Supporting Information for

The Direct Detection of Diphenylsilylene and Tetraphenyldisilene in Solution.

Andrey G. Moiseev and William J. Leigh*

Photolysis of 9 in the presence of methanol (MeOH).

Figure S1. 600 MHz $^1$H NMR spectrum of a 0.048 M solution of 9 in C$_6$D$_{12}$ containing MeOH (0.21 M) and dioxane (0.01 M) after photolysis for 14 minutes with 254 nm light.

Figure S2. Concentration vs. time plots for 254 nm irradiation of deoxygenated solution of 9 (0.048 M) in C$_6$D$_{12}$ containing MeOH (0.21 M) and dioxane (0.01 M).

Photolysis of 9 in the presence of acetone

Figure S3. 600 MHz $^1$H NMR spectrum of a 0.051 M solution of 9 in C$_6$D$_{12}$ containing acetone (0.18 M) and dioxane (0.01 M) after photolysis for 14 minutes with 254 nm light.

Figure S4. Concentration vs. time plots for 254 nm irradiation of deoxygenated solutions of 9 (0.051 M) in C$_6$D$_{12}$ containing acetone (0.18 M) and dioxane (0.01 M).

Laser Flash Photolysis Experiments

Figure S5. (a) Transient decay profiles recorded at 530 nm by laser flash photolysis of a 0.10 mM solution of 1,1,1,3,3,3-hexamethyl-2,2-diphenyltrisilane (4) in hexane and in hexane containing 0.2 mM MeOH. (b) Plots of the pseudo-first order rate constants ($k_{\text{decay}}$) for decay of SiPh$_2$ (monitored at 530 nm) in hexane vs. the concentration of added Et$_3$SiH ( ) and MeOH (○).

Isolation of 1,1,3,3-tetramethyl-2-phenyl-1,2,3-trisilacyclohexane (17) from synthesis of 9, and independent synthesis of 17.

References
Steady State Photolysis Experiments

Photolysis of 9 in the presence of methanol (MeOH).

Diphenylmethoxysilane (14; 93%) was identified as the major SiPh₂-derived product from photolysis of a deoxygenated solution of 9 (0.048 M) in C₆D₁₂ containing MeOH (0.21 M) and dioxane (0.01 M) as internal integration standard, by comparison of its ¹H NMR and mass spectra to those of an authentic sample.¹ One additional minor product (3%) exhibiting a singlet at δ 3.46 was detected by ¹H NMR spectroscopy, while GC/MS showed two minor products of retention time greater than 9 with mass spectra consistent with addition of methanol to an isomer of 9 (M⁺ 372).

Figure S1 shows the NMR spectrum of the reaction mixture after ca. 33% conversion of 9.

Figure S1. 600 MHz ¹H NMR spectrum of a 0.048 M solution of 9 in C₆D₁₂ containing MeOH (0.20 M) and dioxane (0.01 M) after photolysis for 14 minutes with 254 nm light.
The two minor products detected by GC/MS exhibited the following mass spectra: (a) MS, m/z (I) = 372 (6, M+), 356 (16), 281 (18), 256 (8), 219 (14), 208 (21), 209 (19), 207 (100), 196 (6), 159 (10), 135 (19), 119 (7), 59 (16), 44 (9). (b) MS, m/z (I) = 372 (3, M+), 356 (4), 342 (4), 281 (18), 268 (5), 235 (6), 208 (20), 209 (20), 207 (100), 193 (9), 192 (11), 177 (6), 158 (6), 135 (9), 133 (6), 96 (7), 73 (10), 44 (8).

Concentration vs. time plots, constructed from the NMR integration data using the OMe proton resonances to quantitate 14 and the additional minor product, are shown in Figure S2.

**Figure S2.** Concentration vs. time plots for 254 nm irradiation of deoxygenated solutions of 9 (0.048 M) in C₆D₁₂ containing MeOH (0.21 M) and dioxane (0.01 M; internal standard). The solid lines are the linear least squares fits of the data, and are characterized by the following slopes: 9, -0.001148 ± 0.000020; 13, 0.001120 ± 0.000015; 14, 0.001064 ± 0.0000130; minor product, 0.000035 ± 0.000002.

**Photolysis of 9 in the presence of acetone**

Figure S3 shows the NMR spectrum of the reaction mixture after 14 minutes photolysis (ca. 30% conversion of 9) of a deoxygenated solution of 9 (0.051 M) in C₆D₁₂ containing acetone (0.18 M) and dioxane (0.01 M). The two major products were identified as 13 and 2-(diphenylsiloxy)propene (16), the latter on the basis of comparisons of the ¹H NMR and mass spectra
Concentration vs. time plots, constructed from the NMR integration data using the =CCH₃ proton resonance to quantify 16, are shown in Figure S4.

**Figure S3.** 600 MHz $^1$H NMR spectrum of a 0.051 M solution of 9 in C₆D₁₂ containing acetone (0.18 M) and dioxane (0.01 M) after photolysis for 14 minutes with 254 nm light.

**Figure S4.** Concentration vs. time plots for 254 nm irradiation of a deoxygenated solution of 9 (0.051 M) in C₆D₁₂ containing acetone (0.18 M) and dioxane (0.01 M). The solid lines are the linear least squares fits of the data, and are characterized by the following slopes: 9, -0.001206 ± 0.000016; 13, 0.001025 ± 0.000017; 16, 0.001039 ± 0.000017.
Laser Flash Photolysis Experiments

Figure S5. (a) Transient decay profiles recorded at 530 nm by laser flash photolysis of a 0.10 mM solution of 1,1,3,3,3-hexamethyl-2,2-diphenyltrisilane (4) in hexane and in hexane containing 0.2 mM MeOH. (b) Plots of the pseudo-first order rate constants ($k_{\text{decay}}$) for decay of SiPh$_2$ (monitored at 530 nm) in hexane vs. the concentration of added Et$_3$SiH (○) and MeOH (○). The slopes of the plots are $k_{\text{Et}_3\text{SiH}} = (3.5 \pm 0.2) \times 10^9$ M$^{-1}$s$^{-1}$ and $k_{\text{MeOH}} = (1.32 \pm 0.04) \times 10^{10}$ M$^{-1}$s$^{-1}$, respectively.

Isolation of 1,1,3,3-tetramethyl-2-phenyl-1,2,3-trisilacyclohexane (17) during synthesis of 9.

As mentioned in the Experimental section of the paper, the use of THF alone as reaction solvent or use of excessively long reaction times in the synthesis of 9 resulted in over-reduction and the conversion of the desired product to 1,1,3,3-tetramethyl-2-phenyl-1,2,3-trisilacyclohexane (17). An example of a procedure that led to 17 as the exclusive product follows.

In an oven-dried 5 mL roundbottom flask fitted with a rubber septum, magnetic stir bar and argon inlet was placed 30 % lithium dispersion in mineral oil (0.018 g, 2.6 mmol) and THF (2 mL) under an argon atmosphere, and the mixture was cooled with an ice-water bath. A solution
of bis-1,3-(chlorodimethylsilyl)propane (0.200 g, 0.87 mmol) and dichlorodiphenylsilane (0.226 g, 0.89 mmol) in THF (1 mL) was then added dropwise via syringe over 30 minutes. The flask was then fitted with a condenser and left to stir under argon for 12 hours with gradual warming to room temperature. The reaction mixture was quenched with water (20 mL) and extracted with diethyl ether (3×30 mL). The combined organic fractions were dried over sodium sulfate, filtered, and the solvent was removed under vacuum to yield a colorless oil (0.28 g). Column chromatography on silica gel with hexanes as eluant afforded a colorless oil, which was identified as 1,1,3,3-tetramethyl-2-phenyl-1,2,3-trisilacyclohexane (17; 0.065 g, 28 %) on the basis of the following spectroscopic data: $^1$H NMR (600 MHz, CDCl$_3$), δ 7.49 (m, 2H), 7.30 (m, 3H), 3.85 (s, 1H), 1.86 (m, 1H), 1.79 (m, 1H), 0.89 (m, 2H), 0.78 (m, 2H), 0.24 (s, 6H), 0.16 (s, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$), δ 136.15, 133.47, 128.20, 128.03, 19.25, 19.03 -1.03, -2.31; $^{29}$Si NMR (119 MHz, CDCl$_3$), δ -15.7 (SiMe$_2$, $^2$J$_{Si-H}$ = 149.7 Hz), -67.35 (SiPhH, $^1$J$_{Si-H}$ = 173.6 Hz); GC/MS (EI), m/z (I) = 264 (100, M$^+$), 249 (42), 221 (8), 205 (21), 186 (15), 163 (26), 135 (44), 128 (30), 121 (17), 113 (16), 105 (24), 73 (15), 59 (23), 53 (12), 43 (25); IR (thin film), 3067 (m), 2951 (s), 2894 (s), 2864 (s), 2086 (m), 1483 (m), 1462 (m), 1428 (s), 1409 (s), 1331 (m), 1246 (s), 1113 (s), 1100 (m), 1029 (m), 939 (s), 902 (s), 831 (s), 775 (s), 697 (s); Exact mass calculated for C$_{13}$H$_{24}$Si$_3$ 264.1186, found 264.1184.

The same compound was obtained in 43% isolated yield from reaction of phenyltrichlorosilane (0.87 mmol), bis-1,3-(chlorodimethylsilyl)propane (0.91 mmol), and lithium (5.4 mmol) in THF (1 mL) under the same conditions as those described above.

References
