## **Supporting Information**

Metal-ligand cooperativity across two sites of a square planar iron(II) complex ligated by a tetradentate PNNP ligand

Gillian P. Hatzis and Christine M. Thomas

Department of Chemistry and Biochemistry, The Ohio State University, 100 W. 18<sup>th</sup> Ave, Columbus OH 43210 USA. thomasc@chemistry.ohio-state.edu

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## **Experimental Details:**

General Considerations. Unless otherwise noted, all manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques. Glassware was oven-dried before use. All protio solvents were degassed by sparging with ultra-high purity argon and dried via passage through columns of drying agents using a Glass Contours solvent purification system from Pure Process Technologies. Benzene- $d_6$  was degassed via repeated freeze-pump-thaw cycles and dried over 3 Å molecular sieves before use. N,N-bis(2-(diphenylphosphino)phenyl)ethane-1,2-diamine (PN<sup>H</sup>N<sup>H</sup>P) (1)<sup>1</sup> and dimesityliron(II) dimer<sup>2</sup> were synthesized according to literature procedures. NMR spectra were recorded at ambient temperature unless otherwise stated on a Bruker DPX 400 MHz or a Bruker AVIII 600 MHz instrument. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were referenced to residual solvent resonances and are reported in ppm. <sup>31</sup>P NMR and <sup>11</sup>B chemical shifts (in ppm) were referenced using 85% H<sub>3</sub>PO<sub>4</sub> (0 ppm) and BF<sub>3</sub>•OEt<sub>2</sub> (0 ppm) respectively, as external standards. Solid-state attenuated total reflection (ATR) infrared spectra were recorded on a Bruker ALPHA II spectrometer controlled by OPUS software. UV-vis spectra were recorded on a Cary 5000 UV-vis-NIR spectrophotometer using Cary WinUV software. All other reagents and solvents were obtained from commercial sources and used without further purification. Elemental microanalyses were performed by Midwest Microlab, Indianapolis, IN.

**Mössbauer Spectroscopy:** <sup>57</sup>Fe Mössbauer spectra were measured on a constant acceleration spectrometer (SEE Co. Minneapolis, MN) with a Janis SHI-4 cryostat. Isomer shifts are quoted relative to  $\alpha$ -Fe foil (<25 µm thick) at room temperature. Samples were prepared using approximately 50 mg of sample suspended in paratone-N oil and loaded under liquid N<sub>2</sub> to avoid air and moisture. All data were collected at 4 K unless specified otherwise. Data were analyzed using the WMOSS version F software package.<sup>3</sup>

**Magnetic Susceptibility Measurements**: Solid-state magnetic measurements were recorded using a Quantum Designs MPMS 3 magnetometer at 1 T. The sample was contained under nitrogen in a gelcap and suspended in the magnetometer in a plastic straw. The magnetic susceptibility was adjusted for diamagnetic contributions using Pascal's constants. Data were fit using the PHI software package.<sup>4</sup> A suitable fit was obtained for an S = 1 center with *g* = 2.563 ± 0.003 and *D* = 38 ± 1 cm<sup>-1</sup> using the Van Vleck equation<sup>5</sup>:

$$\chi = \frac{Ng^2 \mu_B^2 \exp\left(\frac{-D}{kT}\right) + \binom{2kT}{D} \left[1 - \exp\left(\frac{D}{kT}\right)\right]}{1 + 2\exp\left(\frac{-D}{kT}\right)}$$

**Synthesis of (PNNP)Fe (2)**: A 20 mL vial was charged with dimesityliron(II) dimer (0.508 g, 0.862 mmol) and THF (2 mL). A 100 mL round bottom flask was charged with PN<sup>H</sup>N<sup>H</sup>P (1) (1.00 g, 1.72 mmol), THF (10 mL) and a stir bar then both solutions were frozen in the glovebox coldwell with liquid N<sub>2</sub>. The thawing dimesityliron(II) dimer solution was added to the thawing solution of 1 and the reaction was allowed to stir at room temperature. Gradually, the reaction mixture became a dark red color, and solid began to precipitate. After 1 hour, 90 mL of diethyl ether was added to the round bottom flask to precipitate the product, which was collected on a frit and washed with diethyl ether to yield 2 as an analytically pure solid (0.894 g, 82%). Single crystals of 2 suitable for X-ray diffraction were grown via the diffusion of diethyl ether vapor into a concentrated THF solution of 2 at -35 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  28.86, 19.36, 6.48, 4.86, 1.35 (broad), -13.75, -54.36. The signal corresponding to the methylene backbone protons could not be located in the <sup>1</sup>H NMR spectrum and is likely shifted outside of the available spectral window. UV-vis [THF;  $\lambda$ ,

nm( $\epsilon$ , cm<sup>-1</sup> M<sup>-1</sup>)]: 519 (2.1×10<sup>3</sup>), 463 (2.7×10<sup>3</sup>), 331 (2.4×10<sup>4</sup>), 284 (5.3×10<sup>4</sup>), 255 (6.0×10<sup>4</sup>). Anal. Calcd for C<sub>38</sub>H<sub>32</sub>N<sub>2</sub>P<sub>2</sub>Fe: C, 71.94; H, 5.08; N, 4.42. Found: C, 71.34; H, 4.99; N, 4.01.

Synthesis of (PNNP)Fe(PMe<sub>3</sub>) (3): Solid 2 (0.036 g, 0.057 mmol),  $C_6H_6$  (4 mL) and a stir bar were all added to a 20 mL vial, then trimethylphosphine (8.7 µL, 0.086 mmol) was added via micropipette. The solution immediately became a bright red color, and the reaction was allowed to stir for 1 hour. The reaction mixture was then frozen, and the  $C_6H_6$  was lyophilized to yield a bright red solid. The remaining solids were extracted into diethyl ether, and any insoluble material was removed by filtration through a pipet with a piece of glass microfiber filter paper. Any volatile components were removed in vacuo and the resulting solid was triturated with benzene to yield 3 as an analytically pure solid (0.031 g, 76%). Crystals of 3 suitable for X-ray diffraction were grown via the diffusion of pentane vapor into a concentrated  $C_6H_6$  solution of **3** at room temperature. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.69 (m, Ar-H, 4H), 7.55 (m, Ar-H, 4H), 7.41 (m, Ar-H, 2H), 7.33 (t, Ar-H, J<sub>H-H</sub> = 7.4 Hz, 2H), 7.05 (broad d, Ar-H, J<sub>H-H</sub> = 6.1 Hz, 2H), 6.94 (m, Ar-H, 2H), 6.89 (t, Ar-H, J<sub>H-H</sub> = 7.4 Hz, 4H), 6.84 (t, Ar-H, J<sub>H-H</sub> = 7.2 Hz, 2H), 6.77 (t, Ar-H, J<sub>H-H</sub> = 7.1 Hz, 2H), 6.72 (t, Ar-H, J<sub>H-H</sub> = 7.6 Hz, 4H), 3.87 (q, CH<sub>2</sub>CH<sub>2</sub>, J<sub>H-H</sub> = 5.6 Hz, 2H), 3.50 (q, CH<sub>2</sub>CH<sub>2</sub>, J<sub>H-H</sub> = 5.7 Hz, 2H), 0.08 (d, P(CH<sub>3</sub>)<sub>3</sub>,  ${}^{2}J_{H-P}$  = 9.5 Hz, 9H).  ${}^{31}P{}^{1}H$  NMR (242.9 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  71.7 (d, PPh<sub>2</sub>,  ${}^{2}J_{PPh_2-PMe_3}$  = 45.6 Hz, 2P), 36.0 (t, PMe<sub>3</sub>, <sup>2</sup>J<sub>PMe3-PPh2</sub> = 45.7 Hz, 1P). <sup>13</sup>C{<sup>1</sup>H} NMR (150.9 MHz, C<sub>6</sub>D<sub>6</sub>): δ 168.2 (t, Ar,  $J_{C-P}$  = 13.2 Hz), 137.8 (overlapping m, Ar), 137.6 (overlapping m, Ar), 133.7 (t, Ar,  $J_{C-P}$  = 4.2 Hz), 132.1 (t, Ar, J<sub>C-P</sub> = 5.6 Hz), 132.0 (s, Ar), 131.8 (s, Ar), 129.0 (s, Ar), 128.6 (s, Ar), 128.6 (broad s, Ar), 128.3 (s, Ar), 125.3 (m, Ar), 115.6 (s, Ar), 112.9 (t, Ar, J<sub>C-P</sub> = 5.5 Hz), 54.98 (s, CH<sub>2</sub>CH<sub>2</sub>), 17.8 (d, P(CH<sub>3</sub>)<sub>3</sub>, J<sub>C-P</sub> = 23.9 Hz). UV-vis [THF; λ, nm(ε, cm<sup>-1</sup> M<sup>-1</sup>)]: 895 (4.7×10<sup>3</sup>), 543 3.0×10<sup>3</sup>), 410 (5.0×10<sup>3</sup>), 339 (1.2×10<sup>4</sup>), 284 (3.3×10<sup>4</sup>), 253 (4.7×10<sup>4</sup>). Anal. Calcd for C<sub>41</sub>H<sub>41</sub>N<sub>2</sub>P<sub>3</sub>Fe: C, 69.30; H, 5.82; N, 3.94. Found: C, 69.25; H, 6.03; N, 3.78.

Synthesis of (PN<sup>BPin</sup>N<sup>BPin</sup>P)FeH<sub>2</sub> (4): Solid 2 (0.024 g, 0.038 mmol), C<sub>6</sub>H<sub>6</sub> (3 mL) and a stir bar were added to a 20 mL vial, then pinacolborane (11.0 µL, 0.076 mmol) was added via micropipette. The solution immediately became a bright orange color and was left to stir for 30 minutes. The reaction mixture was subsequently frozen, and the C<sub>6</sub>H<sub>6</sub> was lyophilized. The remaining yellow solid was washed with diethyl ether and collected with C<sub>6</sub>H<sub>6</sub>. The volatile components were removed in vacuo and the resulting solid was triturated with pentane to yield 4 as a pure solid (0.030 g, 89%). Crystals of 4 suitable for X-ray diffraction were grown via the diffusion of pentane vapor into a concentrated THF solution of 4 at -35 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.55 (broad m, Ar-H, 4H), 7.40 (broad m, Ar-H, 4H), 7.34 (broad m, Ar-H, 4H), 7.03 (overlapping m, Ar-H, 10H), 6.85 (t, Ar-H, J<sub>H-H</sub> = 7.3 Hz, 4H), 6.77 (t, Ar-H, J<sub>H-H</sub> = 7.4 Hz, 2H), 4.07 (broad m, CH2CH2, 2H), 3.76 (broad m, CH2CH2, 2H), 1.12 (s, C(CH3)2C(CH3)2, 6H), 1.04 (s, C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>, 6H), 0.56 (s, C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>, 6H), 0.49 (s, C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>, 6H), -15.16 (broad s, Fe-H, 2H). <sup>31</sup>P{<sup>1</sup>H} NMR (242.9 MHz, C<sub>6</sub>D<sub>6</sub>): δ 84.2 (s, PPh<sub>2</sub>, 2P). <sup>11</sup>B{<sup>1</sup>H} NMR (192.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ 4.9 (s, BPin, 2B). <sup>13</sup>C{<sup>1</sup>H} NMR (150.9 MHz, C<sub>6</sub>D<sub>6</sub>): δ 163.6 (m, Ar), 142.3 (m, Ar), 139.0 (m, Ar), 135.7 (m, Ar), 135.0 (t, Ar, J<sub>C-P</sub> = 5.5 Hz), 134.0 (t, Ar, J<sub>C-P</sub> = 5.1 Hz), 131.9 (s, Ar), 129.3 (s, Ar), 128.7 (s, Ar), 128.6 (s, Ar), 128.4 (t, Ar,  $J_{C-P}$  = 13.5 Hz), 127.0 (t, Ar,  $J_{C-P}$  = 4.4 Hz), 123.0 (s, Ar), 120.8 (t, Ar,  $J_{C-P} = 5.3 \text{ Hz}$ ), 80.4 (s,  $C(CH_3)_2C(CH_3)_2$ ), 79.8 (s,  $C(CH_3)_2C(CH_3)_2$ ), 53.9 (s, CH<sub>2</sub>CH<sub>2</sub>), 25.6 (s, C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>), 25.0 (s, C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>), 24.9 (s, C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>), 23.6 (s, C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>). UV-vis [THF; λ, nm(ε, cm<sup>-1</sup> M<sup>-1</sup>)]: 324 (3.5×10<sup>3</sup>), 266 (2.1×10<sup>4</sup>). Anal. Calcd for C<sub>50</sub>H<sub>58</sub>B<sub>2</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Fe: C, 67.44; H, 6.57; N, 3.15. Found: C, 66.92; H, 6.71; N, 2.67.

**Synthesis of (PN**<sup>BH2</sup>**N**<sup>BH2</sup>**P)FeH<sub>2</sub>(4-BH<sub>3</sub>)**: Solid **2** (0.097 g, 0.15 mmol), C<sub>6</sub>H<sub>6</sub> (5 mL) and a stir bar were added to a 20 mL vial, then H<sub>3</sub>B•SMe<sub>2</sub> (36.1  $\mu$ L, 0.38 mmol) was added via micropipette. The solution immediately became a bright orange color and was left to stir for 30 minutes. The reaction mixture was subsequently frozen, and the C<sub>6</sub>H<sub>6</sub> was lyophilized. The remaining orange solid was washed with diethyl ether and collected with C<sub>6</sub>H<sub>6</sub>. The volatile components were removed *in vacuo* and the remaining solid was triturated with pentane to yield **4-BH<sub>3</sub>** as a pure

solid (0.100 g, 99%). Crystals of **4-BH**<sub>3</sub> suitable for X-ray diffraction were grown via the diffusion of pentane vapor into a concentrated THF solution of **4-BH**<sub>3</sub> at -35 °C. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.55 (t, Ar-H, *J*<sub>H-H</sub> = 8.3 Hz, 4H), 7.33 (t, Ar-H, *J*<sub>H-H</sub> = 8.4 Hz, 4H), 7.28 (d, Ar-H, *J*<sub>H-H</sub> = 7.9 Hz, 2H), 7.22 (m, Ar-H, 2H), 7.02 (t, Ar-H, *J*<sub>H-H</sub> = 7.7 Hz, 2H), 6.95 (m, Ar-H, 4H), 6.84 (t, Ar-H, *J*<sub>H-H</sub> = 7.4 Hz, 4H), 6.77 (m, Ar-H, 6H), 3.35 (m, CH<sub>2</sub>CH<sub>2</sub>, 2H), 3.24 (m, CH<sub>2</sub>CH<sub>2</sub>, 2H), 2.59-1.47 (overlapping broad s, BH<sub>2</sub>, 4H), -15.40 (broad s, Fe-H, 2H). <sup>31</sup>P{<sup>1</sup>H} NMR (242.9 MHz, C<sub>6</sub>D<sub>6</sub>): δ 85.3 (s, *P*Ph<sub>2</sub>, 2P). <sup>11</sup>B{<sup>1</sup>H} NMR (192.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ -17.1 (broad s, *B*H<sub>2</sub>, 2B). <sup>13</sup>C{<sup>1</sup>H} NMR (150.9 MHz, C<sub>6</sub>D<sub>6</sub>): 166.9 (t, Ar, *J*<sub>C-P</sub> = 8.7 Hz), 139.4 (m, Ar), 136.1 (m, Ar), 134.2 (t, Ar, *J*<sub>C-P</sub> = 5.1 Hz), 133.8 (m, Ar), 133.4 (t, Ar, *J*<sub>C-P</sub> = 5.2 Hz), 133.0 (s, Ar), 130.1 (s, Ar), 129.2 (s, Ar), 129.0 (s, Ar), 128.6 (s, Ar), 128.4 (s, Ar), 123.7 (s, Ar), 120.1 (t, Ar, *J*<sub>C-P</sub> = 5.4 Hz), 52.7 (s, s, CH<sub>2</sub>CH<sub>2</sub>). UV-vis [THF; λ, nm(ε, cm<sup>-1</sup> M<sup>-1</sup>)]: 340 (2.6×10<sup>3</sup>), 264 (1.9×10<sup>4</sup>). IR (ATR): 2418 (B-H), 2342 (B-H). Anal. Calcd for C<sub>38</sub>H<sub>38</sub>B<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Fe: C, 68.93; H, 6.57; N, 4.23. Found: C, 66.16; H, 6.74; N, 3.54. **4**-**BH**<sub>3</sub> is quite sensitive to air and moisture, so the low C and N values are attributed to oxidation of the phosphorus atoms, while the high H value is attributed to two equivalents of THF in the crystal lattice (e.g. C<sub>46</sub>H<sub>54</sub>B<sub>2</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Fe: C, 65.90; H, 6.49; N, 3.34).



**Figure S1.** <sup>1</sup>H NMR spectrum of **2** (400 MHz,  $C_6D_6$ ). The star denotes residual  $C_6D_5H$ . No additional signals were observed in the -125 to 125 ppm spectral window.



**Figure S2.** <sup>1</sup>H NMR spectrum of **3** (600 MHz,  $C_6D_6$ ). Stars denote residual signals, here  $C_6D_5H$  and diethyl ether.



Figure S4. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 3 (150.9 MHz,  $C_6D_6$ ). The star denotes residual  $C_6D_6$ .



**Figure S5.** <sup>1</sup>H NMR spectrum of **4** (400 MHz,  $C_6D_6$ ). Stars denote residual signals, here  $C_6D_5H$ , diethyl ether, and pentane. Inset shows signal corresponding to the iron hydrides.



Figure S6.  ${}^{31}P{}^{1}H$  NMR spectrum of 4 (242.9 MHz, C<sub>6</sub>D<sub>6</sub>).



Figure S7.  $^{11}B{^{1}H}$  NMR spectrum of 4 (192.5 MHz, C<sub>6</sub>D<sub>6</sub>).



Figure S8. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 4 (150.9 MHz,  $C_6D_6$ ). The star denotes residual  $C_6D_6$ .



**Figure S9.** <sup>1</sup>H NMR spectrum of **4-BH**<sub>3</sub> (600 MHz,  $C_6D_6$ ). The star denotes residual  $C_6D_5H$ . Inset shows signal corresponding to the iron hydrides.



Figure S10.  ${}^{31}P{}^{1}H$  NMR spectrum of 4-BH<sub>3</sub> (242.9 MHz, C<sub>6</sub>D<sub>6</sub>).







Figure S13. UV-Vis-NIR spectra of 2 (black) and 3 (red) at 0.1 mM in THF.



Figure S14. UV-Vis spectra of 2 (black) and 3 (red) at 0.01 mM in THF.



Figure S15. UV-Vis spectra of 4 (red) and  $4-BH_3$  (black) at 0.1 mM in THF.



Figure S16. Solid-state (ATR) IR spectrum of 4.



**Figure S17.** Solid-state (ATR) IR spectrum of **4-BH**<sub>3</sub>. Labelled peaks correspond to the terminal B-H stretches.



**Figure S18.** <sup>57</sup>Fe Mössbauer spectrum of **4-BH**<sub>3</sub>, collected at 8 K. Data is shown with black squares, and the fit is shown with the red line.

Table S1. Mössbauer	parameters for 2	, <b>3</b>	, <b>4</b> ,	, and <b>4-BH</b> ₃
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Complex	δ (mm/s)	<i>∆E<sub>Q</sub></i>   (mm/s)
2	0.17	2.20
3	0.11	1.94
4	0.16	-
4-BH <sub>3</sub>	0.19	-

## X-ray Crystallography Details.

Crystals were coated with Paratone oil and mounted on a MiTeGen MicroLoop that was previously attached to a metallic pin mechanically. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON II CPAD or a Nonius Kappa APEX II system equipped with a graphite monochromator and a Mo K $\alpha$  fine-focus tube ( $\lambda = 0.71073$  Å). Data were corrected for absorption effects with the Multi-Scan method (SADABS).<sup>6</sup> Structures were solved and refined with the Bruker SHELXTL Software Package<sup>7</sup> within APEX3<sup>6</sup> and Olex2.<sup>8</sup> Ordered Non-hydrogen atoms were refined anisotropically. Hydrogen atoms except for terminal B-H atoms and iron hydrides were placed in geometrically calculated positions with  $U_{iso} = 1.2U_{equiv}$  of the parent atom ( $U_{iso} = 1.5U_{equiv}$  for methyl).



**Figure S19**. Displacement ellipsoid (50%) representation of **2**. For clarity, all hydrogen atoms have been omitted.

**Special Structure Solution and Refinement Details for 2:** During the refinement it became clear that the crystal was a racemic twin, so this was modeled with the inversion twin law (-1 0 0, 0 -1 0, 0 0 -1) and BASF value of 0.45634.



**Figure S20**. Displacement ellipsoid (50%) representation of **3**. For clarity, all hydrogen atoms and a second molecule of **3** in the asymmetric unit have been omitted.

**Special Structure Solution and Refinement Details for 3:** During the refinement, it became clear that the reflections corresponding to the Miller indices (0,2,-1), (-2,1,1), (10,1,-3), (-10,1,3), (1,2,-1), (-2,1,0), (2,1,0), (0,2,1) and (-1,2,1) were affected by the shadow of the beamstop (error  $\geq 10$ ), and have been omitted. During the refinement, it became clear that the crystal was twinned, and this was modelled using the PLATON TWINROTMAT<sup>9</sup> technique with the twin law  $(1 \ 0 \ 0, 0 \ 1 \ 0 \ 0, 0 \ -1 \ 2)$  and a BASF value of 0.37147. The benzene solvent molecules were found to be partially disordered and these were modeled with two-component disorder, where the sum of the major and minor components was constrained to be one, and both were restrained with EADP commands.



**Figure S21**. Displacement ellipsoid (50%) representation of **4**. For clarity, all hydrogen atoms except for the iron hydrides have been omitted.

**Special Structure Solution and Refinement Details for 4:** There is a B-level alert in the checkcif that corresponds to the Hirschfield rigid bond test for two carbon atoms, but there is no ambiguity in their assignment, so this was ignored. Electron density difference maps revealed that there was disordered tetrahydrofuran solvent that could not be successfully modeled, so the structure factors were modified using the PLATON SQUEEZE<sup>10</sup> technique. PLATON reported a total electron density of 232 e<sup>-</sup> and total solvent accessible volume of 984 Å<sup>3</sup>, likely representing six tetrahydrofuran molecules per unit cell.



**Figure S22**. Displacement ellipsoid (50%) representation of  $4-BH_3$ . For clarity, a second molecule of  $4-BH_3$  in the asymmetric unit and all hydrogen atoms except for the iron hydrides and terminal B-H's have been omitted.

**Special Structure Solution and Refinement Details for 4-BH<sub>3</sub>:** There is a B-level alert in the checkcif that corresponds to the ratio of maximum to minimum residual electron density, however of the largest remaining Q-peaks did not reveal any disorder in the nearest phenyl rings, so this was ignored. There is another B-level alert corresponding to missing data at low theta values, which is just due to the size of the beam stop on the Bruker D8 Venture PHOTON II CPAD system. During the refinement, it became clear that the reflections corresponding to the Miller indices (-1,2,3), (1,-2,4), (2,-2,2), (3,-1,3), (2,-1,1), (-1,1,4), (3,0,2), (-2,1,4), (1,1,2), (-1,1,3), (-7,1,1), (-7,4,2), (1,-1,6), (0,0,5), (-1,0,4), (0,1,4) and (0,3,2) were affected by the shadow of the beamstop (error  $\geq$ 10), and have been omitted. Electron density difference maps revealed that there was disordered tetrahydrofuran solvent that could not be successfully modeled, so the structure factors were modified using the PLATON SQUEEZE<sup>10</sup> technique. PLATON reported a total electron density of 207 e<sup>-</sup> and total solvent accessible volume of 1753 Å<sup>3</sup>, likely representing five tetrahydrofuran molecules per unit cell. Some of the terminal B-H atoms would not refine properly, so some of these B-H bond lengths were restrained with DFIX commands.

	2	3	4	<b>4-BH</b> ₃
Chemical formula	$C_{42}H_{40}N_2OP_2Fe$	$C_{47}H_{47}N_2P_3Fe$	$C_{50}H_{58}B_2N_2O_4P_2$ Fe	$C_{38}H_{38}B_2N_2P_2Fe$
Fw (g/mol)	706.55	788.62	890.39	662.11
<i>T</i> (K)	100	150	200	200
λ (Å)	0.71073	0.71073	0.71073	0.71073
a (Å)	15.4937(9)	17.3592(13)	11.7019(8)	14.1841(8)
b (Å)	9.7340(6)	16.4666(12)	14.3131(10)	14.9374(9)
c (Å)	12.9942(13)	14.4482(11)	19.1169(14)	23.6074(14)
α (°)	90	90	83.392(2)	104.204(2
β (°)	119.954(2)	106.046(3)	73.967(2)	92.996(2)
γ (°)	90	90	72.760(2)	105.812(2
V (Å <sup>3</sup> )	1698.0(2)	3969.1(5)	2937.2(4)	4627.2(5)
Space Group	C2	Pc	<i>P</i> -1	<i>P</i> -1
Z	2	4	2	2
D <sub>calcd</sub> (g/cm <sup>3</sup> )	1.382	1.320	1.007	0.950
μ (mm <sup>-1</sup> )	0.576	0.537	0.348	0.417
$R_1 (I > 2\sigma(I))^a$	0.0269	0.0448	0.0589	0.0654
wR <sub>2</sub> (all data) <sup>a</sup>	0.0525	0.1152	0.1836	0.1956

**Table S2.** X-ray diffraction experimental details for (PNNP)Fe (2), (PNNP)FePMe<sub>3</sub> (3) and (PN<sup>BPin</sup>P)FeH<sub>2</sub> (4), and (PN<sup>BH2</sup>N<sup>BH2</sup>P)FeH<sub>2</sub> (4-BH<sub>3</sub>).

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{o}|| / \sum |F_{o}|; wR_{2} = \{\sum [w(F_{o}^{2} - F_{c}^{2})_{2}] / \sum [w(F_{o}^{2})^{2}] \}^{1/2}$ 

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