

Substituent Effects on the Reactivity of the Silicon–Carbon Double Bond

TRACY L. MORKIN AND WILLIAM J. LEIGH*

Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, Ontario Canada L8S 4M1

Received April 28, 2000

ABSTRACT

Laser flash photolysis of various organosilicon compounds such as aryl-, vinyl-, and alkynylsilanes, silacyclobutanes and silacyclobutenes, and α -silylketenes and -diazomethanes leads to the formation of reactive silenes which can be detected directly in solution, allowing detailed studies of the kinetics and mechanisms of their reactions with nucleophiles. Over 30 transient silenes have now been studied by these methods, providing the opportunity to systematically assess the effects of substituents at silicon and carbon on the reactivity of the Si=C bond.

Introduction

The study of organosilicon reactive intermediates has been a rapidly growing field over the past 20 years. Gas- and condensed-phase studies of such reactive intermediates as silyl radicals,¹ silylenes,^{2,3} disilenes,^{3,4} and silenes have revealed there to be many of the expected commonalities—and many intriguing differences—between the chemistry of these species and that of their counterparts in organic chemistry. In addition to providing answers to basic questions related to chemical bonding, structure, and reactivity involving the Group 14 elements, the study of these reactive intermediates has the potential of providing useful insight and direction for growing fields such as silicon-based polymers,⁵ photolithography,⁶ and silicon surface science.^{7,8}

The chemistry of the silicon–carbon double bond has been an area of active interest since 1967, when Gusel'nikov and Flowers reported the first evidence of the possible existence of such species as a reactive intermediate in the high-temperature pyrolysis of a silacyclobutane derivative.⁹ Hundreds of examples of *silenes* and many of the qualitative aspects of their reactivity are now known, and the area has been regularly reviewed since the mid-

1970s.¹⁰ While a respectable number of “stable” derivatives have been isolated and identified, most silenes—especially relatively simple ones—are transients, formed as reactive intermediates in various thermal and photochemical reactions of organosilicon compounds. Because of this, their direct detection and study requires either matrix isolation or fast time-resolved spectroscopic techniques. While many simple silenes were studied in the 1980s by low-temperature matrix isolation techniques, information on their absolute reactivities in solution or gas phases requires the use of time-resolved methods that have only become readily available in more recent years. This Account describes our efforts to employ these techniques—laser flash photolysis methods in particular—to study the mechanisms of some of the more commonly known reactions of silenes, and to systematically assess the effects of substituents on the kinetic stability of the silicon–carbon double bond.

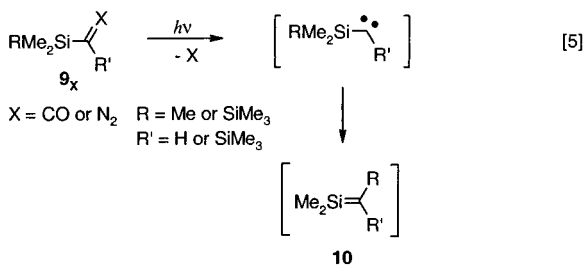
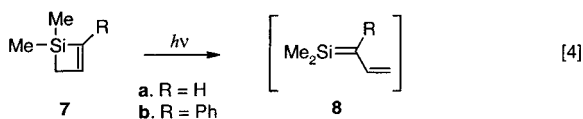
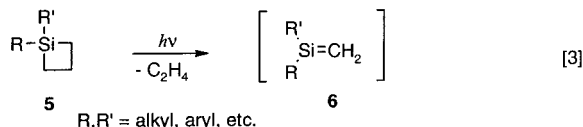
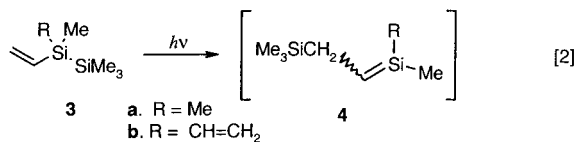
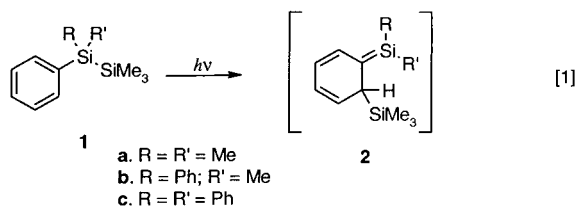
Photochemical Precursors of Transient Silenes

A number of photochemical reactions in organosilicon chemistry afford products consistent with the initial formation of transient silenes,^{11,12} and many of them have proven to be ideal for laser flash photolysis studies of silene reactivity in solution. Our initial efforts employed phenyldisilanes (e.g., **1**) as precursors to the transient (1-sila)hexatriene derivatives **2** (eq 1),¹³ which sprang from the early, product-oriented work of Ishikawa and Kumada on the photochemistry of these compounds under various conditions.¹⁴ Silene formation in these cases is the result of photochemically allowed [1,3]-silyl migration into the ortho position of one of the aromatic rings. This process also occurs in vinylsilanes (**3**; eq 2),^{15–18} which are also useful precursors to transient silenes for time-resolved spectroscopic study.¹⁹ Perhaps the most versatile precursors to simple silenes are silacyclobutanes (**5**), which undergo formal [2 + 2]-photocycloreversion to yield silenes of the type RR'Si=CH₂ (**6**; eq 3).^{20–28} The process occurs with adequate efficiency in derivatives bearing a wide range of aryl and/or alkyl substituents at silicon, using 248-nm laser excitation for aryl-substituted derivatives and 193-nm excitation for non-arylated ones.^{22,29–33} Silacyclobutenes (**7**; eq 4) yield the readily detectable³⁴ 2-vinyl-substituted silenes **8** via photoelectrocyclic ring-opening.^{35–37} Also, α -silyl ketenes (**9_{CO}**) and the analogous diazo compounds (**9_{N2}**) have been used as precursors to the family of carbon-substituted silenes **10** (eq 5).^{38–47} In these cases, silenes are formed by rapid ($k \geq 10^9 \text{ s}^{-1}$) [1,2]-migration (from silicon to carbon)⁴⁷ in the α -silyl carbene formed in the primary photochemical process.

The silenes formed in these reactions generally have lifetimes on the order of several microseconds, decay with second-order kinetics in rigorously dry solution, and exhibit UV absorption maxima ranging from 260 to 320 nm, typically 50–80 nm to the red of the corresponding alkene of the same substitution pattern.

Tracy Morkin was born in Corunna, Ontario, in 1973 and received her B.Sc. in organic chemistry in 1996 from Mount Allison University in Sackville, New Brunswick. Throughout her bachelor's degree studies she was a Woman in Engineering and Science scholar with summer tenure at the National Research Council of Canada under the supervision of D. D. M. Wayner and K. U. Ingold. She is presently a fourth-year Ph.D. candidate and NSERC scholarship holder studying the chemistry of organosilicon reactive intermediates.

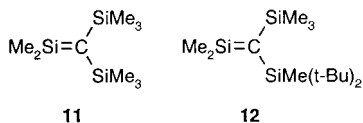
William J. Leigh grew up in Chatham, Ontario. He received the B.Sc. and Ph.D. degrees from the University of Western Ontario, the latter in 1981, and then held postdoctoral positions at the IBM Thomas J. Watson Research Center and the National Research Council of Canada in Ottawa. He joined the Department of Chemistry at McMaster University in 1983, where he is now Professor and Chair. His research is in the areas of organic and organometallic photochemistry, and the chemistry of organosilicon and organogermanium reactive intermediates.



The Addition of Alcohols to Transient Silenes

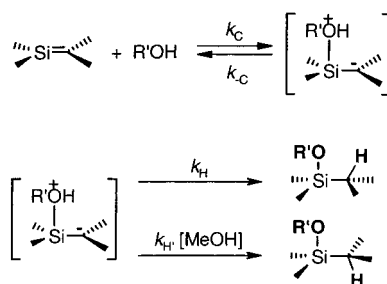
Silenes are potent electrophiles, reacting rapidly with reagents such as water, alcohols, amines, carboxylic acids, and alkoxysilanes by [1,2]-addition, with ketones and aldehydes by ene-addition and/or [2 + 2]-cycloaddition, and with alkenes and dienes by ene-addition, [2 + 2]- and/or [4 + 2]-cycloaddition.^{10,12,48–51} In the absence of such reagents, they undergo dimerization, usually by head-to-tail [2 + 2]-cycloaddition.^{10,52–56} The reactions with nucleophiles are highly regioselective, consistent with the high degree of polarity which is expected to be associated with the $\delta^+\text{Si}=\text{C}^{\delta-}$ bond due to simple electronegativity differences between silicon and carbon.

Wiberg and co-workers first employed competition methods to determine the relative reactivities of a large variety of silene traps with 1,1-dimethyl-2,2-bis(trimethylsilyl)silene (**11**),⁵⁷ a transient silene related to the stable di-*tert*-butylmethylsilyl analogue **12**.^{58,59} This work estab-



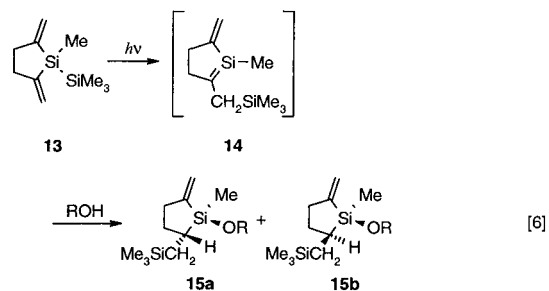
lished that the most rapid reactions of silenes are those with simple alcohols and amines, which led to the

Scheme 1



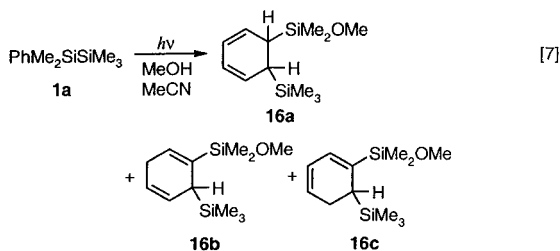
proposal that alcohol addition—the most commonly used trapping reaction for transient silenes—most likely proceeds by a stepwise mechanism involving initial nucleophilic attack at silicon to form a σ -bonded complex, which proceeds to product by proton transfer from oxygen to the silenic carbon. This proposal was supported by the isolation and structural characterization of the THF complex of **12**,⁶⁰ and by the theoretical studies of Nagase and Kudo on the addition of water and HCl to the parent, H₂Si=CH₂.⁶¹

This mechanism was put on a firmer footing by Kira and co-workers, who found that the stereochemistry of addition of various aliphatic alcohols to the transient cyclic silene **14** (formed photolytically from the vinyldisilane **13**; eq 6) varies with the alcohol *and its concentration*. This concentration dependence demands the involvement of an intermediate, such as Wiberg's σ -complex, which collapses to product by competing uni- and bimolecular proton transfer, the latter requiring a second molecule of alcohol (see Scheme 1). It was proposed that the unimolecular pathway yields the *syn*-addition product **15a**, while the *anti*-isomer (**15b**) is formed by the bimolecular H-transfer pathway.⁶²



A more pronounced effect of this type occurs in the addition of MeOH to the transient (1-sila)hexatriene **2a**, from which three regioisomeric addition products (**16a–c**) are obtained in relative yields that vary with MeOH concentration in acetonitrile solution (eq 7).⁶³ The [1,2]-addition product **16a** dominates at very low methanol concentrations (<0.05 M), while the [1,4]- and [1,6]-adducts **16b,c** are the major products in the presence of higher concentrations of methanol. This behavior is also consistent with the intermediacy of a silene–alcohol complex that collapses to product by competing unimolecular and bimolecular proton-transfer processes.

Kinetic evidence in support of this mechanism was obtained from a laser flash photolysis study of the reactivity of **2a** in hydrocarbon and acetonitrile solution.¹³ The



silene was found to react rapidly with water and aliphatic alcohols, and the pseudo-first-order rate constant for decay of **2a** (k_{decay}) was found to vary quadratically with ROH concentration (R = H, Me, Et) according to eq 8, where k_0 is the pseudo-first-order rate constant for silene decay in the absence of ROH, and k_{ROH} and $k_{2\text{ROH}}$ are the second- and third-order rate constants for reaction of the silene with one and two molecules of alcohol, respectively. Figure 1 shows a plot of k_{decay} vs [ROH] for reactive quenching of **2a** by MeOH in acetonitrile solution, fitting of which to eq 8 yields values of $k_{\text{MeOH}} = (2.0 \pm 0.6) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{2\text{MeOH}} = (5.8 \pm 1.0) \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$ for the second- and third-order reaction rate constants, respectively. The ratio of the rate constants for reaction by the second- and third-order pathways ($k_{\text{ROH}}/k_{2\text{ROH}} \approx 0.03$ for **2a**) increases with increasing steric bulk in the alcohol.¹³

$$k_{\text{decay}} = k_0 + k_{\text{ROH}}[\text{ROH}] + k_{2\text{ROH}}[\text{ROH}]^2 \quad (8)$$

This is precisely the behavior predicted by the Kira mechanism, provided that the formation of the silene-ROH complex is reversible and the proton-transfer steps are rate-limiting. The complete mechanism is shown in Scheme 1. Indeed, the first-order term in ROH (k_{ROH}) was found to exhibit a primary deuterium kinetic isotope effect on the order of $k_{\text{H}}/k_{\text{D}} \approx 1.5$ for both H₂O and MeOH addition. Furthermore, k_{decay} was found to obey a linear dependence on [ROH] for addition of 2,2,2-trifluoroethanol and acetic acid,¹³ whose greater acidity and lower nucleophilicity would be expected to result in a change in the rate-determining step from proton transfer (k_{H}) to complexation (k_{C}). In a later, more comprehensive kinetic study of the addition of alcohols to **2a-c**, it was shown that the intercomplex proton-transfer process (represented in Scheme 1 by $k_{\text{H}'}$) most likely proceeds by initial deprotonation of the complex by a second molecule of alcohol or the solvent, followed by fast reprotonation at carbon.⁶³

Such complex kinetic behavior is not observed with simpler silenes of the type Ar₂Si=CH₂ (e.g., **6a,b**), which have been generated in solution by 248-nm photolysis of the corresponding 1,1-diarylsilacyclobutane **5a,b** (eq 9).³⁰ Reaction of these silenes with aliphatic alcohols is significantly faster than is the case with **2**, and the silene decay rate follows a linear dependence on [ROH] over the range of alcohol concentrations that can be studied with our apparatus ([ROH]_{max} ≤ 0.01 M for these silenes). However, evidence that the mechanism of Scheme 1 still operates in these cases has been obtained from steady-state competition studies where the concentration of alcohol used can be much higher. The ratio of alkoxy-

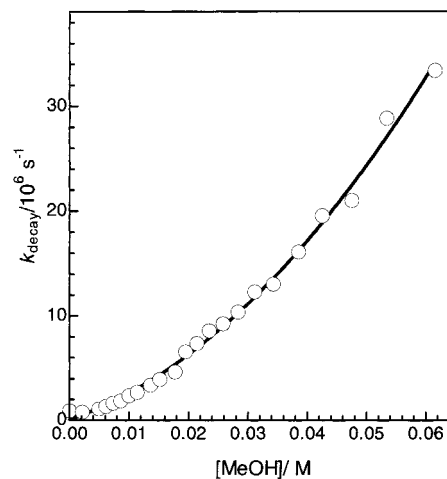
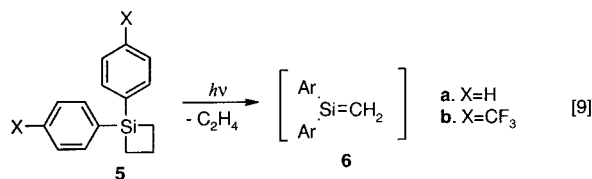


FIGURE 1. Stern–Volmer plot of the pseudo-first-order rate constant for decay of silene **2a** versus MeOH concentration in deoxygenated acetonitrile solution at 23 °C.¹³

lanes obtained from competing reaction of 1,1-diphenylsilene (**6a**) with MeOH and *t*-BuOH was found to vary with bulk alcohol concentration over the 0–0.5 M range.⁶⁴ The results are consistent with the involvement of a second, higher order pathway for reaction, which is more important for MeOH than for *t*-BuOH at any given total ROH concentration.



In these cases, the linear dependence of k_{obs} on [ROH] suggests that $k_{\text{H}} \gg k_{\text{H}'}[\text{ROH}]$ over the range of ROH concentrations that can be studied in our experiments, which simplifies the kinetics considerably. Under these conditions, the overall second-order rate constant for ROH addition (k_{ROH}), using the steady-state approximation for the zwitterionic complex, is given by the product of the rate constant for complexation (k_{C}) and the partitioning ratio for collapse of the complex to starting materials and product ($k_{\text{H}}/(k_{\text{H}} + k_{-\text{C}})$; eq 10). As a result of this and the

$$k_{\text{ROH}} = k_{\text{C}} \frac{k_{\text{H}}}{k_{\text{H}} + k_{-\text{C}}} \quad (10)$$

overall strong exothermicity of the reaction, negative activation energies are observed for addition of MeOH or *t*-BuOH to **6a**; indeed, this behavior appears to be typical of simple silenes of this type.⁶⁵ The negative activation energy results because the rate constant for decomplexation exceeds that of product formation (i.e., $k_{\text{H}} < k_{-\text{C}}$) over the particular range of temperatures studied (–5 to 55 °C), and the latter is strongly entropy-controlled. If all this is correct, then addition of deuterated alcohol (ROD) should lead to a more negative Arrhenius activation energy than ROH addition; indeed, exactly this behavior has been reported for the addition of MeOH to **6a** in acetonitrile (Figure 2).⁶⁶

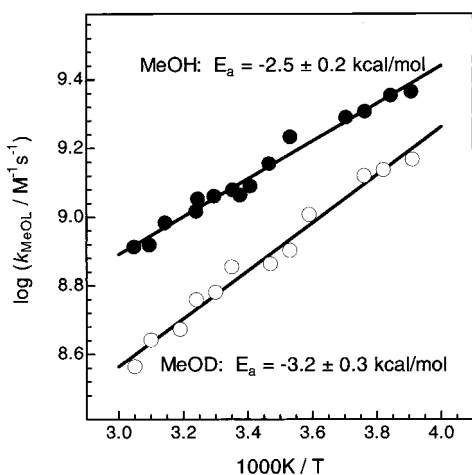


FIGURE 2. Arrhenius plots for the reaction of 1,1-diphenylsilene with MeOH and MeOD in dry acetonitrile solution.⁶⁶

We have also determined absolute rate constants and their Arrhenius parameters for the reactions of **6a** and the ring-substituted derivative **6b** with a number of other nucleophiles, including aliphatic ketones,⁶⁷ acetic acid,⁶⁶ aliphatic amines,⁶⁸ and alkoxysilanes.⁶⁹ All appear to react via two-step mechanisms analogous to that for alcohol addition, with nucleophilic attack occurring in the first step. However, since alcohol addition is the most widely used, most convenient, and mechanistically the best understood of silene trapping reactions, it is the most logical choice of a diagnostic reaction with which to quantify the effects of substituent on silene reactivity.

Substituent Effects on Silene Reactivity

The first systematic study of substituent effects on the electronic structure of the Si=C bond was reported in the mid-1980s by Apeloig and Karni, who carried out ab initio calculations on a series of simple 1- and 2-substituted silenes of the types $RHSi=CH_2$ and $H_2Si=CHR$, respectively.⁷⁰ They suggested that bond polarity factors are primarily responsible for the high intrinsic reactivity of silenes, and that the remarkable stability of isolable silenes such as those of Brook and co-workers ($(Me_3Si)_2Si=C(R)-OSiMe_3$) is due mainly to electronic effects which act to reduce the natural polarity of the $\delta^+Si=C\delta^-$ bond. This proposal was made on the basis of observed variations in calculated Mulliken charge densities, which are reduced by π -acceptor/ σ -donor substituents at silicon and π -donor/ σ -acceptor substituents at carbon. These considerations lead one to predict that Wiberg's silenes (**11** and **12**), having σ -donor substituents at carbon, should in fact be quite potent electrophiles, making the fact that **12** is isolable all the more remarkable. It should be remembered, however, that isolability implies only that the silene is stable toward dimerization. Indeed, both Brook's and Wiberg's silenes were isolated under inert atmosphere conditions, and both evidently disappear rapidly upon exposure to air or moisture.^{58,71} This suggests that they both retain some degree of reactivity toward nucleophiles, the extent of which can only be determined experimentally.

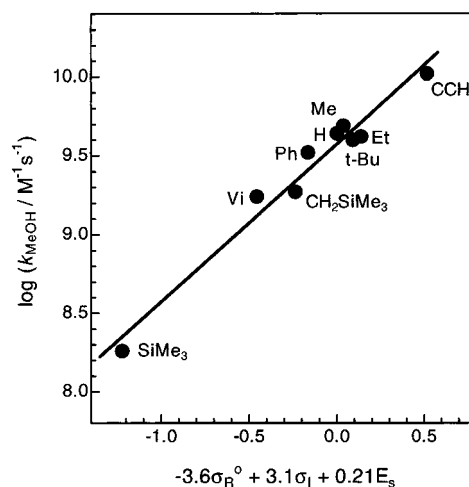
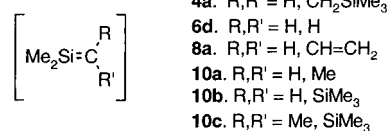
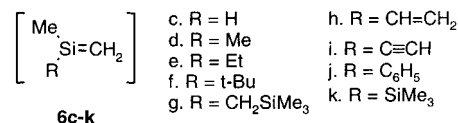


FIGURE 3. Three-parameter substituent correlation of the rates of reaction of Si-substituted 1-methylsilenes (**6c–k**) with methanol in dry hexane solution at 23 °C.³³

Our experimental studies of the effects of substituents at silicon and carbon on silene electrophilicity have focused on two series of simple silenes—of the types $Me-(R)Si=CH_2$ (**6c–k**) and $Me_2Si=C(R)(R')$ (**6d**, **4a**, **8a**, **10**)—and have employed the absolute rate constants for addition of MeOH in hydrocarbon solution as a representative gauge of silene reactivity toward nucleophilic addition. The silenes **6c–k** were generated and detected



by 193- or 248-nm laser flash photolysis of the corresponding 1-methylsilacyclobutanes (**5c–k**; eq 3), while the series of C-substituted 1,1-dimethylsilenes $Me_2Si=C(R)(R')$ were generated in a similar fashion from silacyclobutene (**7a**; eq 4), vinyldisilane (**3a**; eq 2), or α -silylketene or -diazomethane precursors (**9**; eq 5). All of them exhibit characteristically high reactivity toward methanol, with absolute rate constants varying over the range 2×10^8 – $1 \times 10^{10} M^{-1} s^{-1}$, depending on substituent.

The rate constants for reaction of the Si-substituted silenes correlate acceptably with a three-parameter function incorporating standard resonance and inductive and steric substituent parameters (σ_R^0 , σ_I , and E_s , respectively), as is shown in Figure 3.³³ This correlation indicates that the electrophilic reactivity of silicon–carbon double bonds is enhanced by π -donor/ σ -acceptor substituents at silicon, and retarded by steric effects at this position. According to the calculations of Apeloig and Karni, substituents of these types act to increase Si=C bond polarity, an effect which would be expected to enhance reactivity toward both nucleophilic attack at silicon and electrophilic attack

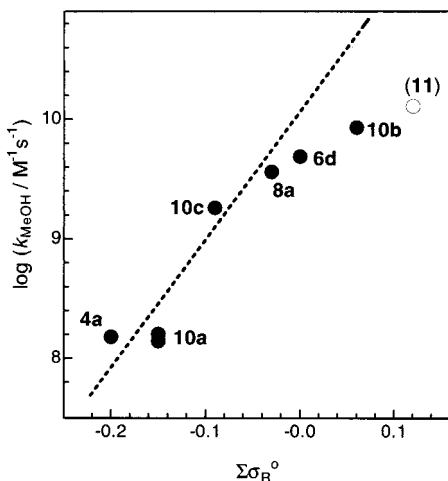
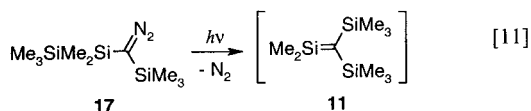


FIGURE 4. Plot of $\log k_{\text{MeOH}}$ versus the resonance substituent parameter σ_R^0 for the reaction of C-substituted 1,1-dimethylsilenes with methanol in dry hexane solution at 23 °C.⁴⁷

at carbon. From the manner in which the (negative) Arrhenius activation energies for MeOH addition vary with substituent for several of the silenes in the series,^{32,33} as well as the variations in absolute reactivity, we conclude that the effect is due to a combination of an increase in both the rate constant for complexation and the partitioning of the complex between product and starting materials; i.e., both k_C and $k_H/(k_H + k_C)$ increase as overall reactivity increases throughout the series.

In contrast, the rate constants for addition of methanol to the series of C-substituted silenes $\text{Me}_2\text{Si}=\text{C}(\text{R})(\text{R}')$ were found to correlate acceptably with the single substituent parameter σ_R^0 ($r^2 = 0.909$; see Figure 4), and nothing is gained upon expanding the analysis to include inductive and steric substituent parameters.⁴⁷ The fit yields a reaction constant $\rho_R = +8.0 \pm 2.2$, which indicates that π -electron donor substituents at carbon stabilize the Si=C bond toward reaction with nucleophiles. Again, this is precisely what theory predicts and is fully consistent with the remarkable kinetic stability of the Brook silenes.

The data discussed above underline the apparent anomaly associated with the stability of Wiberg's isolable silene **12**; silene **10b**, with only one $-\text{SiMe}_3$ substituent at carbon, is the most reactive silene in the series toward nucleophiles—more reactive even than 1,1-dimethylsilene (**6d**). Even greater reactivity is hence expected for Wiberg's bis(trimethylsilyl) analogue **11**. Following an early report of the successful generation and detection of this silene from the low-temperature matrix photolysis of (pentamethyldisilyl)(trimethylsilyl)diazomethane (**17**; eq 11),⁴⁵ we have recently prepared and studied the photochemistry of this compound in solution by steady-state and laser flash photolysis methods.⁷² Laser flash photolysis of



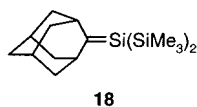
17 (eq 11) in dry hexane affords a short-lived ($\tau \leq 500$ ns) transient species with a UV absorption spectrum which

is similar to that of **10b** ($\lambda_{\text{max}} = 280$ nm) and identical to that reported by Sekiguchi and Ando in their matrix study of **17**.⁴⁵ Most significantly, the transient reacts voraciously with MeOH, exhibiting a second-order rate constant $k_{\text{MeOH}} = (1.3 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in hexane at 23 °C. If our assignment of this transient to silene **11** is correct, the result indicates it to be the most potently electrophilic silene to have yet been studied. Thus, it can be concluded that the isolable analogue **12** owes its kinetic stability solely to steric shielding effects associated with the $-\text{SiMe}(\text{t-Bu})_2$ substituent, which must *far* outweigh the destabilizing influence of methyl substitution at silicon and trialkylsilyl substitution at carbon on the kinetic stability of this silene. Inclusion of the data point for **11** with the others in Figure 4 now makes it clear that the plot exhibits pronounced downward curvature in the more reactive members of the series as k_{MeOH} approaches the diffusional limit, as would clearly be expected. The dashed line of Figure 4 represents the ρ_R value obtained for data points in the linear region of the plot (i.e., $\Sigma\sigma_R < 0$). Thus, the true ρ_R value is likely to be larger than we previously reported; it cannot yet be defined reliably but appears to be more in the range of 9–10.

All of the silenes we have investigated so far appear to react with MeOH by the stepwise mechanism shown in Scheme 1, as judged by the fact that negative Arrhenius activation energies have been observed in every example whose temperature dependence has been studied.⁵¹ Those derivatives for which k_{MeOH} is on the order of $10^9 \text{ M}^{-1} \text{ s}^{-1}$ or higher exhibit linear dependences of k_{decay} on MeOH concentration (i.e., $k_H \gg k_H'[\text{MeOH}]$ under the conditions of our experiments). As overall reactivity is reduced into the $10^8 \text{ M}^{-1} \text{ s}^{-1}$ range, the kinetic plots generally assume some degree of nonlinearity,⁶³ consistent with the bimolecular (general base catalyzed) proton-transfer pathway for collapse of the intermediate complex taking on increased importance. This is presumably due to a reduction in the magnitude of k_H as overall reactivity decreases, as is also indicated by the fact that the Arrhenius activation energies for addition of MeOH to **6c–k** take on increasingly negative values as overall reactivity decreases. Current work in our laboratory is directed at investigating how the mechanisms for addition of nucleophiles to silenes change as overall reactivity is reduced further.

Recent computational studies by Apeloig and co-workers are also consistent with the involvement of silene–alcohol complexes in the reactions of water and MeOH with many of the substituted silenes discussed above, but suggest that the mechanism changes to a concerted one in (relatively nonpolar) silenes of the type $(\text{R}_3\text{Si})_2\text{Si}=\text{CR}'_2$.⁷³ The absolute reactivity of such silenes (e.g., $(\text{Me}_3\text{Si})_2\text{Si}=\text{CMe}_2$) with MeOH is predicted to be on the order of $k_{\text{MeOH}} = 10^4\text{--}10^5 \text{ M}^{-1} \text{ s}^{-1}$ in hexane, by extrapolation of our kinetic data for reaction of MeOH with $\text{Me}_2\text{Si}=\text{CH}_2$ (**6d**; $k_{\text{MeOH}} \approx 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$),³² $(\text{Me}_3\text{Si})(\text{Me})\text{Si}=\text{CH}_2$ (**6k**; $k_{\text{MeOH}} \approx 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$),³³ and $\text{Me}_2\text{Si}=\text{CHMe}$ (**10a**; $k_{\text{MeOH}} \approx 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$).⁴⁷ The behavior of the adamantyl silene **18**,⁷⁴ which we are currently studying in collaboration with Professor Apeloig and his group,⁷⁵

appears to support both of these predictions. Silene **18** is



so unreactive toward MeOH that reaction can be detected only (at least with our laser photolysis system) in essentially neat methanol solution, where the lifetime is on the order of ca. 30 ms at room temperature, and decreases with increasing temperature. In contrast to its sluggish reactivity as an electrophile, it remains reactive toward (head-to-head⁷⁴) dimerization, the absolute rate constant for which is on the order of $10^5 \text{ M}^{-1} \text{ s}^{-1}$ in hexane solution at 25 °C. This should be compared to that for head-to-tail dimerization of 1,1-diphenylsilene (**6a**) under the same conditions, $k_{\text{dim}} = (1.1 \pm 0.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.⁷⁶

Conclusions

Alcohol addition and [2 + 2]-dimerization are the two best-known and most highly exothermic reactions of silene and simple substituted derivatives in the gas phase and in solution. With “naturally polarized” silenes such as $\text{Ph}_2\text{Si}=\text{CH}_2$ (**6a**), these two reactions proceed regiospecifically and with absolute rate constants that are within an order of magnitude of the diffusional rate constant in hexane solution.

The rate of alcohol addition varies markedly with substitution at the Si=C bond in simple silenes. Comparison of absolute rate data with the results of high-level *ab initio* calculations of the structures and electronic properties of substituted silenes verifies earlier suggestions that bond polarity is the main factor affecting the electrophilic reactivity of the Si=C bond; substituents at either silicon or carbon which act to reduce the natural polarity of the bond through resonance and/or inductive effects kinetically stabilize silenes toward addition of nucleophiles. While the regiochemistry of the reaction is substituent-independent, the mechanism of the reaction appears to change as Si=C bond polarity is reduced significantly.

Bond polarity factors also control the regiochemistry of [2 + 2]-dimerization⁷⁷ but appear to have a smaller effect on the absolute rate constant for the reaction. For example, the (head-to-head) dimerization of the 1,1-bis(trimethylsilyl)silene **18** proceeds about 10^5 times slower than the corresponding (head-to-tail) process in 1,1-diphenylsilene (**6a**) under the same conditions.⁷⁵ Given that these two silenes differ by about 9 orders of magnitude in their reactivity toward methanol under similar conditions, the smaller effect of substituents on the rate of silene dimerization is fascinating indeed. Current work in our laboratory is directed at investigating the implications of these results in greater detail.

We gratefully acknowledge the seminal contributions made by a number of co-workers over the past years, in particular Greg Sluggett, Christine Bradaric, Jo-Ann Banisch, Corinna Kerst, Rabah Boukherroub, Nick Tottl, Tom Owens, Xiaojing Li, and Cam

Harrington, as well as stimulating collaborations with Yitzhak Apeloig, Rob Conlin, Peter Gaspar, Keith Pannell, and Tom Tidwell. We are also grateful to the Natural Sciences and Engineering Research Council of Canada for its generous financial support of our work.

References

- (1) Chatgillaloglu, C. Structural and Chemical Properties of Silyl Radicals. *Chem. Rev.* **1995**, *95*, 1229–1251.
- (2) Gaspar, P. P. Silylenes. In *Reactive Intermediates*, Vol. 3; Jones, M., Jr., Moss, R. A., Eds.; John Wiley & Sons: New York, 1985; Chapter 9.
- (3) Weidenbruch, M. Silylenes and Disilenes: Examples of Low Coordinated Silicon Compounds. *Coord. Chem. Rev.* **1994**, *130*, 275–300.
- (4) West, R. Chemistry of the Silicon–Silicon Double Bond. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201–1211.
- (5) Brook, M. A. Silicones. In *Silicon in Organic, Organometallic, and Polymer Chemistry*; Eaborn, C., Ed.; John Wiley and Sons, Inc.: New York, 2000; pp 256–308.
- (6) Moreau, W. M. *Semiconductor Lithography: Principles, Practices, and Materials*; Plenum Press: New York, 1988.
- (7) Lopinski, G. P.; Moffat, D. J.; Wayner, D. D. M.; Zgierski, M. Z.; Wolkow, R. A. Asymmetric Induction at Silicon Surfaces. *J. Am. Chem. Soc.* **1999**, *121*, 4532–4533.
- (8) Lopinski, G. P.; Moffat, D. J.; Wayner, D. D. M.; Wolkow, R. A. How Stereoselective Are Alkene Addition Reactions on Si(100)? *J. Am. Chem. Soc.* **2000**, *122*, 3548–3549.
- (9) Gusel'nikov, L. E.; Flowers, M. C. The Thermal Decomposition of 1,1-Dimethyl-1-Silacyclobutane and Some Reactions of an Unstable Intermediate Containing a Silicon–Carbon Double Bond. *J. Chem. Soc., Chem. Commun.* **1967**, 864–865.
- (10) (a) Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. M. Unstable Silicon Analogs of Unsaturated Compounds. *Acc. Chem. Res.* **1975**, *8*, 18–25. (b) Gusel'nikov, L. E.; Nametkin, N. S. Formation and Properties of Unstable Intermediates Containing Multiple π – π Bonded Group 4B Metals. *Chem. Rev.* **1979**, *79*, 529–577. (c) Coleman, B.; Jones, M. Silenes. *Chem. Intermed.* **1981**, *4*, 297–367. (d) Raabe, G.; Michl, J. Multiple Bonding to Silicon. *Chem. Rev.* **1985**, *85*, 419–509. (e) Brook, A. G.; Baines, K. M. Silenes. *Adv. Organomet. Chem.* **1986**, *25*, 1–44. (f) Raabe, G.; Michl, J. Multiple Bonding to Silicon. In *The Chemistry of Organic Silicon Compounds*, Vol. 1; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; pp 1015–1142. (g) Brook, A. G.; Brook, M. A. The Chemistry of Silenes. *Adv. Organomet. Chem.* **1996**, *39*, 71–158. (h) Sakurai, H. Mechanism and Structures in Alcohol Addition Reactions of Disilenes and Silenes. In *The Chemistry of Organic Silicon Compounds*, Vol. 2; Rappoport, Z., Apeloig, Y., Eds.; Wiley and Sons, Ltd.: New York, 1998; pp 827–855. (i) Muller, T.; Ziche, W.; Auner, N. Silicon–Carbon and Silicon–Nitrogen Multiply Bonded Compounds. In *The Chemistry of Organic Silicon Compounds*, Vol. 2; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons Ltd.: New York, 1998; pp 857–1052.
- (11) (a) Brook, A. G. The Photochemistry of Organosilicon Compounds. In *The Chemistry of Organic Silicon Compounds*, Vol. 1; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; pp 965–1005. (b) Brook, A. G. The Photochemistry of Organosilicon Compounds. In *The Chemistry of Organic Silicon Compounds*, Vol. 2; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: New York, 1998; pp 1233–1310.
- (12) Steinmetz, M. G. Organosilane Photochemistry. *Chem. Rev.* **1995**, *95*, 1527–1588.
- (13) Sluggett, G. W.; Leigh, W. J. Reactive Intermediates From the Photolysis of Methylpentaphenyl- and Pentamethylphenyldisilane. *J. Am. Chem. Soc.* **1992**, *114*, 1195–1201.
- (14) Ishikawa, M.; Kumada, M. Photochemistry of Organopolysilanes. *Adv. Organomet. Chem.* **1981**, *19*, 51–95.
- (15) Barton, T. J.; Wulff, W. D. Silene Generation From a Silyl 1,3-Migration. *J. Organomet. Chem.* **1979**, *168*, 23–31.
- (16) Ishikawa, M.; Fuchikami, T.; Kumada, M. Photochemically Generated Silicon–Carbon Double-Bonded Intermediates VII. A New Route to Silaethene Derivatives From 1-Alkenyldisilanes. *J. Organomet. Chem.* **1978**, *149*, 37–48.
- (17) Ishikawa, M.; Nishimura, Y.; Sakamoto, H. Silicon–Carbon Unsaturated Compounds. 33. Regiochemistry in the Photochemical Formation of Silenes From 1,2,2,2-Tetramethyl-, 1,1,2,2-Tetramethyl-, and 2-Ethyl-1,2,2-Trimethylphenyldisilane. *Organometallics* **1991**, *10*, 2701–2706.

- (18) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. New Photochemical Reactions of Vinylsilanes Through Silaethene or Silacyclopentane Intermediates. *J. Am. Chem. Soc.* **1976**, *98*, 7424–7425.
- (19) Leigh, W. J.; Bradaric, C. J.; Sluggett, G. W.; Venneri, P.; Conlin, R. T.; Dhurjati, M. S. K.; Ezhova, M. B. A Transient Spectroscopic Study of the Photochemistry of Vinylsilanes. *J. Organomet. Chem.* **1998**, *561*, 19–27.
- (20) Damrauer, R. Cyclobutanes Containing Heterocyclic Silicon and Germanium. *Organomet. Chem. Rev. A* **1972**, *8*, 67–133.
- (21) Boudjouk, P.; Sommer, L. H. Photochemical Generation of an Intermediate Containing a Silicon–Carbon Double Bond or Its Equivalent From 1,1-Diphenylsilacyclobutane. *J. Chem. Soc., Chem. Commun.* **1973**, 54–55.
- (22) Brix, Th.; Arthur, N. L.; Potzinger, P. Stationary and Pulsed Photolysis and Pyrolysis of 1,1-Dimethylsilacyclobutane. *J. Phys. Chem.* **1989**, *93*, 8193–8197.
- (23) Dhanya, S.; Kumar, A.; Vatsa, R. K.; Saini, R. D.; Mittal, J. P.; Pola, J. Time-Resolved Study of the Transients Produced in the CO₂ and ArF Laser Flash Photolysis of Gaseous Silacyclobutane and 1,3-Disilacyclobutane. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 179–183.
- (24) Frey, H. M.; Kashoulis, A.; Ling, L. M.; Lodge, S. P.; Pidgeon, I. M.; Walsh, R. The Infra-Red Multiphoton-Induced Decomposition of Silicon-Containing Four-Membered Rings. A New Source of Silaolefins. *J. Chem. Soc., Chem. Commun.* **1981**, 915–917.
- (25) Bertrand, G.; Dubac, J.; Mazerolles, P.; Ancelle, J. Asymmetric Induction at Silicon From Prochiral Silaethylenes. *J. Chem. Soc., Chem. Commun.* **1980**, 382–383.
- (26) Low, H. C.; John, P. The Photolysis of 1,1-Dimethylsilacyclobutane in the Gas Phase. *J. Organomet. Chem.* **1980**, *201*, 363–369.
- (27) Jutzi, P.; Langer, P. Thermolyse und Photolyse Einiger Sila- und Disilacyclobutane. *J. Organomet. Chem.* **1980**, *202*, 401–409.
- (28) Steinmetz, M. G.; Bai, H. Regioselective One- and Two-Bond Cleavages in the Solution-Phase 185-nm Photochemistry of (E)- and (Z)-1,1,2,3-Tetramethylsilacyclobutane. *Organometallics* **1989**, *8*, 1112–1113.
- (29) Vatsa, R. K.; Kumar, A.; Naik, P. D.; Upadhyaya, H. P.; Pavanaja, U. B.; Saini, R. D.; Mittal, J. P.; Pola, J. UV Spectrum and Decay Kinetics of Transient Methylsilene Produced in the 193 nm Photolysis of Gaseous 1-Methyl-1-Silacyclobutane. *Chem. Phys. Lett.* **1996**, *255*, 129–133.
- (30) Leigh, W. J.; Bradaric, C. J.; Sluggett, G. W. 1,1-Diphenylsilene. *J. Am. Chem. Soc.* **1993**, *115*, 5332–5333.
- (31) Leigh, W. J.; Boukherroub, R.; Bradaric, C. J.; Cserti, C. C.; Schmeisser, J. M. Steady State and Time-Resolved Spectroscopic Studies of the Photochemistry of 1-Arylsilacyclobutanes and the Chemistry of 1-Arylsilenes. *Can. J. Chem.* **1999**, *77*, 1136–1147.
- (32) Kerst, C.; Boukherroub, R.; Leigh, W. J. Direct Detection and Absolute Rate Constants for Reaction of 1,1-Dimethylsilene in Solution. *J. Photochem. Photobiol. A: Chem.* **1997**, *110*, 243–246.
- (33) Leigh, W. J.; Boukherroub, R.; Kerst, C. Substituent Effects on the Reactivity of the Silicon–Carbon Double Bond. Resonance, Inductive, and Steric Effects of Substituents at Silicon on the Reactivity of Simple 1-Methylsilenes. *J. Am. Chem. Soc.* **1998**, *120*, 9504–9512.
- (34) Kerst, C.; Byloos, M.; Leigh, W. J. Far-UV Flash Photolysis in Solution. A Time-Resolved Spectroscopic Study of the Chemistry of 1,1-Dimethyl-1,3-(1-Sila)butadiene. *Can. J. Chem.* **1997**, *75*, 975–982.
- (35) Conlin, R. T.; Zhang, S.; Namavari, M.; Bobbitt, K. L.; Fink, M. J. The Rate of Ring Closure of 1,1-Dimethyl-2-Phenyl-1-Silabuta-1,3-Diene to 1,1-Dimethyl-2-Phenyl-1-Silacyclobutene. *Organometallics* **1989**, *8*, 571–573.
- (36) Steinmetz, M. G.; Udayakumar, B. S.; Gordon, M. S. Mechanistic Studies of the Far-UV Photochemical Ring-Opening and Cleavage Reactions of 1,1-Dimethyl-1-Silacyclobut-2-Ene. *Organometallics* **1989**, *8*, 530–541.
- (37) Tzeng, D.; Fong, R. H.; Soysa, H. S. D.; Weber, W. P. Evidence for the Intermediacy of 1,1-Dimethyl-2-Phenyl-1-Sila-1,3-Butadiene in the Photochemistry and Pyrolysis of 1,1-Dimethyl-2-Phenyl-1-Silacyclobut-2-Ene. *J. Organomet. Chem.* **1981**, *219*, 153–161.
- (38) Seyferth, D.; Menzel, H.; Dow, A. W.; Flood, T. C. Trimethylsilyl-Substituted Diazoalkanes. I. Trimethylsilyldiazomethane. *J. Organomet. Chem.* **1972**, *44*, 279–290.
- (39) Haszeldine, R. N.; Scott, D. L.; Tipping, A. E. Carbene Chemistry. Part III. Reactions of Diazomethyltrimethylsilane. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1440–1443.
- (40) Kreeger, R. L.; Shechter, H. The Chemistry of Trimethylsilylcarbene. *Tetrahedron Lett.* **1975**, 2061–2064.
- (41) Chapman, O. L.; Chang, C.-C.; Kolc, J.; Jung, M. E.; Lowe, J. A.; Barton, T. J.; Turney, M. L. 1,1,2-Trimethylsilaethylene. *J. Am. Chem. Soc.* **1976**, *98*, 7844–7846.
- (42) Chedekel, M. R.; Skoglund, M.; Kreeger, R. L.; Shechter, H. Solid State Chemistry. Discrete Trimethylsilylmethylene. *J. Am. Chem. Soc.* **1976**, *98*, 7846–7848.
- (43) Ando, W.; Sekiguchi, A.; Sato, T. Isomerization of Silene to Ketene in the Photolysis of Pentamethylsilyldiazoacetate. *J. Am. Chem. Soc.* **1981**, *103*, 5573–5574.
- (44) Sekiguchi, A.; Ando, W. Photolysis and Pyrolysis of Polysilylated Diazomethanes. Effective Migrating Tendency of Trimethylsilyl Group to a Carbene Center. *Chem. Lett.* **1983**, 871–874.
- (45) Sekiguchi, A.; Ando, W. Decomposition of Polysilylated Diazomethanes. Silene Formation by Selective Silyl Migration. *Organometallics* **1987**, *6*, 1857–1860.
- (46) Sekiguchi, A.; Sato, T.; Ando, W. Intramolecular Reaction of Silene. Evidence for the Isomerization of Silaacylate to Alkoxyketene. *Organometallics* **1987**, *6*, 2337–2341.
- (47) Leigh, W. J.; Kerst, C.; Boukherroub, R.; Morkin, T. L.; Jenkins, S.; Sung, K.; Tidwell, T. T. Substituent Effects on the Reactivity of the Silicon–Carbon Double Bond. UV Spectra and Reactivity of 2-Substituted 1,1-Dimethylsilenes From Far-UV Flash Photolysis of α -Silylketenes and α -Silyldiazomethanes in Solution. *J. Am. Chem. Soc.* **1999**, *121*, 4744–4753.
- (48) Wiberg, N.; Hwang-Park, H.-S.; Lerner, H.-W.; Dick, S. Über das Silaethen t -Bu₂Si=C(SiMe₃)₂ und die Struktur sowie Reaktivität Seines [4+2]-Cycloaddukts mit Ph₂C=O. *Chem. Ber.* **1996**, *129*, 471–478.
- (49) Wiberg, N. Unsaturated Compounds of Silicon and Group Homologues VIII. Unsaturated Silicon and Germanium Compounds of the Types R₂E=C(SiR₃)₂ and R₂E=N(SiR₃) (E = Si, Ge). *J. Organomet. Chem.* **1984**, *273*, 141–177.
- (50) Ishikawa, M. Photolysis of Organopolysilanes. Generation and Reactions of Silicon–Carbon Double-Bonded Intermediates. *Pure Appl. Chem.* **1978**, *50*, 11–18.
- (51) Leigh, W. J. Kinetics and Mechanisms of the Reactions of Si=C and Ge=C Double Bonds. *Pure Appl. Chem.* **1999**, *71*, 453–462.
- (52) Bernardi, F.; Bottoni, A.; Olivucci, M.; Robb, M. A.; Venturini, A. Does a Concerted Path Exist for the Head-to-Tail [2 π _s + 2 π _s] Cycloaddition of Silaethylene? *J. Am. Chem. Soc.* **1993**, *115*, 3322–3323.
- (53) Bernardi, F.; Bottoni, A.; Olivucci, M.; Venturini, A.; Robb, M. A. Dimerization of Silene. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1617.
- (54) Venturini, A.; Bernardi, F.; Olivucci, M.; Robb, M. A.; Rossi, A. Dimerization of Silaethylene: Computational Evidence for a Novel Mechanism for the Formation of 1,3-Disilacyclobutane via a 1,2 Approach. *J. Am. Chem. Soc.* **1998**, *120*, 1912–1913.
- (55) Seidl, E. T.; Grev, R. S.; Schaefer, H. F., III. Mechanistic, Structural, and Vibrational Aspects of the Dimerization of Silaethylene. *J. Am. Chem. Soc.* **1992**, *114*, 3643–3650.
- (56) Zhang, S.; Conlin, R. T.; McGarry, P. F.; Scaiano, J. C. Reaction Kinetics, Quantum Yields, and Product Studies for the Dimerization of a Stabilized Silene. *Organometallics* **1992**, *11*, 2317–2319.
- (57) Wiberg, N.; Preiner, G.; Schieda, O. Reaktivität Des Silaethens Me₂Si=C(SiMe₃)₂: Thermolyse von (Me₃Si)₂(Me₂XSi)ClI (X Z.B. (PhO)₂PO₂) in Anwesenheit von Silaethen-Fangern. *Chem. Ber.* **1981**, *114*, 3518–3532.
- (58) Wiberg, N.; Wagner, G. A Novel Stable Silaethene. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1005–1006.
- (59) Wiberg, N.; Wagner, G. Zur Kenntnis Des Stabilen Silaethens Me₂Si=C(SiMe₃)(SiMe^tBu₂). *Chem. Ber.* **1986**, *119*, 1467–1476.
- (60) Wiberg, N.; Wagner, G.; Müller, G.; Riede, J. Unsaturated Silicon Compounds VII. Preparation and Structure of a Silaethene Tetrahydrofuranate. *J. Organomet. Chem.* **1984**, *271*, 381–391.
- (61) Nagase, S.; Kudo, T. Ab Initio Mechanistic Comparison of Addition of Hydrogen Chloride to Silaethene and Ethene. *J. Chem. Soc., Chem. Commun.* **1983**, 363–364.
- (62) Kira, M.; Maruyama, T.; Sakurai, H. Stereochemistry and Mechanism for the Addition of Alcohols to a Cyclic Silene. *J. Am. Chem. Soc.* **1991**, *113*, 3986–3987.
- (63) Leigh, W. J.; Sluggett, G. W. Aryldisilane Photochemistry. A Kinetic and Product Study of the Mechanism of Alcohol Additions to Transient Silenes. *J. Am. Chem. Soc.* **1994**, *116*, 10468–10476.
- (64) Leigh, W. J.; Bradaric, C. J.; Kerst, C.; Banisch, J. H. Mechanistic Studies of the Reactions of Silicon–Carbon Double Bonds. The Addition of Alcohols to 1,1-Diphenylsilene. *Organometallics* **1996**, *15*, 2246–2253.
- (65) Bradaric, C. J.; Leigh, W. J. Arrhenius Parameters for the Addition of Nucleophiles to the Silicon–Carbon Double Bond of 1,1-Diphenylsilene. *J. Am. Chem. Soc.* **1996**, *118*, 8971–8972.

- (66) Bradaric, C. J.; Leigh, W. J. Substituent Effects on the Reactivity of the Silicon–Carbon Double Bond. Absolute Rate Constants, Kinetic Isotope Effects and Arrhenius Parameters for the Reaction of 1,1-Diarylsilenes With Alcohols and Acetic Acid. *Can. J. Chem.* **1997**, *75*, 1393–1402.
- (67) Bradaric, C. J.; Leigh, W. J. Substituent Effects on the Reactivity of the Silicon–Carbon Double Bond. Mechanistic Studies of the Ene-Addition of Acetone to Reactive Arylsilenes. *Organometallics* **1998**, *17*, 645–651.
- (68) Leigh, W. J.; Harrington, C.; Ovans, R.; Toltl, N. P. Reaction of 1,1-diphenylsilene and 1,1-diphenylgermene with amines. To be published.
- (69) Leigh, W. J.; Morkin, T. L.; Bradaric, C. J.; Li, X. Addition of alkoxy silanes to substituted 1,1-diphenylsilenes. To be published.
- (70) Apeloig, Y.; Karni, M. Substituent Effects on the Carbon–Silicon Double Bond. Monosubstituted Silenes. *J. Am. Chem. Soc.* **1984**, *106*, 6676–6682.
- (71) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.; Wong-Ng, W. Stable Solid Silaethylenes. *J. Am. Chem. Soc.* **1982**, *104*, 5667–5672.
- (72) Morkin, T. L.; Leigh, W. J. Direct detection and absolute rate constants for the reaction of 1,1-dimethyl-2,2-bis(trimethylsilyl)silene in solution. To be published.
- (73) Bendikov, M.; Quadt, S.; Rabin, O.; Moshny, T.; Apeloig, Y. Addition of nucleophiles to silenes. A theoretical study of kinetic stability and regioselectivity. Presented at the 12th International Symposium on Organosilicon Chemistry, 1999, Sendai, Japan.
- (74) Bravo-Zhivotovskii, D.; Braude, V.; Stanger, A.; Kapon, M.; Apeloig, Y. Novel Route to C=Si Double Bonds Via a Peterson-Type Reaction. *Organometallics* **1992**, *11*, 2326–2328.
- (75) Leigh, W. J.; Owens, T.; Bendikov, M.; Bravo-Zhivotovskii, D.; Apeloig, Y. Absolute rate constants and Arrhenius parameters for the [2+2]-cycloaddition of a silene with a disilene. To be published.
- (76) Toltl, N. P.; Stradiotto, M. J.; Morkin, T. L.; Leigh, W. J. The Homo- and Cross-[2+2]-Cycloaddition of 1,1-Diphenylsilene and 1,1-Diphenylgermene. Absolute Rate Constants for Dimerization and the Molecular Structures and Photochemistry of the Resulting 1,3-Dimetallacyclobutanes. *Organometallics* **1999**, *18*, 5643–5652.
- (77) Baines, K. M.; Brook, A. G. Photolysis of Acylpolysilanes Containing α -Hydrogens. Formation of Linear Head-to-Head Silene Dimers. *Organometallics* **1987**, *6*, 692–696.

AR960252Y