

## Dehydrogenative Coupling of Thiol with Hydrosilane Catalyzed by an Iron Complex

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### Experimental Procedures

**General Methods:** All manipulations were carried out with standard Schlenk techniques under a nitrogen atmosphere. Toluene was distilled from sodium and benzophenone prior to use and stored under nitrogen. The other chemicals were commercially available. NMR spectra (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>29</sup>Si{<sup>1</sup>H}) were recorded on a JEOL EX-400 spectrometer. The residual peaks of the solvent were used as the reference for <sup>1</sup>H NMR spectra. For <sup>13</sup>C{<sup>1</sup>H} NMR spectra, solvent signals were used as the chemical-shift reference. Peak positions of the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum were referenced to external tetramethylsilane (δ = 0 ppm).

**Preparation of methyl complexes, silyl-pyridine iron complex 2 and disulfide complex 3:** C<sub>5</sub>R<sub>5</sub>Fe(CO)<sub>2</sub>Me (R<sub>5</sub> = H<sub>5</sub>,<sup>1</sup> Me<sub>5</sub>,<sup>2</sup> H<sub>4</sub>Me,<sup>3</sup> H<sub>4</sub>I<sup>4</sup>), C<sub>5</sub>R<sub>5</sub>Mo(CO)<sub>3</sub>Me ( R<sub>5</sub> =

H<sub>5</sub>,<sup>5</sup> Me<sub>5</sub>,<sup>6</sup> H<sub>4</sub>Me<sup>7</sup>), C<sub>5</sub>H<sub>5</sub>Fe(CO)(pyridine)(SiEt<sub>3</sub>) (**2**)<sup>8</sup> and [C<sub>5</sub>H<sub>5</sub>Fe(CO)SPh]<sub>2</sub> (**3**)<sup>9</sup> were prepared according to the literature methods.

**Dehydrogenative coupling reactions of thiol with Et<sub>3</sub>SiH catalyzed by 1:** Toluene (0.46 mL), CpFe(CO)<sub>2</sub>Me (**1**) (0.112 mmol), thio (1.12 mmol), and Et<sub>3</sub>SiH (11.2 mmol) were charged in a Schlenk tube, and the solution was heated at 80 °C for 24 h. The solvent and Et<sub>3</sub>SiH were removed under vacuum, and then the residue was dissolved in C<sub>6</sub>D<sub>6</sub>. Diphenylmethane (0.560 mmol) was added to the solution as an internal standard and the <sup>1</sup>H NMR spectrum was measured at room temperature. The amount of the triethylsilylthioether produced was evaluated by the relative intensity of signals of the product and the internal standard.

The triethylsilylthioethers produced were identified by the comparison of the NMR spectra of the authentic compounds prepared according to the literature method<sup>10</sup> for EtSSiEt<sub>3</sub>, <sup>t</sup>BuSSiEt<sub>3</sub>, PhSSiEt<sub>3</sub>, PhCH<sub>2</sub>SSiEt<sub>3</sub>. These <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR data were shown below, because of no report in the literature.<sup>10</sup>

**EtSSiEt<sub>3</sub>:** Colorless liquid. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 0.66 (q, *J*<sub>HH</sub> = 7.8 Hz, 6H, CH<sub>3</sub>CH<sub>2</sub>Si), 1.00 (t, *J*<sub>HH</sub> = 7.8 Hz, 9H, CH<sub>3</sub>CH<sub>2</sub>Si), 1.17 (t, *J*<sub>HH</sub> = 7.4 Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>S), 2.32 (q, *J*<sub>HH</sub> = 7.4 Hz, 2H, CH<sub>3</sub>CH<sub>2</sub>S). <sup>13</sup>C {<sup>1</sup>H} NMR (100.4 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 5.71 (CH<sub>3</sub>CH<sub>2</sub>Si), 7.59 (CH<sub>3</sub>CH<sub>2</sub>Si), 18.88 (CH<sub>3</sub>CH<sub>2</sub>S), 20.17 (CH<sub>3</sub>CH<sub>2</sub>S). <sup>29</sup>Si {<sup>1</sup>H} NMR (79.3 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 21.66.

**<sup>t</sup>BuSSiEt<sub>3</sub>:** Colorless liquid. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 0.72 (q, *J*<sub>HH</sub> = 7.7 Hz, 6H, CH<sub>3</sub>CH<sub>2</sub>), 1.01 (t, *J*<sub>HH</sub> = 7.7 Hz, 9H, CH<sub>3</sub>CH<sub>2</sub>), 1.37 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>CS). <sup>13</sup>C {<sup>1</sup>H} NMR (100.4 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 7.10 (CH<sub>3</sub>CH<sub>2</sub>), 7.67 (CH<sub>3</sub>CH<sub>2</sub>), 35.66 (CH<sub>3</sub>CS), 44.28 (CH<sub>3</sub>CS). <sup>29</sup>Si {<sup>1</sup>H} NMR (79.3 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 16.75.

**PhSSiEt<sub>3</sub>**: Colorless liquid. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 0.64 (q, *J*<sub>HH</sub> = 7.8 Hz, 6H, CH<sub>3</sub>CH<sub>2</sub>), 0.96 (t, *J*<sub>HH</sub> = 7.8 Hz, 9H, CH<sub>3</sub>CH<sub>2</sub>), 6.97 (d, *J*<sub>HH</sub> = 7.4 Hz, 2H, Ph), 7.49- 7.51 (m, 3H, Ph). <sup>13</sup>C {<sup>1</sup>H} NMR (100.4 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 5.70 (CH<sub>3</sub>CH<sub>2</sub>), 7.41 (s, CH<sub>3</sub>CH<sub>2</sub>), 126.95, 128.98, 132.01, 135.59 (Ph). <sup>29</sup>Si {<sup>1</sup>H} NMR (79.3 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 23.37.

**PhCH<sub>2</sub>SSiEt<sub>3</sub>**: Colorless liquid. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 0.62 (q, *J*<sub>HH</sub> = 8.0 Hz, 6H, CH<sub>3</sub>CH<sub>2</sub>), 0.95 (t, *J*<sub>HH</sub> = 8.0 Hz, 9H, CH<sub>3</sub>CH<sub>2</sub>), 3.54 (s, 2H, CH<sub>2</sub>Ph), 7.02 (m, 1H, Ph), 7.10 (m, *J*<sub>HH</sub> = 7.3 Hz, 2H, Ph), 7.26 (m, *J*<sub>HH</sub> = 7.3 Hz, 2H, Ph). <sup>13</sup>C {<sup>1</sup>H} NMR (100.4 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 5.69 (CH<sub>3</sub>CH<sub>2</sub>), 7.57 (CH<sub>3</sub>CH<sub>2</sub>), 30.30 (CH<sub>2</sub>Ph), 126.98, 128.60, 128.88, 141.35 (Ph). <sup>29</sup>Si {<sup>1</sup>H} NMR (79.3 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 22.65.

**C<sub>6</sub>H<sub>11</sub>SSiEt<sub>3</sub>**: As this compound has not been reported, it was prepared by modification of the literature method.<sup>10</sup> To a solution of dry ether (50 mL) containing C<sub>6</sub>H<sub>11</sub>SH (44.6 mmol) was added slowly a solution of dry ether (25 mL) containing triethylchlorosilane (44.6 mmol) and triethylamine (44.6 mmol). The mixture was stirred for 24 h at room temperature, and then filtered through Celite. The volatile materials were removed from the filtrate at 420 Pa to leave a colorless liquid of C<sub>6</sub>H<sub>11</sub>SSiEt<sub>3</sub> in 71% yield. The compound was so volatile and hygroscopic that the correct elemental analysis data could not be obtained, though satisfactory spectroscopic data were obtained. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ = <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 0.69 (q, *J*<sub>HH</sub> = 8.0 Hz, 6H, CH<sub>3</sub>CH<sub>2</sub>), 1.00 (t, *J*<sub>HH</sub> = 8.0 Hz, 9H, CH<sub>3</sub>CH<sub>2</sub>), 1.47- 1.50 (m, 2H, Cy), 1.64- 1.68 (m, 4H, Cy), 1.92- 1.96 (m, 4H, Cy), 2.70- 2.76 (t, 1H, Cy). <sup>13</sup>C {<sup>1</sup>H} NMR (100.4 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 6.23 (s, CH<sub>3</sub>CH<sub>2</sub>), 7.68 (s, CH<sub>3</sub>CH<sub>2</sub>), 25.91, 26.58, 38.47, 40.15 (s, Cy). <sup>29</sup>Si {<sup>1</sup>H} NMR (79.3 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 20.78.

***p*-MeOPhSSiEt<sub>3</sub>**: A treatment of *p*-MeOPhSH with Et<sub>3</sub>SiH in a similar manner to that for C<sub>6</sub>H<sub>11</sub>SSiEt<sub>3</sub> gave a colorless liquid of *p*-MeOPhSSiEt<sub>3</sub> in 62% yield. Elemental Analysis C<sub>13</sub>H<sub>22</sub>OSi : C, 61.36; H, 8.71 %. Found : C, 61.39; H, 8.81 %. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 0.66 (q, *J*<sub>HH</sub> = 7.9 Hz, 6H, CH<sub>3</sub>CH<sub>2</sub>), 0.98 (t, *J*<sub>HH</sub> = 7.9 Hz, 9H, CH<sub>3</sub>CH<sub>2</sub>), 3.25 (s, 3H, CH<sub>3</sub>O), 6.61 (d, *J*<sub>HH</sub> = 8.6 Hz, 2H, Ph), 7.39 (d, *J*<sub>HH</sub> = 8.9 Hz, 2H, Ph). <sup>13</sup>C {<sup>1</sup>H} NMR (100.4 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 17.58 (CH<sub>3</sub>CH<sub>2</sub>), 19.41 (CH<sub>3</sub>CH<sub>2</sub>), 66.85 (s, CH<sub>3</sub>O), 126.69, 133.80, 148.71, 171.43 (Ph). <sup>29</sup>Si {<sup>1</sup>H} NMR (79.3 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ = 22.87.

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