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Direct Detection of Diphenylsilylene and Tetraphenyldisilene in Solution

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Photolysis of 1,1,3,3-tetramethyl-2,2-diphenyl-1,2,3-trisilacyclohexane (**9**) in hydrocarbon solvents affords diphenylsilylene ($SiPh_2$) and 1,1,2,2-tetramethyl-1,2-disilacyclopentane in nearly quantitative yields, as shown by the results of steady-state trapping experiments with methanol and acetone. $SiPh_2$ (λ_{max} = 290, 515 nm) can be detected directly by laser flash photolysis of **9** in hexane, where it decays over 1−2 μs with the concomitant growth of a second transient species that is assigned to the dimer, tetraphenyldisilene (Si_2Ph_4; λ_{max} = 290, 370, 460 nm), on the basis of its spectrum and kinetic behavior. The transient spectroscopic behavior is similar to that observed in laser photolysis experiments with the dimethylsilylene ($SiMe_2$) and dimesitylsilylene ($SiMes_2$) precursors dodecamethylcyclohexasilane (**1**) and 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane (**2**), respectively, in the same solvent. Absolute rate constants for the reactions of the three silylenes with methanol and acetone have been measured under common conditions, providing the first quantitative glimpse of the electronic and steric effects of substituents on silylene reactivity in solution. The time-resolved spectroscopic behavior observed in laser photolysis experiments with **9** is also compared to those observed with the related, previously reported $SiPh_2$ precursors, 1,1,3,3-tetramethyl-2,2-diphenyl-1,2,3-trisilacycloheptane (**6**) and 1,1,1,3,3,3-hexamethyl-2,2-diphenyltrisilane (**4**), which are also briefly reinvestigated. The results show that the relatively weak absorptions due to $SiPh_2$ can in fact be detected from the latter compound, superimposed on the much more intense, long-lived transient absorptions due to the conjugated silene derivative that is known to be formed as a coproduct in the photolysis of this compound in solution at room temperature.

Introduction

The chemistry of silylenes has been of great interest for many years,[1] and while a great deal of work has been done toward defining the mechanisms and scope of many of their characteristic reactions, few quantitative kinetic data exist on the reactivity of simple transient derivatives in solution. Silylene itself (SiH_2) and several simple substituted derivatives SiXY (X,Y = H, Me, or halogen) have been studied extensively in the gas phase,[2−4] but, until very recently,[5] only dimethyl- and dimesitylsilylene ($SiMe_2$ and $SiMes_2$, respectively) had been successfully detected and studied in solution by time-resolved spectroscopic methods.[6−10] The prevailing methodology that has been employed for the generation of transient silylenes in condensed phase studies is the photolysis of trisilanes or higher oligosilanes, as silylene extrusion is usually the major photochemical reaction of such compounds.[11−14] This methodology has allowed (inter alia) the determination of the UV/vis spectra of close to two dozen transient silylene derivatives in hydrocarbon glasses at 77 K by West and co-workers.[15]

Four of the tri- or oligosilanes studied in glasses at 77 K have also been studied in solution by laser flash photolysis. These include the $SiMe_2$ and $SiMes_2$ precursors **1**[6−9] and **2**,[10] respectively, which afford very similar transient photoproduct spectra under the two sets of conditions, and the SiMePh and $SiPh_2$ precursors **3**[16,17] and **4**,[18] respectively, which do not. For example, photolysis of 1,1,1,3,3,3-hexamethyl-2,2-diphenyl-

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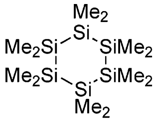
trisilane (**4**) in 3-methylpentane at 77 K yields a species exhibiting $\lambda_{max} \approx 500$ nm, which was assigned to $SiPh_2$,[15] while laser photolysis of the compound in cyclohexane solution affords a species possessing $\lambda_{max} \approx 445$ nm and a lifetime (τ) of several hundred microseconds.[18] Although the latter was initially assigned to $SiPh_2$, its reactivity toward typical silylene scavengers proved to be markedly different from those reported later for $SiMe_2$[6−9] and $SiMes_2$,[10] leading to the eventual recognition that the assignment was probably incorrect.[1a] Its most likely identity is the silene (**5**; eq 1) derived from photochemical 1,3-$SiMe_3$ migration into an ortho-position of one of the phenyl rings in **4**, which trapping experiments have shown is formed in only slightly lower yield than $SiPh_2$ upon photolysis of this compound in solution.[19,20] Migrations of this type are generally the major photoreactions in phenyldisilanes[13,14,21,22] and are also known to compete with silylene extrusion in the photochemistry of other 2-phenyltrisilanes in fluid solution, such as the SiMePh precursor **3**.[23] Silenes of this type are relatively long-lived and absorb quite strongly in the 420−500 nm range of the spectrum[24] and could easily obscure the relatively weak absorptions expected for $SiPh_2$.



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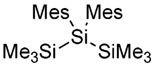
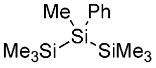


2

(Mes = 2,4,6-trimethylphenyl)



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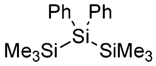

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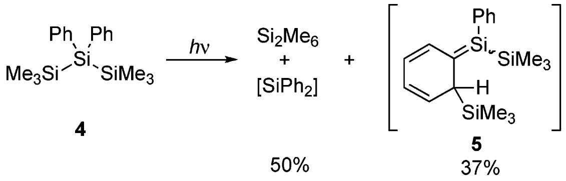
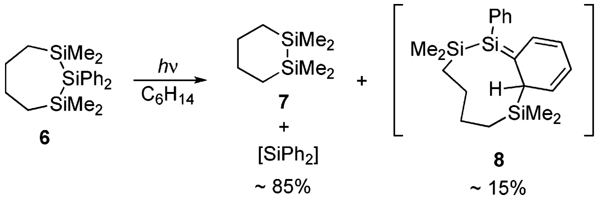


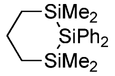
(1)

We recently reported the results of a study of the photochemistry of 1,1,3,3-tetramethyl-2,2-diphenyl-1,2,3-trisilacycloheptane (**6**) (eq 2),[5] which was based on the expectation that the efficiency of silylene extrusion might be enhanced at the expense of silene formation when the undesired 1,3-silyl migration is forced to result in the formation of a (presumably somewhat strained) nine-membered cyclic silene. Indeed, the results indicated that $SiPh_2$ is formed in significantly higher yield from **6** than it is from **4**[19] and allowed the direct detection and characterization of the silylene in solution for the first time. Nevertheless, minor amounts of trapping products consistent with the formation of silene **8** in ca. 15% yield (eq 2) were detected in steady-state photolysis experiments, and flash photolysis of the compound showed evidence of a long-lived transient species ($\lambda_{max} \approx 460$ nm; $\tau > 300$ μs) with spectral and kinetic behavior similar to that reported earlier for **4**. While the presence of this second species did not interfere with the determination of absolute rate constants for scavenging of the silylene, it did necessitate the use of spectral subtraction methods to extract the UV/vis spectrum of $SiPh_2$. The presence of the silene impurity in the transient mixture limits our ability to extract all of the information that is potentially available in experiments of this type, such as the spectra and kinetic behavior of reaction intermediates or transient products. The most important of these is the silylene dimer, tetraphenyldisilene (Si_2Ph_4), which our experiments suggested is the main reaction product from $SiPh_2$ in the absence of silylene scavengers, and which exhibits a UV/vis absorption maximum at the same wavelength as silene (**8**). There thus remained a significant motivation to develop an even cleaner photochemical precursor to $SiPh_2$ than **6**, to enable more detailed study of the reactivity of this fundamentally important species in solution.



(2)

In this Article, we report a steady state and laser flash photolysis study of the homologous trisilacyclohexane derivative, **9**, which we have synthesized in the hope of further optimizing the photochemical yield of $SiPh_2$. Indeed, the compound is shown to extrude $SiPh_2$ almost quantitatively upon photolysis in solution and thus allows full characterization of the UV/vis spectra of both $SiPh_2$ and Si_2Ph_4 without resort to the spectral subtraction methods that were necessary using **6** as the precursor. The assignment is reinforced by a comparison to similar data recorded under the same conditions with the $SiMe_2$ and $SiMes_2$ precursors **1** and **2**, respectively, followed by the determination of absolute rate constants for the reactions of the three silylenes with MeOH and acetone in hexane at 25 °C. Finally, the transient spectroscopic behavior of **9** is compared to those of the trisilacycloheptane derivative, **6**, and the parent acyclic trisilane, **4**, to show that $SiPh_2$ can in fact be detected in laser photolysis experiments with the latter compound, despite its absorptions being buried under the much more intense ones due to the long-lived rearrangement product, silene **5**.



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Our main motivation for this work was to develop a general picture of the common features and differences in the spectroscopic properties and kinetic behavior of these three representative silylene derivatives in solution, laying the groundwork for future kinetic and mechanistic studies of some of their characteristic reactions in solution. The first of these is the subject of the accompanying paper, which presents the results of a survey of the kinetics of the reactions of $SiPh_2$ and $SiMe_2$ with a wide variety of representative silylene scavengers in hexane solution and reveals, in almost every case, new information pertaining to the mechanisms of these reactions.

Results and Discussion

Our initial synthesis of **9** employed a procedure analogous to that used for the preparation of **6**,[5] as shown in eq 3. While

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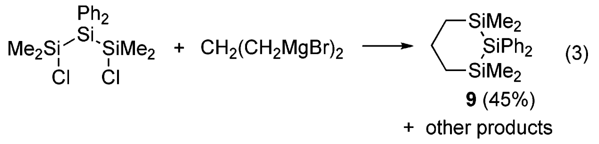
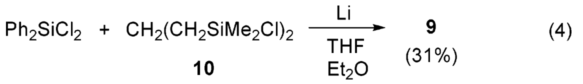
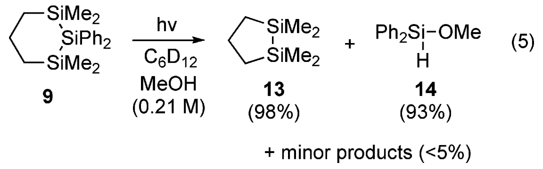
this procedure afforded **9** in acceptable yields, it also produced a number of acyclic byproducts that we were unable to separate completely from the desired compound by column chromatography. We thus turned to the alternate synthetic route shown in eq 4, which afforded **9** in somewhat lower yield, but much higher purity, than the method of eq 3.



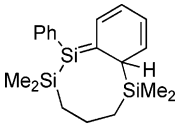


$$Ph_2SiCl_2 + \underset{\mathbf{10}}{CH_2(CH_2SiMe_2Cl)_2} \xrightarrow[THF,\ Et_2O]{Li} \underset{(31\%)}{\mathbf{9}} \qquad (4)$$

Steady-state photolysis (254 nm) of a deoxygenated solution of **9** (0.048 M) in C_6D_{12} containing MeOH (0.21 M) led to the formation of 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**13**) and diphenylmethoxysilane (**14**) in close to quantitative yields, as shown by ^1H NMR spectra of the photolysis mixture recorded at regular intervals between 2% and 60% conversion of **9** (eq 5). Concentration versus time plots for **9**, **13**, and **14** were linear over the 0−35% conversion range, with the slopes of the plots for the two products equal to each other and to the negative slope of the plot for **9** within experimental error (see Supporting Information). The quantum yields for the formation of **13** and **14** were not determined, but are clearly similar to the corresponding values determined previously for product formation from **6**,[5] based on the similarities in the rates of product formation from the two compounds under identical photolysis conditions.



GC/MS analysis of the photolyzed mixture after 60% conversion showed, in addition to **13** and **14**, two very minor products of retention time greater than **9**, which exhibited mass spectra consistent with addition of methanol to an isomer of the starting trisilacyclohexane (M^+ 372). One of these could be tentatively detected in the NMR spectra of the crude photolysate, exhibiting a singlet at δ 3.46 of roughly 3% the intensity of the methoxy singlet due to **14**. These results are consistent with the formation of the isomeric silene derivative **15** in very minor amounts upon photolysis of **9**. As we had hoped, the maximum estimated yield of the species (3−5%) is considerably lower than that of the corresponding products from photolysis of the trisilacyclopheptane derivative **6** (ca. 15%)[5] and the parent acyclic trisilane **4** (ca. 37%).[19]



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Laser flash photolysis of rapidly flowed solutions of **9** ($\sim 10^{-4}$ M) in dry, deoxygenated hexane, with the pulses from a KrF excimer laser (248 nm, ca. 25 ns, ca. 100 mJ), led to the formation of two distinct transient absorptions: a short-lived one that was formed with the laser pulse ($\lambda_{max} \approx 515$ nm; $\tau \approx 0.6-1.2\ \mu s$), and a longer-lived one centered at $\lambda_{max} \approx 460$ nm, the bulk of which grew in after the pulse over a time scale similar to that of the decay of the first species, and then decayed over ca. 400 μs with complex kinetics. Experiments carried out in the presence of 3 mM triethylsilane (Et_3SiH) showed that the absorption centered at 460 nm in pure hexane contains contributions from two transient species, the formation of only one of which is quenched by the silane. Left behind in the presence of Et_3SiH is the 515 nm species ($\tau \approx 65$ ns) and a species exhibiting an absorption band ($\lambda_{max} = 460$ nm) that was approximately one-half as strong as that obtained in the absence of the silane, appeared to be formed with the laser pulse, and decayed over a time scale similar to that of the signal at this wavelength in the absence of silane. A plot of the pseudo-first-order decay rate constant for decay of the 515 nm species (k_{decay}) versus [Et_3SiH] was linear and was analyzed according to eq 6, where k_{decay} and k_0 are the pseudo-first rate constants for decay of the species in the presence and absence of the substrate (Q = Et_3SiH), and k_Q is the second-order rate constant for reaction with the substrate. The analysis afforded $k_Q = (3.3 \pm 0.2) \times 10^9\ M^{-1}\ s^{-1}$ for quenching of the species by Et_3SiH under these conditions.

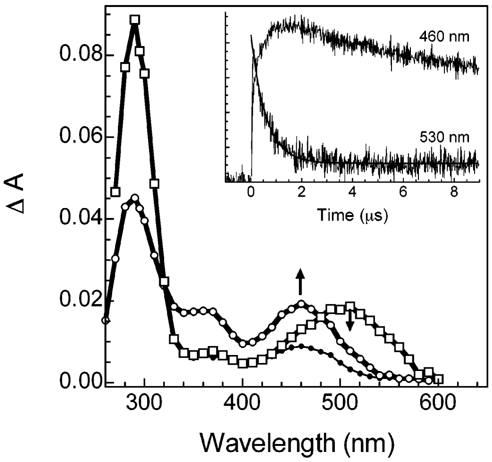

Figure 1. Transient absorption spectra recorded 96−160 ns (−□−) and 1.70−1.81 μs (−○−) after the laser pulse, by laser flash photolysis of a 0.09 mM solution of **9** in deoxygenated, anhydrous hexane; the inset shows transient growth/decay profiles recorded at 460 and 530 nm. The third spectrum (−●−; 350−550 nm) was recorded 1.70−1.81 μs after the laser pulse for the same solution containing 3 mM Et_3SiH, showing the spectrum of the long-lived ($\tau > 400\ \mu s$) transient impurity that underlies the other two spectra.

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

Figure 1 shows time-resolved UV/vis spectra recorded 96−160 ns and 1.70−1.81 μs after the laser pulse for a solution of **9** in deoxygenated hexane, and one recorded 1.70−1.81 μs after the pulse for the same solution after 3 mM Et_3SiH had been added. The gross features of these results are similar to those reported previously for **6**;[5] the main difference is that, with **9**, the slowly decaying, promptly formed transient absorption centered at 460 nm is of much weaker intensity relative to those of the other two transient products. A reasonable assignment for this species is silene **15**; the spectrum and lifetime are both quite similar to those detected in flash photolysis experiments with **6**[5] and **4**,[18] from which the corresponding silenes are formed in much higher yields.[5,19] The NMR and mass spectral signatures of the minor products detected in the steady-state photolysis of **9** in the presence of MeOH (vide supra) are consistent with the

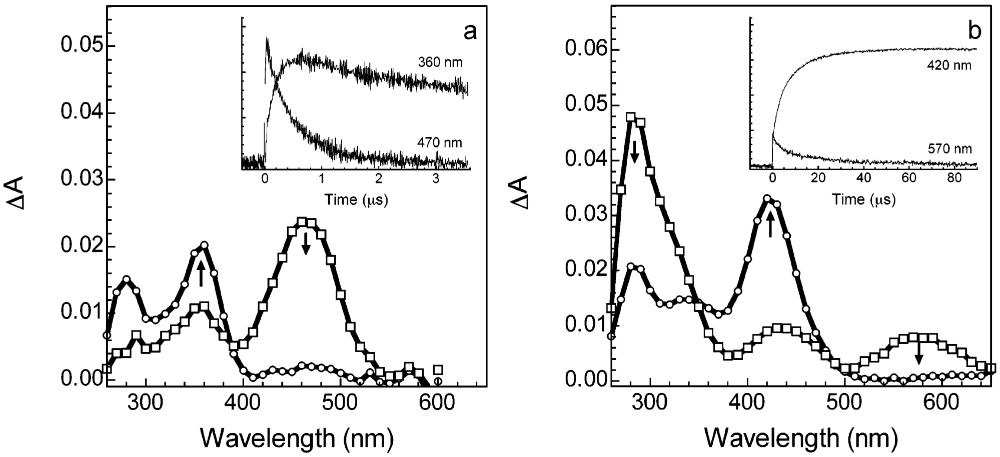

Figure 2. Transient absorption spectra recorded by laser flash photolysis of deoxygenated, anhydrous hexane solutions of (a) the $SiMe_2$/Si_2Me_4 precursor **1** (4.6×10^{-4} M), 90−115 ns (−□−) and 1.45−1.49 μs (−○−) after the laser pulse, and (b) the $SiMes_2$/Si_2Mes_4 precursor **2** (5.8×10^{-5} M), 160−320 ns (−□−) and 89.6−89.9 μs (−○−) after the pulse. The insets show transient decay traces recorded at (a) 470 and 360 nm, and (b) 570 and 420 nm.

products of MeOH addition to **15**, which provides further support for the assignment. The short-lived, promptly formed transient (λ_{max} = 290, 515 nm) and the species formed as a result of its decay (λ_{max} = 290, 370, 460 nm) are both very similar to those observed in our earlier study of **6**[5] and are thus assigned as before to $SiPh_2$ and Si_2Ph_4, respectively. The rate constant for quenching of the former by Et_3SiH is also in excellent agreement with our previously reported value.[5]

Laser photolysis of flowed, deoxygenated solutions of **1** (ca. 5×10^{-4} M) and **2** (ca. 6×10^{-5} M) in anhydrous hexane afforded results that are in good agreement with those reported previously for these compounds in cyclohexane.[6−10] Figure 2a and b shows transient absorption spectra and representative decay traces obtained by laser photolysis of **1** and **2**, respectively, presented in a format similar to those of Figure 1 so as to enable direct comparisons. As in our experiments with **9**, the silylenes are detectable as promptly formed transient absorptions with long-wavelength bands centered at λ_{max} = 465 nm ($SiMe_2$, $\tau \approx$ 250−600 ns) and λ_{max} = 580 nm ($SiMes_2$, $\tau \approx$ 20 μs), which decay with the concomitant growth of absorptions centered at λ_{max} = 360 nm ($\tau \approx$ 20 μs) and λ_{max} = 420 nm (τ > 20 s) due to the corresponding disilenes Si_2Me_4[9,25,26] and Si_2Mes_4,[10,27] respectively. It should be noted that the absorption centered at $\lambda_{max} \approx$ 280 nm in the 1.45 μs spectrum from **1** (see Figure 2a) is due to a long-lived (τ > 1 ms) photolysis coproduct, whose temporal profile in the first ca. 300 ns after excitation is distorted due to intense fluorescence from the sample. The absorption centered at $\lambda_{max} \approx$ 435 nm in the 160−320 ns spectrum from **2** (see Figure 2b) is also due to a long-lived photolysis coproduct. This was confirmed by a transient spectrum recorded with **2** in the presence of 3.9 mM MeOH, which quenched the absorptions due to $SiMes_2$ and Si_2Mes_4 completely, leaving behind a single long-lived species with an absorption band centered at λ_{max} = 440 nm. At present, we are unable to assign structures to either of these species.

The lifetimes of both $SiMe_2$ and $SiPh_2$ in pure hexane varied considerably from experiment to experiment. This is almost certainly due to residual moisture in the system, even though reasonable care was always taken to dry both the solvent and the apparatus used. The implied sensitivity of the lifetimes to the presence of water is borne out by the rate constants for reaction of the two species with MeOH, which are very close to the diffusion-controlled limit in both cases (vide infra). Furthermore, the strength of the signals obtained in experiments with **9** in particular showed a marked dependence on flow rate, because of the high quantum yield associated with the photoextrusion reaction.

It is interesting to compare the UV/vis absorption spectra of the three silylenes and their disilene dimers to those of the corresponding germanium analogues. With the aryl-substituted systems, the absorption maxima of both the silylenes ($SiPh_2$ and $SiMes_2$) and the disilenes (Si_2Ph_4 and Si_2Mes_4) are red-shifted relative to those of the corresponding germylenes ($GePh_2$ (λ_{max} 500 nm) and $GeMes_2$ (λ_{max} 560 nm)) and digermenes (Ge_2Ph_4 (λ_{max} 440 nm) and Ge_2Mes_4 (λ_{max} 410 nm)).[28] Exactly the opposite is true of the methylated derivatives, for which the germylene and digermene are the longer wavelength absorbers: λ_{max} 480 and 375 nm for $GeMe_2$ and Ge_2Me_4, respectively,[28] as compared to λ_{max} 465 and 360 nm for the corresponding silicon analogues. The latter trends presumably most closely represent the intrinsic differences in electronic structure between the two elements; the switch that occurs in the arylated derivatives can then be ascribed to the better π-overlap that is possible between the aryl substituents and the divalent M-atom or M═M bond when M = Si compared to when M = Ge.

Addition of MeOH to the hexane solutions of **1**, **2**, and **9** caused the decay of the silylene absorptions to accelerate in proportion to the methanol concentration and follow clean pseudo-first kinetics, and the growth of the corresponding disilene absorption to accelerate and reach a lower maximum intensity than was the case in pure hexane. Plots of k_{decay} versus [MeOH] were linear in every case (see Figure 2a) and were thus analyzed according to eq 6 to obtain the second-order rate coefficients $k_{MeOH} = (1.8 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1} for $SiMe_2$, $k_{MeOH} = (1.3 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1} for $SiPh_2$, and $k_{MeOH} = (8.2 \pm 0.3) \times 10^{8}$ M^{-1} s^{-1} for $SiMes_2$. The value for $SiPh_2$ is in excellent agreement with that obtained using **6** as precursor,[5] while that for $SiMe_2$ is ca. twice larger than the value reported by Shizuka and co-workers in cyclohexane,[8] as expected given

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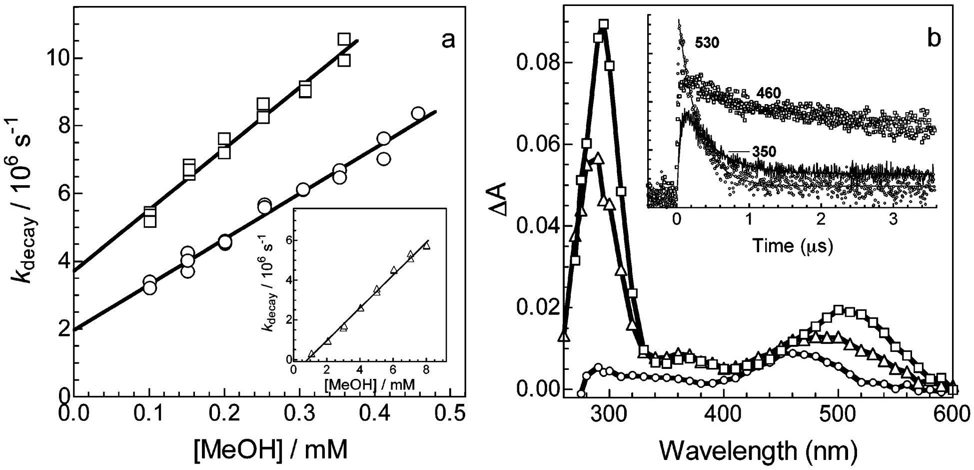
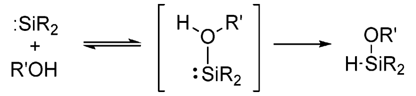


Figure 3. (a) Plots of the pseudo-first-order decay rate constants (k_{decay}) for $SiMe_2$ (□), $SiPh_2$ (○), and $SiMes_2$ (△; see inset) versus [MeOH] in hexane solution at 25 °C; the solid lines are the linear least-squares fits of the data to eq 6. (b) Transient absorption spectra recorded 45−70 ns (−□−), 240−275 ns (−△−), and 1.60−1.63 μs (−○−) after the laser pulse, by laser flash photolysis of a 0.09 mM solution of **9** in deoxygenated hexane containing 0.15 mM MeOH; the inset shows transient growth/decay profiles recorded at 530, 460, and 350 nm.

the lower viscosity of hexane[29] and the fact that the reaction is essentially diffusion-controlled. The rate coefficient for reaction of $SiPh_2$ with the alcohol is only about 25% lower than that for $SiMe_2$, indicating that phenyl-for-methyl substitution has little net effect on this aspect of silylene reactivity. In contrast, the value for $SiMes_2$ is roughly 15 times lower than that for $SiPh_2$, providing a preliminary indication of the effects of steric hindrance on the OH-insertion reaction with this alcohol. It should be noted that the plot of k_{decay} versus [MeOH] for $SiMes_2$ exhibits a negative intercept, indicative of a mixed order dependence of k_{decay} on [MeOH] at low alcohol concentrations.

The mechanism of the formal OH insertion reaction of silylenes with alcohols has been the subject of considerable attention. Weber and co-workers demonstrated using competition experiments that the reactions of $SiMe_2$ and SiMePh with various aliphatic alcohols exhibit primary product isotope effects on the order of $k_H/k_D \approx 2$ in both ether and hydrocarbon solvents, but they were unable to interpret the results in terms of a unique reaction mechanism;[30] a primary isotope effect is consistent with either concerted O−H(D) insertion or a stepwise process involving initial, reversible Si−O complexation followed by rate-determining H-migration. In later low-temperature studies of the Lewis acid−base complexation of $SiMe_2$, $SiMes_2$, and two other hindered silylenes with various heteroatom-containing substrates, Gillette et al. demonstrated that the reaction of $SiMes_2$ with secondary alcohols proceeds via the initial formation of a (transient) silylene−alcohol complex, which could be detected as a discrete intermediate in hydrocarbon solution at ca. 80 K, and on the basis of this concluded that the reaction proceeds via the stepwise mechanism (eq 7).[31] Levin et al. came to a similar conclusion, based on the observation that quenching of $SiMe_2$ by alcohols and ethers is diffusion-controlled in all cases; they were unable to provide discrete transient spectroscopic evidence for the intermediacy of the putative Lewis acid−base complexes in the reactions of $SiMe_2$ with alcohols, but verified that the complexes of $SiMe_2$ with ethers are readily detectable in dilute fluid solution, as long-lived transients with absorption maxima at 305−310 nm.[7] Interestingly, they indicated (in a footnote) that a short-lived species absorbing in the 300−320 nm range was observed in experiments with $SiMe_2$ in the presence of low concentrations of ethanol, which "disappeared on adding more ethanol".[7]



$$\begin{array}{c} :SiR_2 \\ + \\ R'OH \end{array} \rightleftharpoons \left[\begin{array}{c} H\diagdown O \diagup R' \\ | \\ :SiR_2 \end{array} \right] \longrightarrow \begin{array}{c} OR' \\ | \\ H\text{-}SiR_2 \end{array} \qquad (7)$$

Inspection of transient spectra recorded for **9** in the presence of 0.15 mM MeOH suggests that a similar phenomenon may occur with $SiPh_2$; the data are shown in Figure 3b. Of particular note is the weak signal observed at 350 nm, in the spectral range expected for $SiPh_2$–O-donor complexes (see inset, Figure 3b). The signal grows in with a rise time of $\tau \approx 40$ ns and then decays over a time scale similar to that of the silylene absorption, monitored at 530 nm. As Levin et al. indicated in the description of their experiments with $SiMe_2$ in the presence of ethanol,[7] the signal disappears at higher alcohol concentrations. The possibility that the signal is due to the silylene dimerization product (Si_2Ph_4) can be ruled out, because the decay coefficient of the signal at 0.15 mM MeOH ($k_{decay} \approx 2.4 \times 10^6$ s^{-1}) would demand that its reaction with the alcohol proceeds with a rate constant of $k_Q \approx 1.5 \times 10^{10}$ M^{-1} s^{-1}, at least 2 orders of magnitude higher than would be expected on the basis of the values that have been reported for the reactions of other phenylated disilenes with alcohols.[32] Thus, the spectral and kinetic characteristics of the species seem most consistent with a reactive $SiPh_2$–MeOH complex. One possible explanation for why the signal vanishes at higher alcohol concentrations is that the decay rate of the species depends on alcohol concentration, as would occur if a catalytic pathway involving a second molecule of alcohol contributes to the decay. Certainly, the mixed order dependence of the rate law for reaction of $SiMes_2$ with MeOH is consistent with this possibility. It is important to note, however, that our results for $SiPh_2$ (and $SiMe_2$) are consistent with a mechanism in which the rate-determining step for silylene decay is strictly first order in MeOH; thus, if catalysis contributes to the decay of the first-formed intermediate, it does so after the rate-determining step for consumption

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[29] *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1995; pp 6−241.

[30] Steele, K. P.; Weber, W. P. *Inorg. Chem.* **1981**, *20*, 1302.

[31] Gillette, G. R.; Noren, G. H.; West, R. *Organometallics* **1989**, *8*, 487.

[32] Sekiguchi, A.; Maruki, I.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 11460.

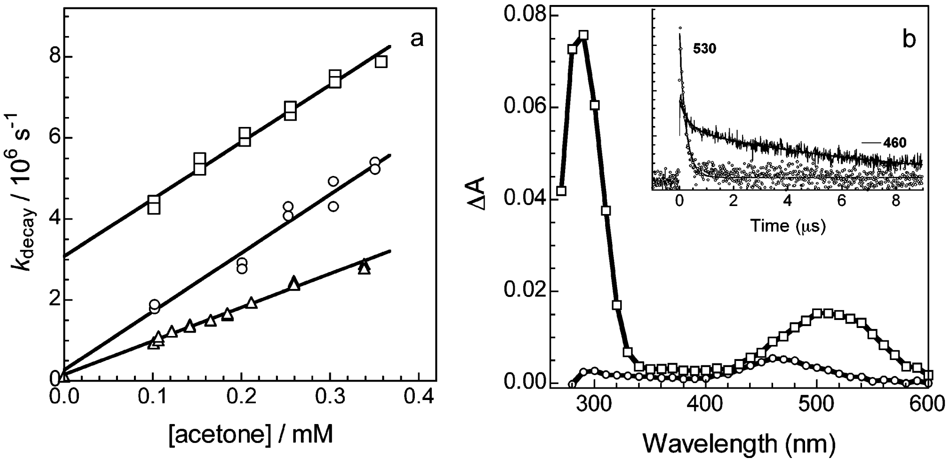
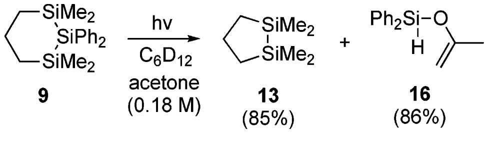


Figure 4. (a) Plots of the pseudo-first-order decay rate constants (k_{decay}) for $SiMe_2$ (□), $SiPh_2$ (○), and $SiMes_2$ (△) versus [acetone] in hexane solution at 25 °C; the solid lines are the linear least-squares fits of the data to eq 6. (b) Transient absorption spectra recorded 32−96 ns (−□−) and 0.88−0.99 μs (−○−) after the laser pulse, by laser flash photolysis of a 0.09 mM solution of **9** in deoxygenated, anhydrous hexane containing 0.35 mM acetone; the inset shows transient growth/decay profiles recorded at 530 and 460 nm.

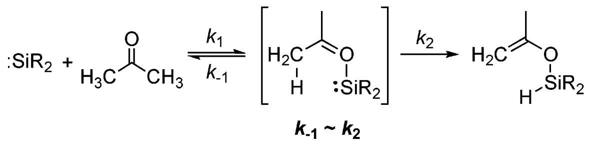
of the silylene, which we identify as complex formation. This is not the case with $SiMes_2$, the results for which cannot be explained by a mechanism in which complexation is the rate-determining step for silylene decay (at very low alcohol concentrations) unless more than one type of complex is formed. Clearly, more detailed studies of the reactions of alcohols with diarylsilylenes will be necessary to fully understand the behavior observed.

We also measured rate constants for the reactions of the three silylenes with acetone, which is known in all three cases to afford the corresponding silyl enol ether derivatives.[10,20,33] Conlin and co-workers reported the reactions of $SiMes_2$ with ketones to be unusually rapid and reported a rate constant of $k_Q = 2.5 \times 10^{10}$ M^{-1} s^{-1} for the reaction with acetone in cyclohexane.[10] However, the value was evidently based on a curved plot of k_{decay} versus [acetone],[10] and because of the unusual mechanistic complexities that this implies we felt the experiment to be worth repeating. As expected, lifetime reductions were observed for all three silylenes in the presence of submillimolar amounts of acetone, and the formation of the corresponding disilenes was also efficiently quenched in all three cases. Furthermore, plots of k_{decay} versus [acetone] were linear in each case (see Figure 4), affording values of $k_{acetone} = (1.4 \pm 0.1) \times 10^{10}$, $(1.4 \pm 0.2) \times 10^{10}$, and $(8.3 \pm 0.4) \times 10^9$ M^{-1} s^{-1} for the reaction of the ketone with $SiMe_2$, $SiPh_2$, and $SiMes_2$, respectively. The value of $k_{acetone}$ determined for $SiMes_2$ is based on data collected over a 15-fold broader range in acetone concentration than that used in the earlier study[10] and can thus be considered the more reliable value. A steady-state photolysis experiment (see eq 8) verified that silyl enol ether **16** is the exclusive product of the reaction of acetone with $SiPh_2$.[20]



(8)

The reactions of silylenes with ketones has also been proposed to occur via a stepwise mechanism involving initial complexation (see eq 9), and indeed spectroscopic evidence for this has been reported for the reaction of a non-enolizable ketone with $SiMes_2$ at cryogenic temperatures.[34] We are unable to detect any signs of intermediate complexes in the reactions of these three silylenes with acetone in fluid solution; for example, Figure 4b shows transient spectra recorded for **9** in the presence of 0.35 mM acetone, where the silylene lifetime is shortened to 230 ns and disilene formation is completely suppressed due to rapid scavenging of the silylene by the ketone. The spectrum recorded at the end of the silylene decay shows only the long-lived residual absorber, which we assigned above to silene **15**. We thus conclude that if intermediate complexes are involved in the reactions of these silylenes with acetone, they must be true steady-state intermediates, rearranging to the final products with rate constants large enough that they do not build up in high enough concentrations to enable detection. Comparison of the rate constants for reaction of acetone with $SiPh_2$ and $SiMes_2$ suggests that this reaction is only marginally sensitive to steric effects in the silylene, in stark contrast to the O−H insertion reaction with alcohols. This is, however, consistent with the expected structure of the transition state for the H-transfer step, in which both of the carbonyl−methyl groups are situated well away from the silylene substituents as the hydrogen is transferred from carbon to silicon.



(9)

It is interesting to note that the lifetime of the residual 460 nm absorption is significantly shorter in the presence of 0.35 mM acetone than in the presence of Et_3SiH (vide supra), suggesting that the species reacts with the ketone. An estimate of $k_Q \approx 4 \times 10^8$ M^{-1} s^{-1} can be derived from the lifetime of the signal ($\tau \approx 8$ μs) under these conditions. The value is similar to those determined for the reaction of aryldisilane-derived silenes in hydrocarbon solvents[24] and is thus consistent with the tentative assignment of silene **15** to this species. The much-reduced intensity of the signal at this wavelength as compared to that observed in pure hexane indicates that formation of Si_2Ph_4 is (at least) largely quenched in the presence of 0.35 mM acetone.

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[33] Ando, W.; Ikeno, M. *Chem. Lett.* **1978**, *7*, 609.

[34] Ando, W.; Hagiwara, K.; Sekiguchi, A. *Organometallics* **1987**, *6*, 2270.

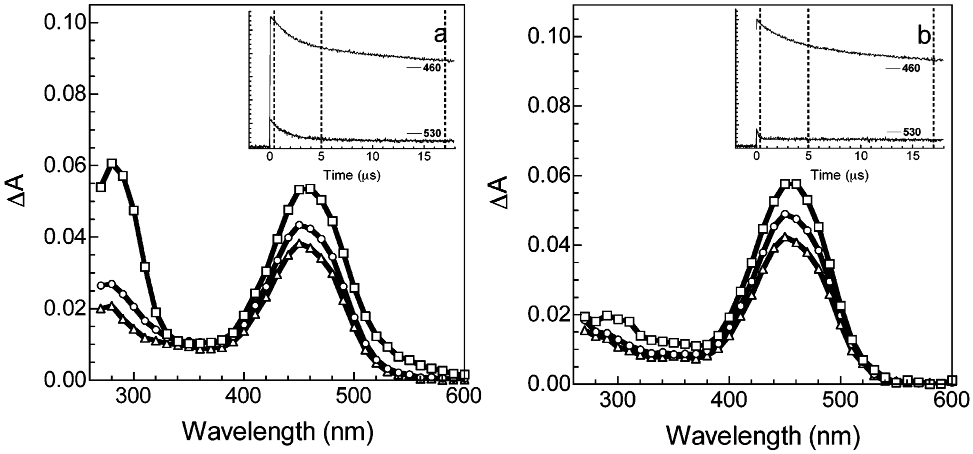

Figure 5. Transient absorption spectra recorded 0.48−0.54 μs (−□−), 5.02−5.25 μs (−○−), and 17.12−17.34 μs (−△−) after the laser pulse, by laser flash photolysis of (a) a 0.10 mM solution of acyclic trisilane **4** in deoxygenated, anhydrous hexane, and (b) the same solution with 3 mM Et_3SiH added. The insets show transient decay profiles recorded at 530 and 460 nm.

With the spectroscopic and kinetic behavior of $SiPh_2$ (vide supra) and the full details of the photochemistry of the acyclic trisilane **4**[19] both now fully established, we thought it would be of interest to re-examine the transient spectroscopic behavior of the latter compound under conditions most appropriate for direct detection of the transient silylene. As expected, laser flash photolysis of a ca. 10^{-4} M solution of **4** in deoxygenated anhydrous hexane afforded results that are in good general agreement with those reported by Gaspar and co-workers in their initial study of this compound in cyclohexane solution;[18] a strongly absorbing transient species exhibiting $\lambda_{max} \approx 460$ nm was produced within the laser pulse and decayed with mixed order kinetics over ca. 300 μs. However, close inspection of the transient spectrum on the microsecond time scale reveals that it changes quite significantly in the first few microseconds after laser excitation, as the spectra of Figure 5a show. Immediately after the pulse, there is, in addition to the 460 nm absorption band, an intense absorption centered at ca. 280 nm, which decays completely within the first ~5 μs after excitation. The 460 nm band also contains some slight distortion on the long wavelength edge, caused by a weak absorption that decays with the same (first order) decay rate constant as the absorption at 280 nm ($\tau \approx 1.8$ μs). These features are, of course, due to $SiPh_2$. Indeed, addition of 3 mM Et_3SiH cleans the transient spectra up considerably (see Figure 5b), reducing the lifetime of the short-lived species to ca. 225 ns without affecting the lifetime of the 460 nm absorption. In fact, rate constants for quenching of $SiPh_2$ by Et_3SiH (and other scavengers) can be determined in straightforward fashion using the signal at 530 nm to monitor the decay of the silylene, and approximating the long- lived underlying tail absorption from the 460 nm band as a non-decaying residual absorption. A value of $k_{Et_3SiH} = (3.5 \pm 0.2) \times 10^9$ M^{-1} s^{-1} was obtained from a (linear) plot of k_{decay} versus [Et_3SiH]; a rate constant of $k_{MeOH} = (1.32 \pm 0.04) \times 10^{10}$ M^{-1} s^{-1} was similarly determined in an experiment using MeOH as the scavenger. Both rate constants are in excellent agreement with the values determined using **6**[5] and **9** as precursors to $SiPh_2$.

The 460 nm transient observed in these experiments can almost certainly be identified as silene **5**, which has been shown to be formed from **4** in ca. 40% yield on the basis of trapping experiments with methanol[19] and acetone,[20] as noted earlier. Kinetic support for the assignment is in fact already available from the early laser photolysis study of **4**, in which rate constants were reported for reaction of the species in cyclohexane with oxygen (~1 × 10^8 M^{-1} s^{-1}), ethyldimethylsilane (~1.5 × 10^3 M^{-1} s^{-1}), MeOH (~4 × 10^7 M^{-1} s^{-1}), and 2,3-dimethyl-1,3-butadiene (~8 × 10^4 M^{-1} s^{-1});[18] these values are all within the ranges expected for conjugated silenes of this general structure,[24,35] taking into account the rate-decelerating effects of trimethylsilyl-substitution at the silenic silicon atom on the reactivity of transient silenes.[36,37]

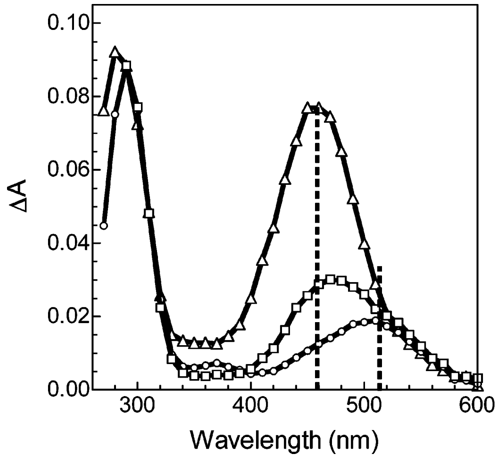

Figure 6. Transient absorption spectra, recorded 96−128 ns after the pulse, by laser flash photolysis of deoxygenated hexane solutions of trisilanes **4** (−△−), **6** (−□−), and **9** (−○−) and normalized at 290 nm, illustrating the variation in the long-wavelength transient absorption band with the relative yields of $SiPh_2$ and the corresponding silene: **5**, ~1.4:1;[19] **8**, ~5:1;[5] **9** ~20:1.

Comparison of the transient spectrum obtained from **4** immediately after the laser pulse to analogous spectra recorded with the cyclic trisilanes **6** and **9** (see Figure 6) further reinforces the assignment in a somewhat different way. The spectra shown in the figure were all recorded under the same conditions, 96−128 ns after laser excitation, and have been normalized using the $SiPh_2$ S_0−S_2 absorption at 290 nm (see Figure 1) to remove differences in the optical yield of $SiPh_2$ between the experiments with the three precursors. As has been shown through steady-state trapping studies, the three trisilanes afford successively

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[35] Leigh, W. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1994**, *116*, 10468.

[36] Leigh, W. J.; Boukherroub, R.; Kerst, C. *J. Am. Chem. Soc.* **1998**, *120*, 9504.

[37] Morkin, T. L.; Owens, T. R.; Leigh, W. J. In *The chemistry of organic silicon compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley and Sons: New York, 2001; Vol. 3, pp 949−1026.

higher yields of $SiPh_2$, and successively lower yields of the corresponding silene derivatives (**5**,[19] **8**,[5] and **15**, respectively), upon photolysis in solution. This is nicely mirrored in the relative intensities of the transient absorptions at ~515 and 460 nm in the three time-resolved spectra.

Summary and Conclusions

Photolysis of 1,1,3,3-tetramethyl-2,2-diphenyl-1,2,3-trisilacyclohexane (**9**) in hydrocarbon solvents in the presence of methanol affords products consistent with the photoextrusion of $SiPh_2$ in close to quantitative chemical yield, along with two minor products in 3−5% combined yield.

Use of the compound in laser flash photolysis experiments in anhydrous hexane solution allows the direct detection of $SiPh_2$ and its dimer, tetraphenyldisilene (Si_2Ph_4), and the determination of their UV/vis absorption spectra and kinetic behavior without resort to spectral subtraction methods. The transient spectroscopic behavior exhibited by **9** is closely analogous to those observed with the well-known $SiMe_2$ and $SiMes_2$ precursors, dodecamethylcyclohexasilane (**1**) and 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane (**2**), respectively, under similar conditions.

Absolute rate constants have been determined for the reactions of the three transient silylenes with MeOH and acetone in hexane solution at 25 °C. The results verify that $SiPh_2$ is only slightly less reactive than the dimethyl analogue toward these two substrates; all four reactions proceed at or very close to the diffusion-controlled rate under these conditions. Comparison of the rate constants for reaction of the two substrates with $SiPh_2$ and $SiMes_2$ affords the first quantitative indication of the extent to which steric bulk associated with the substituents at silicon affects silylene reactivity. The effect is moderate in the case of the O−H insertion reaction and quite small in the case of the reaction with acetone. The magnitude of the effect seems to make sense considering the expected structures of the transition states for the rate-determining steps for silylene decay in the two reactions. In the case of MeOH, this step can be identified as formation of the $SiPh_2$–MeOH Lewis acid−base complex. Our kinetic data for the reaction with acetone are consistent with either a concerted mechanism or a stepwise one involving the silylene−ketone complex as a steady-state reaction intermediate, which cannot be detected; in either case, the rate-determining step involves (1,4)-H transfer from the ketone α-carbon to silicon via a cyclic transition state in which steric interactions between the carbonyl and silylene substituents are practically nonexistent.

1,1,1,3,3,3-Hexamethyl-2,2-diphenyltrisilane (**4**), a well-known precursor for $SiPh_2$ that received considerable use in early product- and time-resolved spectroscopic studies of the reactivity and spectroscopic properties of this silylene in solution and low-temperature glasses, has been briefly reinvestigated in the present Article by laser flash photolysis methods. The silylene is in fact relatively easy to detect using this compound as a precursor, although the task is clearly aided considerably by the fact that we now know exactly what we are looking for. The dominant transient observable in laser photolysis experiments with this compound in hexane solution is assigned to the silene (**5**) formed by photochemical [1,3]-$SiMe_3$ migration into one of the aromatic rings, which others have shown is formed in a chemical yield comparable to that of $SiPh_2$ upon photolysis in solution.

The stage is now set for further kinetic and mechanistic studies of silylene reactivity in solution at a considerable level of detail. The first of these efforts is described in the following paper, which presents kinetic results for a number of well-known silylene reactions—those with other O-donors such as THF, methoxytrimethylsilane, acetic acid, and oxygen, M−H insertions with silyl-, germyl-, and stannyl-hydrides, halogen-atom abstraction from chloroalkanes, and (2 + 1)-addition reactions with alkenes, dienes, and alkynes. The study features a quantitative comparison of the reactivities of $SiMe_2$ and $SiPh_2$ under a common set of conditions, focusing on the direct detection of reaction intermediates that are involved in a number of these processes.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on a Bruker AV200 or AV600 spectrometer 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 (30m × 0.25 mm; 0.25 μm; Varian, Inc.). High-resolution 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. Melting points were recorded using a Mettler FP82 hot stage mounted on a polarizing microscope and are uncorrected. Elemental analyses were performed on a Thermo FlashEA 1112 elemental analyzer. Column chromatography was carried out using a 3 × 60 cm column using Silica Gel 60 (230−400 mesh; Silicycle).

Dichlorodiphenylsilane (Sigma-Aldrich), dimethylchlorosilane (Gelest), dodecamethylcyclohexasilane (**1**; Sigma-Aldrich), and allyl(chloro)dimethylsilane (Sigma-Aldrich) were used as received from the suppliers. 1,3-Bis(chlorodimethylsilyl)propane (**10**) was synthesized by the method of Kumada and co-workers[38] and exhibited ^1H and ^{13}C NMR spectra similar to those reported.[38,39] 1,1,1,3,3,3-Hexamethyl-2,2-diphenyltrisilane (**4**)[40] and 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane (**2**)[41] were synthesized by the published methods, and exhibited similar ^1H NMR and mass spectra to those reported. Acetone (Caledon Reagent) was used as received. Methanol (Baker Photrex) was distilled. Hexanes (EMD OmniSolv), 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 (Cambridge Isotope Laboratories) were used as received from the suppliers.

1,1,3,3-Tetramethyl-2,2-diphenyl-1,2,3-trisilacyclohexane (9). An oven-dried 25 mL two-necked round-bottom flask was fitted with a condenser, argon inlet, and magnetic stir bar, and then purged with argon. Diethyl ether (5 mL) and lithium powder (30% dispersion in mineral oil; 0.37 g, 16 mmol of Li) were added, and the flask was cooled in an ice bath. A solution of 1,3-bis(chlorodimethylsilyl)propane (**10**; 1 g, 4.4 mmol) and chlorodiphenylsilane (1.1 g, 4.3 mmol) in 5 mL of diethyl ether was then added dropwise via syringe to the stirred mixture over 30 min. Anhydrous THF (5 mL) was added, the ice bath was removed, and a further 13 mL of THF was added dropwise over 2 h, at the end of which the mixture turned brown and a black precipitate formed. The mixture was stirred at room temperature for 2 h, following the course of the reaction by TLC ($R_f = 0.24$ for **9**; silica gel/hexanes), until the precipitate turned white. (Note: Excessively long reaction

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(38) Kumada, M.; Tamao, K.; Takubo, T.; Ishikawa, M. *J. Organomet. Chem.* **1967**, *9*, 43.

(39) Muller, T.; Margraf, D.; Syha, Y. *J. Am. Chem. Soc.* **2005**, *127*, 10852.

(40) Tortorelli, V. J.; Jones, M., Jr.; Wu, S.; Li, Z. *Organometallics* **1983**, *2*, 759.

(41) Tan, R. P.; Gillette, G. R.; Yokelson, H. B.; West, R. *Inorg. Synth.* **1992**, *29*, 19.

times or the exclusion of diethyl ether resulted in the conversion of **9** to 1,1,3,3-tetramethyl-2-phenyl-1,2,3-trisilacyclohexane (**17**; $R_f = 0.41$; silica gel/hexanes), spectroscopic data for which are included in the Supporting Information.) The reaction mixture was quenched with water (100 mL) and then extracted with diethyl ether (3 × 50 mL). The combined organic fractions were dried over anhydrous sodium sulfate, filtered, and the solvent was removed on the rotary evaporator to yield a colorless oil (1 g). Column chromatography on silica gel with hexanes as eluant afforded a colorless oil (0.46 g, 31%), which crystallized on standing. The solid was recrystallized twice from methanol to yield colorless needles (mp 50.4−51.0 °C), which were identified as 1,1,3,3-tetramethyl-2,2-diphenyl-1,2,3-trisilacyclohexane (**9**) on the basis of the following data: ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.19 (m, 12H), 0.92 (m, 4H), 1.91 (m, 2H), 7.33 (m, 6H), 7.48 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ −2.25 (SiMe), 19.20 (C5), 19.44 (C4, C6), 128.07 (Ph−C3), 128.36 (Ph−C4), 135.71 (Ph−C1), 136.32 (Ph−*C*2); ^{29}Si NMR (119.2 MHz, $CDCl_3$) δ −16.82 ($SiMe_2$), −42.30 ($SiPh_2$); IR (neat), υ (cm^{-1}) = 3066 (s), 3050 (m), 3019 (m), 2950 (s), 2894 (s), 2862 (s), 1483 (m), 1462 (m), 1428 (s), 1410 (m), 1329 (m), 1246 (s), 1112 (s), 1100 (s), 1028 (m), 938 (s), 900 (s), 829 (s), 760 (m), 737 (m), 698 (s); GC/MS (EI), *m*/*z* = 340 (100; M$^+$), 325 (7), 381 (6), 240 (10), 226 (12), 205 (9), 203 (10), 198 (10), 191(10), 177 (7), 135 (24), 128 (13), 105 (12), 59(10), 43 (10); exact mass calculated for $C_{19}H_{28}Si_3$ 340.1499, found 340.1496. Anal. Calcd for $C_{19}H_{28}Si_3$: C, 66.99; H, 8.28. Found: C, 67.02; H, 8.33.

Steady-State Photolysis Experiments. In a typical procedure, a solution of **9** (0.045−0.051 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 methanol or acetone and dioxane (as internal integration standard) were added with a microliter 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-around and two RPR-2537 lamps, monitoring by 600 MHz ^{1}H NMR spectroscopy in 2 min time intervals throughout the experiment. Each mixture was also analyzed by GC/MS before and after photolysis.

Photolysis of **9** in the presence of MeOH and acetone led to the formation of two major products in each case. One was common to both and was identified as 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**13**) by comparison of its ^{1}H NMR and mass spectra to reported data:[42] ^{1}H NMR (600 MHz, C_6D_{12}) δ 0.07 (s, 12H; $SiMe_2$), 0.67 (m, 4H, $J = 6.6$ Hz; $C^{3,5}H_2$), 1.67 (quint, 2H, $J = 6.6$ Hz; C^4H_2); ^{29}Si NMR (119 MHz, C_6D_{12}) δ −14.14; 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). Methoxydiphenylsilane (**14**) was the second product formed in the MeOH-trapping experiment and was identified by comparison of its ^{1}H NMR and GC/MS characteristics to those of an authentic sample, while 2-(diphenylsiloxy)propene (**16**; ^{1}H NMR δ 1.79 (s, 3H), 4.01 (s, 1H), 4.13 (s, 1H), 5.56 (s, 1H), 7.26 (t, $J = 7.2$ Hz, 4H), 7.31 (t, $J = 7.2$ Hz, 2H), 7.57 (dd, $J = 1.2$, 7.2 Hz, 4H); GC/MS, *m*/*z* = 240 (13, M$^+$), 239 (12), 225 (20), 213 (20), 212 (100), 199 (19), 183 (32), 182 (22), 181 (61), 180 (12), 162 (26), 161 (18), 147 (11), 136 (6), 123 (35), 118 (14), 105 (30), 78 (17), 77 (27), 51 (16), 50 (13), 45 (20), 43 (28)) was the second product formed in the presence of acetone and was identified by comparison of the ^{1}H NMR and mass spectra to the reported spectra for this compound.[20] Product chemical yields were determined from the relative slopes of concentration versus time plots for the products and **9**. Concentrations were calculated from the ^{1}H NMR integrals, using the SiMe proton resonances to characterize **9** and **13** and one of the peaks for the remaining product(s) to characterize it. Details are provided in the Supporting Information.

Laser Flash Photolysis Experiments. Laser flash photolysis experiments employed the pulses from a Lambda Physik Compex 120 excimer laser filled with F_2/Kr/Ne mixtures (248 nm; 25 ns; 90−120 mJ/pulse) and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously.[8] Solutions of **9** in anhydrous hexanes were prepared at concentrations (ca. 9×10^{-5} M), such that the absorbance at the excitation wavelength (248 nm) was ca. 0.7, and were flowed (ca. 3 mL/min) through a 7 × 7 mm Suprasil flow cell from a calibrated 250 mL reservoir, fitted with a glass frit to allow bubbling of argon gas through the solution for at least 30 min prior to and then throughout the duration of each experiment, using a Masterflex 77390 peristaltic pump fitted with Teflon tubing (Cole-Parmer Instrument Co.). The sample cell and transfer lines were dried before use in a vacuum oven at 65−85 °C, while the reservoir was flame-dried and allowed to cool under an argon atmosphere. Reagents were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Transient decay and growth rate constants were calculated by nonlinear least-squares analysis of the absorbance−time profiles using the Prism 4.0 software package (GraphPad Software, Inc.) and the appropriate user-defined fitting equations, after importing the raw data from the Luzchem mLFP software. Rate constants were calculated by linear least-squares analysis of decay rate−concentration data (5−7 points). Errors in absolute second-order rate constants are quoted as twice the standard deviation obtained from the least-squares analyses.

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Supporting Information Available: ^{1}H NMR spectra and concentration versus time plots from steady-state photolysis experiments, transient absorption spectra from laser photolysis of **9** in the presence of MeOH and acetone at low concentrations, and additional details regarding the synthesis of **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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