

Article

Photochemical Generation and Characterization of Di-tertbutylsilylene (Si^tBu₂) in Solution

Ian R. Duffy[®] and William J. Leigh*[®]

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

Supporting Information

ABSTRACT: Di-tert-butylsilylene (Si^tBu₂) has been detected directly in solution and its reactivity characterized by laser flash photolysis methods. Laser photolysis of 7,7-di-tert-butyl-7-silabicyclo[4.1.0]heptane (5) affords a transient product that exhibits $\lambda_{\rm max} \approx 520$ nm and decays on the microsecond time scale, concurrent with the growth of a second, much longer-lived species exhibiting λ_{max} = 290, 430 nm. The two species are assigned to di-tert-butylsilylene (Si^tBu₂) and its disilene dimer, tetratert-butyldisilene ('Bu₂Si=Si^tBu₂, 8), respectively. Transient absorption



spectra recorded by laser photolysis of hexa-*tert*-butylcyclotrisilane (7) are consistent with the prompt formation of both $Si^{t}Bu_{2}$ and 8, the former appearing as a weak shoulder absorption on the red edge of the intense absorption band due to the disilene. Absolute rate constants were determined for the reactions of Si^tBu₂ with a variety of representative silylene substrates in hexanes at 25 °C, including methanol, triethylsilane, acetic acid, acetone, molecular oxygen, and four aliphatic alkenes (1-hexene, cyclohexene, cis-cyclooctene, and 2,3-dimethyl-2-butene). Rate and(or) equilibrium constants for Lewis acid-base complexation of the silylene with diethyl ether, tetrahydrofuran, tetrahydrothiophene, and diethyl- and triethylamine were also determined, along with the UV-vis absorption spectra of the corresponding Lewis acid-base complexes. Rate constants for the reactions of dimethylsilylene (SiMe₂) and dimesitylsilylene (SiMes₂) with cis-cyclooctene, 2,3-dimethyl-2-butene, and 1hexene are also reported, enabling a comprehensive assessment to be made of steric effects on the reactivities of simple (transient) dialkyl- and diarylsilylene derivatives in solution. The kinetic data show the reactivity of Si^BBu₂ to be intermediate between that of SiMe₂ and SiMes₂ under similar conditions, with the (2 + 1)-cycloaddition reactions with alkenes exhibiting the largest variations in rate constant as a function of substitution at Si. Absolute rate constants for the reactions of tetra-tertbutyldisilene (8) with O_2 and acetone are also reported.

INTRODUCTION

Our understanding of the chemistry of silylenes, compounds containing a divalent Si(II) center, has evolved substantially since their debut many years ago as "short-lived intermediates"¹ in various organosilicon reactions.² Contemporary studies are mainly directed at exploring the potential utility of electronically and/or kinetically stabilized isolable silylenes in catalytic applications such as transition-metal-free small molecule activation,⁴ although interest remains in advancing our understanding of basic reactions of the simpler derivatives. The majority of the known isolable silvlenes contain some degree of electronic stabilization, imparted either via intramolecular or intermolecular donor coordination or direct bonding to a heteroatom. Relatively few kinetically stable, electronically unperturbed silylenes have yet been prepared and studied. The notable exception to this generalization is the well-known compound 1, which was first reported by M. Kira and co-workers in 1999⁵ and then studied extensively by them over the next several years.⁶ The rich and diverse reactivity that has been established for this compound has direct analogy in the chemistry of simple transient dialkyl- and diarylsilylenes in solution, which were studied in detail several decades ago.^{2a-c}

Transient silvlenes have been characterized using UV-vis and infrared spectroscopy in frozen matrices,⁷ and in the gas

phase⁸ and fluid solution⁹ by time-resolved UV-vis spectrophotometry, or flash photolysis. This has allowed the direct detection and characterization of the simplest carbonsubstituted silylenes in solution, including SiMe₂,^{9a-c,10} $SiPh_2$ ^{9e-g} SiMePh,^{9h} and SiMes₂ (Mes = 2,4,6-trimethylphe-nyl),^{9d} using oligosilanes such as 2–4 as photoprecursors. Simple hydrido, alkyl, and halo-substituted systems have been studied in the gas phase by the groups of O. P. Strausz,¹¹ J. M. Jasinski,¹² and R. Walsh.^{8a,13}

$$\begin{array}{c|ccccc} \mathsf{Me}_2 & \mathsf{Ph},\mathsf{R} \\ \mathsf{Me}_2\mathsf{Si}, \overset{\mathsf{Si}}{\mathsf{Si}}, \overset{\mathsf{Si}}{\mathsf{Si}} \mathsf{Me}_2 \\ \mathsf{Me}_2\mathsf{Si}, \overset{\mathsf{Si}}{\mathsf{Si}}, \overset{\mathsf{Si}}{\mathsf{Si}} \mathsf{Me}_2 \\ \mathsf{Me}_2 & \mathsf{a}, \mathsf{R} = \mathsf{Ph} \\ \mathsf{Me}_2 & \mathsf{b}, \mathsf{R} = \mathsf{Me} \\ \mathsf{2} & \mathsf{3} \end{array} \xrightarrow{\mathsf{Me}_2 \mathsf{Me}_2 \mathsf{Si}} \mathsf{Me}_2 \\ \end{array}$$

A silylene that has received particular attention in synthetic applications is di-tert-butylsilylene (Si^tBu₂),¹⁴ whose silver-

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mediated transfer from the 1,1-di-*tert*-butylsilirane derivative 5 to a wide variety of substrate types has been demonstrated to be a versatile tool for the stereoselective formation of organosilicon compounds of importance as synthetic intermediates in the preparation of complex natural products.¹⁵ The mechanism of silylene transfer in these reactions is thought to involve silver-assisted extrusion of Si⁶Bu₂ from the silirane to form an intermediary silylsilver complex (eq 1a), preceding formal Si⁶Bu₂ transfer to the substrate.¹⁶



Free, uncoordinated Si^tBu₂ has been proposed as an intermediate in the thermolysis and photolysis of S^{17} (eq 1b) as well as various other substituted 1,1-di-*tert*-butylsilirane derivatives such as **6a** and *cis*- and *trans*-**6b**, from which thermal silylene extrusion (and its reverse) have been shown to proceed stereospecifically.¹⁸ Similarly, photolysis of hexa-*tert*-butylcyclotrisilane (7) in the presence of various trapping agents generates compounds consistent with the formation of both Si^tBu₂ and the marginally stable¹⁹ tetra-*tert*-butyldisilene (**8**) as photoproducts (eq 2),²⁰ and has been used extensively

$${}^{tBu_{2}Si}_{tBu_{2}Si} \xrightarrow{Si'Bu_{2}} \frac{hv}{hexanes} [:Si'Bu_{2}] + {}^{t}Bu_{2}Si = Si'Bu_{2} \quad (2)$$

$$7 \qquad 8$$

$${}^{tBu_{2}Si(N_{3})_{2}} \frac{2hv}{77K} \quad [:Si'Bu_{2}] + 3N_{2} \quad (3)$$

by Weidenbruch and co-workers for the preparation of a wide range of novel organosilicon compounds.²¹ An early laser flash photolysis study of 7 reported the observation of a transient product exhibiting $\lambda_{max} \approx 440$ nm and lifetime $\tau \approx 12$ ms in degassed cyclohexane,²² which was assigned to Si[']Bu₂ on the basis of its lifetime in spite of the spectroscopic similarities to 8.¹⁹ The silylene was subsequently characterized by UV–vis and IR spectroscopy in low temperature matrixes after generation by two-photon photolysis of diazidodi-*tert*-butylsilane (9; eq 3), and found to exhibit a broad visible absorption band over the ca. 430–590 nm spectral range ($\lambda_{max} \approx 480$ nm).^{7d} It has also been the subject of theoretical studies.²³

In the present paper, we report the results of laser flash photolysis of the Si^tBu₂ precursors **5** and 7 in solution under ambient conditions, featuring the direct detection of Si^tBu₂ and characterization of its UV-vis spectrum and reaction kinetics in a variety of well-documented silylene reactions. These include σ -bond insertions with triethylsilane (Et₃SiH) and methanol (MeOH), formal oxa-ene addition with acetic acid (AcOH) and acetone, (2 + 1)-cycloaddition with substituted alkenes (1-hexene, cyclohexene, *cis*-cyclooctene, and 2,3-dimethyl-2-butene (TME)), Lewis acid-base complexation with diethyl ether (Et₂O), tetrahydrofuran (THF), tetrahydrothiophene (THT), and di- and triethylamine (Et₂NH and

 Et_3N , respectively), and reaction with molecular oxygen (O₂). The complete set of reactions and equilibria that have been examined are shown in Scheme 1. The data enable direct

Scheme 1



comparisons to be made between the reactivities of $Si^{t}Bu_{2}$ and the parent dialkylsilylene, $SiMe_{2}$, toward a common set of substrates, thus providing a quantitative assessment of the effects of steric bulk on the kinetics and thermodynamics of transient dialkylsilylene reactions in solution.

RESULTS AND DISCUSSION

Hexa-*tert*-butylcyclotrisilane (7) was prepared from di-*tert*butyldiiodosilane (${}^{t}Bu_{2}SiI_{2}$)²⁴ by a procedure adapted from that of Weidenbruch and co-workers,²⁰ and obtained in \geq 97% purity as determined by ¹H NMR spectroscopy. 7,7-Di-*tert*butyl-7-silabicyclo[4.1.0]heptane (5) was a generous gift from Drs. K. Woerpel and M. Prevost.

Laser photolysis of rapidly flowed, deoxygenated solutions of 5 (ca. 0.004 M) in anhydrous hexanes were carried out using a (pulsed) KrF excimer laser for excitation (248 nm; ca. 25 ns, 40-100 mJ per pulse). Time-resolved UV-vis absorption spectra sampled over selected time intervals after the excitation pulse are shown in Figure 1a. The initially produced (0.16-0.19 μ s) spectrum contains a broad absorption band with an apparent maximum centered at $\lambda_{max} \approx 490$ nm, which decays over ca. 10 μ s with second order kinetics and rate coefficient $2k_{\rm dim}/\varepsilon_{530 \rm nm} = (1.2 \pm 0.4) \times 10^8 \rm cm \ s^{-1} \ (eq \ 4).^{25}$ The spectrum is in good qualitative agreement with that reported previously for Si^tBu₂ in 3-methylpentane at 77 K ($\lambda_{max} \approx 480$ nm).^{7d} Accompanying the silylene decay is the growth of a secondary product, which exhibits $\lambda_{max} = 290, 430$ nm and is stable over a time scale in excess of 1 ms. The spectrum and apparent stability of this species is similarly in very good agreement with that reported for disilene 8 in hydrocarbon solvents (λ_{max} = 305 nm (ε = 5200 M⁻¹ cm⁻¹) and 433 nm (ε = 2800 M^{-1} cm⁻¹)), produced by low-temperature photolysis of compound 10.¹⁹ The laser photolysis results for 5 in hexanes solution are thus consistent with the reaction scheme of eq 5.

$$\Delta A_t = \Delta A_0 / (1 + (2k_{\rm dim}\Delta A_0/\varepsilon l)t) + \Delta A_{\rm res}$$
(4)

In contrast, laser photolysis experiments with deoxygenated hexanes solutions of cyclotrisilane 7 (ca. 4×10^{-5} M) showed evidence of two promptly formed transient photoproducts, as illustrated in the time-resolved spectra of Figure 1b. The more



Figure 1. Transient absorption spectra recorded by laser flash photolysis (a) of 7,7-di-*tert*-butyl-7-silabicyclo[4.1.0]heptane (5; 0.004 M) in hexanes, 0.16–0.19 μ s (- \bullet -) and 17.7–17.8 μ s (- \Box -) after the laser pulse; and (b) of hexa-*tert*-butylcyclotrisilane (7; ca. 4 × 10⁻⁵ M) in hexanes, recorded 0.2–0.5 μ s (- \bullet -) and 7.2–7.7 μ s (- \Box -) after the laser pulse. The solid dark lines in the two figures are the difference spectra (ΔA_{diff}) resulting from subtraction of appropriately scaled spectra of disilene 8 from the ~0.2 μ s spectra, in an attempt to isolate the more rapidly decaying component of the postpulse spectrum in each case (see text). The difference spectrum in (a) is shown on the same scale as the other spectra, while that in (b) is plotted on the scale defined by the right-hand axis. The insets show absorbance vs time profiles recorded at 530, 430, and 290 nm.



prominent transient exhibited strong, long-lived UV-vis absorptions centered at $\lambda_{\rm max} \approx 290{-}295$ and 435 nm which exhibited lifetimes on the order of 0.1 ms and a slight growth over the first ca. 5–10 μ s after the laser pulse, consistent with it being produced both directly (i.e., as a product of photolysis of 7) and in the first few microseconds after the pulse via a secondary (ground state) process. The second photoproduct is evident as a relatively weak transient absorption in the 480-540 nm region of the spectrum, superimposed on the longwavelength tail of the prominent ($\lambda_{max} \approx 435$ nm) transient absorption. It is also formed within the laser pulse and decays over ca. 20 μ s with second-order kinetics and decay rate coefficient $2k/\epsilon_{530 \text{ nm}} = (1.9 \pm 0.5) \times 10^8 \text{ cm s}^{-1,26}$ in reasonable agreement with that of the promptly formed transient from laser photolysis of 5. It can thus be assigned to Si^tBu₂, and the more prominent, long-lived transient that is formed as both a primary and secondary photoproduct to disilene 8 (eq 6).

The UV-vis spectrum of Si^tBu₂ can be extracted from the transient spectral data for 7 (Figure 1b), by subtracting a spectrum sampled 42.1–43.0 μ s after the pulse from the 0.2–0.5 μ s spectrum. The 42.1–43.0 μ s time-window corresponds approximately to the point in the 430 nm absorbance-time profile at which the absorbance has decayed back to its value at the end of the laser pulse, prior to the secondary growth due to Si^tBu₂ dimerization (see inset, Figure 1b); thus, the procedure should (in principle) quantitatively isolate the spectrum of the

silvlene in the absence of contributions from its dimerization product. The resulting difference spectrum is included in Figure 1b, magnified relative to the other spectra in the figure by a factor of 5 for clarity. Indeed, the roughly symmetrical form of the long-wavelength absorption band, which is centered at $\lambda_{\rm max} \approx 520$ nm, suggests the procedure has been more or less successful. Essentially the same difference spectrum is obtained from the data for 5 (see Figure 1a), by subtraction of an appropriately scaled version of the 17.7-17.8 μ s (disilene) spectrum from the prompt spectrum in order to remove the contribution from a small amount of 8 that is formed via dimerization of Si^tBu₂ within the duration of the laser pulse.²⁷ The relative $\Delta A_{520 \text{ nm}}$ values obtained from laser photolysis of the two precursors in approximately optically matched solutions indicate that the quantum yield of Si^tBu₂ extrusion from silirane 5 is 2-3 times higher than from 7.

The spectrum is red-shifted compared to those of both SiMe₂ ($\lambda_{max} = 470 \text{ nm}$),^{9a,c,f} and the stable dialkylsilylene 1 $(\lambda_{\text{max}} = 440 \text{ nm})^5$ under similar conditions; the red shift relative to the spectrum of SiMe₂ has been rationalized as due mainly to a widening of the C-Si-C bond angle by the sterically bulky substituents,^{7d} which destabilizes the filled norbital at silicon and decreases the energy of the $n \rightarrow p$ transition.²⁸ Indeed, DFT calculations predict C-Si-C bond angles of 108.2°, 97.7°, and 93.4° in Si^tBu₂, SiMe₂, and 1, respectively (see Supporting Information); the calculated structure of 1 is in excellent agreement with the reported Xray structure of the compound.⁵ The positions of the lowest energy UV-vis absorption bands in the experimental spectra of the three species are also in reasonable agreement with theoretical predictions, made on the basis of TDB3LYP-D3/6-31+G(d,p) calculations (see Table S1, Supporting Information; the table also compares the calculated and experimental spectra of 5, 7, 8, and SiMes₂, which serves to benchmark the TDDFT method that was employed).

An estimate of the molar extinction coefficient at the Si⁴Bu₂ absorption maximum can be made from the reported value of $\varepsilon_{\rm max}$ for 8¹⁹ and the ratio of the approximate initial absorbances due to the silylene ($\Delta A_0^{520 \text{ nm}}$) and 8 ($\Delta A_0^{430 \text{ nm}}$) at their respective absorption maxima in the difference and 0.2–0.5 μ s spectra of Figure 1b, respectively, assuming that the initial concentrations of Si^fBu₂ and 8 produced upon laser excitation



Figure 2. Plots of k_{decay} vs [Q] for reaction of Si^tBu₂ with (a) cyclohexene, (b) Et₃SiH, and (c) acetone, from laser flash photolysis of solutions of **5** (ca. 0.004 M; O) and 7 (ca. 4×10^{-5} M; \Box) in hexanes solution at 25 °C; the solid lines are from linear regression of the data according to eq 8. Silylene absorbance–time profiles were recorded at a monitoring wavelength of 530 nm in all cases and were analyzed according to eq 7.

of 7 are equal. From the approximate ΔA_0 values of $\Delta A_0^{520 \text{ nm}} = 0.0015 \pm 0.0002$ and $\Delta A_0^{430 \text{ nm}} = 0.016 \pm 0.001$ (see Figure 1b), we thus obtain a value of $\varepsilon_{\text{max}} = 260 \pm 50 \text{ M}^{-1} \text{ cm}^{-1}$ for the long wavelength absorption band in the UV–vis spectrum of Si^tBu₂. The value is in the expected range for a silylene $n \rightarrow 3p$ absorption, as exemplified by SiMe₂ ($\varepsilon_{470 \text{ nm}} = 3400 \text{ M}^{-1} \text{ cm}^{-1}$).⁹ c and the stable dialkylsilylene 1 ($\varepsilon_{440 \text{ nm}} = 500 \text{ M}^{-1} \text{ cm}^{-1}$).⁵ Combined with the second order decay rate coefficient measured with 5 (vide supra) the estimate affords a value of $2k_{\text{dim}} = (3 \pm 1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for the bimolecular rate constant for dimerization of Si^tBu₂ under these conditions. The value is within experimental error of twice the diffusional rate constant in hexanes at 25 °C ($k_{\text{diff}} = 2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).²⁹

The chemical yields of disilene formed via $\mathrm{Si}^{\mathrm{t}}\mathrm{Bu}_2$ dimerization in the laser photolysis experiments with 5 and 7 are only on the order of 20–30%, as estimated by comparison of the final transient absorbance values at 430 nm to the maximum values expected based on the initial ΔA_0 values at 530 nm (from 5; Figure 1a) or 430 nm (from 7; Figure 1b).³⁰ The inefficiency is similar to what we have typically observed previously with other transient silylenes in solution,^{9f-h} and is ascribable to competing reaction of the silylene with adventitious impurities in the solvent, most likely water. Kinetic simulations verified that the presence of only ca. 30 μ M ($\approx 10^{-4}$ wt %) water is sufficient to result in a disilene yield of ca. 25%, assuming an initial silylene concentration of 10 μ M and rate constants of 1 × 10¹⁰ and 6 × 10⁹ M⁻¹ s⁻¹ for dimerization of Si'Bu₂ and its reaction with water, respectively.

Triethylsilane (Et₃SiH), cyclohexene, and acetone have all been shown to be efficient trapping agents for Si^tBu₂, ^{7d,14c,17,18,20,31} as well as other transient silylenes, ^{2,9b,c,g,h} so we used these substrates to compare the reactivities of the promptly formed transients from 5 and 7 to gain further support for a common assignment to Si^tBu₂. As expected, addition of each of these compounds in millimolar concentrations to solutions of 5 and 7 resulted in shortening of the lifetime of the 520 nm transient and a change in its decay kinetics from second to pseudo-first order, indicative of reaction of the species with the added substrate. With each precursor, absorbance-time profiles were recorded at a series of substrate concentrations and analyzed according to eq 7, where k_{decav} is the pseudo-first-order decay rate coefficient at the given substrate ("Q") concentration. Plots of k_{decav} vs [Q] according to eq 8 were linear, the slopes corresponding to the effective second-order rate constants for reaction of the silvlene

with the substrate, $k_{\rm Q}$. Figure 2 shows the plots obtained in the experiments with cyclohexene, Et₃SiH, and acetone as silylene substrates, together with the values of the rate constants obtained with each precursor. Quenching of the silylene absorptions from **5** and 7 by 1-hexene was also examined, affording values of $k_{\rm hex} = (1.4 \pm 0.3) \times 10^9 \,\mathrm{M^{-1} \, s^{-1}}$ and $(1.1 \pm 0.1) \times 10^9 \,\mathrm{M^{-1} \, s^{-1}}$, respectively (see Figure S9).

$$\Delta A_t = \Delta A_{\rm res} + (\Delta A_0 - \Delta A_{\rm res}) \exp(-k_{\rm decay} t)$$
⁽⁷⁾

$$k_{\text{decay}} = k_0 + k_Q[Q] \tag{8}$$

As expected, the changes in the silylene absorptions were accompanied by systematic reductions in the growth of the absorptions due to 8, consistent with silylene dimerization being quenched irreversibly in the presence of the substrate. With both precursors, the formation of 8 via $Si^{f}Bu_{2}$ dimerization was eliminated completely at high substrate concentrations, in the case of 7 leaving behind the (dominant) portion that is formed within the laser pulse.

The results of the parallel quenching experiments with the two precursors clearly support a common assignment of the 520 nm transient to Si^tBu₂, and of the 430 nm species to ^tBu₂Si=Si^tBu₂ (8). However, for all but the reaction with acetone (for which k_0 is very close to the diffusion limit), there appears to be a systematic dependence of the apparent rate constant on the precursor. The values of k_0 obtained with 5 as precursor are consistently 30-60% higher than those obtained using 7, leading to an average of $k_5/k_7 = 1.35 \pm 0.21$ for the ratio of the rate constants from the two precursors, where the error is quoted as the standard deviation from the mean of the four pairs of determinations. It is unclear what causes this discrepancy. The most likely explanation is that the rate constants measured using 5 as precursor are artificially high due to the gradual buildup of minor amounts of reactive decomposition products as the experiments progress, resulting from reaction of 5 with traces of water or oxygen in the substrate solution as it is introduced in increasing amounts throughout the experiment. An alternate possibility is that Si^tBu₂ forms a (nonreactive) complex with disilene 8 which reduces its overall reactivity in experiments carried out using 7 as precursor, though we would not have expected such an interaction to be favorable enough to result in an effect of this magnitude. In any event, it seems most reasonable to attach uncertainty limits of ca. 25% to the measured rate constants, in recognition of these uncertainties in the data.



Figure 3. Complexation of Si⁴Bu₂ with Et₂O in hexanes at 25 °C: (a) plot of $(\Delta A_0)_0/(\Delta A_0)_Q$ vs [Q] from laser photolysis of 7 in hexanes containing Et₂O (see eq 9); (b) transient UV–vis spectra recorded 0.26–0.29 μ s (\bigcirc) and 8.6–8.7 μ s (\square) after the laser pulse, by laser photolysis of 7 in a 0.2 M Et₂O/hexanes solution; and (c) transient UV–vis spectra recorded 0.35–0.43 μ s (\bigcirc) and 8.6–8.7 μ s (\square) after the laser pulse, by laser photolysis of 5 in a 0.4 M Et₂O/hexanes solution. Silylene absorbance–time profiles were recorded at a monitoring wavelength of 530 nm in all cases.

We also examined the reactivity of Si^tBu₂ toward a variety of other silylene substrates with known reactivities toward SiMe₂ in solution (see Scheme 1), in the interest of evaluating quantitatively the effects of the bulky tert-butyl group on dialkylsilylene reactivity. Compound 7 ($\varepsilon_{248 \text{ nm}} \approx 1.6 \times 10^4$ M^{-1} cm⁻¹) was used as the silvlene precursor for most of these experiments, as it is much more conveniently handled than the air- and moisture-sensitive silirane (5; $\varepsilon_{248 \text{ nm}} \approx 1.7 \times 10^2 \text{ M}^{-1}$ cm⁻¹) and has a ca. 100 fold higher molar absorptivity at the excitation wavelength (248 nm), which means that much smaller amounts of material are required for an experiment. The trade-offs are that its photolysis is less efficient than that of 5, which results in weaker silylene absorptions, and the strong, long-lived spectrum of the coproduct (disilene 8), coupled with its own weak absorptions in the 360-370 nm range, complicate the spectra of the transient complexes that the silvlene is expected to form with the various Lewis bases.

Addition of Et₂O led to a decrease in the apparent maximum signal intensity at 530 nm but had no effect on the decay rate coefficient, behavior which is consistent with rapid and reversible reaction between the transient and the substrate, characterized by an equilibrium constant (K_{eq}) smaller than ca. 10^3 M^{-1} ;³² the behavior is similar to that observed for SiMe₂ in the presence of this substrate.^{32a} Plots of $(\Delta A_0)_0/(\Delta A_0)_Q$ vs [Q] according to eq 9, where $(\Delta A_0)_0$ and $(\Delta A_0)_Q$ are the apparent initial absorbances due to the silylene in the absence and presence of the substrate, respectively, are linear, the slope affording the equilibrium constant for Lewis acid-base complexation of the silylene with Et₂O, $K_{eq} = (15 \pm 2) \text{ M}^{-1}$ (Figure 3a).

$$(\Delta A_0)_0 / (\Delta A_0)_Q = 1 + K_{eq}[Q]$$
⁽⁹⁾

The absorption spectrum of the complex was obtained by laser photolysis of a hexanes solution of 7 containing ca. 0.2 M Et₂O, and is shown in Figure 3b. The spectrum shows absorptions due to a short-lived transient exhibiting $\lambda_{max} \approx 300$ nm and a lifetime of ca. 1.5 μ s, whose absorptions are superimposed on the short wavelength absorption band due to disilene 8. A much cleaner spectrum of the species was obtained from a solution of 5 in 0.4 M Et₂O/hexanes (Figure 3c). The spectrum strongly resembles those reported for the SiMe₂-Et₂O and SiMe₂-THF complexes under similar conditions, ^{9b,c,32a} and can be assigned with confidence to the Si^FBu₂-OEt₂ Lewis acid—base complex. The equilibrium constant for complexation with Et₂O is ca. 80 times smaller than the corresponding value for SiMe₂ under similar conditions,^{32a} corresponding to a difference in binding energy of $\Delta(\Delta G^{\circ}) \approx 2.6$ kcal mol⁻¹. This quantifies the steric effect associated with *tert*-butyl- for methyl-substitution at silicon on the thermodynamics of Lewis acid—base complexation with the O-donor. The result can be compared to the difference in the binding free energies of the SiMes₂- and SiPh₂-Et₂O complexes of $\Delta(\Delta G^{\circ}) \approx 5.3$ kcal mol⁻¹ in hexanes at 25 °C.^{32a} The equilibrium constants for complexation of Et₂O with the four transient silylenes span a range of close to 4 orders of magnitude in hexanes at 25 °C, decreasing in the order SiPh₂ ≈ 5.6 SiMe₂ ≈ 470 Si^fBu₂ ≈ 7900 SiMes₂.

Addition of submillimolar concentrations of THF to hexanes solutions of 5 caused the silvlene to decay with two-stage kinetics, consisting of a fast initial decay to a residual absorption that decays over an extended time scale, in a manner consistent with a fast reversible reaction characterized by an equilibrium constant in the range of $10^3 < K_{\rm eq} < 2.5 \times 10^4 \ {\rm M}^{-1.32a}$ The fast initial decay is associated with the approach to equilibrium of the silylene-substrate reaction, while the residual absorption $(\Delta A_{\rm res})$ is associated with free silylene remaining after equilibrium is attained and undergoing relatively slow decay due to dimerization. Analysis of the k_{decay} vs [THF] data according to eq 8 afforded the forward rate constant for complexation of Si^tBu₂ with THF, $k_{\text{THF}} = (1.8 \pm$ $(0.5) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, while a value of $K_{eq} = (2.8 \pm 0.6) \times 10^3$ M⁻¹ was obtained for the equilibrium constant from analysis of the $\Delta A_{\rm res}$ data according to eq 10 (see Figure 4). Laser photolysis of a solution of 7 in hexanes containing 5.0 mM THF afforded a similar transient spectrum as was obtained in the presence of Et_2O (see Figure S1), and can be assigned to the Si^tBu₂-THF complex ($\lambda_{max} = 310 \text{ nm}$; $\tau \approx 7.1 \mu s$).

$$(\Delta A_0)_0 / (\Delta A_{\rm res})_Q = 1 + K_{\rm eq}[Q]$$
⁽¹⁰⁾

The remaining nine substrates of Scheme 1 were all found to react efficiently with Si^tBu₂, causing the silylene to decay with first-order kinetics and with a rate coefficient that increased linearly with concentration according to eq 8. The data are shown in Figures S2–S10 (Supporting Information), while the corresponding rate and equilibrium constants for these and the reactions discussed above are collected in Table 1. The table also lists the reported rate and/or equilibrium constants for the corresponding reactions with SiMe₂ and SiMe₂, for compar-



Figure 4. Plots of k_{decay} (\Box) and $(\Delta A_0)_0/(\Delta A_{\text{res}})_Q$ (O) vs [THF], from laser photolysis of **5** in hexanes containing THF. The solid lines are the least-squares fits of the data to eq 8 and 10, respectively.

Table 1. Absolute Rate Constants (k_Q) and Equilibrium Constants (K_{eq}) for the Reactions of Si^tBu₂, SiMe₂, and SiMes₂ with Various Silylene Substrates in Hydrocarbon Solution at 20–25 °C^{*a*}

	Si ^t Bu ₂ ^b	SiMe ₂	SiMes ₂
	$k_{\rm Q} (10^9 { m M}^{-1} { m s}^{-1})$	$k_{\rm Q} (10^9{ m M}^{-1}{ m s}^{-1})$	$k_{\rm Q} (10^9 {\rm M}^{-1} {\rm s}^{-1})$
substrate	$[K_{\rm eq}/{ m M}^{-1}]$	$[K_{\rm eq}/{ m M}^{-1}]$	$[K_{\rm eq}/{ m M}^{-1}]$
Et_2O	$[15 \pm 2]$	$[1260 \pm 50]^d$	$[0.9 \pm 0.1]^d$
THF	18 ± 5^{c}	17.3 ± 1.5^{e}	$[2.4 \pm 0.4]^d$
	$[2800 \pm 600]^{c}$		
THT	13 ± 2	21 ± 2^{f}	7 ± 2^d
			$[1500 \pm 100]^d$
Et ₂ NH	8 ± 2	16 ± 3^{g}	3.5 ± 0.5^{g}
			$[6300 \pm 600]^{g}$
Et ₃ N	0.54 ± 0.08	9.8 ± 0.8^{g}	$[130 \pm 60]^d$
Et ₃ SiH	0.8 ± 0.1	3.6 ± 0.3^{e}	0.079 ± 0.004^{j}
	$(1.3 \pm 0.1)^{c}$		
MeOH	7 ± 2	21 ± 3^{h}	1.01 ± 0.09^{h}
AcOH	4.4 ± 0.5	16 ± 1^{e}	-
acetone	18 ± 1	20 ± 2^{i}	8.3 ± 0.4^{e}
	$(20 \pm 2)^{c}$		
O ₂	0.20 ± 0.05	0.47 ± 0.04^{e}	0.032 ± 0.004^{j}
cyclohexene	0.18 ± 0.01	7.8 ± 1.0^{e}	0.0028 ± 0.0003^{j}
	$(0.24 \pm 0.02)^{c}$		
cis-cyclooctene	0.99 ± 0.05	8.9 ± 0.4	0.031 ± 0.002
1-hexene	1.1 ± 0.1	7 ± 1^k	0.0102 ± 0.0003
	$(1.4 \pm 0.3)^{c}$		
TME	0.031 ± 0.002	9.1 ± 0.4	0.0017 ± 0.0001
-			

^{*a*}In hexanes at 25 °C, unless otherwise noted. Errors are quoted as twice the standard error from the least-squares analyses. ^{*b*}Determined using 7 as Si^{*i*}Bu₂ precursor unless otherwise noted. ^{*c*}Determined using 5 as Si^{*i*}Bu₂ precursor. ^{*d*}Ref 32a. ^{*e*}Ref 9g. ^{*f*}Ref 33. ^{*g*}Ref 34. ^{*h*}Ref 35. ^{*i*}Ref 36 ^{*j*}Cyclohexane, 23 °C; ref 9d. ^{*k*}Cyclohexane, 22 °C; ref 9b.

ison to the values obtained for $Si^{t}Bu_{2}$; the rate constants for reaction of $SiMe_{2}$ and $SiMes_{2}$ with *cis*-cyclooctene, $SiMe_{2}$ with TME, and $SiMes_{2}$ with 1-hexene (see Figures S11 and S12) were determined as part of the present study and employed oligosilanes **2** and **4** as silylene precursors, respectively.

As with Et_2O and THF, laser photolysis of 5 or 7 in the presence of THT and Et_2NH led to the formation of new transient absorptions at shorter wavelengths, which could also be assigned to the corresponding Lewis acid–base complexes with Si^tBu_2 based on comparisons to the spectra of the

corresponding complexes with SiMe₂.^{9b,33,34} Transient UV-vis spectra were recorded with **5** in hexanes containing 5.0 mM of the sulfide or amine, and are shown in Figures S2b and S3b, respectively. No new transient products were observed with any of the other silylene substrates³⁷ except MeOH, which will be discussed in more detail below. Table 2 summarizes the

Table 2. UV–Vis Absorption Maxima (λ_{max}) of the Lewis Acid–Base Complexes of Si^tBu₂ and SiMe₂ with Chalcogen and Pnictogen Donors in Hydrocarbon Solvents at 20–25 °C^a

λ_{\max} (nm)		
Si ^t Bu ₂	SiMe ₂	
520	465 ^b	
310	305 ^c	
310	310 ^c	
340	325 ^d	
290	280 ^e	
	λ _{max} Si ^t Bu ₂ 520 310 310 340 290	

^{*a*}In hexanes at 25 °C, unless otherwise noted. ^{*b*}Cyclohexane or hexanes. See refs 9a-c, 10. ^{*c*}Cyclohexane, 20 °C. Ref 9b. ^{*d*}Cyclohexane, 20 °C. Ref 9c. ^{*e*}Ref 34.

UV–vis absorption maxima of each of the Lewis acid–base complexes studied in this work, along with those reported previously for the corresponding complexes with $SiMe_2$.^{9b,f,33,34} As can be seen, the spectra of the $Si^{+}Bu_2$ -donor complexes are in most cases red-shifted slightly relative to those of the corresponding SiMe₂-donor complexes, to a similar extent (in terms of transition energy) as is observed with the spectra of the free silylenes.

The absolute rate constants for complexation of $Si^{t}Bu_{2}$ with the disubstituted Lewis bases are all close to the diffusional limit and vary within a factor of 3, in the order THF > THT > Et₂NH; though small, the variation is still larger than that observed for complexation of SiMe₂ with the same series of bases. Significantly greater discrimination between the two silylenes is observed with the bulkier base, Et₃N.

The σ -bond insertion reaction of Si^tBu₂ with Et₃SiH (eq 11) has been well documented,^{17,20} as has the formal oxa-ene

$$\begin{array}{c} :Si^{i}Bu_{2} & k_{1} \\ + & & \\ H-SiEt_{3} & & \\ \end{array} \begin{array}{c} I^{i}Bu_{2}Si^{*} \\ H-SiEt_{3} \end{array} \end{array} \begin{array}{c} \begin{array}{c} k_{2} & SiEt_{3} \\ H-SiEt_{3} \end{array} \begin{array}{c} \\ H \end{array}$$

reaction with acetone, which affords silyl enol ether 11a (eq 12).^{31a} AcOH also reacts with transient silylenes via formal

oxa-ene addition, ^{9g} in the present case to afford (presumably) the corresponding acetoxysilyl hydride **11b**. The mechanisms of these reactions in the case of the parent silylene SiH_2 have been the subject of gas phase kinetics and computational studies, ^{8a,13,38} and are thought to proceed via reversible complexation of the silylene with the basic site in the substrate, with the resulting reactive complex collapsing to product *via* rapid Si- or H-migration (eq 11 and 12, respectively). In these cases the second (unimolecular) step proceeds sufficiently rapidly that the reactive complex plays the role of a steady state intermediate, and thus the reaction follows clean overall

second order kinetics.^{8,9g} This is also observed in the present cases with Si^tBu₂.

With water and alcohols, however, catalysis by a second molecule of substrate provides a lower energy pathway for H-transfer than unimolecular H-migration (see eq 13), which

applies both in solution³⁵ and the gas phase.³⁹ The resulting kinetic behavior in solution is thus more complicated, and varies depending on the stability of the intermediate complex relative to the reactants. With SiMe₂ and SiPh₂ the reaction with alcohols exhibits the characteristics of two distinct, essentially irreversible second order reactions, each first order in ROH concentration, and with the complex building up to detectable amounts at intermediate alcohol concentrations, its lifetime then decreasing as the ROH concentration is increased further. On the other hand, no intermediate complex can be detected in the case of SiMes₂, and the decay of the silylene exhibits a mixed first- and second-order dependence on ROH concentration, consistent with the complex playing the role of a steady state intermediate in the case of the more highly hindered (and much less Lewis acidic) silylene.³⁵

The reaction of Si¹Bu₂ with MeOH leads to kinetic behavior more like that of SiMe₂ and SiPh₂ than SiMes₂, in that the silylene decay rate coefficient follows a first-order dependence on MeOH concentration, affording a linear plot of k_{decay} vs [MeOH] with slope $k_{MeOH} = (7 \pm 2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Figure S5). The rate constant is intermediate between those for the initial complexation step in the reactions of MeOH with SiMe₂ and SiMes₂ ($k_{SiMe2} \approx 3k_{SitBu2} \approx 24k_{SiMes2}$),³⁵ and can thus be associated with the formation of the Si¹Bu₂-MeOH complex. Indeed, a weak, relatively short-lived transient absorption could be detected at 310 nm upon laser photolysis of solutions of 7 in hexanes containing 0.1–1.2 mM MeOH, superimposed on the longer-lived short wavelength band due to disilene 8. The species decayed with first order kinetics, and a plot of k_{decay} vs [MeOH] was linear with slope $k_{cat} = (1.5 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Figure S5). The value is roughly an order of magnitude smaller than that for MeOH-catalyzed H-transfer in the SiMe₂-MeOH complex, $k_{cat} = (1.5 \pm 0.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, presumably the result of steric destabilization of the transition state for the proton-shuttling process (eq 13).

(2 + 1)-Cycloaddition reactions of Si'Bu₂ with simple alkenes have also been well documented, ^{14c,21f,40} as they have as well for other transient silylenes in solution and in the gas phase.⁴¹ In the present work we report bimolecular rate constants for reaction of Si'Bu₂ with 1-hexene, 2,3-dimethyl-2butene (TME), cyclohexene, and *cis*-cyclooctene as representative cyclic and acyclic alkenes with varying degrees of alkyl substitution about the C=C bond. To enable broader comparisons, we have also determined rate constants for reaction of the same series of alkenes with SiMe₂ and SiMes₂ (see Table 1).

The rate constants for reaction of SiMe₂ with the four alkenes are all within a factor of ca. three of the diffusional rate constant in hexanes at 25 °C ($k_{\text{diff}} = 2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) and consequently show no discernible trend with alkene structure, a trend which is similar to that established by Walsh and coworkers for the reactions of SiMe₂ with a more extensive list of aliphatic alkenes in the gas phase.^{41e} In contrast, those for

Si^tBu₂ can be seen to decrease over a 40-fold range with increasing alkyl substitution on the alkene, in the order 1-hexene \approx *cis*-cyclooctene > cyclohexene > TME. Interestingly, there is a 5–6 fold reduction in the rate constant for reaction of Si^tBu₂ with cyclohexene compared to that for *cis*-cyclooctene, which parallels the relative thermal stabilities of the silirane products from the two cycloalkenes (5 and 12, respectively; Figure 5).^{14c} The lower thermodynamic stability



Figure 5. Calculated structures and energies of the most stable conformers of the (2 + 1)-cycloadducts of Si⁶Bu₂ with cyclohexene (5) and *cis*-cyclooctene (12), calculated relative to the isolated reactants at the B3LYP-D3/6-31+G(d,p) level of theory. The methylhydrogens have been omitted for clarity.

of the cyclohexene-adduct (5) relative to 12 is also predicted theoretically (see Figure 5 and Supporting Information), and is due presumably to unfavorable steric interactions between the endo-*tert*-butyl substituent and the flagpole H atoms in the C₆ring of the compound,^{16b} coupled with the increased ring strain that results from the enforced boat-conformation of the C_6 -ring. The ca. 30-fold lower rate constant for reaction of Si^tBu₂ with TME compared to those with *cis*-cyclooctene or 1hexene can be ascribed to steric destabilization of the transition state for the reaction, in which the initial bonding interaction is between the nonbonded p-orbital on silicon (perpendicular to the 3-atom bonding plane of the silvlene) and the π -MO of the alkene, and the silylene is oriented with its substituents approximately bisecting the alkene C=C bond.⁴² The rate constants for reaction of the series of alkenes with SiMes₂ are systematically $20-100 \times$ smaller than those for Si^tBu₂, but the spread in reactivity throughout the series is similar.

In the experiments employing 7 as the Si^tBu₂ precursor, we also monitored the effects of the various substrates on the decay kinetics of the photolysis coproduct, tetra-tertbutyldisilene (8), up to a maximum substrate concentration of at least 5 mM in most cases. Most had no discernible effect on the lifetime of 8, which under the conditions of our laser photolysis experiments was typically on the order of 0.1 ms. The exceptions were molecular oxygen and acetone, which were both found to cause discrete acceleration of the decay rate coefficient of the disilene over the concentration ranges that were studied. The most reactive substrate is oxygen, for which a value of $k_{O2} = (2.3 \pm 0.1) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ was estimated from the slope of a three-point plot of k_{decay} vs $[O_2]$, constructed from rate coefficients obtained in argon-purged, air-saturated, and oxygen-saturated hexanes at 25 °C (Figure S13). The rate constant is in line with those reported previously for tetramethyldisilene (13; $k_{02} = (2.9 \pm 0.4) \times$ $10^8 \text{ M}^{-1} \text{ s}^{-1}$ ^{9g} and tetrakis(trimethylsilyl)disilene (14, k_{O2} = $(1.1 \pm 0.1) \times 10^{6} \text{ M}^{-1} \text{ s}^{-1}$.⁴³ Considering that 8 is known to have a lifetime of several hours in the absence of air and moisture,¹⁹ the ca. 0.1 ms lifetime that is observed for 8 in our experiments with 7 in argon-purged hexanes is consistent with a residual O₂ concentration of ca. 4×10^{-4} M. As expected, the lifetime of 8 could be lengthened to >1 ms when generated by laser photolysis of 7 in freeze–pump–thaw degassed hexanes solution. Acetone was found to react with 8 with an estimated rate constant of $k_{acetone} = (4 \pm 2) \times 10^5$ M⁻¹ s⁻¹.

 $\begin{array}{ccc} Me_2Si{=}SiMe_2 & (Me_3Si)_2Si{=}Si(SiMe_3)_2 \\ 13 & 14 \end{array}$

SUMMARY AND CONCLUSIONS

Laser flash photolysis of 7,7-di-tert-butyl-7-silabicyclo[4.1.0]heptane (5) and hexa-*tert*-butylcyclotrisilane (7) affords $Si^{t}Bu_{2t}$ which has been detected for the first time in solution under ambient conditions. The silylene exhibits a broad absorption band centered at $\lambda_{\rm max} \approx 520$ nm and decays with the concurrent growth of tetra-tert-butyldisilene (8), the spectral characteristics of which (λ_{max} = 290, 430–435 nm) are in good agreement with the previously reported UV-vis spectrum.¹⁹ The silylene is the sole initial transient photoproduct from photolysis of 5, and decays with a second-order rate coefficient of $2k/\varepsilon_{530 \text{ nm}} = (1.2 \pm 0.4) \times 10^8 \text{ cm s}^{-1}$ to form 8. The formation of Si^tBu₂ as a primary photoproduct from cyclotrisilane 7 is less obvious in laser experiments with this precursor because the accompanying formation of 8, with its much stronger absorption at 430-435 nm, obscures the relatively weak silylene absorptions above 500 nm. Nevertheless, the significantly shorter lifetime of Si^tBu₂ compared to 8 allowed for its routine detection at 520-530 nm, on the red edge of the disilene absorption band; the species was again found to decay with second order kinetics and rate coefficient of $2k/\varepsilon_{530 \text{ nm}} = (1.9 \pm 0.5) \times 10^8 \text{ cm s}^{-1}$, in reasonable agreement with the value obtained using 5 as precursor. Combined with the estimate of $\varepsilon_{\rm max} \approx 250 {\rm M}^{-1} {\rm cm}^{-1}$ for the extinction coefficient at 520-530 nm, the kinetic data indicate the dimerization of Si^tBu₂ is fully diffusion-controlled.

Absolute rate or equilibrium constants have been measured for reaction of Si^tBu₂ with 14 substrates in hexanes solution at 25 °C, detailing the reactivity of the silvlene toward Lewis acid-base complexation with ethers, sulfides and amines, σ bond insertion with MeOH and Et₃SiH, oxa-ene addition with acetone and AcOH, (2 + 1)-cycloaddition reactions with a series of aliphatic alkenes, and reaction with molecular oxygen. The Lewis acid-base reactions proceed at close to the diffusion-controlled rate in most cases, to form the corresponding Lewis acid-base complexes, which have also been detected. Their UV-vis spectra are blue-shifted relative to that of the free silylene (as expected), and red-shifted by 5-15 nm relative to the spectra of the corresponding complexes formed with SiMe₂. The equilibrium constant for complexation with Et₂O is ca. 2 orders of magnitude smaller than that for complexation of the ether with SiMe₂; since the rate constants for complexation of the two silvlenes with THF are nearly equal, it can be concluded that the difference in equilibrium constants mainly reflects the difference in thermodynamic stability of the SiMe2- and Si^tBu2-Et2O complexes with respect to dissociation. The rate constants measured for the other 12 reactions are generally smaller than the corresponding ones for SiMe₂, but consistently larger than those of dimesitylsilylene (SiMes₂) under similar conditions, as one would expect from consideration of the differences in steric bulk of the three

substituents. The differences in reactivity between the three silylenes span a particularly large range for the (2 + 1)-cycloaddition reactions, again with Si^tBu₂ exhibiting reactivity intermediate between those of SiMe₂ and SiMes₂.

EXPERIMENTAL SECTION

¹H and ¹³C NMR spectra were recorded at 600.13 MHz (¹H) and 150.90 MHz $({}^{13}C\{{}^{1}H\})$, respectively, on a Bruker AV600 spectrometer in chloroform-d or benzene- d_6 solution, and were referenced to the solvent residual proton and ¹³C signals, respectively. ²⁹Si spectra were also recorded on a Bruker AV600 spectrometer using the 2D ¹H-²⁹Si HMBC pulse sequence and were referenced to an external solution of tetramethylsilane. High-resolution electron impact mass spectra and exact masses were determined on a Waters Micromass GCT Premier mass spectrometer using electron impact ionization (70 eV). Infrared spectra were recorded using a Nicolet 6700 FTIR spectrometer. Melting points were measured using a Mettler FP82 Hot Stage mounted on an Olympus BH-2 microscope and controlled by a Mettler FP80 Central Processor, and are uncorrected. Static UV-visible absorption spectra were recorded using a Cary 50 UV-vis spectrophotometer. Column chromatography and silica microcolumns were prepared using SiliaFlash P60 40-63 μ m (230-400 mesh) silica gel (Silicycle). Alumina packed microcolumns were prepared using neutral (60-325 mesh) Brockmann Activity I alumina (Fisher Scientific).

All commercially available materials were used as received from the suppliers or further purified prior to use as described below; solvents were all reagent grade or better. Lithium wire (99.9%, Sigma-Aldrich) was cut and washed with dry hexanes. Di-tert-butylsilane (^tBu₂SiH₂; 95%, Gelest) and iodine (I2; 99.8%, VWR) were used as received from the suppliers. Naphthalene (99%, Sigma-Aldrich) was purified by sublimation. Hexanes (Caledon) and diethyl ether (Et₂O; Caledon) were dried by passage through activated alumina under nitrogen using a Solv-Tek solvent purification system (Solv-Tek Inc.). Pentane (Caledon) and 35-60 petroleum ether (Caledon) were used as received. Tetrahydrofuran (THF; Caledon) for flash photolysis experiments was dried by stirring over lithium aluminum hydride (LiAlH₄) overnight and distilling immediately prior to use. Alternatively, THF for synthesis was distilled under nitrogen from sodium/benzophenone. Tetrahydrothiophene (THT; 99%, Sigma-Aldrich) was refluxed over anhydrous sodium sulfate and distilled immediately prior to use.⁴⁴ Diethylamine (Et_2NH ; 99.5%, Sigma-Aldrich), and triethylamine (Et₃N; \geq 99%, Sigma-Aldrich) were stirred over solid sodium hydroxide under nitrogen and distilled immediately prior to use. Triethylsilane (Et₃SiH; 98%, Gelest) was stirred over LiAlH₄ overnight and distilled. Glacial acetic acid (AcOH; Caledon) was used as received from the suppliers. Methanol (MeOH; Caledon) was distilled from sodium methoxide. Acetone (Caledon) was distilled from calcium sulfate.⁴⁴ Cyclohexene (≥99%, Sigma-Aldrich) was stirred over maleic anhydride overnight before being distilled and passed through a silica microcolumn.⁴⁴ cis-Cyclooctene (95%, Sigma-Aldrich) was distilled from NaOH pellets and then passed through an alumina microcolumn.⁴⁴ 1-Hexene (99%, Sigma-Aldrich) and 2,3-dimethyl-2-butene (TME; \geq 99%, Sigma-Aldrich) were stirred over calcium hydride or lithium aluminum hydride and distilled immediately prior to use. Sealed ampules of benzene- d_6 (Cambridge Isotope) were used as received from the suppliers, while chloroform-d was dried by distillation from CaH₂.

Di-*tert*-butyldiiodosilane (¹Bu₂SiI₂) and hexa-*tert*-butylcyclotrisilane (7) were prepared according to the procedures of Weidenbruch and co-workers.^{20,24} Compound 7 was purified by column chromatography (silica gel, hexanes), followed by recrystallization from pentane, to a purity of \geq 97% as determined by ¹H NMR spectroscopy (mp 175–188 °C (dec); lit:²⁰ 182 °C (dec)). Spectroscopic data for the compound are in good agreement with the reported spectra,²⁰ except for the chemical shift of the quaternary carbon signal in the ¹³C spectrum, which was reported at 31.0 ppm in C₆D₆; we observed the resonance at 27.2 ppm. Complete spectral data for 7 are as follows: ¹H NMR (C₆D₆) δ 1.42 (s, 54 H); ¹³C{¹H} NMR (C₆D₆) δ 27.2

 $(C(CH_3)_3)$, 35.1 $(C(CH_3)_3)$; ²⁹Si NMR $(C_6D_6) \delta$ 3.6; IR, cm⁻¹ (relative intensity) 2951 (w), 2853 (s), 1483 (m), 1473 (w), 1361 (m), 1165 (m), 937 (w), 810 (s), 481 (w), 438 (m); UV–vis (hexanes) λ_{max} nm 208, 237, 353(sh), 388; EI-MS, m/z (relative intensity) 426.4 (18, M⁺), 376.2 (9), 314.2 (9, $(Si_3t-Bu_4 + 2H)^+$), 285.2 (9, $(Si_2t-Bu_4 + H)^+$), 228.2 (18, $(Si_2t-Bu_3 + H)^+$), 185.1 (12), 169.1 (39, $(Si_2t-Bu_2 - H)^+$), 127.1 (52), 91.1 (51), 73.0 (100), 57.1 (35, C₄H₉⁺); HRMS (C₂₄H₅₄Si₃) calc. 426.3533, found 426.3529. The samples of 7,7-di-*tert*-butyl-7-silabicyclo[4.1.0]heptane (5) employed in this study were provided in sealed ampules by Prof. K. Woerpel and Dr. M. Prevost. Dodecamethylcyclohexasilane (2) and 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane (4) were synthesized and purified according to the previously reported procedures.⁴⁵

Laser flash photolysis experiments were carried out using a Lambda Physik Compex 120 excimer laser filled with F₂/Kr/Ne (248 nm, 20 ns, 40-100 mJ) and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously.⁴⁶ Solutions of the silylene precursors (5 or 7) were prepared in deoxygenated anhydrous hexanes such that the absorbance of the resulting solution at 248 nm in a 7×7 mm quartz cell was in the range 0.4–0.7. The solutions were flowed through a 7 × 7 mm Suprasil flow cell from calibrated 100 or 250 mL reservoirs, which contain a glass frit to allow bubbling of argon gas through the solution for at least 30 min prior to, and then throughout, the experiment. Samples of 5 were dispensed in a glovebox and were transferred rapidly in the required amounts to the (solvent-filled, argon-purged) reservoirs using a microliter syringe to minimize contact with air and moisture. The flow cell was connected to a Masterflex 77390 peristaltic pump fitted with Teflon tubing (Cole-Parmer Instrument Co.) which pulls the solution through the cell at a constant rate of 2-3 mL/min. Solution reservoirs were flamedried under an atmosphere of nitrogen or argon, while the sample cell and transfer lines were dried in a vacuum oven (55-75 °C) before use. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple inserted into the thermostated sample compartment in close proximity to the sample cell. Substrates were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Standard solutions were prepared in 10 or 25 mL volumetric flasks using known quantities (determined by mass and/or volume, in the latter case using literature densities at 25 °C) of substrate. Air and O2-saturated solutions were prepared by bubbling the appropriate gas through the solution for at least 20 min prior to and during measurement.

Transient absorbance-time profiles were recorded by signal averaging of data obtained from 10-50 individual laser shots. Decay rate coefficients were calculated by nonlinear least-squares analysis of the transient absorbance-time profiles using the Prism 7.0d software package (GraphPad Software, Inc.) and the appropriate user-defined fitting equations, after importing the raw data from the Luzchem mLFP software. Rate and equilibrium constants were calculated by linear least-squares analysis of transient absorbance data that spanned as large a range in transient decay rate or initial signal intensity as possible. Errors are quoted as twice the standard error obtained from the least-squares analyses.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00902.

Additional kinetic data determined in laser flash photolysis experiments; details of the computational studies and tables of calculated energies and UV-vis spectra for computed structures (PDF)

Cartesian coordinates for computed structures (XYZ)

AUTHOR INFORMATION

Corresponding Author

*E-mail: leigh@mcmaster.ca.

ORCID 0

Ian R. Duffy: 0000-0001-6805-4943

William J. Leigh: 0000-0002-4905-8436

Notes

The authors declare no competing financial interest.

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(26) Average and standard deviation of 13 determinations made over the course of the study.

(27) An estimate of the appropriate scaling factor to use can be derived by assuming that the extinction coefficient of Si⁴Bu₂ at 420–430 nm is zero; the approximate scaling factor is thus given by the ratio of the transient absorbance at 420–430 nm in the prompt spectrum to that in the 17.7–17.8 μ s spectrum (\approx 0.65).

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7, the maximum expected increase in ΔA^{430nm} is 1/2 the ΔA_0^{430nm} value, or ca. 0.008 AU. The chemical yields of 8 via Si'Bu₂ dimerization are thus $\approx 0.005/0.016 \times 100\% = 31\%$ from 5 and $\approx 0.0015/0.008 \times 100\% = 19\%$ from 7.

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