Thermal C-H Borylation Using CO-Free Iron-Boryl Complexes.

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Supporting Information

General Considerations

Unless otherwise specified, all reactions and manipulations were performed under purified N₂ in a glovebox or using standard Schlenk line techniques. Glassware was oven-dried prior to use. Reaction solvents (tetrahydrofuran, heptane, benzene-d₆, toluene-d₈) were sparged with argon and dried using a Glass Contour Solvent System built by Pure Process technology, LLC, or purified by repeated freeze-pump-thaw cycles followed by prolonged storage over activated, 3-Å molecular sieves. Unless otherwise specified, all chemicals were purchased from commercial sources and used without further purification. Photolysis was conducted using a 450-W Hanovia mercury arc lamp in an immersion well filled with circulating water.

Physical Measurements

NMR spectra were recorded at ambient temperature, unless otherwise noted, using Bruker Avance DPX-400 and Bruker Avance DRX-500 spectrometers. ¹H NMR and $^{13}C{^{1}H}NMR$ chemical shifts were referenced to residual solvent peaks. ^{11}B NMR chemical shifts were referenced to external BF₃·OEt₂ ($\delta = 0$). ³¹P{¹H} NMR chemical shifts were referenced to external H₃PO₄ ($\delta = 0$). ¹⁹F NMR chemical shifts were referenced to external CFCl₃ ($\delta = 0$). FT-IR spectra were recorded on solid samples in a glovebox using a Bruker ALPHA spectrometer fitted with a diamond-ATR detection unit. Elemental analyses were performed by Midwest Microlab, LLC in Indianapolis, IN. GC/MS data was obtained using an Agilent Technologies 7890A GC System interfaced to an Agilent Technologies 5975C VL mass selective detector. Single-crystal X-ray diffraction studies were conducted using a Bruker X2S Smart diffractometer fitted with an Oxford Cryostreams Desktop Cooler (200 K). Solution and refinement was accomplished with SHELXTL suite of programs¹ using standard techniques.² In the case of complex 3, disordered phosphine ethyl and pinacol methyl groups were modeled over multiple positions, resulting in satisfactory refinement. In the case of complex 4, a Level-A checkCIF error indicating positive residual electron density at Fe1 was located; an absorption correction was applied properly using SADABS, and CELLNOW did not indicate twinning, so we believe this error is the result of the marginal data quality for this sample. In the case of complex 5, multiple trifluoromethyl groups were disordered and displayed large thermal motion

¹ G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122.

² P. Müller, *Crystallography Reviews*, 2009, **15**, 57-83.

within the temperature limits of our instrument despite extensive modeling; a Level-A checkCIF error indicating high Max Shift/Error was found despite hundreds of refinement cycles, but the maximum shift invariably involved fluorine positions rather than core atoms.

Metal Complex Synthesis

Literature procedures were used to prepare FpBpin (Fp = $Fe(\eta^5-C_5H_5)(CO)_2$, pin = pinacolate),³ IPrCuOtBu,⁴ [IPrCuH]₂.⁴ The synthesis of CpFe(PEt₃)₂H was modified from a previously reported synthesis.⁵

Synthesis of CpFe(PEt₃)₂H: In a nitrogen filled glovebox, in a 100-mL round bottomed flask, Fe(II)Cl₂ (411.4 mg, 3.25 mmol) was suspended in THF (30 mL). Afterwards, PEt₃ (1.440 mL, 9.75 mmol) was syringed in and the solution turned yellow. To the solution, 2.6 eq. of a Na/Hg amalgam was added, and as soon as the solution started to darken, freshly cracked cyclopentadiene (330 μ L, 3.92 mmol) was quickly syringed in. The reaction was stirred overnight. The dark green solution was filtered through Celite to remove excess Na, and then dried in vacuo. The green powder was extracted with Pentane (3 x 15 mL) and dried in vacuo, resulting in a red oil. Combustion analysis was not obtained because repeated attempts at removing ferrocene (< 5% impurity) were not successful. Yield: 51% (612.0 mg, 1.71 mmol). ¹H NMR (400 MHz, C₆D₆): δ 4.11 (t, *J* = 1.3 Hz, 5H, Cp), 1.23 (m, 12H, CH₂), 0.97 (m, 18H, CH₃), -15.35 (t, *J*= 73.8 Hz, 1H, Fe-H). ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 68.1. ¹³C{¹H} (126 MHz, C₆D₆): δ 73.1 (Cp), 23.7, 8.4. IR (solid, cm⁻¹): 2926, 1865 (Fe-H), 1448, 1027, 808.

³ T. J. Mazzacano, N. P. Mankad, J. Am. Chem. Soc., 2013, 135, 17258-17261.

⁴ N. P. Mankad, D. S. Laitar, J. P. Sadighi, *Organometallics*, 2004, 23, 3369-3371.

⁵ M. L. H. Green, J. B. Leach, M. A. Kelland, J. Organomet. Chem., 2007, 692, 4147-4156.



Figure S1: ¹H NMR spectrum of CpFe(PEt₃)₂H



Figure S2: ${}^{31}P{}^{1}H$ NMR spectrum of CpFe(PEt₃)₂H



Figure S3: ${}^{13}C{}^{1}H$ NMR spectrum of CpFe(PEt₃)₂H



Figure S4: IR spectrum of CpFe(PEt₃)₂H

General Synthesis of $CpFe(PR_3)_2Bpin$: In a nitrogen filled glovebox, in a 250-mL Schlenk flask, FpBpin was dissolved in heptane (10 mL). Phosphine (5-7 equivs.) was added and the flask was sealed. The flask was removed from the glovebox and placed under N₂ on a Schlenk line. The flask was then placed approximately 3 inches away from a 450-W Hanovia Mercury Arc UV Lamp for 16 h. After 16 h, the flask was dried in vacuo. Sample was recrystallized in pentane at -35°C to obtain spectroscopically pure material.

CpFe(PMe₃)₂Bpin: Crude Yield: 83%, Crystal Yield: 38%. NMR: ¹H NMR (400 MHz, C₆D₆): δ 4.12 (t, J = 1.7 Hz, 5H, Cp), 1.19 (m, 30H). ¹¹B NMR (128 MHz, C₆D₆): δ 55.4. ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 36.5. ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 79.9, 77.4, 25.9, 24.6. IR (solid, cm⁻¹): 2969, 2897, 1048, 931. Anal. Calcd. for C₁₇H₃₅BFeO₂P₂: C, 51.04; H, 8.82. Found: C, 52.17; H, 9.11.

CpFe(PEt₃)₂Bpin: Crude Yield: 93%, Crystal Yield: 33%. ¹H NMR (400 MHz, C₆D₆): δ 4.27 (t, *J* = 1.3 Hz, 5H, Cp), 1.70 (m, 6H, CH₂), 1.39 (m, 6H, CH₂), 1.23 (s, 12H, CH₃), 1.00 (m, 18H). ¹¹B NMR (128 MHz, C₆D₆): δ 55.2. ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 58.8. ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 80.0, 76.2-77.5 (m), 23.4-27.1 (m), 9.08 (m). IR (solid, cm⁻¹): 2965, 2932, 2875, 1025, 1060. Anal. Calcd. for C₂₃H₄₇BFeO₂P₂: C, 57.05; H, 9.78. Found: C, 58.11; H, 10.05.

CpFe(P(OMe)₃)₂**Bpin**: Crude Yield: 99%, Crystal Yield: 80%. ¹H NMR (400 MHz, C₆D₆): δ 4.51 (m, 5H, Cp), 3.55 (m, 18H, CH₃), 1.19 (s, 12H, CH₃). ¹¹B NMR (128 MHz, C₆D₆): δ 53.2. ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 194.1. ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 80.5, 78.7, 51.5 (O-CH₃), 25.5 (CH₃). IR (solid, cm⁻¹): 2939, 1199, 1013. Combustion analysis was not obtained due to a trace impurity (<5%) that could not be removed even after repeated recrystallizations.

CpFe(P(OCH₂CF₃)₃)₂Bpin: Crude Yield: 77%, Crystal Yield: 56%. ¹H NMR (400 MHz, C₆D₆): δ 4.21 (m, 12H, CH₂), 4.16 (s, 5H, Cp), 0.91 (s, 12H, CH₃). ¹¹B NMR (128 MHz, C₆D₆): δ 51.0. ³¹P{¹H} NMR (162 MHz, C₆D₆). δ 190.0. ¹⁹F NMR (376 MHz, C₆D₆): -75.1. ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 124.0 (q, *J*=277.5, CF₃), 82.3, 79.6, 62.4 (q, *J*=36.5, CH₂), 25.0 (s, CH₃). IR (solid, cm⁻¹): 1414, 1276, 1155, 1059, 958. Anal. Calcd. for C₂₃H₂₉BF₁₈FeO₈P₂: C, 30.56; H, 3.23. Found: C, 30.87; H, 3.35.



Figure S5: ¹H NMR spectrum of CpFe(PMe₃)₂Bpin



Figure S6: ¹¹B NMR spectrum of CpFe(PMe₃)₂Bpin



Figure S7: ³¹P{¹H} NMR spectrum of CpFe(PMe₃)₂Bpin



Figure S8: ${}^{13}C{}^{1}H$ NMR spectrum of CpFe(PMe₃)₂Bpin



Figure S9: Infrared spectrum of CpFe(PMe₃)₂Bpin



Figure S10: ¹H NMR spectrum of CpFe(PEt₃)₂Bpin



Figure S11: ¹¹B NMR spectrum of CpFe(PEt₃)₂Bpin



Figure S12: ³¹P{¹H} NMR spectrum of CpFe(PEt₃)₂Bpin



Figure S13: ¹³C{¹H} spectrum of CpFe(PEt₃)₂Bpin



Figure S14: Infrared spectrum of CpFe(PEt₃)₂Bpin



Figure S15: Solid-state structure of $CpFe(P(OMe)_3)_2Bpin$ determined by single-crystal X-ray diffraction. Atoms are shown as 50% thermal ellipsoids, and hydrogen atoms have been omitted in the depiction. Selected bond lengths; Fe1-B1, 2.002(10), Fe1-P1, 2.087(2), Fe1-P2, 2.102(2).



Figure S16: ¹H NMR spectrum of CpFe(P(OMe)₃)₂Bpin



Figure S17: ¹¹B NMR spectrum of CpFe(P(OMe)₃)₂Bpin



Figure S18: ${}^{31}P{}^{1}H$ spectrum of CpFe(P(OMe)₃)₂Bpin



Figure S19: ${}^{13}C{}^{1}H$ spectrum of CpFe(P(OMe)_3)₂Bpin



Figure S20: Infrared spectrum of CpFe(P(OMe)₃)₂Bpin



Figure S21: Solid-state structure of CpFe(P(OCH₂CF₃)₃)₂Bpin determined by single-crystal X-ray diffraction. Atoms are shown as 50% thermal ellipsoids, and hydrogen atoms have been omitted in the depiction. Selected bond lengths; Fe1-B1, 1.997(3), Fe1-P1, 2.087(1), Fe1-P2, 2.0677(9).



Figure S22: ¹H NMR spectrum of CpFe(P(OCH₂CF₃)₃)₂Bpin



Figure S23: ¹¹B NMR spectrum of CpFe(P(OCH₂CF₃)₃)₂Bpin



Figure S24: ³¹P $\{^{1}H\}$ NMR spectrum of CpFe(P(OCH₂CF₃)₃)₂Bpin



Figure S25: ¹⁹F NMR spectrum of CpFe(P(OCH₂CF₃)₃)₂Bpin



Figure S26: ¹³C{¹H} NMR spectrum of CpFe(P(OCH₂CF₃)₃)₂Bpin



Figure S27: Infrared spectrum of CpFe(P(OCH₂CF₃)₃)₂Bpin

General Thermal Reaction of CpFe(PR₃)₂Bpin: In a nitrogen filled glovebox, CpFe(PR₃)₂Bpin and internal standard were dissolved in C_6D_6 (1 mL) and filtered through a Celite filled pipette into a J-Young NMR tube. The tube was sealed and placed in an oil bath at 70°C for 24 hr.



Figure S28: ¹H NMR spectrum for the thermal borylation of C₆D₆ by CpFe(PEt₃)₂Bpin at 70°C for 24 h.



Figure S29: ¹¹B NMR spectrum for the thermal borylation of C_6D_6 by $CpFe(PEt_3)_2Bpin$ at 70°C for 24 h.



Figure S30: ³¹P{¹H} NMR spectrum for the thermal borylation of C_6D_6 by $CpFe(PEt_3)_2Bpin$ at 70°C for 24 h.



Figure S31: ¹H NMR spectrum for the thermal borylation of C₆D₆ by CpFe(PEt₃)₂Bpin at 80°C for 4 h.



Figure S32: ¹¹B NMR spectrum for the thermal borylation of C_6D_6 by $CpFe(PEt_3)_2Bpin$ at 80°C for 4 h.



Figure S33: ³¹P{¹H} NMR spectrum for the thermal borylation of C_6D_6 by $CpFe(PEt_3)_2Bpin$ at 80°C for 4 h.



Figure S34: ¹H NMR spectrum for the thermal borylation of C_6D_6 by $CpFe(PMe_3)_2Bpin$ at 70°C for 24 h.



Figure S35: ¹¹B NMR spectrum for thermal borylation of C₆D₆ by CpFe(PMe₃)₂Bpin at 70°C for 24 h.



Figure S36: ³¹P{¹H} NMR spectrum for the thermal borylation of C_6D_6 by $CpFe(PMe_3)_2Bpin$ at 70°C for 24 h.



Figure S37: ¹H NMR spectrum for the thermal borylation of C_6D_6 by $CpFe(P(OCH_2CF_3)_3)_2Bpin$ at 70°C for 24 h.



Figure S38: ¹¹B NMR spectrum for the thermal borylation of C_6D_6 by $CpFe(P(OCH_2CF_3)_3)_2Bpin$ at 70°C for 24 h.



Figure S39: ³¹P{¹H} NMR spectrum for the thermal borylation of C_6D_6 by $CpFe(P(OCH_2CF_3)_3)_2Bpin$ at 70°C for 24 h.



Figure S40: ¹⁹F NMR spectrum for the thermal borylation of C_6D_6 by $CpFe(P(OCH_2CF_3)_3)_2Bpin$ at 70°C for 24 h.



Figure S41: ¹H NMR spectrum for the thermal borylation of C_6D_6 by $CpFe(P(OMe)_3)_2Bpin$ at 70°C for 24 h.



Figure S42: ¹¹B NMR spectrum for the thermal borylation of C_6D_6 by $CpFe(P(OMe)_3)_2Bpin$ at 70°C for 24 h.



Figure S43: ³¹P{¹H} NMR spectrum for the thermal borylation of C_6D_6 by $CpFe(P(OMe)_3)_2Bpin$ at 70°C for 24 h.



Figure S44: ¹H NMR spectrum for the thermal borylation of C_6D_6 by FpBpin at 70°C for 24 h.



Figure S45: ¹¹B NMR spectrum for the thermal borylation of C_6D_6 by FpBpin at 70°C for 24 h.

Thermal Borylation of CpFe(PR₃)₂Bpin with toluene-d₈: In a nitrogen filled glovebox,

 $CpFe(PEt_3)_2Bpin$ and hexamethylbenzene were dissolved in toluene-d₈ (1 mL) and filtered through a Celite filled pipette into a J-Young NMR tube. The tube was sealed and placed in an oil bath at 70°C for 24 h. Because the ¹H NMR resonances for the *meta* and *para* isomers were not well resolved, their isomeric ratio was determined by GC-MS (average of 4 independent runs).



Figure S46: ¹H NMR spectrum for the thermal borylation of toluene-d₈ by CpFe(PEt₃)₂Bpin at 70°C for 24 h.



Figure S47: ¹¹B NMR spectrum for the thermal borylation of toluene-d₈ by CpFe(PEt₃)₂Bpin at 70°C for 24 h.



Figure S48: ³¹P{¹H} NMR spectrum for the thermal borylation of toluene-d₈ by CpFe(PEt₃)₂Bpin at 70°C for 24 h.

General Photolytic Reaction of CpFe(PR₃)₂Bpin: In a nitrogen filled glovebox, CpFe(PR₃)₂Bpin and hexamethylbenzene were dissolved in C_6D_6 (1 mL) and filtered through a Celite filled pipette into a J-Young NMR tube. The tube was sealed and placed approximately 0.75 inches away from a 450-W Hanovia Mercury Arc lamp for 1 h. After the reaction, the resulting solutions were filtered through a Celite filled pipette into a new J-Young NMR tube. The ¹H, ¹¹B, ³¹P and ¹⁹F spectra were recorded.



Figure S49: ¹H NMR spectrum for the photolytic borylation of C_6D_6 by CpFe(PEt₃)₂Bpin for 1 h.



Figure S50: ³¹B NMR spectrum for the photolytic borylation of C_6D_6 by CpFe(PEt₃)₂Bpin for 1 h.



Figure S51: ³¹P{¹H} NMR spectrum for the photolytic borylation of C_6D_6 by $CpFe(PEt_3)_2Bpin$ for 1 h.



Figure S52: ¹H NMR spectrum for the photolytic borylation of C_6D_6 by $CpFe(PMe_3)_2Bpin$ for 1 h.



Figure S53: ¹¹B NMR spectrum for the photolytic borylation of C_6D_6 by CpFe(PMe₃)₂Bpin for 1 h.



Figure S54: ³¹P{¹H} NMR spectrum for the photolytic borylation of C_6D_6 by CpFe(PMe₃)₂Bpin for 1 h.



Figure S55: ¹H NMR spectrum for the photolytic borylation of C_6D_6 by $CpFe(P(OMe)_3)_2Bpin$ for 1 h.



Figure S56: ¹¹B NMR spectrum for the photolytic borylation of C_6D_6 by $CpFe(P(OMe)_3)_2Bpin$ for 1 h.



Figure S57: ³¹P{¹H} NMR spectrum for photolytic borylation of C_6D_6 by $CpFe(P(OMe)_3)_2Bpin$ for 1 h.



Figure S58: ¹H NMR spectrum for photolytic borylation of C₆D₆ by CpFe(P(OCH₂CF₃)₃)₂Bpin for 1 h.



Figure S59: ¹¹B NMR spectrum for the photolytic borylation of C_6D_6 by $CpFe(P(OCH_2CF_3)_3)_2Bpin$ for 1 h.



Figure S60: ³¹P{¹H} NMR spectrum for the photolytic borylation of C_6D_6 by $CpFe(P(OCH_2CF_3)_3)_2Bpin$ for 1 h.



Figure S61: ¹⁹F NMR spectrum for photolytic borylation of C_6D_6 by $CpFe(P(OCH_2CF_3)_3)_2Bpin$ for 1 h.

Kinetic Study of CpFe(PEt₃)₂Bpin: In a nitrogen filled glovebox, CpFe(PEt₃)₂Bpin (5.4 mg, 0.0111 mmol) and hexamethylbenzene (3.7 mg, 0.0228 mmol) were dissolved in C₆D₆ (2 mL). Two separate 1 mL aliquots were removed and filtered through a Celite filled pipette into a J-Young NMR tube. The tubes were sealed. The reaction was monitored over the course of 6 hours at 70°C on an Avance Bruker 500 MHz NMR.



5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 fl (ppm)

Figure S62: Monitored thermal borylation of C_6D_6 with $CpFe(PEt_3)_2Bpin$ for 6 h at 70°C. The peak at 4.22 ppm is representative of the Cp resonance for $CpFe(PEt_3)_2Bpin$. The peak at 4.08 ppm is representative of Cp resonance of $CpFe(PEt_3)_2H$. Each data point corresponds to 5.5 minutes between scans.



Figure S63: Mass balance of monitored thermal borylation of C_6D_6 with $CpFe(PEt_3)_2Bpin 6$ h at 70°C. I.S. = internal standard

Kinetic Study of CpFe(PEt₃)₂Bpin with 1 eq. of PEt₃: In a nitrogen filled glovebox, CpFe(PEt₃)₂Bpin (10.5 mg, 0.0217 mmol) and hexamethylbenzene (6.0 mg, 0.0370 mmol) were dissolved in C_6D_6 (2 mL). Into that vial, PEt₃ (3.1 mg, 0.0264 mmol) was added. Two separate 1 mL aliquots were removed and filtered through a Celite filled pipette into a J-Young NMR tube. The tubes were sealed. The reaction was monitored over the course of 6 hours at 70°C on an Avance Bruker 500 MHz NMR.



Figure S64: Monitored thermal borylation of C_6D_6 with $CpFe(PEt_3)_2Bpin$ and 1 eq. of PEt₃ for 6 h at 70°C. The peak at 4.22 ppm is representative of the Cp resonance for $CpFe(PEt_3)_2Bpin$. The peak at 4.08 ppm is representative of Cp resonance of $CpFe(PEt_3)_2H$. Each data point corresponds to 5.5 minutes between scans.



Figure S65: Mass balance of monitored thermal borylation of C_6D_6 with $CpFe(PEt_3)_2Bpin$ and 1 eq. of PEt₃ for 6 h at 70°C. I.S. = internal standard

Catalytic Thermal Borylation of Benzene-d₆ by CpFe(PEt₃)₂Bpin and HBpin: In a nitrogen filled glovebox, CpFe(PEt₃)₂Bpin (4.1 mg, 0.00847 mmol) and hexamethylbenzene (2.7 mg, 0.166 mmol) were dissolved in benzene-d₆ (1 mL) and filtered through a Celite filled pipette into a J-Young NMR tube. Pinacolborane (13.3 μ L, 0.0917 mmol) was syringed into the NMR tube. The tube was sealed and placed in an oil bath at 70°C for 24 h.



Figure S66: ¹H NMR spectrum for the catalytic thermal borylation of benezene- d_6 by CpFe(PEt₃)₂Bpin and HBpin at 0 h.



Figure S67: ¹¹B NMR spectrum for the catalytic thermal borylation of benezene-d₆ by $CpFe(PEt_3)_2Bpin$ and HBpin at 0 h.



Figure S68: ³¹P{¹H} NMR spectrum for the catalytic thermal borylation of benezene-d₆ by $CpFe(PEt_3)_2Bpin$ and HBpin at 0 h.



Figure S69: ¹H NMR spectrum for the catalytic thermal borylation of benezene- d_6 by CpFe(PEt₃)₂Bpin and HBpin at 70°C for 24 h.



Figure S70: ¹¹B NMR spectrum for the catalytic thermal borylation of benezene- d_6 by CpFe(PEt₃)₂Bpin and HBpin at 70°C for 24 h.



Figure S71: ³¹P{¹H} NMR spectrum for the catalytic thermal borylation of benezene-d₆ by $CpFe(PEt_3)_2Bpin$ and HBpin at 70°C for 24 h.

Reaction between CpFe(PEt₃)₂H and HBpin: In a nitrogen filled glovebox, CpFe(PEt₃)₂H (9.5 mg, 0.0265 mmol) and pinacolborane (3.8μ L, 0.0261 mmol) were dissolved in benzene-d₆ (1 mL) and filtered through a Celite filled pipette into a J-Young NMR tube. The tube was sealed and placed in an oil bath at 70°C for 24 h.



Figure S72: ¹H NMR spectrum for reaction of CpFe(PEt₃)₂H and HBpin at 0 h.



Figure S73: ¹¹B NMR spectrum for reaction of CpFe(PEt₃)₂H and HBpin at 0 h.



Figure S74: ³¹P{¹H} NMR spectrum for reaction of CpFe(PEt₃)₂H and HBpin at 0 h.



Figure S75: ¹H NMR spectrum for reaction of CpFe(PEt₃)₂H and HBpin at 70°C for 24 h.



Figure S76: ¹¹B NMR spectrum for reaction of CpFe(PEt₃)₂H and HBpin at 70°C for 24 h.



Figure S77: ³¹P{¹H} NMR spectrum for reaction of CpFe(PEt₃)₂H and HBpin at 70°C for 24 h.

Reaction between CpFe(PEt₃)₂H and [IPrCuH]₂: In a nitrogen filled glovebox, in a scintillation vial, CpFe(PEt₃)₂H (7.9 mg, 0.02221 mmol) was dissolved in benzene (5 mL). In a separate vial, IPrCuOtBu (12.0 mg, 0.0228 mmol) was dissolved in benzene (5 mL). Into that vial, (EtO)₃SiH (4.2 μ L, 0.0228) was syringed in and the solution turned bright yellow. The bright yellow solution of [IPrCuH]₂ was transferred to the vial containing CpFe(PEt₃)₂H. After 30 minutes, the solution turned black. It was dried *in vacuo* and analyzed via NMR. The resulting products were IPr free carbene, which matched with according literature values, and CpFe(PEt₃)₂H.



Figure S78: ¹H NMR spectrum for reaction of CpFe(PEt₃)₂H and [IPrCuH]₂.



Figure S79: ³¹P{¹H} NMR spectrum for reaction of CpFe(PEt₃)₂H and [IPrCuH]₂.