





**Figure 1.** Transient absorption spectra recorded 64–80 ns (○) and 1.5–1.6  $\mu$ s (□) after the laser pulse, from laser flash photolysis of a 0.09 mM solution of **3** in deoxygenated, anhydrous hexane containing 0.6 mM Et<sub>3</sub>SiH. Also shown is the difference spectrum (●; 80 ns minus 1.6  $\mu$ s) and the spectrum obtained after 254 nm photolysis of **3** in a MP glass at 78 K (---). The inset shows transient decays recorded at 460 and 530 nm.

**Table 1.** Absolute Rate Constants ( $k_Q/10^9 \text{ M}^{-1}\text{s}^{-1}$ ) for Reaction of SiPh<sub>2</sub>, SiMe<sub>2</sub>, and GePh<sub>2</sub> with Selected Scavengers in Hydrocarbon Solvents at 25 °C

scavenger (Q)	$k_Q/10^9 \text{ M}^{-1}\text{s}^{-1}$		
	SiPh <sub>2</sub> <sup>a</sup>	SiMe <sub>2</sub> <sup>b</sup>	GePh <sub>2</sub> <sup>c</sup>
MeOH	13.2 ± 0.3	9.1	6.1 <sup>d</sup>
Et <sub>3</sub> SiH	2.8 ± 0.1	3.6	0.0006
isoprene	11.8 ± 1.0	9.4	5.5 <sup>d</sup>
4,4-dimethyl-1-pentene	8.7 ± 0.4	7.3	4.2 <sup>d</sup>
<i>tert</i> -butylacetylene	9.7 ± 0.4	8.0	5.2

<sup>a</sup> From plots of the pseudo-first-order rate constants ( $k_{\text{decay}}$ ) for decay of SiPh<sub>2</sub> in hexane, monitored at 530 nm, versus scavenger concentration; errors are reported as  $\pm 2\sigma$ . <sup>b</sup> Data from refs 2, 3 (cyclohexane, 22 °C); diene = 2,5-dimethyl-1,3-hexadiene; alkene = 1-hexene; alkyne = trimethylsilylacetylene. <sup>c</sup> Data from refs 13, 14. <sup>d</sup> Reversible, with equilibrium constants in the range 2000–6000 M<sup>-1</sup> in hexane at 25 °C (see refs 13, 14).

homologue, GePh<sub>2</sub>,<sup>13,14</sup> with the same or similar substrates. The close correspondence between the rate constants for reaction of the 520 nm species from **3** and of SiMe<sub>2</sub> with corresponding substrates provides strong support for a silylene assignment. Further support is provided by the excellent agreement between the absolute rate constant ratio for reaction of the species with MeOH and Et<sub>3</sub>SiH ( $k_{\text{MeOH}}/k_{\text{Et}_3\text{SiH}} = 4.7 \pm 0.3$ ) and the value determined above by competitive steady-state trapping.

Each of these reagents also quenched the formation of the short-lived 460 nm transient completely, suggesting it is a product of reaction of SiPh<sub>2</sub> that is eliminated in the presence of silylene scavengers. A likely candidate is the dimerization product, tetraphenyldisilene (Si<sub>2</sub>Ph<sub>4</sub>); its spectrum can be compared to that of tetraphenyldigermene (Ge<sub>2</sub>Ph<sub>4</sub>;  $\lambda_{\text{max}} = 440 \text{ nm}$ ), which is similarly formed from GePh<sub>2</sub> under the same conditions and similarly quenched in the presence of added scavengers.<sup>13,15</sup> Time-dependent DFT calculations (see Supporting Information) reproduce the red-shifts in the absorption maxima of SiPh<sub>2</sub> and Si<sub>2</sub>Ph<sub>4</sub> relative to those of the corresponding germanium analogues<sup>13</sup> and yield values of  $\lambda_{\text{max}}$  (equal to 565 and 486 nm for SiPh<sub>2</sub> and Si<sub>2</sub>Ph<sub>4</sub>, respectively) that are in acceptable agreement with the experimental spectra.

SiPh<sub>2</sub> and GePh<sub>2</sub> exhibit the same large differences in reactivity toward Si–H insertion as do the parent (MH<sub>2</sub>) and dimethyl (MMe<sub>2</sub>) metallylene analogues.<sup>16,17</sup> The kinetic differences are much less pronounced in the reactions with C–C multiple bonds and MeOH, despite substantial differences in the stabilities of the primary

products of these reactions. The latter is evident from the fact that GePh<sub>2</sub> reacts reversibly with MeOH, the alkene, and the diene on the microsecond time scale,<sup>13,14</sup> while SiPh<sub>2</sub> appears to react irreversibly. The trends are similar to those exhibited by the methylated counterparts, SiMe<sub>2</sub> and GeMe<sub>2</sub>, under similar conditions.<sup>16</sup>

The insensitivity of the lifetime of the long-lived 460 nm species to added Et<sub>3</sub>SiH was mirrored in the experiments with the other scavengers studied. This is the behavior expected<sup>10</sup> of a silylene intermediate analogous to that formed in the photolysis of **1**.<sup>9</sup> As discussed above, minor products consistent with addition of MeOH to such a species were observed in the steady-state experiments, though they have not yet been isolated owing to their very low individual yields. More complete identification of the minor transient products of photolysis of **3** and analogous studies of the transient photoproducts from **1** will be reported in due course, as will the results of further studies of the reactivities of simple transient silylenes in solution.

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**Supporting Information Available:** Synthesis and characterization of compounds; detailed descriptions of product studies; flash photolysis experiments; TD–DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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