Synthesis and Electronic Structure of Bis(imino)pyridine Iron Carbene Complexes.

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Supporting Information

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I. General Considerations. All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk, and cannula techniques or in an MBraun inert atmosphere dry box containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were initially dried and deoxygenated using literature procedures.[1] Benzene-*d*$_6$ was purchased from Cambridge Isotope Laboratories and dried over 4 Å molecular sieves. Diphenyldiazomethane[2] and 2,4,6-trimethylphenyl azide [3] were prepared according to literature procedures. The compounds: (^{iPr}PDI)Fe(N$_2$)$_2$, [4] [(^{Et}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$) [5] and [(^{Me}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$)[5] were prepared according to literature procedures.

^{1}H NMR spectra were recorded on Varian Mercury 300, Inova 400, 500, and 600 spectrometers operating at 299.76, 399.78, 500.62, and 599.78 MHz, respectively. ^{13}C NMR spectra were recorded on an Inova 500 spectrometer operating at 125.893 MHz. All ^{1}H and ^{13}C NMR chemical shifts are reported relative to SiMe$_4$ using the ^{1}H (residual) and ^{13}C chemical shifts of the solvent as a secondary standard. Peak widths at half heights are reported for paramagnetically broadened and shifted resonances. For diamagnetic complexes, many assignments were made based on COSY and HSQC NMR experiments. Solution magnetic moments were determined by the method described by Evans[6] using a ferrocene standard and are the average value of at least two independent measurements. Magnetic susceptibility balance measurements were performed with a Johnson Matthey instrument that was calibrated with HgCo(SCN)$_4$. Infrared spectra were collected on a Thermo Nicolet spectrometer. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker X8 APEX2 diffractometer equipped with a molybdenum X-ray tube (λ = 0.71073 Å). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of 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.

SQUID magnetization data of crystalline powdered samples were recorded with a SQUID magnetometer (Quantum Design) at 10 kOe between 5 and 300 K for all samples. Values of the magnetic susceptibility were corrected for the underlying diamagnetic increment by using tabulated Pascal constants and the effect of the blank sample holders (gelatin capsule/straw). Samples used for magnetization measurement were recrystallized multiple times and checked for chemical composition by ^{1}H NMR spectroscopy. The program julX written by E. Bill was used for the simulation and analysis of magnetic susceptibility data.[7]

Zero-field ^{57}Fe Mössbauer spectra were recorded on a SEE Co. Mössbauer spectrometer (MS4) at 80 K in constant acceleration mode. ^{57}Co/Rh was used as the radiation source. WMOSS software was used for the quantitative evaluation of the spectral parameters (least-squares fitting to Lorentzain peaks). The minimum experimental line widths were 0.23 mm/s. The temperature of the sample was controlled by a Janis Research Co. CCS-850 He/N_2 cryostat within and accuracy of ± 0.3 K. Isomer shifts were determined relative to α-iron at 298 K.

Samples for X-ray absorption spectroscopy were prepared in an inert atmosphere nitrogen glovebox as finely ground dilutions in boron nitride pressed into 1 mm Al spacers and shipped to the experimental site in triple glass jars with fluoropolymer seals on the lids and sealed with Teflon and electrical tape. X-ray absorption spectra were recorded at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline BL9-3 under standard ring conditions. The beamline optics were optimized, and the monochromator was fully tuned at 7500 eV. The incident energy was calibrated by setting the first inflection of an iron foil to 7111.2 eV. Data were measured in transmission mode. All DFT calculations were carried out as described previously.[8]

II. Preparation of Iron Compounds

Preparation of (^{iPr}PDI)Fe(N_2CPh_2). A 20 mL scintillation vial was charged with 0.098 g (0.165 mmol) of (^{iPr}PDI)Fe(N_2)$_2$ and approximately 10 mL of diethyl ether. A solution of diphenyldiazomethane (0.032 g, 0.165 mmol) in approximately 5 mL of diethyl ether was added to the vial resulting in vigorous bubbling and an immediate color change from green to blue-green was observed. The solution was stirred for 5 minutes after which time the solvent was removed *in vacuo* and yielded 0.117 g (97%) of a blue-green solid identified as (^{iPr}PDI)Fe(N_2CPh_2). Analysis for $C_{46}H_{53}N_5Fe$: Calc. C, 75.50; H, 7.30; N, 9.57. Found C, 75.65; H, 7.54; N, 9.23. Magnetic susceptibility: μ_{eff} = 3.1 μ_B (benzene-*d*$_6$, 20°C), ^{1}H NMR (benzene-*d*$_6$): δ = -3.68 (160.2 Hz), -0.13 (82.46 Hz), 0.98 (180.80 Hz), 6.03 (44.75 Hz), 9.03 (24.99 Hz). IR(pentane): ν(NN) = 2042 cm^{-1}.

Preparation of (^{Et}PDI)FeCPh$_2$. A 20 mL scintillation vial was charged with 0.200 g (0.191 mmol) of [(^{Et}PDI)Fe(N_2)]$_2$(μ_2-N_2) and approximately 10 mL of diethyl ether. A solution of diphenyldiazomethane (0.074 g, 0.382 mmol) in 5 mL of diethyl ether was added to the vial resulting in vigorous bubbling and a color change from brown to green was observed. Removal of the solvent *in vacuo* yielded 0.240 g (97%) of a green solid identified as (^{Et}PDI)Fe(CPh$_2$). Crystals suitable for X-ray analysis were obtained from a pentane solution stored at -35 °C. Analysis for $C_{42}H_{45}N_3Fe$: Calc. C, 77.89; H, 7.00; N, 6.49. Found C, 77.67; H, 7.17; N, 6.38. Magnetic susceptibility: μ_{eff} = 3.2 μ_B (benzene-*d$_6$*, 20 °C); 3.2 μ_B (magnetic susceptibility balance, 23°C). ^{1}H NMR (benzene-*d$_6$*, 20 °C): δ = -68.32 (72.38 Hz, 6H, C(C*H$_3$*)), -55.88 (177.9 Hz, 4H, C*H$_2$*CH$_3$), -45.91 (107.3 Hz, 4H, C*H$_2$*CH$_3$), -27.30 (29.33 Hz, 4H, Ph), -14.96 (24.67 Hz, 12H, CH$_2$C*H$_3$*), -3.32 (18.58 Hz, 2H, *p-Ar*), -3.00 (17.32 Hz, 4H, *m-Ar*), 54.45 (50.61 Hz, 2H, *m-py* or *Ph*), 101.72 (432.6 Hz, 4H, *Ph*), 118.22 (124.5 Hz, 2H, *m-py* or *Ph*), 155.56 (150.3 Hz, 1H, *p-py*).

Preparation of (^{Me}PDI)FeCPh$_2$. A 20 mL scintillation vial was charged with 0.200 g (0.214 mmol) of [^{Me}PDIFe(N$_2$)]$_2$(μ_2-N$_2$) and approximately 10 mL of diethyl ether. A solution of diphenyldiazomethane (0.083g, 0.428 mmol) in diethyl ether was added to the vial resulting in vigorous bubbling and a color change from brown to green was observed. Removal of the solvent *in vacuo* yielded 0.238 g (94%) of a green solid identified as (^{Me}PDI)FeCPh$_2$. Analysis for $C_{38}H_{37}N_3Fe$: Calc. C, 77.15; H, 6.30; N, 7.10. Found C, 76.93; H, 6.39; N, 6.86. Magnetic susceptibility: μ_{eff} = 3.0 μ_B (benzene-*d$_6$*, 20 °C), μ_{eff} = 3.4 μ_B (magnetic susceptibility balance, 23°C). ^{1}H NMR (benzene-*d$_6$*, 20 °C): δ = -56.76 (64.90 Hz, 6H, C(C*H$_3$*)), -33.07 (71.57 Hz, 12H, Ar C*H$_3$*), -24.27 (26.89 Hz, 4H, *Ph*), -3.23 (16.47 Hz, 2H, *p-Ar*), -2.15 (16.12 Hz, 4H, *m-Ar*), 50.23 (49.01 Hz, 2H, *m-py* or *Ph*), 92.96 (350.1 Hz, 4H, *Ph*), 107.28 (104.5 Hz, 2H, *m-py* or *Ph*), 133.40 (123.8 Hz, 1H, *p-py*).

Independent preparation of (^{Me}PDI)FeN(2,4,6-Me$_3$C$_6$H$_2$). A 20 mL scintillation vial was charged with 0.200 g (0.21 mmol) of [^{Me}PDIFe(N$_2$)]$_2$(μ_2-N$_2$) and approximately 10 mL of diethyl ether. A solution containing 2,4,6-trimethylphenyl azide (0.068 g, 0.43 mmol) in diethyl ether was added to the vial resulting in vigorous bubbling and a color change from brown to dark blue was observed. Removal of the solvent yielded 0.167 g (70 %) of a dark blue solid identified as (^{Me}PDI)FeN(2,4,6-$Me_3C_6H_2$). Magnetic susceptibility: μ_{eff} = 3.0 μ_B (magnetic susceptibility balance, 296K). ^{1}H NMR (benzene-*d$_6$*, 20 °C): δ = -109.44 (43.45 Hz, 6H, C(C*H$_3$*)), -19.67 (32.30 Hz, 12H, Ar C*H$_3$*), 0.88 (14.52 Hz, 6H, mes o-C*H$_3$*), 7.41 (21.66 Hz, 2H, mes C*H*), 45.54 (26.45 Hz, 4H, *m-Ar*), 98.20 (31.85 Hz, 2H, *p-Ar*), 125.40 (66.30 Hz, 2H, *m-py*), 239.18 (169.73 Hz, 1H, *p-py*).

Preparation of [(^{Me}EtPDI)Fe(N_2)](μ_2-N_2). A 100 mL round bottom flask was charged with 0.300 g (0.572 mmol) of ^{Me}EtPDIFeCl_2 and approximately 20 mL of toluene. To the resulting slurry, 0.066 g (2.861 mmol) of sodium and 13.200 g (65.806 mmol) of mercury was added. The reaction mixture was stirred for 1 hour, filtered through Celite and removal of the solvent *in vacuo* yielded 0.218 g (77%) of a red solid identified as [(^{Me}EtPDI)Fe(N_2)](μ_2-N_2). Analysis for $C_{54}H_{62}N_{12}Fe_2$: Calc. C, 65.46; H, 6.31; N, 16.96. Found C, 65.50; H, 6.65; N, 17.22. ^{1}H NMR (benzene-*d$_6$*, 20 °C): δ = 1.03 (7.62 Hz, 12H, CH_2C*H$_3$*), 1.37 (22.45 Hz, 24H, Ar C*H$_3$*), 2.49 (13.72 Hz, 8H, C*H$_2$*CH_3), 6.93 (8.25 Hz, 12H, *m-* and *p-Ar*), 7.54 (7.94 Hz, 2H, *p-py*), 8.17 (17.35 Hz, 4H, *m-py*). IR(toluene): $\nu(N_2)$ = 2102, 2086 cm^{-1}.

Preparation of (^{Me}EtPDI)FeCPh$_2$. A 20 mL scintillation vial was charged with 0.332 g (0.335 mmol) of [^{Me}EtPDIFe(N_2)]$_2$(μ_2-N_2) and approximately 10 mL of diethyl ether. A solution of diphenyldiazomethane (0.137 g, 0.704 mmol) in diethyl ether was added to the vial resulting in vigorous bubbling and a color change from red to green. Removal of the solvent *in vacuo* yielded 0.395 g (0.638 mmol, 95%) of a green solid identified as (^{Me}EtPDI)Fe(CPh_2). Analysis for $C_{40}H_{41}N_3Fe$: Calc. C, 77.54; H, 6.67; N, 6.78. Found C, 77.31; H, 6.39; N, 6.59. Magnetic susceptibility: μ_{eff} = 2.8 μ_B (benzene-d_6, 20 °C), μ_{eff} = 3.0 μ_B (magnetic susceptibility balance, 23 °C). ^{1}H NMR (benzene-d_6, 20 °C): δ = -34.19 (87.32 Hz, 12H, Ar C*H*$_3$), -24.45 (39.34 Hz, 4H, *Ph*), -20.01 (53.77 Hz, 4H, C*H*$_2$CH$_3$), -3.69 (19.96 Hz, 6H, CH$_2$C*H*$_3$) -3.35 (18.00 Hz, 2H, *p-Ar*), -2.03 (13.44 Hz, 4H, *m-Ar*), 52.87 (74.12 Hz, 2H, *m-py* or *Ph*), 93.89 (419.4 Hz, 4H, *Ph*), 108.11 (130.46 Hz, 2H, *m-py* or *Ph*), 132.65 (135.71 Hz, 1H, *p-py*).

Preparation of [(2,6-Et$_2$C$_6$H$_3$)((6-Et)(2-(C=CH$_2$)C$_6$H$_3$)N=CMe)$_2$C$_5$H$_3$N]Fe. A 20 mL scintillation vial was charged with 0.195 g (0.302 mmol) of (^{Et}PDI)Fe(CPh$_2$) and approximately 10 mL of diethyl ether. The solution was stirred 24 hours after which time it was filtered through Celite and the solvent removed in *vacuo*. To the residue was added approximately 2 mL of pentane and stirred for 5 minutes. The resulting solid was collected on a glass frit yielding 0.053 g (37%) of a dark brown solid. Analysis for C$_{29}$H$_{33}$N$_3$Fe: Calc. C, 72.65; H, 6.94; N, 8.76. Found C, 72.29; H, 6.74; N, 8.74. Magnetic susceptibility: μ_{eff} = 2.7 μ_B (benzene-d_6, 20 °C). Mössbauer parameters: δ= 0.34 mm/s, ΔE_Q = 0.74 mm/s.

Degradation Experiment. A solution of (^{Et}PDI)Fe(CPh$_2$) was dissolved in benzene-d_6 and filtered into a J. Young tube. The solution was allowed to stand at room temperature for 24 hours during which time a color change from green to brown was observed. The ^{1}H NMR signals of (^{Et}PDI)Fe(CPh$_2$) had disappeared over the course of 24 hours with liberation of H$_2$CPh$_2$. The resulting iron product is NMR silent and was identified by Mössbauer spectroscopy.

III. Additional Characterization Data

A. Magnetic Data

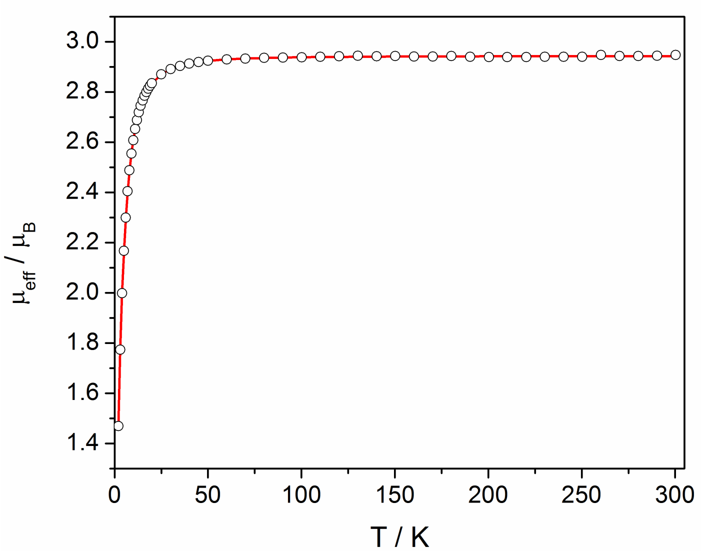

Figure S1. Variable temperature SQUID magnetization data for (^{iPr}PDI)Fe(N_2CPh_2) from 4 to 300 K. Experimental data are represented by the open circles, the simulation with the red curve. The fit of the data yielded g = 2.081, D = -16 cm^{-1}, E/D =0.24 with TIP = 55 x10^{-6} emu.

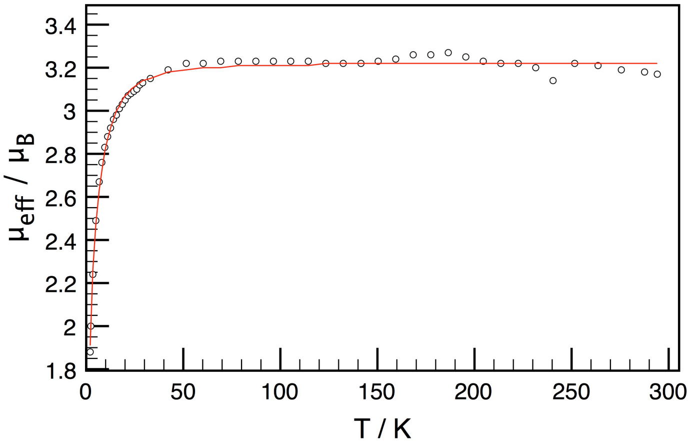

Figure S2. Variable temperature SQUID magnetization data for (^{Me}EtPDI)Fe(CPh_2) from 4 to 300 K. Experimental data are represented by the open circles, the simulation with the red curve. The fit of the data yielded g = 2.277, D = 21.37 cm^{-1}, E/D =0.10 with TIP = 0 x10^{-6} emu.

B. ^{57}Fe Mössbauer Spectra

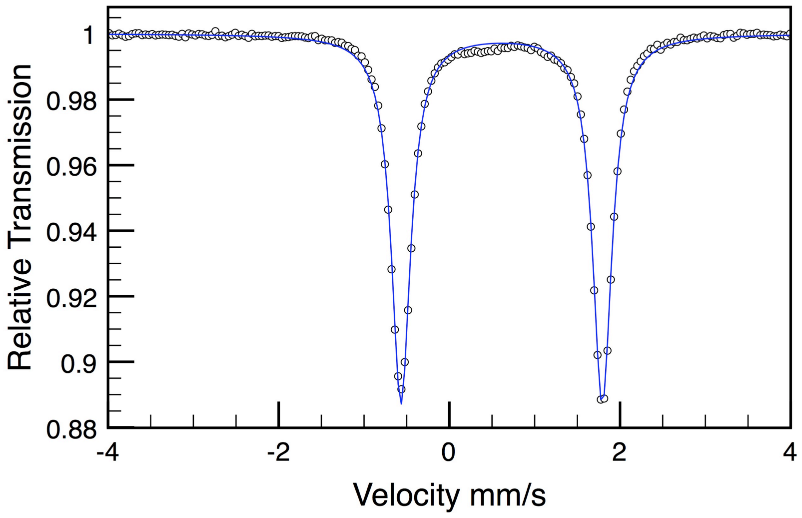

Figure S3. Zero field ^{57}Fe Mössbauer spectrum of (^{iPr}PDI)Fe(N_2CPh_2) recorded at 80 K.

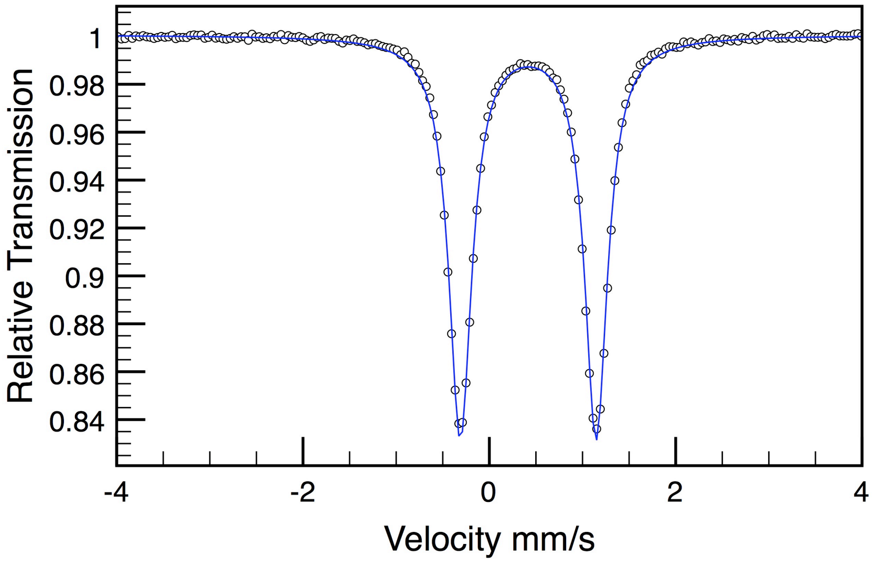

Figure S4. Zero field ^{57}Fe Mössbauer spectrum of (^{Et}PDI)FeCPh_2 recorded at 80 K.

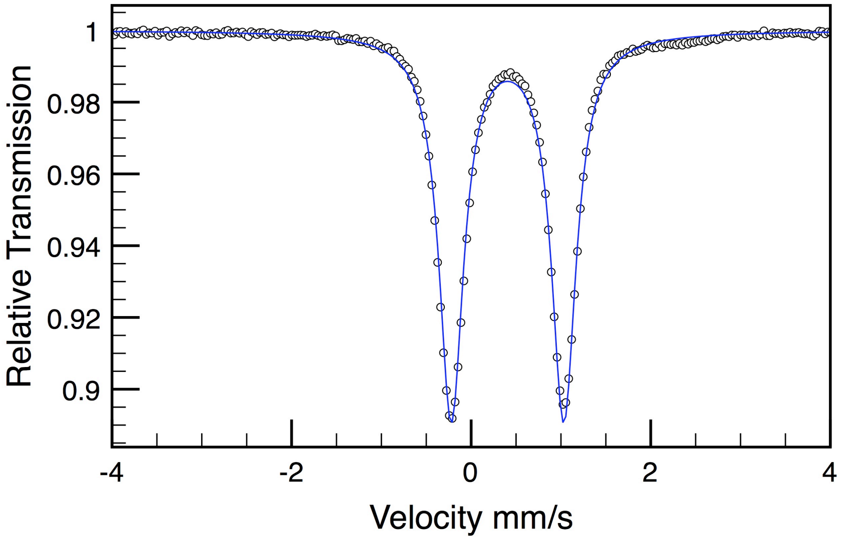

Figure S5. Zero field ^{57}Fe Mössbauer spectrum of (^{Me}PDI)FeCPh$_2$ recorded at 80 K.

C. X-ray Crystallographic Data

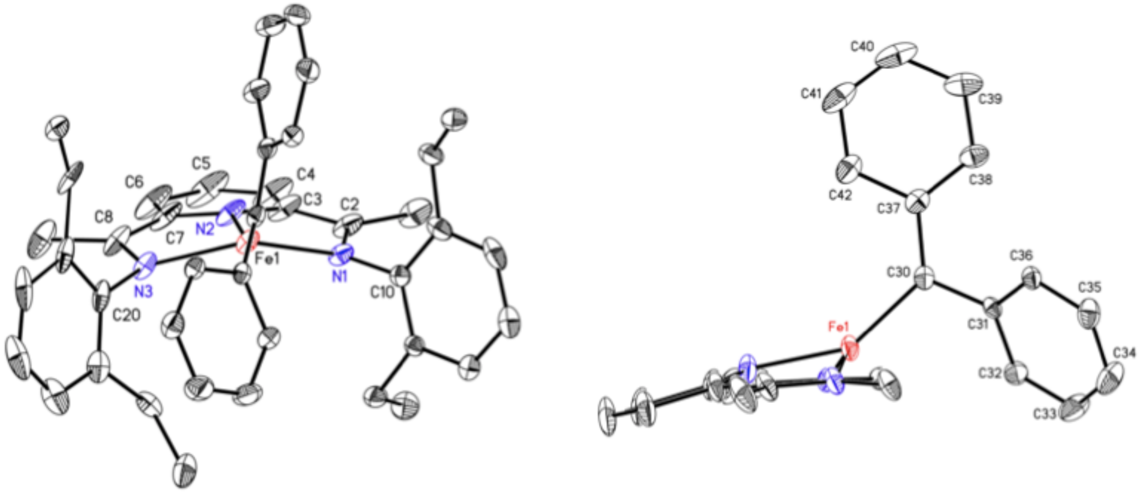

Figure S6. Representations of the solid state structure of (^{Et}PDI)FeCPh$_2$ at 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

Tabe S1. Selected bond distances (Å) and angles (deg) for (^{Et}PDI)FeCPh$_2$.

Fe(1)-N(1)	2.047(2)	N(2)-Fe(1)-C(30)	147.82(8)
Fe(1)-N(2)	1.955(2)	Fe(1)-C(30)-C(31)	112.31(13)
Fe(1)-N(3)	2.093(2)	Fe(1)-C(30)-C(37)	127.52(14)
Fe(1)-C(30)	1.921(2)	C(31)-C(30)-C(37)	119.87(17)
N(1)-C(2)	1.330(3)	N(1)-Fe(1)-N(3)	140.43(7)
N(3)-C(8)	1.322(2)		
C(2)-C(3)	1.432(3)	Deviation of Fe(1) from N(1), N(2), N(3) plane	0.647
C(7)-C(8)	1.436(3)		

D. Representative NMR Spectra

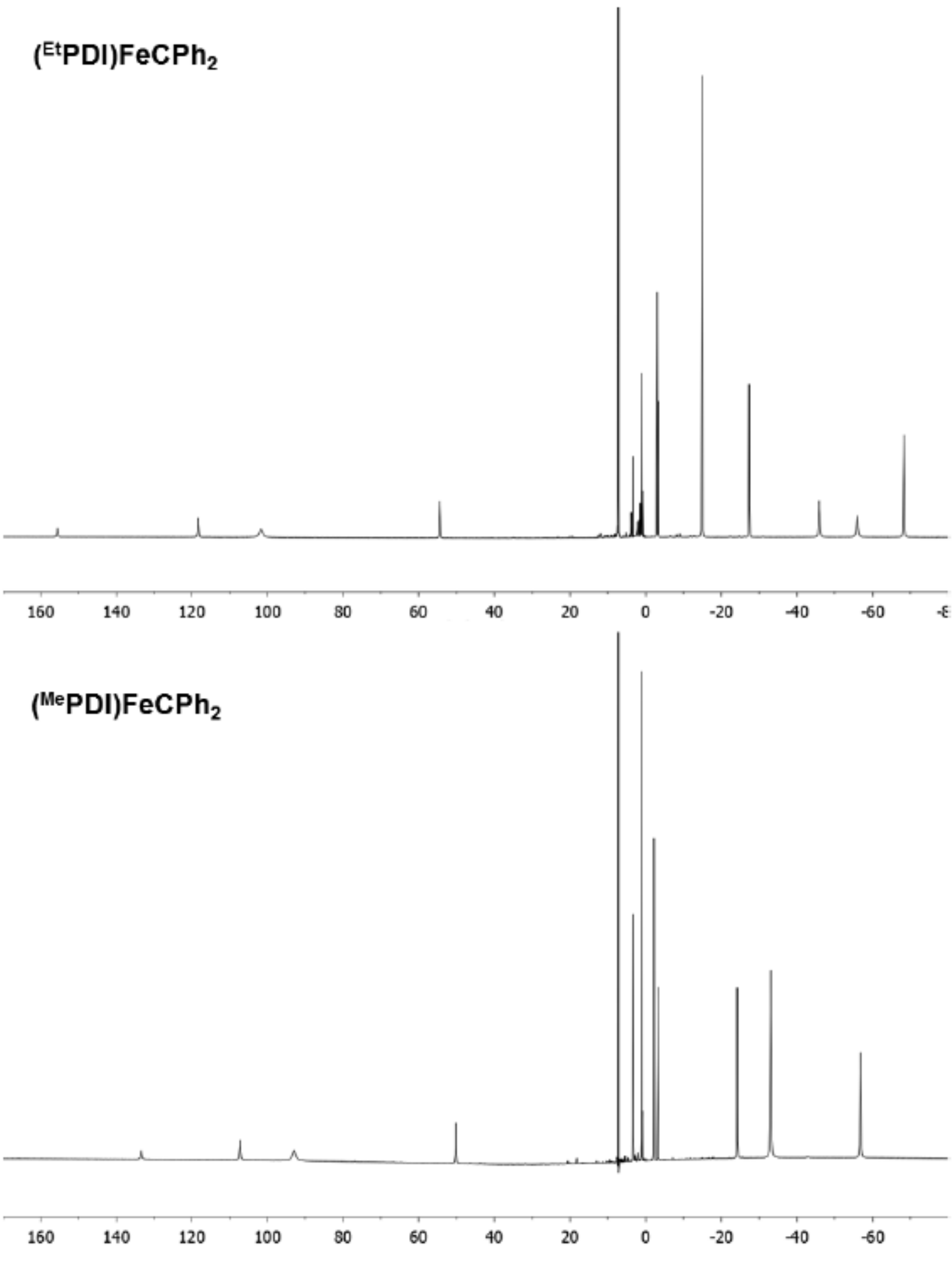

Figure S7. Representative ^{1}H NMR spectra of (^{Et}PDI)FeCPh$_2$ and (^{Me}PDI)FeCPh$_2$ in benzene-d_6 at 20°C.

IV. Computational Results

Table S1. Comparison of experimental and computed bond distances for (^{iPr}PDI)Fe(N_2CPh_2).

	Experimental	Calculated (Fixed M-L)	Calculated (Not Fixed)
Fe(1)-N(1)	2.072(2)	2.072	2.234
Fe(1)-N(2)	1.882(2)	1.882	1.986
Fe(1)-N(3)	2.063(2)	2.063	2.266
Fe(1)-N(4)	1.903(2)	1.964	2.020
Fe(1)-N(5)	1.894(2)	1.899	1.899
N(1)-C(2)	1.315(3)	1.321	1.305
N(3)-C(8)	1.324(3)	1.323	1.312
C(2)-C(3)	1.445(3)	1.447	1.464
C(7)-C(8)	1.437(3)	1.445	1.456
N(4)-N(5)	1.280(3)	1.254	1.249
N(5)-C(34)	1.331(3)	1.322	1.325

Table S2. Comparison of experimental and computed bond distances for (^{Et}PDI)FeCPh$_2$.

	Experimental	Calculated
Fe(1)-N(1)	2.047(2)	2.244
Fe(1)-N(2)	1.955(2)	2.032
Fe(1)-N(3)	2.093(2)	2.197
Fe(1)-C(30)	1.921(2)	2.010
N(1)-C(2)	1.330(3)	1.317
N(3)-C(8)	1.322(2)	1.307
C(2)-C(3)	1.432(3)	1.450
C(7)-C(8)	1.436(3)	1.460

Table S3. Comparison of experimental and computed bond distances for (^{Me}Et PDI)FeCPh$_2$.

	Experimental	Calculated
Fe(1)-N(1)	2.082(1)	2.206
Fe(1)-N(2)	1.976(2)	2.008
Fe(1)-N(3)	2.048(2)	2.258
Fe(1)-C(30)	1.936(2)	1.983
N(1)-C(2)	1.320(3)	1.312
N(3)-C(8)	1.328(3)	1.318
C(2)-C(3)	1.445(3)	1.465
C(7)-C(8)	1.440(2)	1.455

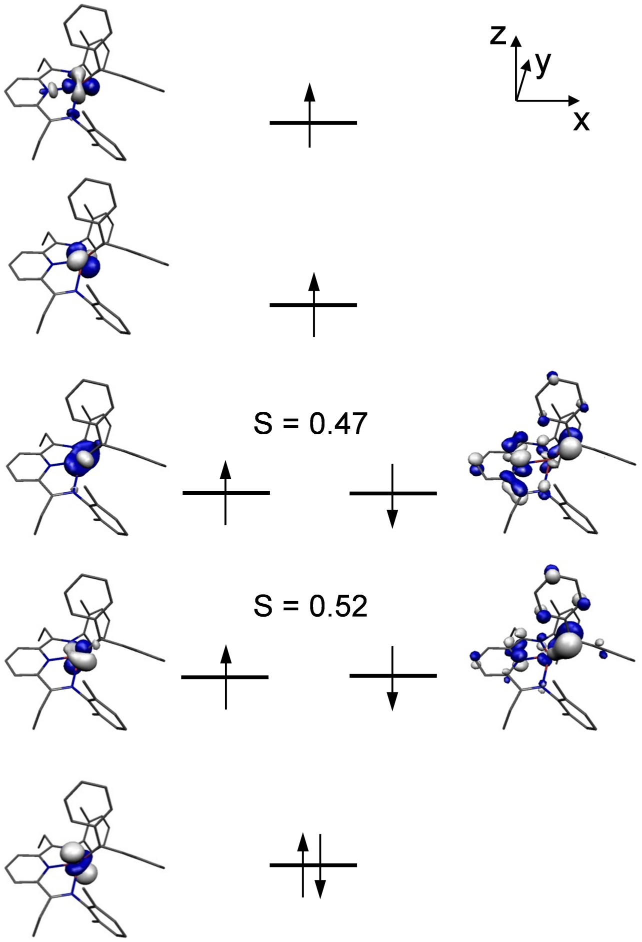

Figure S8. Qualitative molecular orbital diagram for (^{Me}Et PDI)FeCPh$_2$ from a geometry optimized DFT calculation at the B3LYP level of theory.

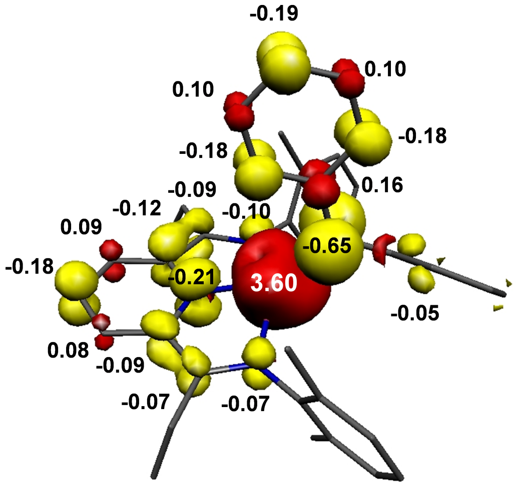

Figure S9. Spin density plot obtained from the Mulliken population analysis of (^{Me}Et PDI)FeCPh$_2$.

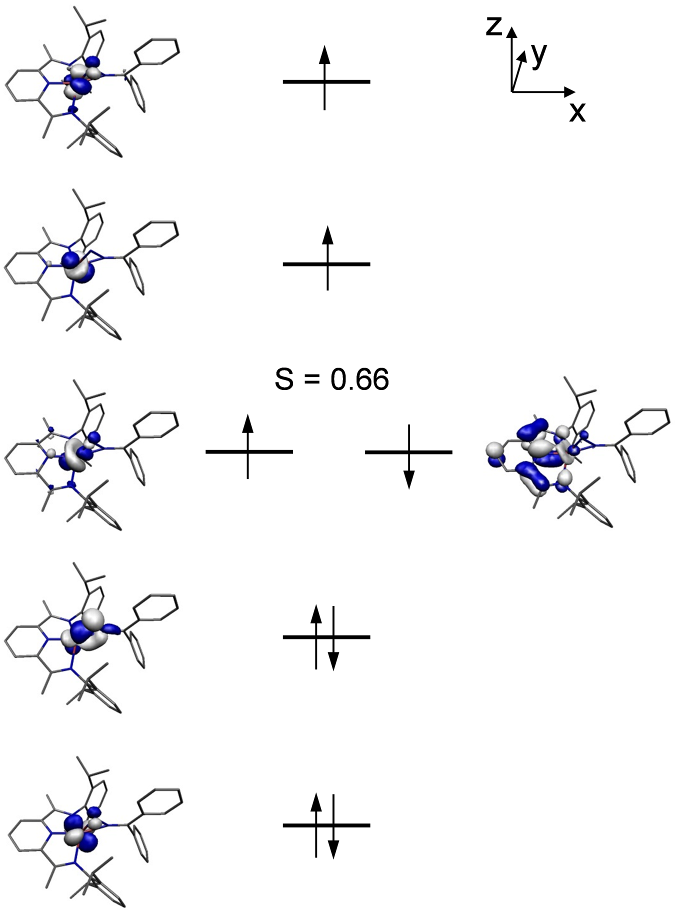

Figure S10. Qualitative molecular orbital diagram for $(^{iPr}\text{PDI})\text{Fe}(\text{N}_2\text{CPh}_2)$ from a geometry optimized DFT calculation at the B3LYP level of theory.

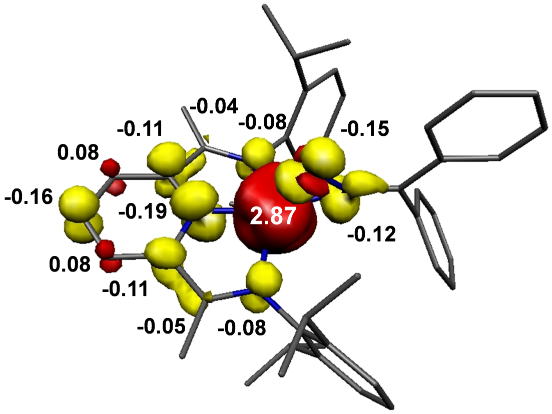

Figure S11. Spin density plot obtained from the Mulliken population analysis of $(^{iPr}\text{PDI})\text{Fe}(\text{N}_2\text{CPh}_2)$.

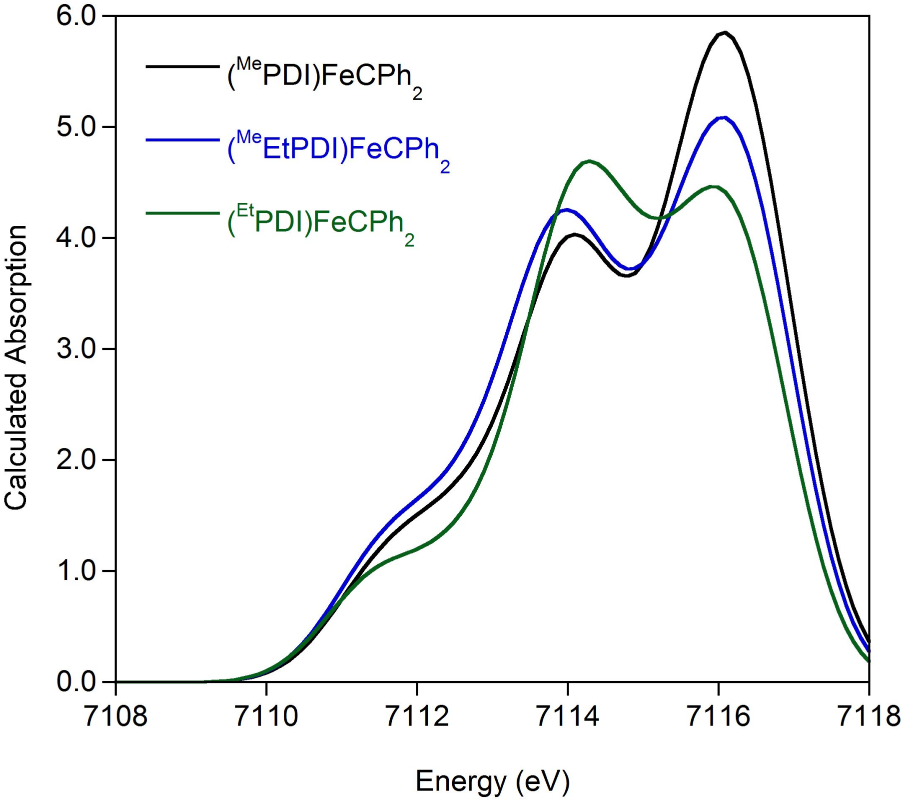

Figure S12. Calculated XAS spectra using TDDFT methods as described previously.[8]

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