

## Supplementary Information

### Steric Effects on Silene Reactivity. The Effects of *ortho*-Methyl-Substituents on the Kinetics and Mechanisms of the Reactions of 1,1-Diarylsilenes with Nucleophiles.

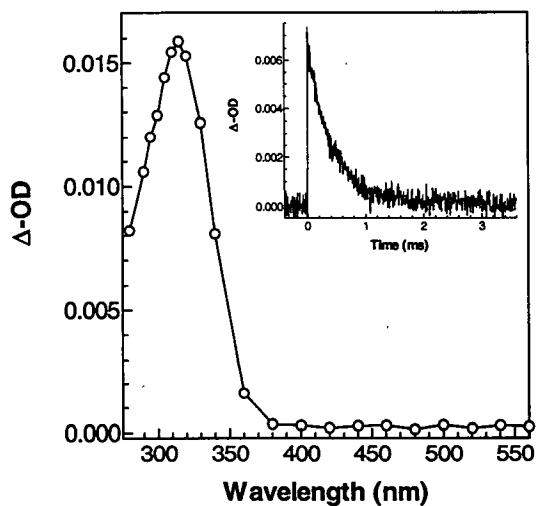
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**Figure 1.** Transient absorption spectrum of 1-(2,4,6-trimethylphenyl)-1-phenylsilene (**5e**) in acetonitrile solution at 25 °C, recorded 12.5-17.5  $\mu$ s after laser excitation. The Insert shows a transient absorption profile recorded at a monitoring wavelength of 315 nm. The short-lived component exhibits  $\lambda_{\text{max}} = 300$  nm.

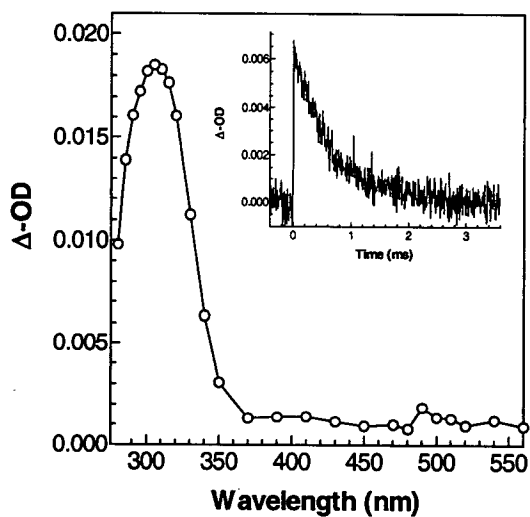
**Figure 2.** Transient absorption spectrum of 1-(2-methylphenyl)-1-(2,6-dimethylphenyl)silene (**5f**) in acetonitrile solution at 25 °C, recorded 12.8-17.8  $\mu$ s after laser excitation. The Insert shows a transient absorption profile recorded at a monitoring wavelength of 310 nm. The short-lived component exhibits  $\lambda_{\text{max}} = 300$  nm.

### Preparation and Characterization of Compounds

**Figure 1.** Transient absorption spectrum of 1-(2,4,6-trimethylphenyl)-1-phenylsilene in acetonitrile solution at 25 °C, recorded 12.5-17.5  $\mu$ s after laser excitation. The Insert shows a transient absorption profile recorded at a monitoring wavelength of 315 nm. The short-lived component exhibits  $\lambda_{\text{max}} = 300$  nm.



**Figure 2.** Transient absorption spectrum of 1-(2-methylphenyl)-1-(2,6-dimethylphenyl)silene in acetonitrile solution at 25 °C, recorded 12.8-17.8  $\mu\text{s}$  after laser excitation. The Insert shows a transient absorption profile recorded at a monitoring wavelength of 310 nm. The short-lived component exhibits  $\lambda_{\text{max}} = 300 \text{ nm}$ .



## Preparation and Characterization of Compounds

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra were recorded in chloroform-*d* using Bruker AV200, DRX500 or AV600 spectrometers, and are referenced to tetramethylsilane. Ultraviolet absorption spectra were recorded on a Varian Cary 50 spectrometer. Gas chromatographic (GC) separations employed a Hewlett-Packard 5890 Series II gas chromatograph equipped with a HP3396A integrator, a flame ionization detector and a DB-5 column (30m, 0.25  $\mu\text{m}$ ; Chromatographic Specialties, Inc.). Gas chromatographic/mass spectrometric (GC/MS) experiments were carried out on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a HP-5971A mass selective detector and a SPB-5 capillary column (30 m, 0.25-ID, 1.0  $\mu\text{m}$ ; Supelco, Inc.). High-resolution electron impact mass spectra and exact masses were determined by on a VG Analytical ZAB-R mass spectrometer. Radial chromatographic separations were carried out using a Chromatotron<sup>®</sup> (Harrison Research, Inc.), with silica gel 60 plates (2-4 mm thick) and using hexane as the elutant. Steady state photolyses were carried out in a Rayonet<sup>®</sup> photochemical reactor (Southern New England Ultraviolet Co.) equipped with a merry-go-round apparatus and 6 RPR-2537 lamps (254 nm). Elemental analyses were performed by Guelph Chemical Laboratories, Inc.

2-Bromo-1,3,5-trimethylbenzene (Aldrich), magnesium (Aldrich), 1,1-dichlorosilacyclobutane (Gelest), pentane (Caledon Reagent), phenyl magnesium bromide (3 M solution in ether; Aldrich), hexanes (BDH Omni-Solv), cyclohexane-*d*<sub>12</sub> (Cambridge Isotope Laboratories, Inc.), 2-bromotoluene (Aldrich), (2-bromo-*m*-xylene (Aldrich), methanol (Aldrich), methanol-*O-d* (Aldrich), glacial acetic acid (Fisher), acetic acid-*O-d* (Aldrich), and dodecane (Lancaster) were used as received from the suppliers. Diethyl ether (BDH Omni-Solv), tetrahydrofuran (Caledon Reagent) and acetonitrile ("190-grade"; Caledon) were dried by

passage through columns of activated alumina. n-Butylamine (Aldrich) was distilled from anhydrous potassium hydroxide.

The 1,1-diarylsilacyclobutanes studied in this work were prepared by modifications of the procedures of Auner and Grobe.<sup>1</sup>

*Preparation of 1,1-bis(2-methylphenyl)silacyclobutane (6c).*

Magnesium (1.95 g, 0.080 mol) was added to a 250 mL 2-neck round bottom flask fitted with an addition funnel and gas inlet, and the apparatus was flame-dried under a flow of dry nitrogen. After cooling, a stir bar and dried THF (80 mL) were added to the reaction vessel, and then 2-bromotoluene (12.05 g, 0.071 mol) was added to the mixture dropwise with stirring over 30 minutes. The reaction mixture was stirred at room temperature for a further 3 hours, resulting in a dark brown solution.

1,1-Dichlorosilacyclobutane (3.11 g, 0.022 mol) and dry THF (10 mL) were placed in the addition funnel and added dropwise with stirring over 30 minutes. The reaction mixture was stirred overnight at room temperature, and then quenched by the slow addition of saturated aqueous ammonium chloride solution (15 mL). The resulting mixture was placed in a 500 mL separatory funnel, diethyl ether (100 mL) was added, the layers were separated, and the organic layer was washed with distilled water (3 x 25 mL). The ether layer was dried over anhydrous magnesium sulfate, filtered, and the solvent was removed on a rotary evaporator to yield the crude product as a yellow oil (2.91 g, 0.012 mol, 68%), which crystallized on cooling.

Recrystallization from 1:4 acetone:hexane afforded colorless crystals, which were recrystallized three more times from a minimum amount of hexane. The compound (m.p. = 109.6 – 110.2 °C) was identified as 1,1-bis(2-methylphenyl)silacyclobutane (**6c**) on the basis of the following spectroscopic data: <sup>1</sup>H NMR,  $\delta$  = 1.56 (t, 4H), 2.25 (m, 2H), 2.27 (s, 6H), 7.11 (d, 2H), 7.23 (t,

2H), 7.30 (t, 2H), 7.68 (d, 2H);  $^{13}\text{C}$  NMR,  $\delta$  = 14.2, 18.6, 22.6, 125.1, 129.7, 129.9, 135.0, 136.0, 143.9;  $^{29}\text{Si}$  NMR,  $\delta$  = 6.16; MS,  $m/z$  (I) = 252 (15), 224 (30), 209 (100), 195(6), 179(23), 178 (30), 160 (23), 133 (33), 119 (31), 105 (30), 93 (27), 53 (26); Exact mass; calculated for  $\text{C}_{17}\text{H}_{20}\text{Si}$ , 252.1334; found 252.1334; Elemental analysis: calculated for  $\text{C}_{17}\text{H}_{20}\text{Si}$ , C = 80.98%, H = 7.99%; found, C = 81.14%, H = 8.15%.

#### *Preparation of 1-phenyl-1-(2,6-dimethylphenyl)silacyclobutane (6d)*

Magnesium (0.71 g, 0.029 mol) was added to a 250 mL 2-neck round bottom flask fitted with an addition funnel and gas inlet, and the apparatus was flame-dried under a flow of dry nitrogen. After cooling, a stir bar and dried THF (70 mL) were added to the reaction vessel, and then 2-bromo-*m*-xylene (4.81 g, 0.026 mol) was added to the mixture dropwise with stirring over 30 minutes. The reaction mixture was stirred at room temperature for a further 2 hours, resulting in a dark brown solution.

A solution of 1,1-dichlorosilacyclobutane (3.41 g, 0.024 mol) in dry THF (10 mL) was added dropwise with stirring over 30 minutes, and the resulting mixture was then stirred at room temperature for a further 15 hours.

Phenyl magnesium bromide (9.7 mL, 0.029 mol) was placed in the addition funnel with a syringe, added dropwise to the reaction mixture over 20 minutes, and the resulting mixture was stirred under reflux for 16 hours. The reaction mixture was cooled to room temperature and quenched by the slow addition of saturated aqueous ammonium chloride solution (15 mL). The resulting solution was placed in a 500 mL separatory funnel, diethyl ether (100 mL) was added, and the layers were separated. The organic layer was washed with distilled water (3 x 25 mL), dried over anhydrous magnesium sulfate, filtered, and the solvent was removed on a rotary evaporator to yield a yellow oil (2.46 g, 0.0098 mol, 41%). The product was obtained as

colorless crystals (m.p. = 34.0 – 34.5 °C) after purification by radial chromatography and three recrystallizations from hexane. It was identified as 1-(2,6-dimethylphenyl)-1-phenylsilacyclobutane (**6d**,) on the basis of the following spectroscopic data:  $^1\text{H}$  NMR,  $\delta$  = 1.63 (m, 4H), 2.24 (m, 1H), 2.34 (s, 6H), 2.41 (m, 1H), 7.02 (d, 2H), 7.23 (t, 1H), 7.38 (m, 3H), 7.59 (d, 1H), 7.61 (d, 1H);  $^{13}\text{C}$  NMR,  $\delta$  = 18.2, 19.8, 22.9, 127.3, 128.2, 129.7, 129.9, 134.4, 134.9, 137.1, 144.1;  $^{29}\text{Si}$  NMR,  $\delta$  = 4.45; MS (EI),  $m/z$  (I) = 252 (86), 237 (9), 224 (74), 209 (100), 195 (14), 179 (53), 165 (25), 146 (28), 131 (24), 119 (21), 105 (93), 91 (17), 79 (17), 55 (6); Exact mass; Calculated for  $\text{C}_{17}\text{H}_{20}\text{Si}$ , 252.1334; found 252.1349; Elemental analysis: for  $\text{C}_{17}\text{H}_{20}\text{Si}$ , C = 80.98% H = 7.99%; found, C = 81.27%, H = 8.22%.

#### *Preparation of 1-mesityl-1-phenylsilacyclobutane (6e)*

Magnesium (3.0 g, 0.12 mol) was placed in a 250 mL 2-neck round bottom flask fitted with an addition funnel under dry nitrogen, and the apparatus was flame-dried. A stir bar and anhydrous diethyl ether (50 mL) were added to the vessel, and then 2-bromo-1,3,5-trimethylbenzene (23.0 g, 0.12 mol) was added dropwise through the addition funnel over a 60-minute period. The reaction mixture was stirred for 24 hours, resulting in the formation of a dark red solution.

A 250 mL 2-neck round bottom flask fitted with an addition funnel, condenser, and gas inlet was flame-dried under dry nitrogen. 1,1-Dichlorosilacyclobutane (16.0 g, 0.10 mol), anhydrous diethyl ether (40 mL), and THF (10 mL) were added to the reaction vessel, the solution of mesityl magnesium bromide was transferred to the addition funnel using a syringe, and was then added dropwise to the reaction mixture over a 60-minute period. The reaction mixture was heated to reflux and stirred for 24 hours, causing it to turn from light green to dark brown in color. The mixture was filtered, the solvents were distilled off at atmospheric pressure,

and then the product was distilled under vacuum (0.2 mm Hg, head temp. = 120°C), yielding crude 1-chloro-1-mesitylsilacyclobutane (14 g), which was identified by comparison of its mass and  $^1\text{H}$  NMR spectra to previously reported data.<sup>2</sup>

A portion of the crude chlorosilacyclobutane (5 g, 0.022 mol) was placed in a flame-dried 250 mL 2-neck round bottom flask fitted with an addition funnel and condenser under dry nitrogen, and dissolved in anhydrous diethyl ether (40 mL). A solution of phenylmagnesium bromide (9 mL, 0.027 mol) was placed in the addition funnel with a syringe and then added dropwise to the reaction mixture over a 30-minute period. The reaction mixture was stirred under reflux for 72 hours, cooled to room temperature, and then quenched by the slow addition of saturated aqueous ammonium chloride solution (15 mL). The resulting mixture was placed in a 500 mL separatory funnel, the aqueous layer was discarded, the remaining solution was washed with distilled water (3 x 25 mL), dried over anhydrous magnesium sulfate, and filtered. The solvent was removed on a rotary evaporator to yield a yellow oil (5.30 g, 0.020 mol, 91%). The product was obtained as colorless crystals (m.p. = 51.0 – 51.5°C) after purification by radial chromatography and three recrystallizations from hexane. It was identified as 1-mesityl-1-phenylsilacyclobutane (**6e**) on the basis of the following spectroscopic data:  $^1\text{H}$  NMR,  $\delta$  = 1.56 (m, 4H), 2.22 (m, 9H), 6.74 (s, 2H), 7.21 (m, 3H), 7.52 (m, 2H);  $^{13}\text{C}$  NMR,  $\delta$  = 17.8, 19.7, 21.2, 22.7, 128.0, 128.6, 129.4, 131.2, 134.2, 137.1, 139.6, 144.0;  $^{29}\text{Si}$  NMR,  $\delta$  = 4.05; MS (EI),  $m/z$  (I) = 266 (89), 238 (78), 237 (54), 225 (69), 224 (94), 223 (100), 221 (22), 195 (25), 193 (43), 179 (22), 178 (23), 146 (29), 145 (25), 119 (27), 105 (77), 53 (27); Exact mass; calculated for  $\text{C}_{18}\text{H}_{22}\text{Si}$ , 266.1491; found 266.1487; Elemental analysis: calculated for  $\text{C}_{18}\text{H}_{22}\text{Si}$ , C = 81.22%, H = 8.33%; found, C = 81.57%, H = 8.41%.



*Preparation of 1-(2,6-dimethylphenyl)-1-(2-methylphenyl)silacyclobutane (6f)*

Magnesium (0.74 g, 0.030 mol) was added to a 250 mL 2-neck round bottom flask fitted with an addition funnel and gas inlet, and the apparatus was flame-dried under a flow of dry nitrogen. After cooling, a stir bar and dried THF (50 mL) were added to the reaction vessel, and then 2-bromo-*m*-xylene (5.0 g, 0.027 mol) was added. The reaction mixture was refluxed for 4 h and then stirred at room temperature for a further 24 hours. Most of the THF was distilled off under nitrogen, hexane (50 mL) was added, and the resulting mixture was stirred for 20 minutes. The hexane solution was transferred to a fresh flask using a pipette to separate it from the magnesium salts, the solvent was distilled off, and the resulting yellow liquid was distilled under vacuum to yield a colorless liquid (b.p. 115 °C (0.02 mm Hg), 1.08 g, 0.0051 mol, 19%), which was identified as pure 1-chloro-1-(2,6-dimethylphenyl)silacyclobutane on the basis of its NMR spectrum: <sup>1</sup>H NMR, δ = 1.83 (m, 4H), 2.35 (m, 2H), 2.46 (s, 6H), 7.04 (d, 2H), 7.28 (t, 1H); <sup>13</sup>C NMR, δ = 18.0, 22.2, 23.8, 127.5, 131.0, 133.6, 143.5

The chlorosilacyclobutane from above was added to a solution of 2-methylphenylmagnesium bromide (prepared from 2-bromotoluene (1.25 g, 0.0073 mol) as described for the synthesis of 6c) in dry THF (40 mL), and the resulting mixture was refluxed under nitrogen for 24 h. The mixture was cooled to room temperature and then quenched with saturated aqueous ammonium chloride (40 mL). Ether (100 mL) was added, the layers were separated, and the organic fraction was washed with saturated aqueous ammonium chloride (25 mL) and water (25 mL). The aqueous fractions were combined and washed with ether (2 x 50 mL). The combined organic fractions were washed with water (2 x 25 mL), saturated brine (25 mL), dried over magnesium sulfate, and filtered. The solvents were removed on the rotary evaporator to yield a colorless oil, which crystallized upon addition of 3:1 methanol:acetone and

cooling. The material was recrystallized twice more from the same solvent mixture and then twice from hexane to yield colorless crystals (0.72 g, 0.00271 mol, 52%; m.p. = 51 – 53°C), which were identified as 1-(2,6-dimethylphenyl)-1-(2-methylphenyl)silacyclobutane (**6f**) on the basis of the following spectroscopic and analytical data:  $^1\text{H}$  NMR,  $\delta$  = 1.83 (m, 4H), 2.34 (m, 1H), 2.52 (m, 1H), 2.55 (d, 6H), 2.58 (d, 3H), 7.14 (d, 2H), 7.35 (m, 3H), 7.45 (t, 1H), 7.88 (d, 1H);  $^{13}\text{C}$  NMR,  $\delta$  = 18.0, 19.4, 22.9, 23.1, 125.1, 127.2, 127.6, 129.7, 129.8, 129.9, 135.3, 135.4, 143.9, 144.1;  $^{29}\text{Si}$  NMR,  $\delta$  = 3.93; MS (EI),  $m/z$  (I) = 266 (27), 251 (7), 238 (7), 223 (100), 209 (7), 192 (18), 178 (20), 165 (8), 145 (7), 131 (13), 119 (15), 105 (17), 91 (11), 77 (6); Exact mass; calculated for  $\text{C}_{18}\text{H}_{24}\text{Si}$ , 266.1491; found 266.1493; Elemental analysis: calculated for  $\text{C}_{18}\text{H}_{24}\text{Si}$ , 81.22%, H = 8.33%; found, C = 81.47%, H = 8.46%.

#### *Preparation of 1,1-bis(2,6-dimethylphenyl)silacyclobutane (6g)*

2,6-Dimethylphenylmagnesium bromide was prepared as described above for **6d**, from 2-bromo-*m*-xylene (11.65 g, 0.063 mol) in dry THF (150 mL), in a 500 mL 2-neck round bottom flask fitted with an addition funnel and condenser under dry nitrogen. A solution of 1,1-dichlorosilacyclobutane (4.23 g, 0.03 mol) in dry THF (100 mL) was then added dropwise over ca. 30 minutes, and the resulting mixture was stirred at reflux for five days. The reaction was quenched by the slow addition of saturated aqueous ammonium chloride solution (100 mL), the mixture was placed in a 500 mL separatory funnel, diethyl ether (150 mL) was added, and the aqueous layer was discarded. The solution was washed with distilled water (2 x 100 mL), dried over anhydrous magnesium sulfate, filtered, and the solvent was removed on a rotary evaporator to yield the product as yellow crystals (4.20 g, 0.015 mol, 50%). These were purified by several recrystallizations from hexane to yield colorless crystals (m.p. = 80 – 81 °C), which were identified as 1,1-bis(2,6-dimethylphenyl)silacyclobutane (**6g**) on the basis of the following

spectroscopic data:  $^1\text{H}$  NMR,  $\delta(\text{ppm}) = 1.67$  (t, 2H), 2.23 (m, 4H), 2.48 (s, 12H), 6.95 (d, 4H), 7.15 (t, 2H);  $^{13}\text{C}$  NMR,  $\delta(\text{ppm}) = 20.3, 22.1, 23.4, 128.1, 129.4, 136.2, 144.1$ ;  $^{29}\text{Si}$  NMR,  $\delta(\text{ppm}) = 0.45$ ; MS (EI),  $m/z$  (I) = 252 (58), 224 (95), 211 (84), 210 (71), 209 (100), 181 (32), 179 (62), 178 (74), 133 (86), 119 (68), 105 (61), 93 (49), 91 (27), 67 (22), 53 (35); Exact mass; calculated for  $\text{C}_{19}\text{H}_{24}\text{Si}$ , 280.1647; found 280.1637; Elemental analysis: calculated for  $\text{C}_{19}\text{H}_{24}\text{Si}$ , C = 81.45%, H = 8.63%; found, C = 81.25%, H = 8.85%.

### *Steady State Photolysis Experiments*

A 0.05M solution of the compound of interest (**6c-g**) 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 20 minutes, and then methanol (20  $\mu\text{L}$ , 0.5 M) was added *via* syringe. The solutions were photolyzed for 1 hour (10 – 15% conversion) with six RPR-2537 lamps, with periodic monitoring by GC, GC/MS and  $^1\text{H}$  NMR spectroscopy. In each case, the NMR spectrum showed evidence for the formation of ethylene and the corresponding methoxysilane (**7c-g**), which could be identified by their characteristic singlets at  $\delta$  0.63-0.84 and  $\delta$  3.49-3.58 ppm due to the Si-Me and Si-OMe methyl groups, respectively.<sup>3</sup> The latter products were also detected by GC and GC/MS analysis of the crude photolysis mixtures, along with one or two additional products whose mass spectra indicated to be isomeric with the starting silacyclobutane. The alkoxy silanes **7c** and **7g** were rigorously identified by GC coinjection with authentic samples, prepared as described below, while **7d-f** were identified by GC/MS and  $^1\text{H}$  NMR analysis of the crude reaction mixtures. A single isomeric product was obtained in the photolysis of **6c**, and was identified as 1-(2-methylphenyl)-1-(3-methylphenyl)silacyclobutane (**8c**) by GC coinjection with an authentic sample, whose preparation and characterization are also

described below. Product yields were determined by GC, without correction for fid response factors, and are listed in Table A1.

*Preparation of methoxymethylbis(2-methylphenyl)silane (7c).*

Magnesium (4.3 g, 0.176 mol) was added to a 250 mL 2-neck round bottom flask fitted with an addition funnel under dry nitrogen, and the apparatus was flame-dried. A stir bar and dry THF (120 mL) were added to the reaction vessel. 2-Bromotoluene (15.00 g, 0.088 mol) was then added dropwise over 1.5 h., and the reaction mixture was stirred for 1 h.

Trichloromethylsilane (6.12 g, 0.041 mol) was added dropwise to the reaction mixture over 15 minutes, and the resulting mixture was then stirred at reflux for three days. The mixture was filtered into a clean, dry flask, to which methanol (30 mL) was added over five minutes. Diethyl ether (150 mL) and saturated aqueous sodium chloride (100 mL) were added, the mixture was placed in a 500 mL separatory funnel, and the aqueous layer was discarded. The ether layer was washed with distilled water (2 x 50 mL), dried over anhydrous magnesium sulfate, filtered, and the solvent was removed on a rotary evaporator to yield the crude product as a yellow oil (5.39 g, 0.021 mol, 51%). The material was distilled under vacuum to yield clear colorless oil identified as **7c** (b.p. 139 °C (0.5 torr)) on the basis of the following spectroscopic data: <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.79 (s, 3H), 2.36 (s, 6H), 3.58 (s, 3H), 7.21 (d, 2H), 7.27 (t, 2H), 7.38 (t, 2H), 7.66 (d, 2H); <sup>13</sup>C NMR: -2.1, 22.7, 50.8, 125.1, 129.9, 130.0, 130.1, 135.5, 144.0; <sup>29</sup>Si NMR: -0.59; GC/MS (EI): 256(6), 241(100), 223(17), 209(31), 193(6), 181(8), 179(17), 165(47), 152(7), 149(19), 135(17), 119(17), 105(10), 91(22), 65(11), 59(8). Exact mass: calculated for C<sub>16</sub>H<sub>20</sub>OSi, 256.1283; found, 256.1272.

*Preparation of bis(2,6-dimethylphenyl)methoxymethylsilane (7g).*

The compound was prepared by refluxing the corresponding ethoxysilane (1.34 g, 0.0045 mol) in dry methanol for 2 h, followed by removing the solvent on the rotary evaporator. The light yellow oil that was obtained was distilled under vacuum, affording the compound as a colorless oil (1.03 g, 0.0036 mol, 81%) (b.p. 80 °C (0.02 torr)). It was identified as 7g on the basis of the following spectroscopic data: <sup>1</sup>H NMR,  $\delta$  = 0.79 (s, 3H), 2.37 (s, 12H), 3.41 (s, 3H), 6.97 (d, 4H), 7.17 (t, 2H); <sup>13</sup>C NMR,  $\delta$  = 4.5, 23.6, 49.9, 128.2, 129.2, 136.1, 143.7; MS (EI), *m/z* (I) = 284 (4), 269 (18), 237 (8), 178 (100), 163 (100), 146 (25), 133 (27), 105 (29), 91, 21), 59 (38); Exact mass; calculated for C<sub>17</sub>H<sub>20</sub>Si, 284.1596; found 284.1565

Ethoxymethylbis(2,6-dimethylphenyl)silane was inadvertently prepared by stirring a solution of 2,6-dimethylphenylmagnesium bromide (prepared from 2-bromo-*m*-xylene (10.0 g, 0.054 mol) and magnesium (1.44 g, 0.059 mol) in anhydrous ether, as described above) and methyltrichlorosilane (15.0 g, 0.1 mol) in anhydrous ether (150 mL) for 72 h at room temperature, in an attempt to synthesize dichloro(methyl)(2,6-dimethylphenyl)silane. The solvent and excess methyltrichlorosilane were distilled off, dry hexane (25 mL) was added to the oily solid residue, and the resulting solution was transferred to a 100 mL round bottom flask with a pipet. The latter was repeated with two more 25 mL portions of dry hexane. The combined hexane extracts were distilled at atmospheric pressure to remove the solvent, and then the distillation was continued under vacuum. Two fractions were collected: 2-bromo-*m*-xylene (0.68 g; b.p. 35 °C (0.1 torr)) and ethoxymethylbis(2,6-dimethylphenyl)silane (3.50 g, 0.0117 mol, 22%) (b.p. 120 °C (0.1 torr)), which was identified on the basis of the following spectroscopic data: <sup>1</sup>H NMR,  $\delta$  = 0.96 (s, 3H), 1.36 (t, 3H), 2.54 (s, 12H), 3.89 (q, 2H), 7.11 (d, 4H), 7.31 (t, 2H); <sup>13</sup>C NMR,  $\delta$  = 5.4, 18.5, 23.8, 58.3, 128.3, 129.3, 136.5, 143.8; <sup>29</sup>Si NMR,  $\delta$  =

-1.93; MS (EI),  $m/z$  (I) = 298 (1), 283 (20), 239 (12), 207 (5), 192 (75), 177 (100), 165 (10), 149 (80), 133 (20), 105 (39), 91 (34), 77 (25).

*Methoxymethyl(2,6-dimethylphenyl)phenylsilane (7d)*. MS (EI),  $m/z$  (I) = 256 (5), 197 (20), 196 (100), 195 (74), 183 (20), 182 (15), 181 (75), 180 (14), 165 (12), 155 (6), 146 (6), 106 (7), 105 (51), 103 (7), 79 (10), 77 (5), 53 (7).

*Methoxymethyl(2,4,6-trimethylphenyl)phenylsilane (7e)*. MS (EI),  $m/z$  (I) = 270 (15), 257 (5), 256 (23), 255 (100), 224 (8), 223 (37), 195 (6), 193 (16), 192 (28), 179 (6), 178 (10), 177 (21), 165 (7), 151 (11), 147 (5), 145 (5), 121 (17), 119 (9), 115 (5), 105 (10), 91 (11), 78 (6), 77 (6), 59 (15).

*Methoxymethyl(2,6-Dimethylphenyl)(2-methylphenyl)silane (7f)*. MS (EI),  $m/z$  (I) = 270 (9), 256 (20), 255 (95), 237 (6), 224 (9), 223 (46), 195 (6), 193 (7), 192 (6), 180 (8), 179 (32), 178 (100), 166 (8), 163 (56), 149 (23), 147 (8), 145 (6), 135 (16), 133 (16), 131 (10), 119 (17), 107 (7), 105 (17), 103 (5), 92 (5), 91 (14), 77 (7), 65 (6), 59 (12).

*Preparation of 1-(2-methylphenyl)-1-(3-methylphenyl)silacyclobutane (8c)*.

Magnesium filings (5.3 g, 0.2 mol) were added to a 250 mL 2-neck round bottom flask fitted with an addition funnel under dry N<sub>2</sub>. The apparatus was flame dried. A stir bar and 100 mL of dried THF were added to the reaction vessel. 2-Bromotoluene (3.74 g, 0.022 mol) was added to the reaction vessel dropwise through the addition funnel over a 120-minute period, and the resulting mixture was stirred for 1 hour.

1,1-Dichlorosilacyclobutane (2.82 g, 0.02 mol) was placed in the addition funnel and added dropwise to the reaction mixture over a 30-minute period and stirred overnight under reflux conditions. 3-Bromotoluene (3.74 g, 0.022 mol) was added to the reaction vessel dropwise through the addition funnel over a 30-minute period. The reaction mixture was stirred for 2 days

under reflux. The reaction was quenched by the slow addition of saturated aqueous ammonium chloride solution (100 mL). The resulting mixture was then placed in a 500 mL separatory funnel, ether (100 mL) was added, and the aqueous layer was discarded. The remainder was washed with distilled water (2 x 100 mL), dried over anhydrous magnesium sulfate, filtered, and the solvent was removed on a rotary evaporator to yield the crude product (4.7 g, 0.0186 mol, 93%).

The crude product was purified by a radial chromatography using hexane as eluant to yield a clear colorless oil, which was identified as **8c** on the basis of the following spectroscopic data: <sup>1</sup>H NMR, (CDCl<sub>3</sub>): 1.58 (t, 4H), 2.31 (m, 2H), 2.33 (s, 3H), 2.38 (s, 3H), 7.22-7.49 (m, 6H), 7.69 (d, 2H); <sup>13</sup>C NMR: 14.41, 18.7, 21.6, 22.7, 125.2, 128.1, 129.6, 130.1, 130.5, 131.3, 134.8, 135.00, 135.5, 137.2, 137.5, 143.9; <sup>29</sup>Si: 6.70; GC/MS (EI), m/z: 252(14), 225(11), 224(49), 223(25), 222(5), 211(18), 210(21), 209(100), 207(9), 195(6), 181(7), 179(16), 178(9), 165(9), 119(10), 105(5), 93(6), 91(5); Exact mass: calculated for C<sub>17</sub>H<sub>20</sub>Si, 252.1334; found, 252.1333.

## References

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