

### Supporting Material for:

The substituent-dependent base-treatment chemistry of ( $\eta^5$ - $C_5H_5$ )Fe(CO) $_2$ SiR $_2$ SiR $_2$ Cl: Formation of 1,2-disila-3-metallacyclobutanes, their ring-opened polymers, migrations and substitutions

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### Experimental Procedures:

**Synthesis of PhSiMeBuSiMeBuPh:** Lithium wire (0.68 g, 97.1 mmol, Aldrich) was quickly cut into small pieces and added to 200 mL of dry THF in a 500 mL three-necked flask equipped with pressure-equalized addition funnel. The system was purged with dry argon. The chlorosilane, PhMeBuSiCl (20.7 g, 97.4 mmol,) in 30 mL THF was added over 2 h at 0 °C. The reaction mixture was stirred for 3 days at room temperature, the color of the mixture changed from dark brown to colorless with the precipitation of salts. THF was pumped off, and 100 mL hexane was added to the

mixture, which was filtered on Celite to remove lithium chloride and unreacted lithium. Hexane was evaporated from the solution, and the fractional distillation gave 12.6 g, (35 %) of disilane as a colorless viscous liquid, bp 150-158 °C (0.1 torr). NMR spectra showed mixture of two diastereomers in the ratio of 1:1. <sup>1</sup>H NMR (300 MHz) (CDCl<sub>3</sub>): δ 0.41, 0.42 (s, 6H, Me), 0.91, 1.36 (m, 18 H, Bu), 7.34-7.36, 7.43-7.44 (m, 10 H, Ph). <sup>13</sup>C NMR (75.4 MHz) (CDCl<sub>3</sub>): δ -5.94, -5.79 (Me), 13.18, 13.27, 13.69, 26.55, 26.63 (Bu), 127.6, 128.3, 134.1, 138.3, (ipso), <sup>29</sup>Si NMR (59.6 MHz) (CDCl<sub>3</sub>): δ -19.64, -19.62. Anal. Calcd. for C<sub>23</sub>H<sub>37</sub>Si<sub>2</sub>: C, 74.72; H, 10.09. Found: C, 74.41; H, 9.91.

**Synthesis of ClSiMeBuSiMeBuCl:** A 250- ml Schlenk flask was charged with 6.6 g, 17.85 mmol of disilane, PhMeBuSiSiMeBuPh in 50 mL of dry benzene, and 0.26 g of anhydrous AlCl<sub>3</sub>. Dry HCl gas was bubbled slowly into the reaction flask through septum at room temperature. An exothermic reaction occurred. The progress of the chlorination was monitored by <sup>29</sup>Si NMR spectroscopy. After 4 h, the chlorination was complete. Benzene was distilled out under reduced pressure (30 - 40 mm Hg) and 50 ml of hexane was added. White gelatinous precipitate was filtered over Celite and hexane was evaporated under reduced pressure (40-50 mm Hg). The fractional distillation of the residue gave 2.6 g ( 54 %) of ClSiMeBuSiMeBuCl. bp 80-82 °C at 1 mm Hg. NMR spectra showed mixture of two diastereomers in the ratio of 1:1. <sup>1</sup>H NMR (300 MHz) (CDCl<sub>3</sub>): δ 0.54, 0.545 (s, 6H, Me), 0.90, 0.93, 1.40 (m, 18 H, Bu). <sup>13</sup>C NMR (75.4 MHz) (CDCl<sub>3</sub>): δ -0.11, 0.014 (Me), 13.61, 17.40, 17.44, 25.15, 25.20, 26.01 (Bu), <sup>29</sup>Si NMR (59.6 MHz) (CDCl<sub>3</sub>): δ 19.17, 19.37. Anal. Calcd. for C<sub>10</sub>H<sub>24</sub>Cl<sub>2</sub>Si<sub>2</sub>: C, 44.26; H, 8.91. Found: C, 45.51; H, 8.97.

**Data for PhSiMe<sub>2</sub>SiBu<sub>2</sub>Ph:** bp 135-140 °C at 0.3 mm Hg. <sup>1</sup>H NMR (300 MHz) (CDCl<sub>3</sub>): δ 0.41, (s, 6H, Me), 0.90, 1.36 (m, 18 H, Bu), 7.32-7.35, 7.40-7.41 (m, 10 H, Ph). <sup>13</sup>C NMR (75.4 MHz) (CDCl<sub>3</sub>): δ -2.86, (Me), 11.40, 13.67, 26.74, 26.78 (Bu), 127.6, 128.3, 133.9, 134.4, 137.4, 137.4 (ipso), 139.5 (ipso), <sup>29</sup>Si NMR (59.6 MHz) (CDCl<sub>3</sub>): δ -21.69, -17.75. Anal. Calcd. for C<sub>23</sub>H<sub>37</sub>Si<sub>2</sub>: C, 74.72; H, 10.09. Found: C, 73.91; H, 10.05.

**Data for ClSiMe<sub>2</sub>SiSiBu<sub>2</sub>Cl:** bp 96-100 °C at 3 mm Hg. <sup>1</sup>H NMR (300 MHz) (CDCl<sub>3</sub>): δ 0.57, (s, 6H, Me), 0.90, 0.92, 1.39 (m, 18 H, Bu). <sup>13</sup>C NMR (75.4 MHz) (CDCl<sub>3</sub>): δ 2.28 (Me), 13.61, 15.86, 25.37, 26.14 (Bu), <sup>29</sup>Si NMR (59.6 MHz, CDCl<sub>3</sub>): δ 18.47, 19.62. Anal. Calcd. for C<sub>10</sub>H<sub>24</sub>Cl<sub>2</sub>Si<sub>2</sub>: C, 44.26; H, 8.91. Found: C, 45.41; H, 9.43.

**Synthesis of FpSiMe<sub>2</sub>SiBu<sub>2</sub>Cl, 1c:** To 50 mL of a THF solution of Fp<sup>-</sup>Na<sup>+</sup> (prepared from 2.0 g (5.65 mmol) of [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>]<sub>2</sub>) was added *via* a syringe 3.06 g (11.3 mmol) of 1,2-dichloro-1,1-dibutyl-2,2-dimethylidisilane in 10 mL of THF at -78 °C. The solution was stirred at low temperature for 2 h and then warmed to room temperature and further stirred overnight. The solvent was removed under vacuum and the residue was extracted with 70 mL of hexane. The solution was filtered over Celite and the solvent was removed under vacuum. The molecular distillation of the red oily residue at 135-150 °C at 0.08 mm Hg afforded red oil. Yield: 2.8 g (60 %). The NMR spectral data indicated the exclusive formation of only FpSiMe<sub>2</sub>SiBu<sub>2</sub>Cl. No isomeric iron complex, FpSiBu<sub>2</sub>SiMe<sub>2</sub>Cl was obtained. <sup>1</sup>H NMR (300 MHz) (C<sub>6</sub>D<sub>6</sub>): δ 0.60, (s, 6H, Me), 0.92, 1.02, 1.39, 1.56, (m, 18 H, Bu), 4.28 (s, 5 H, Cp). <sup>13</sup>C NMR (75.4 MHz) (C<sub>6</sub>D<sub>6</sub>): δ 4.11 (Me), 13.96, 18.00, 26.25, 26.85 (Bu), 83.42

(Cp), 215.43 (CO).  $^{29}\text{Si}$  NMR (59.6 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  17.53, 30.34. IR ( $\nu$  CO,  $\text{cm}^{-1}$ , hexane): 1999.8, 1949.1. Anal. Calcd. for  $\text{C}_{17}\text{H}_{29}\text{ClFeO}_2\text{Si}_2$ : C, 49.45; H, 7.08. Found: C, 49.66; H, 7.30.

**Data for FpSiMeBuSiMeBuCl, 1d:** (Mixture of two diastereomers in 1:1 ratio)  $^1\text{H}$  NMR (300 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.54, 0.55, (s, 6H, Me), 0.91, 0.92, 0.94, 1.38, 1.40, 1.48, (m, 18 H, Bu), 4.32 (s, 5 H, Cp).  $^{13}\text{C}$  NMR (75.4 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.62, 0.83, 2.18 (Me), 13.94, 14.00, 19.81, 21.09, 25.88, 25.94, 26.64, 27.10, 28.97, 29.03 (Bu), 83.42 (Cp), 215.30, 215.51 (CO).  $^{29}\text{Si}$  NMR (59.6 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  20.82, 20.89 (Si-Cl), 30.01 (Fe-Si). IR ( $\nu$  CO,  $\text{cm}^{-1}$ , hexane): 1999.8, 1949.1. Anal. Calcd. for  $\text{C}_{17}\text{H}_{29}\text{ClFeO}_2\text{Si}_2$ : C, 49.45; H, 7.08. Found: C, 50.36; H, 7.76.

**Data for FpSiBu<sub>2</sub>SiBu<sub>2</sub>Cl, 1b:**  $^1\text{H}$  NMR (300 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.92, 0.96, 1.38, 1.42, (m, 36 H, Bu), 4.38 (s, 5 H, Cp).  $^{13}\text{C}$  NMR (75.4 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  13.92, 13.96, 19.41, 19.48, 26.30, 26.83, 27.22, 29.28 (Bu), 83.52 (Cp), 215.82 (CO).  $^{29}\text{Si}$  NMR (59.6 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  31.24, 25.28. IR ( $\nu$  CO,  $\text{cm}^{-1}$ , hexane): 1998.8, 1948.3. Anal. Calcd. for  $\text{C}_{23}\text{H}_{41}\text{ClFeO}_2\text{Si}_2$ : C, 55.58; H, 8.31. Found: C, 55.66; H, 8.60.

**Synthesis of polymer 2:** In a 50 mL round-bottomed Schlenk flask was placed 1.21 g (3.68 mmol) of FpSiMe<sub>2</sub>SiMe<sub>2</sub>Cl in 15 mL of THF. To this solution at  $-5^\circ\text{C}$  was added 8 mL (3.70 mmol) of freshly prepared LDA in the same solvent via cannula. The color of the reaction mixture changed to dark red-brown immediately. The solution was stirred for 30 min at low temperature and for 2 h at room temperature. Light brown polymeric material dropped out of solution. The polymer was filtered on sintered crucible and washed repeatedly with hexanes and dried under vacuum. Yield

0.8 g (2.73 mmol, 74 %).  $^1\text{H}$  NMR (300 MHz) (THF- $d_8$ ):  $\delta$  0.42 (bd, Me), 4.77, 4.85 (unresolved m, Cp),  $^{13}\text{C}$  NMR (75.4 MHz) (THF- $d_8$ ):  $\delta$  -1.59 (Me), 3.69 (Me), 86.9, 89.2 (Cp), 216.7 (CO). Solid state  $^{13}\text{C}$  NMR (62.9MHz, CP MS) -0.76, 1.85, 3.75 (Me), 85.8, 92.3 (bd, Cp), 219.4 (CO);  $^{29}\text{Si}$  NMR (59.6 MHz, THF- $d_8$ ):  $\delta$  21.5, -10.9.  $^{29}\text{Si}$  NMR (49.7 MHz, CP, MS) 22.0, -8.2 IR ( $\nu$  CO,  $\text{cm}^{-1}$ , THF): 1986, 1934. The carbon values obtained from the combustion based elemental analysis for polymer was found to be low by ca. 2% presumably due to the formation of thermally stable ceramics at elevated temperature.

**Synthesis Disilametallacycle, 3c:** A 50 mL Schlenk flask was charged with 0.62 g (1.50 mmol) of  $\text{FpSiMe}_2\text{SiBu}_2\text{Cl}$  in 10 mL of dry THF. To this solution at  $-25^\circ\text{C}$  was added 8 mL (1.51 mmol) of freshly prepared LDA in the same solvent via cannula. The color of the reaction mixture changed to dark red-brown immediately. The solution was stirred for 30 min at low temperature and overnight at room temperature. The solvent was evaporated and the red residue was extracted with 20 mL of hexane and filtered on Celite. Evaporation of the solvent yielded red oil of **3c**, yield: 0.35g (62%).  $^1\text{H}$  NMR (300 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.21, (s, 6H, Me), 0.97, 1.16, 1.46, (m, 18 H, Bu), 4.19 (unresolved m, 2H Cp), 4.71 (unresolved m, 2 H, Cp).  $^{13}\text{C}$  NMR (75.4 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  -2.09 (Me), 14.03, 15.91, 27.00, 29.61 (Bu), 83.71, 85.2 (ipso), 90.33 (Cp), 216.70 (CO).  $^{29}\text{Si}$  NMR (59.6 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  -41.42, -19.26. IR ( $\nu$  CO,  $\text{cm}^{-1}$ , hexane): 1990.9, 1940.4. Anal. Calcd. for  $\text{C}_{17}\text{H}_{28}\text{FeO}_2\text{Si}_2$ : C, 54.24; H, 7.50. Found: C, 54.92; H, 7.62.

**Data for Disilametallacycle, 3b** (81% yield):  $^1\text{H}$  NMR (300 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.87, 0.90, 0.94, 1.26, 1.37, 1.46, (m, 36 H, Bu), 4.27, 4.75 (unresolved m, 4 H, Cp).  $^{13}\text{C}$

NMR (75.4 MHz) ( $C_6D_6$ ):  $\delta$  12.66, 13.96, 14.01, 16.16, 26.36, 26.88, 27.11, 29.60 (Bu), 84.13 (ipso), 84.25, 90.31 (Cp), 216.81 (CO).  $^{29}Si$  NMR (59.6 MHz) ( $C_6D_6$ ):  $\delta$  -39.81, -15.57. IR ( $\nu$  CO,  $cm^{-1}$ , hexane): 1989.8, 1939.3; LRMS (FAB 3-NBA):  $m/z$  (%) 460 (100)  $[M]^+$ , 432 (85)  $[M-CO]^+$ , HRMS (FAB): Found 460.193741; Calculated for  $C_{23}H_{40}FeO_2Si_2$ : 460.191627. Anal. Calcd. for  $C_{23}H_{40}FeO_2Si_2$ : C, 59.98; H, 8.75. Found: C, 59.95; H, 9.23.

**Synthesis of FpSiMeBuSiMeBu<sub>2</sub>, 4:** A 50 mL Schlenk flask was charged with 0.5g (1.21 mmol) of FpSiMeBuSiBuMeCl in 10 mL of dry THF. To this solution at  $-25\ ^\circ C$  was added 0.75 ml (1.21 mmol) of 1.6 M BuLi (Aldrich) via syringe. The color of the reaction mixture changed to dark red-brown immediately. The solution was stirred for 30 min at low temperature and overnight at room temperature. The solvent was evaporated and the red residue was extracted with 20 mL of hexane and filtered on Celite. Evaporation of the solvent produced red oil which was redissolved in hexane and chromatographed on silica gel. Elution of the yellow band with hexane and evaporation of hexane produced 0.2 g (38 %) of red oil.  $^1H$  NMR (300 MHz) ( $C_6D_6$ ):  $\delta$  0.23, 0.61 (s, 6H, Me), 0.96, 1.43 (m, 27 H, Bu), 4.21 (s, 5 H, Cp).  $^{13}C$  NMR (75.4 MHz) ( $C_6D_6$ ):  $\delta$  -3.68, 1.71 (Me), 14.00, 15.23, 22.21, 27.39, 29.33 (Bu), 83.10 (Cp), 215.93, 216.26 (CO).  $^{29}Si$  NMR (59.6 MHz) ( $C_6D_6$ ):  $\delta$  -8.61 (Si-MeBu), 20.47 (Fe-Si). IR ( $\nu$  CO,  $cm^{-1}$ , hexane): 1996.7, 1945.4. HRMS (FAB) Calcd. for  $C_{21}H_{38}FeO_2Si_2$ : 434.17597; Found: 434.179194, fit 1.4 ppm.

**Synthesis of (MeOSiMe<sub>2</sub>SiMe<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)Fe(CO)<sub>2</sub>SnPh<sub>3</sub>, 5:** A 50 mL round-bottomed Schlenk flask was charged with 1.0 g (3.09 mmol) of FpSiMe<sub>2</sub>SiMe<sub>2</sub>OMe in 15 mL THF. To this solution was added 10 mL THF solution of freshly prepared LDA (3.10

mmol) at  $-25^{\circ}\text{C}$ . The reaction reaction after the addition of LDA became dark red-brown. The reaction mixture was stirred at  $-10^{\circ}\text{C}$  for 2h. Then 1.19 g (3.08 mmol) of  $\text{Ph}_3\text{SnCl}$  dissolved in 10 mL THF was added at  $-25^{\circ}\text{C}$ . The reaction mixture was stirred at low temperature for 1h and then at room temperature for 16 h. The solvent was evaporated in vacuum and the residue was extracted with 30 mL of benzene and filtered on Celite. The filtrate was concentrated to 5 mL and placed in (2 x 10 cm) silica gel column. Yellow band developed was eluted with 1:1 hexane/ benzene mixture (v/v). The yellow waxy compound obtained after evaporation of solvent was obtained in 70 % yield (1.45g, 2.16 mmol). The waxy material solidifies in the refrigerator.  $^1\text{H}$  NMR (300 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.14, 0.23, (s, 12H, Me), 3.16 (s, 3H, OMe), 4.30(t, 2H, J =2.1Hz, Cp), 4.36 (t, 2H, J = 2.1 Hz, Cp), 7.18-7.21, 7.75-7.78 (m, 15 H, Ph).  $^{13}\text{C}$  NMR (75.4 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  -2.75, -1.08 (Me), 50.8 (OMe), 84.7, 88.3, 89.8 (ipso) ( $\text{C}_5\text{H}_4$ ), 128.7, 137.1, 144.5 (ipso), 215.4 (CO).  $^{29}\text{Si}$  NMR (59.6 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  14.8, -26.0.  $^{119}\text{Sn}$  NMR ( $\text{C}_6\text{D}_6$ ): 61.6. IR (v CO,  $\text{cm}^{-1}$ , hexane): 1994, 1947. Anal. Calcd. for  $\text{C}_{30}\text{H}_{34}\text{FeO}_3\text{Si}_2\text{Sn}$ : C, 53.52; H, 5.09. Found: C, 53.47.57; H, 5.23.