ORGANOMETALLICS

Electronic Effects in 4-Substituted Bis(imino)pyridines and the Corresponding Reduced Iron Compounds

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Supporting Information

ABSTRACT: A family of 4-substituted bis(imino)pyridines, 4-X-^{iPr}PDI (4-X-^{iPr}PDI = 2,6-(2,6-ⁱPr₂-C₆H₃N=CMe)₂-4-X-C₃H₂N; X = CF₃, ^tBu, Bn, NMe₂), has been synthesized and the iron coordination chemistry studied. Sodium amalgam reduction of the iron dihalides (4-X-^{iPr}PDI)FeX₂ (X = Cl, Br) in the presence of excess carbon monoxide furnished the corresponding iron dicarbonyl compounds (4-X-^{iPr}PDI)Fe-(CO)₂. Equilibrium mixtures of the four- and five-coordinate iron dinitrogen compounds (4-X-^{iPr}PDI)FeN₂ and (4-X-^{iPr}PDI)Fe(N₂)₂ were prepared by performing the sodium



amalgam reduction of the iron dihalides under a dinitrogen atmosphere. Electrochemical and spectroscopic measurements were conducted on the free ligands and the iron derivatives to systematically evaluate the influence of each para pyridine substituent on the electronic structure of the compound.

INTRODUCTION

Iron is an attractive precious-metal surrogate due to its natural abundance, low cost, and biocompatibility.¹ Aryl-substituted bis(imino)pyridine iron compounds have emerged as an important class of catalysts. Interest in these compounds intensified with the discovery of high-activity ethylene polymerization upon activation of (^{Ar}PDI)FeCl₂ with methyl-aluminoxane (MAO).^{2,3} Numerous modifications have been made to the bis(imino)pyridine ligand scaffold to alter the degree of oligomerization or polymerization,⁴ while investigations into the nature of the propagating species have established the efficacy of high-spin iron(II) alkyl cations with a neutral bis(imino)pyridine chelate.^{5,6} Inspired by the thermal⁷⁻¹⁰ and photochemical¹¹ activity of

Inspired by the thermal^{7–10} and photochemical¹¹ activity of $Fe(CO)_5$ in unactivated olefin hydrogenation and hydrosilylation reactions,¹² our laboratory sought to prepare a modular mimic of the proposed [Fe(CO)₃] active species^{13–20} by two-electron reduction of (^{Ar}PDI)FeX₂ (X = halide) derivatives. Stirring (^{iPr}PDI)FeBr₂ (^{iPr}PDI = 2,6-(2,6-ⁱPr₂-C₆H₃N=CMe)₂C₅H₃N) with excess 0.5% sodium amalgam under an N₂ atmosphere yielded, following filtration and recrystallization, the five-coordinate bis(imino)pyridine iron dinitrogen compound (^{iPr}PDI)Fe(N₂)₂. This compound is in equilibrium with the four-coordinate iron mono(dinitrogen) derivative (^{iPr}PDI)FeN₂ where the relative concentrations of each species depend on the N₂ pressure. Investigations into the electronic structures of the two compounds established participation of the bis(imino)pyridine chelate in both cases, a well-established phenomenon with this ligand class.^{21–23} The five-coordinate compound (^{iPr}PDI)Fe(N₂)₂ is a highly covalent compound best described as a hybrid structure between $[({}^{iPr}PDI^{2-})Fe^{II}]$ and $[({}^{iPr}PDI^{0})Fe^{0}]$ resonance forms, analogous to the case for the dicarbonyl derivative $({}^{iPr}PDI)Fe(CO)_2$.²⁴ In this bonding regime, the bis(imino)pyridine is classified as "redox non-innocent", a term coined by Jørgensen in the context of nitrosyl ligands to signal ambiguity in metal oxidation state assignment.²⁵

The electronic structure of the four-coordinate bis(imino)pyridine iron dinitrogen compound (^{iPr}PDI)FeN₂ differs from that of its five-coordinate counterpart. Variable-temperature NMR, Mössbauer, X-ray absorption, and X-ray emission spectroscopy, in combination with DFT calculations, support an intermediate-spin ferrous compound antiferromagnetically coupled to a bis(imino)pyridine triplet diradical.²⁶ Population of a thermally accessible paramagnetic excited state gives rise to temperature-dependent ¹H NMR chemical shifts, a phenomenon attributed to poor overlap of an iron SOMO with the ligand-centered radicals. This behavior is distinct from that of (^{iPr}PDI)Fe(DMAP) and other related four-coordinate iron compounds with principally σ -donating ligands, where a triplet excited state mixes into the diamagnetic ground state via spinorbit coupling, giving rise to temperature-independent para-magnetism.^{23a,27} The ground states of this class of compounds are also best described as intermediate-spin ferrous derivatives antiferromagnetically coupled to bis(imino)pyridine triplet diradicals. In both ($^{\rm iPr}PDI)FeN_2$ and ($^{\rm iPr}PDI)Fe(DMAP)$, we refer to the bis(imino)pyridine chelate as "redox active" to signify direct participation in the electronic structure and the presence of ligand-centered radicals. This terminology is used

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Figure 1. 4-Substituted bis(imino)pyridines used in this study and associated shorthand designations.

to distinguish this situation, where the metal oxidation state is unambiguously iron(II), from the "redox non-innocent" examples such as $({}^{iPr}PDI)Fe(N_2)_2$ and $({}^{iPr}PDI)Fe(CO)_2$, where a single oxidation state formalism is inadequate.

The equilibrium mixture of the four- and five-coordinate bis(imino)pyridine iron dinitrogen compounds serves as an effective precatalyst for alkene hydrogenation,²⁸⁻³¹ hydrosilvlation, 28,29,32 and [2 + 2] cycloaddition reactions. 33 Since the initial preparation and discovery of the catalytic performance of $({}^{iPr}PDI)Fe(N_2)_n$ (n = 1, 2), our laboratory has been engaged in efforts to improve catalytic activity and substrate scope through systematic modification of the bis(imino)pyridine architecture. Replacement of the imine methyl groups with phenyl substituents yielded an iron dinitrogen compound, $({}^{iPr}BPDI)Fe(N_2)_2$ $({}^{iPr}BPDI = 2,6-(2,6-{}^{i}Pr_2-C_6H_3N=$ CPh)₂C₅H₃N), that exhibited increased initial hydrogenation activity for α -olefins such as 1-hexene, but rapid intramolecular coordination of phenyl or 2,6-diisopropyl aryl groups resulted in catalyst deactivation and shorter lifetimes. Reducing the size of the 2,6-aryl substituents from isopropyl to ethyl or methyl resulted in dimeric iron dinitrogen complexes, [(RPDI)Fe- $(N_2)_2(\mu_2-N_2)$ (^RPDI = 2,6-(2,6-R_2-C_6H_3N=CMe)_2C_5H_3N; R = Me, Et), that exhibited significantly increased activity for the hydrogenation of ethyl 3-methylbut-2-enoate.³⁴ However, replacing the aryl imino substituents with alkyl groups³⁵ or the bis(imino)pyridine with related α -diimines³⁶ is deleterious, as catalytically inactive bis(ligand) iron or arene complexes are formed.

Given the now well-established redox activity of bis(imino)pyridines,²³ in-plane electronic modifications may impact the electronic structure and ultimately the reactivity/catalytic activity of the resulting iron complex. Zhu and Budzelaar have evaluated substituent effects on the σ -donating and π accepting properties of aryl-substituted bis(imino)pyridines and other related tridentate chelates.³⁷ Variations in the 4-positions of the pyridine ring were found to change both the donating and accepting properties of the chelate significantly and have inspired preparation of several new iron dinitrogen compounds. Here we describe our efforts toward this objective with the synthesis, characterization, and systematic evaluation of the electronic effects of 4-substituted bis(imino)pyridine iron dinitrogen complexes.

RESULTS AND DISCUSSION

Synthesis of 4-Substituted Bis(imino)pyridine Com-pounds. The series of 4-substituted bis(imino)pyridine ligands targeted for this study is presented in Figure 1. In each case, the 2,6-diisopropyl aryl imine variant was used such that the steric environment of the resulting iron series remains, to a first approximation, constant. Substituents were also selected that

are likely compatible with the reducing methods used to prepare the corresponding iron dinitrogen complexes. The two alkyl-substituted bis(imino)pyridines, 4-Bn-^{iPr}PDI and 4-^tBu-PDI, were synthesized according to the previously reported methods of Cámpora³⁸ and Burger,³⁹ respectively. The CF₃ and NMe₂ derivatives, 4-CF₃-^{iPr}PDI and 4-

The CF₃ and NMe₂ derivatives, $4\text{-}CF_3\text{-}^{\mu\nu}PDI$ and $4\text{-}Me_2N\text{-}^{iP}PDI$, were prepared as outlined in Scheme 1. Both syntheses began with chlorination of chelidamic acid with SOCl₂. Introduction of the NMe₂ substituent was accomplished by initial hydrolysis to the diacid chloride followed by treatment with aqueous dimethylamine at 160 °C.⁴⁰ With this material in hand, conversion to the 4-NMe₂-substituted diacetylpyridine and ultimately the bis(imino)pyridine proceeded via standard methods.⁴¹

For the CF₃ example, esterification of the trichloro compound with methanol at 45 °C furnished the 4-chloro methyl ester, which was then treated with NaI in the presence of CH₃C(O)Cl in acetonitrile to yield the corresponding iodide.⁴² Introduction of the CF₃ group was accomplished with FSO₂CF₂CO₂CH₃ in the presence of 5 equiv of CuI and 5% (dppf)PdCl₂ at 100 °C, following the procedure of Johnson utilized to prepare 4-substituted pyridine bis(oxazolines).⁴³ As with the NMe₂ derivative, conversion to diacetylpyridine and the bis(imino)pyridine was accomplished using standard methods.⁴¹

Synthesis of the iron dihalide complexes of each of the 4-substituted bis(imino)pyridine ligands was accomplished in a straightforward manner^{2,3} by stirring the free ligand with either $FeCl_2$ or $FeBr_2$ in THF for 12–24 h followed by precipitation with pentane and collection by filtration (eq 1). Each of the



bis(imino)pyridine iron dihalides was isolated as a blue or bluegreen powder in high yield (88–98%) and exhibits an S = 2ground state, as determined by magnetic susceptibility balance measurements. Two examples, (4-Me₂N-^{iPr}PDI)FeCl₂ and (CF₃-^{iPr}PDI)FeCl₂, were characterized by X-ray diffraction, and representations of the solid-state structures are presented Scheme 1. Synthesis of 4-Me₂N-^{iPr}PDI and 4-CF₃-^{iPr}PDI Ligands^{*a*}



^aReagents and conditions: (i) $SOCl_2$; (ii) H_2O , 0–45 °C; (iii) Me_2NH (aq, 35%), 160 °C; (iv) $SOCl_2$, MeOH; (v) NaOEt, EtOAc; HCl; (vi) 2,6-diisopropylaniline, MeOH, H^+ (cat); (vii) MeOH, 45 °C; (viii) NaI, $CH_3C(O)Cl$, CH_3CN ; (ix) $FSO_2CF_2CO_2CH_3$, 5 equiv of CuI, 5% (dppf)PdCl₂·CH₂Cl₂, DMF, 100 °C.

in Figure 2. Selected metrical parameters, along with those for $({}^{iPr}PDI)FeCl_{2}{}^{2b}$ are presented in Table 1.

To probe the electronic effects of each of the 4-substituents, the corresponding series of bis(imino)pyridine iron dicarbonyl complexes was prepared. Sodium amalgam reduction of each of the iron dihalide complexes in toluene solution under 1 atm of carbon monoxide furnished the corresponding bis(imino)-pyridine iron dicarbonyl complexes (eq 2). Each (4-X-^{iPr}PDI)-Fe(CO)₂ compound was isolated as a diamagnetic green or yellow-brown crystalline solid in moderate (63–69%) yield and



was routinely characterized by ¹H and ¹³C NMR spectroscopy, solution infrared spectroscopy, and combustion analysis.

The solid-state structure of one example, $(4-Me_2N^{-i^{p_r}}PDI)$ -Fe(CO)₂, was determined by X-ray diffraction, and a representation of the molecular structure is presented in Figure 3. Selected metrical parameters are reported in Table 2. As with the structure of $(^{i^{p_r}}PDI)$ Fe(CO)₂,²⁸ an idealized squarepyramidal geometry is observed with apical and basal carbonyl ligands. The observation of a C_{2v} -symmetric molecule by benzene- d_6 ¹H and ¹³C NMR spectroscopy at 23 °C indicates rapid exchange between these positions under these conditions. The [NMe₂] group is nearly coplanar with the pyridine ring, with a dihedral angle of 10.3(3)° between the two idealized planes. The bond distances in the bis(imino)pyridine are statistically indistinguishable from those in ($^{i^{p_r}PDI$)Fe(CO)₂ (Table 2) and support back-bonding between the iron center and the terdentate chelate.

Given their rich catalytic and stoichiometric chemistry, the synthesis of the corresponding bis(imino)pyridine iron dinitrogen complexes was also explored. Inspired by the conditions used to prepare $({}^{iPr}PDI)Fe(N_2)_2$,²⁸ each of the bis(imino)pyridine iron dihalide complexes was stirred with an excess of 0.5% sodium amalgam in toluene under a dinitrogen atmosphere. In one case, with $(4-Me_2N-{}^{iPr}PDI)FeCl_2$, an equal volume of THF was added to the mixture to improve solubility and facilitate the reduction. Filtration and recrystallization from pentane or pentane–diethyl ether mixtures at -35 °C furnished green and green-brown solids identified as the desired iron dinitrogen compounds $(4-X-{}^{iPr}PDI)Fe(N_2)_2$, in modest to good yields (39–65%, eq 3).



One exception was $(4-CF_{3}-i^{Pr}PDI)FeCl_2$. Reduction of this compound yielded an intractable mixture of products, mostly comprised of free bis(imino)pyridine ligand. The solid-state (KBr) infrared spectrum of the residue isolated following reduction did not contain any strong bands assignable to N₂ stretches, suggesting that no iron dinitrogen complex was present in the mixture. More careful monitoring of the reduction reaction by analyzing aliquots by ¹H NMR spectroscopy revealed a smooth one-electron reduction to yield a paramagnetic intermediate, $(4-CF_3-i^{Pr}PDI)FeCl.^{44}$



Figure 2. Molecular structures of (4-CF₃-^{iPr}PDI)FeCl₂ (left) and (4-Me₂N-^{iPr}PDI)FeCl₂ (right) with 30% probability ellipsoids. In both cases, only one molecule from the asymmetric unit is shown. Hydrogen atoms are omitted for clarity.

Table 1. Bond Distances (Å) and Angles (deg) for (4-
CF ₃ - ^{iPr} PDI)FeCl ₂ , (4-Me ₂ N- ^{iPr} PDI)FeCl ₂ , and (^{iPr} PDI)FeCl ₂

	$\begin{array}{c} (\text{4-CF}_3\text{-}^{\text{iPr}}\text{PDI})\\ \text{FeCl}_2 \end{array}$	$(4-Me_2N-^{iPr}PDI)$ FeCl ₂	${{}^{(^{iPr}PDI)}_{FeCl_2}}^{a}$
Fe(1) - N(1)	2.177(3)	2.284(3)	2.222(4)
Fe(1) - N(2)	2.058(3)	2.100(2)	2.091(4)
Fe(1) - N(3)	2.184(3)	2.253(3)	2.225(5)
Fe(1)-Cl(1)	2.2535(9)	2.3339(10)	2.2627(17)
Fe(1)-Cl(2)	2.2940(10)	2.2828(9)	2.3173(19)
N(1)-C(2)	1.291(4)	1.286(4)	1.301(7)
N(3) - C(8)	1.285(4)	1.284(4)	1.295(7)
C(2) - C(3)	1.479(4)	1.497(4)	1.466(8)
C(7) - C(8)	1.480(5)	1.497(4)	1.482(8)
N(1)-Fe(1)-N(2)	73.92(10)	71.90(10)	73.67(16)
N(1)-Fe(1)-Cl(1)	96.31(7)	100.22(8)	98.14(12)
N(1)-Fe(1)-Cl(2)	103.81(7)	104.19(8)	100.57(12)
N(2)-Fe(1)-Cl(1)	149.11(8)	96.77(8)	147.90(13)
N(2)-Fe(1)-Cl(2)	93.92(8)	152.67(8)	94.52(13)
N(2)-Fe(1)-N(3)	73.01(10)	72.92(9)	72.59(16)
N(3)-Fe(1)-Cl(1)	101.68(7)	101.28(7)	99.28(12)
N(3)-Fe(1)-Cl(2)	98.22(7)	98.78(7)	102.47(12)
Cl(1)-Fe(1)-Cl(2)	116.95(4)	110.47(4)	117.58(7)
^a Values taken from ref	f 2b.		

However, continued reduction resulted in consumption of this intermediate, and no new iron compounds were identified.

Each of the $(4-X^{-i^{Pr}}PDI)Fe(N_2)_2$ complexes was routinely characterized by ¹H and ¹³C NMR infrared and zero-field Mössbauer spectroscopy. As has been observed previously,²⁸ the five-coordinate iron bis(dinitrogen) complexes were isolated upon recrystallization but reverted to a mixture of $(4-X^{-i^{Pr}}PDI)Fe(N_2)_2$ and $(4-X^{-i^{Pr}}PDI)Fe(N_2)$ compounds in solution. Benzene- d_6 solution infrared spectra of two examples, $(4^{-t}Bu^{-i^{Pr}}PDI)Fe(N_2)_n$ and $(4-Me_2N^{-i^{Pr}}PDI)Fe(N_2)_n$ (n = 1, 2), are presented in the Supporting Information. The ¹H and ¹³C NMR spectra exhibit the appropriate number of resonances for a single $C_{2\nu}$ -symmetric compound, demonstrating rapid interconversion between the four- and five-coordinate compounds in solution on the NMR time scale. The presence of both species can be detected by techniques with shorter



Figure 3. Solid-state structure of $(4-Me_2N-^{Pr}PDI)Fe(CO)_2$ with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

observation time scales such as infrared and Mössbauer spectroscopy (vide infra).

Two of the new bis(imino)pyridine iron bis(dinitrogen) compounds, $(4-Me_2N^{-i^{pr}}PDI)Fe(N_2)_2$ and $(4-^{t}Bu^{-i^{pr}}PDI)Fe(N_2)_2$, were also characterized by single-crystal X-ray diffraction. Representations of the solid-state structures are presented in Figure 4, and selected bond distances and angles are presented in Table 3. For $(4-^{t}Bu-^{i^{pr}}PDI)Fe(N_2)_2$, two independent molecules were located in the asymmetric unit that were statistically indistinguishable. Only the values for one of these molecules are presented in Table 3. Rapid loss of dinitrogen in the solid state made isolation and handling of the crystals of both samples challenging; specifically, how each sample was individually handled produced varying amounts of the four- and five-coordinate compounds.

As is frequently observed in five-coordinate bis(imino)pyridine iron compounds bearing two neutral ligands, nearidealized square-pyramidal geometries are observed with N₂ ligands in the apical and basal positions. For (4-Me₂N-^{iPr}PDI)-Fe(N₂)₂, the [NMe₂] group is essentially coplanar with the pyridine ring, with a dihedral angle between the two idealized planes of approximately 3°. All three crystallographically characterized dinitrogen compounds, (^{iPr}PDI)Fe(N₂)₂, (4-^tBu-^{iPr}PDI)Fe(N₂)₂, and (4-Me₂N-^{iPr}PDI)Fe(N₂)₂, exhibit

	$(4-Me_2N-^{iPr}PDI)Fe(CO)_2$	$(^{iPr}PDI)Fe(CO)_2^a$
Fe(1) - N(1)	1.9540(14)	1.9622(15)
Fe(1) - N(2)	1.8648(14)	1.8488(14)
Fe(1) - N(3)	1.9582(14)	1.9500(14)
Fe(1) - C(36)	1.7806(18)	1.7809(19)
Fe(1) - C(37)	1.7839(18)	1.7823(19)
N(1)-C(2)	1.330(2)	1.330(2)
N(3)-C(8)	1.327(2)	1.335(2)
C(2) $C(2)$	1 427(2)	1 425(2)
C(2) = C(3)	1.42/(2)	1.423(2)
C(7) - C(8)	1.438(2)	1.423(2)
N(1)-Fe(1)-N(2)	78.49(6)	79.10(6)
N(1)-Fe(1)-N(3)	148.83(6)	152.56(6)
N(1)-Fe(1)-C(36)	103.98(7)	101.54(7)
N(1)-Fe(1)-C(37)	97.41(7)	96.36(7)
N(2)-Fe(1)-N(3)	78.55(6)	79.32(6)
N(3)-Fe(1)-C(36)	102.33(7)	100.30(7)
N(3)-Fe(1)-C(37)	97.35(7)	97.27(7)
C(36)-Fe(1)-C(37)	93.56(8)	97.01(9)
^a Data taken from ref 28.		

Table 2. Metrical Parameters for $(4-Me_2N-i^{Pr}PDI)Fe(CO)_2$ and $(i^{Pr}PDI)Fe(CO)_2$

near-identical metrical parameters, suggesting an iron(0)-iron(II) hybrid for all three compounds. Addition of a 4-substituent does not significantly alter the steric environment imparted by the bis(imino)pyridine ligand.

Evaluation of the Electronic Effects of the 4-Substituent. A series of electrochemical and spectroscopic measurements were made on each class of compounds (free ligands and iron dicarbonyl and iron dinitrogen derivatives) to assay the electronic influence of each of the 4-substituents. Electrochemical studies were carried out on the free bis-(imino)pyridines, and representative cyclic voltammograms are presented in Figure 5. The measured reduction potentials (versus ferrocene/ferrocenium and SCE) are reported in Table 4. Also included in Table 4 are ^{iPr}BPDI, a 2,6-diisopropylsubstituted bis(imino)pyridine known to be electron withdrawing relative to ^{iPr}PDI,³¹ and ^{Cy}APDI, a bis(imino)pyridine

1	Table 3. Metrical Parameters for $(4-Me_2N-PPDI)Fe(N_2)_2$,
($(4-{}^{t}Bu-{}^{iPr}PDI)Fe(N_2)_2$, and $({}^{iPr}PDI)Fe(N_2)_2$

		$\begin{array}{c} (\text{4-Me}_2\text{N-}^{\text{iPr}}\text{PDI}) \\ \text{Fe}(\text{N}_2)_2 \end{array}$	$(4-^{t}Bu-^{iPr}PDI)$ Fe $(N_2)_2$	${(^{iPr}PDI) \over Fe(N_2)_2}^a$
	Fe(1)-N(1)	1.9738(14)	1.9444(16)	1.9473(16)
	Fe(1) - N(2)	1.8500(14)	1.8415(16)	1.8362(14)
	Fe(1) - N(3)	1.9134(14)	1.9444(16)	1.9452(16)
	Fe(1) - N(4)	1.8386(16)	1.9013(19)	1.8800(19)
	Fe(1) - N(6)	1.8670(15)	1.8347(18)	1.8341(16)
	N(1)-C(2)	1.332(2)	1.342(2)	1.333(2)
	N(3) - C(8)	1.362(2)	1.334(3)	1.333(2)
	C(2) - C(3)	1.464(3)	1.423(3)	1.427(2)
	C(7) - C(8)	1.419(3)	1.425(3)	1.428(3)
	N(1) - Fe(1) - N(2)	80.42(6)	79.42(7)	79.90(6)
	N(1)-Fe(1)-N(4)	104.73(6)	99.33(7)	98.92(7)
	N(1)-Fe(1)-N(6)	94.17(6)	97.00(7)	97.41(7)
	N(2)-Fe(1)-N(4)	97.49(7)	103.16(7)	
	N(2)-Fe(1)-N(6)	161.58(7)	159.45(8)	159.09(8)
	N(2)-Fe(1)-N(3)	79.31(6)	79.64(7)	79.49(6)
	N(3)-Fe(1)-N(4)	94.78(6)	99.06(7)	99.74(7)
	N(3)-Fe(1)-N(6)	99.71(6)	97.65(7)	96.65(7)
	N(4)-Fe(1)-N(6)	100.91(7)	97.38(8)	98.02(8)
a	Data taken from ref 2	8.		

where the aryl substituents have been replaced by cyclohexyl groups. $^{\rm 35}$

Each bis(imino)pyridine exhibits a reversible reduction wave in THF solution with $[Bu_4N][PF_6]$ as an electrolyte, silver wire as the reference electrode, and glassy carbon as the working electrode. No other reversible oxidation or reduction waves were observed in this solvent window. As expected, 4-CF₃-^{iPr}PDI exhibits the least negative reduction potential (most easily reduced) followed by the phenylated derivative ^{iPr}BPDI. The difference in reduction potentials between these two compounds is 200 mV. Replacing the 4-[CF₃] substituent by hydrogen changes the reduction potential by 270 mV, while introduction of either a [Bn] or [^tBu] group in the 4-position of the ligand results in 330 and 380 mV shifts, respectively, as compared to (4-CF₃-^{iPr}PDI). The most electron donating member of the series, (4-Me₂N-^{iPr}PDI), is as expected the most



Figure 4. Solid-state structures of $(4-{}^{t}Bu-{}^{iPr}PDI)Fe(N_2)_2$ (left) and $(4-Me_2N-{}^{iPr}PDI)Fe(N_2)_2$ (right) with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.



Potential (V) vs Fc/Fc⁺

Figure 5. Cathodic CV scans of 4-substituted bis(imino)pyridine ligands: 4-CF₃-^{iPr}PDI (red), ^{iPr}PDI (orange), 4-Bn-^{iPr}PDI (green), 4-^tBu-^{iPr}PDI (blue), and 4-Me₂N-^{iPr}PDI (purple).

Table 4. Reduction Potentials of Various Bis(imino)pyridines

ligand	redn potential (V vs Fc/Fc ⁺)	redn potential (V vs SCE) ^{a}
4-CF3- ^{iPr} PDI	-2.35	-1.79
^{iPr} BPDI	-2.55	-1.99
^{iPr} PDI	-2.62	-2.06
4-Bn- ^{iPr} PDI	-2.72	-2.16
4- ^t Bu- ^{iPr} PDI	-2.76	-2.20
4-Me ₂ N- ^{iPr} PDI	-2.82	-2.26
$^{Cy}PDI^{b}$	-2.83	-2.27
-	. /0	

^aFormal potential for the ferrocene^{+/0} couple vs SCE with $[Bu_4N]$ - $[PF_6]$ taken from ref 45. ^bData taken from ref 46.

challenging to reduce, with a reduction potential 200 mV more negative than that of ^{iPr}PDI. It is noteworthy that the reduction potential of the series of bis(imino)pyridine ligands can be tuned by 470 mV by simply altering the substituents from $[CF_3]$ to $[NMe_2]$ in the 4-position of the pyridine ring, highlighting the modular electronic nature of this chelate class.

Electrochemical studies were also carried out on the series of 4-substituted bis(imino)pyridine iron dicarbonyl complexes, (4- $X^{-iPr}PDI)Fe(CO)_2$, using the same conditions as for the free ligands. Representative cyclic voltammagrams are presented in Figure 6, and the oxidation and reduction potentials for each compound are reported in Table 5. As was reported previously for $({}^{iPr}PDI)Fe(CO)_{\mathcal{V}}^{24}$ each of the 4-substituted bis(imino)pyridine iron dicarbonyl complexes exhibits clean and reversible one-electron oxidation and reduction waves. On the basis of chemical oxidation and reduction and isolation of the corresponding cations and anions, respectively, the electronic structures of these species have been elucidated. The oxidation event is principally ligand-based to form an iron(I) compound with a neutral bis(imino)pyridine chelate, $[(^{iPr}PDI^{0}) Fe^{I}(CO)_{2}^{+}$. In contrast, the reduction event is primarily metal-based and also yielded an iron(I) compound, but with a dianionic chelate, [(^{iPr}PDI²⁻)Fe^I(CO)₂]^{-.24} Computational studies established that these formalisms are slight oversimplifications, as contributions from covalency complicate oxidation state assignment and suggest redox non-innocence.

For the series of 4-substituted compounds $(4-X-^{iPr}PDI)Fe-(CO)_2$ (Figure 6, Table 5), the reduction potentials follow the same overall trend as the free bis(imino)pyridines. The [CF₃]-



Figure 6. CV scans of 4-substituted bis(imino)pyridine iron dicarbonyl complexes: $(4\text{-}CF_3-^{iPr}\text{PDI})\text{Fe}(\text{CO})_2$ (red), $(^{iPr}\text{PDI})\text{Fe}(\text{CO})_2$ (orange), $(4\text{-}Bn-^{iPr}\text{PDI})\text{Fe}(\text{CO})_2$ (green), $(4\text{-}^tBu-^{iPr}\text{PDI})\text{Fe}(\text{CO})_2$ (blue), and $(4\text{-}Me_2\text{N}-^{iPr}\text{PDI})\text{Fe}(\text{CO})_2$ (purple). The scans were initiated anodically.

Table 5. Cyclic Voltammetry Data for $(4-X-^{iPr}PDI)Fe(CO)_2$ Complexes

compd	oxidn (V vs Fc/Fc ⁺)	redn (V vs Fc/Fc ⁺)	oxidn (V vs SCE) ^a	redn (V vs SCE) ^a
$\begin{array}{c} (4\text{-}CF_3\text{-}^{iPr}\text{PDI})\\ Fe(CO)_2 \end{array}$	-0.27	-2.27	0.29	-1.71
(^{iPr} PDI) Fe(CO) ₂ ^b	-0.49	-2.46	0.07	-1.90
$(4-Bn-^{iPr}PDI)$ Fe(CO) ₂	-0.53	-2.47	0.03	-1.91
$(4-^{t}Bu-^{iPr}PDI)$ Fe(CO) ₂	-0.56	-2.53	0.00	-1.97
$(4-Me_2N-^{iPr}PDI)$ Fe(CO) ₂	-0.86	-2.53	-0.30	-1.97

^{*a*}Formal potential for the ferrocene^{+/0} couple vs SCE with $[Bu_4N]$ - $[PF_6]$ taken from ref 45. ^{*b*}Data taken from ref 24.

substituted compound has the least negative reduction potential, followed by the parent compound, (^{iPr}PDI)Fe(CO)₂. The difference of 190 mV is smaller than the 270 mV difference measured for free ligands. A similar trend is observed in oxidation potentials where the parent compound, (^{iPr}PDI)Fe(CO)₂, is more readily oxidized than (4-CF₃-^{iPr}PDI)Fe(CO)₂ by 220 mV. The oxidations of the alkyl-substituted compounds, (4-Bn-^{iPr}PDI)Fe(CO)₂ and (4-^tBu-^{iPr}PDI)Fe(CO)₂, are essentially indistinguishable, while the reduction events differ slightly. The most electron rich member of the series, (4-Me₂N-^{iPr}PDI)Fe(CO)₂, is more readily oxidized by 370 mV than the parent compound, while the reduction potential differs by only 7 mV and is much less sensitive than the free ligand. A plot of the potential of the (4-X-^{iPr}PDI)Fe(CO)₂^{+/0} redox event versus σ_p^{47} gives a linear relationship (Figure 7). The carbonyl stretching frequencies of each of the (4-

The carbonyl stretching frequencies of each of the (4- $X^{-i^{pr}PDI}$)Fe(CO)₂ compounds were measured in pentane solution by infrared spectroscopy, and the values are reported in Table 6. The carbonyl stretching frequencies are sensitive to the identity of the 4-substituent, with the most electron poor member of the series, (4-CF₃-^{i^{pr}PDI})Fe(CO)₂, exhibiting the highest stretching frequencies while the most electron rich member, (4-Me₂N-^{i^{pr}PDI})Fe(CO)₂, has the lowest values. There is little difference in the stretching frequencies of the parent compound (^{i^{pr}PDI})Fe(CO)₂ and the alkyl-substituted



Figure 7. Plot of the (4-X-^{iPr}PDI)Fe(CO)₂^{+/0} redox couple vs σ_p value (y = 0.432x - 0.496; $R^2 = 0.999$).

Table 6. Carbonyl Stretching Frequencies of (4-X-^{iPr}PDI)Fe(CO)₂ Measured by Infrared Spectroscopy

complex	$\nu(C\equiv O) \ (cm^{-1})$
$(4-CF_3-^{iPr}PDI)Fe(CO)_2$	1925, 1983
(^{iPr} BPDI)Fe(CO) ₂	1921, 1979 ^{<i>a</i>}
$(^{iPr}PDI)Fe(CO)_2$	1914, 1974 ^{<i>a</i>}
$(4-Bn-^{iPr}PDI)Fe(CO)_2$	1913, 1972
$(4-^{t}Bu-^{iPr}PDI)Fe(CO)_{2}$	1911, 1971
$(4-Me_2N-i^{Pr}PDI)Fe(CO)_2$	1906, 1965

^aData from ref 31; all values recorded in pentane solution.

derivatives $(4-Bn-^{iPr}PDI)Fe(CO)_2$ and $(4-^tBu-^{iPr}PDI)Fe(CO)_2$, similar to the results of the electrochemical measurements.

To probe whether introduction of the 4-substituents induced a gross change in electronic structure, zero-field ⁵⁷Fe Mössbauer spectra were collected on each (4-X-^{iPr}PDI)Fe-(CO)₂ compound in the solid state at 80 K. The Mössbauer parameters, δ and ΔE_{Q2} are reported in Table 7. In each case,

Table 7. Zero-Field 57 Fe Mössbauer Parameters for (4-X- iPr PDI)Fe(CO)₂

compd	$\delta~({ m mm/s})$	$\Delta E_{\rm Q} ({\rm mm/s})$
$(4-CF_3-^{iPr}PDI)Fe(CO)_2$	0.02	1.14
(^{iPr} PDI)Fe(CO) ₂ ^{<i>a</i>}	0.03	1.17
$(4-Bn-^{iPr}PDI)Fe(CO)_2$	0.02	1.09
$(4-^{t}Bu-^{iPr}PDI)Fe(CO)_{2}$	0.03	1.08
$(4-Me_2N-^{iPr}PDI)Fe(CO)_2$	0.04	1.23
^{<i>a</i>} Data from ref 23a.		

both parameters for each $(4-X-{}^{iPr}PDI)Fe(CO)_2$ compound are essentially invariant and indicate no change in the gross electronic structure of the molecules as a function of the 4substituent.

Similar spectroscopic measurements were carried out on the bis(imino)pyridine iron dinitrogen complexes. The N_2 stretching frequencies of the four- and five-coordinate iron dinitrogen compounds as determined by pentane solution infrared spectroscopy are reported in Table 8. Within the series of four-coordinate iron dinitrogen compounds, the alkyl-substituted derivatives exhibit slightly more reduced N_2 stretching frequencies as compared to those of the parent compound, signaling a modestly more electron rich iron center.

Table 8. Dinitrogen Stretching Frequencies for $(4-X^{-i^{pr}}PDI)Fe(N_2)_n$ (n = 1, 2) Compounds Recorded in Pentane Solution

	$\nu(N\equiv N) \ (cm^{-1})$	
complex	n = 1	<i>n</i> = 2
$(^{iPr}PDI)Fe(N_2)_n^a$	2046	2132, 2073
$(4-Bn-^{iPr}PDI)Fe(N_2)_n$	2044	2129, 2071
$(4-^{t}Bu-^{iPr}PDI)Fe(N_2)_n$	2041	2128, 2067
$(4-Me_2N-^{iPr}PDI)Fe(N_2)_n$	2034	2117, 2055 ^b
^a Data from ref 28. ^b Values were recorded in toluene at -30 °C.		

Introduction of a $[Me_2N]$ substituent reduces the N_2 stretching frequency by 12 cm⁻¹ from (^{iPr}PDI)Fe(N_2)₂, also consistent with a more electron rich metal center. Similar effects are observed within the series of five-coordinate bis(dinitrogen) compounds, with the 4-alkyl-substituted compounds exhibiting a slightly more electron rich iron center than the parent compound and the $[NMe_2]$ derivative being the most significant.

Analogous to the carbonyl derivatives, the Mössbauer parameters within the series of $(4-X-{}^{iPr}PDI)Fe(N_2)$ and $(4-X-{}^{iPr}PDI)Fe(N_2)_2$ compounds, respectively, are essentially indistinguishable and suggest a similar electronic structure for each class of molecule (Table 9). Representative spectra are

Table 9. Zero-Field ⁵⁷ Fe Mössbauer Parameters for (4-
$X^{iPr}PDI$)Fe $(N_2)_n$ Compounds Recorded at 80 K	

compd	$\delta~({ m mm/s})$	$\Delta E_{\rm Q} ({\rm mm/s})$
$(^{iPr}PDI)Fe(N_2)_2^a$	0.39	0.53
$(^{iPr}PDI)Fe(N_2)^a$	0.38	1.72
$(4-Bn^{-iPr}PDI)Fe(N_2)_2$	0.39	0.51
$(4-Bn^{-iPr}PDI)Fe(N_2)$	0.36	1.81
$(4-^{t}Bu-^{iPr}PDI)Fe(N_2)_2$	0.37	0.51
$(4-^{t}Bu-^{iPr}PDI)Fe(N_2)$	0.36	1.74
$(4-Me_2N-^{iPr}PDI)Fe(N_2)_2$	0.37	0.44
$(4-Me_2N-^{iPr}PDI)Fe(N_2)$	0.35	1.79
Data from ref 27.		

presented in Figure 8, and each exhibits a mixture of four- and five-coordinate compounds, the ratio of which was largely determined by how the sample was manipulated. The isomer shifts are consistent with iron(II) compounds in all cases. As has been observed previously,²⁷ the four-coordinate compounds exhibit a larger quadrupole splitting than the corresponding five-coordinate derivatives, likely due to a change in electric field gradient in the two coordination geometries.

CONCLUDING REMARKS

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A family of 4-substituted bis(imino)pyridine ligands and their corresponding iron dihalide, dicarbonyl, and dinitrogen complexes have been synthesized. The influence of the 4substituent on the electronic properties of the free ligand and the resulting iron compounds has been evaluated using electrochemical, vibrational, and Mössbauer spectroscopy. While the introduction of electron-withdrawing or electrondonating substituents does not influence the redox activity of the bis(imino)pyridine ligand and hence the overall electronic structure of the corresponding iron compounds, the remote substituents have a measurable influence on the electronic properties of the metal. Electrochemical measurements on the



Figure 8. Zero-field ⁵⁷Fe Mössbauer spectra of $(4 - X^{-i^{pr}}PDI)Fe(N_2)_n$ (n = 1, 2): $(4 - Bn^{-i^{pr}}PDI)Fe(N_2)_n$ (left), $(4 - Bu^{-i^{pr}}PDI)Fe(N_2)_n$ (middle), and $(4 - Me_2N^{-i^{pr}}PDI)Fe(N_2)_n$ (right).

free bis(imino)pyridines appear to be the most sensitive to 4subsitution. The influence of these effects on the catalytic performance of these compounds will be reported in due course.

EXPERIMENTAL SECTION

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 drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were initially dried and deoxygenated using literature procedures.⁴⁸ Benzene- d_6 was purchased from Cambridge Isotope Laboratories and dried over 4 Å molecular sieves. The following compounds were prepared according to literature procedures: $4-Bn-^{iPr}PDI,^{38} 4-{}^{t}Bu-^{iPr}PDI,^{39}$ dimethyl 4-(trifluoromethyl)pyridine-2,6-dicarboxylate, and dimethyl 4-(dimethylamino)pyridine-2,6-dicarboxylate.⁴⁰

¹H NMR spectra were recorded on Varian Mercury 300 and Inova 400, 500, and 600 spectrometers operating at 299.76, 399.78, 500.62, and 599.78 MHz, respectively. ¹³C NMR spectra were recorded on an Inova 500 spectrometer operating at 125.893 MHz. All ¹H and ¹³C NMR chemical shifts are reported relative to SiMe₄ using the ¹H (residual) and ¹³C chemical shifts of the solvent as a secondary standard. For diamagnetic complexes, many assignments were made on the basis of COSY and HSQC NMR experiments. Solution magnetic moments were determined by the Evans method⁴⁹ 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 $HgCo(SCN)_4$. All solid-state values were recorded at 21 °C unless otherwise noted. Peak widths at half-heights are reported for paramagnetically broadened and shifted resonances. Infrared spectra were collected on a Thermo Nicolet spectrometer. Highresolution mass spectra were collected on an Agilent 6220 Accurate-Mass Time-of-Flight LC/MS. The mass spectrometer was calibrated externally before each use with purine and the Agilent ES-TOF tuning mix (part number G1969-85000). These compounds were assigned $(M + H)^+ m/z$ ratios of 121.050 873 and 922.009 798, respectively. Elemental analyses were performed by Robertson Microlit Laboratories, Inc., in Ledgewood, NJ.

Cyclic voltammograms (CVs) were collected in THF solution (1 mM in compound) with $[^nBu_4N][PF_6]$ (0.1 M), using a 3 mm glassycarbon working electrode, platinum wire as the counter electrode, and silver wire as the reference in a drybox equipped with electrochemical outlets. CVs were recorded using a BASi EC Epsilon electrochemical workstation and analyzed using the BASi Epsilon-EC software. All CVs were run at a scan rate of 100 mV/s at 295 K. Potentials are reported versus ferrocene/ferrocenium and were obtained using the in situ method.⁵⁰

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. Data for $(4-Me_2N^{-iPr}PDI)$ -Fe $(N_2)_2$ were collected using a Bruker X8 APEX2 diffractometer

equipped with a molybdenum X-ray tube ($\lambda = 0.71073$ Å). 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. A Bruker APEX2 Duo diffractometer equipped with molybdenum and copper X-ray tubes ($\lambda = 0.71073$ and 1.54178 Å, respectively) was used to collect data for (4-CF₃-^{iPr}PDI)FeCl₂ (Cu source), (4-Me₂N-^{iPr}PDI)FeCl₂ (Cu source), (4-⁴Bu-^{iPr}PDI)Fe(N₂)₂ (Cu source), and (4-Me₂N-^{iPr}PDI)Fe(CO)₂ (Cu source). The space groups were identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SIR92) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

⁵⁷Fe Mössbauer spectra were recorded on a SEE Co. Mössbauer spectrometer (MS4) at 80 K in constant-acceleration mode. ⁵⁷Co/Rh was used as the radiation source. WMOSS software was used for the quantitative evaluation of the spectral parameters (least-squares fitting to Lorentzian peaks). The temperature of the samples was controlled by a Janis Research Co. CCS-850 He/N₂ cryostat within an accuracy of ±1 K. Isomer shifts were determined relative to α-iron at 298 K.

Preparation of 4-Dimethylamino-2,6-diacetylpyridine. A 250 mL round-bottom flask was charged with dimethyl 4-(dimethylamino)pyridine-2,6-dicarboxylate (5.00 g, 21.0 mmol) and sodium ethoxide (6.14 g, 90.2 mmol, 4.3 equiv). To this mixture was added 50 mL of ethyl acetate with rapid stirring. After 1 h, the reaction mixture was brought to reflux, and an additional 75 mL of ethyl acetate was added once the reaction mixture thickened. After 6 h, the mixture was cooled to room temperature and 20 mL of concentrated HCl was added dropwise. Refluxing was resumed for an additional 12 h, after which the reaction was cooled to room temperature and water was added until the salt was dissolved. The resulting mixture was neutralized with sodium bicarbonate and extracted three times with dichloromethane. The organic extracts were dried with magnesium sulfate, filtered, and concentrated in vacuo to give 3.67 g (84% yield) of a light brown solid identified as 4-dimethylamino-2,6-diacetylpyridine. HR-MS (+ESI): calcd for $C_{11}H_{15}N_2O_2$, $[M + H]^+$, m/z 207.112 80; found, *m*/*z* 207.112 84. ¹H NMR (chloroform-*d*, 22 °C): δ 2.78 (s, 6H, CCH₃), 3.17 (s, 6H, N(CH₃)₂), 7.46 (s, 2H, *m*-pyr). ¹³C NMR (chloroform-d, 22 °C): $\delta = 25.9 (C(O)CH_3)$, 39.6 (N(CH₃)₂), 106.8 (*m*-pyr), 153.4 (*o*-pyr), 155.6 (*p*-pyr), 201.2 (*C*(O)CH₃). **Preparation of 4-Me₂N-^{iPr}PDI.** A 100 mL round-bottom flask was

Preparation of 4-Me₂N-^{IP}PDI. A 100 mL round-bottom flask was charged with 2.0 g (9.7 mmol) of 4-dimethylamino-2,6-diacetylpyridine, 4.3 g (24 mmol) of 2,6-diisopropylaniline, 2 drops of formic acid, and 25 mL of methanol. The reaction mixture was brought to reflux and stirred for 72 h. After this time, the reaction mixture was cooled to room temperature and then placed in an ice bath. Filtration of the resulting solid gave 3.2 g (63% yield) of a pale yellow solid identified as 4-Me₂N-^{IP}PDI. HR-MS (+ESI): calcd for C₃₅H₄₉N₄, [M + H]⁺, *m/z* 525.395 17; found, *m/z* 525.395 21. ¹H NMR (benzene-*d₆*, 22 °C): δ 1.19 (d, 7 Hz, 12H, CH(CH₃)₂), 1.25 (d, 7 Hz, 12H, CH(CH₃)₂), 2.38 (s, 6H, N(CH₃)₂ or CCH₃), 2.43 (s, 6H, N(CH₃)₂), or CCH₃), 3.05 (spt, 4H, CH(CH₃)₂), 7.16–7.23 (m, 6H, *m-*, *p*-aryl),

8.04 (s, 2H, *m*-pyr). ¹³C NMR (benzene- $d_{6^{j}}$ 22 °C): δ 17.7 (C(N) CH₃), 23.1 (CH(CH₃)₂), 23.5 (CH(CH₃)₂), 28.8 (CH(CH₃)₂), 38.6 (N(CH₃)₂), 105.3 (*m*-pyr), 123.6 (aryl), 124.1 (aryl), 136.1 (aryl), 147.4 (aryl), 155.6 (*o*-pyr), 156.1 (*p*-pyr), 168.1 (C(N)CH₃).

Preparation of 4-CF₃-^{iPr}PDI. 4-Trifluoromethyl-2,6-diacetylpyridine was first prepared in a manner similar to that for 4dimethylamino-2,6-diacetylpyridine with 1.76 g (6.65 mmol) of dimethyl 4-(trifluoromethyl)pyridine-2,6-dicarboxylate, 1.96 g (36.3 mmol) of sodium ethoxide, and 15 mL of ethyl acetate. An additional 50 mL of ethyl acetate was added during the course of the reaction. The crude, golden oil (1.50 g) isolated from the reaction, identified as 4-trifluoromethyl-2,6-diacetylpyridine, was used without purification for the synthesis of 4-CF₃-^{iPr}PDI. ¹H NMR (chloroform-d, 22 °C): δ 2.82 (s, 6H, CCH₃), 8.43 (s, 2H, *m*-pyr). ¹⁹F NMR (benzene-*d*₆, 22 °C): δ –63.5. 4-CF₃-^{iPr}PDI was prepared in a manner similar to that for 4-Me2N-iPrPDI with 1.00 g (4.32 mmol) of 4-trifluoromethyl-2,6diacetylpyridine, 2.30 g (12.9 mmol) of 2,6-diisopropylaniline, and two drops of formic acid in 15 mL of methanol. Following filtration, 0.78 g (33% yield) of 4-CF₃-^{iPr}PDI was isolated as a light yellow solid. HR-MS (+ESI): calcd for $C_{10}H_9F_3NO_2$, $[M + H]^+$, m/z 550.340 36; found, m/z 550.340 72. ¹H NMR (benzene- d_6 , 22 °C): δ 1.11 (d, 4 Hz, 12H, CH(CH₃)₂), 1.13 (d, 4 Hz, 12H, CH(CH₃)₂), 2.18 (s, 6H, CCH₃), 2.82 (m, 4H, CH(CH₃)₂), 7.12-7.18 (m, 6H, m-, p-aryl), 8.88 (s, 2H, *m*-pyr). ¹³C{¹H} NMR (benzene-*d*₆, 22 °C): δ 17.2 (C(N)CH₃), 23.0 (CH(CH₃)₂), 23.4 (CH(CH₃)₂), 28.9 (CH(CH₃)₂), 118.0 (3 Hz, mpyr), 123.1 (aryl), 123.5 (273 Hz, CF₃), 123.6 (aryl), 135.8 (aryl), 140.1 (q, 34 Hz, p-pyr), 146.4 (aryl), 157.1 (o-pyr), 166.1 $(C(N)CH_3)$. ¹⁹F{¹H} NMR (benzene- d_6 , 22 °C): δ -63.3.

Preparation of (4-Me₂N-^{iPr}PDI)FeCl₂. A 20 mL scintillation vial was charged with 0.083 g (0.65 mmol) of FeCl₂ and 2 mL of THF. A solution of 0.36 g (0.68 mmol) of 4-Me₂N-^{iPr}PDI in 5 mL of THF was then added to the slurry with rapid stirring, causing an immediate color change to dark blue-green. After 12 h, 10 mL of pentane was added, causing the product to precipitate from solution. Filtration from THF/pentane and washing with diethyl ether gave 0.42 g (98% yield) of analytically pure blue-green solid identified as (4-Me₂N-^{iPr}PDI)FeCl₂. Anal. Calcd for C₃₅H₄₈N₄FeCl₂: C, 64.52; H, 7.43; N, 8.60. Found: C, 64.58; H, 7.69; N, 8.34. Solid-state magnetic susceptibility: $\mu_{eff} = 4.5 \mu_{B}$. ¹H NMR (dichloromethane- d_2 , 22 °C): δ –22.4 (200 Hz, 4H, CH(CH₃)₂), -7.6 (22 Hz, 2H, *p*-aryl), -4.7 (42 Hz, 6H, CCH₃), -4.6 (66 Hz, 12H, CH(CH₃)₂), -3.7 (21 Hz, 12H, CH(CH₃)₂), 15.2 (21 Hz, 4H, *m*-aryl), 27.8 (22 Hz, 6H, N(CH₃)₂), 91.9 (45 Hz, 2H, *m*-pyr).

Preparation of (4-^tBu-^{iPr}PDI)FeBr₂. The compound was prepared in a manner similar to that for (4-Me₂N-^{iPr}PDI)FeCl₂ with 1.50 g (2.79 mmol) of 4-^tBu-^{iPr}PDI and 0.57 g (2.6 mmol) of FeBr₂. Filtration from THF/pentane and washing with diethyl ether gave 1.93 g (97% yield) of analytically pure, dark blue solid identified as (4-^tBu-^{iPr}PDI)FeBr₂. Anal. Calcd for C₃₇H₅₁N₃FeBr₂: C, 58.98; H, 6.82; N, 5.58. Found: C, 59.11; H, 6.71; N, 5.29. Magnetic susceptibility (magnetic susceptibility balance): $\mu_{\text{eff}} = 4.5 \ \mu_{\text{B}}$. ¹H NMR (dichloromethane- d_2 , 22 °C): δ –23.7 (30 Hz, 6H, CCH₃), -14.2 (290 Hz, 4H, CH(CH₃)₂), -10.6 (18 Hz, 2H, *p*-aryl), -5.2 (15 Hz, 12H, CH(CH₃)₂), -1.9 (66 Hz, 12H, CH(CH₃)₂), 4.8 (7 Hz, 9H, C(CH₃)₃), 14.8 (16 Hz, 4H, *m*-aryl), 78.0 (44 Hz, 2H, *m*-pyr).

Preparation of (4-Bn-^{iPr}PDI)FeCl₂. The compound was prepared in a manner similar to that for (4-Me₂N-^{iPr}PDI)FeCl₂ with 0.40 g (0.70 mmol) of 4-Bn-^{iPr}PDI and 0.084 g (0.66 mmol) of FeCl₂. Filtration from THF/pentane and washing with diethyl ether gave 0.41 g (88% yield) of analytically pure, blue solid identified as (4-Bn-^{iPr}PDI)FeCl₂. Anal. Calcd for C₄₀H₄₉N₃FeCl₂: C, 68.77; H, 7.07; N, 6.02. Found: C, 68.75; H, 6.71; N, 5.82. Magnetic susceptibility (magnetic susceptibility balance): $\mu_{eff} = 4.6 \ \mu_{B}$ -¹H NMR (dichloromethane- d_2 , 22 °C): δ –35.1 (19 Hz, 2H, p-Bn), –32.8 (39 Hz, 6H, CCH₃), –25.2 (279 Hz, 4H, CH(CH₃)₂), –10.6 (21 Hz, 2H, p-aryl), –6.8 (19 Hz, 12H, CH(CH)₃), –5.6 (70 Hz, 12H, CH(CH₃)₂), 9.3 (20 Hz, 1H, p-Bn), 9.7 (23 Hz, 2H, p-Bn), 13.2 (20 Hz, 2H, p-Bn), 14.4 (23 Hz, 4H, m-aryl), 83.5 (49 Hz, 2H, m-pyr).

14.4 (23 Hz, 4H, *m*-aryl), 83.5 (49 Hz, 2H, *m*-pyr). **Preparation of (4-CF₃-^{iPr}PDI)FeCl₂.** The compound was prepared in a manner similar to that for (4-Me₂N-^{iPr}PDI)FeX₂ with 0.40 g (0.73) mmol) of 4-CF₃-^{iP}PDI and 0.090 g (0.71 mmol) of FeCl₂. Filtration from THF/pentane and washing with diethyl ether gave 0.47 g (98% yield) of analytically pure blue-green solid identified as (4-CF₃-^{iP}PDI)-FeCl₂. Anal. Calcd for C₃₄H₄₂F₃N₃FeCl₂: *C*, 60.37; H, 6.26; N, 6.21. Found: C, 60.32; H, 6.54; N, 5.92. Solid-state magnetic susceptibility: $\mu_{\text{eff}} = 4.5 \ \mu_{\text{B}}$. ¹H NMR (benzene- d_6 , 22 °C): δ -75.1 (120 Hz, 6H, CCH₃), -13.5 (26 Hz, 2H, *p*-aryl), -3.6 (191 Hz, 12H, CH(CH₃)₂), -3.3 (75 Hz, 16H, CH(CH₃)₂ and *m*-aryl), 16.2 (44 Hz, 4H, CH(CH₃)₂), 67.9 (98 Hz, 2H, *m*-pyr).

Preparation of (4-Me₂N-^{iPr}PDI)Fe(CO)₂. A thick-walled vessel was charged with 8.8 g of mercury, approximately 10 mL of toluene, and a stir bar. Sodium (0.044 g, 1.9 mmol) was cut into small pieces and added slowly to the rapidly stirred slurry. The resulting amalgam was stirred for an additional 30 min to ensure complete dissolution. A slurry of (4-Me₂N-^{iPr}PDI)FeCl₂ (0.25 g, 0.38 mmol) in 10 mL of toluene was added to the reaction vessel, which was then sealed. The resulting mixture was brought to -196 °C, and the vessel was evacuated. One atmosphere of CO was introduced, and the reaction mixture was stirred for 24 h. The resulting green-yellow mixture was then decanted away from the amalgam and filtered through a pad of Celite. The solvent was removed in vacuo and the residue recrystallized from pentane/ether at -35 °C to give 0.16 g (65% yield) of an olive green solid identified as (4-Me₂N-^{iPr}PDI)Fe(CO)₂. Dissolving the compound in benzene gave a dark yellow-brown solution. Anal. Calcd for C37H48N4O2Fe: C, 69.80; H, 7.60; N, 8.80. Found: C, 69.46; H, 7.57; N, 8.66. ¹H NMR (benzene- d_{6} , 22 °C): δ 1.04 (d, 7 Hz, 12H, CH(CH₃)₂), 1.47 (d, 7 Hz, 12H, CH(CH₃)₂), 2.10 (s, 6H, CCH₃ or N(CH₃)₂), 2.65 (s, 6H, CCH₃ or N(CH₃)₂), 2.98 (spt, 7 Hz, 4H, CH(CH₃)₂), 7.16-7.17 (m, 6H, m-, p-aryl), 7.33 (s, 2H, *m*-pyr). ¹³C{¹H} NMR (benzene- d_6 , 22 °C): δ 16.5 (C(N) CH₃), 24.8 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 27.9 (CH(CH₃)₂), 40.6 (N(CH₃)₂), 106.6, 123.9, 126.6, 140.47, 146.9, 150.5, 153.3, 184.3 (aryl, pyr, imine), 215.2 (CO). IR (pentane): ν_{CO} 1905, 1965 cm⁻¹.

Preparation of (4-ⁱBu-^{iPr}PDI)Fe(CO)₂. The compound was prepared in a manner similar to that for (4-Me₂N-^{iPr}PDI)Fe(CO)₂ with 0.25 g (0.32 mmol) of (4-ⁱBu-^{iPr}PDI)FeBr₂, 10.9 g of mercury, and 0.053 g (2.3 mmol) of sodium. Recrystallization from pentane/ ether at -35 °C gave 0.15 g (69% yield) of a yellow-brown solid identified as (4-ⁱBu-^{iPr}PDI)Fe(CO)₂. Anal. Calcd for C₃₉H₅₃FeN₃O₂: C, 71.88; H, 8.20; N, 6.45. Found: C, 72.03; H, 7.96; N, 6.55. ¹H NMR (benzene-*d*₆, 22 °C): δ 0.97 (d, 7 Hz, 12H, CH(CH₃)₂), 1.37 (s, 9H, C(Me)₃), 1.41 (d, 7 Hz, 12H, CH(CH₃)₂), 2.19 (s, 6H, CMe), 2.84 (spt, 7 Hz, 4 Hz, CH(CH₃)₂), 7.10-7.18 (m, *p*, *m*-aryl), 8.04 (s, *m*-pyr, 2H). ¹³C{¹H} NMR (benzene-*d*₆, 22 °C): δ 16.4 (C(N)CH₃), 24.8 (CH(CH₃)₂), 25.2 (CH(CH₃)₂), 27.9 (CH(CH₃)₂), 31.5 (C(CH₃)₃), 35.1 (C(CH₃)₃), 118.5, 123.9, 126.8, 140.5, 142.0, 145.9, 150.1, 155.4 (aryl, pyr, imine), 214.8 (CO). IR (pentane): ν_{CO} 1911, 1971 cm⁻¹.

Preparation of (4-Bn-^{iPr}PDI)Fe(CO)₂. The compound was prepared in a manner similar to that for (4-Me₂N-^{iPr}PDI)Fe(CO)₂ with 0.15 g (0.21 mmol) of (4-Bn-^{iPr}PDI)FeCl₂, 7.0 g of mercury and 0.035 g (1.5 mmol) of sodium. Recrystallization from pentane/ether at -35 °C gave 0.10 g (68% yield) of a yellow-brown solid identified as (4-Bn-^{iPr}PDI)Fe(CO)₂. Anal. Calcd for C₄₂H₄₉N₃O₂Fe: C, 73.78; H, 7.22; N, 6.15. Found: C, 73.68; H, 7.48; N, 6.05. ¹H NMR (benzene-d₆, 22 °C): δ 0.99 (d, 7 Hz, 12H, CH(CH₃)₂), 1.45 (d, 7 Hz, 12H, CH(CH₃)₂), 2.08 (s, 6H, CCH₃), 2.85 (spt, 4H, CH(CH₃)₂), 4.06 (s, 2H, CH₂Ph), 7.10–7.28 (m, 11H, CH₂Ph, m-, p-aryl), 7.76 (s, 2H, m-pyr). ¹³C{¹H} NMR (benzene-d₆, 22 °C): δ 16.4 (C(N)CH₃), 24.8 (CH(CH₃)₂), 25.2 (CH(CH₃)₂), 27.9 (CH(CH₃)₂), 42.4 (CH₂(C₆H₅)), 122.0, 123.9, 126.8, 128.1, 129.1, 129.5, 131.7, 140.4, 140.6, 150.0, 155.5, 198.0 (aryl, phenyl, pyr, imine), 228.1 (CO). IR (pentane): ν_{CO} 1913, 1972 cm⁻¹.

Preparation of (4-CF₃-^{iPr}PDI)Fe(CO)₂. The compound was prepared in a manner similar to that for $(4-Me_2N-^{iPr}PDI)Fe(CO)_2$ with 0.11 g (0.20 mmol) of $(4-CF_3-^{iPr}PDI)FeCl_2$, 3.67 g of mercury, and 0.018 g (0.78 mmol) of sodium. Recrystallization from pentane/ ether at -35 °C gave 0.083 g (63% yield) of a yellow-brown solid identified as $(4-CF_3-^{iPr}PDI)Fe(CO)_2$. Anal. Calcd for $C_{36}H_{42}F_3N_3O_2Fe: C, 65.36; H, 6.40; N, 6.35. Found: C, 65.09; H,$

6.58; N, 6.30. ¹H NMR (benzene- d_6 , 22 °C): δ 0.91 (d, 7 Hz, 12H, CH(CH₃)₂), 1.36 (d, 7 Hz, 12H, CH(CH₃)₂), 1.87 (s, 6H, CCH₃), 2.61 (spt, 4H, CH(CH₃)₂), 7.06–7.20 (m, 6H, *m*-, *p*-aryl), 8.02 (s, 2H, *m*-pyr). ¹³C NMR (benzene- d_6 , 22 °C): δ 16.2 (C(N)CH₃), 24.8 (CH(CH₃)₂), 25.0 (CH(CH₃)₂), 27.9 (CH(CH₃)₂), 117.4, 124.1, 127.2, 138.2, 140.2, 144.4, 149.4, 158.4 (aryl, pyr, CF₃, imine). ¹⁹F NMR (benzene- d_6 , 22 °C): δ –59.9. IR (pentane): ν_{CO} 1925, 1983 cm⁻¹.

Preparation of (4-Me2N-iPrPDI)Fe(N2)2. A round-bottom flask was charged with 17.6 g of mercury, approximately 10 mL of toluene, and a stir bar. Sodium (0.088 g, 3.8 mmol) was cut into small pieces and added slowly to the rapidly stirred slurry. The resulting amalgam was stirred for an additional 30 min to ensure complete dissolution. A solution containing 0.50 g (0.77 mmol) of (4-Me₂N-^{iPr}PDI)FeCl₂ in 10 mL of toluene and 10 mL of THF was added to the vessel. The reaction mixture was stirred vigorously, forming a brown solution. After 3 h, the reaction mixture was decanted from the amalgam and concentrated in vacuo to remove the THF. The residue was extracted with pentane and yielded a brown-green mixture that was filtered through a pad of Celite and concentrated to ~15 mL. The concentrated solution was stored at -35 °C and deposited 0.19 g (39%) of a green-brown solid identified as $(4-Me_2N-i^{\tilde{P}r}PDI)Fe(N_2)_2$. ¹H NMR (benzene- d_6 , 22 °C): δ –0.17 (d, 7 Hz, 12H, CH(CH₃)₂), 1.28 (d, 7 Hz, 12 H, CH(CH₃)₂), 1.98 (spt, 7 Hz, 4H, CH(CH₃)₂), 2.95 (s, $\Delta \nu_{1/2} = 11$ Hz, 6H, N(CH₃)₂), 4.23 (bs, 6H, CCH₃), 7.56 (d, 7 Hz, 4H, *m*-aryl), 7.63 (m, 2H, *p*-aryl), 9.13 (s, 2H, *m*-pyr). ¹³C{¹H} NMR (benzene- d_{6} , 22 °C): δ 13.7 (C(N)CH₃), 24.0 (CH(CH₃)₂), 27.5 (CH(CH₃)₂), 34.6 (CH(CH₃)₂), 40.8 (N(CH₃)₂), 80.5 (m-pyr), 125.3 (aryl), 125.6 (aryl), 145.6 (aryl), 151.2 (aryl), 162.4 (pyr or C(N)CH₃), 173.0 (pyr or C(N)CH₃), 190.5 (pyr or C(N)CH₃). In solution, under a dinitrogen atmosphere, the compound is in equilibrium with (4-Me₂N-^{iPr}PDI)Fe(N₂). IR (pentane, 23 °C): $\nu_{\rm NN}$ 2034 cm⁻¹.

Preparation of (4-^tBu-^{iPr}PDI)Fe(N₂)₂. The compound was prepared in a manner similar to that for (4-Me₂N-^{iPr}PDI)Fe(N₂)₂ with 0.25 g (0.33 mmol) of (4-tBu-tPrDI)FeBr2, 10.7 g of mercury, 0.055 g (2.4 mmol) of sodium, and approximately 30 mL of toluene. Filtration of the green reaction mixture through Celite, concentration in vacuo, and recrystallization from pentane/ether at -35 °C gave 0.10 g (49%) of a green solid identified as $(4-{}^{t}Bu-{}^{iPr}PDI)Fe(N_2)_2$. ^IH NMR (benzene- d_6 , 22 °C): δ –0.26 (d, 5 Hz, 12H, CH(CH₃)₂), 1.08–1.20 (m, 16H, CH(CH₃)₂ and CH(CH₃)₂), 1.66 (s, 9H, C(CH₃)₃), 7.59-7.68 (m, 6H, m- and p-aryl), 10.18 (s, 2H, m-pyr), 10.93 (bs, $\Delta \nu_{1/2}$ = 28 Hz, 6H, CCH₃). ¹³C{¹H} NMR (benzene- d_6 , 22 °C): δ -0.9 $(C(N)CH_3)$, 24.4 $(CH(CH_3)_2)$, 27.7 $(C(CH_3)_3)$, 30.7 $(CH(CH_3)_2)$, 38.6 (CH(CH₃)₂), 39.5 (C(CH₃)₃), 125.5 (aryl), 79.8 (m-pyr), 126.3 (aryl), 143.1 (aryl), 148.4 (o-pyr), 153.2 (aryl), 187 (p-pyr, located by HMBC), one resonance not located. IR (pentane, 23 °C): $\nu_{\rm NN}$ 2128, 2067 cm^{-1} . In solution, under a dinitrogen atmosphere, the compound is in equilibrium with (4-^tBu-^{iPr}PDI)Fe(N₂). IR (pentane, 23 °C): ν_{NN} 2041 cm^{-1} .

Preparation of $(4-Bn-i^{Pr}PDI)Fe(N_2)_2$. The compound was prepared in a manner similar to that for $(4-Me_2N-i^{Pr}PDI)Fe(N_2)_2$ with 0.25 g (0.36 mmol) of (4-Bn-^{iPr}PDI)FeCl₂, 8.4 g of mercury, 0.042 g (1.8 mmol) of sodium, and 20 mL of toluene. Filtration of the green reaction mixture through Celite, concentration in vacuo, and recrystallization from pentane/ether at -35 °C gave 0.16 g (65% yield) of a green solid identified as $(4-Bn-{}^{iPr}PDI)Fe(N_2)_2$. IR (pentane): $\nu_{\rm NN}$ 2129, 2071 cm⁻¹. In solution, under a dinitrogen atmosphere, the compound is in equilibrium with (4-Bn-^{iPr}PDI)Fe-(N₂). IR (pentane, 23 °C): ν_{NN} 2044 cm⁻¹. ¹H NMR (benzene- d_{6} , 22 °C): δ -0.36 (d, 7 Hz, 12H, CH(CH₃)₂), 1.06 (spt, 7 Hz, 4H, CH(CH₃)₂), 1.17 (d, 7 Hz, 12H, CH(CH₃)₂), 7.10 (t, 7 Hz, 1H, pphenyl), 7.23 (t, 7 Hz, 2H, m-phenyl), 7.37 (d, 7 Hz, 2H, o-phenyl), 7.70-7.61 (m, 6H, m- and p-aryl), 7.97 (s, 2H, CH₂ phenyl), 10.09 (s, 2H, *m*-pyr), 11.62 (bs, $\Delta v_{1/2} = 20$ Hz, 6H, CCH₃). ¹³C{¹¹H} NMR (benzene- d_{6} , 22 °C): δ -1.6 (C(N)CH₃), 24.4 (CH(CH₃)₂ or $CH(CH_3)_2$), 31.2 ($CH(CH_3)_2$), 33.8 (CH_2Ph), 39.5 ($CH(CH_3)_2$ or CH(CH₃)₂), 81.9 (m-pyr), 125.5 (aryl), 126.3 (aryl), 126.8 (phenyl), 129.1 (phenyl), 142.3 (aryl), 147.1 (phenyl), 147.7 (o-pyr), 153.9

(aryl), 154.4 (phenyl), 181 (*p*-pyr, located by HMBC), one resonance not located.

ASSOCIATED CONTENT

Supporting Information

Figures and CIF files giving additional spectroscopic data and complete crystallographic data for $(4-CF_3-^{iPr}PDI)FeCl_2$, $(4-Me_2N-^{iPr}PDI)Fe(CO)_2$, and $(4-Me_2N-^{iPr}PDI)FeN_2$. This material is available free of charge via the Internet at http://pubs. acs.org.

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Notes

The authors declare no competing financial interest.

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