Supporting Information for

Diphenylsilylene

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Synthesis and Characterization of Compounds

^{1}H and ^{13}C NMR spectra were recorded on Bruker AV200 or AV600 spectrometers in deuterated chloroform and were referenced to the residual solvent 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×0.25mm; 0.25 μm; Varian, Inc.). High-resolution electron mass spectra and exact masses were determined on a Micromass TofSpec 2E mass spectrometer using electron impact ionization (70 eV). Infrared spectra were recorded as thin-films on potassium bromide plates using a Bio-Rad FTS-40 FTIR spectrometer. Column chromatography was carried out using a 3×60 cm column using Silica Gel 60 (230-400 mesh; Silicycle). Low temperature UV/vis spectrophotometry employed 2 x 1 x 1 cm cuvettes constructed from Suprasil quartz tubing (Vitro Dynamics, Inc.), an Oxford Optistat™ cryostat and Oxford ITC601 temperature controller, and a Varian Cary 50 spectrophotometer.

Dichlorodiphenylsilane (Sigma-Aldrich), dimethylchlorosilane (Gelest), and 1,4-dichloro-butane (Lancaster) were used as received from the suppliers. Triethylsilane (Sigma-Aldrich) was purified by vacuum distillation (p = 20 mmHg) after stirring for 10 hours over lithium aluminum hydride. Isoprene (Sigma-Aldrich) was purified by distillation from sodium. *Tert*-butylacetylene (Sigma-Aldrich) was purified by distillation. 4,4-Dimethyl-1-pentene (Sigma-Aldrich) was purified by passage through a short silica gel column. Deuterated solvents were used as received from Cambridge Isotope Laboratories. 1,1,1,3,3,3-Hexamethyl-2,2-diphenyltrisilane was prepared by the method of Berry et al.[1]

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).

Synthesis of 2,2-Diphenyl-1,1,3,3-tetramethyl-1,2,3-trisilacycloheptane (**3**)
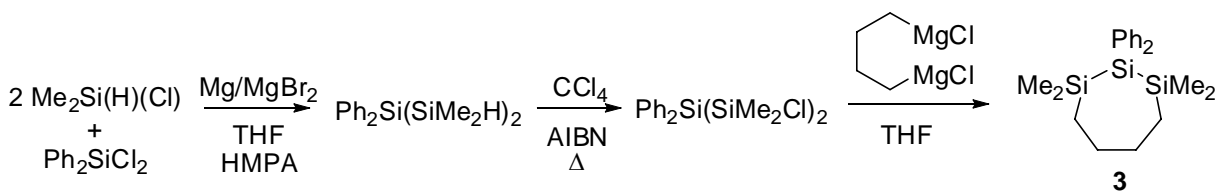
1,1,3,3-Tetramethyl-2,2-diphenyltrisilane was prepared by a procedure similar to that used by Ando and coworkers.[2] An oven-dried 500 mL round-bottom flask containing magnesium turnings (33.4 g, 1.4 g-atom) under nitrogen was fitted with a reflux condenser, nitrogen inlet, and magnetic stir bar. Anhydrous THF (130 mL) was added, and then 1,2-dibromoethane (56.7 g, 0.30 mol) was added dropwise with stirring *via* syringe over ca. 3 hours at a rate appropriate to sustain reflux. After the addition was complete, hexamethylphosphoramide (60 mL) was added, the resulting solution was stirred for 20 minutes, and then chlorodimethylsilane (26.4 g, 0.28 mol) was added dropwise *via* syringe over 2 hours. Dichlorodiphenylsilane (34.92 g, 0.14 mol) was then added in similar fashion, and the reaction mixture was stirred at reflux for 18 hours. After cooling to room temperature, the reaction mixture was quenched with 5% aqueous ammonium chloride (1 L), placed in a separatory funnel, and extracted with diethyl ether (3×300 mL). The combined organic fractions were dried over magnesium sulfate, filtered, and the solvent was removed under vacuum to yield a colorless oil (44.8 g), which was distilled under reduced pressure (115-117^{0}C, p = 0.05 mmHg). The colorless oil that was collected (10.6 g, 26 %) was identified as 1,1,3,3-tetramethyl-2,2-diphenyltrisilane on the basis of the following spectroscopic data. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.51 (m, 6H), 7.35 (m, 4H), 4.14 (sept, J = 4.5 Hz, 2H), 0.27 (d, J = 4.5 Hz, 12H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 136.1, 134.9, 128.7, 128.2, -5.4; MS, m/z (I) = 300 (48) (M$^+$), 299 (100), 285 (47), 239 (27), 223 (50), 164 (26), 135 (31), 105 (65), 59 (12), 43 (24); IR (film) 3067 (m), 2958 (m), 2094 (s), 1483 (w), 1428 (s), 1247 (m), 1098 (w), 884 (s), 838 (s), 736 (s); Exact mass calculated for C$_{16}$H$_{24}$Si$_3$ 300.1186, found 300.1175.

A portion of the product from above (2.0 g, 6.7 mmol) was placed in a nitrogen-flushed 25 mL round-bottom flask, and carbon tetrachloride (15.94 g, 0.103 mol) and 2,2'-azobis(2-methylpropionitrile) (0.010 g, 0.061 mmol) were added. A reflux condenser, magnetic stirrer, and nitrogen inlet were attached and the mixture was refluxed for 14 hours, until TLC analysis (silica gel, hexanes) indicated reaction to be complete. The excess carbon tetrachloride was removed on the rotary evaporator to yield a colorless oil, which was further pumped on under high vacuum for 1 hour (2.3 g, 93%). A portion of the material (0.1 g) was removed for NMR analysis, and the remainder was dissolved in anhydrous THF (20 mL) and used in the next step without further purification. The ^{1}H NMR spectrum of the material (200 MHz, CDCl$_3$; δ 7.23 (m, 4H), 7.77 (m, 6H), 0.6 (s, 12 H)) was consistent with the desired product, 1,3-dichloro-1,1,3,3-tetramethyl-2,2-diphenyltrisilane.

To an oven-dried 25 mL round-bottom flask containing magnesium turnings (0.32 g, 0.13 g-atom) and fitted with a reflux condenser, magnetic stirrer, and nitrogen inlet was added anhydrous THF (6 mL), followed by a solution of 1,4-dichlorobutane (0.76 g, 6.0 mmol) in anhydrous THF (6 mL), dropwise *via* syringe over 2 hours under nitrogen. A crystal of iodine was added to the solution to initiate reaction, and the mixture was then stirred under reflux for 2.5 hours. The resulting mixture was cooled to room temperature, the THF solution from the preceding step was added dropwise *via* syringe to the stirred solution over 1 h, and the resulting mixture was stirred at room temperature for a further 18 hours. The reaction mixture was quenched with 5% aqueous ammonium chloride (200 mL), placed in a separatory funnel, and extracted with diethyl ether (3 × 100 mL). The combined organic fractions were dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure to afford the crude product (2.25 g) as a slightly yellow oil. Column chromatography on silica gel with hexanes as eluant afforded 2,2-diphenyl-1,1,3,3-tetramethyl-1,2,3-trisilacycloheptane (**3**; 0.83 g,

35 %) as a colorless oil. ^{1}H NMR (600 MHz, CDCl$_3$), δ 7.48 (m, 4H), 7.32 (m, 6H), 1.74 (m, 4H), 0.91 (m, 4H), 0.16 (s, 12H); ^{13}C NMR (150 MHz, CDCl$_3$), δ 136.5, 136.4, 128.2, 127.9, 25.1, 14.6, -1.4; ^{29}Si NMR (119 MHz, CDCl$_3$), δ -12.46 (SiMe$_2$), -39.70 (SiPh$_2$); GC/MS (EI), m/z = 354 (100; M$^+$), 339 (80) 277 (38), 240 (7), 217 (9), 142 (7), 105(11); IR (film), 3021 (m), 2948 (m), 2907 (m), 1427 (s), 1245 (s), 1096 (s), 869 (m), 832 (m), 699 (m); Exact mass calculated for C$_{20}$H$_{30}$Si$_3$ (EI) 354.1655, found 354.1638.

Synthesis of 1,1,2,2-Tetramethyl-1,2-disilacyclohexane (**5**)

The synthesis of **5**[3,4] followed the procedure outlined above for the last step in the synthesis of **3**. From 5 g (0.027 mol) of 1,2-dichloro-1,1,3,3-tetramethyldisilane was obtained 2.57 g (56%) of 1,1,2,2-tetramethyl-1,2-disilacyclohexane after vacuum distillation of the crude reaction product (115-118^{0}C, p = 20 mm Hg). ^{1}H NMR (600 MHz, CDCl$_3$), δ 1.58 (m, 4H), 0.71 (m, 4H), 0.06 (s, 12H) ; ^{13}C NMR (150 MHz, CDCl$_3$), δ 26.3, 17.1, -3.9; MS *m/z* (I) = 172 (63; M$^+$), 157 (100), 144 (13), 129 (33), 116 (60), 97 (49), 85 (14), 73 (85), 59 (30), 43 (37).

Steady State Photolysis of 3 in the Presence of Methanol

A 0.051 M solution of **3** in cyclohexane-*d$_{12}$* 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 minutes, and then the appropriate volumes of methanol and dioxane were added with a syringe to result in concentrations of 0.16 M and 0.016 M, respectively. The solution was photolyzed for 20 minutes (ca. 60% conversion of **3**) in a Rayonet photochemical reactor (Southern New England Ultraviolet Co.) equipped with a merry-go-round and two RPR-2537 lamps, monitoring by 600 MHz ^{1}H NMR spectroscopy in 2 minute intervals; the mixture was also analyzed by GC/MS before and after photolysis. Figure S1 shows the NMR spectra of the mixture before and after 20 minutes photolysis. The two major products were identified as diphenylmethoxysilane (**4**; ^{1}H NMR, δ 7.54

(dd, J = 8.1, 1.8 Hz, 4H), 7.30 (dt, J = 7.2, 1.8 Hz, 2H), 7.26 (dt, J = 7.2, 1.8 Hz, 4H), 5.36 (s, 1H),

3.52 (s, 3H), 0.06 (s, 12H); MS, m/z (I) = 214 (6), 213 (16), 184 (5), 183 (11), 138 (7), 136 (100),

107 (9), 105 (13), 92 (10), 91 (11), 59 (42)) and 1,1,2,2-tetramethyl-1,2-disilacyclohexane (**5**; vide

supra) on the basis of comparisons to the reported spectra (for **4**)[5] and those of the authentic sample

of **5** prepared above, respectively.
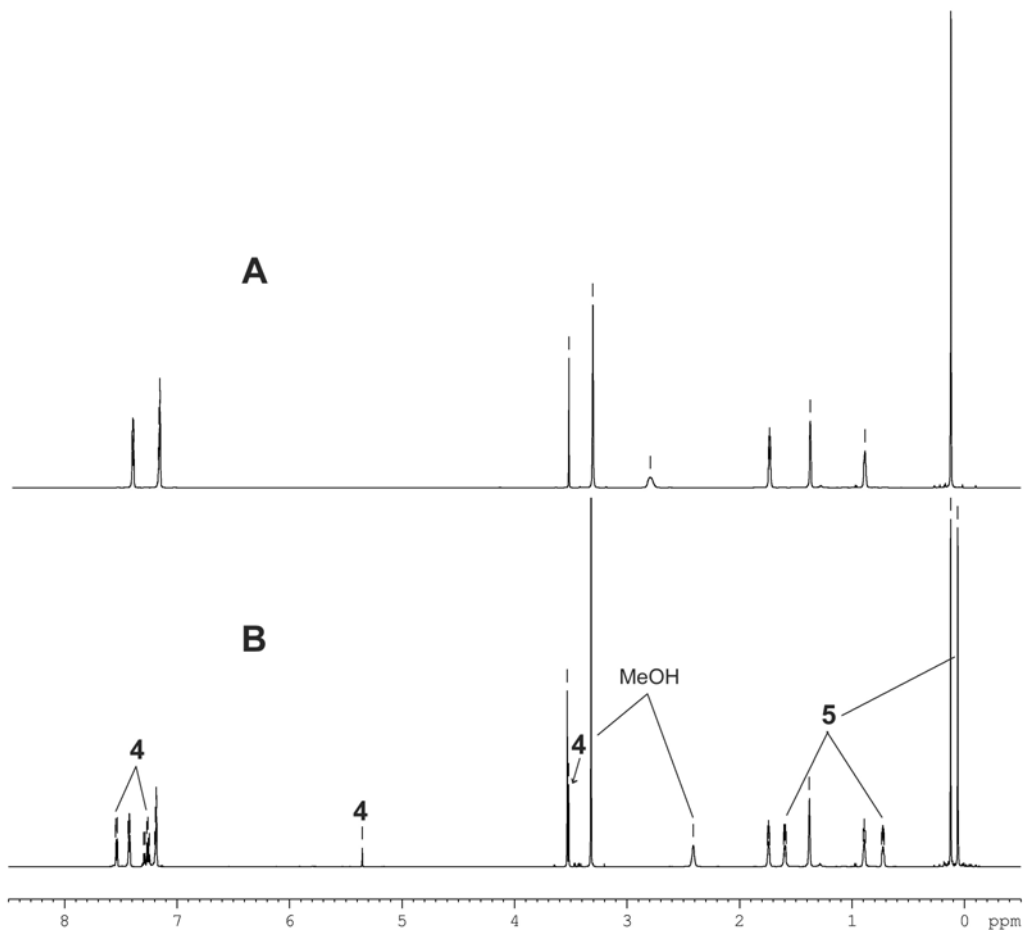
Figure S1. 600 MHz ^{1}H NMR spectrum of a 0.051 M solution of **3** in C_6D_{12} containing MeOH
(0.16 M) and dioxane (0.016 M) before (A) and after photolysis for 20 minutes with 254 nm
light (B).

An expansion of the δ 3.15-3.70 region of the spectrum of the photolyzed mixture (Figure

S2A) shows the presence of at least five minor methoxylated products, which are characterized

by singlets of similar intensities at δ 3.41, 3.43, 3.46, 3.47, and 3.65; the sum of the areas of

these five peaks was ca. $1/5^{th}$ of that of the singlet at δ 3.52 due to **4**. The intensity of the δ 3.46

peak increased continuously relative to the others throughout the course of the photolysis, while

the other four grew in with similar relative intensities; this suggests that the δ 3.46 peak is due to

a secondary thermal or photochemical decomposition product. A complex pattern of resonances

also grew in throughout the δ 4.7-6.8 region of the spectrum, as shown in Figure S2B. GC/MS

analysis of the mixture showed four minor peaks with retention times greater than that of **3**, in

addition to those due to **4** and **5**. The mass spectra of three of these exhibited molecular ions of

$m/z = 386$, consistent with the products of addition of methanol to an isomer of **3**. The spectrum

of the fourth peak exhibited a molecular ion of $m/z = 384$, consistent with a dehydrogenation

product of one or more of the other three minor adducts. While no attempt was made to isolate

these compounds because of their very low individual yields, their spectral characteristics are

consistent with the products of addition of MeOH to silene **6**, for which three regioisomers (**7a-c**;

eqn. 1) are possible (**7**; eq. 1), and the associated dehydrogenation product **8**.[6,7] The 1,4- and 1,3-

regioisomers **7a** and **7b** are the type that have been most widely isolated from photolysis of

aryldisilanes and –trisilanes in the presence of alcohols.[6-11]
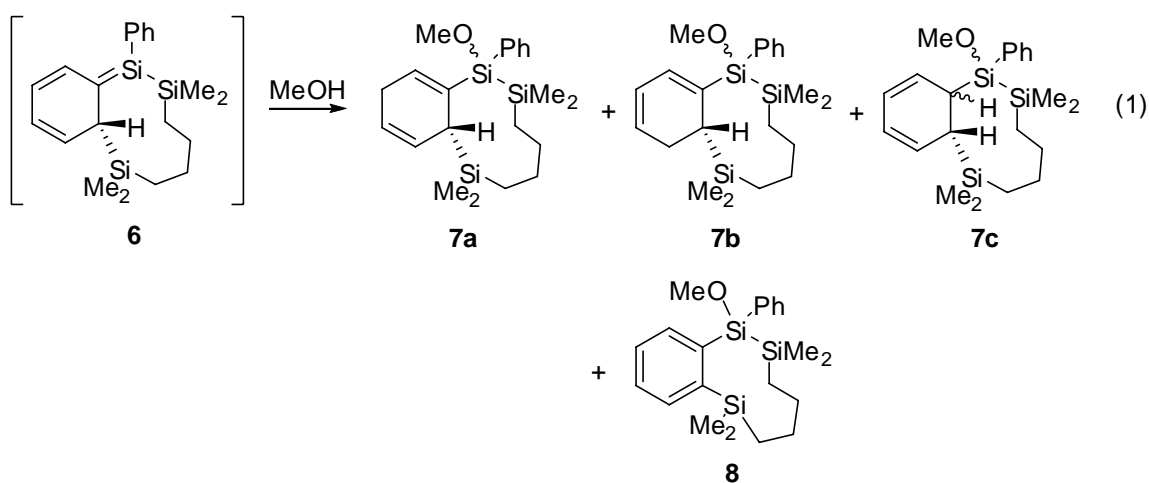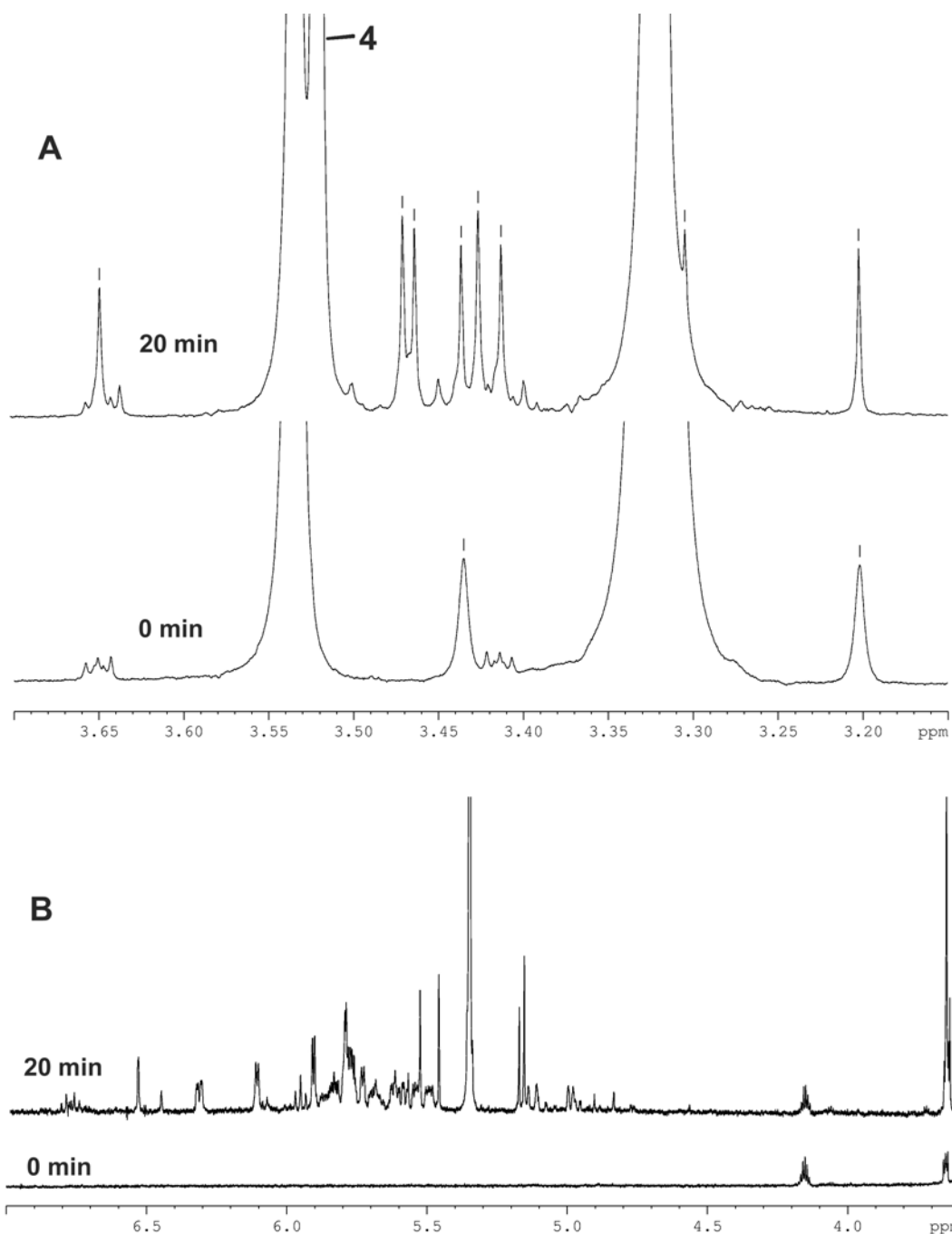
Figure S2. Expansions of the δ 3.15-3.70 (A) and δ 3.6-7.0 (B) regions of the 600 MHz ^{1}H NMR spectra of Figure S1, before and after photolysis for 20 minutes with 254 nm light.

Concentration vs. time plots were constructed from the NMR integration data for **3** (SiMe protons), **4** (OMe protons), and **5** (SiMe protons) and are shown in Figure S3. The figure also shows a plot of the sum of the concentrations of the five minor products discussed above

(Σ[minor products]) versus time. The product yields listed in eqn. 2 of the paper were calculated

from the slopes of these plots relative to that of the plot of [**3**] vs. time.

Figure S3. Concentration *vs.* time plots for 254 nm irradiation of deoxygenated solution of **3** (0.051 M) in C_6D_{12} containing MeOH (0.162 M) and dioxane (0.0156 M; internal standard). The solid lines are the linear least squares fits of the data, and are characterized by the following slopes: **3**, -0.00141 ± 0.00007; **4**, 0.00097 ± 0.00003; **5**, 0.00116 ± 0.00002; Σ(minor products), 0.00019 ± 0.00001.

Quantum Yield of Photolysis of 3

The quantum yield for photolysis of **3** was determined by merry-go-round photolysis of

deoxygenated solutions of **3** (0.041 M) and 1,1-diphenylsilacyclobutane (Ph$_2$SCB; 0.054 M) in

cyclohexane-d_{12} containing methanol (0.179 M) and dioxane (0.009 M), in a Rayonet

photochemical reactor equipped with 2 RPR-2537 low pressure Hg lamps. The photolyses were

monitored at time intervals between 0 and ca. 30 % conversion of **1** by 600 MHz ^{1}H NMR

spectroscopy. The quantum yield for consumption the formation of **3** was calculated from the

relative slopes of concentration vs time plots for it and Ph$_2$SCB (Fig. S4), and the reported

quantum yield of the latter reaction ($\Phi = 0.21 \pm 0.03$).[12] The slopes of the plots were: **3**, -

0.00140 ± 0.00003; Ph$_2$SCB, -0.00054 ± 0.00006. This affords a value of $\Phi_{-3} = 0.54 \pm 0.09$ for

the quantum yield for photolysis of **3**.
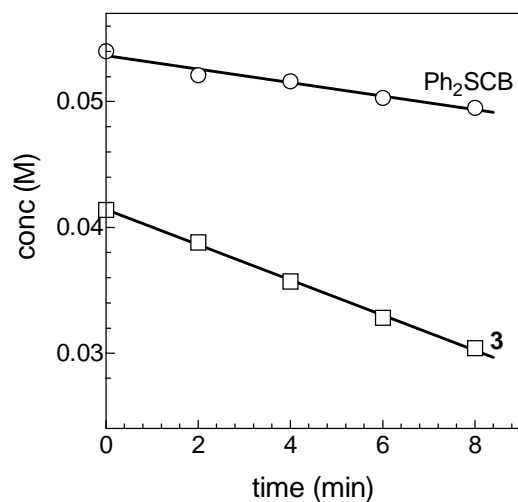
Figure S4. Concentration vs. time plots from merry-go-round photolysis of solutions of **3** (0.041 M;) and 1,1-diphenyl-1-silacyclobutane (Ph$_2$SCB, 0.041 M) in cyclohexane-d_{12} containing MeOH (0.179 M) and dioxane (0.009 M) as internal standard.

Steady State Photolysis of 3 in the Presence of Triethylsilane

A 0.045 M solution of **3** in cyclohexane-d_{12} 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 minutes, and then the appropriate volumes of Et$_3$SiH and dioxane were added with a syringe to result in concentrations of 0.24 M and 0.018 M, respectively. The solution was photolyzed for 18 minutes (ca. 58% conversion of **3**) with two RPR-2537 lamps, monitoring by 600 MHz ^{1}H NMR spectroscopy in 2 minute intervals; the mixture was also analyzed by GC/MS before and after photolysis. Figure S5 shows concentration vs. time plots constructed from the NMR integration data for **3** (SiMe protons), **5** (SiMe protons), and **6** (SiH proton x 1.19); the correction factor necessary for the Si-H proton integrals in the spectrum of **6** was determined from the NMR spectrum of the authentic compound (*vide infra* and Fig. S6).
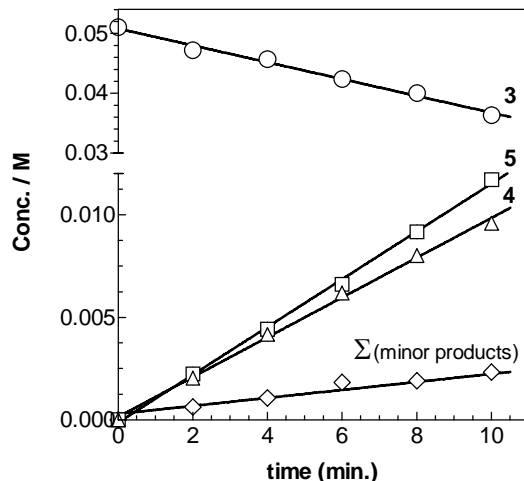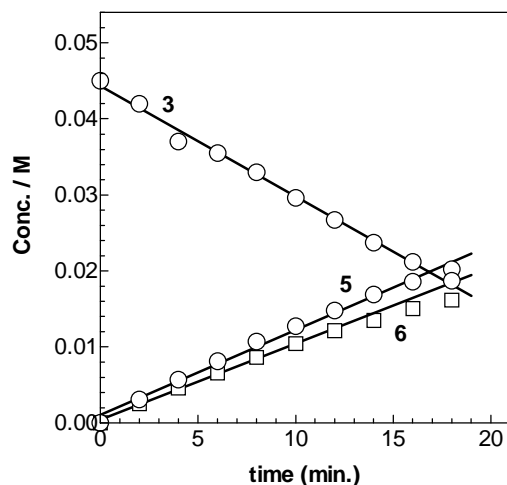
Figure S5. Concentration *vs.* time plots for 254 nm irradiation of deoxygenated solution of **3** (0.045 M) in C_6D_{12} containing Et_3SiH (0.240 M) and dioxane (0.0179 M; internal standard). The solid lines are the linear least squares fits of the data, and are characterized by the following slopes: **3**, -0.00145 ± 0.00004; **5**, 0.00112 ± 0.00003; **6**, 0.00101 ± 0.00003.

Removal of the solvent on the rotary evaporator, followed by pumping on the resulting oil under vacuum (0.1 mm Hg) for 2 hours, afforded a mixture of **3** (54%) and a single major reaction product (46%), which was identified as 1,1,1-triethyl-2,2-diphenyldisilane (**6**) on the basis of the following spectral data: ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.56 (m, 4H), 7.34 (m, 6H), 4.89 (s, 1H), 0.94 (t, *J* = 7.8 Hz, 9H), 0.74 (q, *J* = 7.8 Hz , 6H); ^{13}C NMR (150 MHz, $CDCl_3$), δ 135.9, 129.4, 129.0, 128.1, 8.4, 4.0; ^{29}Si NMR (119 MHz, $CDCl_3$), δ -6.57 ($SiEt_3$), -33.00 (Ph_2SiH; J_{Si-H} = 179.7 Hz); GC/MS, *m/z* (I) = 298 (100), 269 (32), 241 (19), 221 (21), 213 (26), 183 (18), 163 (13), 115 (65), 105 (58), 87 (73), 59 (57), 53 (15), 43 (10); Exact mass, calculated for $C_{18}H_{26}Si_2$, 298.1573; found 298.1574. The ^{1}H NMR spectrum of the mixture is shown in Figure S6.
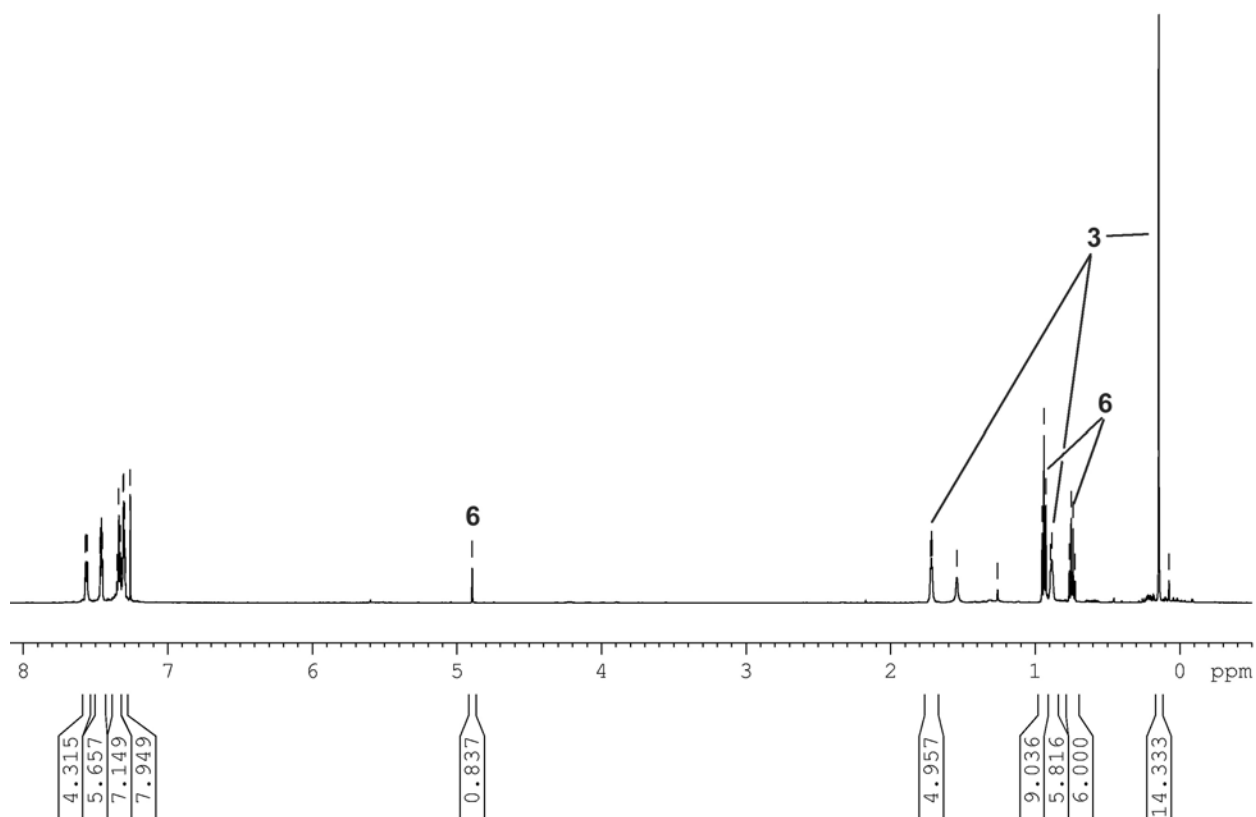
Figure S6. 600 MHz ^{1}H NMR spectrum (in CDCl$_3$) of the crude mixture from photolysis of **3** in the presence of Et$_3$SiH (0.24 M), after evaporation of excess Et$_3$SiH and **5**.

Competitive Steady State Trapping of SiPh$_2$ by MeOH and Et$_3$SiH

A 0.023 M solution of **1** in cyclohexane-d_{12} 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 minutes, and then the appropriate volumes of methanol and Et$_3$SiH were added with a syringe to result in concentrations of 0.089 M and 0.251 M, respectively. The solution was photolyzed for 10 minutes with two RPR-2537 lamps, with monitoring by 600 MHz ^{1}H NMR spectroscopy at 1 minute time intervals. The relative concentrations of **4** and **6** present were determined from the relative peak areas of the Si-H proton singlets due to the two products at δ 4.89 and 5.36, respectively. Figure S7 shows a plot of the [**4**]/[**6**] concentration ratios vs. photolysis time. The intercept of the plot (= 1.59 ± 0.02) is the **4/6** product ratio extrapolated to zero% conversion.

From this value and the relative scavenger concentrations is obtained the rate constant ratio for trapping by the two reagents, $k_{MeOH}/k_{Et3SiH} = 4.48 \pm 0.18$.
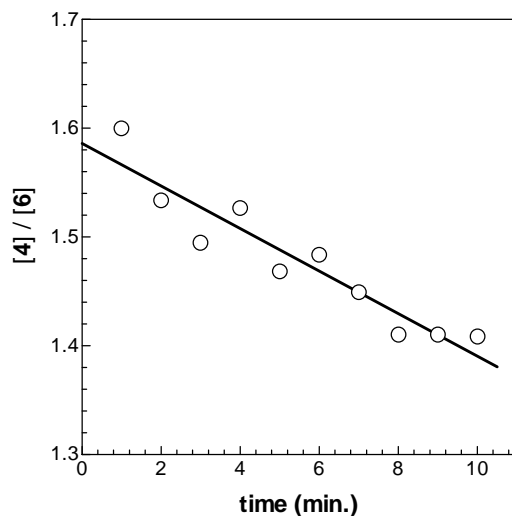
Figure S7. Plot of the **4/6** product ratio *vs.* time for the 254 nm photolysis of a deoxygenated solution of **3** (0.023 M) in cyclohexane-d_{12} containing MeOH (0.089 M) and Et$_3$SiH (0.251 M).

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 **3** in anhydrous hexanes were prepared at concentrations (ca. 8.4×10^{-5} M) such that the absorbance at the excitation wavelength (248 nm) was ca. 0.7, and were flowed through a 7 × 7 mm Suprasil flow cell from to a calibrated 250 nm reservoir, fitted with a glass frit to allow bubbling of argon gas through the solution for at least 30 minutes prior to and then throughout the duration of each experiment, using a Masterflex^{TM} 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. 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.

Figure S8a shows transient absorption spectra recorded for a deoxygenated solution of **3** in anhydrous hexane over three time slices within the first 9 μs after excitation, and transient absorbance vs. time profiles at monitoring wavelengths of 460 nm and 530 nm. The latter was fit to the two-exponential decay equation (i), which afforded decay constants of $k_1 = (9.5 \pm 0.6)$ x 10^5 s^{-1} and $k_2 = (6.3 \pm 0.7)$ x 10^4 s^{-1} and pre-exponentials of $A_1 = 0.0140 \pm 0.004$ and $A_2 = 0.0089 \pm 0.004$ ($r^2 = 0.9218$). Figure S8b shows transient spectra recorded for a similar solution over an extended time scale, along with transient absorbance vs. time profiles recorded at 460 nm and 300 nm.

$$k_{decay} = A_1 exp(-k_1 t) + A_2 exp(-k_2 t) \qquad (i)$$

The data are consistent with the presence of three transient species, two that are formed with the laser pulse ($\lambda_{max} \sim 515$ nm [$\tau \sim 1$ μs] and $\lambda_{max} = 460$ nm [$\tau > 100$ μs]) and one formed within the first ~1 μs after the pulse ($\lambda_{max} \sim 460$ nm [$\tau \sim 10$ μs]). The very long-lived species decays with mixed 1st and 2nd order kinetics at high laser intensities, but with reasonably clean 1st order kinetics and $\tau \sim 300$ μs when the intensity is reduced with neutral density filters. The behavior depicted in Figure S8a is exquisitely sensitive to the presence of moisture in the solvent or apparatus, which shortened the lifetime of the 515 nm species and quenched the growth of the short-lived 460 nm species; i.e., the latter was a distinct component of the signal at 460 nm only when water is rigorously excluded from the system. Similar behavior was noted when silylene scavengers such as Et_3SiH or the other reagents listed in Table 1 of the paper were added to the solution. It can thus be concluded that the short-lived 460 nm transient is a product of the decay
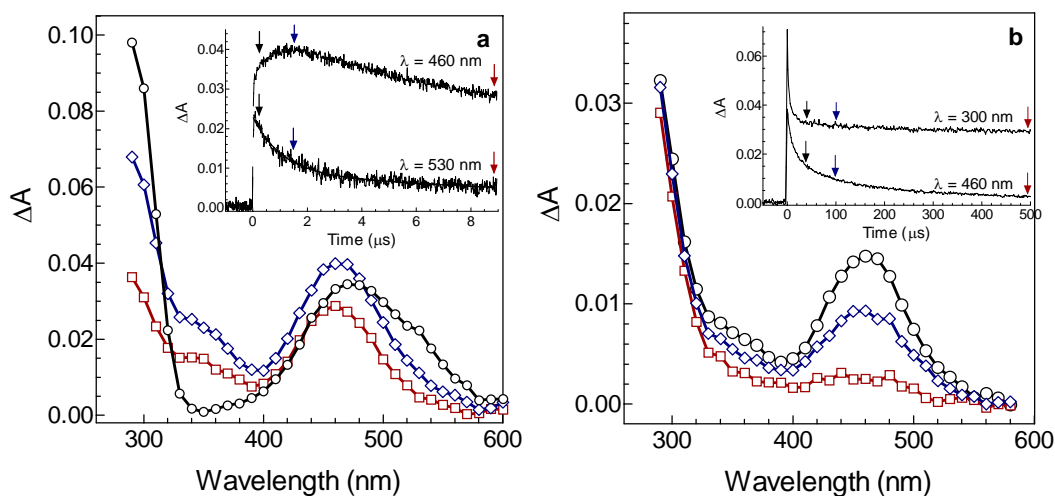
Figure S8. Transient UV/vis absorption spectra recorded for a deoxygenated solution of **3** (ca. 85 μM) in anhydrous hexane at 25 °C. (a) Short time-scale spectra, recorded 0.18-0.24 μs (-○-), 1.44-1.52 μs (-◇-), and 8.58-8.69 μs (-□-) after the laser pulse. The inset shows two of the decay traces used to construct the spectra, recorded at monitoring wavelengths of 460 nm and 530 nm; the solid line in the 530 nm decay is the fit to a two-exponential decay equation, which yielded decay constants of $k_1 = (9.5 \pm 0.6) \times 10^5$ s^{-1} and $k_2 = (6.3 \pm 0.7) \times 10^4$ s^{-1}. (b) Long time-scale spectra, recorded 41.6-44.8 μs (-○-), 101-106 μs (-◇-), and 498-502 μs (-□-) after the laser pulse; the inset shows transient decay profiles recorded at 460 and 300 nm.

of the 515 nm species in the absence of reagents that react with the 515 nm species. The lifetime of

the long-lived 460 nm species is approximately independent of the presence of water in the sample.

Addition of sub-millimolar concentrations of MeOH, Et$_3$SiH, isoprene, 4,4-dimethyl-1-

pentene, or *tert*-butylacetylene to solutions of **3** led to an increase in the rate constant for decay

of the 515 nm transient, and reduced and eventually eliminated the growth due to the short-lived

460 nm transient. Plots of k_{decay} versus substrate concentration according to equation (ii) are

shown in Figure S9 for the five scavengers studied; the slopes are the absolute second order rate

constants for reaction (k_Q) listed in Table 1 of the paper. None of these reagents exerted a

discernible effect on the lifetime of the long-lived 460 nm transient at these concentrations.

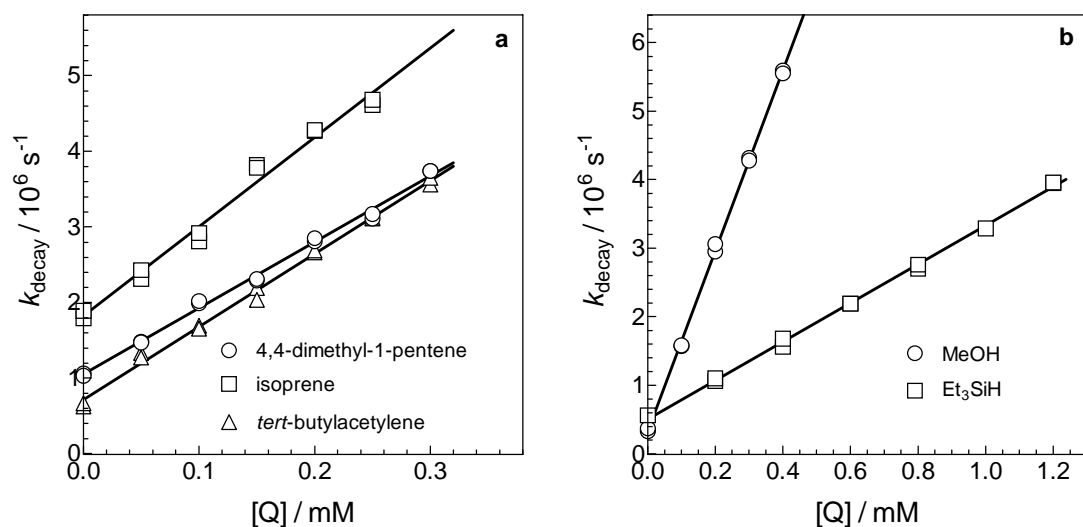$$k_Q = k_0 + k_Q[Q] \hspace{3cm} \text{(ii)}$$

Figure S9. Plots of k_{decay} *vs*. concentration for quenching of $SiPh_2$ (monitored at 530 nm) in deoxygenated hexane at 25 °C by (a) 4,4-dimethyl-1-pentene (○), isoprene (□), and *tert*-butylacetylene (△); (b) MeOH (○) and Et_3SiH (□). The solid lines are the linear least squares fits of the data to eq. (ii).

Low Temperature UV/vis Spectroscopy

For low temperature UV/vis absorption spectra, solutions of **1** or **3** (ca. 0.001 M; $A_{254\ nm} \sim$ 0.8) in 3-methylpentane (Aldrich spectrophotometric grade) were sealed in a Suprasil quartz cuvette with a rubber septum and degassed by bubbling with a fine stream of argon for 5 minutes. The sample was placed in the cryostat, which was then cooled to 78 K. The entire assembly was placed in a Rayonet photochemical reactor equipped with 4-10 RPR-253.7 lamps in order to irradiate the sample, with UV/vis spectra being obtained before and during the photolysis procedure at selected time intervals. The photoproduct spectra were then calculated as the difference between the spectra of the photolyzed and unphotolyzed samples. Figure S10 shows the spectra obtained from **1** and **3**.
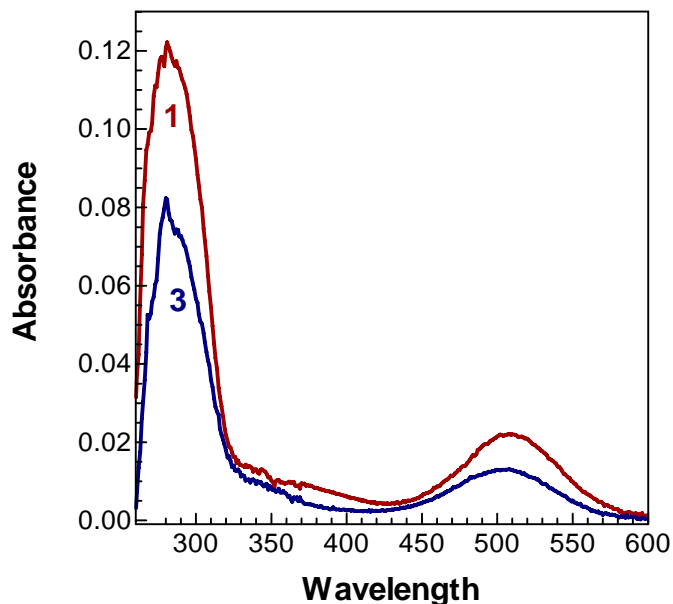
Figure S10. UV/vis difference spectra of 3-methylpentane (MP) solutions of **1** (---) and **3** (---) at 78K, after brief photolysis with 254 nm light. The difference in the intensities of the two spectra is not significant.

Time Dependent DFT Calculations.

Calculations were performed with the ADF 2004.01 density functional theory package (SCM).[13-15] Time-dependent density functional theory (TD-DFT) calculations for $SiPh_2$ and Si_2Ph_4 (**7**) were carried out on the previously reported PW91/TZ2P geometries;[16] the Adiabatic Local Density Approximation (ALDA) was used for the exchange-correlation kernel[17,18] and the differentiated static LDA expression was used with the Vosko-Wilk-Nusair parametrization.[19] Zero-order relativistic corrections (ZORA) were applied in both cases, though they had minimal effects on the electronic transition energies in the two molecules. For the exchange-correlation potentials in the zeroth-order KS equations, the first ten excitation energies and oscillator strengths were obtained using the Davidson iterative diagonalization method, and are listed in Table S1.

Table S1. Calculated energies and oscillator strengths (f) of the first 10 allowed electronic transitions of $SiPh_2$ and Si_2Ph_4 (**7**).

SiPh$_2$ (C$_2$ symmetry)				Si$_2$Ph$_4$ (**7**; C$_i$ symmetry)			
Sym.	ΔE(eV)	λ$_{max}$(nm)	f	Sym.	ΔE(eV)	λ$_{max}$(nm)	f
1B	2.19	565	2.76E-02	1A$_u$	2.55	486	2.23E-01
1A	3.33	372	1.25E-03	2A$_u$	2.74	452	1.29E-01
2A	3.50	354	7.47E-03	3A$_u$	2.85	435	1.11E-01
3A	3.52	352	2.01E-03	4A$_u$	3.09	401	6.23E-04
2B	3.60	344	1.64E-03	5A$_u$	3.86	321	5.90E-02
3B	3.68	337	6.14E-03	6A$_u$	4.09	303	5.28E-03
4B	3.76	329	1.24E-01	7A$_u$	4.18	297	9.65E-03
4A	3.83	323	3.07E-02	8A$_u$	4.31	287	1.33E-02
5A	4.21	294	3.09E-02	9A$_u$	4.37	283	4.76E-02
5B	4.31	288	1.34E-01	10A$_u$	4.59	270	3.61E-03

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