Supporting Information

A Diiron Amido-Imido Complex [(Cp*Fe)₂(µ₂-NHPh)(µ₂-NPh)]: Synthesis and a Net Hydrogen Atom Abstraction Reaction to Form a Bis(imido) Complex

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Experimental Section

Figure S1. X-band EPR spectrum (77K, toluene) of [(Cp*Fe)₂(µ₂-NHPh)(µ₂-NPh)] (1).
Figure S2. SQUID magnetization data for [(Cp*Fe)₂(µ₂-NHPh)(µ₂-NPh)] (1).
Figure S3. ¹H NMR spectrum of [Cp*Fe(µ₂-NPh)]₂ (2).
Experimental Procedures.

General. All manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. Toluene, hexanes, and THF were distilled from sodium benzophenone ketyl and degassed before use. Deuterated solvents were degassed by three freeze-pump-thaw cycles and stored over 4A molecular sieves. \([\text{Cp}^*\text{FeCl}]_x\) was generated in situ by a method analogous to that reported in the literature.\(^1,2\) 2,2'-azobis(2,4-dimethylvaleronitrile) was purchased from Wako Pure Chemicals Industries, Ltd. and used as received.

NMR spectra were recorded on a JEOL EX400 NMR spectrometer operating at 399.65 MHz (\(^1\)H) and 100.40 MHz (\(^{13}\)C); chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. IR spectra were recorded on a JASCO FT-IR spectrometer. Elemental analyses were performed on a Perkin Elmer CHNS series II microanalyzer. Mass spectra were measured on a JEOL JMS-700 spectrometer. X-band EPR spectra were obtained on a JEOL RE1X spectrometer. Magnetic measurements were recorded using a Quantum Designs SQUID magnetometer at 5 kOe. Samples were suspended in the magnetometer in a clear plastic straw with a gelatin capsule. Data were acquired at 2 – 20 K (one data point every 2 K), 10 – 60 K (one data point every 2.5 K), and 60 – 300 K (one data point every 5 K). The magnetic susceptibility was adjusted for diamagnetic contributions using the constitutive corrections of Pascal’s constants. The molar magnetic susceptibility (\(\chi_m\)) was calculated by converting the calculated magnetic susceptibility (\(\chi\)) obtained from the magnetometer to a molar susceptibility (using the multiplication factor \([(\text{molecular weight})/\{\text{sample weight}\}^*\text{(field strength)}]\)). Effective magnetic moments were calculated using the equation \(\mu_{\text{eff}} = \sqrt{(7.997 \chi_m T)}\).

Preparation of \([((\text{Cp}^*\text{Fe})_2(\mu_2\text{-NHP})_2)(\mu_2\text{-NPh})]\) (1). To a stirred solution of 1,2,3,4,5-pentamethylcyclopentadiene (0.72 mL, 4.6 mmol) in 12 mL of THF was added \(n\)-BuLi (1.85 mL, 2.5 M solution in \(n\)-hexane) at 0 ºC. The resulting white suspension was cooled to −80 ºC and then transferred via cannula to a cooled (−80 ºC) suspension of anhydrous FeCl\(_2\) (583 mg, 4.6 mmol) in THF (15 mL). After the transfer was complete, the mixture was stirred for 30 min, while the temperature was maintained at −80 ºC. Separately, a THF solution of LiNHPPh was prepared by adding \(n\)-BuLi (1.85 mL, 2.5 M solution in \(n\)-hexane) to a solution of aniline (0.43 mL, 4.6 mmol) in THF (10 mL) at −80 ºC followed by warming to room temperature. The solution of LiNHPPh was cooled again to −80 ºC and then transferred via cannula to the cooled suspension of \([\text{Cp}^*\text{FeCl}]_x\). After the addition was complete, the mixture was allowed to warm slowly to room temperature and stirred for 16 h. The dark greenish brown solution obtained was evaporated to dryness, and the residue was extracted with hexanes (70 mL). The extract was concentrated to ca. 35 mL, and then stored in a freezer (−25 ºC).
After two days, dark green brown crystals of 1 were collected by filtration and dried in vacuo. Yield 565 mg, 44%. Anal. Calcd for C_{32}H_{41}N_{2}Fe_{2}: C, 67.98; H, 7.31; N, 4.95. Found: C, 67.26; H, 7.66; N, 4.32. The low carbon percentage could be due to the extreme oxygen sensitivity of the compound. Repeated analyses failed to give the expected results. IR (THF): 3296 cm\(^{-1}\) (\(\nu\)(N–H)). MS (FAB): \[m/z\] 565 [M]+. \(^1\)H NMR (toluene-\(d_8\)): \(\delta\) 16.1 (br, 2H), 7.53 (br, 2H), 4.39 (br, 1H), 3.76 (br, 30H), 0.20 (br, 2H), −34.48 (br, −2H), −43.43 (br, −2H). The spectral pattern retains over the temperature range of 80 to −20 °C. The signals became extremely broad at lower temperature. The EPR and SQUID results are depicted in Figures S1 and S2, respectively.

**Preparation of [(Cp*Fe)(\(\mu_2\)-NPh)(\(\mu_2\)-NPh)]OTf (1\(^{\cdot}\)OTf\(^{-}\)).** To a cooled (−80 °C) solution of 1 (359 mg, 0.635 mmol) in 20 mL of THF was added [Cp\(_2\)Fe]OTf (212 mg, 0.631 mmol), and the mixture was allowed to warm to room temperature with stirring over 17 h to form a green suspension. The mixture was evaporated to dryness and the residue was extracted with acetone (20 mL). Evaporation of the solvent gave an olive green solid, which was washed twice with diethyl ether (15 mL) and dried in vacuo. Yield 317 mg, 70%. Anal. Calcd for C\(_{33}\)H\(_{41}\)N\(_2\)O\(_3\)F\(_3\)SFe\(_2\): C, 55.48; H, 5.78; N, 3.92. Found: C, 55.06; H, 5.37; N, 4.02. \(^1\)H NMR (acetone-\(d_6\)): \(\delta\) 8.82 (d, 1H, Ph), 7.62 (m, 2H, Ph), 7.55 (t, 2H, Ph), 7.34 (m, 1H, Ph), 7.27 (t, 1H, Ph), 7.12 (d, 1H, Ph), 6.71 (t, 1H, Ph), 3.82 (d, 1H, Ph), 3.76 (s, 1H, NH), 1.16 (s, 30H, Cp*). \(^{13}\)C\({\{^1\}H}\) NMR (acetone-\(d_6\)): \(\delta\) 171.39 (s, Ph), 164.09 (s, Ph), 130.24 (s, Ph), 130.18 (s, Ph), 129.79 (s, Ph), 129.69 (s, Ph), 128.76 (s, Ph), 126.16 (s, Ph), 124.48 (s, Ph), 121.54 (q, CF\(_3\)), 120.23 (s, Ph), 119.14 (s, Ph), 118.63 (s, Ph), 97.48 (s, C\(_5\)Me\(_5\)), 9.38 (s, C\(_5\)Me\(_5\)).

**Preparation of [Cp*Fe(\(\mu_2\)-NPh)]\(_2\) (2).** Method A: To a stirred solution of 1 (162 mg, 0.287 mmol) in 10 mL of hexanes was added 2,2’-azobis(2,4-dimethylvaleronitrile) (71 mg, 0.287 mmol). The mixture was stirred at 50 °C for 24 h, at which time the dark brown mixture was filtered hot. Standing the filtrate at −25 °C afforded dark brown plates of 2 during the period of 18 h. The crystals were collected by filtration, washed twice with cold hexanes (3mL, −25 °C) and then dried in vacuo. Yield 73 mg, 45%. Method B: To a stirred suspension of 1\(^{\cdot}\)OTf\(^{-}\) (97 mg, 0.136 mmol) in 10 mL of THF was added NaN(SiMe\(_3\))\(_2\) (0.15 mL, 1.1 M solution in THF, 0.165 mmol) at room temperature. After stirring for 2 h, the mixture was evaporated to dryness and the residue extracted with hexanes (15 mL). Concentration to ca 5 mL and cooling to −25 °C afforded dark brown plates, which were collected by filtration and dried in vacuo. Yield 39 mg, 51%. \(^1\)H NMR (C\(_6\)D\(_6\)): \(\delta\) 7.98 (m, 4H, Ph), 7.28 (m, 2H, Ph), 6.62 (m, 4H, Ph), 2.48 (s, 30H, Cp*). Anal. Calcd for C\(_{32}\)H\(_{40}\)N\(_2\)Fe\(_2\): C, 68.10; H, 7.14; N, 4.96. Found: C, 67.01; H, 7.31; N, 5.05. Repeated analyses failed to give the expected results.
X-ray Crystallography. Reflection data were collected at 296 K with a Rigaku RAXIS Rapid diffractometer equipped with an imaging plate detector. The frame data were processed using the Rigaku PROCESS-AUTO program, and the reflection data were corrected for absorption with the ABSCOR program. The structures were solved by direct method and refined on $F^2$ by full-matrix least-squares method with the SHELX97 program package. Anisotropic refinement was applied to all non-hydrogen atoms. Hydrogen atoms were located at the calculated positions and treated as riding models.

References
**Figure S1.** X-band EPR spectrum (77K, toluene) of $[(\text{Cp^*Fe})_2(\mu_2-N\text{HPh})(\mu_2-N\text{Ph})] \ (1)$. 

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g_1 = 2.231 \\
g_2 = 2.051 \\
g_3 = 1.966
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Figure S2. SQUID magnetization data for [(Cp*Fe)$_2$(µ$_2$-NPh)(µ$_2$-NPh)] (1).
Figure S3. $^1$H NMR spectrum of [Cp*Fe($\mu_2$-NPh)]$_2$ (2).