Comparison of the Reactivities of Dimethylsilylene (SiMe₂) and Diphenylsilylene (SiPh₂) in Solution by Laser Flash Photolysis Methods

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Laser flash photolysis studies have been carried out with the goal of comparing the reactivities of dimethyl- and diphenylsilylene (SiMe₂ and SiPh₂, respectively) toward a comprehensive series of representative substrates in hexane solution under common conditions. The silylenes are generated using dodecamethylcyclohexasilane (**1**) and 1,1,3,3-tetramethyl-2,2-diphenyl-1,2,3-trisilacyclohexane (**9**), respectively, as photochemical precursors. The reactions examined include O−H, O−Si, and M−H (M = Si, Ge, Sn) bond insertions, Lewis acid−base complexation with tetrahydrofuran, (1+2) cycloaddition to C=C and C≡C multiple bonds, chlorine atom abstraction from CCl₄, and reaction with molecular oxygen; the kinetic data for SiPh₂ are accompanied by product studies in most cases. Further insight into the mechanisms of these reactions is provided by the identification of reaction intermediates and/or transient products in some cases; notable examples include the reactions of SiPh₂ with methoxytrimethylsilane, carbon tetrachloride, and molecular oxygen. With several of the substrates that were studied, comparison of the kinetic data for SiPh₂ to previously reported rate constants for reaction of dimesitylsilylene in cyclohexane allows an assessment of the role of steric effects in affecting silylene reactivity. Rate constants could also be determined for quenching of tetramethyldisilene (Si₂Me₄) with molecular oxygen, CCl₄, and several other reagents that were studied.

Introduction

Despite great experimental and theoretical interest over the past several decades in the chemistry of divalent organosilicon compounds (silylenes),[1] relatively little is known of their reaction kinetics in solution. The parent molecule (SiH₂) and several simple substituted derivatives SiXY (X,Y = H, Me, or halogen) have received extensive attention in gas-phase kinetic studies,[2−5] and the results of this work have served to provide a useful link between theoretical and experimental studies of silylene reactivity in the gas phase. Until very recently however,[6] only dimethyl- and dimesitylsilylene (SiMe₂ and SiMes₂, respectively) had been successfully detected and studied in solution by time-resolved spectroscopic methods,[7−11] using the well-known oligosilane derivatives **1** and **2** as photochemical precursors to the silylenes of interest. The first attempts to study reactive silylenes by laser flash photolysis methods in solution employed the acyclic trisilanes **3**[12,13] and **4**[14] as precursors to the phenylated silylenes SiMePh and SiPh₂, respectively, as it was well known that photolysis of both compounds (as well as **1** and **2** and a number of other aryltrisilane derivatives) in low-temperature glasses afforded the corresponding silylenes cleanly, allowing their UV/vis absorption spectra to be characterized.[15] These compounds were also well known to afford the corresponding silylenes in high yields upon photolysis in solution at room temperature. Unfortunately, they also undergo competing photorearrangements under the latter conditions, producing transient silene derivatives (e.g., **5**; eq 1) whose strong UV/vis absorptions occur in a similar spectral range as the more weakly absorbing silylenes, obscuring the transient spectra to the point where the silylenes of primary interest were missed altogether.
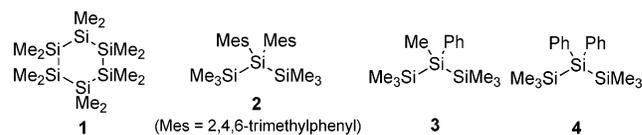

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(1)

4

50%   **5**   37%
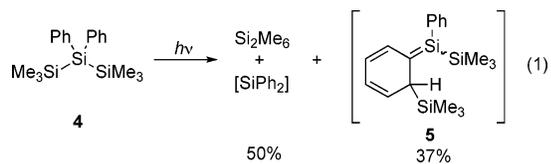
As outlined in the preceding paper,[16] we have recently developed two photochemical precursors to SiPh$_2$ with the idea of exploiting ring-strain effects to suppress the undesired photorearrangements characteristic of 2-phenyl-substituted trisilanes, which occur at the expense of silylene extrusion. Indeed, preliminary product and laser photolysis studies demonstrated the approach to be successful. The first compound studied, trisilacycloheptane **6**, affords SiPh$_2$ and the accompanying disilacyclohexane derivative (**7**) in significantly higher yields than **4** (eq 2), allowing the UV/vis spectrum of SiPh$_2$ to be recorded in fluid solution and its reaction kinetics studied in spite of still-significant interference from transient absorptions assignable to the silene coproduct, **8**.[6] Even better results were obtained with the trisilacyclohexane derivative **9**, which affords SiPh$_2$ and disilacyclopentane **10** in close to quantitative yields under the same conditions (eq 3).[16] This was shown by the results of steady-state photolysis experiments with methanol (MeOH) and acetone, which trap the silylene as the formal O—H insertion and ene-addition products **12** and **13**, respectively.[16] Though the isomeric silene (**11**) still appears to be formed, its yield is so low that it presents minimal interference in laser flash photolysis studies with the molecule. The UV/vis spectrum of SiPh$_2$ thus emerges in almost identical form to that recorded in earlier matrix experiments with **4**.[15] In hexane solution in the absence of scavengers, SiPh$_2$ dimerizes to afford tetraphenyldisilene (Si$_2$Ph$_4$), whose spectrum was also recorded. Interestingly, it coincides almost exactly with that of the minor silene coproduct; the situation thus remains complicated, but is nevertheless tractable. It is now possible to study the chemistry of this benchmark transient silylene in solution directly and at an unprecedented level of detail.

(2)

6

~ 85%   **8**   ~ 15%

(3)

9

95-97%   **11**   ≤ 5%

12   **13**
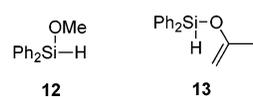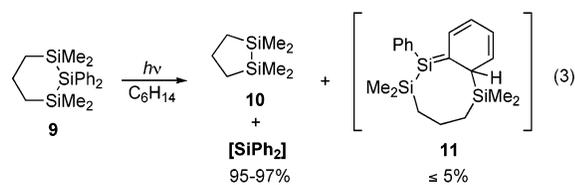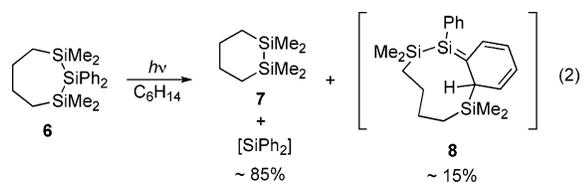
The first such study is the subject of the present paper: a preliminary survey of the kinetics of a broad selection of well-known silylene reactions in solution, focusing on SiPh$_2$ and its methylated counterpart, SiMe$_2$, with data recorded under a common set of conditions so as to enable direct comparisons between the two silylene derivatives. The specific reactions studied are shown in Chart 1 and include Lewis acid—base

complexation with THF, O—H, O—Si, and group 14 M—H (M = Si, Ge, Sn) σ-bond insertions, reaction with molecular oxygen, (2+1) cycloaddition to alkenes, dienes, and alkynes, and chlorine atom abstraction from CCl$_4$. Advantage is taken of the fact that the presence of the phenyl chromophore in SiPh$_2$ results in a red-shift of the absorption spectra of the silylene and its reaction products relative to those of SiMe$_2$, enhancing our ability to detect and characterize intermediates that may be involved in a given silylene—substrate reaction. In several cases, this provides important new insight into the mechanisms of these reactions.

Results and Discussion

Laser flash photolysis experiments were carried out as described in the preceding paper,[16] using rapidly flowed solutions of **9** ($\sim$10^{-4} M) and **1** (ca. 5 × 10^{-4} M) in dry, deoxygenated hexane and the pulses from a KrF excimer laser (248 nm, ca. 25 ns, ca. 100 mJ) for excitation. Silylene decays were monitored at 530 nm for SiPh$_2$ and 470 nm for SiMe$_2$; they generally fit acceptably to first-order decay kinetics in the absence of added scavenger, with lifetimes that varied over the ranges 0.6–1.5 μs and 250–600 ns, respectively. As detailed in the preceding paper,[16] the decay of the silylenes was accompanied by the growth of absorptions at shorter wavelengths, due to the formation of the corresponding disilenes Si$_2$Ph$_4$ (λ_{max} = 290, 370, 460 nm) and Si$_2$Me$_4$ (λ_{max} = 360 nm) by silylene dimerization. The variation in the lifetimes of the silylenes is due to an acute sensitivity to the presence of moisture in the solvent and the glassware, which was difficult to control (particularly on humid days) despite the routine of flame-drying the apparatus prior to each experiment. As expected, the initial intensities of the disilene signals also varied from experiment to experiment, correlating inversely with the silylene lifetimes.

Addition of the substrates shown in Chart 1 caused the pseudo-first-order decay of the silylenes to accelerate in proportion to the substrate concentration; in all cases but THF, this was accompanied by increases in the growth rates of the disilene absorptions and reductions in their maximum intensities. Rate constants were determined by linear least-squares analysis of plots of the pseudo-first-order decay rate constants for decay (k_{decay}) of SiPh$_2$ and SiMe$_2$ according to eq 6, where k_0 is the pseudo-first-order rate constant for decay of the species in the absence of the substrate (Q) and k_Q is the second-order rate constant for the reaction with Q; these plots were linear in all but one case (*vide infra*). The data are summarized in Table 1, along with reported rate constants for reaction of seven of the substrates with SiMes$_2$ in cyclohexane or hexane solution.[11,16] Each experiment was completed by recording transient spectra in the presence of the scavenger at a concentration where the silylene lifetime was reduced to ca. 300 ns or less, and is hence determined mainly by reaction with the substrate. This was done in an effort to probe for the formation of the primary product(s) of the silylene-trapping reaction. These additional details will be presented later in the paper.

$$k_{decay} = k_0 + k_Q[Q] \qquad (6)$$

The outcomes of these reactions are all well documented for SiMe$_2$ and/or other transient silylenes,[1,17] but only those with Et$_3$SiH, dienes, alkenes, and acetone have been studied previously for SiPh$_2$.[6,16,18–20] We therefore carried out NMR-scale photolyses of ca. 0.05 M solutions of **9** in C$_6$D$_{12}$ containing ca.

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Chart 1
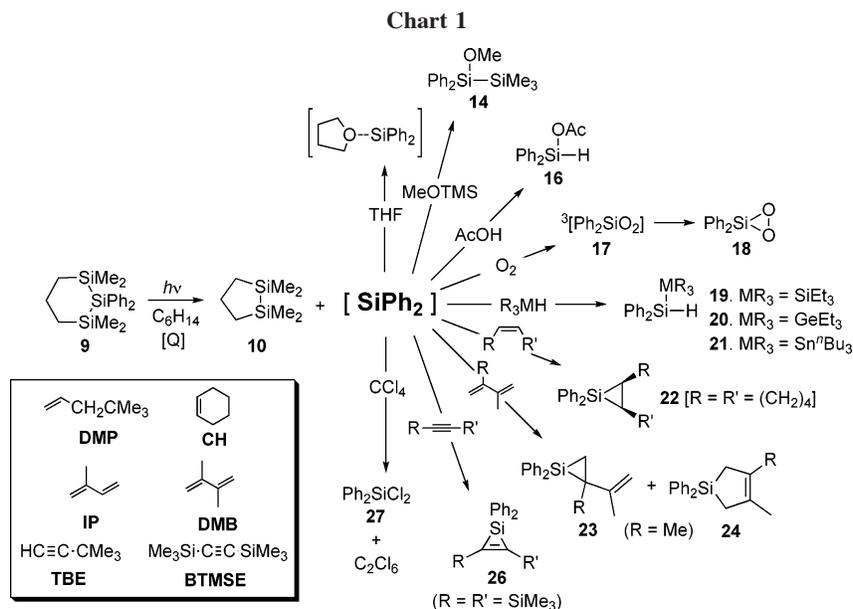
Table 1. Diphenylsilylene Trapping Products and Absolute Rate Constants for Reaction of Diphenyl-, Dimethyl-, and Dimesitylsilylene with Various Silylene Scavengers in Hexane Solution at 25 °C

trapping agent	product(s)	$k_Q^{SiPh_2}/10^9\ M^{-1}\,s^{-1}$	$k_Q^{SiMe_2}/10^9\ M^{-1}\,s^{-1}$	$k_Q^{SiMes_2}/10^9\ M^{-1}\,s^{-1}$
MeOH[a]	**12** (93%)	13.4 ± 1.0	18.1 ± 1.5	0.82 ± 0.03
acetone[a]	**13** (86%)	14.4 ± 2.0	14.1 ± 1.2	8.3 ± 0.4
THF	Ph₂Si−THF complex	15.2 ± 1.3	17.3 ± 1.5	
MeOSiMe₃	**14** (54%)	4.2 ± 0.7	6.2 ± 0.6[b]	< 0.001[d]
AcOH	**16** (84%)	10.1 ± 1.0	15.9 ± 1.0	
O₂	**17** (R = Ph)[c]	0.12 ± 0.02	0.47 ± 0.04	0.032 ± 0.004[d]
Et₃SiH	**19**	3.3 ± 0.2[a]	3.6 ± 0.3	0.079 ± 0.004[d]
Et₃GeH	**20** (90%)	3.1 ± 0.2	2.5 ± 0.2	
n-Bu₃SnH	**21** (87%)	5.3 ± 0.6	18.9 ± 1.4	
cyclohexene	**22**[18]	7.9 ± 0.7	7.8 ± 1.0	0.0028 ± 0.0003[d]
DMP	c	7.9 ± 1.6[e]	11.7 ± 0.5	
DMB	**23** (87%) + **24** (<18%)	14.5 ± 1.3	15.9 ± 0.7	0.0088 ± 0.0007[d]
isoprene	c	13.6 ± 1.4	19.8 ± 0.7	
BTMSE	**26** (67%)	7.6 ± 0.6	13.8 ± 0.5	
TBE	c	8.3 ± 0.7[e]	17.8 ± 0.6	
CCl₄	**27** (78%)	1.37 ± 0.09	3.4 ± 0.2	

[a] Data from ref 16. [b] Rate constant obtained from linear least-squares analysis of k_{decay} data at low concentrations (0.1−0.5 mM). [c] Product not determined. [d] In cyclohexane at 25 °C; data from ref 11. [e] Data from ref 6.

0.20 M AcOH, MeOTMS, Et₃GeH, Bu₃SnH, BTMSE, DMB, and CCl₄, following the course of the photolyses by ¹H NMR spectroscopy and GC/MS, the latter being recorded before and after photolysis to 50−60% conversion of **9**. The products formed in these experiments (see Chart 1) were in most cases identified by comparison of the NMR and GC/MS data for the crude reaction mixtures to the corresponding data for authentic samples or to literature data; only two of them (vinylsilirane **23** and silirene **26**) were tentatively identified by comparison of the spectral data to reported data for closely related compounds. As in the MeOH- and acetone-trapping experiments described in the preceding paper,[16] yields were determined relative to consumed **9** from the slopes of concentration versus time plots constructed from the NMR data over the 0−25% conversion range. The photolysis mixtures were generally quite clean, with the yield of disilacyclopentane **10** matching that of the SiPh₂-derived product(s) reasonably closely in most cases. The chemical yields of the SiPh₂-derived products identified in these experiments are shown in Table 1 along with the kinetic data. Additional specific details pertaining to the steady state

and laser flash photolysis experiments with each of the substrates studied are presented below.

Finally, for several of the reagents studied with the SiMe₂ precursor **1** (AcOH, CCl₄, TBE, acetone, DMP, isoprene, O₂, and BTMSE), the reduction in the maximum transient absorbance at 360 nm (due to Si₂Me₄) with increasing substrate concentration was accompanied by a distinct shortening of the lifetime of the absorption over the substrate concentration ranges studied, with the decays fitting well to first-order kinetics. Rate constants for quenching of Si₂Me₄ were determined from plots of k_{decay} versus [Q] according to eq 6 and are listed in Table 2.

Reactions of SiPh₂ and SiMe₂ with Oxygenated Substrates. The Lewis acid−base complexation of silylenes with ethers and other heteroatom-containing substrates is well known and has been studied extensively in low-temperature matrixes with SiMe₂ and a number of other reactive silylene derivatives.[21−25]

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Table 2. Rate Constants for Quenching of Si₂Me₄ by Various Substrates in Hexane Solution at 25 °C, Determined from Plots of k_{decay} vs [Q] According to Eq 6

reagent	$k_Q/10^9 \ M^{-1} \ s^{-1}$
AcOH	2.7 ± 0.2
CCl₄	2.3 ± 0.2
O₂	0.29 ± 0.04^b
DMP	0.5 ± 0.2^b
isoprene	0.4 ± 0.2
TBE	0.81 ± 0.04
BTMSE	0.59 ± 0.05

[a] In most cases, the plots were constructed using data recorded at 5–9 substrate concentrations; errors are reported as $\pm 2\sigma$. [b] From k_{decay} values recorded at only two concentrations.

Kinetic studies have been limited to SiH₂ and SiMe₂ in the gas phase[26,27] and SiMe₂ in solution.[8,10] Though the complexation process is ultimately nonproductive in the cases of unstrained dialkyl ethers,[28] it has the effect of moderating the reactivity of silylenes toward other substrates in ether compared to hydrocarbon solvents[8,24,29,30] and forms the basis for our current understanding the mechanisms of the reactions of silylenes with alcohols, alkoxysilanes, ketones, and strained cyclic ethers such as oxetanes and oxiranes.[1]

Lewis acid–base complexation of SiPh₂ with THF proceeds at close to the diffusion limit in hexane solution and leads to the formation of new, longer-lived absorptions at shorter wavelengths ($\lambda_{max} \approx 350$ nm), which appear to grow in over a similar time scale as the silylene decay over the 0.1–0.5 mM concentration range in THF (see Figure 1a). The spectrum of the species is similar to that reported for the 2-methyltetrahydrofuran complex of SiMes₂ ($\lambda_{max} \approx 350$ nm) at 77 K[21] and is red-shifted compared to that of the complex of SiMe₂ ($\lambda_{max} \approx 310$ nm) with THF in cyclohexane;[8,10] it can thus be assigned with confidence to the SiPh₂–THF Lewis acid–base complex. A similar trend in λ_{max} is known for the complexes of the germanium analogues of the three silylenes with THF.[31] Disilene formation is slowed quite substantially over this concentration range, but appears to proceed in similar yield to that in pure hexane solution. The behavior is illustrated in Figure 1a, which shows transient absorption spectra recorded with a solution of **9** in hexane containing 0.3 mM THF at four time intervals after the laser pulse and transient growth/decay profiles at 530, 460, and 350 nm. A dotted line has been placed at the 500 ns point of the growth/decay profiles to emphasize the equivalence of the silylene decay rate and the growth rate of the complex, which are both just discernible on the time scale employed for this particular experiment. The absorption intensity at 460 nm grows to a maximum over the first 5 μs after the pulse, 4–5 times slower than in the absence of THF, and then decays at the same rate as the absorption due to the complex.

The long-lived residual absorption present in the 530 nm decay profile is due to silene **11**, which absorbs very weakly at this wavelength, and not to residual free SiPh₂ in equilibrium with the complex. This conclusion is supported by the fact that the long-lived absorption remained of similar relative intensity with solutions of **9** containing up to 0.05 M THF, where the lifetime of the free silylene was too short to be detected, and is consistent with an equilibrium constant in excess of $10^5 \ M^{-1}$ for formation of the silylene–ether complex under these conditions. On the other hand, the temporal profiles of the absorptions at 350 and 460 nm varied only modestly over this concentration range. This indicates that disilene formation occurs mainly via a mechanism involving dimerization of the complex under these conditions, even in the presence of as little as 0.3 mM THF. The lengthening of both the growth and decay times of the disilene absorption in the presence of the ether compared to those in its absence indicates that this process occurs significantly more slowly than that involving the free silylene, which is close to diffusion-controlled.[16] Analysis of the 350 nm signal as a second-order decay afforded a rate coefficient of $2k/\epsilon \approx 10^6 \ cm \ s^{-1}$.

Addition of dioxane to hexane solutions of **9** led to similar effects; the ether quenched the lifetime of SiPh₂ at the diffusion-controlled rate ($k_Q = (1.8 \pm 0.1) \times 10^{10} \ M^{-1} \ s^{-1}$) and led to the formation of a new species exhibiting $\lambda_{max} = 370$ nm. The species decayed with a lifetime $\tau \approx 5$ μs in the presence of 11 mM dioxane, with the concomitant growth of the disilene absorption at 460 nm. These results are relevant to the interpretation of the various steady-state photolysis experiments reported throughout this paper, in which dioxane was employed as an internal integration standard. It clearly also serves as a moderator in the silylene-trapping reactions, though it appears to have no effect on their ultimate outcomes.

Laser photolysis of hexane solutions of **1** in the presence of THF afforded quite similar results to those described previously in cyclohexane solution[8,9] and allowed the determination of $k_{THF} = 1.73 \times 10^{10} \ M^{-1} \ s^{-1}$ for formation of the SiMe₂–THF complex ($\lambda_{max} = 310$ nm) in hexane at 25 °C. The rate constant is the same within experimental error as that for formation of the SiPh₂–THF complex under the same conditions.

The behavior observed in the presence of the reactive ether methoxytrimethylsilane (MeOTMS) was markedly different from that observed with THF. As with THF, addition of the alkoxysilane to hexane solutions of **9** led to reductions in the lifetime of SiPh₂ over the 0–1 mM concentration range, affording the second-order rate constant $k_{MeOTMS} = 4.2 \times 10^9 \ M^{-1} \ s^{-1}$ from the resulting linear plot of k_{decay} versus [MeOTMS]. Growth/decay profiles recorded at 460 nm showed the formation of Si₂Ph₄ to be strongly quenched over the 0.1–4.0 mM concentration range in added MeOTMS, which is characteristic of essentially irreversible scavenging of SiPh₂, the immediate precursor to the disilene. At 350 nm, the characteristic growth/decay associated with the $S_0 \rightarrow S_2$ transition of Si₂Ph₄ in pure hexane[16] was replaced with a stronger, more rapidly decaying signal whose maximum intensity increased with increasing alkoxysilane concentration, superimposed on a longer-lived decay which decreased in overall intensity with increasing concentration. No further changes in either component of the 350 nm signal were observed upon increasing the alkoxysilane concentration above 4 mM. The lifetime of the rapidly decaying component of the 350 nm signal was determined by two-exponential decay analysis of traces recorded in the presence of 1, 2, and 4 mM MeOTMS and was found to be independent of concentration within this range ($\tau = 730 \pm 5$ ns). The only unusual feature noted in these experiments was that the initial intensity of the silylene signal (at 530 nm)

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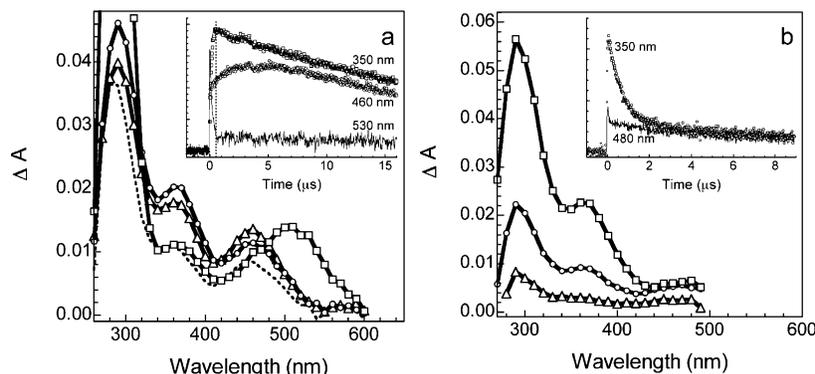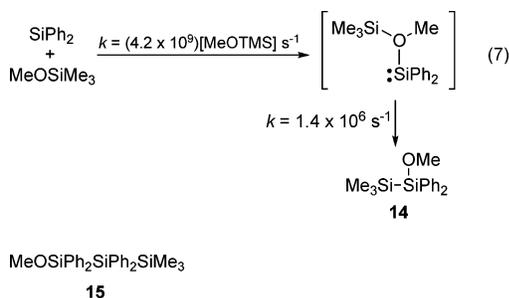(30) Steele, K. P.; Weber, W. P. *Inorg. Chem.* **1981**, *20*, 1302.
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Figure 1. (a) Transient absorption spectra recorded 64−128 ns (-□-), 0.64−0.70 μs (-O-), 3.52−3.58 μs (-△-), and 17.76−17.92 μs (---) after the laser pulse, from laser flash photolysis of a 0.09 mM solution of **9** in deoxygenated hexane containing 0.3 mM THF. The inset shows transient growth/decay profiles recorded at 350, 460, and 530 nm; a dotted line has been drawn at ∼0.6 μs to illustrate the coincidence in the decay of the signal at 530 nm and the growth at 350 nm. (b) Transient absorption spectra recorded 0−64 ns (-□-), 1.01−1.07 μs (-O-), and 8.5−8.6 μs (-△-) after the pulse, from laser photolysis of **9** in hexane containing 4.0 mM MeOTMS; the inset shows transient decay profiles recorded at 350 and 480 nm.

appeared to be reduced in the presence of MeOTMS, to an extent that increased systematically with increasing concentration. We do not yet understand the reasons for this behavior, but can at least rule out excited-state quenching on the basis of the product studies described below.

Figure 1b shows transient absorption spectra recorded over various time windows after the laser pulse with a hexane solution of **9** containing 4 mM MeOTMS, along with decay profiles recorded at 350 and 480 nm. The decay profiles show that the long-lived component of the 350 nm signal is in fact associated with the minor transient coproduct formed along with SiPh₂ in the photolysis pulse, which we assign to silene **11**.[16] The lifetime of the species is largely unaffected in the presence of the alkoxysilane, which is consistent with the silene assignment.[32] The short-lived component can be assigned to the Lewis acid−base complex of SiPh₂ with MeOTMS on the basis of its similarity to the spectrum of the SiPh₂−THF complex (see Figure 1a), while its first-order decay can be associated with the rate of SiMe₃ migration to yield the final product formed in the reaction, alkoxydisilane **14** (eq 7). The identity of the final product was confirmed by steady-state photolysis of **9** in C₆D₁₂ containing 0.19 M MeOTMS, which afforded **10** and **14** in yields of 74% and 46%, respectively. A third product was also detected by GC/MS of the crude photolysate after ca. 60% conversion of **9** and was tentatively identified as trisilane **15**, the (secondary) product of competing trapping of SiPh₂ by **14**. Its formation was in fact expected, as it is known that alkoxydisilanes are considerably more effective silylene scavengers than alkoxysilanes.[33,34]

$$
\begin{array}{c}
\text{SiPh}_2 \\
+ \\
\text{MeOSiMe}_3
\end{array}
\xrightarrow{k = (4.2 \times 10^9)[\text{MeOTMS}] \text{ s}^{-1}}
\left[
\begin{array}{c}
\text{Me}_3\text{Si} \diagdown \diagup \text{Me} \\
\text{O} \\
:\text{SiPh}_2
\end{array}
\right]
\quad (7)
$$

$$
k = 1.4 \times 10^6 \text{ s}^{-1} \downarrow
$$

$$
\begin{array}{c}
\text{OMe} \\
| \\
\text{Me}_3\text{Si}-\text{SiPh}_2 \\
\mathbf{14}
\end{array}
$$

$$
\text{MeOSiPh}_2\text{SiPh}_2\text{SiMe}_3
$$
15

The quenching of SiMe₂ by MeOTMS was found to be somewhat different than the behavior observed with SiPh₂. Addition of the alkoxysilane to hexane solutions of **1** resulted in the expected increase in the silylene decay rate constant, but the resulting plot of k_{decay} versus [MeOTMS] exhibited downward curvature over the 0.1−5.0 mM concentration range. An estimate of the limiting second-order rate constant (i.e., as [MeOTMS] → 0) of $k_Q = 6.2 \times 10^9$ M^{-1} s^{-1} was therefore determined by linear least-squares analysis of data recorded over the 0.1−0.4 mM concentration range. The value is ca. 3 times lower than the rate constant for reaction of SiMe₂ with MeOH under the same conditions, in reasonable agreement with the rate constant ratio determined by Steele et al. for reaction of SiMe₂ with MeOTMS and ethanol in dilute hydrocarbon solution, which was based on competition experiments.[34] Quenching of the silylene was accompanied by the appearance of a new transient absorption centered at $\lambda_{max} \approx 310$ nm, which can be assigned to the SiMe₂−MeOTMS complex on the basis of *its* similarity to the spectrum of the SiMe₂−THF complex.[8] The absorption decayed with clean first-order kinetics and a lifetime $\tau = 150$ ns in hexane containing 5.3 mM MeOTMS, nearly the same as that exhibited by the much weaker signal at 470 nm due to free SiMe₂ at this concentration ($\tau \approx 110$ ns). The formation of Si₂Me₄, which is barely detectable in the presence of 1.4 mM MeOTMS (see Supporting Information), could not be detected at the higher alkoxysilane concentration, and so we interpret the similar lifetimes at 470 and 350 nm as being due to the free silylene and the complex in mobile equilibrium and decaying predominantly via unimolecular rearrangement of the complex to yield the formal O−Si insertion product. The underlying reasons for the nonlinear dependence of the silylene decay rate on alkoxysilane concentration are not clear at the present time, though we note that the behavior is consistent with saturation kinetics, as would result if there were a pathway for reaction of the complex that involves a second molecule of alkoxysilane and regenerates SiMe₂.

Our results are consistent with the two-step mechanism originally proposed by Weber and co-workers for the O−Si insertion reaction with alkoxysilanes, involving initial Lewis acid complexation of silylene with the substrate,[34] but add considerable new insight into the finer mechanistic details of the reaction. As with MeOH,[16] formation of the complex is the rate-determining step for silylene decay at low substrate concentrations; however, this stage of the process is considerably slower in the case of MeOTMS, as might be expected consider-

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ing the lower basicity of the alkoxysilane compared to the ether and alcohol.[35] Our results also show that the intermediate complex is not a steady-state intermediate, but rather constitutes a bottleneck in the reaction pathway owing to its relatively slow rate of conversion to the final product, **14**. It is interesting to note that Conlin and co-workers found the reaction of SiMes$_2$ with MeOTMS to be too slow to be detected under the conditions of their kinetic experiments with this silylene in fluid solution and estimated an upper limit for the rate constant of $k_{MeOTMS} < 10^6$ M^{-1} s^{-1}.[11] This suggests that complexation with the alkoxysilane is significantly more sensitive to steric effects than is the case for the reaction with MeOH, as might be expected on the basis of the fact that complexation is the rate-determining step for silylene decay in both cases and considering the differences in steric bulk between the two substrates.

While the rate constants for formation of the silylene-methoxysilane complexes from SiPh$_2$ and SiMe$_2$ (see Table 1) are quite similar, larger differences are observed in the first-order rate constants for their decay. The decay process can most reasonably be associated with the 1,2-SiMe$_3$ migration that takes the intermediate complex to the final product of the reaction. The ca. 5-fold slower decay rate constant observed for the SiPh$_2$−MeOTMS complex ($k_{decay} \approx 1.4 \times 10^6$ s^{-1}) relative to that of the SiMe$_2$−MeOTMS complex under the same conditions ($k_{decay} \approx 6.6 \times 10^6$ s^{-1}) is consistent with a somewhat higher secondary barrier for formation of the net O−Si insertion product in the phenylated system. The rate constants for decay of the complexes are consistent with activation energies for the second step in the reaction on the order of $E_a \approx 7.5$ kcal mol^{-1}, assuming pre-exponential factors on the order of 10^{12} s^{-1}. However, it is clear from the unusual concentration dependence observed with SiMe$_2$ that the reaction is significantly more complicated than this analysis might suggest, and further work will be necessary in order to understand it completely.

The reactions of SiPh$_2$ with acetone and acetic acid afford the formal ene-type addition products **13**[16,18] and **16** (see eq 8), respectively, and both proceed with rate constants close to the diffusion-controlled limit. As might therefore be expected, the rate constants are also quite similar to those measured for reaction of SiMe$_2$ with these substrates. While it is reasonable to expect that these reactions also proceed via initial complexation, and indeed spectroscopic evidence for this has been reported for the reaction of a nonenolizable ketone with SiMes$_2$ at cryogenic temperatures,[36] we have been unable to detect any signs of intermediate complexes in the reactions of these three silylenes with acetone[16] or AcOH in fluid solution (see Supporting Information). We thus conclude that if such species are indeed generally involved in the reactions with these two substrates, they must be true steady-state intermediates, rearranging to the final products with rate constants large enough that the intermediates do not build up in high enough concentrations to enable detection (eq 9). This is consistent with the results of theoretical calculations for the reaction of SiH$_2$ with acetone.[26b]

The reaction of transient silylenes with molecular oxygen has been studied in low-temperature matrixes in the cases of SiMes$_2$,[37] SiMe$_2$,[38] and SiMePh[39] and has also been the subject
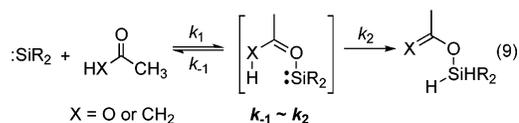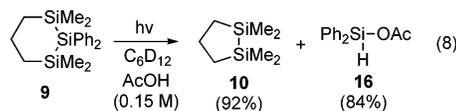
of theoretical calculations by several groups;[37,39−41] kinetic studies of the reaction of the parent molecule (SiH$_2$) with O$_2$ in the gas phase have also been reported.[41] Ando and co-workers first studied the reaction of SiMes$_2$ with O$_2$ by UV/vis and IR spectroscopy in an oxygen matrix at 16 K.[37] They reported the formation of a species exhibiting a weak UV/vis absorption maximum at $\lambda_{max} \approx 320$ nm, which they assigned to the corresponding triplet silanone oxide (**17**; see eq 10) on the basis of IR spectroscopic evidence and RHF/6-31(g) calculations on the triplet state of the parent silanone oxide, ^{3}(H$_2$Si−O$_2$). Sander and co-workers later studied the reactions of O$_2$ with SiMe$_2$[38] and SiMePh[39] in 0.5% O$_2$-doped argon matrixes by IR spectroscopy and showed that the two species react rapidly at ca. 40 K to form the corresponding dioxasiliranes (**18**), without the intervention of detectable intermediates. It is thus clear that following intersystem crossing to the singlet (ground) state surface, the initially formed silanone oxide closes to the corresponding dioxasilirane derivative via an extremely low activation barrier. This is supported by theoretical calculations, which place the height of the barrier at ca. 5 kcal mol^{-1} for the parent silanone oxide[41] and lower still in substituted systems such as that derived from SiMePh.[39]
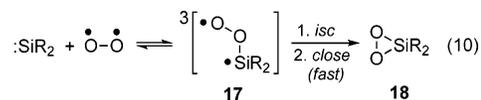
We have measured absolute rate constants for the reactions of SiPh$_2$ and SiMe$_2$ with oxygen in hexane in the present study, obtaining values of $k_{O2} = 1.2 \times 10^8$ and 4.7×10^8 M^{-1} s^{-1}, respectively, from the slopes of three-point plots of k_{decay} in argon-, air-, and O$_2$-saturated hexane versus [O$_2$]. The value for SiPh$_2$ is only ca. 4 times higher than that reported by Conlin and co-workers for SiMes$_2$ in cyclohexane solution,[11] showing that steric effects on the rate constant for the process are quite small, as might be expected. Interestingly, the reaction with O$_2$ is the slowest that we have examined with SiMe$_2$ and SiPh$_2$, which most likely reflects the fact that the reaction yields in the first step a relatively high-energy triplet 1,3-biradical product. The present value for SiMe$_2$ of $k_{O2} = 4.7 \times 10^8$ M^{-1} s^{-1} revises the ca. 5-fold higher value reported by Levin et al., which was based on a single lifetime determination in air-saturated cyclohexane.[8]

Transient absorption spectra were recorded by laser photolysis of an O$_2$-saturated hexane solution of **9**, where the lifetime of SiPh$_2$ is reduced to $\tau \approx 330$ ns; the results of the experiment are shown in Figure 2. Transient decays recorded at 460 nm suggest that disilene formation is largely quenched under these conditions; the transient absorption observed at 460 nm appears

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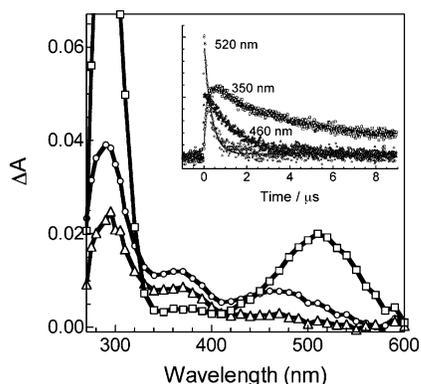
Figure 2. Transient absorption spectra recorded 0−48 ns (-□-), 0.54−0.62 μs (-○-), and 2.14−2.22 μs (-△-) after the laser pulse, by laser flash photolysis of a 0.09 mM solution of **9** in oxygen-saturated hexane at 25 °C; the inset shows transient growth/decay profiles recorded at 520 (○), 460 (△), and 350 nm (□).

to consist of only a single component, which is formed with the laser pulse and decays to the prepulse level with clean first-order kinetics and a lifetime $\tau \approx 1.6$ μs. The much reduced lifetime of the transient absorption at this wavelength in O₂-compared to Ar-saturated hexane provides additional support for its assignment to silene **11**, as the estimated second-order rate constant for its reaction with O₂ ($k \approx 4 \times 10^7$ M⁻¹ s⁻¹; calculated from the 1.6 μs lifetime and a value of [O₂] = 15 mM[42]) is of the magnitude expected on the basis of reported kinetic data for other silenes of this general structure.[32] It is difficult to rule out the possibility that the 460 nm signal in O₂-saturated solution contains minor contributions from the silylene dimer, Si₂Ph₄. However, if this is the case, then the fact that the signal decays with clean first-order kinetics suggests that Si₂Ph₄ and **11** have similar lifetimes and hence similar rate constants for reaction with O₂. This is, in fact, consistent with reported data for other phenyl-substituted disilenes.[43]

In addition to the prompt absorptions due to SiPh₂ ($\tau \approx 330$ ns) and silene **11** ($\tau \approx 1.6$ μs), transient spectra recorded with the O₂-saturated solution (see Figure 2) showed clear evidence for the formation of a new transient product ($\lambda_{max} \approx 370$ nm), which grows in over a similar time scale as the silylene decay and is then consumed on a time scale of several microseconds ($\tau \approx 3.3$ μs). While we clearly have insufficient data for a reliable assignment for the species to be made at the present time, the lifetime seems rather short and the absorption maximum too far to the red for it to be due to 1,1-diphenyl-dioxasilirane (**18**; R = Ph); the similarity in the spectrum to those of the complexes of SiPh₂ with the other O-donors studied herein suggests the triplet silanone oxide may be the most likely candidate for the species. It should be noted that the spectrum of the species is strikingly similar to the matrix spectrum of the SiMes₂-O₂ adduct reported by Ando and co-workers.[37] It should also be noted that the fact that the species is significantly longer-lived than free SiPh₂ under the same conditions indicates that it is formed irreversibly.

Nothing but SiMe₂ ($\tau \approx 100$ ns), Si₂Me₄ ($\tau \approx 250$ ns), and the long-lived photolysis coproduct ($\lambda_{max} = 280$ nm) could be detected in experiments with **1** in O₂-saturated hexane, so unfortunately we cannot address the mechanistic details of the reaction of SiMe₂ with O₂ in fluid solution. We can, however,

provide an estimate of $k_{O2} = (2.9 \pm 0.4) \times 10^8$ M⁻¹ s⁻¹ for the rate constant for reaction of Si₂Me₄ with O₂ under these conditions, based on the lifetimes of the species in air- and O₂-saturated solution. The value compares favorably with those that have been measured for other transient disilenes in solution[43] and is a factor of about 5 larger than that for the corresponding reaction of the germanium analogue, Ge₂Me₄.[44]

Further studies of the reactions of arylsilylenes with molecular oxygen in hydrocarbon solvents are in progress.

Reactions of SiPh₂ and SiMe₂ with Group 14 Hydrides R₃MH (M = Si, Ge, Sn). The Si−H insertion reaction of silylenes with hydridosilanes is among the best known of silylene reactions and has been particularly extensively studied in the gas phase with several simple silylene derivatives such as SiH₂, SiMeH, SiPhH, SiClH, and SiMe₂ as a function of methyl substitution in the silane (Me$_n$SiH$_{4-n}$; $n = 0-3$).[4,5] The accepted mechanism involves the initial formation of a weakly bound H-bonded silylene(acceptor)−hydridosilane(donor) complex, which rearranges to yield the final insertion product (eq 11); the latter is thought to be the rate-determining step in the reactions of the substituted silylenes that have been studied.[4,45] The effects of substituents on the high-pressure-limiting rate constants for these reactions in the gas phase vary somewhat depending on the degree of methyl substitution in the silane, but with trimethylsilane (Me₃SiH) vary in the order PhSiH ∼ MeSiH ∼ SiH₂ ≫ SiMe₂ > ClSiH.[5] The effect has been rationalized as the result of destabilization of both the intermediate complex and the barrier for the second step, relative to the situation in the corresponding reaction of the parent molecule (SiH₂), with the effect being much greater for SiMe₂ than for MeSiH and PhSiH.[45] Ge−H insertions have also received attention in gas-phase studies, though much less extensively than is the case for Si−H insertions. Surprisingly, SiMe₂ has recently been found to react close to 10 times more slowly with Me₂-GeH₂ than with Me₂SiH₂, which runs counter to what might be expected on the basis of the relative strengths of the M−H bonds in the two substrates.[5]

$$R_2Si: \;+\; HSiRR'R'' \;\rightleftharpoons\; \left[\begin{array}{c} H^{\nearrow SiRR'R''} \\ | \\ R_2Si: \end{array} \right] \;\longrightarrow\; R_2Si\begin{array}{c} H \\ \diagdown SiRR'R'' \end{array} \quad (11)$$

The rate constant determined in the present work for reaction of SiMe₂ with Et₃SiH in hexane ($k_{Et3SiH} = (3.6 \pm 0.3) \times 10^9$ M⁻¹ s⁻¹) is the same as the values reported previously in cyclohexane within experimental error,[8,9] as should be expected given that it is well below the diffusion-controlled limit, and is also in good agreement with the value reported for reaction of the same silylene with Me₃SiH in the gas phase ($k = 2.7 \times 10^9$ M⁻¹ s⁻¹).[46] The value is also quite similar to the value found for SiPh₂ + Et₃SiH in hexane,[6,16] indicating once again the close similarities in the reactivities of SiMe₂ and SiPh₂. The two silylenes are ca. 40 times more reactive toward Si−H insertion than SiMes₂ in cyclohexane under similar conditions,[11] indicating that steric effects on the Si−H insertion reaction are moderate and of a similar magnitude to those observed in the reaction with MeOH.[16]

Silylene insertions into Ge−H and Sn−H bonds have been much less widely studied than Si−H insertions, but at least one

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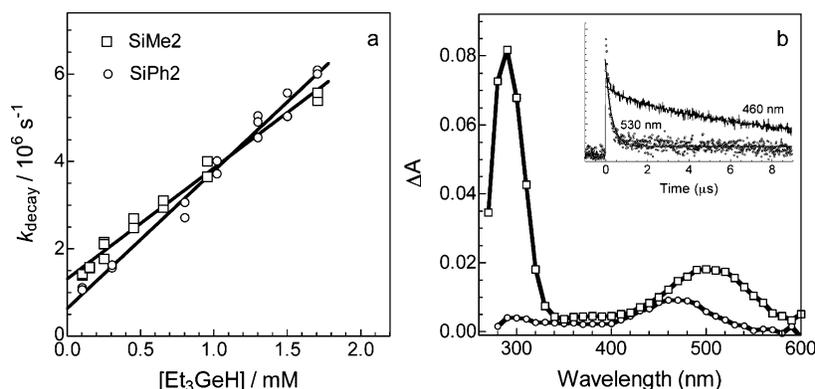
Figure 3. (a) Plots of the pseudo-first-order decay rate constants (k_{decay}) for SiMe$_2$ (□) and SiPh$_2$ (○) vs [Et$_3$GeH] in hexane solution at 25 °C. The solid lines are the linear least-squares fits of the data to eq 6. (b) Transient absorption spectra recorded 16−80 ns (-□-) and 0.86−0.98 μs (-○-) after the laser pulse, by laser flash photolysis of a 0.09 mM solution of **9** in deoxygenated hexane containing 1.7 mM Et$_3$GeH. The inset shows transient growth/decay profiles recorded at 460 and 530 nm.

example of each process is known for transient silylenes such as SiMe$_2$[47] and SiMePh[19] in solution. The expected M−H insertion products from SiPh$_2$ (**20** and **21**; eq 12) are obtained along with **10** in excellent yields upon photolysis of **9** in C$_6$D$_{12}$ in the presence of Et$_3$GeH and *n*-Bu$_3$SnH, respectively (see eq 12). Figure 3a shows the plots of k_{decay} versus [Et$_3$GeH] for SiMe$_2$ and SiPh$_2$ in hexane at 25 °C, while Figure 3b shows time-resolved absorption spectra recorded by flash photolysis of a solution of **9** containing 1.7 mM Et$_3$GeH, where the lifetime of SiPh$_2$ is reduced to $\tau \approx 300$ ns and the formation of Si$_2$Ph$_4$ is strongly quenched. The spectra illustrate the absence of detectable intermediates in the primary reaction of SiPh$_2$ with Et$_3$GeH; similar results were obtained with Bu$_3$SnH.
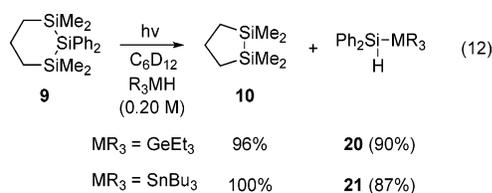
Perhaps surprisingly given the systematic decrease in M−H bond strengths throughout the series M = Si > Ge > Sn,[48] the rate constants for the reactions of SiPh$_2$ with the three metallyl hydrides are all quite similar, with those for the Si−H and Ge−H insertions being essentially identical and less than a factor of 2 lower than that for the Sn−H insertion. A somewhat larger spread in reactivity is observed for SiMe$_2$, with the reaction with Et$_3$GeH proceeding slightly slower than with Et$_3$SiH, and that with Bu$_3$SnH ca. 5 times faster. The difference in rate constants for reaction of SiMe$_2$ with the germane and silane is small, but is in the same direction that has been observed for the reactions of Me$_2$GeH$_2$ and Me$_2$SiH$_2$ with SiMe$_2$ in the gas phase,[5] as mentioned above. The absence of detectable transient products in laser photolysis experiments with SiPh$_2$ in the presence of these substrates verifies, for the Sn−H insertion in particular, that the reaction does not proceed via H atom abstraction, as the tributylstannyl radical should be readily detectable if it was formed as a discrete intermediate.[49,50]

Reactions of SiPh$_2$ and SiMe$_2$ with Alkenes and Alkynes. The reactions of silylenes with C−C unsaturated compounds have had a long and fascinating history, which is well documented in early reviews.[1] The corresponding three-membered ring compounds—siliranes from alkenes and silirenes from alkynes—are well known to be the primary products of these reactions, which proceeds stereospecifically in the case of addition to alkenes.[20,51−53] The stereochemistry of the addition to alkenes was in fact first established with SiMe$_2$ and SiPh$_2$, employing the photolysis of **1** and **4** to generate the two species in the presence of high concentrations of *cis*- or *trans*-2-butene and trapping the resulting siliranes, which are often rather unstable, as their methanolysis products.[20,51]

The kinetics of the reactions of both SiMe$_2$ and SiMes$_2$ with alkenes were examined in the earlier flash photolysis studies of these species in cyclohexane solution, with values of 7.3×10^9 and 5.9×10^9 M^{-1} s^{-1} being reported for SiMe$_2$ with 1-hexene and trimethylsilylethylene, respectively,[8] and $k = 2.8 \times 10^6$ M^{-1} s^{-1} for SiMes$_2$ with cyclohexene.[11] Rate constants for the reactions of SiMe$_2$ and SiPh$_2$ with cyclohexene and the terminal alkene 3,3-dimethyl-1-pentene (DMP) have been measured in the present work and again reveal close similarities between the reactivities of the two species. Though we have not carried out product studies in either case, Tortorelli et al. showed that SiMe$_2$ and SiPh$_2$ both react with cyclohexene by 1,2-addition, the latter yielding **22** (see Chart 1).[20] Steric effects are felt considerably more strongly in this reaction than in MeOH or Et$_3$SiH insertions, as shown by the ca. 2000-fold lower rate constant for reaction of SiMes$_2$ with cyclohexene[11] compared to that for SiPh$_2$ ($k = 7.9 \times 10^9$ M^{-1} s^{-1}). The difference is of a similar magnitude to that observed for the complexation reaction with MeOTMS; in both cases, it is impossible to avoid some degree of nonbonded interaction between the substituents on the silylene and the substrate in the transition state for the rate-determining step of the reaction, and hence the sensitivity of the rate constant to steric bulk associated with the silylene substituents is greater.

The rate constants for reaction of the three silylenes with 2,3-dimethyl-1,3-butadiene (DMB) and isoprene are 2−3 times larger than those for reaction with the alkenes, but exhibit a similar trend with silylene structure, decreasing in the order

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$k_{SiMe_2} \sim k_{SiPh_2} \sim 1600 k_{SiMes_2}$. The reaction is thought to proceed analogously to that with alkenes, forming the corresponding 2-vinyl-1-silirane derivative as the main primary product, which undergoes rapid secondary rearrangement to the isomeric 1-silacyclopent-3-ene and (under photochemical conditions) other (acyclic) isomers.[1] The evidence for vinylsilirane formation has come largely from trapping experiments, but was put on a firm footing by Zhang and Conlin's successful isolation of several vinylsilirane derivatives from reaction of SiMes₂ with aliphatic dienes.[56] The isomeric 1-silacyclopent-3-ene is apparently always formed in the reactions of silylenes with dienes, but has been suggested to arise mainly via secondary thermal and/or photochemical rearrangement of the vinylsilirane as opposed to a direct (4+1) cycloaddition pathway.[1,18]


(13)
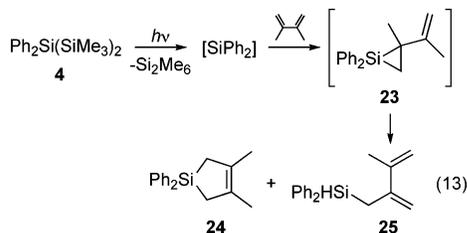
The reaction of SiPh₂ with DMB was first studied by Jones and co-workers, who isolated silacyclopentene **24** and the formal ene-type product **25** from photolysis of **4** in the presence of the diene (eq 13).[20] Both compounds were suggested to arise from "rapid isomerization" of vinylsilirane **23**, citing the earlier conclusions of Ishikawa, Ohi, and Kumada regarding the origins of the analogous products from photolysis of the SiMePh precursor **3** in the presence of DMB under similar conditions.[54,55] In light of this and a recent study of our own of the photochemistry of **24**,[57] we were surprised to discover that vinylsilirane **23** is easily detectable by NMR spectroscopy upon photolysis of **9** in C₆D₁₂ in the presence of DMB, where it is formed in a chemical yield of ca. 87% along with minor amounts of silacyclopentene **24** (eq 14). The structural assignment is based on comparison of the ¹H and ²⁹Si NMR spectra of the photolyzed mixture (see Supporting Information) to the data reported by Zhang and Conlin for the corresponding vinylsilirane obtained from reaction of DMB with SiMes₂.[56] As expected, the compound shows marked thermal instability, rearranging within 48 h (in the dark) to yield **24**. Isomer **25** could not be detected as a coproduct in this experiment, indicating that the quantum yield for its formation by secondary photolysis of **23** is substantially lower than that for formation of **24** by the same route. The concentration versus time plot for product **24** shows good linearity over the 0−30% conversion range in **9** (see Supporting Information), which would seem to be inconsistent with it being formed *exclusively* via secondary rearrangement of vinylsilirane **23**, but rather also via direct (4+1) cycloaddition. However, it should be pointed out that the lowest conversion probed in our steady-state photolysis experiment was ca. 5%, and the ratio of **24**:**23** present appeared to be significantly lower than its value at ca. 10% conversion. It thus seems more likely that **24** is formed mainly via secondary rearrangement of **23**,

which is consistent with the results of Bobbitt and Gaspar for the reaction of SiPh₂ with 1,3-butadiene in the presence of acetone.[1,18]

(14)
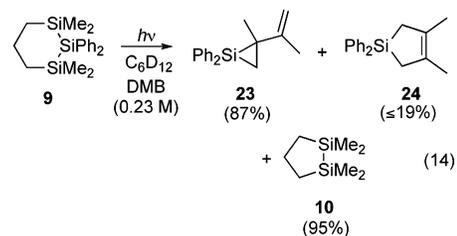
While numerous examples illustrating the course of the reaction of silylenes with alkynes have been reported, to our knowledge none have specifically addressed SiPh₂. We thus photolyzed **9** in the presence of bis(trimethylsilyl)acetylene (BTMSE) to verify the course of the reaction expected on the basis of the reported studies of the reaction of SiMe₂[58] and SiMes₂[59] with this alkyne. Indeed, a single major (SiPh₂-derived) product was formed in the reaction and was assigned to silirene **26** on the basis of the ¹H and ²⁹Si NMR spectra of the crude photolysate (see eq 15). The ²⁹Si spectrum showed, in addition to the resonances due to **9** and the coproduct **10**, resonances at δ −11.37 and −114.46 due to the SiMe₃ and ring-silicon atoms, respectively, in **26**; the latter is in close correspondence with the analogous data reported for the silirenes derived from reaction of the same alkyne with SiMe₂[58] and SiMes₂.[59] As with the other C−C unsaturated compounds studied, near diffusion-controlled quenching was observed for both SiMe₂ and SiPh₂ in hexane solutions of **1** and **9** containing submillimolar concentrations of BTMSE, leading to absolute rate constants of $k_{BTMSE} = 1.38 \times 10^{10}$ and 7.6×10^9 M⁻¹ s⁻¹ for SiMe₂ and SiPh₂, respectively.

(15)
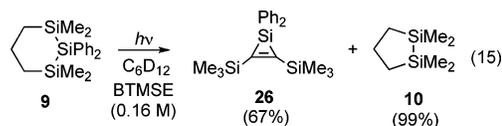
Transient absorption spectra recorded with hexane solutions of **9** containing 0.4−1.0 mM DMP, DMB, and BTMSE, conditions under which the lifetime of SiPh₂ is reduced to $\tau <$ 200 ns, showed absorptions centered at ca. 280 nm that did not decay during the maximum time window (of 0.9 s) that can be monitored with our system (see Supporting Information). The spectra and extended lifetimes of these species are consistent with their assignment to the corresponding three-membered-ring compounds. The UV/vis spectrum of the product formed from DMB (see Supporting Information) is identical to that reported by us previously for the long-lived product detected in laser photolysis experiments with silacyclopentene **24**, which was assigned to vinylsilirane **23**.[57] No spectroscopic evidence for intermediate complexes could be obtained for any of these reactions.

Reactions of SiPh₂ and SiMe₂ with CCl₄. The reactions of silylenes with halocarbons have also been of considerable interest.[17,47,60−70] The reaction varies in overall course depending

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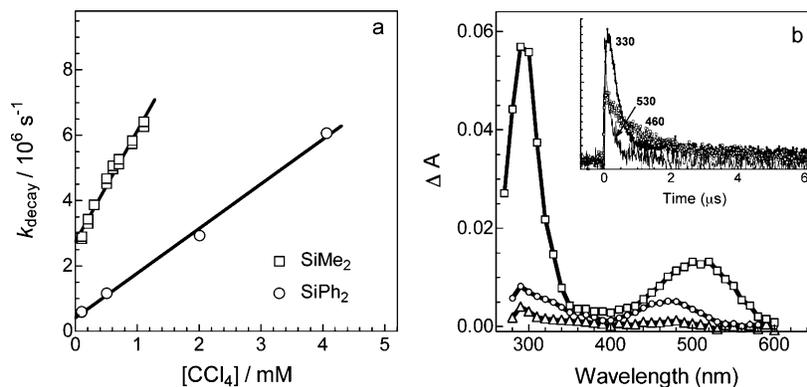
Figure 4. (a) Plots of the pseudo-first-order decay rate constants (k_{decay}) for SiMe$_2$ (-□-) and SiPh$_2$ (-O-) vs [CCl$_4$] in hexane solution at 25 °C. The solid lines are the linear least-squares fits of the data to eq 6. (b) Transient absorption spectra recorded 48−80 ns (-□-), 0.32−0.43 (-O-), and 0.88−0.99 μs (-△-) after the laser pulse, by laser flash photolysis of a 0.09 mM solution of **9** in deoxygenated hexane containing 4 mM CCl$_4$. The inset shows transient growth/decay profiles recorded at 330, 460, and 530 nm.

on the silylene and the halocarbon; for example, transient silylenes such as SiMe$_2$ undergo C−Cl insertion with monochloroalkanes[60,71] and halogen atom abstraction with CCl$_4$, the latter leading ultimately to the formation of the corresponding dichlorosilane and other radical-derived products.[62−65,69] The latter is precisely the behavior exhibited by SiPh$_2$, as shown by the results of steady-state photolysis of a solution of **9** in C$_6$D$_{12}$ containing 0.2 M CCl$_4$ (eq 16). The reaction affords dichlorodiphenylsilane (**27**; 78%) as the main SiPh$_2$-derived product, in addition to **10** (89%), CHCl$_3$ (25%), and hexachloroethane, with the latter being detected (but not quantified) by GC/MS; we did not determine whether chloroform-*d* was formed along with the protiated isotopomer in the reaction. At least one additional product was detected by ^{1}H NMR spectroscopy, which indicated it to be formed in ca. 25% yield relative to consumed **9**. This could not be confirmed by GC/MS, however. The NMR spectrum suggests that the product retains the ring structure of the starting material, and thus it seems most likely that it is a radical-derived product resulting from reaction of **9** with trichloromethyl radicals. Chlorodiphenylsilane-*d* (Ph$_2$Si-(D)Cl) was ruled out as a possible product by spiking the crude sample with a small quantity of an authentic sample of the protiated isotopomer.

The reaction is thought to proceed in general via the intermediacy of a silylene−halocarbon Lewis acid−base complex,[60,66,69,70] whose partitioning between halogen atom abstraction and other pathways depends primarily on the nature of the halocarbon; Cl abstraction is known to be very strongly favored in the case of CCl$_4$.[47,63,66] No absolute rate constants have yet been reported for a silylene−halocarbon reaction, although
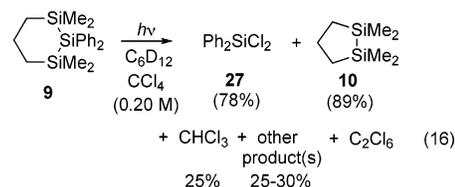
Taraban and co-workers have studied the photochemistry of a benzosilanorbornadiene-type precursor to SiMe$_2$ (**28**) in the presence of CCl$_4$ by flash photolysis and CIDNP methods and assigned a relatively long-lived transient they observed by flash photolysis in hexane containing 2 M CCl$_4$ to the SiMe$_2$−CCl$_4$ complex.[69] The free silylene cannot be detected directly in laser photolysis experiments with this precursor,[72,73] and so an indirect method was employed to estimate a value of $k \approx 10^6$ M^{-1} s^{-1} for the rate constant for complexation of the (singlet) silylene with CCl$_4$.[69]
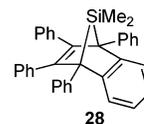
Addition of CCl$_4$ to hexane solutions of **1** and **9** led in both cases to linear dependences of the silylene decay rate constants on CCl$_4$ concentration (see Figure 4a) and concomitant quenching of the disilene signal intensities, as was observed with the other scavengers. Analysis of the k_{decay}−concentration data according to eq 6 afforded absolute rate constants of $k_{CCl_4} = 3.4 \times 10^9$ and 1.37×10^9 M^{-1} s^{-1} for SiMe$_2$ and SiPh$_2$, respectively. Transient absorption spectra recorded by laser photolysis of **9** in the presence of 4 mM CCl$_4$, where the lifetime of SiPh$_2$ was reduced to $\tau \approx 225$ ns, showed the characteristic absorption bands due to SiPh$_2$ and the long-lived residual absorber ($\lambda_{max} = 460$ nm), both of which were formed promptly with the laser pulse (see Figure 4b). The lifetime of the latter species ($\tau \approx 1.4$ μs) was roughly 100-fold shorter than its value in neat hexane; this indicates a quenching rate constant of $k_Q \approx 2 \times 10^8$ M^{-1} s^{-1}, which is again consistent with the silene (**11**) assignment.[32] Interestingly, the signals in the 330−350 nm region of the spectrum of **9** in the presence of 4 mM CCl$_4$ exhibited somewhat longer lifetimes compared to those at 300 and 530 nm (see inset, Figure 4b), suggesting the presence of

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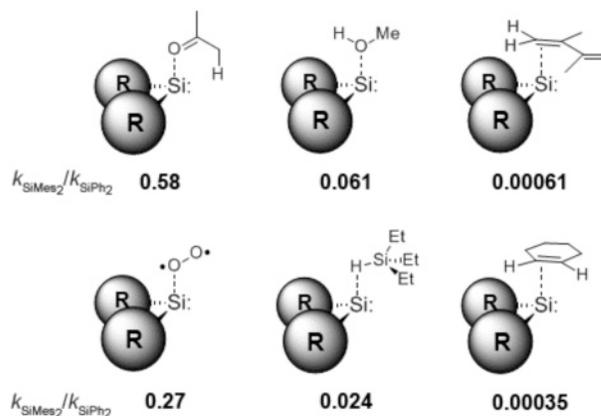
a transient product that absorbs in this wavelength range. The identity of this species is uncertain, but we consider the most likely possibility to be the chlorodiphenylsilyl radical (Ph$_2$SiCl), which the product studies suggest is formed as the primary product of the reaction of the silylene with the halocarbon. The lifetime of the species shows a similar (but slightly lower) sensitivity to CCl$_4$ concentration than SiPh$_2$; a plot of k_{decay} values at 330 nm versus [CCl$_4$] was linear, affording a rate constant of $k_Q = (8 \pm 1) \times 10^8$ M^{-1} s^{-1}. The value is similar to those reported for the (Cl abstraction) reactions of other arylsilyl radicals with CCl$_4$.[74]

Transient spectra recorded with a solution of **1** containing 0.6 mM CCl$_4$ showed *only* the characteristic absorptions due to SiMe$_2$ ($\tau \approx$ 180 ns), Si$_2$Me$_4$ (peak intensity ca. 25% of that in pure hexane; $\tau \approx$ 680 ns), and the long-lived photoproduct that is characteristic of all the experiments carried out with this precursor; no new transient products or intermediates could be detected in the experiment (see Supporting Information). The lifetime of Si$_2$Me$_4$ under these conditions provides an estimate of $k \approx 2.4 \times 10^9$ M^{-1} s^{-1} for the rate constant for reaction of the disilene with CCl$_4$, which is thought to proceed via initial Cl atom abstraction.[75,76] This is 10 orders of magnitude higher than the value reported by Kira and co-workers for reaction of CCl$_4$ with a stable tetrasilyldisilene in solution under similar conditions.[75] The value for Si$_2$Me$_4$ can also be compared to that for reaction of the germanium analogue, Ge$_2$Me$_4$, with CCl$_4$ in hexane at 25 °C, $k = 2.3 \times 10^7$ M^{-1} s^{-1}.[44] The difference in rates for the two tetramethyldimetallenes is in order-of-magnitude agreement with the recent calculations of Su on the energetics of Cl atom abstraction from CCl$_4$ by these compounds.[76]

Summary and Conclusions

Absolute rate constants have been determined for the reactions of the transient silylenes SiMe$_2$ and SiPh$_2$ with a wide variety of representative reagents, under a common set of conditions. The reactions that have been studied are all well known, and many of the associated mechanistic details have already been reasonably well established with the aid of product studies, competition experiments, and low-temperature (matrix) spectroscopic studies. Gas-phase kinetics and theoretical studies of the parent molecule and the few other small molecules that lend themselves readily to work of this type have also played a particularly significant role in developing our understanding of silylene reactivity. In particular, this work provides a quantitative link between the behavior of the parent molecule, for which kinetic studies are limited to the gas phase, and simple substituted derivatives such as SiMe$_2$, which can be studied in both the gas phase and solution.

The present work has been directed at further developing the links between these various efforts and exploring some of the finer mechanistic details that are associated with silylene chemistry. We have shown that substitution of methyl with phenyl groups generally leads to almost no change in intrinsic reactivity toward a wide variety of representative substrates; where differences do exist, they are invariably small, with SiPh$_2$ being only slightly less reactive than SiMe$_2$. Similar trends are evident in the relative reactivities of Si(H)Ph and Si(H)Me toward the methylsilanes (Me$_n$SiH$_{4-n}$; $n = 0-3$) in the gas phase, as mentioned earlier in the paper.[5] We have fewer data available at present to address the differences in reactivity

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Figure 5. Representations of the transition states for the rate-determining steps in the reactions of silylenes with various substrates, illustrating the variation in silylene−substrate steric interactions with reaction type. Also shown are the rate constant ratios k_{SiMes_2}/k_{SiPh_2} for each of the systems pictured, which provides a quantitative description of the effect.

between SiMe$_2$- and SiPh$_2$-derived reaction intermediates, as only a few of the reactions studied in the present work proceed via intermediates that build up in sufficient concentrations for us to detect them. Nevertheless, the few examples for which this is the case indicate that the differences here are also small. Those derived from SiPh$_2$ tend to be longer-lived, absorb at longer wavelengths, and exhibit more intense UV/vis spectra than their SiMe$_2$-derived counterparts, all distinct advantages in studies of this type. Though it has not been specifically quantified, dimerization appears to be somewhat slower in the case of SiPh$_2$, which imparts scavenging reactions with intrinsically greater efficiency; this makes kinetic analyses more reliable at low substrate concentrations and provides better sensitivity in experiments directed at the detection and characterization of reaction intermediates that are involved in some cases. The phenylated system has the additional advantage of being readily amenable to the introduction of polar ring substituents, which will undoubtedly prove to be very useful in future, more detailed mechanistic studies of silylene reactivity.

Wherever possible, we have made a point of comparing our kinetic data for SiPh$_2$ to previously reported rate constants for the corresponding reactions of the sterically hindered diarylsilylene, SiMes$_2$,[11] in the interest of developing kinetic benchmarks describing the sensitivity of various silylene reaction types to steric effects. A convenient measure of this sensitivity is the relative rate constants for reaction of SiMes$_2$ and SiPh$_2$ with a given substrate, subject to the proviso that these rate ratios may also contain contributions to the rate constants from the electronic effects of the mesityl methyl groups; there are six of them, so this effect may not be insignificant. The list of reactions for which direct comparisons can be made is somewhat limited at present, but it is nevertheless already clear that trends of valuable predictive power will emerge from further comparisons of this type. The seven substrates for which we have data divide into three groups: those with little apparent sensitivity to steric effects (acetone, O$_2$; $k_{SiMes_2}/k_{SiPh_2} > 0.1$), those with moderate sensitivity (MeOH, Et$_3$SiH; $0.01 < k_{SiMes_2}/k_{SiPh_2} < 0.1$), and those with high sensitivity (cyclohexene, DMB, MeOTMS; $k_{SiMes_2}/k_{SiPh_2} \leq 10^{-3}$). These trends make good sense when considered against the expected structures of the transition states for the rate-determining steps in the various reactions and the degree of nonbonded interactions that must develop between the substrate and the silylene substituents. This is illustrated pictorially in Figure 5 for the reactions with acetone, O$_2$, MeOH,

Et$_3$SiH, DMB, and cyclohexene. The reader is directed to the extensive body of theoretical work that has been done on most of these reactions in the case of the parent molecule, for more accurate depictions of the transition-state structures.[40,41,45,77−80]

A few of the systems studied in this and the preceding paper have afforded particularly rich mechanistic information as a result of the successful detection of intermediates formed as the primary products of the silylene−substrate reactions. These include the reactions of SiPh$_2$ with methanol,[16] methoxytrimethylsilane, CCl$_4$, and oxygen. In all four cases, intriguing preliminary results have been obtained, underlining the fact that much remains to be learned of the mechanistic details of many silylene reactions. Future work from our laboratory will address these reactions, and others, in greater detail.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on Bruker AV200 or AV600 spectrometers in deuterated chloroform and were referenced to the solvent residual proton and ^{13}C signals, respectively, while ^{29}Si spectra were recorded on the AV600 using the HMBC pulse sequence and referenced to an external solution of tetramethylsilane. GC/MS analyses were determined on a Varian Saturn 2200 GC/MS/MS system equipped with a VF-5ms capillary column (30 m × 0.25 mm; 0.25 μm; Varian, Inc.). High-resolution electron mass spectra and exact masses were determined on a Micromass TofSpec 2E mass spectrometer using electron impact ionization (70 eV). Infrared spectra were recorded as thin films on potassium bromide plates using a Bio-Rad FTS-40 FTIR spectrometer. Column chromatography was carried out using a 3 × 60 cm column using silica gel 60 (230−400 mesh; Silicycle).

1,1,3,3-Tetramethyl-2,2-diphenyl-1,2,3-trisilacyclohexane (**9**) was synthesized according to the method described in the preceding paper,[16] while dodecamethylcyclohexasilane (**1**) was used as received from Sigma-Aldrich. Methoxytrimethylsilane was synthesized by reaction of methanol with excess hexamethyldisilazane and purified by distillation (bp 56−58 °C).[81] All the other scavengers investigated in this work were obtained from commercial sources in the highest purity available. Triethylsilane (Et$_3$SiH), triethylgermane (Et$_3$GeH), and tri-*n*-butylstannane (Bu$_3$SnH) were stirred at room temperature for 18 h over lithium aluminum hydride and then either distilled at atmospheric pressure (Et$_3$SiH) or under mild vacuum (Bu$_3$SnH) or passed through a short silica gel column in the case of Et$_3$GeH. CCl$_4$ was refluxed over phosphorus pentoxide and distilled. 4,4-Dimethyl-1-pentene (DMP), isoprene, and 2,3-dimethyl-1,3-butadiene (DMB) were purified by passage of the neat liquids through a silica gel column. 3,3-Dimethyl-1-butyne (TBE) and cyclohexene were distilled. Bis(trimethylsilyl)acetylene (Gelest), acetone (Caledon Reagent), and glacial acetic acid (Sigma-Aldrich) were used as received from the suppliers. Hexanes (EMD Omni-Solv), diethyl ether (Caledon Reagent), and tetrahydrofuran (Caledon Reagent) were dried by passage through activated alumina under nitrogen using a Solv-Tek solvent purification system (Solv-Tek, Inc). Deuterated solvents were used as received from Cambridge Isotope Laboratories.

Triethyl(diphenylsilyl)germane (20). In an oven-dried 15 mL two-necked round-bottom flask fitted with condenser, argon inlet, and magnetic stir bar was placed diisopropylamine (0.17 g, 1.7 mmol) in THF (2 mL) under argon, and the solution was cooled to

−78 °C with a dry ice/acetone bath. A 2 M solution of *n*-butyllithium (0.82 mL, 1.65 mmol) in pentane was added dropwise via syringe over 20 min, and the mixture was warmed to ca. 0 °C in an ice bath and then kept at this temperature for 15 min. The mixture was recooled to −78 °C, and a solution of triethylgermane (0.27 g, 1.69 mmol) in THF (1.5 mL) was added dropwise over 1 h. The bath was removed, and the contents were taken up in a syringe and then added dropwise over 1 h to a solution of chlorodiphenylsilane (0.31 g, 1.42 mmol) in THF (2 mL) under argon at −40 °C (acetonitrile−dry ice bath) in an oven-dried 25 mL two-necked round-bottom flask fitted with condenser, argon inlet, and magnetic stir bar. The reaction mixture was left to stir overnight, with the temperature rising slowly to room temperature. The mixture was diluted with diethyl ether (5 mL) and filtered through a short silica gel column to remove white precipitate and polar impurities, and the solvent was removed under vacuum to yield a colorless oil (0.27 g). Column chromatography on silica gel with hexanes as eluant afforded triethyl(diphenylsilyl)germane (**20**; 0.077 g, 16%), which was identified on the basis of the following spectroscopic data: ^{1}H NMR (600 MHz, CDCl$_3$) δ 0.96 (q, J = 7.8 Hz, 6H), 1.05 (t, J = 7.8 Hz, 9H), 5.08 (s, 1H), 7.37-(m,6H), 7.58 (dd, J = 1.8, 7.8 Hz, 4H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 9.0, 13.8, 27.5, 30.1, 128.2, 129.1, 135.0, 135.8; ^{29}Si NMR (119 MHz, CDCl$_3$) δ −29.25 (Ph$_2$SiH, $J_{Si−H}$ = 186.0 Hz); IR (neat) ν (cm^{-1}) = 3068 (m), 3052 (m), 2950 (s), 2928 (s), 2909 (s), 2874 (s), 2099 (s), 1486 (m), 1459 (m), 1430 (s), 1104 (m), 1014 (m), 791 (s), 754 (s), 722 (s); GC/MS (EI) m/z = 344(8; M$^+$), 317 (17), 316 (18), 315 (65), 314 (32), 313 (61), 311 (47), 289 (23), 288 (22), 287 (100), 286 (40), 285 (80), 284 (17), 283 (56), 261 (14), 260 (9). 259 (49), 258 (19), 257 (49), 256 (13), 255 (39), 253 (9), 212 (16), 184 (16), 183 (83), 181 (26), 151 (31), 149 (25), 147 (15), 135 (15), 133 (12), 131 (11), 107 (18), 105 (65), 103 (27), 101 (13), 75 (10), 53 (17); exact mass calculated for C$_{18}$H$_{26}$Si^{74}Ge 344.1016, found 344.1024.

Tri-*n*-butyl(diphenylsilyl)stannane (21). The compound was prepared in identical fashion to **20**, from tri-*n*-butyltin hydride (0.37 g, 1.27 mmol) and chlorodiphenylsilane (0.26 g, 1.19 mmol). Column chromatography of the crude reaction mixture on silica gel with hexanes as eluant afforded tri-*n*-butyl(diphenylsilyl)-stannane (**21**; 0.055 g, 10%), which was identified on the basis of the following spectroscopic data: ^{1}H NMR (600 MHz, CDCl$_3$) δ 0.84 (t, J = 7.8 Hz, 9H), 1.00 (t, J = 7.8 Hz, 6H), 1.26 (sextet, J = 7.8 Hz, 6H), 1.46 (quint, J = 7.8 Hz, 6H), 7.36 (m,6H), 5.28 (s, 1H), 7.57 (m, 4H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 9.0, 13.8, 27.5, 30.1, 128.2, 129.1, 135.0, 135.8; ^{29}Si NMR (119 MHz, CDCl$_3$) δ −28.23 (Ph$_2$SiH, $J_{Si−H}$ = 187.4 Hz); IR (neat) ν (cm^{-1}) = 3068 (m), 2958 (s), 2871 (s), 2853 (s), 2099 (s), 1464 (m), 1428 (s), 1376 (m), 1102 (s), 787 (s), 714 (s), 698 (s); GC/MS (EI) m/z = 417 (10; M$^+$ − *n*-Bu), 416 (7), 415 (9), 414 (6), 361 (31), 360 (17), 359 (31), 358 (16), 357 (16), 309 (16), 307 (21), 306 (20), 305 (100), 304 (39), 303 (87), 301 (46), 197 (12), 195 (10), 184 (11), 183 (50), 181 (14), 177 (9), 121 (8), 105 (17), 79 (3), 53 (5); exact mass calculated for C$_{24}$H$_{38}$SiSn 474.1765, found 474.1794; exact mass calculated for C$_{20}$H$_{29}$SnSi (M$^+$ − *n*-Bu) 417.1060, found 417.1043.

Steady-State Photolysis Experiments. In a typical procedure, a solution of **9** (0.039−0.051 M) in cyclohexane-d_{12} (0.7 mL) was placed in a quartz NMR tube and the tube was capped with a rubber septum. The solution was deoxygenated with dry argon for 15 min, and then the appropriate volumes of trapping agent and dioxane (as internal integration standard) were added with a microlitre syringe to result in concentrations of ca. 0.20 and 0.01 M, respectively. The solution was then photolyzed for 18−24 min (ca. 44−60% conversion of **9**) in a Rayonet photochemical reactor (Southern New England Ultraviolet Co.) equipped with a merry-go-round and two RPR-2537 lamps, monitoring by 600 MHz ^{1}H NMR spectroscopy in 2 min time intervals throughout the experi-

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ment. Each mixture was also analyzed by GC/MS before and after photolysis.

With most of the trapping agents studied, photolysis led to the formation of two major products. The first was common to all and was identified as 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**10**) by comparison of its ^{1}H NMR and mass spectra to reported data:[82] ^{1}H NMR (600 MHz, C_6D_{12}) δ 0.07 (s, 12H; $SiMe_2$), 0.67 (t, 4H, J = 6.6 Hz; $C^{3,5}H_2$), 1.67 (quint, 2H, J = 6.6 Hz; C^4H_2); GC/MS (EI) m/z = 158 (42; M⁺), 143 (43), 130 (41), 117 (33), 116 (44), 115 (100), 99 (8), 85 (10), 73 (41), 59 (19), 45 (13), 43 (28). The second major product was unique to each of the trapping agents studied and could be assigned to the product of reaction of the trap with $SiPh_2$. Additional minor product(s) were evident in a few cases. In the majority of cases, the silylene-trapping products were identified by comparison of the ^{1}H NMR and mass spectra to literature data or to the corresponding spectra of authentic, independently prepared samples. Two of the products (**23** and **26**) were tentatively identified from the ^{1}H NMR spectra of the crude photolysis mixtures, on the basis of comparisons to the reported spectra of closely related analogues. Chemical yields of the major products formed were determined from the relative slopes of concentration

versus time plots for the product(s) and **9** in each case. Concentrations were calculated from the ^{1}H NMR integrals, using the SiMe proton resonances to characterize **9** and **10** and one of the peaks for the remaining product(s) to characterize it; C—H resonances were used wherever possible. Details are provided in the Supporting Information.

Laser Flash Photolysis Experiments. Laser flash photolysis experiments were carried out as described in the preceding paper.[16] Rate constants were calculated by linear least-squares analysis of decay rate—concentration data. Errors in absolute second-order rate constants are quoted as twice the standard deviation obtained from the least-squares analyses.

Supporting Information Available: Representative ^{1}H NMR spectra and concentration versus time plots from steady-state photolysis experiments, plots of k_{decay} versus [Q] for quenching of $SiMe_2$ and $SiPh_2$, and transient absorption spectra from laser photolysis of **9** and **1** in the presence of scavengers. This material is available free of charge via the Internet at http://pubs.acs.org.

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