

## Investigation of Formally Zerovalent Triphos Iron Complexes

*Supplementary Information*

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## Experimental Procedures

**General Considerations.** All synthetic reactions were performed in an MBraun glovebox under an atmosphere of purified nitrogen. Aldrich or Acros anhydrous solvents were sparged with argon and stored in the glovebox over activated 4Å molecular sieves and sodium (Alfa Aesar) before use. Benzene-*d*<sub>6</sub> and tetrahydrofuran-*d*<sub>8</sub> were purchased from Cambridge Isotope Laboratories and dried over 4Å molecular sieves prior to use. Bis(2-diphenylphosphinoethyl)phenylphosphine (Triphos) and iron(II) bromide were purchased from Acros, while iron(III) chloride, diphenylacetylene, and 2,2'-bipyridine were used as received from Aldrich. Iron(III) bromide and potassium metal were used as obtained from Strem. All of the gases in this study were obtained from Praxair, with the exception of carbon monoxide which was purchased from Aldrich. [(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh]FeCl<sub>2</sub> (**1-Cl**<sub>2</sub>) was prepared from the straightforward addition of Triphos to iron dichloride (Strem) in THF solution, an adaptation of literature procedure.<sup>1</sup> Solution <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were recorded at room temperature on either a Bruker AVANCE 400 MHz spectrometer or Varian MR 400. All <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported relative to SiMe<sub>4</sub> using <sup>1</sup>H (residual) and <sup>13</sup>C chemical shifts of the solvent as secondary standards. <sup>31</sup>P NMR data is reported relative to H<sub>3</sub>PO<sub>4</sub>. Elemental analyses were performed at Robertson Microlit Laboratories Inc., in Ledgewood, NJ. Solid state magnetic susceptibilities were determined at 23 °C using a Johnson Matthey magnetic susceptibility balance calibrated with HgCo(SCN)<sub>4</sub> and K<sub>3</sub>Fe(CN)<sub>6</sub>.

**Electrochemistry.** Electrochemical measurements were run with an EG&G Princeton Applied Research model 263A potentiostat. A conventional three-electrode setup was used for cyclic voltammetry, with a glassy carbon working electrode, a Pt-wire auxiliary electrode, and a Ag/Ag<sup>+</sup> reference electrode (0.01 M AgNO<sub>3</sub>; 0.10 M NBu<sub>4</sub>PF<sub>6</sub>). Extra dry, deoxygenated tetrahydrofuran was used as solvent to prepare sample solutions. All measurements were made in a glovebox under inert atmosphere (Ar) at room temperature.

**X-Ray Crystallography.** Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox and transferred to a nylon loop which was then mounted on the goniometer head of a Bruker APEX II diffractometer equipped with Mo K<sub>α</sub> radiation. A hemisphere routine was used for data collection and determination of the lattice constants. The

space group was identified and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS), completed by subsequent Fourier synthesis, and refined by full-matrix, least-squares procedures on  $|F|^2$  (SHELXL). For  $(\kappa^2\text{-Triphos})_2\text{FeCl}_2$ , a molecule of toluene was located at an inversion centre and disordered by symmetry. The two components overlap such that some carbons could be modeled with full occupancy, others with half occupancy, to yield the proper total occupancies after superposition. Hydrogen atoms were not located for this molecule.

**Preparation of  $[(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}]\text{FeBr}_2$  (**1-Br<sub>2</sub>**):** In the glove box, a 250 mL round-bottomed flask was charged with 0.250 g Triphos (0.468 mmol), 0.101 g (0.468 mmol) of  $\text{FeBr}_2$ , and approximately 75 mL of tetrahydrofuran. The resulting yellow solution was set to stir at an ambient temperature. After 17 hours, the reaction mixture was filtered through Celite and the filtrate was concentrated to yield a dark orange film. This material was scraped from the sides of the filter flask in the presence of approximately 5 mL of pentane and dried *in vacuo*. After repeating this process 2 additional times (to ensure removal of residual tetrahydrofuran), 0.327 g of a dark orange microcrystalline solid identified as **1-Br<sub>2</sub>** was collected (93% yield). Analysis for  $\text{C}_{34}\text{H}_{33}\text{Br}_2\text{FeP}_3$ : Calcd. C, 54.41%; H, 4.40%. Found: C, 54.19%; H, 4.33%. Magnetic Susceptibility (Gouy Balance, 23 °C):  $\mu_{\text{eff}} = 4.8 \mu_{\text{B}}$ .  $^1\text{H}$  NMR (tetrahydrofuran- $d_8$ , 23 °C):  $\delta$  (ppm) = 98.38 (2959.1 Hz, 2H,  $\text{CH}_2$ ), 43.10 (1511.7 Hz, 2H,  $\text{CH}_2$ ), 34.24 (1527.8 Hz, 2H,  $\text{CH}_2$ ), 26.2 (855.48 Hz, 2H,  $\text{CH}_2$ ), 16.3 (105.95 Hz, 4H, *phenyl*), 11.74-11.20 (m, 16H, *phenyl*), 9.94 (46.41 Hz, 1H, *phenyl*), 3.07 (71.64 Hz, 2H, *phenyl*), 2.44 (55.28 Hz, 2H, *phenyl*).

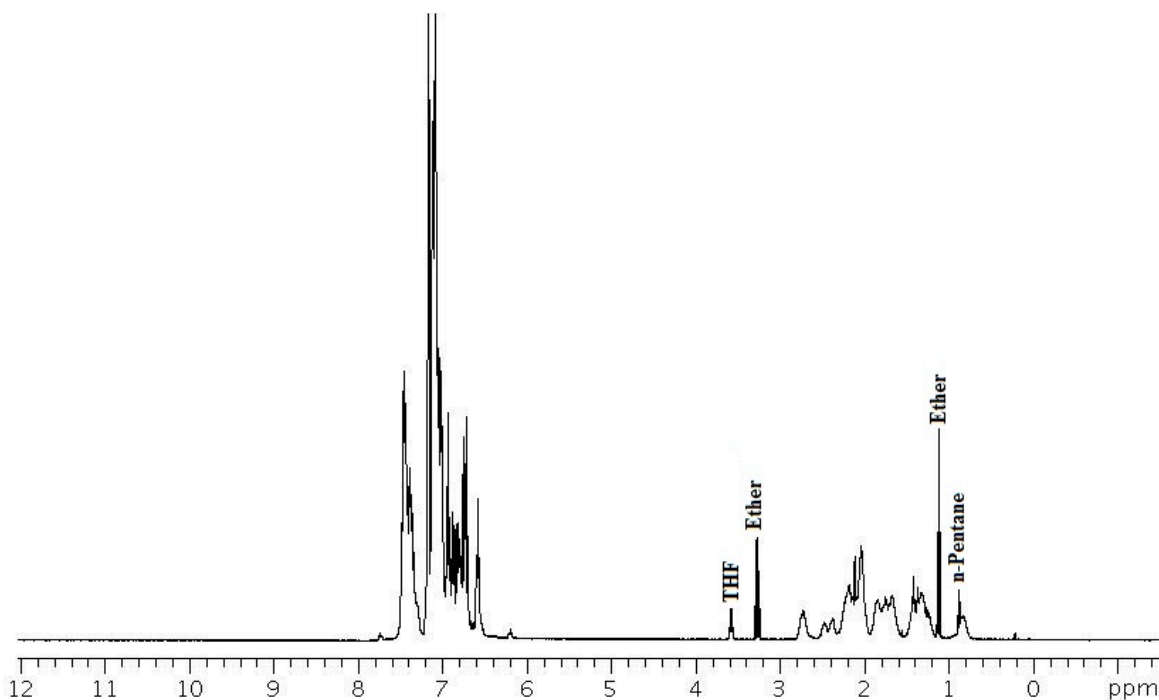
**Preparation of  $[(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}]\text{FeCl}_3$  (**1-Cl<sub>3</sub>**):** In the glove box, a 250 mL round-bottomed flask was charged with 0.141 g (0.869 mmol) of  $\text{FeCl}_3$  and approximately 50 mL of tetrahydrofuran resulting in the formation of yellow solution. A second solution containing 0.465 g Triphos (0.870 mmol) in approximately 15 mL of tetrahydrofuran was prepared and added drop-wise to the iron trichloride solution while stirring. The reaction mixture darkened from yellow to reddish-orange in color until the halfway point of addition, at which point it began to turn green in color. Upon stirring at ambient temperature for 90 min, the resulting emerald green solution was filtered through Celite and the solvent was evacuated. The resulting solid was washed twice with about 10 mL of diethylether and then twice with 10 mL of pentane to remove

any residual Triphos or tetrahydrofuran. After drying under vacuum, 0.586 g (0.843 mmol, 97% yield) of a dark green solid identified as **1-Cl<sub>3</sub>** was collected. Analysis for C<sub>34</sub>H<sub>33</sub>Cl<sub>3</sub>FeP<sub>3</sub>: Calcd. C, 58.59%; H, 4.74%. Found: C, 58.38%; H, 4.88%. Magnetic Susceptibility (Gouy Balance, 23 °C):  $\mu_{eff} = 4.3 \mu_B$ . <sup>1</sup>H NMR (tetrahydrofuran-*d*<sub>8</sub>, 23 °C):  $\delta$  (ppm) = 13.22 – 4.65 (m, *phenyl*), -19.34 (615.72 Hz, 2H, CH<sub>2</sub>), -24.32 (725.55 Hz, 2H, CH<sub>2</sub>), -46.02 (1918.85 Hz, 2H, CH<sub>2</sub>), -49.62 (2529.81 Hz, 2H, CH<sub>2</sub>).

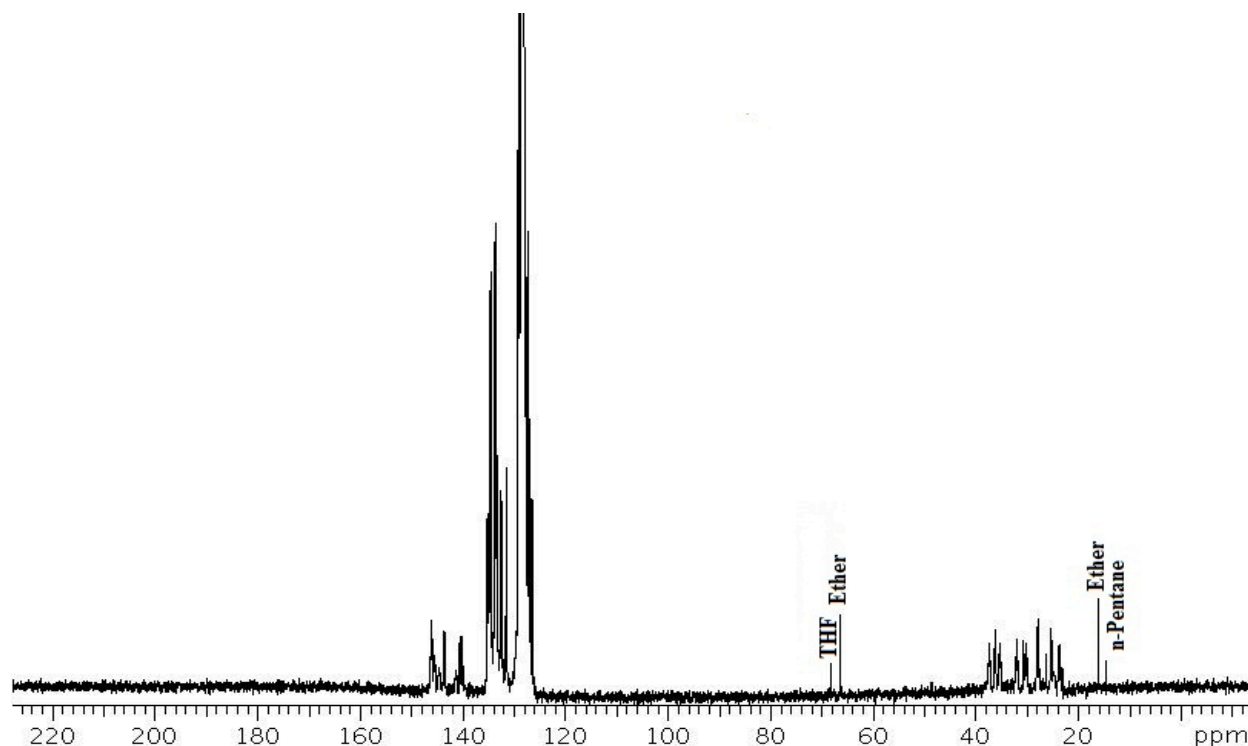
**Preparation of [(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh]FeBr<sub>3</sub> (**1-Br<sub>3</sub>**):** In the glove box, a 250 mL round-bottomed flask was charged with 0.425 g of Triphos (0.796 mmol), 0.235 g (0.795 mmol) of FeBr<sub>3</sub> and approximately 100 mL of tetrahydrofuran. The resulting yellow solution was set to stir at ambient temperature. After 1 hour, the reaction had turned dark red-orange in color. After 20 hours, the resulting bright orange solution was filtered through Celite and the solvent was evacuated to yield a yellow film. The material was scraped from the sides of the filter flask in the presence of approximately 5 mL of pentane and then dried *in vacuo* to yield 0.571 g (0.688 mmol, 86% yield) of an olive green solid identified as **1-Br<sub>3</sub>**. Analysis for C<sub>34</sub>H<sub>33</sub>Br<sub>3</sub>FeP<sub>3</sub>: Calcd. C, 49.22%; H, 3.98%. Found: C, 48.64%; H, 4.11%. Magnetic Susceptibility (Gouy Balance, 23 °C):  $\mu_{eff} = 5.6 \mu_B$ . <sup>1</sup>H NMR (tetrahydrofuran-*d*<sub>8</sub>, 23 °C):  $\delta$  (ppm) = 27.51 ppm (772.8 Hz), 9.84 (m), 8.68 (m), 6.55 (m), several resonances not located. <sup>31</sup>P{<sup>1</sup>H} NMR (tetrahydrofuran-*d*<sub>8</sub>, 23 °C):  $\delta$  (ppm) = -22.10 (449.9 Hz).

**Preparation of [ $\kappa^3$ -(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh]Fe[ $\kappa^2$ -(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh] [1-( $\kappa^2$ -Triphos)]:** In the glove box, a 20 mL vial was charged with 0.159 g (0.213 mmol) of **1-Br<sub>2</sub>** and approximately 15 mL of tetrahydrofuran. To this resulting yellow solution, 0.025 g (1.065 mmol, 5 equivalents) of sodium metal was added and the vial was set to stir. After 2 hours it had turned reddish-yellow in color. After 16 hours the resulting dark red solution was filtered through Celite and the solvent was evacuated to obtain a dark red film. It was washed with approximately 10 mL of pentane and then dried under vacuum to yield 0.076 g (0.068 mmol, 32% recrystallized yield) of a dark red microcrystalline solid identified as **1-( $\kappa^2$ -Triphos)**. Elemental Analysis for C<sub>68</sub>H<sub>66</sub>FeP<sub>6</sub>: Calcd. C, 72.64%; H, 5.87%. Found: C, 71.90%, H 5.71%. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta$  (ppm) = 7.48-7.30 (m, 12H, *phenyl*), 7.12-6.99 (m, 20H, *phenyl*), 6.93 (t, *J* = 7.6 Hz, 3H, *phenyl*), 6.86 (m, 2H, *phenyl*), 6.81 (m, 4H, *phenyl*), 6.73 (m, 4H, *phenyl*), 6.58 (t, *J* = 8.0 Hz, 2H, *phenyl*), 2.72 (broad

m, 1H,  $\text{CH}_2\text{P}$ ), 2.42 (broad m, 1H,  $\text{CH}_2\text{P}$ ), 2.18 (broad m, 2H,  $\text{CH}_2\text{P}$ ), 2.04 (broad m, 3H,  $\text{CH}_2\text{P}$ ), 1.75 (broad m, 4H,  $\text{CH}_2\text{P}$ ), 1.31 (broad m, 4H,  $\text{CH}_2\text{P}$ ), 0.82 (broad m, 1H,  $\text{CH}_2\text{P}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzene- $d_6$ ):  $\delta$  (ppm) = 146.3 (m, *i*-phenyl), 145.9 (m, *i*-phenyl), 145.4 (m, *i*-phenyl), 144.5 (m, *i*-phenyl), 143.5 (m, *i*-phenyl), 141.2 (m, *i*-phenyl), 140.4 (d,  $J_{\text{CP}} = 16.6$  Hz, *i*-phenyl), 140.0 (d,  $J_{\text{CP}} = 16.5$  Hz, *i*-phenyl), 135.1 (d,  $J_{\text{CP}} = 10.5$  Hz, *i*-phenyl), 134.8 (d,  $J_{\text{CP}} = 11.9$  Hz, phenyl), 134.5 (s, phenyl), 134.4 (m, phenyl), 133.8 (d,  $J_{\text{CP}} = 8.4$  Hz, phenyl), 133.7 (s, phenyl), 133.6 (s, phenyl), 133.4 (s, phenyl), 133.3 (d,  $J_{\text{CP}} = 8.9$  Hz, phenyl), 132.5 (d,  $J_{\text{CP}} = 6.8$  Hz, phenyl), 131.4 (d,  $J_{\text{CP}} = 7.0$  Hz, phenyl), 129.2 (d,  $J_{\text{CP}} = 6.0$  Hz, phenyl), 129.0 (m, phenyl), 128.9 (s, phenyl), 128.5 (s, phenyl), 128.3 (s, phenyl), 128.0 (s, phenyl), 127.9 (m, phenyl), 127.7 (d,  $J_{\text{CP}} = 7.1$  Hz, phenyl), 127.6 (s, phenyl), 127.4 (d,  $J_{\text{CP}} = 8.3$  Hz, phenyl), 127.1 (d,  $J_{\text{CP}} = 8.3$  Hz, phenyl), 126.8 (d,  $J_{\text{CP}} = 8.3$  Hz, phenyl), 126.4 (s, phenyl), 37.3 (pseudo t,  $J_{\text{CP}} = 19.8$  Hz,  $\text{CH}_2\text{P}$ ), 36.1 (m,  $\text{CH}_2\text{P}$ ), 35.3 (pseudo t,  $J_{\text{CP}} = 16.8$  Hz,  $\text{CH}_2\text{P}$ ), 31.9 (pseudo t,  $J_{\text{CP}} = 26.1$  Hz,  $\text{CH}_2\text{P}$ ), 30.1 (dd,  $J_{\text{CP}} = 27.2$  Hz,  $\text{CH}_2\text{P}$ ), 27.8 (pseudo t,  $J_{\text{CP}} = 23.6$  Hz,  $\text{CH}_2\text{P}$ ), 25.2 (pseudo q,  $J_{\text{CP}} = 9.2$  Hz,  $\text{CH}_2\text{P}$ ), 23.6 (m,  $\text{CH}_2\text{P}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (benzene- $d_6$ ):  $\delta$  (ppm) = 119.23 (m, Fe-*P*), 99.11 (m, Fe-*P*), 82.74 (m, Fe-*P*), 76.95 (m, Fe-*P*), 68.24 (m, Fe-*P*), -12.08 (d,  $J_{\text{PP}} = 19.65$  Hz,  $\text{CH}_2\text{CH}_2\text{PPh}_2$ ).



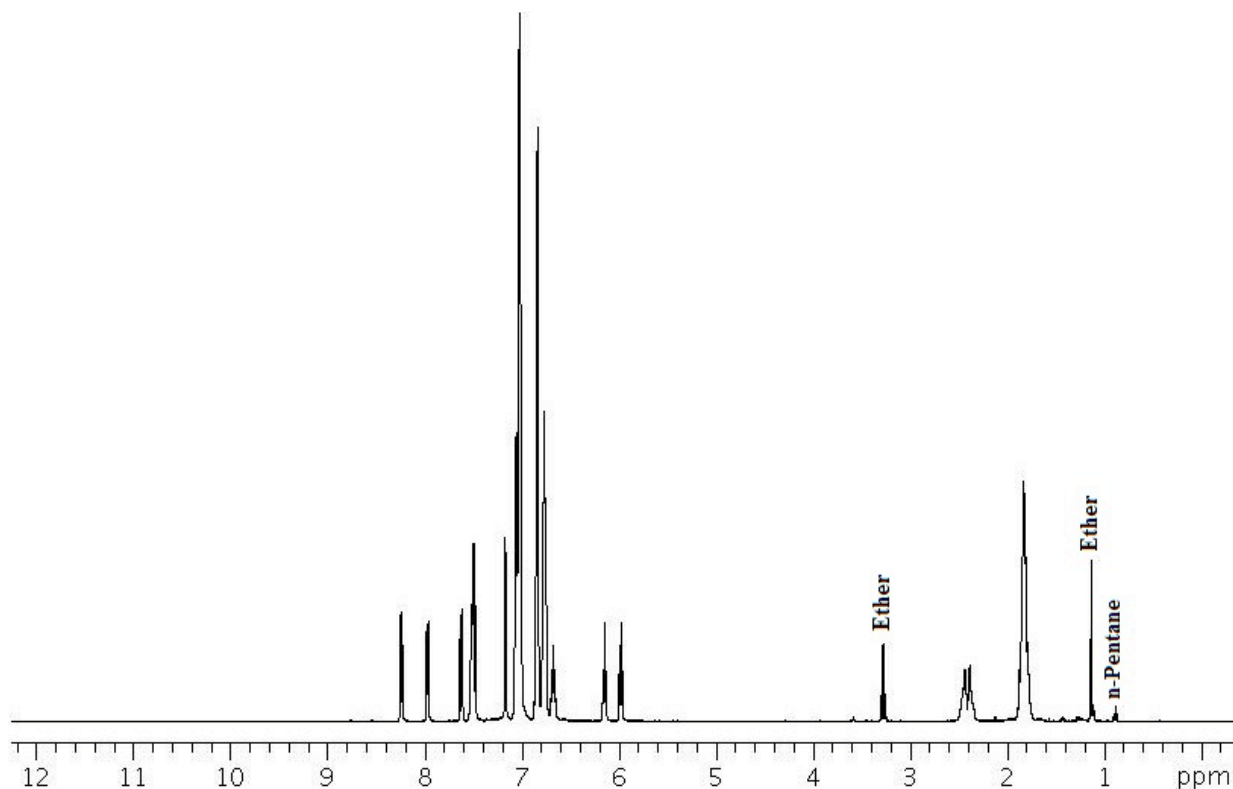
$^1\text{H}$  NMR spectrum of **1-( $\kappa^2$ -Triphos)** in benzene- $d_6$ .



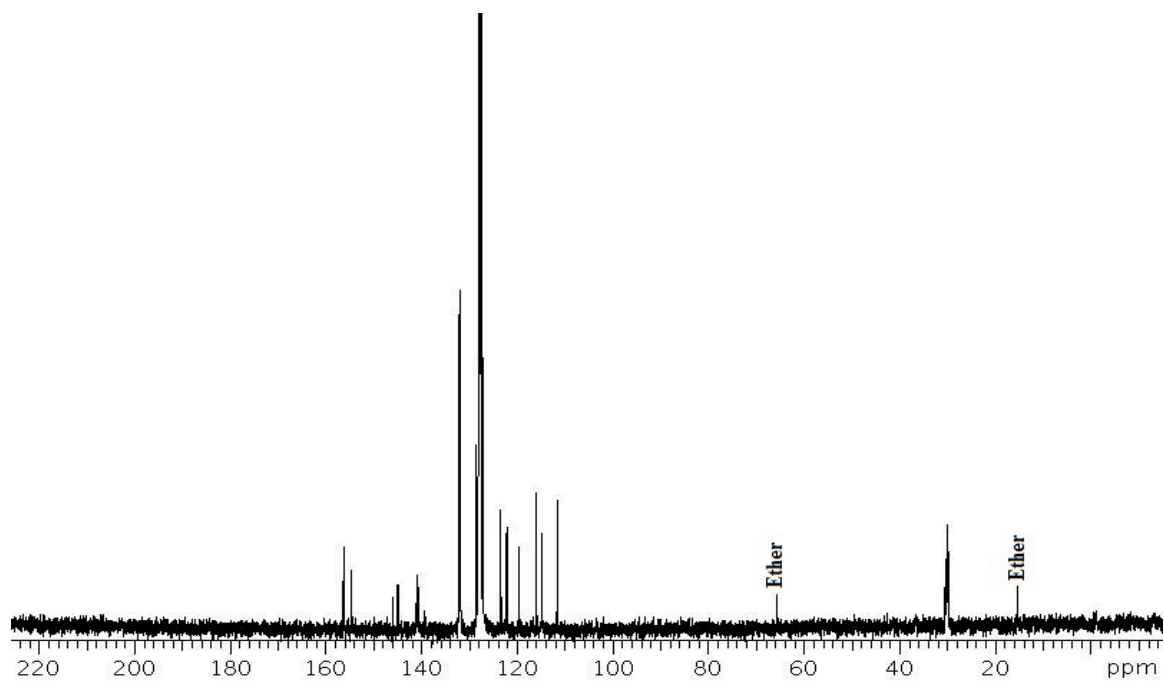
$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1-( $\kappa^2$ -Triphos)** in benzene- $d_6$ .

**Preparation of [ $\kappa^3$ -(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh]Fe( $\kappa^2$ -2,2'-bipyridine) (1-Bpy).** In the glove box, a 250 mL round-bottomed flask was charged with 0.208 g (0.278 mmol) of **1-Br<sub>2</sub>**, 0.217 g (1.390 mmol, 5 equivalents) of 2,2'-bipyridine and approximately 100 mL of diethylether. The mixture was allowed to cool at -35 °C for 30 min when a dark red color was observed. Then to the mixture, 0.032 g (1.390 mmol, 5 equivalents) of sodium metal was added and set to stir at ambient temperature. After 1 hour the resulting solution had turned deep purple. After 18 hours the solution was filtered through Celite and the solvent was evacuated to obtain 0.202 g of a dark purple microcrystalline solid. This was dissolved in approximately 10 mL of toluene and twice filtered through a Celite column (to remove any residual salt). The toluene was removed *in vacuo* to yield a dark purple solid identified as **1-Bpy** (0.165g, 76%). This solid was dissolved in minimum amount of diethylether (approximately 10 mL), filtered through Celite and stored in the freezer (-35 °C) until dark purple color crystals were deposited at the bottom of the vial. After decanting the residual solvent, crystals of **1-Bpy** were dried and collected (0.093 g, 45% recrystallized yield). Alternatively, this complex was prepared upon heating a mixture of 0.0106 g (0.0094 mmol) **1-( $\kappa^2$ -Triphos)** and 0.0074 g (0.047 mmol) 2,2'-bipyridine in benzene- $d_6$  to

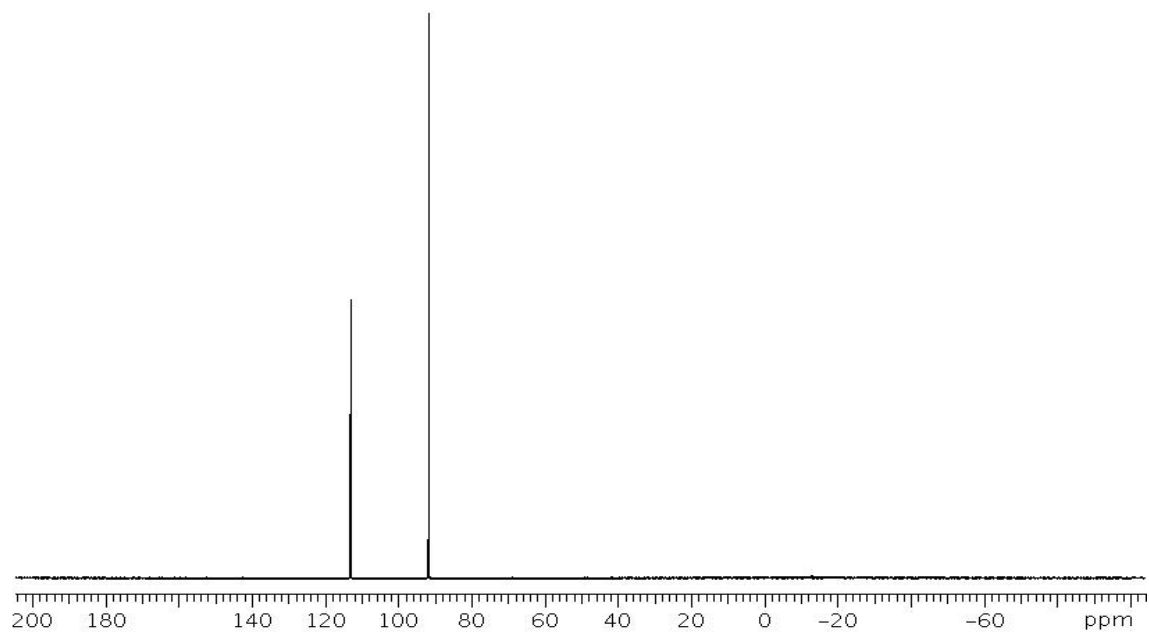
80°C for 23.5 hours.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  (ppm) = 8.23 (d,  $J$  = 6.8 Hz, 1H, *bpy*), 7.96 (d,  $J$  = 6.4 Hz, 1H, *bpy*), 7.61 (d,  $J$  = 8.4 Hz, 1H, *bpy*), 7.51 (m, 2H, *phenyl*), 7.47 (d,  $J$  = 8.0 Hz, 1H, *bpy*), 7.05 (m, 4H, *phenyl*), 7.01 (m, 9H, *phenyl*), 6.83 (m, 6H, *phenyl*), 6.76 (m, 5H, *bpy* and *phenyl*), 6.66 (t,  $J$  = 7.2 Hz, 1H, *bpy*), 6.14 (t,  $J$  = 6.4 Hz, 1H, *bpy*), 5.97 (t,  $J$  = 6.4 Hz, 1H, *bpy*), 2.40 (m, 2H,  $\text{CH}_2\text{P}$ ), 1.82 (m, 6H,  $\text{CH}_2\text{P}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzene- $d_6$ ):  $\delta$  (ppm) = 156.8 (s, *bpy*), 155.1 (d,  $J_{\text{CP}}$  = 11.7 Hz, *bpy*), 146.5 (s, *phenyl*), 145.7 (s, *phenyl*), 141.6 (m, *phenyl*), 141.4 (m, *phenyl*), 139.8 (m, *phenyl*), 132.7 (m, *phenyl*), 132.5 (m, *phenyl*), 132.4 (s, *phenyl*), 129.2 (s, *phenyl*), 129.1 (s, *phenyl*), 129.0 (m, *phenyl*), 127.7 (s, *phenyl*), 123.9 (s, *bpy*), 122.7 (s, *bpy*), 120.1 (s, *bpy*), 116.5 (s, *bpy*), 115.4 (s, *bpy*), 112.2 (s, *bpy*), 30.0 (m,  $\text{PCH}_2\text{CH}_2\text{P}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (benzene- $d_6$ ):  $\delta$  (ppm) = 112.93 (t,  $J_{\text{PP}}$  = 7.7 Hz, Fe-PPh), 91.59 (d,  $J_{\text{PP}}$  = 7.7 Hz, Fe-PPh $_2$ ).



$^1\text{H}$  NMR spectrum of **1-Bpy** in benzene- $d_6$ .

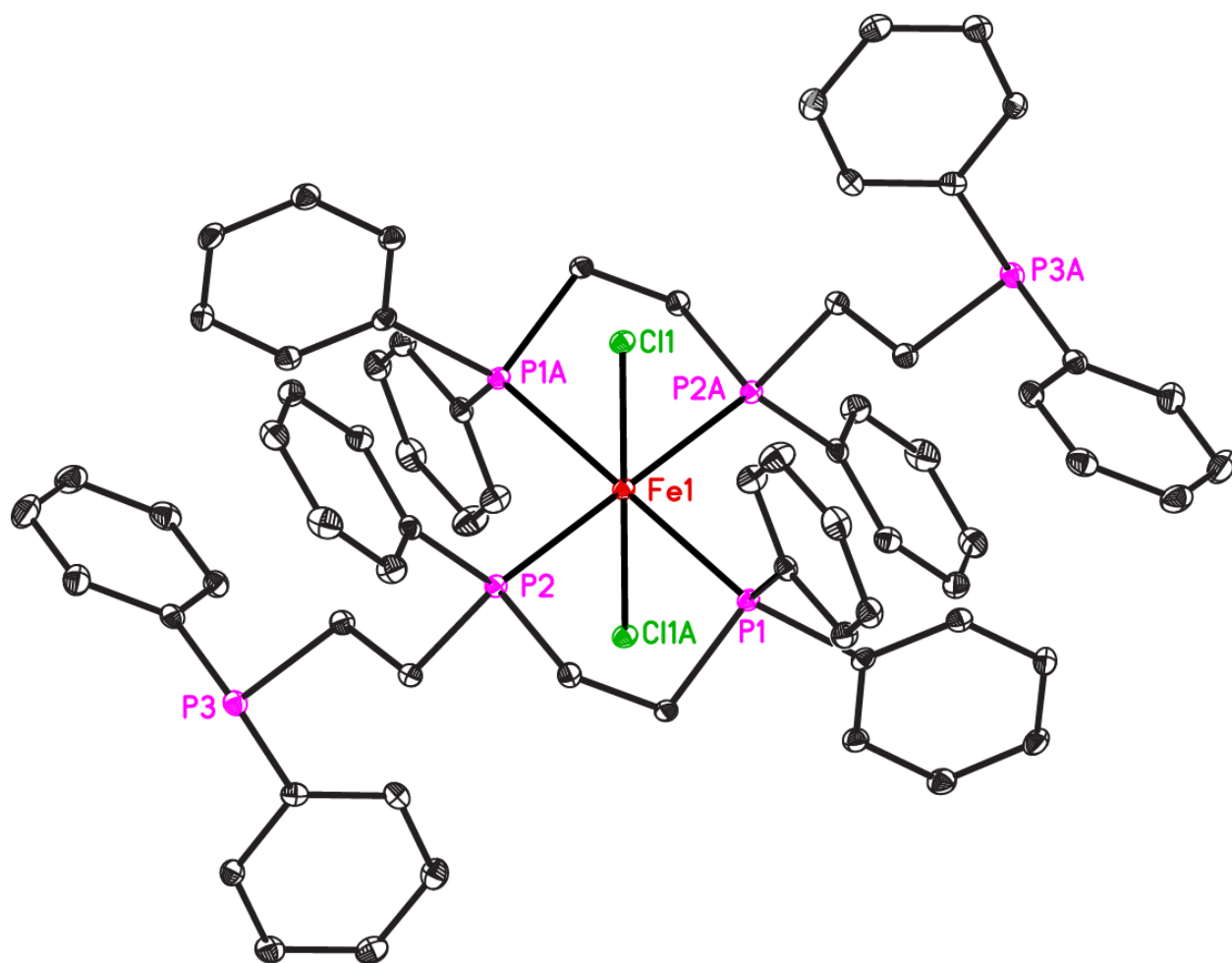


$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1-Bpy** in benzene- $d_6$ .

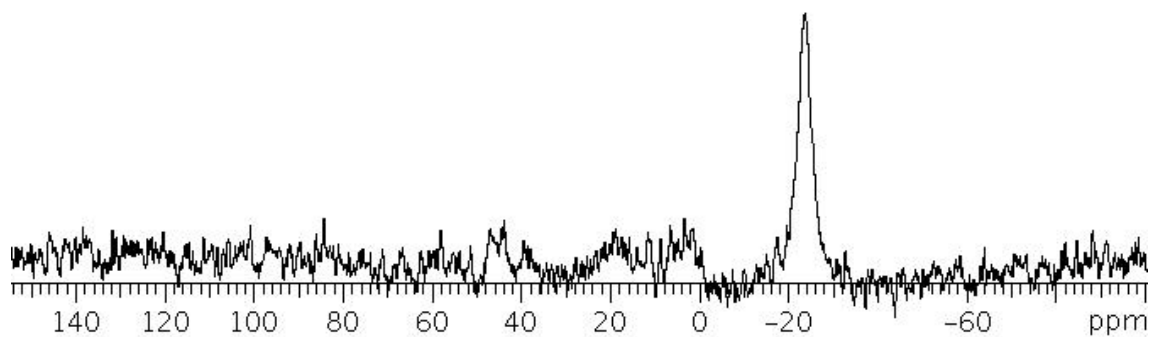


$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1-Bpy** in benzene- $d_6$ .

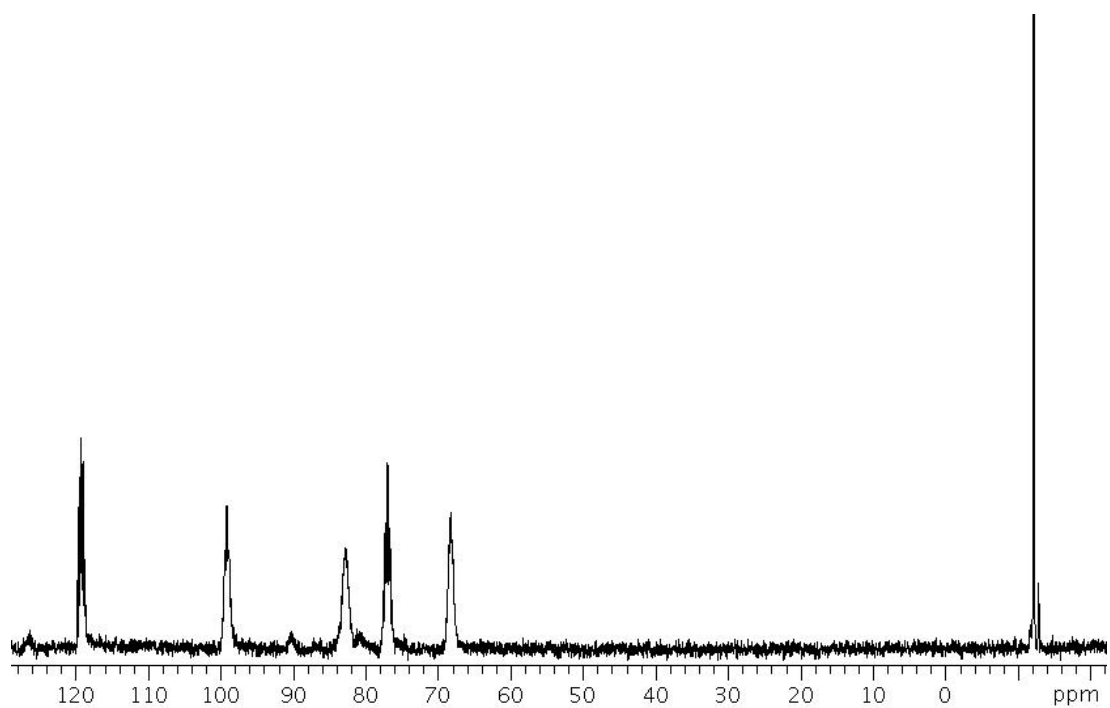




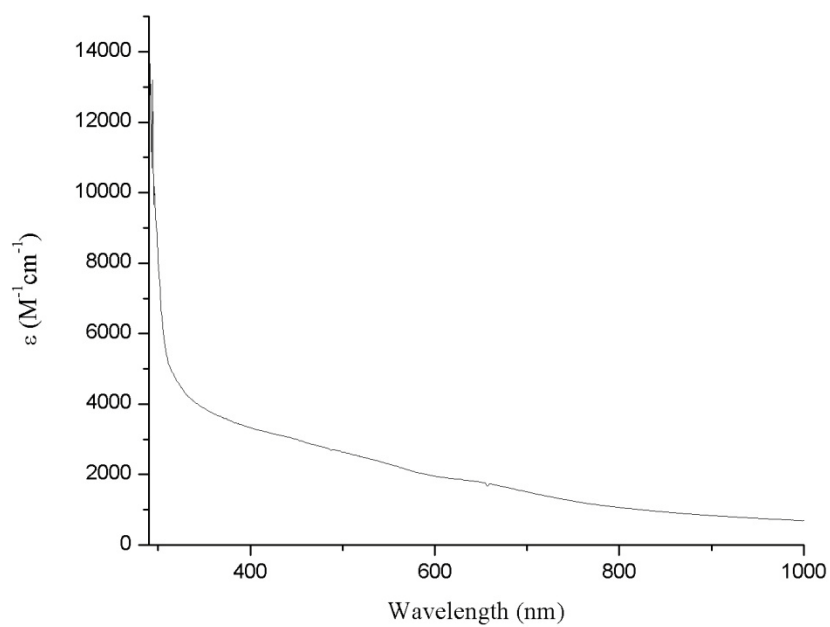
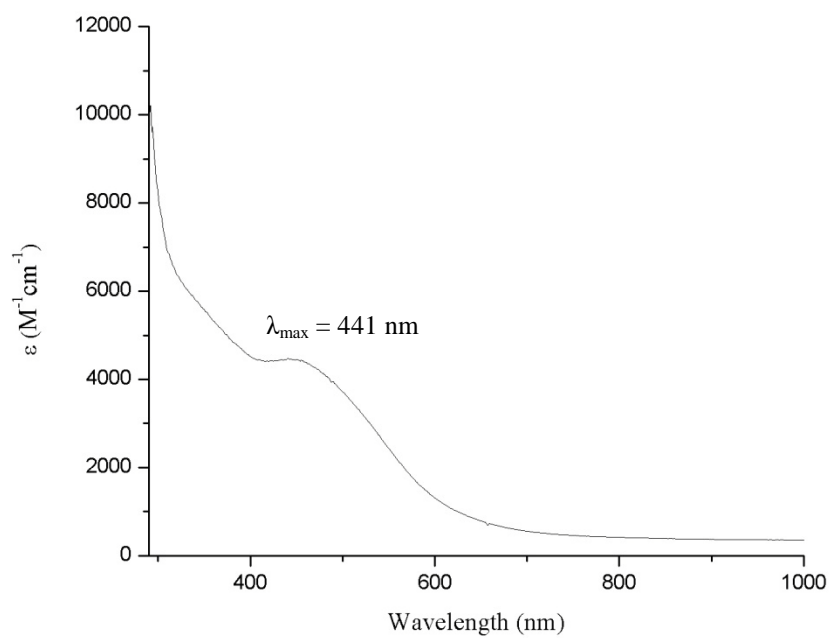
**Figure S1.** The molecular structure of  $(\kappa^2\text{-Triphos})_2\text{FeCl}_2$  at 30% probability ellipsoids. Hydrogen atoms and the co-crystallized toluene molecule have been omitted for clarity. A: 2-x, 1-y, 1-z.



**Figure S2.** Observation of the free phosphine substituent in **1-Br<sub>3</sub>** by  $^{31}\text{P}$  NMR spectroscopy (tetrahydrofuran-*d*<sub>8</sub>, 23°C).



**Figure S3.**  $^{31}\text{P}$  NMR spectrum of **1-( $\kappa^2$ -Triphos)** (benzene- $d_6$ , 23 °C).



**Figure S4.** Electronic absorption spectra of **1-( $\kappa^2$ -Triphos)** (top) and **1-Bpy** (bottom).

**Table S1.** Crystallographic Parameters for  $(\kappa^2\text{-Triphos})_2\text{FeCl}_2$ .

Empirical formula	$\text{C}_{75} \text{H}_{74} \text{Cl}_2 \text{Fe P}_6$	
Formula weight	1287.91	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 10.3077(7) \text{ Å}$	$\alpha = 71.48(1)^\circ$ .
	$b = 10.9001(8) \text{ Å}$	$\beta = 84.08(1)^\circ$ .
	$c = 15.4955(11) \text{ Å}$	$\gamma = 77.60(1)^\circ$ .
Volume	$1611.2(2) \text{ Å}^3$	
Z	1	
Density (calculated)	$1.327 \text{ Mg/m}^3$	
Absorption coefficient	$0.510 \text{ mm}^{-1}$	
F(000)	674	
Crystal size	$0.25 \times 0.15 \times 0.15 \text{ mm}^3$	
Theta range for data collection	2.01 to $25.89^\circ$ .	
Index ranges	$-12 \leq h \leq 12$ , $-13 \leq k \leq 13$ , $-19 \leq l \leq 19$	
Reflections collected	16475	
Independent reflections	6231 [R(int) = 0.0306]	
Completeness to theta = $25.89^\circ$	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9274 and 0.8831	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	6231 / 30 / 394	
Goodness-of-fit on $F^2$	1.050	
Final R indices [I > 2sigma(I)]	$R1 = 0.0346$ , $wR2 = 0.0864$	
R indices (all data)	$R1 = 0.0432$ , $wR2 = 0.0927$	
Largest diff. peak and hole	0.551 and $-0.261 \text{ e.Å}^{-3}$	

**Table S2.** Selected bond distances (Å) and angles (°) for ( $\kappa^2$ -Triphos)<sub>2</sub>FeCl<sub>2</sub>.

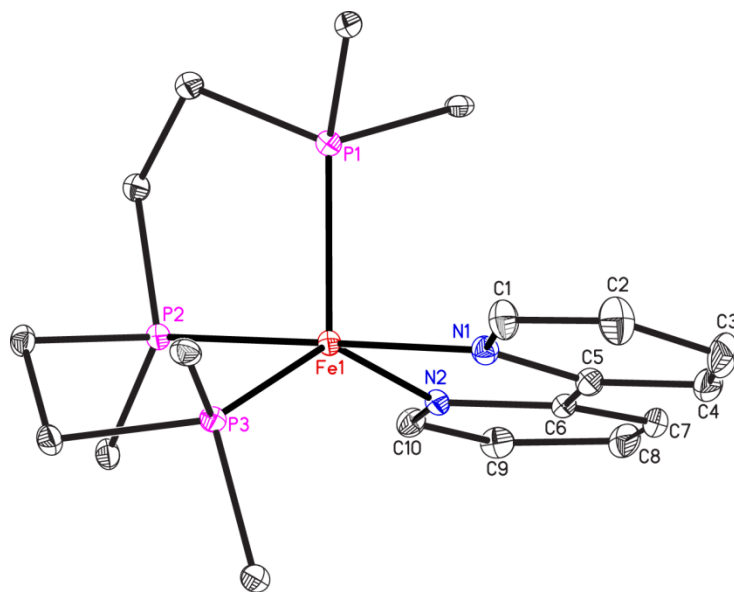
Fe(1)-Cl(1)	2.3656(5)
Fe(1)-P(1)	2.6861(5)
Fe(1)-P(2)	2.6166(5)
Cl(1)-Fe(1)-P(1)	96.745(16)
Cl(1)-Fe(1)-P(2)	93.143(17)
Cl(1A)-Fe(1)-P(1)	83.255(16)
P(2)-Fe(1)-P(1)	77.858(16)
P(2)A-Fe(1)-P(1)	102.142(16)

**Table S3.** Crystallographic Parameters for **1-Bpy**.

Empirical formula	$C_{44} H_{41} Fe N_2 P_3$	
Formula weight	746.55	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	$a = 14.8559(19)$ Å	$\alpha = 90^\circ$ .
	$b = 14.3443(18)$ Å	$\beta = 109.030(1)^\circ$ .
	$c = 18.850(2)$ Å	$\gamma = 90^\circ$ .
Volume	$3797.4(8)$ Å <sup>3</sup>	
Z	4	
Density (calculated)	1.306 Mg/m <sup>3</sup>	
Absorption coefficient	0.557 mm <sup>-1</sup>	
F(000)	1560	
Crystal size	0.40 x 0.30 x 0.10 mm <sup>3</sup>	
Theta range for data collection	2.03 to 27.68°.	
Index ranges	$-19 \leq h \leq 19$ , $-18 \leq k \leq 18$ , $-24 \leq l \leq 24$	
Reflections collected	41383	
Independent reflections	8717 [R(int) = 0.0735]	
Completeness to theta = 27.68°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9464 and 0.8078	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	8717 / 0 / 451	
Goodness-of-fit on F <sup>2</sup>	1.021	
Final R indices [I > 2σ(I)]	R1 = 0.0473, wR2 = 0.1064	
R indices (all data)	R1 = 0.0799, wR2 = 0.1204	
Largest diff. peak and hole	1.699 and -0.575 e.Å <sup>-3</sup>	

**Table S4.** Selected bond distances (Å) and angles (°) for **1-Bpy**.

Fe(1)-N(1)	1.956(2)
Fe(1)-N(2)	1.936(2)
Fe(1)-P(1)	2.1628(8)
Fe(1)-P(2)	2.1608(8)
Fe(1)-P(3)	2.2045(8)
N(1)-C(1)	1.361(3)
N(1)-C(5)	1.383(3)
N(2)-C(10)	1.378(3)
N(2)-C(6)	1.399(3)
C(1)-C(2)	1.360(4)
C(2)-C(3)	1.412(4)
C(3)-C(4)	1.355(4)
C(4)-C(5)	1.409(4)
C(5)-C(6)	1.420(4)
C(6)-C(7)	1.401(4)
C(7)-C(8)	1.366(4)
C(8)-C(9)	1.408(4)
C(9)-C(10)	1.366(4)
N(2)-Fe(1)-N(1)	80.75(9)
N(2)-Fe(1)-P(2)	98.38(7)
N(1)-Fe(1)-P(2)	179.09(7)
N(2)-Fe(1)-P(1)	104.83(7)
N(1)-Fe(1)-P(1)	95.43(7)
P(2)-Fe(1)-P(1)	85.02(3)
N(2)-Fe(1)-P(3)	138.77(7)
N(1)-Fe(1)-P(3)	95.74(7)
P(2)-Fe(1)-P(3)	84.75(3)
P(1)-Fe(1)-P(3)	116.38(3)
C(5)-N(1)-Fe(1)	116.18(17)
C(6)-N(2)-Fe(1)	115.90(17)
N(1)-C(5)-C(6)	113.2(2)
N(2)-C(6)-C(5)	113.3(2)





## References

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