Supporting Information for:

**Silyl-Migrations in Frustrated Lewis Pair Chemistry: Reactions of**

$$((\text{CH}_3)_3\text{Si})_3\text{P~and~B(C}_6\text{F}_4\text{H})_3$$ with **H**$_2$ and **CO**$_2$

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**General considerations:**

All preparations and manipulations were performed on a double manifold **N**$_2$/vacuum line with Schlenk-type glassware or in a **N**$_2$-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 ($^1\text{H}$, $^{13}\text{C}$) or externally ($^{11}\text{B}; \text{BF}_3\text{OEt}_2$, $^{19}\text{F}; \text{CFCl}_3$, $^{31}\text{P}; 85\% \text{H}_3\text{PO}_4$). NMR solvents were purchased from Cambridge Isotopes, dried over CaH$_2$, 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$_6$F$_4$H)$_3$ was prepared as previously described.

**[(TMS)$_4$P][HB(p-C$_6$F$_4$H)$_3$] (1) and (TMS)$_2$(H)P–B(p-C$_6$F$_4$H)$_3$ (2):**

In a well-dried Schlenk flask, (TMS)$_3$P (55 mg, 0.22 mmol) and B(p-C$_6$F$_4$H)$_3$ (98 mg, 0.21 mmol) were dissolved in toluene (3 mL). About 3 atm of **H**$_2$ was introduced to the Schlenk flask. After standing for 24 h, colorless crystals were precipitated. The $^1\text{H}$ 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$_2$Cl$_2$ (0.5 ml) at $-30^\circ \text{C}$ to give 1 as colorless crystals (80 mg, 43% yield). Single crystals of 1 suitable for X-ray
diffraction were grown by layering a C₆D₅Br solution of the product at room temperature. 

$$^1$$H NMR (CD₂Cl₂, δ): 0.76 (d, $$^3$$JₜHP = 6.2 Hz, 36 H, SiMe₃), 3.85 (q, $$^1$$JₜHB = 91 Hz, 1 H, BH), 6.80-6.93 (m, 3 H, p-CH); 
$$^{11}$$B NMR (CD₂Cl₂, δ): –24.7 (d, $$^1$$JₜHB = 91 Hz); 
$$^{13}$$C{¹H} NMR (CD₂Cl₂, δ): 0.0 (d, $$^2$$JₜCP = 8.1 Hz, SiMe₃), 98.4 (t, $$^2$$JₜCF = 23 Hz, p-CH), 131.5 (weak, br, ipso-C), 143.1 (dm, $$^1$$JₜCF = 245 Hz, m-CF), 146.3 (dm, $$^1$$JₜCF = 236 Hz, o-CF); 
$$^{19}$$F NMR (CD₂Cl₂, δ): –24.7 (d, $$^1$$JₜBP = 91 Hz); 
$$^{31}$$P{¹H} NMR (CD₂Cl₂, δ): –201.2; Anal. calcd for C₂₉H₃₀BO₄F₁₂Si₃P + 2/3(CH₂Cl₂): 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). 

$$^1$$H NMR (CD₂Cl₂, δ): 0.25 (d, $$^3$$JₜHP = 5.6 Hz, 27 H, SiMe₃), 3.79 (d, $$^1$$JₜHP = 322 Hz, 1 H, PH), 6.95 (tt, $$^3$$JₜHF = 9.3 Hz, $$^4$$JₜHF = 6.6 Hz, 3 H, p-CH); 
$$^{11}$$B NMR (CD₂Cl₂, δ): –14.5 (br); 
$$^{13}$$C{¹H} NMR (CD₂Cl₂, δ): 1.4 (d, $$^2$$JₜCP = 7.8 Hz, SiMe₃), 104.4 (t, $$^2$$JₜCF = 23 Hz, p-CH), 125.8 (weak, br, ipso-C), 146.1 (dm, $$^1$$JₜCF = 245 Hz, m-CF), 148.2 (dm, $$^1$$JₜCF = 242 Hz, o-CF); 
$$^{19}$$F NMR (CD₂Cl₂, δ): –141.7 (m, br, m-CF), –129.8 (m, br, o-CF); 
$$^{29}$$Si{¹H} NMR (CD₂Cl₂, δ): 12.5; 
$$^{31}$$P{¹H} NMR (CD₂Cl₂, δ): –139.3 (d, $$^1$$JₜHP = 322 Hz); Anal. calcd for C₂₄H₂₂BF₁₂Si₂P: C, 45.30; H, 3.48%; found: C, 44.85; H, 3.35%.

$$(TMS)_2P$$_{−}$$C(OTMS)=O→B(p-C$_{6}$F$_{4}$H)$_{3}$ (3):

In a well-dried Schlenk flask, (TMS)$_3$P (60 mg, 0.24 mmol) and B(p-C$_6$F$_4$H)$_3$ (110 mg, 0.24 mmol) were dissolved in pentane (10 mL). 1 atm of CO$_2$ 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$_2$Cl$_2$ (0.5 ml) at –30 °C to give 3 as colorless crystals (106 mg, 59% yield). (TMS)$_2$P$^{13}$C(OTMS)=O→B(p-C$_6$F$_4$H)$_3$ (3-$^{13}$C) was also synthesized by same
method using $^{13}\text{CO}_2$. $^1\text{H}$ NMR (CD$_2$Cl$_2$, δ): 0.29 (s, 9 H, OSiMe$_3$), 0.33 (d, $^3J_{HF} = 5.5$ Hz, 18 H, P(SiMe$_3$)$_2$), 7.00-7.15 (m (br), 3 H, p-CH); $^{11}\text{B}$ NMR (CD$_2$Cl$_2$, δ): −13.5 (br); $^{13}\text{C}$ {$^1\text{H}$} NMR (CD$_2$Cl$_2$, δ): 0.7 (s, OSiMe$_3$), 1.5 (d, $^2J_{CP} = 12$ Hz, PSiMe$_3$), 107.3 (br, p-CH), 123.3 (weak, br, ipso-C), 146.1 (dm, $^1J_{CF} = 247$ Hz, m-CF), 148.0 (dm, $^1J_{CF} = 246$ Hz, o-CF), 194.2 (very br, quaternary C, using $^{13}\text{C}$ labeled CO$_2$); $^{13}\text{C}$ {$^1\text{H}$} NMR (233 K, CD$_2$Cl$_2$, δ): 199.4 (d, $^1J_{PC} = 66$ Hz, quaternary C, using $^{13}\text{C}$ labeled CO$_2$); $^{19}\text{F}$ NMR (CD$_2$Cl$_2$, δ): −13.5 (br); $^{13}\text{C}$ {$^1\text{H}$} NMR (233 K, CD$_2$Cl$_2$, δ): 199.4 (d, $^1J_{CP} = 66$ Hz, quaternary C, using $^{13}\text{C}$ labeled CO$_2$); $^{19}\text{F}$ NMR (CD$_2$Cl$_2$, δ): −13.5 (br); $^{29}\text{Si}$ {$^1\text{H}$} NMR (CD$_2$Cl$_2$, δ): 7.3 (d, $^1J_{SiP} = 23$ Hz, PSiMe$_3$), 38.6 (OSiMe$_3$); $^{31}\text{P}$ {$^1\text{H}$} NMR (CD$_2$Cl$_2$, δ): −104.5 (very br); $^{31}\text{P}$ {$^1\text{H}$} NMR (233 K, CD$_2$Cl$_2$, δ): −101.6 (d, $^1J_{PC} = 66$ Hz, using $^{13}\text{C}$ labeled CO$_2$); Anal. calcd for C$_{28}$H$_{30}$BO$_2$F$_{12}$Si$_3$P: C, 44.69; H, 4.02%; found: C, 45.08; H, 3.79%.

(TMSO)$_2$C=P–C(OTMS)=O→B(p-C$_6$F$_4$H)$_3$ (4)

In a well-dried Schlenk flask, (TMS)$_3$P (55 mg, 0.22 mmol) and B(p-C$_6$F$_4$H)$_3$ (105 mg, 0.23 mmol) were dissolved in CH$_2$Cl$_2$ (10 mL). 1 atm of CO$_2$ was introduced to the Schlenk flask. After standing for 24 h, the reaction mixture was recrystallized from CH$_2$Cl$_2$ at −30 ºC to give 4 as pale yellow crystals (140 mg, 80% yield). $^1\text{H}$ NMR (CD$_2$Cl$_2$, δ): 0.15 (s, 27 H, SiMe$_3$ x 3), 6.74 (tt, $^3J_{HF} = 9.0$ Hz, $^4J_{HF} = 7.4$ Hz, 3 H, p-CH); $^{11}\text{B}$ NMR (CD$_2$Cl$_2$, δ): −0.7; $^{13}\text{C}$ NMR (CD$_2$Cl$_2$, δ): −0.04 (s, SiMe$_3$), 0.00 (s, SiMe$_3$), 0.04 (s, SiMe$_3$), 104.0 (t, $^2J_{CF} = 23$ Hz, p-CH), 126.1 (weak, br, ipso-C), 145.8 (dm, $^1J_{CF} = 241$ Hz, m-CF), 148.3 (dm, $^1J_{CF} = 243$ Hz, o-CF), 202.0 (d, $^1J_{CP} = 95$ Hz, quaternary C), 205.5 (d, $^1J_{CP} = 91$ Hz, quaternary C); $^{19}\text{F}$ NMR (CD$_2$Cl$_2$, δ): −142.9 (m, br, m-CF), −134.1 (m, br, o-CF); $^{29}\text{Si}$ {$^1\text{H}$} NMR (CD$_2$Cl$_2$, δ): 7.4, 33.0, 33.4; $^{31}\text{P}$ {$^1\text{H}$} NMR (CD$_2$Cl$_2$, δ): 2.4; Anal. calcd for C$_{29}$H$_{30}$BO$_2$F$_{12}$Si$_3$P: C, 43.73; H, 4.02%; found: C, 43.66; H, 3.55%.
Reaction of 3 with $^{13}$CO$_2$:

In a well-dried J-Young NMR tube, 3 (105 mg, 0.23 mmol) was dissolved in CD$_2$Cl$_2$ (0.5 mL). 1 atm of $^{13}$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 (TMSO)$_2$C=P-$^{13}$C(OTMS)=O→B(p-C$_6$F$_4$H)$_3$ 4-1-$^{13}$C and (TMSO)$_2^{13}$C=P–C(OTMS)=O→B(p-C$_6$F$_4$H)$_3$ 4-2-$^{13}$C was produced quantitatively.

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