Comparative Study of the Reactivity of Brook and Couret Silenes: Aldehyde Addition

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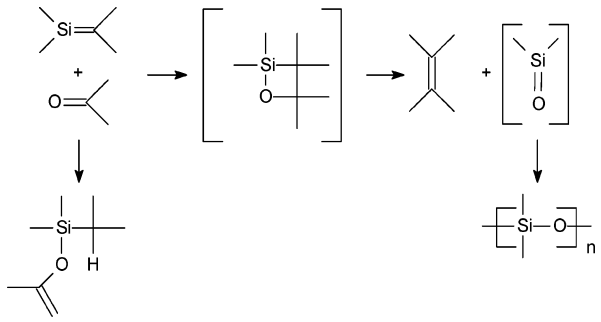
The addition of the mechanistic probe *trans*-2-phenylcyclopropanecarbaldehyde (**10**) to the naturally polarized Couret silene $Mes_2Si{=}C(H)(CH_2\text{-}t\text{-}Bu)$ (**2**) and the relatively nonpolar Brook silenes $(Me_3Si)_2Si{=}C(R)(OSiMe_3)$, where R = *t*-Bu (**1a**), 1-Ad (**1b**), respectively, was examined. The addition of aldehyde **10** to silene **2** produces vinylsilane **17**, siloxetanes **18a**−**c**, and ester **19**. Upon chromatography, siloxetanes **18a**−**c** were found to undergo conversion to the alkenes *trans*-**20** and *cis*-**20** and $(Mes_2SiO)_2$. The formation of siloxetanes **18a**−**c** and ester **19** is consistent with the formation of a 1,4-zwitterionic intermediate during the course of the addition of the aldehyde to silene **2**. The addition of the cyclopropyl aldehyde **10** to Brook silenes produces the *cis*,*trans*-dienes **23** and **26**, siloxetanes **24a**,**b** and **27a**,**b**, and acylsilanes **25a**,**b** and **28a**,**b** derived from silenes **1a** and **1b**, respectively. The formation of the *cis*,*trans*-dienes and the siloxetanes provides compelling evidence for the formation of an α-cyclopropylcarbinyl radical during the course of the addition of the aldehyde to the Brook silenes. This work provides a unique comparison of the reactivities of the naturally polarized Couret silene **2** and the relatively nonpolar Brook silenes **1a**,**b** toward aldehydes. It is evident from the results that the polarity of the Si=C bond of the silene has a profound influence on the mechanism of the addition of aldehydes to silenes.

Introduction

The addition of carbonyl compounds to silenes, compounds containing a silicon−carbon double bond, to give an alkene and a cyclosiloxane was one of the first and remains one of the most common and important reactions of these species.[1,2] For many years, the alkene and cyclosiloxane were postulated to be secondary products of the reaction derived from a formal [2 + 2] retrocyclization of the primary product, an intermediate siloxetane. Retrocyclization of a siloxetane would result in the formation of an alkene and a silanone; however, since silanones are unstable, they were believed to undergo rapid oligomerization to yield the observed cyclosiloxanes. The overall transformation is often described as a pseudo-Wittig reaction (Scheme 1). In early experiments, no direct evidence for the formation of a siloxetane was obtained, and thus, for many years, the isolation of a "Wittig" alkene and a cyclosiloxane from a reaction between a carbonyl compound and a putative silene was accepted as good evidence not only for the formation of an intermediate siloxetane but, more importantly, of a transient silene.[2] The addition of an enolizable carbonyl compound to a silene often results in the formation of an ene-addition product which does provide some direct evidence for an intermediate carbonyl adduct of the silene. To verify the hypothesis that a siloxetane was indeed the primary product of addition of a nonenolizable carbonyl compound to a silene, a stable derivative of such a compound became an important and challenging target.

Scheme 1. Addition of a Carbonyl Compound to a Silene



One of the first examples of a stable siloxetane was provided by Märkl et al.[3] Addition of tetrasubstituted cyclopentadienones to $(Me_3Si)_2Si{=}C(R)(OSiMe_3)$, where R = Ph, *t*-Bu, resulted in the formation of stable siloxetanes (Scheme 2). Since Märkl's initial report, a number of other stable siloxetanes, derived from the addition of a carbonyl compound to a silene, have been reported.[4−6] For many of these siloxetanes, the stability is

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(1) (a) Morkin, T. L.; Leigh, W. J. *Acc. Chem. Res.* **2001**, *34*, 129. (b) Morkin, T. L.; Owens, T. R.; Leigh, W. J. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 2001; Chapter 17. (c) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71. (d) Müller, T.; Ziche, W.; Auner, N. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Chapter 16. (e) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1989; Chapter 17. (f) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1. (g) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (h) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141. (i) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. (j) Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. M. *Acc. Chem. Res.* **1975**, *8*, 18.

(2) (a) Bush, R. D.; Golino, C. M.; Homer, G. D.; Sommer, L. H. *J. Organomet. Chem.* **1974**, *80*, 37. (b) Golino, C. M.; Bush, R. D.; Roark, D. N.; Sommer, L. H. *J. Organomet. Chem.* **1974**, *66*, 29. (c) Roark, D. N.; Sommer, L. H. *J. Chem. Soc., Chem. Commun.* **1973**, 167.

(3) Märkl, G.; Horn, M. *Tetrahedron Lett.* **1983**, *24*, 1477.

(4) (a) Toltl, N. P.; Leigh, W. J. *Organometallics* **1996**, *15*, 2554. (b) Barton, T. J.; Bain, S.; Ijadi-Maghsoodi, S.; Magrum, G. R.; Paul, G.; Robinson, L. R.; Yeh, M. H. In *Silicon Chemistry*; Corey, E. R., Corey, J. Y., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, U.K., 1988; p 201. (c) Saso, H.; Yoshida, H.; Ando, W. *Tetrahedron Lett.* **1988**, *29*, 4747. (d) Wiberg, N.; Preiner, G.; Schieda, O. *Chem. Ber.* **1981**, *114*, 3518.

(5) (a) Brook, A. G.; Chatterton, W. J.; Hughes, D. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246. (b) Brook, A. G.; Chatterton, W. J.; Lough, A. L. *Organometallics* **1991**, *10*, 2752.

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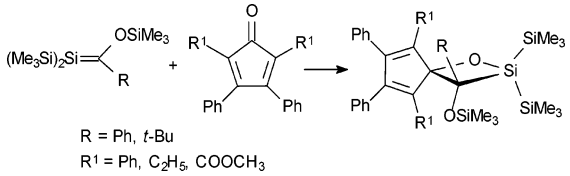
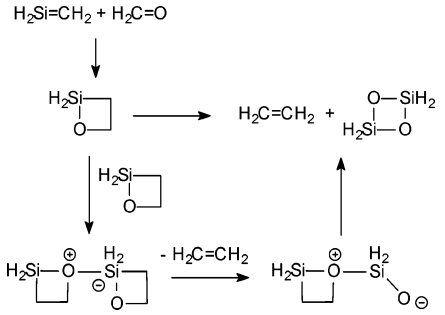
Scheme 2. First Example of Stable Siloxetanes

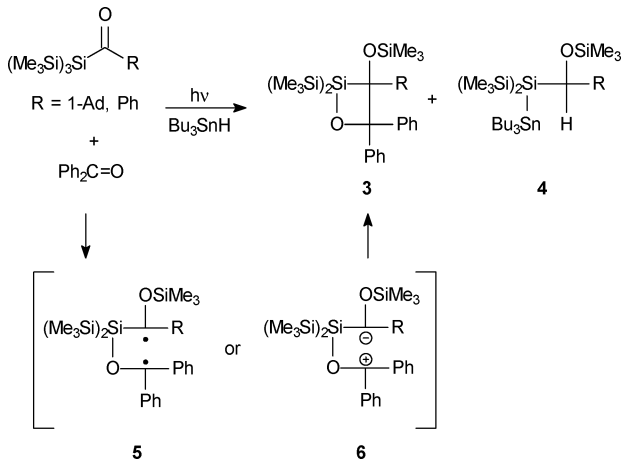


Scheme 3. Formation of Cyclodisiloxane and Ethene from Siloxetane



attributed to the presence of bulky substituents, although this is counterintuitive, since the relief of steric strain presumably would provide a driving force for the retrocyclization. However, in most cases, stable siloxetanes with bulky substituents do not undergo retrocyclization. To provide insight into this matter, the addition of formaldehyde to the parent silene, $H_2Si{=}CH_2$, to form the intermediate siloxetane and its decomposition to ethene and the 1,3-cyclodisiloxane was examined using ab initio methods.[7] The formation of the silanone did not lower the relative energy of the products relative to the siloxetane; however, the formation of the 1,3-cyclodisiloxane, the dimer of silanone, does provide a sufficient decrease in the total energy of the products to drive the reaction forward (Scheme 3). The oxygen of the siloxetane was found to carry a significant negative charge, and thus, it was concluded that the oxygen center of one siloxetane can nucleophilically add to the silicon center of a second molecule of siloxetane to yield, after elimination of ethene, the 1,3-cyclodisiloxane without the intermediate formation of silanone. These results provide a reasonable explanation for why retrocyclization of siloxetanes bearing bulky substituents is not typically observed. Thus, our current understanding is that nonenolizable ketones and aldehydes add to silenes to give siloxetanes, which, depending on the substituents, may undergo a subsequent bimolecular reaction to give a Wittig alkene and a cyclosiloxane. The focus of this work is the mechanism of the first step of this transformation: the addition of the carbonyl compound to the silene. The relatively nonpolar Brook silenes $(Me_3Si)_2Si{=}C(R)(OSiMe_3)$, where R = *t*-Bu (**1a**), 1-Ad (**1b**),[8,9] and the naturally polarized Couret silene $Mes_2Si{=}C(H)(CH_2\text{-}t\text{-}Bu)$ (**2**)[10] were selected as ideal substrates for a comparative study to examine the influence of the polarity of the Si=C group on the mechanism of the addition of the C=O group.

Scheme 4. Formation of Siloxetane 3 in the Presence of Bu_3SnH



The addition of benzaldehyde and acetophenone to the stable neopentylsilene $Mes_2Si{=}C(H)(CH_2\text{-}t\text{-}Bu)$ (**2**) has been examined.[10b] In both cases, siloxetanes and ene-addition products were obtained. The addition of acetophenone to silene **2** yielded products derived from both the silene and acetophenone acting as the enophile. The siloxetanes were proposed to form by way of a zwitterionic intermediate; however, no evidence for this proposal was provided. The addition of carbonyl compounds to Brook silenes, of the type $(Me_3Si)_2Si{=}C(R)(OSiMe_3)$, typically forms siloxetanes.[3,5,11] The addition of an α,β-unsaturated aldehyde or ketone to a Brook silene often results in the formation of a [4 + 2] cycloaddition product; in some cases, two regioisomers of the [4 + 2] cycloadduct are observed.[5b]

Benzaldehyde is the *only* carbonyl compound that has been added to both Couret's neopentylsilene **2** and a Brook silene (**1a**).[10b,5a] In both cases, a siloxetane is formed. An ene-addition product was also observed in the addition to silene **2**, where benzaldehyde acted as the enophile; however, this type of product is not possible with the Brook silene.

There is a good deal of speculation in the literature regarding the mechanism for the addition of carbonyl compounds to silenes: the intermediacy of both zwitterions and biradicals has been proposed;[10b,12−14] however, little evidence, experimental or theoretical, has been presented.

Brook and co-workers examined the addition of benzophenone to silenes $(Me_3Si)_2Si{=}C(R)(OSiMe_3)$, R = 1-Ad, Ph, formed by irradiation of the corresponding acyltris(trimethylsilyl)silane, in the presence of an excess of the radical trap Bu_3SnH.[5a] The observed products were siloxetane **3** and the Bu_3SnH-trapped silene **4** in a ratio of 90:10, respectively (Scheme 4). Brook rationalized that, if a biradical intermediate were formed (**5**; Scheme 4), products derived from the addition of Bu_3SnH to the putative intermediate biradical should have been observed. Since this was not the case, these results were taken as evidence that the intermediate formed during the addition of benzophenone to the silene was zwitterionic in nature

(6) (a) Schmohl, K.; Reinke, H.; Oehme, H. *Eur. J. Inorg. Chem.* **2001**, 481. (b) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1999**, *121*, 11336. (c) Suginome, M.; Takama, A.; Ito, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1930. (d) Trommer, M.; Miracle, G. E.; Eichler, B. E.; Powell, D. R.; West, R. *Organometallics* **1997**, *16*, 5737.

(7) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 1186.

(8) Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676.

(9) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

(10) (a) Delpon-Lacaze, G.; Couret, C. *J. Organomet. Chem.* **1994**, *480*, C14. (b) Delpon-Lacaze, G.; de Battisti, C.; Couret, C. *J. Organomet. Chem.* **1996**, *514*, 59.

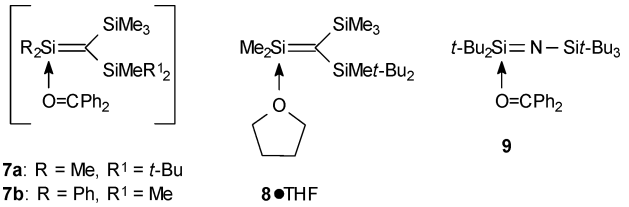
(11) Ishikawa, M.; Matsui, S.; Naka, A.; Ohshita, J. *Organometallics* **1996**, *15*, 3836.

(12) Barton, T. J. *Pure Appl. Chem.* **1980**, *52*, 615.

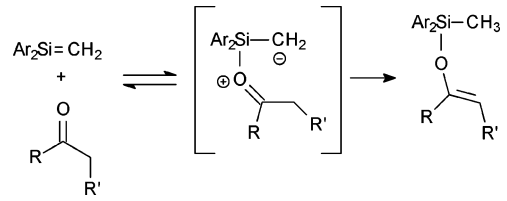
(13) Auner, N.; Seidenschwarz, C. *Z. Naturforsch., B* **1990**, *45*, 909.

(14) (a) Wiberg, N.; Hwang-Park, H.-S.; Lerner, H.-W.; Dick, S. *Chem. Ber.* **1996**, *129*, 471. (b) Wiberg, N.; Link, M. *Chem. Ber.* **1995**, *128*, 1231.

Chart 1. Selected Zwitterionic Complexes of Silenes or Silanimines



Scheme 5. Mechanism for the Addition of Enolizable Carbonyl Compounds to Diarylsilenes



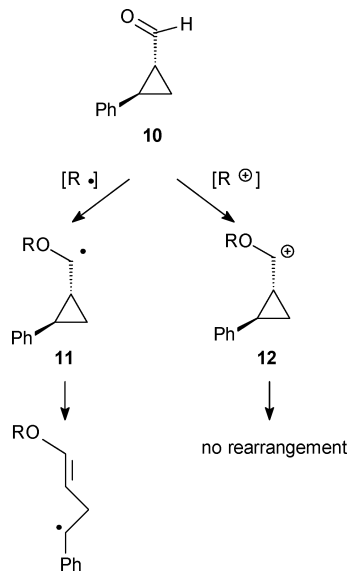
(**6**; Scheme 4). The conclusions of this experiment will be revisited in the Discussion.

Wiberg proposed that the addition of benzophenone to the silenes $R_2Si{=}C(SiMe_3)(SiMeR^1{}_2)$, where R = Me and R^1 = *t*-Bu or R = Ph and R^1 = Me, forms the zwitterionic complexes **7a**,**b** as intermediates during the cycloaddition (Chart 1).[1h,14] The proposal is reasonable, given that the THF complex of a related silene has been isolated and characterized by X-ray crystallography (**8**·THF; Chart 1).[15] Similarly, the molecular structure of a zwitterionic adduct between benzophenone and a silanimine has been determined (**9**; Chart 1).[16]

Evidence in support of the formation of a zwitterionic complex between a silene and a carbonyl compound, as proposed by Wiberg, was provided by Leigh and co-workers by examination of the kinetics of the addition of a series of enolizable carbonyl compounds to substituted diarylsilenes.[17] Both electron-withdrawing substituents on the silenic silicon center and electron-donating substituents on the carbonyl carbon resulted in an increase in the rate constant of the addition reaction. The effect of solvent polarity on the addition of the carbonyl compound to the silene was also examined; the additions were carried out in isooctane, hexane, or acetonitrile. The rate constant for the addition of acetone to the diarylsilenes decreased in acetonitrile, presumably due to coordination of the solvent with the silene.[17a] Furthermore, when deuterated acetone was added to the diarylsilene, a primary kinetic isotope effect was observed.[17a] These findings provide convincing evidence for the reversible formation of a zwitterionic complex between the silene and the carbonyl compound followed by rate-limiting proton transfer (Scheme 5). Leigh and co-workers also examined the addition of acetone to $Ph_2Si{=}C(H)(CH_2\text{-}t\text{-}Bu)$ and found similar results, which led to the conclusion that the mechanism was analogous to that of the related $Ar_2Si{=}CH_2$ derivative: i.e., a mechanism of addition passing through a zwitterionic intermediate.[18]

A detailed examination of the mechanism of the addition of formaldehyde to the parent silene, $H_2Si{=}CH_2$, has been performed by Mosey et al. using density functional theory.[19] Three reaction pathways were explored: a concerted addition and stepwise additions through either biradical or zwitterionic intermediates. The concerted pathway for addition was found to be the highest in energy, and thus, was ruled out as a reasonable possibility. However, when the relative energies of the pathways passing through either a biradical or a zwitterionic intermediate were compared, it was noted that the addition pathway through a zwitterionic intermediate was only slightly lower in energy than that of the pathway involving a biradical intermediate. The effect of solvent polarity on the addition of formaldehyde to $H_2Si{=}CH_2$ was also examined; it was found that polar solvents stabilize a zwitterionic intermediate to a greater degree than a biradical intermediate. Thus, it was concluded that the mechanism of the addition of aldehydes to silenes may be influenced by the polarity of the solvent. Furthermore, the authors noted that, due to the competitiveness of the two pathways, the nature of the substituents on the silene would likely determine which mechanism is operative.

Scheme 6. Reactivity of the Oxy-Substituted α-Cyclopropylcarbinyl Intermediates Derived from Aldehyde 10



We have used the cyclopropyl aldehyde **10** (Scheme 6) as an effective mechanistic probe to study the reactivity of group 14 dimetallenes ($Mes_2Si{=}SiMes_2$, $Mes_2Ge{=}SiMes_2$, and $Mes_2Ge{=}GeMes_2$) toward aldehydes.[20−22] The function of the probe is based on the hypersensitive cyclopropylcarbinyl radical probes developed by Newcomb and co-workers.[23] Although the absolute rate constant for the ring-opening rearrangement of an oxy-substituted cyclopropylcarbinyl radical, **11**, is unknown, there are several estimates in the literature which demonstrate that

(15) (a) Wiberg, N.; Wagner, G.; Reber, G.; Riede, J.; Müller, G. *Organometallics* **1987**, *6*, 35. (b) Wiberg, N.; Wagner, G. *J. Organomet. Chem.* **1984**, *271*, 381.

(16) Wiberg, N.; Schurz, K.; Müller, G.; Riede, J. *Angew. Chem., Int. Ed.* **1988**, *27*, 935.

(17) (a) Bradaric, C. J.; Leigh, W. J. *Organometallics*, **1998**, *17*, 645. (b) Leigh, W. J.; Bradaric, C. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1993**, *115*, 5332.

(18) Owens, T. R.; Grinyer, J.; Leigh, W. J. *Organometallics* **2005**, *24*, 2307.

(19) Mosey, N. J.; Baines, K. M.; Woo, T. K. *J. Am. Chem. Soc.* **2002**, *124*, 13306.

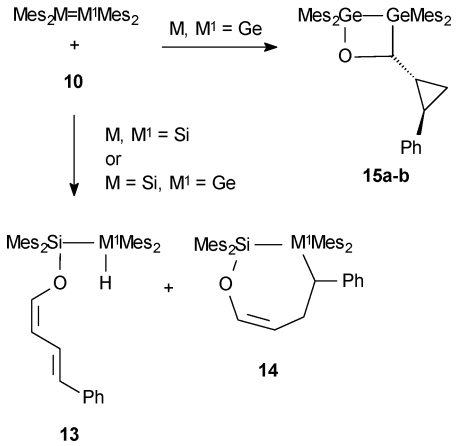
(20) Dixon, C. E.; Hughes, D. W.; Baines, K. M. *J. Am. Chem. Soc.* **1998**, *120*, 11019.

(21) Samuel, M. S.; Jenkins, H. A.; Hughes, D. W.; Baines, K. M. *Organometallics* **2003**, *22*, 1603.

(22) Samuel, M. S.; Baines, K. M. *J. Am. Chem. Soc.* **2003,** *125*, 12702.

(23) (a) Le Tadic-Biadatti, M.-H.; Newcomb, M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1467. (b) Newcomb, M.; Chestney, D. L. *J. Am. Chem. Soc.* **1994**, *116*, 9753. (c) Newcomb, M.; Johnson, C. C.; Manek, M. B.; Varick, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 10915. (d) Newcomb, M.; Manek, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 9662.

Scheme 7. Addition of Aldehyde 10 to $Mes_2Si{=}SiMes_2$, $Mes_2Ge{=}SiMes_2$, and $Mes_2Ge{=}GeMes_2$



the lower limit of the rate constant is likely 10^{10} s^{-1}.[20,24−26] In contrast, the oxy-substituted α-cyclopropylcarbinyl cation **12** derived from aldehyde **10** is not expected to undergo a ring-opening rearrangement, on the basis of the observation that acid-catalyzed removal of an acetal protecting group from a phenyl-substituted cyclopropyl aldehyde does not give any ring-opened products; only the aldehyde was isolated.[27] Thus, aldehyde **10** can be used to discriminate between the formation of oxy-substituted cyclopropylcarbinyl radicals and cations (Scheme 6).

When cyclopropyl aldehyde **10** was added to tetramesityl-disilene or -germasilene, the *cis*,*trans*-diene **13** and the oxa-cycloheptene **14** were formed (Scheme 7).[20] In all cases, the cyclopropane ring had opened toward the phenyl substituent, leading to the conclusion that a *biradical* intermediate had formed along the reaction pathway. In contrast, when the cyclopropyl aldehyde **10** was added to tetramesityldigermene, the only products formed were the diastereomeric digermoxetanes **15a**,**b** (Scheme 7).[22] There is a remarkable difference in the reactivity of tetramesityldigermene compared to those of the disilene and germasilene derivatives. This difference was also evident in the theoretical study of the addition of formaldehyde to $H_2Si{=}SiH_2$, $H_2Si{=}GeH_2$, and $H_2Ge{=}GeH_2$.[19] In the addition of formaldehyde to both $H_2Si{=}SiH_2$ and $H_2Si{=}GeH_2$, the lowest energy pathways were found to pass through a biradical intermediate.[19] Our experimental results (Scheme 7) are totally consistent with these findings, since the structures of the products formed (**13** and **14**) are best explained as being derived from a biradical intermediate.[20,21] In the case of $H_2Ge{=}GeH_2$, however, the lowest energy pathway located proceeded through a zwitterionic intermediate; the concerted pathway was found to be too high in energy to be competitive.[19] We have argued that the oxy-substituted α-(2-phenylcyclopropyl)carbinyl cation **12** (Scheme 6) does not undergo rapid ring opening, and thus, the formation of digermoxetanes **15a**,**b** is completely consistent with the intermediacy of a zwitterion in the addition of aldehyde **10** to tetramesityldigermene.[22]

As with group 14 dimetallenes, mechanistic studies of silenes are hindered by the inherent reactivity of these compounds. Since silenes react rapidly with many functional groups, including carbonyl, hydroxyl and amino groups, few solvents are suitable for examining the effect of solvent polarity on the rate constants for the addition reactions of silenes. Furthermore, the range of substituents which can be employed in studies of the effect of substituents on the rate constants of reactions is also limited. Only a few stable geometric isomers of silenes are known, and these exist as mixtures.[28] Since it is extremely difficult either to stereoselectively synthesize or separate geometric isomers of silenes, stereochemical studies of addition reactions have not been used, in general, as a mechanistic tool. We believe the molecular probe method is an effective means for studying this class of compounds, and thus, we have examined the addition of aldehyde probe **10** to two different types of silenes: the relatively nonpolar Brook silenes $(Me_3Si)_2Si{=}C(R)(OSiMe_3)$, where R = *t*-Bu (**1a**), 1-Ad (**1b**),[9,29] and the naturally polarized Couret silene $Mes_2Si{=}C(H)(CH_2$-*t*-Bu) (**2**).[10] We were particularly interested in the examination of the influence of the polarity of the Si=C on the nature of the reactive intermediate (if any).

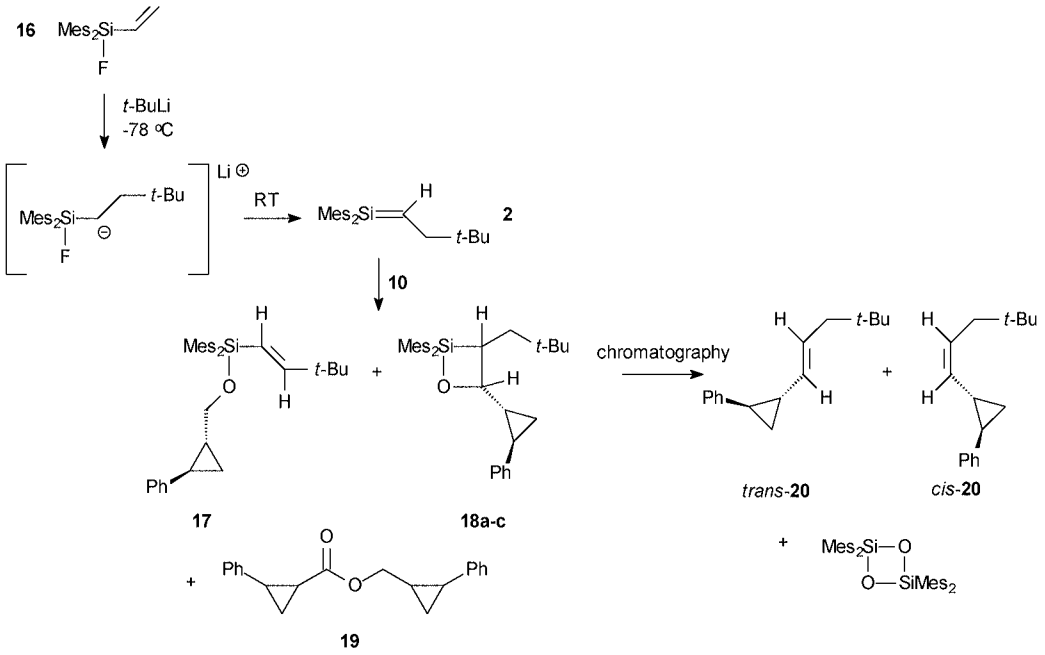
Results

1,1-Dimesityl-2-neopentylsilene (**2**) was prepared by the addition of *t*-BuLi to a pentane solution of fluorodimesitylvinylsilane (**16**) at −78 °C.[10] When the reaction mixture is warmed to room temperature, LiF is eliminated, forming silene **2**. Addition of *trans*-2-phenylcyclopropanecarbaldehyde (**10**) to the solution of 1,1-dimesityl-2-neopentylsilene (**2**) yielded a mixture of vinylsilane **17**, siloxetanes **18a**−**c** (in a ratio of 54:23:14:9, respectively), and ester **19** as well as unreacted **16** and **10**, as determined by ^{1}H NMR spectroscopy (Scheme 8). Examination of the ratio of the products from a number of reactions revealed that the relative amount of ester **19** was quite variable, ranging from 6 to 55% of the product mixture; the relative amounts of **17** and **18a**−**c** remained fairly constant.

Separation of the crude reaction mixture by chromatography yielded a mixture of vinylsilane **17**, alkenes *trans*-**20** and *cis*-**20**, and fluorosilane **16** (in a ratio of 46:15:6:33, respectively), a mixture of **19** and tetramesityl-1,3-cyclodisiloxane,[30] and a mixture of tetramesityl-1,3-cyclodisiloxane[30] and *trans*-2-phenylcyclopropyl carbinol contaminated with unidentified impurities.[31] Vinylsilane **17**, ester **19**, and *trans*-**20** and *cis*-**20** could be separated after extensive chromatography. Siloxetanes **18a**−**c** decompose upon prolonged exposure to the atmosphere or upon adsorption to silica gel. Alkenes *trans*-**20** and *cis*-**20** and tetramesityl-1,3-cyclodisiloxane are only observed after chromatographic separation of the crude reaction mixture. Due to difficulties encountered during the attempted isolation of the products of this reaction, the recovered yields are quite low and, as such, do not reflect the amount of the products formed. The products of several reactions had to be combined in order to obtain sufficient amounts of material for purification and characterization.

(24) (a) Ha, C.; Horner, J. H.; Newcomb, M.; Varick, T. R.; Arnold, B. R.; Lusztyk, J. *J. Org. Chem.* **1993**, *58*, 1194. (b) Johnson, C. C.; Horner, J. H.; Tronche, C.; Newcomb, M. *J. Am. Chem. Soc.* **1995**, *117*, 1684.
(25) Zelechonok, Y.; Silverman, R. B. *J. Org. Chem.* **1992**, *57*, 5785.
(26) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7512.
(27) (a) Barrett, A. G. M.; Doubleday, W. W.; Tustin, G. J.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1783. (b) Mori, A.; Arai, I.; Yamamoto, H. *Tetrahedron* **1986**, *42*, 6447. (c) Abdallah, H.; Grée, R.; Carrié, R. *Bull. Soc. Chim. Fr.* **1985**, *5*, 794.
(28) (a) Brook, A. G.; Baumegger, A.; Lough, A. J. *Organometallics* **1992**, *11*, 3088. (b) Lassacher, P.; Brook, A. G.; Lough, A. J. *Organometallics* **1995**, *14*, 4359.
(29) (a) Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83. (b) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.
(30) (a) Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, *5*, 531. (b) Fink, M. J.; DeYoung. D. J.; West, R. *J. Am. Chem. Soc.* **1983**, *105*, 1070.
(31) Smart, R. P.; Peelen, T. J.; Blankespoor, R. L.; Ward, D. L. *J. Am. Chem. Soc.* **1997**, *119*, 461.

Scheme 8. Addition of Aldehyde 10 to Silene 2

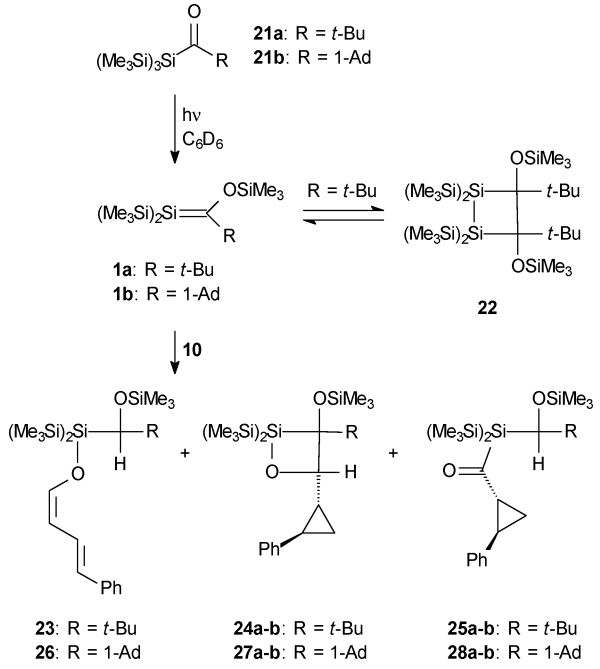


Vinylsilane **17**, ester **19**, and alkenes *trans*-**20** and *cis*-**20** were isolated and identified by IR, ^{1}H, ^{13}C, gCOSY, ^{1}H−^{13}C gHSQC and gHMBC, and ^{1}H−^{29}Si gHMBC (in the case of **17**) NMR spectroscopy, and mass spectrometry.[32] Because of the sensitivity of siloxetanes **18a**−**c**, they were identified as part of the crude product mixture. Due to signal overlap, it was difficult to identify all the signals attributable to siloxetanes **18a**−**c** in the 1D and 2D NMR spectra of the crude reaction mixture. The only unobscured signals in the ^{1}H NMR spectrum of the product mixture which could be assigned to siloxetanes **18a**−**c** were those at 4.77 ppm (dd, J = 2.4, 3.6 Hz), 4.66 ppm (t, J = 4.2 Hz), and 4.27 ppm (t, J = 8.4 Hz). On the basis of the chemical shifts and multiplicities of these signals, they were assigned to the ^{1}H geminal to the oxygen on the four-membered ring for the three diastereomers of **18a**−**c**. Accordingly, in the ^{1}H−^{29}Si gHMBC NMR spectrum of the crude reaction mixture, a correlation between these three signals and signals at ∼20 ppm in the ^{29}Si dimension, assigned to the siloxetane ring silicon, were observed. The chemical shifts of ∼20 ppm are comparable to those assigned to the ring silicon atoms of similarly substituted siloxetanes.[33]

The identity of tetramesityl-1,3-cyclodisiloxane was confirmed by mass spectrometry[34] and by comparison of the ^{1}H and ^{29}Si NMR chemical shifts to the literature data.[30] The identity of *trans*-2-phenylcyclopropyl carbinol was confirmed by comparison of the ^{1}H NMR chemical shifts to those of an authentic sample and to the literature data.[31] The alcohol was not observed in the crude product mixture, and thus, it was likely formed by hydrolysis of one of the primary products upon chromatography.

The addition of aldehyde **10** to Brook silenes **1a**,**b** was also examined. A solution of acyltris(trimethylsilyl)silane **21a** or **21b** was irradiated, producing silene **1a** or **1b**, respectively.[9,29] Silene

Scheme 9. Addition of Aldehyde 10 to Silenes 1a,b



1a reversibly dimerizes, forming the 1,2-disilacyclobutane **22**. Although aldehyde **10** reacts very quickly with silene **1a**, dissociation of dimer **22** to the silene is relatively slow. Thus, the reaction mixture was stirred for several hours. The addition of aldehyde **10** to the Brook silenes produces a mixture of *cis*,*trans*-dienes **23** and **26**, siloxetanes **24a**,**b** and **27a**,**b**, and acylsilanes **25a**,**b** and **28a**,**b** for silenes **1a** and **1b**, respectively (Scheme 9). The products derived from silene **1a** were formed in a ratio of 74:11:10:2:3 for **23**:**24a**,**b**:**25a**,**b**, and those from **1b** were formed in a ratio of 73:13:12:1:1 for **26**:**27a**,**b**:**28a**,**b**, as determined by ^{1}H NMR spectroscopy. When silenes **1a**,**b** are formed by irradiation in the presence of aldehyde **10**, similar product mixtures are obtained; however, products which appear to be derived from isomerization of the *cis*,*trans*-dienes are also formed. Addition of **10** to the preformed silene provided a less complex product mixture.

(32) A discussion of the NMR spectral data for compounds **17**, **19**, *trans*- and *cis*-**20**, **23**, **25a**,**b**, **26**, and **27a**,**b** can be found in the structure elucidation section of the Supporting Information.

(33) Toltl, N. P.; Leigh, W. J. *Organometallics* **1996**, *15*, 2554.

(34) A sample of $(Mes_2SiO)_2$ was isolated from the addition of aldehyde **10** to silene **2** after chromatography. Tetramesityl-1,3-cyclodisiloxane: high-resolution CI-MS for $C_{36}H_{45}O_2Si_2$ (M + H$^+$) *m/z* calcd 565.2958, found 565.2963.

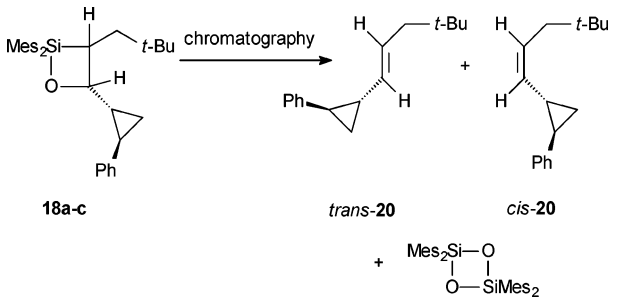
The *cis,trans*-dienes **23** and **26** and acylsilanes **25a**,**b** are readily separated and purified by chromatography and were identified by IR, ^{1}H, ^{13}C, gCOSY, ^{1}H−^{13}C gHSQC and gHMBC, and ^{1}H−^{29}Si gHMBC NMR spectroscopy, and mass spectrometry.[32] Despite many attempts, acylsilanes **28a**,**b** could not be isolated, even as part of a mixture by chromatography. Siloxetanes **24a**,**b** and **27a**,**b** are somewhat sensitive to ambient atmospheric conditions. They remain unchanged after exposure to the atmosphere for short time periods (typically hours); however, upon prolonged exposure they decompose. Siloxetanes **24a**,**b** and **27a**,**b** also readily decompose upon adsorption on silica gel; however, no decomposition products could be isolated or identified. The identity of siloxetanes **24a**,**b** and **27a**,**b** was, therefore, confirmed by several characteristic features in the NMR spectra of the crude reaction mixtures. The spectral features which led to the identification of both diastereomers of siloxetanes **24** and **27** are essentially the same; as such, only diastereomer **24a** will be discussed.[32] A doublet was observed in the ^{1}H NMR spectrum of the crude reaction mixture at 4.34 ppm; the magnitude of the coupling constant for this signal was 9.0 Hz. This signal is attributable to the siloxetane ring ^{1}H, geminal to the oxygen of siloxetane **24a**. The gCOSY NMR spectrum of the crude reaction mixture showed a correlation between the doublet at 4.34 ppm and a multiplet at ∼1.8 ppm.[35] The multiplet at ∼1.8 ppm also correlated to three multiplets at ∼0.9−1.3 ppm in the gCOSY NMR spectrum of the crude reaction mixture. The chemical shifts and correlations can be assigned to the cyclopropyl ^{1}H's, and thus, the downfield signal at ∼1.8 ppm was assigned to the ^{1}H vicinal to the siloxetane ring ^{1}H of **24a**. The ^{1}H−^{29}Si gHMBC NMR spectrum of the crude reaction mixture revealed that the signal at 4.34 ppm in the ^{1}H dimension correlated to a signal at 57.4 ppm in the ^{29}Si dimension. This ^{29}Si resonance also showed a correlation to two types of $SiMe_3$ protons, each in the range of 0.1−0.4 ppm in the ^{1}H dimension, which implies that the silicon atom resonating at 57.4 ppm is of the type $Si(SiMe_3)_2$. Thus, the signal at 57.4 ppm was assigned to the siloxetane ring silicon of **24a**. The chemical shifts of the ring ^{29}Si of a number of siloxetanes derived from the addition of carbonyl compounds to Brook-type silenes have been determined. The chemical shift of the siloxetane ring ^{29}Si ranges from 42 to 65 ppm, with the majority of the chemical shifts falling within the much narrower range of 50−56 ppm.[5a] Thus, the observed ^{29}Si chemical shift of siloxetane **24a** is completely consistent with the known data.

Discussion

The addition of aldehyde **10** to silene **2** yielded vinylsilane **17**, siloxetanes **18a**−**c**, and ester **19** (Scheme 8). Vinylsilane **17** is the product of a formal ene addition between aldehyde **10** and silene **2**. In this case, the aldehyde has exclusively acted as the enophile; no products were observed that could be attributed to an ene addition where the silene acted as the enophile. Interestingly, the addition of acetophenone to silene **2** forms both types of ene-addition products.[10b]

Upon chromatography of the crude product mixture from the addition of aldehyde **10** to silene **2**, alkenes *trans*-**20** and *cis*-**20** and tetramesityl-1,3-cyclodisiloxane were isolated; these products were not present in the crude product mixture. Alkenes *trans*-**20** and *cis*-**20** are the expected products from the corresponding siloxetanes **18a**−**c**, which were detected by ^{1}H NMR spectroscopy in the crude product mixture. The formation of the Wittig alkene provides additional evidence for the formation of a siloxetane from the addition of the aldehyde to the silene (Scheme 10).[1,2] Interestingly, the siloxetanes derived from the addition of benzaldehyde or benzophenone to silene **2** were not reported to undergo transformation to the Wittig alkenes and $(Mes_2SiO)_n$.[10b] It is likely that the siloxetanes were only characterized as part of the crude product mixture and not isolated. No products were isolated or observed in the NMR spectra of the crude reaction mixture where the cyclopropyl ring had opened. As such, we believe that a biradical intermediate is not formed during the addition of aldehyde **10** to silene **2**. The possibility of a concerted addition of the aldehyde was also ruled out, since the concerted addition of formaldehyde to $H_2Si{=}CH_2$ follows a significantly higher energy pathway than the pathways passing through either a biradical or a zwitterionic intermediate, as determined by density functional theory.[19] Thus, siloxetanes **18a**−**c**, from the addition of aldehyde **10** to silene **2**, are likely formed by cyclization of an intermediate 1,4-zwitterion.

Scheme 10. Conversion of Siloxetanes 18a−c to Alkenes 20 and $(Mes_2SiO)_2$



The formation of the ester **19** was unexpected. The formation of an ester from dimerization of an aldehyde via Lewis acid catalysis is a well-known reaction: the Tishchenko reaction.[36] Typically, the Lewis acid catalyst employed is an aluminum alkoxide; however, other catalysts, including transition-metal complexes containing Zr, Hf, Fe, Ru, Os, Rh, and Ir, are known to catalyze the dimerization. The proposed mechanism for the catalytic process is dependent on which catalyst is employed.[36,37]

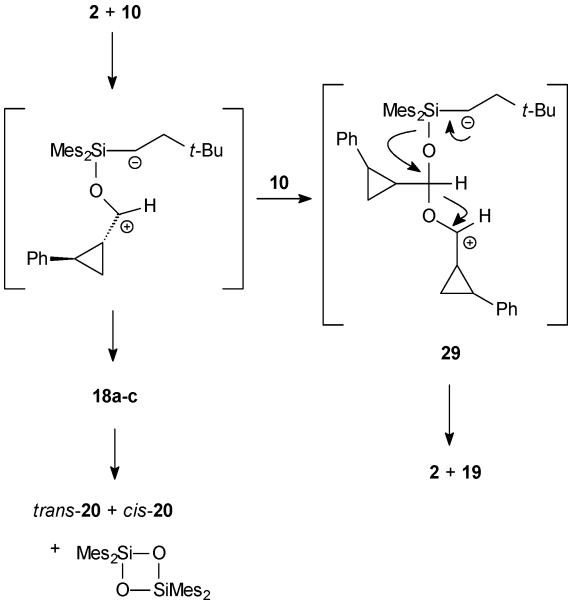
In this case, we believe silene **2** is acting as a Lewis acid, catalyzing the dimerization of aldehyde **10** to form ester **19**. Thus, the addition of *trans*-2-phenylcyclopropanecarbaldehyde (**10**) to $Mes_2Si{=}C(H)(CH_2$-*t*-Bu) (**2**) initially yields a 1,4-zwitterion (Scheme 11). The zwitterion can then cyclize to give siloxetanes **18a**−**c** or add a second equivalent of aldehyde **10** to yield the 1,6-zwitterion **29**. Loss of silene **2** from zwitterion **29** accompanied by a [1,3]-hydride shift results in the formation

(35) Due to overlap in the ^{1}H NMR spectrum of the crude reaction mixture, it was not possible to observe the precise chemical shifts of some signals, and thus, the chemical shifts have been estimated from the gCOSY NMR spectrum.

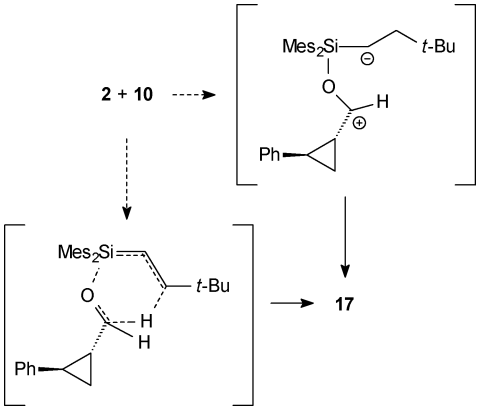
(36) A recent review: Seki, T.; Nakajo, T.; Onaka, M. *Chem. Lett.* **2006**, *35*, 824.

(37) Although there are no reports in the literature of Pt catalyzing the dimerization of an aldehyde, the possibility that the formation of ester **19** was catalyzed by a Pt species was also considered. Fluorodimesitylvinylsilane (**16**), the precursor to silene **2**, is formed by the H_2PtCl_6-catalyzed hydrosilylation of acetylene by Mes_2SiHF. Although fluorosilane **16** was purified by multiple filtrations through a bed of silica gel to remove the catalyst, it seemed possible that traces of a Pt species of unknown composition remained. The formation of ester **19** by a Pt-catalyzed reaction was discarded on the basis of the following evidence. A mixture of fluorosilane **16** and aldehyde **10**, in both the presence and absence of LiF, afforded no reaction. When a catalytic amount of H_2PtCl_6 was added to a solution of aldehyde **10**, a number of products were formed; however, ester **19** was not. Finally, a sample of fluorosilane **16** was analyzed by energy dispersive X-ray spectroscopy (EDS) and no signals attributable to platinum could be observed (detection limit: 2 ppt). The upper limit of Pt in this case, 2 ppt, is significantly lower than the amounts typically required in catalytic reactions.

Scheme 11. Mechanism of Addition of Aldehyde 10 to Silene 2



Scheme 12. Possible Routes for the Formation of Vinylsilane 17

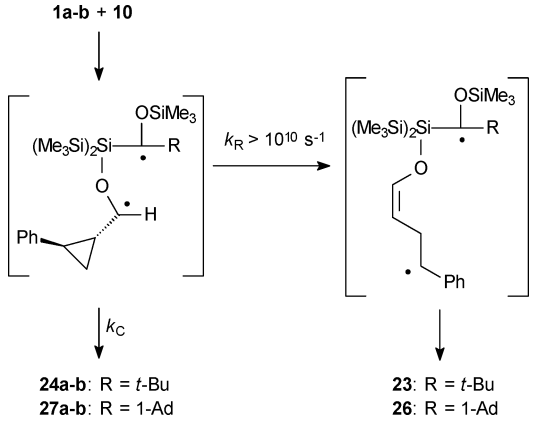


of ester **19** (Scheme 11). The formation of ester **19**, therefore, provides further evidence that, in the case of aldehyde addition to this type of silene, a 1,4-zwitterion is formed along the reaction pathway.

The mechanism by which vinylsilane **17** is formed is more ambiguous. The vinylsilane could be formed by a [1,6]-hydride shift from the 1,4-zwitterionic intermediate or by a concerted ene addition (Scheme 12). Interestingly, the ene product derived from a proton transfer from the 1,4-zwitterion (that is, with the silene acting as the enophile) was not observed. Further experiments are required to provide evidence for the mechanism by which this product is formed.

The addition of aldehyde **10** to silenes **1a**,**b** yielded the *cis*,*trans*-dienes **23** and **26**, siloxetanes **24a**,**b** and **27a**,**b**, and acylsilanes **25a**,**b** and **28a**,**b**, respectively (Scheme 9). The *cis*,*trans*-dienes **23** and **26**, derived from the addition of aldehyde **10** to Brook silenes **1a**,**b**, respectively, clearly result from ring-opening rearrangement of the cyclopropyl group toward the phenyl substituent. On the basis of the known behavior of aldehyde **10** (vide supra), we believe that this rearrangement occurs from an intermediate biradical. Thus, the aldehyde initially adds to the Brook silenes **1a**,**b**, forming a 1,4-biradical intermediate which can either cyclize to give siloxetanes **24a**,**b** and **27a**,**b** or undergo ring-opening rearrangement toward the

Scheme 13. Mechanism of Addition of Aldehyde 10 to Silenes 1a,b



phenyl substituent to form a 1,7-biradical intermediate. This 1,7-biradical intermediate then disproportionates, yielding the observed *cis*,*trans*-dienes **23** and **26** (Scheme 13). No evidence for the formation of products derived from cyclization of the 1,7-biradical intermediate was observed.

The proposed mechanism by which siloxetanes **24a**,**b** and **27a**,**b** are formed, via a biradical intermediate, contrasts with our earlier conclusion that siloxetanes **18a**−**c**, detected as a product of the addition of aldehyde **10** to silene **2**, are formed via a 1,4-zwitterion. Although the possibility that siloxetanes **24a**,**b** and **27a**,**b** are formed by ring closure of a 1,4-zwitterion cannot be rigorously ruled out, we believe that, in this reaction, these products are more likely formed by cyclization of the 1,4-biradical. If we assume that the 1,4-biradical undergoes competitive ring closure or rearrangement and we assume that the rate constant for ring opening of the oxy-substituted cyclopropylcarbinyl radical, k_R, is on the same order as that of the unsubstituted derivative, 10^{11} s^{-1},[23] the rate constant of cyclization, k_C, of the 1,4-biradical can be estimated using the following equation: $k_C = k_R([\mathbf{24}]/[\mathbf{23}])$. The ratio of **24**:**23** is 21:74, and thus, k_C is estimated to be on the order of 10^{10} s^{-1}. Although the value of k_C is only an estimate, it is likely that the order of magnitude is correct. Thus, siloxetanes **24a**,**b** and **27a**,**b** are likely formed by the cyclization of a 1,4-biradical intermediate. Since the *cis*,*trans*-dienes and the siloxetanes formed from the addition of aldehyde **10** to the Brook silenes can be explained from the same 1,4-biradical intermediate, there is no need to invoke the intermediacy of a zwitterion.

With an estimate of k_C, the interpretation of the Bu_3SnH-trapping experiments reported by Brook et al. should be re-examined. During the formation of the silene $(Me_3Si)_2Si{=}C(R)(OSiMe_3)$, R = 1-Ad, Ph, in the presence of benzophenone and Bu_3SnH, no product(s) derived from the reaction of Bu_3SnH with a putative 1,4-biradical intermediate (**5**; Scheme 4) was observed.[5a] Siloxetane **3** and a small amount of **4**, derived from the addition of Bu_3SnH to the silene, were formed (Scheme 4). The absence of Bu_3SnH adducts of biradical **5** was taken as evidence that no biradical intermediate was formed during the addition of $Ph_2C{=}O$ to the silene. Thus, Brook and co-workers concluded that the addition proceeded via a zwitterionic intermediate (**6**; Scheme 4). Our results indicate that the rate constant for cyclization of the 1,4-biradical intermediate is very fast, on the order of 10^{10} s^{-1}. The rate constant for hydrogen atom abstraction from Bu_3SnH by most alkyl radicals is on the order of 10^6-10^7 $M^{-1}s^{-1}$ and is 10^4 $M^{-1}s^{-1}$ in the case of a benzyl radical.[38] Since the rate constant for hydrogen atom abstraction by an alkyl radical is at *least* 3 orders of magnitude

less than that for cyclization of the biradical intermediate, the relative amount of products derived from reaction with Bu_3-SnH would be very small and, in all probability, not be within the detection limit of ^{1}H NMR spectroscopy. Thus, Brook's experiments do not rule out the possibility of the intermediacy of a biradical during the addition of carbonyl compounds to Brook silenes.

The formation of acylsilanes **25a**,**b** and **28a**,**b** is more perplexing. A reasonable mechanism for their formation involves the addition of aldehyde **10** to silenes **1a**,**b** to form a biradical intermediate, where the carbonyl carbon has added to the silenic silicon center. A subsequent [1,3]-hydrogen transfer forms acylsilanes **25a**,**b** and **28a**,**b**.

Conclusions

We have examined the addition of *trans*-2-phenylcyclopropanecarbaldehyde (**10**) to two different types of silenes. In the case of the addition of aldehyde **10** to the naturally polarized Couret silene **2**, three different types of products are obtained: vinylsilane **17**, siloxetanes **18a**−**c**, and ester **19**. Upon chromatography, siloxetanes **18a**−**c** undergo conversion to alkenes *trans*-**20** and *cis*-**20** and $(Mes_2SiO)_2$. The formation of siloxetanes **18a**−**c** and ester **19** are best explained from the same intermediate: a 1,4-zwitterion. The absence of cyclopropyl ring-opened products rules out the formation of an α-cyclopropylcarbinyl radical along the reaction pathway. Vinylsilane **17** is likely formed via a [1,6]-hydride shift from the 1,4-zwitterionic intermediate, but a concerted ene addition cannot be ruled out.

The formation of ester **19**, the dimer of aldehyde **10**, via a silene-catalyzed Tishchenko reaction is a unique example of a silene behaving as a Lewis acid catalyst. While the catalytic activity of silene **2** is very intriguing, the silene-catalyzed reaction is not efficient, due to the multiple modes of reactivity that are possible and, as such, silene **2** is unlikely to gain common use as a Lewis acid.

In the case of the less polar Brook silenes, three types of products were also obtained: *cis*,*trans*-dienes **23** and **26**, siloxetanes **24a**,**b** and **27a**,**b**, and acylsilanes **25a**,**b** and **28a**,**b**, derived from silenes **1a** and **1b**, respectively. The formation of the *cis*,*trans*-dienes and the siloxetanes are best explained from the same intermediate: a 1,4-biradical. This is the first time that unequivocal experimental evidence for the formation of a biradical intermediate has been found during the addition of a carbonyl compound to silenes.

We have provided convincing evidence for the formation of both biradicals and zwitterions during the addition of aldehydes to silenes. The preferred reaction pathway is dependent on the nature of the substituents and, thus, the polarity of the silene. This work provides the first clear example of a dramatic difference in reactivity between the relatively nonpolar Brook silenes and naturally polarized Couret silene toward aldehydes. Although the structures of the products are analogous, we have shown that the mechanisms of the addition are quite different. Our results are in very good agreement with the results of the theoretical study of the addition of formaldehyde to the parent silene, $H_2Si{=}CH_2$, where the biradical and zwitterionic pathways were shown to be relatively close in energy.[19] The authors indicated that, because of the competitiveness of the two pathways, the substituents on the silene will have a significant influence on the preferred mechanism of aldehyde addition, as we have shown here experimentally.

(38) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151.

Silenes, particularly the readily available Brook silenes, have been recently recognized as promising substrates for organic synthesis because of their selective and efficient cycloaddition reactions.[39] Our results are important not only because of the fundamental nature of the work but also because a thorough understanding of the mechanisms of cycloaddition reactions will be critical for the continued and fruitful development of applications of this chemistry.

Experimental Section

Addition of *trans*-2-Phenylcyclopropanecarbaldehyde (10) to 1,1-Dimesityl-2-neopentylsilene (2). A solution of fluorodimesitylvinylsilane (**16**; 248 mg, 0.79 mmol) in pentane (3 mL) was cooled to −78 °C. A pentane solution of *t*-BuLi (0.45 mL, 1.7 M) was then added to the cold solution. The reaction mixture was warmed to room temperature and stirred for 1 h, after which time the color had deepened to orange and a fine precipitate of LiF had formed. The pentane was removed under vacuum, the orange residue was dissolved in C_6D_6 (1.0 mL), and this solution was transferred to a septum-sealed NMR tube. The solution consisted of a mixture of silene **2** and fluorosilane **16** in a ratio of 71:29, respectively, as determined by ^{1}H NMR spectroscopy.[40] A solution of *trans*-2-phenylcyclopropanecarbaldehyde (**10**; 94 mg, 0.64 mmol) in C_6D_6 (0.5 mL) was added to the silene solution. Upon addition of the aldehyde, the orange color immediately faded to pale yellow; the reaction mixture was stirred at room temperature for 2 h. The solvent was removed by rotary evaporation, yielding an orange residue (332 mg) consisting of vinylsilane **17**, siloxetanes **18a**−**c** (in a ratio of 54:23:14:9, respectively), and ester **19** as well as fluorosilane **16** and unreacted aldehyde **10**, as determined by ^{1}H NMR spectroscopy.

The crude reaction mixture was separated by column chromatography (silica gel, 1:1 hexanes−CH_2Cl_2), yielding a mixture of vinylsilane **17**, alkenes *trans*-**20** and *cis*-**20**, and fluorosilane **16** (46:15:6:33, 158 mg), ester **19** contaminated with tetramesityl-1,3-cyclodisiloxane (16 mg),[30] and a mixture of tetramesityl-1,3-cyclodisiloxane[30] and *trans*-2-phenylcyclopropyl carbinol[31] (34:66, 30 mg). The mixture of vinylsilane **17**, alkenes *trans*-**20** and *cis*-**20**, and fluorosilane **16** was further separated by repetitive preparative thin-layer chromatography (silica gel, hexanes). The mixture containing **19** was further separated by preparative thin-layer chromatography (silica gel, 2:1 CH_2Cl_2−hexanes). It proved to be very difficult to purify any of the products from this reaction, and as such, the product mixtures of several reactions had to be combined in order to obtain sufficient amounts for characterization of vinylsilane **17**, alkenes *trans*-**20** and *cis*-**20**, and ester **19**. Vinylsilane **17** and ester **19** remained contaminated with minor amounts of unidentifiable impurities. Alkenes *trans*-**20** and *cis*-**20** were obtained as a colorless oil in a ratio of 75:25, respectively (98% pure by GC analysis). **17**: IR (cm^{-1}) 3026 (m), 2958 (s), 2865 (m), 2735 (w), 1606 (s), 1452 (s), 1411 (m), 1236 (m), 1072 (s), 1030 (m), 849 (m), 817 (w), 792 (w), 748 (m), 698 (w), 632 (s); ^{1}H NMR (C_6D_6) δ 7.11 (t, 2H, *m*-Ph *H*, J = 7.8 Hz), 7.02 (tt, 1H, *p*-Ph *H*, J = 1.4, 7.8 Hz), 6.95 (d, 2H, *o*-Ph *H*, J = 7.8 Hz), 6.76 (s, 2H, *m*-Mes *H*), 6.75 (s, 2H, *m*-Mes *H*), 6.30 (AB spin system, 1H, SiC(H)=C(*H*)*t*-Bu, J = 18.6 Hz, $^3J_{Si-H}$ = 8.1 Hz), 6.23 (AB spin system, 1H, SiC(*H*)=C(H)-*t*-Bu, J = 18.6 Hz, $^2J_{Si-H}$ = 6.9 Hz), 3.67 (dd, 1H, OCH_2, J = 6.0, 10.2 Hz), 3.55 (dd, 1H, OCH_2, J = 6.3, 10.5 Hz), 2.50 (s, 6H, *o*-Mes CH_3), 2.49 (s, 6H, *o*-Mes CH_3), 2.104 (s, 3H, *p*-Mes CH_3), 2.102 (s, 3H, *p*-Me CH_3), 1.66 (dt, 1H, Ph C*H*, J = 8.8, 4.0 Hz), 1.35−1.40 (m, 1H, OCH_2CH), 0.93 (s, 9H, *t*-Bu), 0.75 (dt, 1H, CH_2, J = 8.2, 5.0 Hz),

(39) Ottosson, H.; Steel, P. G. *Chem. Eur. J.* **2006**, *12*, 1576.

(40) It was necessary to add <1 equiv of *t*-BuLi to fluorosilane **16** when forming silene **2**, to prevent decomposition of the silene. As such, silene **2** was always contaminated with residual fluorosilane **16**.

0.71 (dt, 1H, CH_2, J = 8.6, 5.3 Hz); ^{13}C NMR (C_6D_6) δ 158.07 (SiC(H)=*C*(H)-*t*-Bu), 144.39 (*o*-Mes *C*), 143.29 (*i*-Ph *C*), 139.08 (*p*-Mes *C*), 132.15 (*i*-Mes *C*), 132.10 (*i*-Mes *C*), 129.67 (*m*-Mes *C*), 128.49 (*m*-Ph *C*), 126.20 (*o*-Ph *C*), 125.66 (*p*-Ph *C*), 122.89 (Si*C*(H)=C(H)*t*-Bu), 66.48 (O*C*H_2), 34.91 (*C*$(CH_3)_3$), 28.79 (C(*C*$H_3)_3$), 25.41 (OCH$_2$*C*H), 24.39 (*o*-Mes-*C*H_3), 21.80 (Ph *C*H), 21.08 (*p*-Mes-*C*H_3), 14.21 (*C*H_2); ^{29}Si NMR (C_6D_6) δ -10.4 (Mes$_2$*Si*); high-resolution EI-MS for $C_{34}H_{44}OSi$ (M^+) *m/z* calcd 496.3161, found 496.3152. **18a**−**c**: ^{1}H NMR (C_6D_6) δ 4.77 (dd, 1H, OC*H*, J = 2.4, 3.6 Hz, **18a**), 4.66 (t, 1H, OC*H*, J = 4.2 Hz, **18b**), 4.27 (t, 1H, OC*H*, J = 8.4 Hz, **18c**); ^{29}Si NMR (C_6D_6) δ ∼20 (Mes$_2$*Si*, **18a**−**c**). **19**: IR (cm^{-1}) 3063 (w), 3029 (w), 2950 (w), 1723 (s), 1605 (w), 1498 (w), 1459 (w), 1404 (m), 1338 (m), 1262 (w), 1173 (s), 754 (m), 697 (m); ^{1}H NMR (C_6D_6)[41] δ 7.06−7.10 (m, 2H, *m*-Ph *H* ring B), 6.96−7.02 (m, 4H, *m*-Ph *H* ring A, *p*-Ph *H* ring A and B), 6.86−6.88 (m, 2H, *o*-Ph *H* ring B), 6.74−6.76 (m, 2H, *o*-Ph *H* ring A), 3.97, 3.90 (AB portion of an ABX spin system, 2H, OCH_2 of one diastereomer, J_{AB} = 11.4 Hz, J_{AX} = 7.0 Hz, J_{BX} = 7.6 Hz), 3.95, 3.92 (AB portion of an ABX spin system, 2H, OCH_2 of one diastereomer, J_{AB} = 11.6 Hz, J_{AX} = 7.1 Hz, J_{BX} = 6.9 Hz), 2.59−2.63 (m, 1H, PhC*H* ring A), 1.88 (dt, 1H, C*H*C=O, J = 8.6, 4.3 Hz), 1.60−1.63 (m, 1H, PhC*H* ring B), 1.55−1.60 (m, 1H, CH_2 ring A), 1.28−1.34 (m, 1H, OCH$_2$C*H*), 0.95 (1H, ddd, CH_2 ring A, J = 4.2, 6.3, 8.4 Hz), 0.71 (dt, 1H, CH_2 ring B of one diastereomer, J = 10.6, 5.4 Hz), 0.71 (q, 1H, CH_2 ring B of one diastereomer, J = 5.6 Hz), 0.64 (dt, 1H, CH_2 ring B of one diastereomer, J = 11.8, 5.4 Hz), 0.64 (q, 1H, CH_2 ring B of one diastereomer, J = 5.6 Hz); ^{13}C NMR (C_6D_6) δ 173.04 (*C*=O), 142.29 (*i*-Ph *C* ring B), 140.31 (*i*-Ph *C* ring A), 128.62 (*m*-Ph *C* ring A), 128.56 (*m*-Ph *C* ring B), 126.53 (*p*-Ph *C* ring B), 126.35 (*o*-Ph *C* ring A), 126.23 (*o*-Ph *C* ring B), 125.96 (*p*-Ph *C* ring A), 68.25, 68.19 (O*C*H$_2$ × 2 diastereomers), 26.45 (Ph *C*H ring A), 24.45, 24.44 (*C*(H)C=O × 2 diastereomers), 22.02, 22.00 (Ph *C*H × 2 diastereomers, ring B), 21.76 (OCH$_2$*C*H), 17.11 (*C*H$_2$ ring A), 13.97 (*C*H$_2$ ring B); high-resolution EI-MS for $C_{20}H_{20}O_2$ (M^+) *m/z* calcd 292.1463, found 292.1453. *trans*-**20**: ^{1}H NMR (C_6D_6) δ 7.09−7.12 (m, 2H, *m*-Ph *H*), 7.01−7.04 (m, 1H, *p*-Ph *H*), 6.91−6.93 (m, 2H, *o*-Ph *H*), 5.53 (1H, ddt, CH=C*H*CH$_2$-*t*-Bu, J = 0.6, 15.0, 7.5 Hz), 5.05 (1H, ddt, C*H*=CHCH$_2$-*t*-Bu, J = 8.2, 15.2, 1.0 Hz), 1.89 (dt, 1H, CH_2-*t*-Bu, J = 7.2, 1.4 Hz), 1.76 (dt, 1H, PhC*H*, J = 9.0, 4.6 Hz), 1.60 (tt, 1H, CH=CHC$H_{cycloprop}$, J = 4.5, 8.6 Hz), 1.01 (dt, 1H, CH_2, J = 8.4, 5.1 Hz), 0.88−0.92 (m, 1H, CH_2), 0.88 (s, 9H, *t*-Bu); ^{13}C NMR (C_6D_6) δ 142.92 (*i*-Ph *C*), 134.85 (CH=*C*HCH$_2$-*t*-Bu), 128.56 (*m*-Ph *C*), 126.07 (*C*H=CHCH$_2$-*t*-Bu), 125.96 (*o*-Ph *C*), 125.73 (*p*-Ph *C*), 47.38 (*C*H$_2$-*t*-Bu), 30.97 (*C*$(CH_3)_3$), 29.36 (C(*C*$H_3)_3$), 26.82 (CH=CH*C*H$_{cycloprop}$), 25.31 (Ph *C*H), 16.85 (*C*H$_2$). *cis*-**20**: ^{1}H NMR (C_6D_6) δ 7.09−7.12 (m, 2H, *m*-Ph *H*), 7.00−7.03 (m, 1H, *p*-Ph *H*), 6.95−6.96 (m, 2H, *o*-Ph *H*), 5.49 (1H, ddt, CH=C*H*CH$_2$-*t*-Bu, J = 1.0, 11.0, 8.0 Hz), 4.97 (1H, ddt, C*H*=CHCH$_2$-*t*-Bu, J = 9.6, 11.0, 1.4 Hz), 2.02 (ddd, 1H, CH_2-*t*-Bu, J = 1.5, 4.2, 7.8 Hz), 1.83−1.88 (m, 1H, CH=CHC$H_{cycloprop}$), 1.76 (dt, 1H, PhC*H*, J = 9.0, 4.6 Hz), 1.09 (dt, 1H, CH_2, J = 8.8, 5.4 Hz), 0.88 (s, 9H, *t*-Bu), 0.81−0.85 (m, 1H, CH_2); ^{13}C NMR (C_6D_6) δ 142.70 (*i*-Ph *C*), 134.34 (CH=*C*HCH$_2$-*t*-Bu), 128.60 (*m*-Ph *C*), 126.10 (*C*H=CHCH$_2$-*t*-Bu), 125.96 (*o*-Ph *C*), 125.83 (*p*-Ph *C*), 41.84 (*C*H$_2$-*t*-Bu), 30.97 (*C*$(CH_3)_3$), 29.34 (C(*C*$H_3)_3$), 25.57 (Ph *C*H), 23.07 (CH=CH-*C*H$_{cycloprop}$), 17.19 (*C*H$_2$). *trans*- and *cis*-**20**: high-resolution EI-MS for $C_{16}H_{22}$ (M^+) *m/z* calcd 214.1721, found 214.1718.

Addition of *trans*-2-Phenylcyclopropanecarbaldehyde (10) to 2-*tert*-Butyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene (1a). A solution of pivaloyltris(trimethylsilyl)silane (**21a**; 73 mg, 0.22 mmol) was irradiated in C_6D_6 (1.5 mL), forming a mixture of silene **1a** and its dimer **22**. The progress of the irradiation was monitored by ^{1}H NMR spectroscopy, and after 13 h of irradiation the solution consisted of a mixture of silene **1a**, dimer **22**, and pivaloylsilane **21a** in a ratio of 54:33:13, respectively, as determined by ^{1}H NMR spectroscopy. A solution of *trans*-2-phenylcyclopropanecarbaldehyde (**10**; 38 mg, 0.26 mmol) in C_6D_6 (0.5 mL) was added to the yellow solution of **1a**, **22**, and **21a**. Upon addition of aldehyde **10**, the color of the reaction mixture changed to light orange; however, after sitting for 18 h, the color of the solution had completely disappeared. The crude reaction mixture contained *cis*,*trans*-diene **23**, siloxetanes **24a**,**b**, and acylsilanes **25a**,**b** in a ratio of 74:11:10:2:3, respectively, as well as pivaloylsilane **21a** and aldehyde **10**, as determined by ^{1}H NMR spectroscopy. The solvent was removed from the crude reaction mixture, yielding a pale yellow residue (98 mg). The mixture was separated by preparative thin-layer chromatography (silica gel, 1:1 hexanes−CH_2Cl_2), yielding *cis*,*trans*-diene **23** (21.1 mg), pivaloylsilane **21a**, an impure mixture of pivaloylsilane **21a** and acylsilanes **25a**,**b** (2.3 mg), and aldehyde **10**. Since such a small amount of the mixture containing acylsilanes **25a**,**b** was obtained, the products of several reactions were combined to obtain a sufficient amount for further purification and characterization. **23**: IR (cm^{-1}) 3026 (m), 2954 (s), 2898 (m), 1636 (s), 1596 (s), 1405 (s), 1248 (s), 1058 (s), 838 (s), 743 (s), 690 (s); ^{1}H NMR (C_6D_6) δ 7.61 (ddd, 1H, OCH=CHC*H*=CH, J = 0.9, 10.9, 16.1 Hz), 7.45−7.48 (m, 2H, *o*-Ph *H*), 7.13 (tt, 2H, *m*-Ph *H*, J = 7.6, 1.8 Hz), 6.99 (tt, 1H, *p*-Ph *H*, J = 7.6, 1.4 Hz), 6.46 (d, 1H, OCH=CHCH=C*H*, J = 16.0 Hz), 6.35 (dt, 1H, OC*H*=CHCH=CH, J = 1.0, 5.6 Hz), 5.40 (ddd, 1H, OCH=C*H*CH=CH, J = 0.8, 5.6, 10.8 Hz), 3.89 (s, 1H, Me$_3$SiOC*H*), 0.99 (s, 9H, *t*-Bu), 0.35 (s, 9H, SiMe$_3$), 0.26 (s, 9H, SiMe$_3$), 0.22 (s, 9H, OSiMe$_3$); ^{13}C NMR (C_6D_6) δ 143.88 (O*C*H=CHCH=CH), 138.86 (*i*-Ph *C*), 128.89 (*m*-Ph *C*), 128.85 (OCH=CHCH=*C*H), 127.05 (*p*-Ph *C*), 126.35 (*o*-Ph *C*), 122.78 (OCH=CH*C*H=CH), 111.12 (OCH=*C*HCH=CH), 80.03 (Me$_3$SiO*C*H), 35.69 (*C*$(CH_3)_3$), 28.66 (C(*C*$H_3)_3$), 1.16 (OSiMe$_3$), 0.58 (SiMe$_3$), 0.21 (SiMe$_3$); ^{29}Si NMR (C_6D_6) δ 16.3 (O*Si*Me$_3$), 13.7 (*Si*(SiMe$_3$)$_2$), −16.8 (*Si*Me$_3$), −17.8 (*Si*Me$_3$); high-resolution EI-MS for $C_{24}H_{46}O_2Si_4$ (M^+) *m/z* calcd 478.2575, found 478.2568. **24a**,**b**: ^{1}H NMR (C_6D_6) δ 4.39 (d, 1H, OC*H*, J = 8.4 Hz, **24b**), 4.34 (d, 1H, OC*H*, J = 9.0 Hz, **24a**), ∼1.95 (m, OCHC*H*$_{cycloprop}$, **24b**), ∼1.80 (m, OCHC*H*$_{cycloprop}$, **24a**), ∼0.9−1.3 (six m, C*H*$_{cycloprop}$, **24a**,**b**); ^{29}Si NMR (C_6D_6) δ 57.6 (*Si*(SiMe$_3$)$_2$, **24b**), 57.4 (*Si*(SiMe$_3$)$_2$, **24a**). **25a**,**b**: IR (cm^{-1}) 2956 (s), 2899 (m), 1615 (s), 1249 (s), 1052 (s), 1028 (m), 839 (s), 749 (m), 694 (m). **25a**: ^{1}H NMR (C_6D_6) δ 6.96−7.08 (m, 3H, *m*,*p*-Ph *H*), 6.87−6.88 (m, 2H, *o*-Ph *H*), 4.42 (s, 1H, Me$_3$SiOC*H*), 2.79 (ddd, 1H, C*H*C=O, J = 3.8, 5.3, 7.7 Hz), 2.67 (ddd, 1H, PhC*H*, J = 3.9, 6.3, 9.0 Hz), 1.91 (ddd, 1H, CH_2, J = 3.8, 5.3, 8.9 Hz), 1.17−1.20 (m, 1H, CH_2), 0.98 (s, 9H, *t*-Bu), 0.38 (s, 9H, SiMe$_3$), 0.23 (s, 9H, SiMe$_3$), 0.20 (s, 9H, OSiMe$_3$); ^{13}C NMR (C_6D_6) δ 241.15 (*C*=O), 141.15 (*i*-Ph *C*), 128.67 (*m*-Ph *C*), 126.42 (*p*-Ph *C*), 125.75 (*o*-Ph *C*), 79.83 (Me$_3$SiO*C*H), 41.90 (*C*HC=O),[42] 36.05 (*C*$(CH_3)_3$), 30.49 (Ph *C*H), 28.91 (C(*C*$H_3)_3$), 20.21 (*C*H$_2$),[42] 2.07 (SiMe$_3$), 1.20 (SiMe$_3$), 0.88 (SiMe$_3$);[43] ^{29}Si NMR (C_6D_6) δ 15.0 (O*Si*Me$_3$), −15.7 (SiMe$_3$), −15.9 (SiMe$_3$), −37.5 (*Si*(SiMe$_3$)$_2$). **25b**: ^{1}H NMR (C_6D_6) δ 6.96−7.08 (m, 3H, *m*,*p*-Ph *H*), 6.94−6.96 (m, 2H, *o*-Ph *H*), 4.44 (s, 1H, Me$_3$SiOC*H*), 2.79 (ddd, 1H, C*H*C=O, J = 3.8, 5.3, 7.7 Hz), 2.75 (ddd, 1H, PhC*H*, J = 4.0, 6.5, 8.6), 1.86 (ddd, 1H, CH_2, J = 3.8, 5.3, 9.2 Hz), 1.17−1.20 (m, 1H, CH_2), 0.97 (s, 9H, *t*-Bu), 0.34 (s, 9H, SiMe$_3$), 0.23 (s, 9H, OSiMe$_3$), 0.19 (s, 9H, SiMe$_3$); ^{13}C NMR (C_6D_6) δ 241.04 (*C*=O), 141.15 (*i*-Ph *C*), 128.67 (*m*-Ph *C*), 126.49 (*p*-Ph *C*), 125.92 (*o*-Ph *C*), 79.83 (Me$_3$SiO*C*H), 41.61 (*C*HC=O),[42] 36.05 (*C*$(CH_3)_3$), 30.61 (Ph *C*H), 28.94 (C(*C*$H_3)_3$),[42] 20.04 (*C*H$_2$),[42] 2.07 (SiMe$_3$), 1.29 (SiMe$_3$), 0.88 (SiMe$_3$);[43] ^{29}Si NMR (C_6D_6) δ 15.0 (O*Si*Me$_3$), −15.0 (SiMe$_3$), −15.4 (SiMe$_3$),

(41) The cyclopropyl ring attached to the carbonyl carbon is assigned as ring A, and the cyclopropyl ring attached to the OCH$_2$ is assigned as ring B.

(42) A number of the carbon signals were difficult to assign to a specific isomer, and thus, their assignments may be reversed.

(43) The ^{13}C signals for compounds **25a** and **25b** attributable to the SiMe$_3$ groups could not be specifically assigned as SiMe$_3$ or OSiMe$_3$, due to overlap of the signals.

−37.4 (*Si*($SiMe_3$)$_2$). **25a**,**b**: high-resolution CI-MS for $C_{24}H_{47}O_2Si_4$ ($M + H^+$) *m/z* calcd 479.2653, found 479.2652.

Addition of *trans*-2-Phenylcyclopropanecarbaldehyde (10) to 2-(1-Adamantyl)-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-silene (1b). Aldehyde **10** was added to silene **1b** as described for silene **1a**. Specific experimental details can be found in the Supporting Information. **26**: IR (cm^{-1}) 2906 (s), 2852 (m), 1637 (s), 1453 (w), 1405 (w), 1248 (s), 1143 (w), 1050 (s), 839 (s), 745 (w), 691 (w); ^{1}H NMR (C_6D_6) δ 7.63 (ddd, 1H, OCH═CHC*H*═CH, J = 1.0, 11.0, 16.0 Hz), 7.47−7.50 (m, 2H, *o*-Ph *H*), 7.11−7.15 (m, 2H, *m*-Ph *H*), 6.97−7.01 (m, 1H, *p*-Ph *H*), 6.47 (d, 1H, OCH═CHCH═C*H*, J = 16.0 Hz), 6.38 (dt, 1H, OC*H*═CHCH═CH, J = 1.0, 5.6 Hz), 5.42 (ddd, 1H, OCH═C*H*CH═CH, J = 0.8, 5.7, 10.7 Hz), 3.83 (s, 1H, Me_3SiOCH), 1.96 (bs, 3H, Ad C*H*), 1.64−1.72 (m, 12H, Ad CH_2), 0.39 (s, 9H, $SiMe_3$), 0.30 (s, 9H, $SiMe_3$), 0.25 (s, 9H, $OSiMe_3$); ^{13}C NMR (C_6D_6) δ 144.02 (O*C*H═CHCH═CH), 138.89 (*i*-Ph *C*), 128.89 (*m*-Ph *C*), 128.78 (OCH═CHCH═*C*H), 127.03 (*p*-Ph *C*), 126.34 (*o*-Ph *C*), 122.84 (OCH═CH*C*H═CH), 111.06 (OCH═*C*HCH═CH), 81.30 (Me_3SiOCH), 41.41 (Ad CH_2), 37.85 (4° Ad *C*), 37.31 (Ad CH_2), 28.99 (Ad *C*H), 1.24 ($OSiMe_3$), 0.69 ($SiMe_3$), 0.29 ($SiMe_3$); ^{29}Si NMR (C_6D_6) δ 16.3 (O*Si*Me_3), 14.0 (*Si*($SiMe_3$)$_2$), −16.6 (*Si*Me_3), −17.9 (*Si*Me_3); high-resolution EI-MS for $C_{30}H_{52}O_2Si_4$ (M^+) *m/z* calcd 556.3044, found 556.3054. **27a**,**b**: ^{1}H NMR (C_6D_6) δ 4.38 (d, 1H, OC*H*, J = 9.2 Hz, **27b**), 4.33 (d, 1H, OC*H*, J = 9.6 Hz, **27a**); ^{29}Si NMR (C_6D_6) δ 58.4 (*Si*($SiMe_3$)$_2$, **27a**), 58.0 (*Si*($SiMe_3$)$_2$, **27b**). **28a**,**b**: ^{1}H NMR (C_6D_6) δ 4.45 (s, Me_3SiOCH, **28b**), 4.43 (s, Me_3SiOCH, **28a**).

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Supporting Information Available: Text and figures giving a structure elucidation section for compounds **17**, **19**, *trans*- and *cis*-**20**, **23**, **25a**,**b**, **26**, and **27a**,**b**, general experimental details, experimental details of the addition of **10** to **1b**, and ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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