

Synthesis and Characterization of Iron Derivatives Having a Pyridine-Linked Bis(anilide) Pincer Ligand

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A pyridine-linked bis(anilide) pincer ligand, $[2]H_2$ ($[2]H_2 = (2,6-NC_5H_3(2-(2,4,6-Me_3C_6H_2)-NHC_6H_4)_2)_2$), has been synthesized in two steps. Deprotonation with Me_3SiCH_2Li followed by metalation with $FeCl_2$ yielded a $LiCl$ adduct of $[2]Fe$. The complex is freed of $LiCl$ with excess $TIPF_6$ or by crystallization from toluene/petroleum ether, giving $[2]Fe(THF)$. $[2]Fe(THF)$ reacts with I_2 and O_2 to generate $[2]FeI$ and $([2]Fe)_2O$, respectively. The complexes have been characterized by 1H NMR spectroscopy, elemental analysis, X-ray crystallography, and UV–vis spectroscopy. $[2]Fe(THF)$ has been examined using cyclic voltammetry.

Introduction

Noble metals have been dominant in many areas of catalytic organic transformations: a fact that may be partially due to their readily accessible two electron redox couples, as well as their oxygen, water, and functional group tolerance.¹ These abilities are counterbalanced, however, by those same metals' cost, and in some cases by environmental or toxicological considerations. By comparison, iron is cheap, relatively nontoxic, and environmentally benign.² For these reasons, this decade has seen an emergence of research in areas not historically associated with iron,^{3–6} including hydrogenation,^{7–13} hydrosilylation,⁸ hydrodefluorination,¹⁴ and

cross-coupling.^{15–17} Additionally, the well-studied area of oxidation chemistry with iron complexes has made great strides in mechanistic understanding, substrate scope, chemo-, regio-, and enantioselectivity, and pertinence to industrial applications.^{18–22}

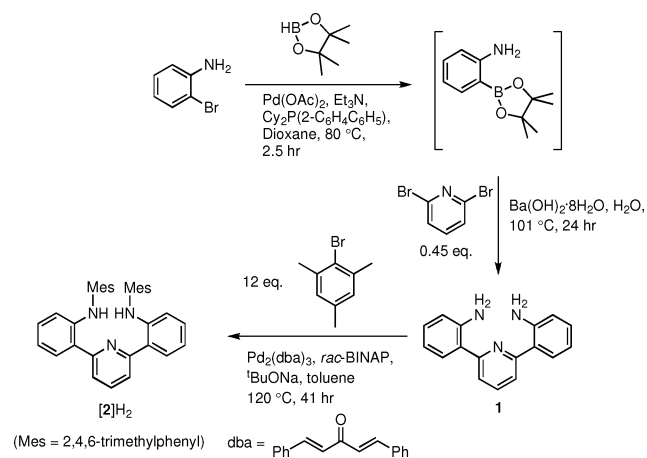
The new ligand investigated herein, $[2]H_2$ ($[2]H_2 = (2,6-NC_5H_3(2-(2,4,6-Me_3C_6H_2)-NHC_6H_4)_2)_2$), possesses two features which may engender unique properties upon complexation with iron. First, the ligand forms two six-membered chelate rings with the metal center. This ring size is less common than the five-membered chelated rings found in many iron chelates. Second, the deprotonated ligand $[2]^{2-}$ is dianionic, unlike the neutral or monoanionic ligands more common to iron chemistry.

The relative rarity of the two aforementioned motifs is surprising in light of the rich and diverse chemistry available

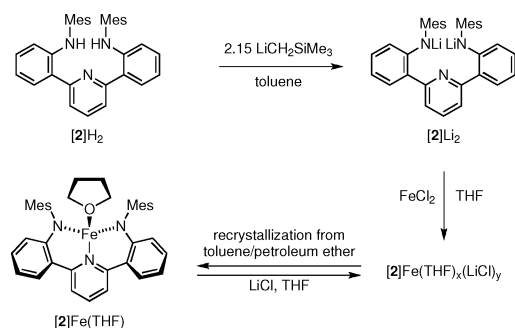
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Scheme 1. Synthesis of [2]H₂

Scheme 2. Synthesis of [2]Fe(THF)



to iron porphyrins,²³ which are dianionic and form six-membered rings upon chelation. With respect to that goal, we report herein a chelating pyridine-linked bis(anilide) ligand and iron complexes derived therefrom.

Results and Discussion

The synthesis of the ligand precursor **1** was accomplished via in situ borylation of 2-bromoaniline, followed by a 2-fold Suzuki coupling with 2,6-dibromopyridine. The arylation of **1** with an excess of mesityl bromide was accomplished with Buchwald–Hartwig coupling, yielding the ligand [2]H₂ (Scheme 1). X-ray quality crystals of the ligand were obtained by slow evaporation of a diethyl ether solution (see Supporting Information). [2]H₂ was deprotonated with a slight excess of trimethylsilylmethyl lithium in toluene, giving the dilithium salt [2]Li₂ as a bright yellow solid (Scheme 2).

[2]Li₂ was subsequently allowed to react with anhydrous ferrous chloride in tetrahydrofuran (THF) for 1 day, yielding a lithium chloride adduct of [2]Fe. Lithium chloride-free [2]Fe(THF) may be obtained by addition of thallium hexafluorophosphate or by crystallization from a toluene-petroleum ether mixture. Reaction of [2]Fe(THF) with lithium chloride in THF regenerates the lithium chloride adduct.

The magnetic moment of [2]Fe(THF) was measured via Evans method in benzene-*d*₆,²⁴ giving $\mu_{\text{eff}} = 4.8 \mu_{\text{B}}$, which

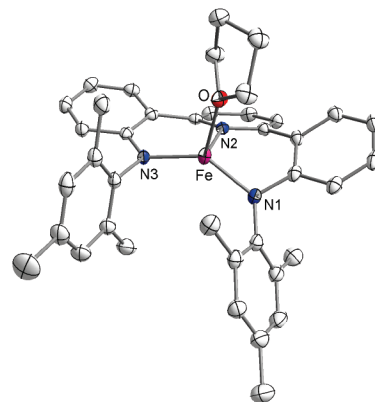


Figure 1. Structure of [2]Fe(THF) with displacement ellipsoids at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles(deg): Fe–N3, 1.928(1); Fe–N1, 1.932(1); Fe–N2, 2.036(1); Fe–O, 2.113(1); N3–Fe–N1, 139.52(4); N3–Fe–N2, 94.97(4); N1–Fe–N2, 96.44(4); N3–Fe–O, 110.45(4); N1–Fe–O, 106.54(4); N2–Fe–O, 96.85(4); Sum of angles N3–Fe–N1, N3–Fe–O, and N1–Fe–O = 356.5°.

is close to the spin-only value of $4.9 \mu_{\text{B}}$ for a quintet ground state. X-ray quality crystals were obtained by cooling a saturated toluene/petroleum ether solution at $-30 \text{ }^{\circ}\text{C}$ overnight. [2]Fe(THF) (Figure 1) does not closely resemble any regular polyhedron, but can best be described as having a distorted trigonal monopyramidal geometry, with the THF and the anilide nitrogens forming the basal plane and the pyridine nitrogen at the apex. Tetrahedral, and to a lesser extent square planar, are the dominant geometries for four-coordinate iron. In contrast, there are only a handful of structurally characterized iron complexes with a trigonal monopyramidal geometry.^{25–28} Although the sum of the angles in the basal plane is close to 360° , the individual angles are all quite different from 120° (approximately 140° , 110° , 107°).

The binding pocket of the ligand is too small to accommodate a C_{2v} -type ligand geometry, which is partially a result of the two six-membered chelate rings that are formed upon metalation. Chirik has reported several iron compounds from a bis(enamide)pyridine ligand with two five-membered chelate rings;²⁹ these complexes comprise the only other crystallographically characterized iron pincer compounds with anilide arms. The most useful comparison (Figure 2) may be made with his pyridinebis(anilide) iron (II) amine adduct **3**. In contrast to [2]Fe(THF), **3** supports a slightly

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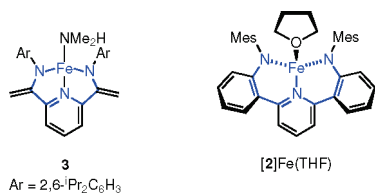


Figure 2. Comparison between five and six-membered chelate rings in pyridinebis(anilide) iron complexes.

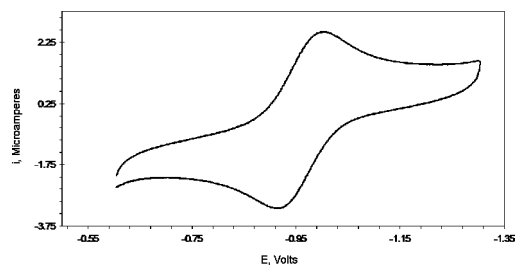
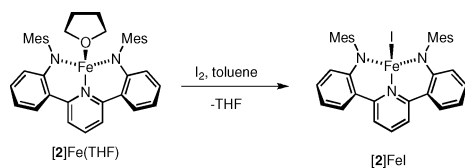


Figure 3. Voltammogram of 0.003 M **[2]Fe(THF)** in THF with 0.3 M ^tBu₄NBF₄ as supporting electrolyte. Data were recorded at 100 mV/s, and peaks were referenced to the ferrocene/ferrocenium couple.

Scheme 3. Synthesis of **[2]FeI**



distorted square planar configuration (the sum of the four angles about iron is $\sim 361^\circ$).

Cyclic voltammetry studies were performed on **[2]Fe(THF)** (Figure 3). A quasireversible, diffusion controlled³⁰ reduction occurs at $E_{1/2} = -0.96$ V (versus the ferrocene/ferrocenium couple), and an irreversible oxidation is also observed at -0.37 V. Two new reduction waves (-0.92 V, -1.14 V) are coupled to the irreversible oxidation event, which are observed in addition to the original reversible reduction wave. The electrochemical data suggest that the **[2]Fe** framework is capable of supporting either reduced or oxidized species.

In light of the electrochemical data, chemical oxidation of **[2]Fe(THF)** was attempted. Oxidation using molecular iodine generates **[2]FeI**, which resembles a chelated version of a previously reported complex (Scheme 3).³¹

[2]FeI exhibits a solution magnetic moment of $5.8 \mu_B$ in benzene-*d*₆, consistent with a sextet ground state. The solid state structure of **[2]FeI** (Figure 4) reveals a more tetrahedral, but still quite distorted geometry about the iron center, in contrast to the more trigonal monopyramidal geometry observed for **[2]Fe(THF)**. Oxidation of **[2]Fe(THF)** via dioxygen generates a bridging oxo dimer, **([2]Fe)₂O** (Scheme 4, Figure 5).

Bridging-oxo diiron complexes are well-known.^{32,33} **[2]FeI** and **([2]Fe)₂O** possess significantly smaller anilide nitrogen

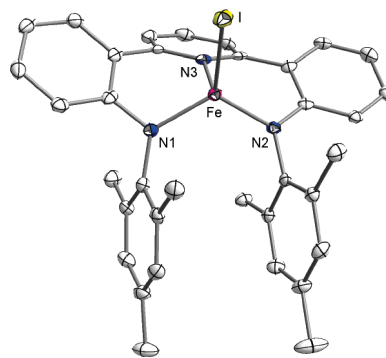


Figure 4. Structure of **[2]FeI** with displacement ellipsoids at the 50% probability level. Two virtually identical **[2]FeI** molecules were present in the asymmetric unit. Hydrogen atoms, solvent molecules, and the other **[2]FeI** molecule were omitted for clarity. Selected bond lengths (Å) and angles(deg): Fe–N1, 1.8993(1); Fe–N2, 1.8834(1); Fe–N3, 2.0274(1); Fe–I, 2.5784(1); N1–Fe–N2, 118.297(5); N1–Fe–N3, 93.436(4); N2–Fe–N3, 94.660(4); N1–Fe–I, 115.771(4); N2–Fe–I, 118.771(4); N3–Fe–I, 108.740(4).

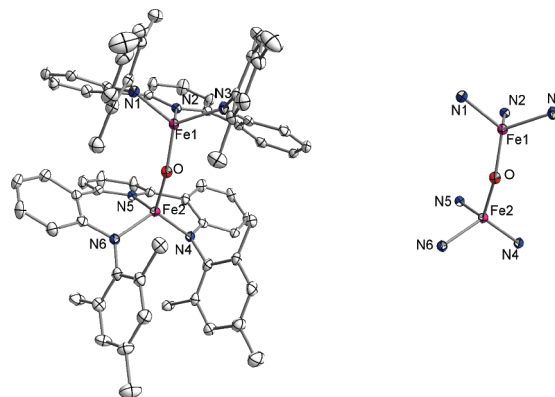
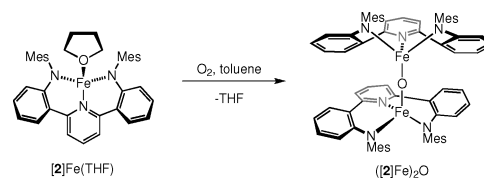


Figure 5. Structure of **([2]Fe)₂O** (left) and iron coordination sphere (right) with displacement ellipsoids at the 50% probability level. Hydrogen atoms and solvent were omitted for clarity. Selected bond lengths (Å) and angles(deg): Fe1–N1, 1.9174(1); Fe1–N2, 2.0161(1); Fe1–N3, 1.9262(1); Fe1–O, 1.7802(1); Fe2–N4, 1.9263(1); Fe2–N5, 2.0154(1); Fe2–N6, 1.9234(1); Fe2–O, 1.7761(1); Fe1–O–Fe2, 156.601(3); N1–Fe1–N3, 117.501(2); N1–Fe1–N2, 92.864(2); N2–Fe1–N3, 95.140(2); N1–Fe1–O, 120.084(3); N3–Fe1–O, 116.843(3); N2–Fe1–O, 104.570; N6–Fe2–N4, 116.394(2); N6–Fe2–N5, 95.056(2); N5–Fe2–N4, 93.669; N6–Fe2–O, 117.267(3); N4–Fe2–O, 119.968(3); N5–Fe2–O, 106.367(2).

Scheme 4. Synthesis of **([2]Fe)₂O**



iron anilide nitrogen angles (118.13° and 117.50° , respectively) than does **[2]Fe(THF)** (139.52°); the reasons for this distortion are not immediately apparent.

In conclusion, the syntheses of iron complexes based on the new ligand **[2]²⁻** has been accomplished. Investigations of the reactivity of this class of compounds are currently underway.

Experimental Section

General Methods. Unless otherwise specified, air exposed solids were dried under vacuum prior to use, liquids were degassed or bubbled with argon, protio solvents were dried via Grubbs'

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method,³⁴ reagents were used as received from the supplier, and reactions were performed under an inert atmosphere or vacuum. All air and moisture sensitive compounds were handled using standard glovebox, Schlenk, and high-vacuum line techniques. Deuterated chloroform, benzene, and THF were obtained from Cambridge Isotope Laboratories. Deuterated chloroform was used as received and not stored under inert atmosphere. Deuterated benzene and THF were dried with disodium benzophenone. Deuterated benzene was subsequently dried using titanocene dihydride. 2-Bromoaniline was obtained from Avocado. 2-(Dicyclohexylphosphino)biphenyl, tris(dibenzylideneacetone) dipalladium (0), and thallium hexafluorophosphate were obtained from Strem. Palladium (II) acetate, racemic 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), sodium tert-butoxide, mesityl bromide, triethylamine, 2,6-dibromopyridine, 3 Å Linde type molecular sieves, and calcium hydride were obtained from Aldrich. Sodium and benzophenone were obtained from Lancaster and MCB reagents, respectively. Mesityl bromide was dried on 3 Å Linde type molecular sieves for 6 days prior to use. Triethylamine was stirred on calcium hydride for several days, then vacuum transferred onto 3 Å Linde type molecular sieves prior to use. 1,4-Dioxane was obtained from EMD, dried sequentially with 3 Å Linde type molecular sieves and disodium benzophenone, then vacuum transferred before use. Pinacolborane was obtained from Aldrich or Alfa Aesar, and stored at -30 °C. Barium hydroxide octahydrate was obtained from Mallinckrodt, and stored open to the atmosphere. Trimethylsilylmethylolithium was sublimed before use. Ferrous chloride 99.99% was obtained from Aldrich as anhydrous beads. NMR spectra were recorded on Varian Mercury 300 Megahertz NMR spectrometers, and referenced according to the solvent residual peak.³⁵ Solution magnetic moments were determined via Evans Method.²⁴ The paramagnetism of the iron complexes precluded assignment of peaks in their ¹H NMR spectra. The paramagnetism also implies that the integrations must only be regarded as rough estimations. Electrochemical measurements were performed using a glassy carbon rod as a working electrode, a platinum wire as auxiliary electrode, and partitioned Ag/AgCl wire as a pseudoreference electrode. Data were obtained using BAS100W software, on a BAS100A Electrochemical Analyzer. 0.3 M ⁿBu₄NBF₄ THF solutions were employed, with 0.003 M concentration for the analyte. Ferrocene was employed as the internal standard, and all potentials were referenced to the ferrocene/ferrocenium couple. All data were obtained in an inert atmosphere glovebox. X-ray diffraction data were obtained on a Bruker SMART 1000 or Bruker KAPPA APEXII. UV-vis spectra were recorded on an Agilent 8453 UV-vis spectrometer. High resolution mass spectra (HRMS) were obtained at the California Institute of Technology Mass Spectral Facility using a JEOL JMS-600H magnetic sector mass spectrometer. Elemental analyses were carried out by Desert Analytics, Tucson, AZ 85714.

Synthesis of Bis(aniline) 1.³⁶ In a glovebox, 2-bromoaniline (34.48 g, 200.5 mmol), palladium (II) acetate (2.33 g, 10.4 mmol), and 2-(dicyclohexylphosphino) biphenyl (13.80, 19.36 mmol) were added to a 2 L, 3 neck round-bottom flask, and the flask was sealed. Under an argon purge, the flask was equipped with a reflux condenser and an addition funnel. Triethylamine (112 mL, 803 mmol) and 425 mL of dioxane were added via cannula. Pinacolborane

(88 mL, 610 mmol) was cannulated into the addition funnel and added dropwise to the stirring solution over 43 min. Upon addition, vigorous bubbling occurred, and the solution turned olive green. After addition was complete, the reaction mixture was heated to 80 °C for 2.5 h, then allowed to cool to room temperature. Under an argon purge, solid barium hydroxide octahydrate (195.2 g, 618.7 mmol) was slowly added until the bubbling ceased, then the remainder was added. Subsequently a solution of 2,6-dibromopyridine (21.58 g, 91.11 mmol) in 140 mL of dioxane was added via cannula. Finally, 97 mL of deionized water was bubbled with argon for approximately 10 min, then cannulated into the reaction mixture. The reaction was heated to 101 °C for approximately 24 h, then allowed to cool to room temperature. The solvent was removed in vacuo. The remaining solid was repeatedly pulverized then washed with methylene chloride (1.7 L) to remove trapped product from insoluble barium hydroxide, as indicated by the washings no longer darkening. The solution was extracted with an equal amount of water, then concentrated in vacuo. The crude black sludge was purified by column chromatography using methylene chloride and ethyl acetate. Because the separation is somewhat nontrivial, it is reported in detail in the Supporting Information. After chromatography, the resulting yellow solid was washed repeatedly with large amounts of diethyl ether until the ether lost most of its yellow color (though the pure compound is very faintly yellow). After the washings, the solid was dried in vacuo, giving 7.91 g of **1** as an off-white solid in 33% yield. ¹H NMR (CDCl₃): δ 5.38 (s(broad), 2H, NH), 6.76 (dd, *J*_{H-H} = 8 Hz, 1 Hz, 2H, CH), 6.82 (td, *J*_{H-H} = 8 Hz, 1 Hz, 2H, CH), 7.19 (dd, *J*_{H-H} = 12 Hz, 7 Hz, CH), 7.52 (s(broad), 2H, CH), 7.54 (s(broad), 2H, CH), 7.86 (t, *J*_{H-H} = 8.0 Hz, 1H, *p*-NC₅H₃). ¹³C NMR (CDCl₃): δ 117.1, 117.8, 120.2, 123.0, 129.9, 130.0, 138.1, 146.1, 157.7. HRMS (FAB+) *m/z* calcd for C₁₇H₁₆N₃: 262.1344. Found: 262.1348 (M + H), 245.0991 (M - NH₂).

Synthesis of Ligand [2]H₂.³⁷ In a glovebox, **1** (7.91 g, 30.3 mmol), tris(dibenzylideneacetone)-dipalladium (0) (1.39 g, 1.51 mmol), *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (2.34 g, 3.75 mmol), sodium tert-butoxide (8.82 g, 91.7 mmol), 300 mL of toluene, and mesityl bromide (56 mL, 360 mmol) were combined in a 3-neck, 1 L round-bottom flask. The solution was refluxed under an argon atmosphere for approximately 41 h. Under an argon purge, the reaction was quenched with 20 mL of water, and then concentrated in vacuo. Excess mesityl bromide was distilled away by heating the solid at 70 °C under high vacuum. The solid was washed with 50 mL of petroleum ether, then dissolved in 250 mL of methylene chloride. The solution was extracted with an equal amount of water, filtered, and concentrated in vacuo, giving a yellow solid. Any palladium containing species were removed by passing a methylene chloride solution of the product through 1 L of silica gel packed with methylene chloride. The solution was concentrated to a yellow solid. The solid was washed repeatedly with methanol until the solid appeared off-white. [2]H₂ was obtained in 46% yield (6.93 g). ¹H NMR (C₆D₆): δ 2.01 (s, 12H, *o*-CH₃), 2.15 (s, 6H, *p*-CH₃), 6.50 (d, *J*_{H-H} = 8 Hz, 2H, CH), 6.74 (s, 4H, mesityl-CH), 6.82 (s, 4H, CH), 7.03 (t, *J*_{H-H} = 8 Hz, 2H, CH), 7.2-7.4 (m, 3H, CH), 7.55 (d, *J*_{H-H} = 8 Hz, 2H, CH), 8.53 (s, 2H, NH). ¹H NMR (d₈-THF): δ 1.97 (s, 12H, *o*-CH₃), 2.23 (s, 6H, *p*-CH₃), 6.20 (d, *J*_{H-H} = 8 Hz, 2H, CH), 6.69 (t, *J*_{H-H} = 8 Hz, 2H, CH), 6.82 (s, 4H, CH), 7.02 (t, *J*_{H-H} = 8 Hz, 2H, CH), 7.59 (d, *J*_{H-H} = 8 Hz, 2H, CH), 7.76 (d, *J*_{H-H} = 8 Hz, 2H, CH), 7.97 (t, *J*_{H-H} = 8 Hz, 1H, *p*-NC₅H₃), 8.42 (s, 2H, NH). ¹H NMR (CDCl₃): δ 2.01 (s,

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12H, *o*-CH₃), 2.27 (s, 6H, *p*-CH₃), 6.27 (d, $J_{\text{H-H}} = 8$ Hz, 2H, CH), 6.76 (t, $J_{\text{H-H}} = 7$ Hz, 2H, CH), 6.85 (s, 4H, mesityl-CH), 7.09 (t, $J_{\text{H-H}} = 8$ Hz, 2H, CH), 7.57 (d, $J_{\text{H-H}} = 8$ Hz, 2H, CH), 7.66 (d, $J_{\text{H-H}} = 8$ Hz, 2H, CH), 7.91 (t, $J_{\text{H-H}} = 8$ Hz, 1H, *p*-NC₅H₃), 8.14 (s, 2H, NH). ¹³C NMR (CDCl₃): δ 18.5, 21.0, 113.2, 117.1, 120.8, 123.3, 129.1, 130.0, 130.1, 135.1, 136.0, 136.1, 137.9, 145.4, 158.1. HRMS (FAB+) *m/z* calcd. for C₃₅H₃₅N₃: 497.2831. Found: 497.2849 (M⁺), 482.2596 (M-CH₃). UV-vis (THF, nm (M⁻¹ cm⁻¹)): 275 (sh), 354 (1.3 × 10⁴). X-ray quality crystals were obtained by slow evaporation of a saturated diethyl ether solution. The crystal data are summarized as follows: formula, C₃₅H₃₅N₃; formula weight, 497.66; lattice system, monoclinic; space group *P*2₁/*n* (No. 14); temperature 100 K; lattice parameters *a* = 12.1774(12) Å, *b* = 8.3901(8) Å, *c* = 27.039 (3) Å, β = 93.803(2)°; unit cell volume *V* = 2756.5(5) Å³; calculated density *D*_{calc} = 1.199 g/cm³; number of molecules in the unit cell *Z* = 4; linear absorption coefficient μ = 0.070 mm⁻¹; no empirical absorption correction; Mo Kα radiation recorded on a Bruker SMART 1000 diffractometer; 34841 reflections collected, 6476 unique reflections (4122 with *I* > 2σ(*I*)); θ_{max} = 28.41°; 349 parameters; 0 restraints; H atoms were placed in calculated positions; all other atoms were refined anisotropically, full matrix least-squares on *F*² refinement method; reliability factor *R* for all data = 0.0900 (for data *I* > 2σ(*I*) = 0.0554), weighted reliability factor *R*_w = 0.0939 (for data *I* > 2σ(*I*) = 0.0907), goodness-of-fit on *F*², 1.579. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. Copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 65353 or by visiting http://www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of [2]Li₂. In a glovebox, [2]H₂ (2.222 g, 4.465 mmol) and trimethylsilylmethylolithium (0.943 g, 10.01 mmol) were combined as solids. On the high vacuum line, ~100 mL of toluene were vacuum transferred from a titanocene dihydride pot onto the solids at -78 °C. After transfer was complete, the mixture was stirred and allowed to warm to room temperature. Upon warming, the solids dissolved. After 2 h, the orange solution was concentrated in vacuo. In the glovebox, the orange solid was suspended in 30 mL of pentane (obtained by vacuum transfer from a disodium benzophenone/tetraglyme pot). The orange suspension was cooled via a liquid nitrogen cooled cold well, then filtered. The aforementioned procedure was repeated with an additional 30 mL of pentane. The remaining solid was dried in vacuo, giving 2.256 g of [2]Li₂ as a bright yellow solid in 99% yield. ¹H NMR (d₈-THF): δ 1.65 (s, 12H, *o*-CH₃), 2.20 (s, 6H, *p*-CH₃), 5.99 (d, $J_{\text{H-H}} = 8$ Hz, 2H, *o*-anilide CH), 6.14 (t, $J_{\text{H-H}} = 7$ Hz, 2H, *p*-anilide CH), 6.58 (s, 4H, mesityl aryl-CH), 6.70 (t, $J_{\text{H-H}} = 7$ Hz, 2H, *m*-anilide CH *para* to pyridine ring), 7.54 (d, $J_{\text{H-H}} = 8$ Hz, 2H, *m*-anilide CH *ortho* to pyridine ring), 7.64 (d, $J_{\text{H-H}} = 8$ Hz, 2H, *m*-NC₅H₃), 7.84 (t, $J_{\text{H-H}} = 8$ Hz, *p*-NC₅H₃). ¹³C NMR (C₆D₆) δ 18.54, 20.91, 112.34, 116.36, 119.56, 120.74, 129.52, 130.53, 131.44, 131.92, 131.97, 139.62, 147.51, 156.84, 160.77. Anal. Calcd. for C₃₅H₃₃Li₂N₃: C, 82.50; H, 6.53; N, 8.25. Found1: C, 81.25; H, 6.14; N, 7.34. Found2: C, 80.85; H, 5.93; N, 7.33.

Synthesis of [2]Fe(THF). Ferrous chloride (199 mg, 1.57 mmol) and [2]Li₂ (800 mg, 1.57 mmol) were combined as solids, then dissolved in 20 mL of THF. The reaction mixture was stirred for 25 h, then concentrated in vacuo to give the lithium chloride adduct [2]Fe(THF)_x(LiCl)_y. ¹H NMR (d₈-THF): δ -51.32 (s, 2H, CH), -38.59 (s, 2H, CH), 18.25 (s, 4H), 19.82 (s, 2H, CH), 28.43 (s, 2H, CH), 41.07 (s, 6H), 44.42 (s, 2H, CH), 47.59 (s, 2H, CH), 66.06 (s, 2H, CH), 73.51 (s, 1H, *p*-NC₅H₃), 77.72 (s, 4H). The lithium chloride adduct was dissolved in 55 mL of toluene, filtered, diluted with 100 mL of petroleum ether, and left at -30 °C

overnight. A 531 mg quantity of black crystalline [2]Fe(THF) was obtained after drying in vacuo in 54% yield. ¹H NMR (C₆D₆): δ -52.03 (s, 2H, CH), -27.83 (s, 2H, CH), 2.85 (s, 4H), 33.41 (s, 4H), 47.42 (s, 2H, CH), 52.78 (s, 6H, *p*-CH₃), 54.28 (s, 2H, CH), 55.40 (s, 2H, CH), 63.46 (s, 1H, *p*-NC₅H₃). ¹H NMR (d₈-THF): δ -52.39 (s, 2H, CH), -31.47 (s, 2H, CH), 33.04 (s, 4H), 44.15 (s, 10H), 46.66 (s, 2H, CH), 52.35 (s, 2H, CH), 52.78 (s, 6H, CH₃), 56.97 (s, 2H, CH), 66.25 (s, 1H, *p*-NC₅H₃). Anal. Calcd for C₃₉H₄₁FeN₃O: C, 75.11; H, 6.63; N, 6.74. Found1: C, 74.90; H, 6.74; N, 6.67. Found2: C, 73.72; H, 6.50; N, 6.64. CV (THF): *E*_{1/2}, V versus Ferrocene at 100 mV/s (Δ*E*_p, *i*_{pa}/*i*_{pc}): -0.96 V (90 mV, 0.88) and -0.37 V (irreversible). UV-vis (THF, nm (M⁻¹ cm⁻¹)): 275 (sh), 371 (1.1 × 10⁴), 410 (sh).

X-ray quality crystals were obtained from a toluene/petroleum ether solution at -30 °C. The crystal data are summarized as follows: formula, C₃₉H₄₁N₃OFe; formula weight, 623.60; lattice system, monoclinic; space group *P*2₁/*c* (No. 14); temperature 100 K; lattice parameters *a* = 14.5396(6) Å, *b* = 13.5644(6) Å, *c* = 16.6014(7) Å, β = 98.247(2)°; unit cell volume *V* = 3240.3(2) Å³; calculated density *D*_{calc} = 1.278 g/cm³; number of molecules in the unit cell *Z* = 4; linear absorption coefficient μ = 0.501 mm⁻¹; no empirical absorption correction; Mo Kα radiation recorded on a Bruker KAPPA APEX II diffractometer; 97719 reflections collected, 14879 unique reflections (10317 with *I* > 2σ(*I*)); θ_{max} = 36.53°; 403 parameters; 0 restraints; H atoms were placed in calculated positions; all other atoms were refined anisotropically, full matrix least-squares on *F*² refinement method; reliability factor *R* for all data = 0.0792 (for data *I* > 2σ(*I*) = 0.0501), weighted reliability factor *R*_w = 0.0860 (for data *I* > 2σ(*I*) = 0.0848), goodness-of-fit on *F*², 2.823. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. Copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 678268 or by visiting http://www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of [2]FeI. [2]Fe(THF) (116.8 mg, 187.3 μmol) and iodine (23.8 mg, 93.6 μmol) were combined as solids, dissolved in 10 mL of toluene, and left stirring for 15 min. The solution was then concentrated in vacuo. A 126 mg quantity of [2]FeI was isolated in 77% yield. X-ray quality crystals were obtained by dissolution with benzene, dilution in an equal quantity of petroleum ether, and cooling to -30 °C. The crystal data are summarized as follows: formula, 2(C₃₅H₃₃N₃FeI) 1.5(C₆H₆); formula weight, 1473.98; lattice system, triclinic; space group *P* $\bar{1}$ (No. 2); temperature 100 K; lattice parameters *a* = 14.8740(7) Å, *b* = 14.9489(7) Å, *c* = 16.9750(8) Å, α = 69.528(3)°, β = 72.061(3)°, γ = 76.207(3)°; unit cell volume *V* = 3327.7(3) Å³; calculated density *D*_{calc} = 1.471 g/cm³; number of molecules in the unit cell *Z* = 4; linear absorption coefficient μ = 1.413 mm⁻¹; semiempirical absorption correction from equivalents; Mo Kα radiation recorded on a Bruker KAPPA APEX II diffractometer; 85468 reflections collected, 22141 unique reflections (13476 with *I* > 2σ(*I*)); θ_{max} = 32.13°; 1102 parameters; 0 restraints; H atoms were located via a Difference Fourier map; all other atoms were refined anisotropically, full matrix least-squares on *F*² refinement method; reliability factor *R* for all data = 0.1132 (for data *I* > 2σ(*I*) = 0.0507), weighted reliability factor *R*_w = 0.0647 (for data *I* > 2σ(*I*) = 0.0602), goodness-of-fit on *F*², 1.524. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. Copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 695390 or by visiting http://www.ccdc.cam.ac.uk/data_request/cif. ¹H NMR (d₈-THF): δ -208.67 (s, 2H), -187.22 (s, 2H), 38.38 (s, 1H), 64.06 (s, 4H), 88.58 (2 overlapping peaks, s, 6H) 96.40 (s, 2H), 109.64 (s, 2H),

115.71 (s, 6H), 121.91 (s, 2H), 137.74 (s, 2H). Anal. Calcd for $C_{35}H_3FeN_3I$: C, 61.97; H, 4.90; N, 6.19. Found1: C, 62.25; H, 4.46; N, 6.15. Found2: C, 62.42; H, 4.47; N, 5.95. UV-vis (THF, nm ($M^{-1} \text{ cm}^{-1}$)): 371 (1.8×10^4), 456 (6.2×10^3), 510 (sh), 741 (7.3×10^3).

Synthesis of $[(2)Fe]_2O$. In the glovebox, $[(2)Fe(THF)]$ (167.9 mg, 269 μmol) was dissolved in 25 mL of toluene. On the high vacuum line, the solution was degassed. ~ 1 atm of dioxygen was dried via a dry ice/acetone trap for 1 h, then exposed to the solution. The solution immediately turned from dark red to dark green. After 30 min, the solution was concentrated in vacuo to an intractable sludge. The sludge was treated with petroleum ether, stirred briefly, then concentrated in vacuo to a green powder and isolated in 85% yield. X-ray quality crystals were obtained by vapor diffusion of petroleum ether into a saturated toluene solution. The crystal data are summarized as follows: formula, $C_{70}H_{66}N_6OFe_2 \cdot 0.5(C_7H_8)$; formula weight, 1165.05; lattice system, orthorhombic; space group $Iba2$ (No. 45); temperature 100 K; lattice parameters $a = 19.8707(9)$ Å, $b = 39.4031(19)$ Å, $c = 15.1038(6)$ Å; unit cell volume $V = 11825.8(9)$ Å³; calculated density $D_{\text{calc}} = 1.309 \text{ g/cm}^3$; number of molecules in the unit cell $Z = 8$; linear absorption coefficient $\mu = 0.542 \text{ mm}^{-1}$; no empirical absorption correction; Mo $K\alpha$ radiation recorded on a Bruker KAPPA APEX II diffractometer; 121688 reflections collected, 18216 unique reflections (14462 with $I > 2\sigma(I)$); $\theta_{\text{max}} = 32.23^\circ$; 757 parameters; 10 restraints; H atoms were placed in calculated positions; all other atoms were refined anisotropically, full matrix least-squares on F^2 refinement method; reliability factor R for all data = 0.0600 (for data $I > 2\sigma(I) =$

0.0416), weighted reliability factor $R_w = 0.0567$ (for data $I > 2\sigma(I) = 0.0558$), goodness-of-fit on F^2 , 1.792. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. Copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 697910 or by visiting http://www.ccdc.cam.ac.uk/data_request/cif.

^1H NMR (C_6D_6): δ -10.59 (s), δ -8.66 (s), δ 10.35 (s), δ 11.24 (s), δ 12.86 (s), δ 13.64 (s), δ 15.99 (s), δ 16.67 (s) (the overlap of peaks precluded integration). Anal. Calcd for $C_{70}H_{66}N_6OFe_2$ (and 0.5 equiv C_7H_8): C, 75.77; H, 6.06; N, 7.21. Found1: C, 75.40; H, 5.81; N, 5.71. Found2: C, 75.32; H, 5.90; N, 6.32.

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Supporting Information Available: UV-vis spectra, diffraction data, and voltammograms. Crystallographic data in CIF file format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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