-halo- and 1-sulfonyl-substituted alkynes form silylene insertion products through migratory insertion/elimination/recombination (mechanism (b), Figure 1). Attempts at copper-catalyzed insertion of carbonyl compounds into sulfonamidosilacyclopropene **3c** and thiolatosilacyclopropene **3d** led to a similar rearrangement, providing a net silylene insertion into the carbon−heteroatom bond. A mechanism involving transmetalation/elimination that proceeds through the vinyl copper complex **B**, analogous to the silver-mediated intermediate **A**, was supported by the observation of a crossover for **3d**. The lack of crossover for silacyclopropene **3c** was postulated to arise from intramolecular trapping of the sulfonamide upon elimination. The insertion of acetophenone into silacyclopropene **3h** to form oxasilacyclopentene **24** displays the ability to construct heteroatom-substituted oxasilacyclopentenes utilizing an appropriate alkyne substituent. Current efforts are focused on expanding the types of alkyne substituents that tolerate the copper-catalyzed insertion of carbonyl compounds, thus providing oxasilacyclopentenes with functionalized alkenes.

Experimental Section

General Procedures. Melting points were obtained using a Büchi 510 melting point apparatus and were reported uncorrected. Analytical gas chromatography (GC) was performed on an Agilent 6850 series chromatograph, equipped with an Agilent 6850 autosampler, and a flame ionization detector with a fused silica capillary column (30 m × 0.32 mm × 0.25 μm) wall-coated with HP-1 (J & W Scientific) was used with helium as the carrier gas or on a gas chromatography−mass spectrometry (GCMS) Thermo-Finnigan Trace Mass Spectrometer Plus quadrupole system with a fused silica capillary column (30 m × 0.32 mm × 0.25 μm) wall-coated with DB-5 (J & W Scientific) using electron ionization (70 eV). Analytical thin-layer chromatography was performed on EM Reagents 0.25 mm silica gel 60-F plates. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on EM Reagents silica gel (SiO_2) 60 (230−400) mesh or on Aldrich Davasil silica gel (SiO_2) as indicated. ^1H NMR and ^{13}C NMR spectra were recorded at 25 °C at 400 and 100 MHz and 500 and 125 MHz, respectively, using Bruker DRX 400 and DRX 500 spectrometers, as indicated. ^{29}Si NMR spectra were recorded at 25 °C at 99.3 MHz. The ^1H NMR data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sext = sextet, m = multiplet, and br = broad), coupling constants (Hz), and integration. The ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane on the δ scale, using tetramethylsilane as an internal standard. The ^{29}Si NMR chemical shifts are reported in ppm from tetramethylsilane on the δ scale, using tetramethylsilane as an external standard. High-resolution mass spectra were

(38) For examples of sulfonyl oxygen nucleophilic reactivity, including stable γ-sultinium ions, see: (a) Braverman, S.; Duar, Y. *J. Am. Chem. Soc.* **1983**, *105*, 1061−1063. (b) Carretero, J. C.; Garcia Ruano, J. L.; Martinez, M. C.; Rodriguez, J. H. *Tetrahedron* **1987**, *43*, 4417−4423. (c) Lucchini, V.; Modena, G.; Pasquato, L. *J. Chem. Soc., Chem. Commun.* **1992**, 293−294. (d) Saginova, L. G.; Polyakova, O. V.; Shabarov, Y. S. *J. Org. Chem. USSR* **1992**, *28*, 938−942. (e) Leca, D.; Song, K.; Amatore, M.; Fensterbank, L.; Lacote, E.; Malacria, M. *Chem. Eur. J.* **2004**, *10*, 906−916.

(39) For the bond dissociation enthalpies of S=N, S=O, Si−N, and Si−O, see: (a) Parsons, S.; Passmore, J. *Inorg. Chem.* **1992**, *31*, 526−528. (b) Roux, M. V.; Temprado, M.; Jimenez, P.; Davalos, J. Z.; Notario, R.; Guzman-Mejia, R.; Juaristi, E. *J. Org. Chem.* **2003**, *68*, 1762−1770. (c) Johnson, E. R.; Clarkin, O. J.; DiLabio, G. A. *J. Phys. Chem. A* **2003**, *107*, 9953−9963.

(40) Challis, B. C.; Iley, J. N. *J. Chem. Soc., Perkin Trans. 2* **1985**, 699−703.

acquired on a LCT Premier quadrupole time-of-flight spectrometer and were obtained by peak matching. Microanalyses were performed by Atlantic Microlabs, Atlanta, GA, or Desert Analytics, Tucson, AZ. Silacyclopropane **1** was stored and manipulated in an Innovative Technologies nitrogen atmosphere drybox. All reaction mixtures to form silacyclopropenes and rearrangement products, unless otherwise specified, were prepared in the drybox. All other reactions, unless specified, were carried out under an atmosphere of nitrogen or argon in glassware that had been flame-dried under a stream of nitrogen or under vacuum. Solvents were distilled or filtered before use. Unless otherwise noted, all reagents and substrates were commercially available. ((Trimethylsilyl)ethynyl)iodonium triflate,[41] *N*-benzyl-*N*-((trimethylsilanyl)ethynyl)-4-methylbenzenesulfonamide (**2c**),[42] 1-hexynylpinacolatoborane (**2h**),[43] 1-bromo-1-hexyne (**4**),[44,45] 1-iodo-1-octyne (**8**),[46,47] ethynyl phenyl sulfone (**12**),[48,49] and cyclohexenesilacyclopropane (**1**)[50,51] were constructed by known methods, and spectral data matched the literature values.

1-(Methylthio)-1-octyne (2d). A procedure reported by Livinghouse[52] was adapted to prepare **2d**. To a cooled (−78 °C) solution of 1-octyne (1.89 mL, 12.8 mmol) in 30 mL of tetrahydrofuran was slowly added *n*-BuLi (9.00 mL, 13.5 mmol, 2.44 M solution in hexanes). After 30 min, methyl disulfide (1.15 mL, 12.8 mmol) was slowly added and the reaction mixture was warmed to room temperature slowly. After 1 h at room temperature, 20 mL of aqueous saturated ammonium chloride was added and the resulting solution was extracted with Et_2O (2 × 20 mL). The organic extracts were rinsed with saturated aqueous sodium chloride (20 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo to provide a pale yellow oil. Purification by bulb-to-bulb distillation (55−65 °C/0.5 mmHg) afforded **2d** as a pale yellow oil (1.62 g, 81 %): ^{1}H NMR (C_6D_6, 500 MHz) δ 2.35 (s, 3H), 2.28 (t, J = 7.0, 2H), 1.50 (p, J = 7.1, 2H), 1.32 (m, 6H), 0.89 (t, J = 7.0, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 93.6, 70.0, 31.5, 28.9, 28.7, 22.7, 20.3, 19.5, 14.2; IR (thin film) 2928, 2858, 1466 cm^{-1}. Anal. Calcd for $C_9H_{16}S$: C, 69.16; H, 10.32. Found: C, 69.24; H, 10.47.

1-(*p*-Tolylsulfonyl)-2-deuterioethyne (13). Alkyne **13** was prepared from *p*-tolyl 2-(trimethylsilyl)ethynyl sulfone, which was constructed by a procedure reported by Stang[49] and matched the spectroscopic data.[53]

A procedure reported by Trudell[48] was adapted to prepare **13.** Silica gel (10 g) was flame-dried under vacuum; upon cooling, D_2O (3.60 mL, 198 mmol) was added, followed by 50 mL of CH_2Cl_2. **A** (0.500 g, 1.98 mmol) was added to the resulting slurry, which was stirred vigorously for 19 h and was filtered and concentrated in vacuo to provide **13** as a white solid (0.352 g, 98%, ∼95% deuterium incorporation by ^{1}H NMR spectroscopy using a single scan). The spectroscopic data matched the reported data.[54]

Alkynamide 2e. A procedure reported by Witulski[55] was adapted to prepare **2e**. To a cooled (0 °C) solution of *N*-methyl-*p*-toluenesulfonamide (2.80 g, 15.1 mmol) in 200 mL of toluene was slowly added *n*-BuLi (6.19 mL, 15.1 mmol, 2.44 M solution in hexanes). The reaction mixture was warmed to room temperature, at which time ((trimethylsilyl)ethynyl)iodonium triflate (4.00 g, 8.88 mmol) was added in small portions (4 × 1.0 g) and the mixture stirred for 16 h. The reaction mixture was passed through a short column of silica gel and was rinsed with 250 mL of Et_2O. The unpurified reaction mixture was concentrated in vacuo to give a yellow oil. Purification by column chromatography (90:10 pentane:Et_2O) afforded **2e** as a yellow solid (1.10 g, 44%): mp 43−45 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.78 (d, J = 8.4, 2H), 7.36 (d, J = 8.4, 2H), 3.05 (s, 3H), 2.46 (s, 3H), 0.15 (s, 9H); ^{13}C NMR (C_6D_6, 125 MHz) δ 145.0, 133.4, 129.9, 128.2, 96.8, 71.6, 39.3, 21.9, 0.3; IR (thin film) 2959, 2167, 1368, 1172, 845 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{19}NO_2SSi$ $(M + Na)^+$ 304.0804, found 304.0801. Anal. Calcd for $C_{13}H_{19}NO_2SSi$: C, 55.48; H, 6.80; N, 4.98. Found: C, 55.67; H, 6.71; N, 4.81.

1-(Butylthio)-1-hexyne (2f). A procedure reported by Livinghouse[52] was adapted to prepare **2f**. To a cooled (−78 °C) solution of 1-hexyne (2.02 mL, 17.6 mmol) in 42 mL of tetrahydrofuran was slowly added *n*-BuLi (7.60 mL, 18.5 mmol, 2.44 M solution in hexanes). After 30 min, butyl disulfide (3.35 mL, 17.6 mmol) was slowly added and the reaction mixture was warmed to room temperature slowly. After 1 h at room temperature, 30 mL of aqueous saturated ammonium chloride was added and the resulting solution was extracted with Et_2O (2 × 30 mL). The organic extracts were rinsed with saturated aqueous sodium chloride (30 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo to provide a pale yellow oil. Purification by bulb-to-bulb distillation (50−65 °C/0.5 mmHg) afforded **2f** as a colorless oil (1.38 g, 46%): ^{1}H NMR (C_6D_6, 500 MHz) δ 2.67 (t, J = 7.3, 2H), 2.31 (t, J = 7.0, 2H), 1.70 (p, J = 7.4, 2H), 1.45 (m, 6H), 0.95−0.89 (t, J = 7.4, 3H; t, J = 7.3, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 94.4, 68.5, 35.4, 31.5, 31.1, 22.1, 21.6, 20.0, 13.82, 13.79; IR (thin film) 2958, 2871, 1462 cm^{-1}.

Alkynamide 2g. To a cooled (−78 °C) solution of *N*-tosyl-*N*-(4-methylbenzyl)ethynylamine[56] (0.890 g, 2.97 mmol) in 15 mL of tetrahydrofuran was slowly added *n*-BuLi (1.28 mL, 3.12 mmol, 2.44 M solution in hexanes). The reaction mixture was stirred at −78 °C for 15 min, at which time chlorodimethylethylsilane (0.458 mL, 3.27 mmol) was added dropwise. After it was stirred at −78 °C for 30 min, the reaction mixture was warmed to room temperature, diluted with 25 mL of saturated aqueous ammonium chloride, and extracted with Et_2O (2 × 25 mL). The organic extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to give **2g** as a yellow solid (1.10 g, 96%): mp 63−64 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.74 (d, J = 8.3, 2H), 7.29 (d, J = 7.9, 2H), 7.16 (d, J = 8.0, 2H), 7.09 (d, J = 7.8, 2H), 4.44 (s, 2H), 2.45 (s, 3H), 2.33 (s, 3H), 0.87 (t, J = 8.0, 3H), 0.50 (q, J = 7.7, 2H), 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.7, 138.3, 134.9, 131.6, 129.7, 129.24, 129.16, 128.0, 95.8, 73.2, 55.5, 21.9, 21.4, 8.4, 7.4, −2.0; IR (thin film) 3030, 2955, 2873, 2169, 1364, 1171, 812 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{27}NO_2SSi$ $(M + Na)^+$ 408.1429, found 408.1434. Anal. Calcd for $C_{21}H_{27}NO_2SSi$: C, 65.41; H, 7.06; N, 3.63. Found: C, 65.54; H, 6.96; N, 3.65.

Silacyclopropene 3a. Representative Procedure A for the NMR Reactions of Silver-Catalyzed Silacyclopropenation. To an NMR tube containing ethoxyacetylene **2a** (0.03 mL, 0.12 mmol, 40% solution in hexanes) and **1** (0.600

(41) Kitamura, T.; Kotani, M.; Fujiwara, Y. *Synthesis* **1998**, 1416−1418.
(42) Witulski, B.; Buschmann, N.; Bergstraber, U. *Tetrahedron* **2000**, *56*, 8473−8480.
(43) Ali, H. A.; El Aziz Al Quntar, A.; Goldberg, I.; Srebnik, M. *Organometallics* **2002**, *21*, 4533−4539.
(44) Inoue, Y.; Fukunaga, T.; Hakushi, T. *J. Org. Chem.* **1983**, *48*, 1732−1737.
(45) Jiang, M. X.-W.; Rawat, M.; Wulff, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 5970−5971.
(46) Trost, B. M.; Rudd, M. T. *Org. Lett.* **2003**, *5*, 4599−4602.
(47) Barluenga, J.; Gonzalez, J. M.; Rodriguez, M. A.; Campos, P. J.; Asensio, G. *Synthesis* **1987**, 661−662.
(48) Chen, Z. M.; Trudell, M. L. *Synth. Commun.* **1994**, *24*, 3149−3155.
(49) Tykwinski, R. R.; Williamson, B. L.; Fischer, D. R.; Stang, P. J.; Arif, A. M. *J. Org. Chem.* **1993**, *58*, 5235−5237.
(50) Driver, T. G.; Franz, A. K.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 6524−6525.
(51) Boudjouk, P.; Black, E.; Kumarathason, R. *Organometallics* **1991**, *10*, 2095−2096.
(52) Duncan, D.; Livinghouse, T. *J. Org. Chem.* **2001**, *66*, 5237−5240.
(53) Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1983**, *48*, 3077−3084.
(54) Kosack, S.; Himbert, G. *Chem. Ber.* **1987**, *120*, 71−77.
(55) Witulski, B.; Stengel, T. *Angew. Chem., Int. Ed.* **1998**, *37*, 489−492.
(56) *N*-Tosyl-*N*-(4-methylbenzyl)ethynylamine was prepared by a three-step sequence; see the Supporting Information for details.

mL, 0.150 mmol, 0.250 M solution of **1** and 0.133 M solution of $PhSiMe_3$ in C_6D_6) was added Ag_3PO_4 (0.005 g, 0.01 mmol). After 10 h, the reaction yield was 89% by ^1H NMR spectroscopy (compared to the $PhSiMe_3$ internal standard) using a single scan.

Representative Procedure B for the Isolation of Silacyclopropenes. To a sealed tube containing ethoxyacetylene **2a** (0.344 mL, 1.41 mmol, 40% solution in hexanes), 7 mL of C_7H_8, and **1** (0.380 g, 1.69 mmol) was added Ag_3PO_4 (0.059 g, 0.14 mmol). After 24 h, the reaction mixture was filtered through a short column of Celite with excess C_7H_8 and concentrated in vacuo. Purification by bulb-to-bulb distillation (30−40 °C/0.5 Torr) gave **3a** as a colorless oil (0.143 g, 48%): ^1H NMR (C_6D_6, 500 MHz) δ 5.89 (s, 1H), 3.84 (q, J = 7.1, 2H), 1.15 (t, J = 7.1, 3H), 1.10 (s, 18H); ^{13}C NMR (C_6D_6, 125 MHz) δ 172.4, 98.5, 68.1, 30.1, 22.0, 15.5; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ −48.7; IR (thin film) 2931, 2857, 1556, 1471 cm^{-1}. Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.58; H, 11.21.

Silacyclopropene 3b. Representative procedure B was followed using 4-((trimethylsilanyl)alkynyl)morpholine **2b** (0.300 mL, 1.54 mmol), **1** (0.413 g, 1.84 mmol), and Ag_3PO_4 (0.065 g, 0.16 mmol), and the mixture was heated to 70 °C for 4 days. Purification by bulb-to-bulb distillation (75−85 °C/0.5 Torr) gave **3b** as a colorless oil (0.372 g, 74%): ^1H NMR (C_6D_6, 500 MHz) δ 3.45 (t, J = 4.9, 4H), 3.11 (t, J = 4.9, 4H), 1.10 (s, 18H), 0.25 (s, 9H); ^{13}C NMR (C_6D_6, 125 MHz) δ 170.3, 101.4, 67.3, 52.1, 30.9, 21.6, 2.7; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ −63.6, −17.2; IR (thin film) 2956, 2855, 1575, 1470 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{17}H_{35}NOSi_2$ $(M + H)^+$ 326.2336, found 326.2331. Anal. Calcd for $C_{17}H_{35}NOSi_2$: C, 62.70; H, 10.83; N, 4.30. Found: C, 62.92; H, 10.62; N, 3.71.

Silacyclopropene 3c. Representative procedure B was followed using alkyne **2c** (0.715 g, 2.00 mmol), **1** (0.539 g, 2.40 mmol), and Ag_3PO_4 (0.084 g, 0.20 mmol) and was heated to 50 °C for 21 h. Filtration of the reaction mixture through Celite and concentration in vacuo provide **3c** as a pale yellow solid (1.06 g, 106%) in >90% purity: mp 93−95 °C; ^1H NMR (C_6D_6, 500 MHz) δ 7.62 (d, J = 8.2, 2H), 7.21 (m, 2H), 7.07 (t, J = 7.3, 2H), 7.00 (m, 1H), 6.71 (dd, J = 8.6, 0.6, 2H), 5.09 (s, 2H), 1.86 (s, 3H), 1.10 (s, 18H), 0.03 (s, 9H); ^{13}C NMR (C_6D_6, 125 MHz) δ 163.3, 143.7, 138.6, 137.8, 130.0, 129.9, 128.9, 128.4, 127.7, 118.3, 52.5, 30.4, 22.2, 21.4, 2.0; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ −61.8, −15.7; IR (thin film) 3054, 2987, 1422, 1265 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{41}NO_2SSi_2$ $(M + H)^+$ 500.2475, found 500.2491. Anal. Calcd for $C_{27}H_{41}NO_2SSi_2$: C, 64.88; H, 8.27; N, 2.80. Found: C, 64.95; H, 8.40; N, 2.61.

Silacyclopropene 3d. Representative procedure B was followed using **2d** (0.250 g, 1.60 mmol), **1** (0.467 g, 2.08 mmol), and Ag_3PO_4 (0.067 g, 0.16 mmol) and heated to 50 °C for 25 h. Purification by bulb-to-bulb distillation (70−85 °C/0.5 Torr) gave **3d** as a colorless oil (0.340 g, 71%): ^1H NMR (C_6D_6, 500 MHz) δ 2.51 (t, J = 7.4, 2H), 2.23 (s, 3H), 1.61 (p, J = 7.4, 2H), 1.33 (m, 6H), 1.08 (s, 18H), 0.90 (t, J = 7.0, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 147.0, 146.5, 32.6, 31.0, 30.47, 30.44, 30.1, 23.5, 22.1, 21.1, 14.8; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ −58.9; IR (thin film) 2957, 2856, 1470 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{17}H_{34}SSi$ $(M + H)^+$ 299.2229, found 299.2234. Anal. Calcd for $C_{17}H_{34}SSi$: C, 68.38; H, 11.48. Found: C, 68.00; H, 11.18.

Silacyclopropene 3f. Representative procedure A was followed using **2f** (0.250 mL, 0.125 mmol, 0.500 M solution in C_6D_6), **1** (0.250 mL, 0.125 mmol, 0.500 M solution in C_6D_6), and Ag_3PO_4 (0.005 g, 0.01 mmol). After 6 h at 50 °C, the reaction yield was 75% by ^1H NMR spectroscopy: ^1H NMR (C_6D_6, 500 MHz) δ 2.77 (t, J = 7.4, 2H), 2.51 (t, J = 7.5, 2H), 1.68 (p, J = 7.4, 2H), 1.60 (p, J = 7.4, 2H), 1.40 (p, J = 7.4, 2H), 1.34 (p, J = 7.4, 2H), 1.07 (s, 18H), 0.92 (t, J = 7.4, 3H), 0.84 (t, J = 7.4, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 146.2, 145.8, 37.8, 33.1, 32.5, 30.7, 30.4, 23.4, 22.5, 22.2, 14.5, 14.2; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ −59.1.

Silacyclopropene 3g. Representative procedure A was followed using **2g** (0.250 mL, 0.125 mmol, 0.500 M solution in C_6D_6), **1** (0.250 mL, 0.125 mmol, 0.500 M solution in C_6D_6), and Ag_3PO_4 (0.005 g, 0.01 mmol). After 40 h at 50 °C, the reaction yield was 99% by ^1H NMR spectroscopy: ^1H NMR ($CDCl_3$, 500 MHz) δ 7.62 (d, J = 8.3, 2H), 7.15 (d, J = 8.2, 2H), 6.90 (d, J = 8.5, 2H), 6.71 (d, J = 8.2, 2H), 5.11 (s, 2H), 2.07 (s, 3H), 1.86 (s, 3H), 1.12 (s, 18H), 0.89 (t, J = 7.9, 3H), 0.55 (q, J = 7.9, 2H), 0.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.0, 143.6, 138.6, 137.0, 134.8, 129.7, 129.5, 128.3, 127.7, 117.1, 52.8, 30.4, 23.5, 22.2, 10.2, 8.3, −0.5, −0.8; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ −61.7, −12.7.

Representative Procedure for Crossover Experiments. To an NMR tube containing 1-bromo-1-hexyne **4** (0.200 mL, 0.100 mmol, 0.500 M solution of **4** and 0.133 M solution of $PhSiMe_3$, the internal standard, in C_6D_6) and 1-iodo-1-octyne **8** (0.200 mL, 0.100 mmol, 0.500 M solution of **8** and 0.133 M solution of $PhSiMe_3$, the internal standard, in C_6D_6) and **1** (0.480 mL, 0.240 mmol, 0.500 M solution of **1** and 0.133 M solution of $PhSiMe_3$ in C_6D_6) was added Ag_3PO_4 (0.017 g, 0.04 mmol). After 5 h at 50 °C, the reaction mixture was filtered through a short column of Davasil with CH_2Cl_2 and concentrated in vacuo. The unpurified reaction mixture was analyzed by GCMS to provide the given ratio of products **5** and **9**−**11**.

Alkynylsilane 5. Representative Procedure C for the Silver-Catalyzed Silylene Insertion and Direct Formation of Alkynylsilanes. To an NMR tube containing 1-bromo-1-hexyne **4** (0.300 mL, 0.150 mmol, 0.500 M solution of 1-bromo-1-hexyne and 0.133 M solution of $PhSiMe_3$, the internal standard, in C_6D_6) and **1** (0.360 mL, 0.180 mmol, 0.500 M solution of **1** and 0.133 M solution of $PhSiMe_3$ in C_6D_6) was added Ag_3PO_4 (0.012 g, 0.03 mmol). After 2 h at 50 °C, the reaction yield was 88% by ^1H NMR spectroscopy. The unpurified reaction mixture was filtered through a short column of Davasil with CH_2Cl_2 and concentrated in vacuo to afford **5** as a colorless oil in >90% purity (0.049 g): ^1H NMR (C_6D_6, 500 MHz) δ 2.32 (t, J = 7.0, 2H), 1.54 (m, 2H), 1.44 (m, 2H), 1.13 (s, 18H), 0.92 (t, J = 7.3, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 111.9, 77.8, 30.6, 27.6, 22.2, 22.1, 19.8, 13.7; IR (thin film) 2935, 2862, 2176, 1470, 822 cm^{-1}; LRMS (GCMS) *m/z* calcd for $C_{14}H_{27}BrSi$ $(M - C_4H_9)^+$ 245.0, found 245.0.

Alkynylsilane 7. Representative procedure C was followed using *p*-tolyl ethynyl sulfone **6** (0.450 mL, 0.225 mmol, 0.500 M solution in C_6D_6), **1** (0.500 mL, 0.250 mmol, 0.500 M solution in C_6D_6) and Ag_3PO_4 (0.009 g, 0.02 mmol). After 7 h the reaction yield was 93% by ^1H NMR spectroscopy. Purification by column chromatography (40:60 hexanes/CH_2Cl_2) afforded **7** as a colorless solid (0.063 g, 83%). Crystallization by slow evaporation of pentane afforded crystals suitable for X-ray crystallographic analysis (crystallographic data are provided, vide infra): mp 51−52 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.67 (d, J = 8.1, 2H), 7.31 (d, J = 7.9, 2H), 2.64 (s, 1H), 2.42 (s, 3H), 1.14 (s, 9H), 1.00 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.4, 142.6, 129.8, 124.3, 97.6, 83.0, 27.2, 27.0, 21.8, 20.34, 20.32; IR (thin film) 3221, 2967, 2935, 2862, 2034, 1471, 1141, 858 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{26}O_2SSi$ $(M + Na)^+$ 345.1320, found 345.1321.

Alkynylsilane 9. Representative procedure C was followed using 1-iodo-1-octyne **8** (0.230 mL, 0.115 mmol, 0.500 M solution in C_6D_6), **1** (0.280 mL, 0.140 mmol, 0.500 M solution in C_6D_6), and Ag_3PO_4 (0.019 g, 0.04 mmol). After 5 h at 50 °C, the reaction yield was 88% by ^1H NMR spectroscopy. The unpurified reaction mixture was filtered through a short column of Davasil with CH_2Cl_2 and concentrated in vacuo afforded **9** as a colorless oil in ~80% purity (0.049 g): ^1H NMR (C_6D_6, 500 MHz) δ 2.33 (t, J = 7.0, 2H), 1.54 (p, J = 7.2, 2H), 1.42 (m, 2H), 1.29 (m, 4H), 1.16 (s, 18H), 0.89 (t, J = 7.0, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 112.8, 77.9, 31.3, 28.5, 28.3, 27.8, 22.6, 22.0, 20.0, 14.1; IR (thin film) 2933, 2860, 2173, 1470, 819 cm^{-1}; LRMS (GCMS) *m/z* calcd for $C_{16}H_{31}ISi$ $(M - C_4H_9)^+$ 321.1, found 321.0.

Alkynylsilane 14. Representative procedure C was followed using phenyl ethynyl sulfone **12** (0.250 mL, 0.125 mmol, 0.500 M solution in C_6D_6), **1** (0.250 mL, 0.125 mmol, 0.500 M solution in C_6D_6), and Ag_3PO_4 (0.005 g, 0.01 mmol). After 7 h the reaction yield was 90% by ^{1}H NMR spectroscopy. Purification by column chromatography (40:60 hexanes/CH_2Cl_2) afforded **14** as a pale yellow oil (0.026 g, 67%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.79 (m, 2H), 7.52 (m, 3H), 2.66 (s, 1H), 1.15 (s, 9H), 1.00 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.2, 132.1, 129.2, 124.3, 97.8, 82.9, 27.2, 27.0, 20.34, 20.31; IR (thin film) 3223, 2967, 2936, 2862, 2035, 1471, 1142, 860 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{24}O_2SSi$ $(M + Na)^+$ 331.1164, found 331.1163. Anal. Calcd for $C_{16}H_{24}O_2SSi$: C, 62.29; H, 7.84. Found: C, 62.45; H, 7.90.

Alkynylsilane 15. Representative procedure C was followed using *p*-tolyl 2-deuterioethynyl sulfone **13** (0.300 mL, 0.150 mmol, 0.500 M solution in C_6D_6, 95% D incorporation), **1** (0.390 mL, 0.195 mmol, 0.500 M solution in C_6D_6) and Ag_3PO_4 (0.006 g, 0.01 mmol). After 7 h the reaction yield was 79% by ^{1}H NMR spectroscopy. Purification by column chromatography (40:60 hexanes/CH_2Cl_2) afforded **15** as a colorless solid (0.039 g, 80%): mp 46−51 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.67 (d, J = 8.1, 2H), 7.31 (d, J = 8.3, 2H), 2.42 (s, 3H), 1.14 (s, 9H), 1.00 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.4, 142.6, 129.8, 124.3, 97.4 (t, J = 36.5 Hz), 82.5 (t, J = 5.9 Hz), 27.2, 27.0, 21.8, 20.32, 20.30; IR (thin film) 2935, 2862, 2360, 1896, 1471, 1141, 856 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{25}DO_2SSi$ $(M + Na)^+$ 346.1384, found 346.1383.

Alkynylsilane 17. Representative Procedure D for the Copper-Catalyzed Rearrangement of Silacyclopropenes to Alkynylsilanes. To an NMR tube (fitted with an airtight seal) containing in situ generated silacyclopropene **3c** was added acetophenone (0.015 mL, 0.13 mmol) and CuI (0.004 g, 0.02 mmol), and this mixture was heated to 50 °C for 18 h, providing **17** in 94% yield by ^{1}H NMR spectroscopy (compared to the $PhSiMe_3$ internal standard) using a single scan. The unpurified reaction mixture was filtered through a short column of Davasil with CH_2Cl_2 and concentrated in vacuo to give a pale yellow solid. Recrystallization by slow evaporation from CH_2Cl_2/hexanes provided **17** as a colorless solid (0.035 g, 56%, crystallographic data are provided, vide infra): mp 124−125 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.53 (d, J = 8.3, 2H), 7.00 (m, 7H), 4.85 (s, 2H), 2.28 (s, 3H), 1.31 (s, 18H), 0.01 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.0, 138.1, 137.8, 129.0, 128.3, 127.9, 127.6, 126.5, 119.5, 110.0, 53.2, 29.4, 23.4, 21.5, −0.5; IR (thin film) 2957, 2933, 2860, 1316, 1152, 843 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{41}NO_2SSi_2$ $(M + Na)^+$ 522.2294, found 522.2307. Anal. Calcd for $C_{27}H_{41}NO_2SSi_2$: C, 64.88; H, 8.27; N, 2.80. Found: C, 65.08; H, 8.31; N, 2.84.

Alkynylsilane 18. Representative procedure D was followed using silacyclopropene **3d** and CuI (0.004 g, 0.02 mmol) at 50 °C for 18 h to provide **18**. Purification by column chromatography (95:5 hexanes/CH_2Cl_2) afforded **18** as a colorless oil (0.037 g, 95%): ^{1}H NMR (C_6D_6, 500 MHz) δ 2.31 (t, J = 7.0, 2H), 2.16 (s, 3H), 1.55 (p, J = 7.2, 2H), 1.43 (m, 2H), 1.30 (m, 4H), 1.09 (s, 18H), 0.89 (t, J = 7.0, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 112.4, 77.4, 31.5, 28.8, 28.6, 28.2, 22.8, 22.3, 20.1, 14.2, 11.8; IR (thin film) 2931, 2859, 2171, 1470, 821 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{34}SSi$ $(M + Na)^+$ 321.2048, found 321.2054. Anal. Calcd for $C_{17}H_{34}SSi$: C, 68.38; H, 11.48. Found: C, 68.48; H, 11.60.

Alkynylsilane 20. Representative procedure D was followed using silacyclopropene **3f** and CuI (0.004 g, 0.02 mmol) at 50 °C for 43 h to provide **20**. Purification by column chromatography (90:10 hexanes/CH_2Cl_2) afforded **20** as a colorless oil (0.024 g, 61%): ^{1}H NMR (C_6D_6, 500 MHz) δ 2.69 (t, J = 7.4, 2H), 2.30 (t, J = 6.9, 2H), 1.63 (p, J = 7.4, 2H), 1.53 (m, 2H), 1.44 (octet, J = 7.4, 4H), 1.08 (s, 18H), 0.95−0.89 (t, J = 7.2, 3H; t, J = 7.2, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 111.8, 77.9, 35.3, 30.9, 29.4, 28.2, 22.13, 22.12, 22.08, 19.8, 13.9, 13.7; IR (thin film) 2933, 2859, 2172, 1468, 820 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{36}SSi$ $(M + Na)^+$ 335.2205, found 335.2206. Anal. Calcd for $C_{18}H_{36}SSi$: C, 69.15; H, 11.61. Found: C, 69.16; H, 11.80.

Alkynylsilane 23. Representative procedure D was followed using silacyclopropene **3g**, acetophenone (0.015 mL, 0.13 mmol), and CuI (0.004 g, 0.02 mmol) at 50 °C for 27 h to provide **23**. Purification by column chromatography (65:35 hexanes/CH_2Cl_2) afforded **23** as a colorless solid (0.062 g, 94%): mp 95 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.53 (d, J = 8.3, 2H), 6.99 (d, J = 8.5, 2H), 6.94 (d, J = 8.0, 2H), 6.81 (d, J = 8.1, 2H), 4.80 (s, 2H), 2.31 (s, 3H), 2.23 (s, 3H), 1.30 (s, 18H), 0.89 (t, J = 7.9, 3H), 0.47 (q, J = 7.9, 2H), 0.04 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.9, 138.0, 136.1, 135.0, 129.0, 128.29, 128.28, 128.1, 118.8, 110.6, 53.0, 29.5, 23.3, 21.5, 21.1, 7.9, 7.4, −2.6; IR (thin film) 2959, 2860, 2361, 1317, 824 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{29}H_{45}NO_2SSi_2$ $(M + Na)^+$ 550.2607, found 550.2612. Anal. Calcd for $C_{29}H_{45}NO_2SSi_2$: C, 65.98; H, 8.59; N, 2.65. Found: C, 66.06; H, 8.52; N, 2.59.

Oxasilacyclopentene 24. Representative procedure B was followed using **2h** (0.298, 1.43 mmol), **1** (0.480 g, 2.14 mmol), and Ag_3PO_4 (0.059 g, 0.14 mmol) at 23 °C for 14 h. Purification by bulb-to-bulb distillation (80−90 °C/0.5 Torr) gave **3h** as a colorless oil (0.288 g, 58%): ^{1}H NMR (C_6D_6, 500 MHz) δ 2.75 (t, J = 7.4, 2H), 1.70 (p, J = 7.6, 2H), 1.44 (p, J = 7.3, 2H), 1.15 (s, 12H), 1.12 (s, 18H), 0.94 (t, J = 7.3, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 176.6, 127.7, 83.2, 35.1, 32.1, 30.8, 25.3, 23.3, 21.6, 14.7; ^{29}Si NMR (C_6D_6, 99.3 MHz) δ −68.2; IR (thin film) 2933, 2859, 1470 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{20}H_{39}BO_2Si$ $(M + H_3O)^+$ 369.3000, found 369.2997. Anal. Calcd for $C_{20}H_{39}BO_2Si$: C, 68.55; H, 11.22. Found: C, 68.36; H, 11.13.

To an in situ prepared solution of silacyclopropene **3h**, generated following representative procedure A, was added acetophenone (0.036 mL, 0.31 mmol) and $Cu(OTf)_2$ (0.006 g, 0.02 mmol). After 1.5 h, the reaction mixture was filtered through a short column of Davasil with CH_2Cl_2 and concentrated in vacuo. Purification by column chromatography (70:30 hexanes/CH_2Cl_2) afforded **24** as a colorless oil (0.030 g, 63%): ^{1}H NMR (C_6D_6, 500 MHz) δ 7.43 (d, J = 7.3, 2H), 7.26 (t, J = 7.5, 2H), 7.19 (t, J = 7.3, 1H), 2.76 (m, 1H), 2.14 (m, 1H) 1.75 (s, 3H), 1.70 (heptet, J = 5.4, 2H), 1.37−1.28 (m, 2H; d, J = 2.2, 12H), 1.05 (s, 9H), 0.88 (t, J = 7.4, 3H), 0.79 (s, 9H); ^{13}C NMR (C_6D_6, 125 MHz) δ 179.8, 146.2, 127.8, 127.2, 127.0, 91.0, 82.9, 35.0, 34.5, 28.6, 28.5, 28.0, 25.3, 25.1, 23.9, 20.94, 20.88, 14.1 (two peaks overlap); IR (thin film) 2933, 2857, 1340, 1145, 823 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{47}BO_3Si$ $(M + Na)^+$ 493.3291, found 493.3306. Anal. Calcd for $C_{28}H_{47}BO_3Si$: C, 71.47; H, 10.07. Found: C, 71.54; H, 10.11.

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Supporting Information Available: Experimental procedures and characterization data for the preparation of *N*-tosyl-*N*-(4-methylbenzyl)ethynylamine and spectroscopic, analytical, and X-ray data for the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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