

Supporting Information for:

## Silyl-Migrations in Frustrated Lewis Pair Chemistry: Reactions of ((CH<sub>3</sub>)<sub>3</sub>Si)<sub>3</sub>P and B(C<sub>6</sub>F<sub>4</sub>H)<sub>3</sub> with H<sub>2</sub> and CO<sub>2</sub>

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### General considerations:

All preparations and manipulations were performed on a double manifold N<sub>2</sub>/vacuum line with Schlenk-type glassware or in a N<sub>2</sub>-filled M-Braun glove box. Solvents (Aldrich) were dried using an Innovative Technologies solvent system. NMR spectra were obtained on a Bruker or Varian System 400 MHz spectrometer and spectra were referenced to residual solvent (<sup>1</sup>H, <sup>13</sup>C) or externally (<sup>11</sup>B; BF<sub>3</sub>OEt<sub>2</sub>, <sup>19</sup>F; CFCl<sub>3</sub>, <sup>31</sup>P; 85% H<sub>3</sub>PO<sub>4</sub>). NMR solvents were purchased from Cambridge Isotopes, dried over CaH<sub>2</sub>, distilled prior to use, and stored over 4 Å molecular sieves in the glove box. Combustion analysis was performed in house on a Perkin-Elmer CHN Analyzer. B(C<sub>6</sub>F<sub>4</sub>H)<sub>3</sub> was prepared as previously described.

### [(TMS)<sub>4</sub>P][HB(*p*-C<sub>6</sub>F<sub>4</sub>H)<sub>3</sub>] (1) and (TMS)<sub>2</sub>(H)P–B(*p*-C<sub>6</sub>F<sub>4</sub>H)<sub>3</sub> (2):

In a well-dried Schlenk flask, (TMS)<sub>3</sub>P (55 mg, 0.22 mmol) and B(*p*-C<sub>6</sub>F<sub>4</sub>H)<sub>3</sub> (98 mg, 0.21 mmol) were dissolved in toluene (3 mL). About 3 atm of H<sub>2</sub> was introduced to the Schlenk flask. After standing for 24 h, colorless crystals were precipitated. The <sup>1</sup>H NMR spectrum of the reaction mixture showed that the salt **1** and phosphine–borane adduct **2** were afforded in ratio of 1:1. After removal of the toluene solution, the residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> (0.5 ml) at -30 °C to give **1** as colorless crystals (80 mg, 43% yield). Single crystals of **1** suitable for X-ray

diffraction were grown by layering a C<sub>6</sub>D<sub>5</sub>Br solution of the product at room temperature. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ): 0.76 (d, <sup>3</sup>J<sub>HP</sub> = 6.2 Hz, 36 H, SiMe<sub>3</sub>), 3.85 (q, <sup>1</sup>J<sub>HB</sub> = 91 Hz, 1 H, BH), 6.80-6.93 (m, 3 H, *p*-CH); <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ): -24.7 (d, <sup>1</sup>J<sub>HB</sub> = 91 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ): 0.0 (d, <sup>2</sup>J<sub>CP</sub> = 8.1 Hz, SiMe<sub>3</sub>), 98.4 (t, <sup>2</sup>J<sub>CF</sub> = 23 Hz, *p*-CH), 131.5 (weak, br, *ipso*-C), 143.1 (dm, <sup>1</sup>J<sub>CF</sub> = 245 Hz, *m*-CF), 146.3 (dm, <sup>1</sup>J<sub>CF</sub> = 236 Hz, *o*-CF); <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ): -144.5 (m, br, *m*-CF), -134.1 (m, br, *o*-CF); <sup>29</sup>Si{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ): 12.5; <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ): -201.2; Anal. calcd for C<sub>29</sub>H<sub>30</sub>BO<sub>4</sub>F<sub>12</sub>Si<sub>3</sub>P + 2/3(CH<sub>2</sub>Cl<sub>2</sub>): C, 43.88; H, 4.96%; found: C, 44.24; H, 5.10%.

On the other hand, evaporation of the separated toluene solution and recrystallization of the residue from pentane (0.5 ml) at -30 °C gave **2** as colorless powders (32 mg, 25% yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ): 0.25 (d, <sup>3</sup>J<sub>HP</sub> = 5.6 Hz, 27 H, SiMe<sub>3</sub>), 3.79 (d, <sup>1</sup>J<sub>HP</sub> = 322 Hz, 1 H, PH), 6.95 (tt, <sup>3</sup>J<sub>HF</sub> = 9.3 Hz, <sup>4</sup>J<sub>HF</sub> = 6.6 Hz, 3 H, *p*-CH); <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ): -14.5 (br); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ): 1.4 (d, <sup>2</sup>J<sub>CP</sub> = 7.8 Hz, SiMe<sub>3</sub>), 104.4 (t, <sup>2</sup>J<sub>CF</sub> = 23 Hz, *p*-CH), 125.8 (weak, br, *ipso*-C), 146.1 (dm, <sup>1</sup>J<sub>CF</sub> = 245 Hz, *m*-CF), 148.2 (dm, <sup>1</sup>J<sub>CF</sub> = 242 Hz, *o*-CF); <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ): -141.7 (m, br, *m*-CF), -129.8 (m, br, *o*-CF); <sup>29</sup>Si{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ): 11.3 (d, <sup>1</sup>J<sub>SiP</sub> = 16.8 Hz); <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ): -139.3 (d, <sup>1</sup>J<sub>HP</sub> = 322 Hz); Anal. calcd for C<sub>24</sub>H<sub>22</sub>BF<sub>12</sub>Si<sub>2</sub>P: C, 45.30; H, 3.48%; found: C, 44.85; H, 3.35%.

### (TMS)<sub>2</sub>P-C(OTMS)=O→B(*p*-C<sub>6</sub>F<sub>4</sub>H)<sub>3</sub> (**3**):

In a well-dried Schlenk flask, (TMS)<sub>3</sub>P (60 mg, 0.24 mmol) and B(*p*-C<sub>6</sub>F<sub>4</sub>H)<sub>3</sub> (110 mg, 0.24 mmol) were dissolved in pentane (10 mL). 1 atm of CO<sub>2</sub> was introduced to the Schlenk flask. After standing for 24 h, colorless powder was precipitated. After evaporation of the solvent, the residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> (0.5 ml) at -30 °C to give **3** as colorless crystals (106 mg, 59% yield). (TMS)<sub>2</sub>P<sup>13</sup>C(OTMS)=O→B(*p*-C<sub>6</sub>F<sub>4</sub>H)<sub>3</sub> (**3**-<sup>13</sup>C) was also synthesized by same

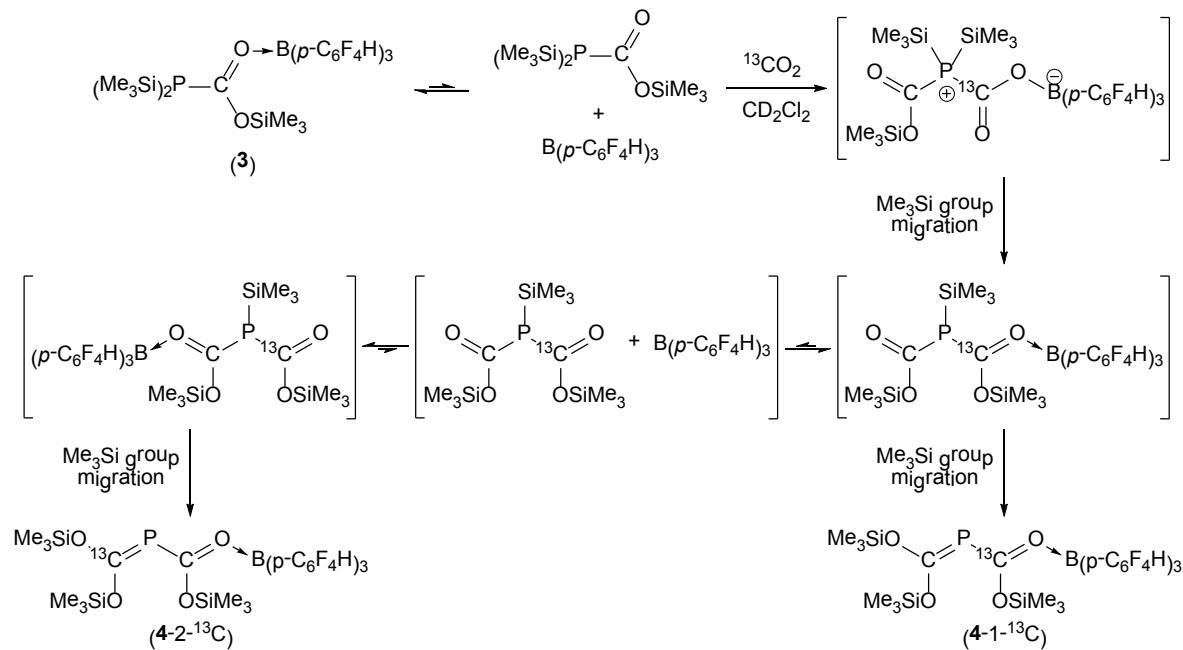
method using  $^{13}\text{CO}_2$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): 0.29 (s, 9 H,  $\text{OSiMe}_3$ ), 0.33 (d,  $^3J_{\text{HP}} = 5.5$  Hz, 18 H,  $\text{P}(\text{SiMe}_3)_2$ ), 7.00-7.15 (m (br), 3 H, *p*-CH);  $^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): -13.5 (br);  $^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): 0.7 (s,  $\text{OSiMe}_3$ ), 1.5 (d,  $^2J_{\text{CP}} = 12$  Hz,  $\text{PSiMe}_3$ ), 107.3 (br, *p*-CH), 123.3 (weak, br, *ipso*-C), 146.1 (dm,  $^1J_{\text{CF}} = 247$  Hz, *m*-CF), 148.0 (dm,  $^1J_{\text{CF}} = 246$  Hz, *o*-CF), 194.2 (very br, quaternary C, using  $^{13}\text{C}$  labeled  $\text{CO}_2$ );  $^{13}\text{C}\{\text{H}\}$  NMR (233 K,  $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): 199.4 (d,  $^1J_{\text{CP}} = 66$  Hz, quaternary C, using  $^{13}\text{C}$  labeled  $\text{CO}_2$ );  $^{19}\text{F}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): -141.1 (m, br, *m*-CF), -131.9 (m, br, *o*-CF);  $^{29}\text{Si}\{\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): 7.3 (d,  $^1J_{\text{SiP}} = 23$  Hz,  $\text{PSiMe}_3$ ), 38.6 ( $\text{OSiMe}_3$ );  $^{31}\text{P}\{\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): -104.5 (very br);  $^{31}\text{P}\{\text{H}\}$  NMR (233 K,  $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): -101.6 (d,  $^1J_{\text{PC}} = 66$  Hz, using  $^{13}\text{C}$  labeled  $\text{CO}_2$ ); Anal. calcd for  $\text{C}_{28}\text{H}_{30}\text{BO}_2\text{F}_{12}\text{Si}_3\text{P}$ : C, 44.69; H, 4.02%; found: C, 45.08; H, 3.79%.

#### (TMSO)<sub>2</sub>C=P-C(OTMS)=O→B(*p*-C<sub>6</sub>F<sub>4</sub>H)<sub>3</sub> (4)

In a well-dried Schlenk flask,  $(\text{TMS})_3\text{P}$  (55 mg, 0.22 mmol) and  $\text{B}(\text{p-C}_6\text{F}_4\text{H})_3$  (105 mg, 0.23 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  (10 mL). 1 atm of  $\text{CO}_2$  was introduced to the Schlenk flask. After standing for 24 h, the reaction mixture was recrystallized from  $\text{CH}_2\text{Cl}_2$  at -30 °C to give **4** as pale yellow crystals (140 mg, 80% yield).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): 0.15 (s, 27 H,  $\text{SiMe}_3 \times 3$ ), 6.74 (tt,  $^3J_{\text{HF}} = 9.0$  Hz,  $^4J_{\text{HF}} = 7.4$  Hz, 3 H, *p*-CH);  $^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): -0.7;  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): -0.04 (s,  $\text{SiMe}_3$ ), 0.00 (s,  $\text{SiMe}_3$ ), 0.04 (s,  $\text{SiMe}_3$ ), 104.0 (t,  $^2J_{\text{CF}} = 23$  Hz, *p*-CH), 126.1 (weak, br, *ipso*-C), 145.8 (dm,  $^1J_{\text{CF}} = 241$  Hz, *m*-CF), 148.3 (dm,  $^1J_{\text{CF}} = 243$  Hz, *o*-CF), 202.0 (d,  $^1J_{\text{CP}} = 95$  Hz, quaternary C), 205.5 (d,  $^1J_{\text{CP}} = 91$  Hz, quaternary C);  $^{19}\text{F}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): -142.9 (m, br, *m*-CF), -134.1 (m, br, *o*-CF);  $^{29}\text{Si}\{\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): 7.4, 33.0, 33.4;  $^{31}\text{P}\{\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): 2.4; Anal. calcd for  $\text{C}_{29}\text{H}_{30}\text{BO}_4\text{F}_{12}\text{Si}_3\text{P}$ : C, 43.73; H, 3.80%; found: C, 43.66; H, 3.55%.

### Reaction of 3 with $^{13}\text{CO}_2$ :

In a well-dried J-Young NMR tube, **3** (105 mg, 0.23 mmol) was dissolved in  $\text{CD}_2\text{Cl}_2$  (0.5 mL). 1 atm of  $^{13}\text{CO}_2$  was introduced to the Schlenk flask. After standing for 24 h, the NMR spectra of the reaction mixture showed that the almost 1:1 mixture of  $(\text{TMSO})_2\text{C}=\text{P}^{13}\text{C}(\text{OTMS})=\text{O} \rightarrow \text{B}(p\text{-C}_6\text{F}_4\text{H})_3$  **4-1- $^{13}\text{C}$**  and  $(\text{TMSO})_2^{13}\text{C}=\text{P}-\text{C}(\text{OTMS})=\text{O} \rightarrow \text{B}(p\text{-C}_6\text{F}_4\text{H})_3$  **4-2- $^{13}\text{C}$**  was produced quantitatively.



**Scheme S1** Plausible mechanism for the reaction of **3** with  $^{13}\text{CO}_2$  giving **4-1- $^{13}\text{C}$**  and **4-2- $^{13}\text{C}$** .