**Supplementary Information** – W.J. Leigh and X. Li, “Intramolecular nucleophile-induced photorearrangements and silene formation from an ortho-(methoxymethyl)phenylsilacyclobutane.”

1H NMR spectra were recorded in deuteriochloroform or (where noted) cyclohexane-$d_{12}$ solution on Bruker AC200 or DRX500 spectrometers, and are referenced relative to tetramethylsilane. Infrared spectra were recorded as neat liquids on a BioRad FTS-40 FT/IR spectrometer and are reported in wavenumbers (cm$^{-1}$). Ultraviolet absorption spectra were recorded on a Varian Cary 50 spectrophotometer. Low-resolution electron impact mass spectra were determined by GC/MS, using a Hewlett-Packard 5890II gas chromatograph equipped with a HP-5971 mass selective detector and a DB-5 fused silica capillary column (30 m x 0.25 mm; 0.25 µm film; Agilent Technologies). High-resolution electron impact mass spectra and exact masses were determined using a VGH ZABE mass spectrometer.

1-(2-Methoxymethylphenyl)-1-phenylsilacyclobutane (1) was prepared in 73% isolated yield from 1-bromo-2-(methoxymethyl)benzene$^1$ and 1-chloro-1-phenylsilacyclobutane$^2$ according to the method of Auner and Grobe.$^2$ It was isolated as a colorless oil by silica gel column chromatography using 4% ethyl acetate in hexanes as eluant, and identified on the basis of the following spectroscopic data: $^1$H NMR (200 MHz), $\delta$ = 7.78 (d, 1H), 7.56 (m, 2H), 7.37 (m, 6H), 4.36 (s, 2H), 3.09 (s, 3H), 2.22 (m, 2H), 1.56 (t, 4H, $J$ = 8.1 Hz); $^{13}$C NMR (50 MHz), $\delta$ = 144.1, 137.8, 135.6, 135.0, 133.8, 129.6, 129.0, 127.7, 127.0, 126.8, 74.7, 57.8, 17.8, 15.34; $^{29}$Si NMR (99 MHz), $\delta$ = 4.26; IR (film): 3066(m), 3054(m), 2963(m), 2926(s), 2872(m), 1429(s), 1381(m), 1196(s), 1111(s), 963(m), 852(m), 751(m), and 701(m); EIMS, m/z (I) = 268 (1), 253 (22), 240 (10), 225 (27), 211 (24), 209 (23), 208 (100), 195 (35), 181 (14), 178 (18), 165 (49), 163 (41), 162 (61), 131 (20), 119 (23), 105 (55), 91 (20), 59 (62); HRMS, Calcd. for C$_{17}$H$_{20}$OSi (M$^+$): 268.1237; found 268.1283.

**Isolation and Identification of Photoproduts**

1. A solution of 1-(2-methoxymethylphenyl)-1-phenylsilacyclobutane (1, 0.25 g, 0.93 mmol) in hexane (8 mL) was placed in a 1×9 cm quartz tube, sealed with a rubber septum, and deoxygenated with a stream of argon. The solution was irradiated with 11 RPR-2537 lamps in a Rayonet photochemical reactor for 16h to ca. 95% conversion of 1, as estimated by GC. The
solvent was removed on the rotary evaporator to yield a yellow oil, from which 4-6 were isolated as colorless oils by silica gel column chromatography (5% ethyl acetate in hexanes).

**Allyl-methoxy-(2-methylphenyl)-phenylsilane (4):** $^1$H NMR (500 MHz), δ 7.63 (d, 1H), 7.58 (d, 2H), 7.35-7.45 (m, 4H), 7.24 (t, 1H), 7.19 (d, 1H), 5.86 (sx, 1H), 5.01 (d, 1H, J = 16.9 Hz), 4.93 (d, 1H, J = 10.1 Hz), 3.58 (s, 3H), 2.34 (s, 3H), 2.27 (d, 2H, J = 7.8 Hz); $^{13}$C NMR (125 MHz), δ 144.5, 136.0, 135.0, 134.6, 133.3, 132.8, 130.4, 130.1, 130.0, 128.0, 125.0, 115.1, 51.5, 22.9, 21.9; $^{29}$Si NMR (99 MHz), δ -5.39; IR (film), 3003 (m), 2936 (m), 2835 (m), 1631 (m), 1591 (w), 1430 (m), 1187 (m), 1158 (m), 1114 (s), 1086 (s), 993 (m), 901 (m), 742 (m), 701 (m);

EIMS, m/z (I) = 268 (0.4), 228 (20), 227 (100), 195 (30), 165 (11), 119 (9), 105 (13), 59 (22); HRMS, Calc for C$_{17}$H$_{20}$OSi (M$^+$), 268.1283; Found, 268.1276.

**5-Methoxy-5-phenyl-6,7,8,9-tetrahydro-5H-(5-sila)benzocycloheptene (5):** $^1$H NMR (500 MHz), δ 7.63 (d, 2H), 7.57 (d, 1H), 7.42 (m, 4H), 7.27 (d, 1H), 7.18 (d, 1H), 3.61 (s, 3H), 2.89 and 2.75 (m, 2H), 1.78 (m, 4H), 1.17 (m, 2H); $^{13}$C NMR (125 MHz), δ 148.0, 135.5, 135.2, 134.6, 134.5, 130.5, 130.0, 128.7, 128.3, 128.1, 125.5, 51.6, 34.9, 29.3, 22.0, 11.0; $^{29}$Si NMR (99 MHz), δ -2.49; IR (film): 3052 (m), 3004 (m), 2927 (s), 2859 (m), 2833 (m), 1590 (m), 1458 (m), 1430 (s), 1187 (m), 1114 (s), 1084 (s), 782 (s), 739 (s), 704 (s); EIMS, m/z (I) = 268 (4), 227 (16), 208 (15), 191 (21), 190 (100), 177 (22), 163 (36), 162 (52), 136 (19), 131 (39), 105 (45), 91 (23), 59 (82); HRMS, Calc for C$_{17}$H$_{20}$OSi (M$^+$), 268.1283; Found, 268.1267.

**6-Methoxy-6-phenyl-6,7,8,9-tetrahydro-6H-(6-sila)benzocycloheptene (6):** $^1$H NMR (500 MHz), δ 7.54 (d, 2H), 7.39 (m, 3H), 7.10 (s, 4H), 3.45 (s, 3H), 2.87 and 2.80 (p, 2H), 2.60 and 2.57 (AB, 2H, $J_{AB}$ = 14.45 Hz, $I_{inner}/I_{outer}$ = 6.3), 1.96 (m, 2H), 1.13 and 1.00 (p, 2H); $^{13}$C NMR (125 MHz), δ 141.1, 137.6, 135.8, 133.8, 130.0, 129.7, 129.6, 128.1, 126.7, 125.5, 51.3, 35.0, 23.8, 23.6, 13.7; $^{29}$Si NMR (99 MHz), δ -1.15; IR (film), 3069 (m), 3015 (m), 2930 (s), 2861 (m), 2833 (m), 1487 (m), 1453 (m), 1428 (m), 1186 (m), 1154 (m), 1115 (s), 1085 (s), 968 (m), 794 (m), 758 (m), 727 (m), 701 (m); EIMS, m/z (I) = 268 (45), 227 (7), 208 (58), 178 (10), 177 (11), 163 (32), 162 (69), 137 (12), 136 (11), 107 (24), 105 (34), 91 (24), 78 (17), and 58 (100); HRMS, Calc for C$_{17}$H$_{20}$OSi (M$^+$), 268.1283; Found, 268.1274.

2. A solution of 1 (0.25 g, 0.93 mmol) in methanol (16 mL) was placed in a 1×17 cm quartz tube, sealed with a rubber septum, and deoxygenated with a stream of argon. The solution was irradiated with 11 RPR-2537 lamps in a Rayonet photochemical reactor for 2.5h to ca. 95%
conversion of 1, as estimated by GC. The solvent was removed on the rotary evaporator to yield a yellow oil, from which 3, 4, 5, and 7 were isolated as colorless oils after silica gel column chromatography (5% ethyl acetate in hexanes):

**Methoxy-(2-methoxymethylphenyl)-methyl-phenylsilane** (3): $^1$H NMR (200 MHz), $\delta$ 7.73 (d, 1H), 7.57 (m, 2H), 7.40 (m, 6H), 4.44 and 4.34 (AB, 2H, $J_{AB} = 11.8$ Hz, $I_{inner}/I_{outer} = 2.9$), 3.53 (s, 3 H), 3.13 (s, 3H), 0.71 (s, 3H); $^{13}$C NMR (50 MHz), $\delta$ 144.4, 136.4, 135.8, 134.0, 130.0, 129.6, 128.0, 127.9, 126.9, 74.4, 57.7, 51.0, -2.8; $^{29}$Si NMR (99 MHz), $\delta$ -1.36; IR(film), 3054 (m), 2933 (m), 2831 (m), 1591 (m), 1528 (m), 1428 (m), 1410 (m), 1378 (m), 1256 (m), 1191 (m), 1090 (s), 805 (m), 793 (m), 751 (m), 740 (m), 704 (m); EIMS, m/z (I) = 257 (13), 240 (7), 225 (100), 209 (12), 195 (50), 179 (62), 165 (75), 149 (31), 135 (10), 121 (21), 119 (13), 105 (26), 91 (15), 59 (33); HRMS, Calc for C$_{17}$H$_{20}$O$_2$Si (M$^+$-CH$_3$), 257.0998; Found, 257.0996. The NMR and MS data for this compound were identical to those obtained from an authentic sample, prepared in 63% isolated yield by reaction of 1-lithio-2-methoxymethylbenzene (7.46 mmol) with methyl-phenyl-dimethoxysilane (1.63 g, 8.94 mmol) in hexane (50 mL) for 3h at 25 °C, followed by isolation by silica gel column chromatography (10% ethyl acetate in hexane).

**Dimethoxy-phenyl-(3-o-tolyl-propyl)-silane** (7): $^1$H NMR (500 MHz), $\delta$ 7.61 (d, 2H), 7.38-7.45 (m, 3H), 7.09 (m, 4H), 3.58 (s, 6H), 2.61 (t, 2H, $J = 7.8$ Hz), 2.26 (s, 3H), 1.68 (p, 2H), 0.96 (dd, 2H); $^{13}$C NMR (125 MHz), $\delta$ 140.6, 136.0, 134.4, 133.0, 130.3, 130.2, 129.1, 128.1, 126.0, 125.9, 50.8, 36.8, 23.5, 19.4, 12.4; $^{29}$Si NMR (99 MHz), $\delta$ -16.5; IR (film), 3070 (m), 3016 (m), 2938 (s), 2868 (m), 2838 (m), 1491 (m), 1461 (m), 1430 (m), 1188 (s), 1121 (s), 1085 (s), 809 (s), 739 (s), 703 (m); EIMS, m/z (I) = 222 (36), 194 (11), 167 (100), 137 (22), 107 (14), 105 (13), 91 (12) 59 (6); HRMS, Calc for C$_{18}$H$_{24}$O$_2$Si, 300.1546; Found, 300.1538.

3. 1-Methoxy-10-methylene-1-phenyl-(1-sila)spiro[4.5]deca-6,8-diene (8) was detected (along with 4-6) by $^1$H NMR spectroscopy on the crude mixture from photolysis of an argon-saturated 0.1 M solution of 1 in cyclohexane-$d_{12}$ with 11 RPR-2357 lamps to ca. 5% conversion of 1: $^1$H NMR (500 MHz), $\delta$ 6.15 (d, 1H), 5.63 (m, 1H), 5.45 (m, 2H), 4.81 (s, 1H), 4.72 (s, 1H), 3.47 (s, 3H). It was also detected after photolysis of deoxygenated 0.026 M solutions of 1 in hexane and methanol, in a quartz cuvette (1 x 3 cm) equipped with a micro-stirring bar, with 11 RPR-2537 lamps for 5 minutes. The cuvettes were quickly transferred to the Varian Cary 50 spectrophotometer equipped with a magnetic stirrer for spectral and kinetic analysis (see Figure
1). Least squares analysis of log(absorbance) vs. time data afforded pseudo first order rate constants for decay of 8 in hexane and methanol of $(5.7 \pm 1.5) \times 10^{-4} \text{ s}^{-1}$ and $(5.5 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$, respectively.

References


Figure 1. Static and time-resolved UV absorption spectra, recorded on 0.05 M solutions of 9a in hexane or methanol, after brief photolysis with 254 nm light. (a) static UV spectrum in hexane solution; (b) decay of the 333 nm absorption in hexane and methanol solution.

Figure 2. Time-resolved UV absorption spectrum of silene 2, recorded by laser flash photolysis of flowed, 0.003 M acetonitrile solutions of 1. The spectrum shown is the difference between spectra recorded 1-5 µs and 95-100 µs after the 248 nm laser pulse. The insert shows a typical decay trace, recorded at a monitoring wavelength of 330 nm.