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Article

Synthesis of Aryl-Substituted Bis(imino)pyridine Iron Dinitrogen Complexes

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The synthesis and characterization of dimeric, aryl-substituted bis(imino)pyridine iron dinitrogen complexes is described. In contrast to reduction with sodium amalgam where bis(chelate) iron compounds were isolated, stirring (^{Ar}PDI)FeBr$_2$ or (^{Me}BPDI)FeBr$_2$ (PDI = 2,6-(ArN=CMe)$_2$C$_5$H$_3$N; Ar = 2,6-Et$_2$-C$_6$H$_3$N (^{Et}PDI), 2,6-Me$_2$-C$_6$H$_3$N (^{Me}PDI), 2-^{i}Pr,6-Me-C$_6$H$_3$N (^{Me,iPr}PDI); ^{Me}BPDI = 2,6-(2,6-Me$_2$-C$_6$H$_3$N=CPh)$_2$C$_5$H$_3$N) with sodium naphthalenide resulted in isolation of the desired iron dinitrogen compounds as diamagnetic solids. Two examples, [(^{Et}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$) and [(^{Me}BPDI)Fe(N$_2$)]$_2$(μ_2-N$_2$), were characterized by X-ray diffraction. The solid state metrical parameters, in combination with infrared and Mössbauer spectroscopic data, establish ferrous compounds with doubly reduced chelates. Each new bis(imino)pyridine iron dinitrogen compound was screened for the catalytic hydrogenation of ethyl-3-methylbut-2-enoate, and the compound bearing the smallest aryl substituent, [(^{Me}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$), offers significant improvement over the original (^{iPr}PDI)Fe(N$_2$)$_2$ pre-catalyst and is one of the most active iron pre-catalysts known.

Introduction

The hydrogenation of olefins and ketones catalyzed by homogeneous transition metal compounds is one of the most well-studied and powerful transformations in organic synthesis. Since Wilkinson's discovery of (Ph$_3$P)$_3$RhCl over four decades ago, precious metal catalysts based on rhodium, iridium, and ruthenium have been widely studied and have resulted in several commercial processes for the synthesis of pharmaceuticals as well as fine and commodity chemicals. The environmental and cost advantages of iron have renewed interest in using earth abundant elements as alternatives to precious metal catalysts for organic and commodity chemical synthesis.[1−4]

The aryl-substituted bis(imino)pyridine iron bis(dinitrogen) complex, (^{iPr}PDI)Fe(N$_2$)$_2$ (^{iPr}PDI = 2,6-(2,6-^{i}Pr$_2$-C$_6$H$_3$N=CMe)$_2$C$_5$H$_3$N), exhibits rich catalytic chemistry including the hydrogenation,[5,6] hydrosilylation,[5] and [$2\pi + 2\pi$] cycloisomerization[7] of olefins.[8] (^{iPr}PDI)Fe(N$_2$)$_2$ has also proven to be an effective catalyst for the hydrogen-mediated reductive cyclization of enynes and diynes with substrate scope and turnover frequencies comparable to rhodium catalysts.[9] These results are not surprising in light of the enormous success of aryl-substituted bis(imino)pyridine ligands in iron- and cobalt-catalyzed olefin polymerization.[10−13] In both polymerization and small molecule catalysis, the redox-activity of the bis(imino)pyridine chelate, defined as the ability to undergo reversible transfer of 1−3 electrons with the metal, appears to be a key ingredient for high activity catalysts.[14−17] In olefin polymerization chemistry, studies into the interaction of the bis(imino)pyridine iron

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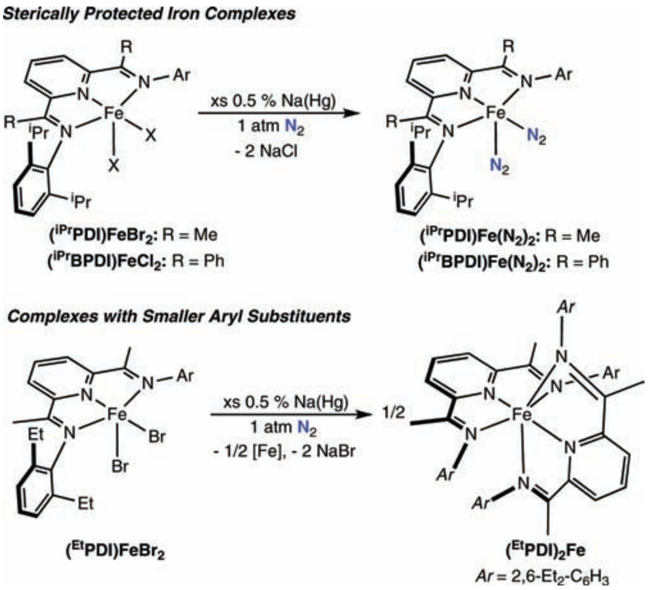
dihalide precursors with methylalumoxane (MAO) or trialkylaluminums have demonstrated that a variety of processes including chelate alkylation as well as metal and chelate redox events accompany activation.[18]

One of the attractive features of bis(imino)pyridine chelates is their modularity.[19,20] Libraries of ligands are easily accessed from condensation of the appropriate amine or aniline with 2,6-diacetylpyridine. In principle, scores of new iron dinitrogen compounds could be prepared with improved properties as compared to (^{iPr}PDI)Fe(N_2)$_2$. In addition to iron, the aryl-substituted bis(imino)pyridine chelate has been used to support dinitrogen complexes of vanadium,[21] chromium,[22] cobalt,[23] and ruthenium.[24] To date, the only other neutral bis(imino)pyridine iron bis(dinitrogen) complex reported is (^{iPr}BPDI)Fe(N_2)$_2$ (^{iPr}BPDI = 2,6-(2,6-$^{i}Pr_2$-$C_6H_3N{=}CPh)_2C_5H_3N$) where the imine methyl substituents have been replaced with phenyl rings.[25] While improved hydrogenation activity is observed with this catalyst for simple unactivated olefins such as 1-hexene, η^6-coordination of both the imine phenyl ring and the diisopropyl aryl group have been identified as catalyst deactivation pathways. Gambarotta and co-workers[26] have since reported the synthesis of a family of anionic iron dinitrogen complexes following treatment of (^{iPr}PDI)FeCl_2 with various amounts of NaH. In certain instances, deprotonation of an imine methyl group of the chelate accompanied dinitrogen complex formation.

Attempts to prepare bis(imino)pyridine iron dinitrogen compounds with aryl substituents on the imine smaller than 2,6-diisopropyl or with alkyl groups have been unsuccessful. For example, stirring the closely related precursor, (^{Et}PDI)FeBr_2 (^{Et}PDI = 2,6-(2,6-Et_2-$C_6H_3N{=}CMe)_2C_5H_3N$) with excess 0.5% Na(Hg) under a dinitrogen atmosphere, the conditions used to prepare (^{iPr}PDI)Fe(N_2)$_2$, did not yield the desired N_2 complex. The catalytically inactive bis(chelate) iron derivative, (^{Et}PDI)$_2$Fe, was obtained instead (Scheme 1).[27] Similar outcomes were observed for alkyl-substituted bis(imino)pyridines and pyridine bis(oxazoline) complexes as sodium amalgam reduction of (^{R}APDI)FeBr_2 (^{R}APDI = 2,6-(R-N$=$CMe)$_2C_5H_3N$; R = Cy, ^{i}Pr) or (^{iPr}Pybox)FeCl_2 also yielded the bis(chelate) iron complexes, (^{R}APDI)$_2$Fe or (^{iPr}Pybox)$_2$Fe,[28] respectively. In this contribution, we describe the exploration of alternative reductants and reaction conditions for the preparation of new aryl-substituted bis(imino)pyridine iron dinitrogen complexes. Each new iron dinitrogen compound was evaluated for the catalytic hydrogenation of ethyl-3-methylbut-2-enoate (ethyl 3,3-dimethylacrylate), and iron pre-catalysts with vastly improved hydrogenation activities over (^{iPr}PDI)Fe(N_2)$_2$ have been discovered.

Scheme 1



Results and Discussion

Synthesis of Aryl-Substituted Bis(imino)pyridine Iron Dinitrogen Complexes. Different reduction conditions were screened in an attempt to prepare bis(imino)pyridine iron complexes bearing *N*-aryl groups smaller than 2,6-diisopropyl phenyl. Initial experiments focused on the reduction of (^{Et}PDI)FeBr_2 with excess 0.5% sodium amalgam in tetrahydrofuran (THF). The motivation for these studies was the observation of reversible THF coordination to (^{iPr}PDI)Fe(N_2)$_2$ to form (^{iPr}PDI)Fe(THF)$_2$. A similar outcome was observed upon addition of THF to (^{iPr}BPDI)Fe(N_2)$_2$.[25] We reasoned that if (^{Et}PDI)Fe(THF)$_2$ could be generated as the kinetic product of the reduction in THF perhaps bis(chelate) iron complex formation could be suppressed. Stirring a THF solution of (^{Et}PDI)FeBr_2 with 0.5% Na(Hg) under a dinitrogen atmosphere furnished a mixture of products, one of which was likely the desired N_2 compound. Notably, the amount of (^{Et}PDI)$_2$Fe observed by ^{1}H NMR spectroscopy was diminished compared to reductions carried out in either toluene or pentane where the bis(chelate) iron complex was the exclusive product.[27]

Inspired by the improved results observed in THF, alternative reduction conditions were explored in an attempt to obtain the desired iron dinitrogen compound. Stirring a THF solution of (^{Et}PDI)FeBr_2 with 2 equiv of sodium naphthalenide for 1 h under a dinitrogen atmosphere furnished [(^{Et}PDI)Fe(N_2)]$_2$(μ_2-N_2) as a dark brown solid. The stoichiometric naphthalene byproduct proved difficult to remove completely without decomposition of the iron dinitrogen compound. Because naphthalene is required both to synthesize the reductant, sodium naphthalenide, and is a byproduct of the synthesis of the iron dinitrogen compound, we reasoned it could be

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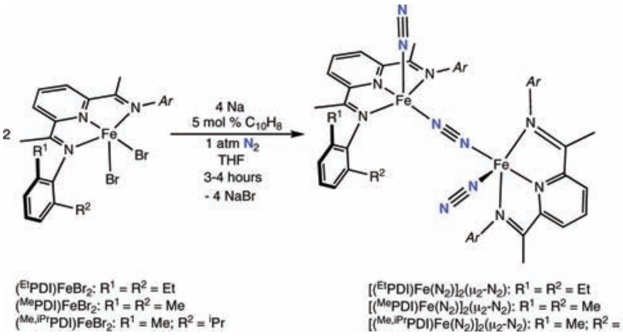
used in catalytic rather than stoichiometric amounts. Stirring a THF solution of (^{Et}PDI)FeBr$_2$ with 2 equiv of sodium metal in the presence of 5 mol % of naphthalene for 3−4 h followed by solvent removal, extraction into diethyl ether, and recrystallization at −35 °C furnished pure [(^{Et}PDI)-Fe(N$_2$)]$_2$(μ_2-N$_2$), free of naphthalene contamination.

With a new reduction protocol in hand, the synthesis of other bis(imino)pyridine iron dinitrogen complexes was explored. Both (^{Me}PDI)FeBr$_2$ and *rac*/*meso*-(^{Me,iPr}PDI)-FeBr$_2$ underwent smooth conversion to the corresponding dinitrogen complexes, [(^{Me}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$) and [(^{Me,iPr}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$), respectively (eq 1). Because (^{Me,iPr}PDI)FeBr$_2$ was prepared as a 9: 1 mixture of *rac* and *meso* diastereomers,[29] the dinitrogen complex, [(^{Me,iPr}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$), was also likely isolated as a mixture of isomers. However, the benzene-d_6 ^{1}H NMR spectrum of the compound at 23 °C is broadened because of dynamics (vide infra), and both infrared and Mössbauer spectroscopies exhibit the number of peaks consistent with formation of only one compound. It is possible that both techniques are insensitive to stereochemistry and that multiple diastereomers are actually present. To address this issue, a benzene-d_6 solution of [(^{Me,iPr}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$) was treated with excess carbon monoxide, and a 4:1 mixture of two isomers of the corresponding, monomeric bis(imino)pyridine iron dicarbonyl compound, (^{Me,iPr}PDI)Fe(CO)$_2$, was obtained.[5,28] Because we are unable to differentiate *rac* and *meso* diastereomers based on NMR spectroscopy,[29] it is not known whether the *rac* isomer predominates and if epimerization occurred during the synthesis of the dinitrogen compound or upon carbonylation. The major isomer of (^{Me,iPr}PDI)Fe(CO)$_2$ was isolated free of the minor following recrystallization.

The same dinitrogen compound, [(^{Me,iPr}PDI)Fe(N$_2$)]$_2$-(μ^2-N$_2$), was also obtained from 0.5% sodium amalgam reduction of (^{Me,iPr}PDI)FeBr$_2$ in toluene under a dinitrogen atmosphere, the only new iron dinitrogen compound reported in this study that could be prepared in this manner. In the sodium amalgam reductions, no resonances for the bis(chelate) iron complex, (^{Me,iPr}PDI)$_2$Fe, were detected in the benzene-d_6 ^{1}H NMR spectrum. Treatment of the resulting iron dinitrogen complex with carbon monoxide furnished the same 4:1 ratio of carbonyl compounds as material prepared with sodium naphthalenide. For preparation of the dinitrogen compound, [(^{Me,iPr}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$), the sodium with catalytic naphthalenide method was preferred because of its relative operational simplicity over the sodium amalgam route.



(1)

Previous studies from our laboratory have demonstrated that replacing the backbone imine methyl group with a phenyl substituent resulted in a more active iron catalyst for the hydrogenation of simple unactivated olefins such as 1-hexene.[25] This iron dinitrogen complex, (^{iPr}BPDI)Fe(N$_2$)$_2$, also underwent competitive intramolecular reactions to form catalytically inactive η^6-aryl and -phenyl compounds thereby reducing the overall hydrogenation activity with more hindered olefins. With the application of the new sodium naphthalenide reduction protocols, we sought to prepare an example of an iron dinitrogen complex with a phenylated bis(imino)pyridine chelate bearing a smaller 2,6-disubstituted imine aryl ring. Stirring a THF solution of (^{Me}BPDI)FeCl$_2$ with 2 equiv of sodium naphthalenide for 30 min at ambient temperature followed by extraction and repeated recrystallizations from diethyl ether furnished the desired iron dinitrogen compound, [(^{Me}BPDI)Fe(N$_2$)]$_2$(μ_2-N$_2$), as an intensely dark brown solid. The recrystallized material also contained significant quantities of (^{Me}BPDI)Fe(THF)$_2$ and the corresponding η^6-aryl compound, (κ^2-^{Me}BPDI)Fe-(η^6-aryl) (vide infra) as judged by Mössbauer spectroscopy (see Supporting Information for details). Unfortunately, the [(^{Me}BPDI)Fe(N$_2$)]$_2$(μ_2-N$_2$)/(^{Me}BPDI)Fe(THF)$_2$ mixture obtained from this method could not be isolated free of residual naphthalene. In a typical batch approximately 25% (w/w) naphthalene remained. Attempts to remove this byproduct by sublimation resulted in decomposition of the iron dinitrogen compound while attempts at selective recrystallization failed to achieve separation. The THF compound, (^{Me}BPDI)Fe(THF)$_2$, was independently prepared by reduction of (^{Me}BPDI)-FeCl$_2$ under vacuum but was not isolated in pure form because of competing formation of the η^6-aryl compound, (κ^2-^{Me}BPDI)Fe(η^6-aryl), as judged by Mössbauer spectroscopy (see Supporting Information). Attempts to obviate contamination by this compound by using shorter reduction times resulted in mixtures of (^{Me}BPDI)Fe(THF)$_2$ and (^{Me}BPDI)FeCl.

To avoid the complications of contamination with free naphthalene, the reduction of (^{Me}BPDI)FeCl$_2$ was repeated using 2 equiv of sodium with 5 mol % of naphthalene (eq 2). This method provided [(^{Me}BPDI)Fe(N$_2$)]$_2$-(μ_2-N$_2$) along with (^{Me}BPDI)Fe(THF)$_2$ as judged by Mössbauer spectroscopy (see Supporting Information) and degradation experiments. In a typical batch, approximately 10−20% of the mixture was (^{Me}BPDI)Fe(THF)$_2$. The benzene-d_6 ^{1}H NMR spectrum of this mixture was broad and featureless. However, simply adding 1−2 drops of THF allowed observation of the diamagnetic C_{2v} symmetric (because of rapid interchange of the THF ligands) (^{Me}BPDI)Fe(THF)$_2$ with sharp signals. Because of the inability to reproducibly separately these compounds on a preparative scale and the sensitivity of (^{Me}BPDI)Fe(THF)$_2$ to dinitrogen, meaningful combustion analysis was not obtained. It should also be noted that the reduction using sodium with catalytic naphthalene was best accomplished with concentrated (∼0.24 M) iron solutions and short reaction times (∼1 h) to prevent formation of significant quantitites of η^6-arene compounds.

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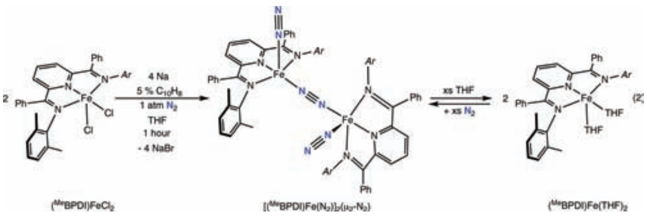
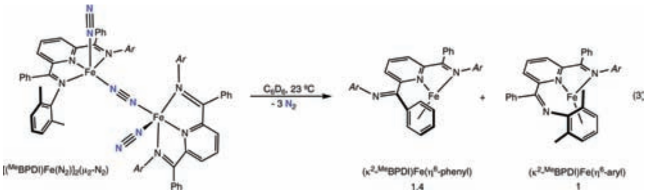


As with monomeric (^{iPr}BPDI)Fe(N_2)$_2$, [(^{Me}BPDI)Fe(N_2)]$_2$(μ_2-N_2) is prone to N_2 dissociation and irreversible formation of intramolecular η^6-arene compounds. Allowing a benzene-d_6 solution of the compound to stand at 23 °C for 48 h resulted in smooth conversion to a 1.4:1 mixture of (κ^2-^{Me}BPDI)Fe(η^6-phenyl) and (κ^2-^{Me}BPDI)Fe(η^6-aryl), respectively (eq 3). Each of the η^6-arene compounds is diamagnetic and was readily identified by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR resonances for the hydrogens of the coordinated arene ring shift upfield and are diagnostic of coordination to iron (see Experimental Section for details). Because the formation of η^6-arene compounds is irreversible,[25] the ratio of the phenyl to the aryl compound is kinetically controlled and did not change over time



Although the sodium naphthalenide reduction methods were successful for the preparation of new dinitrogen compounds, it has not proven completely general. Iron compounds with bis(imino)pyridine ligands bearing aryl rings with a single ortho-substituent (R = ^{i}Pr, ^{t}Bu), 3,5-dimethyl or an *N*-alkyl (R^1 = cyclohexyl) group produced a mixture of unidentified products using either stoichiometric sodium naphthalenide or 2 equiv of sodium with catalytic naphthalene. The specific iron compounds explored are presented in Figure 1. In cases where *rac* and *meso* diastereomers are possible, a mixture of isomers was used in the reduction reaction.

In contrast to monomeric (^{iPr}PDI)Fe(N_2)$_2$ and (^{iPr}BPDI)Fe(N_2)$_2$, all of the compounds prepared in this study were isolated as dimers with two terminal and one bridging N_2 ligand. The dinitrogen ligands are labile as evidenced by exchange with $^{15}N_2$ and detection of compounds where the two metal centers are four-coordinate and bridged with a terminal dinitrogen ligand. This structural type has been observed by Berry and co-workers in related bis(imino)pyridine ruthenium chemistry.[24,30]

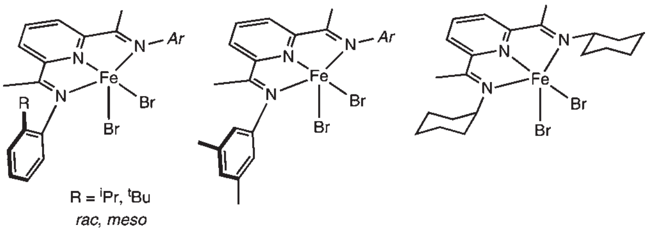


Figure 1. Aryl- and alkyl-substituted bis(imino)pyridine iron compounds that failed to yield a dinitrogen compound following sodium naphthalenide reduction.

Table 1. Infrared Stretching Frequencies of [(^{Ar}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$) and [(^{Me}BPDI)Fe(N$_2$)]$_2$(μ_2-N$_2$) Compounds Recorded in Toluene Solution

compound	ν(N≡N) (cm^{-1})
(^{iPr}PDI)Fe(N$_2$)$_2$	2122, 2058
[(^{Me,iPr}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$)	2099, 2084
[(^{Et}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$)	2101, 2086
[(^{Me}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$)	2102, 2085
[(^{Me}BPDI)Fe(N$_2$)]$_2$(μ_2-N$_2$)	2104, 2094[a] 2120, 2109[b]

[a] Values recorded in KBr. [b] Toluene solution values observed by React-IR spectroscopy at 10 °C.

Toepler pump experiments were conducted to quantitate the amount of bulk dinitrogen per sample. Addition of PbCl$_2$ to [(^{Et}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$) resulted in collection of 2.6 equiv of dinitrogen per dimer. Analysis of this specific sample by Mössbauer spectroscopy (vide infra) prior to addition of the PbCl$_2$ established a mixture of dimers with five- and four-coordinate monomeric subunits in a 9:1 ratio. When taking this mixture into account, 93% of the total amount of the expected N$_2$ was obtained. It should be noted that depending on the specific handling and recrystallizations conditions, [(^{Et}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$) can be isolated exclusively. In the case of [(^{Me}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$), the combination of Mössbauer spectroscopy and Toepler pump experiments yielded 2.9 equiv of dinitrogen per two iron centers (97% of the expected total) and demonstrated little contamination from the dimeric structure composed of two four-coordinate iron monomers lacking terminal N$_2$ ligands.[24,30]

The dimeric structures with two terminal dinitrogen ligands were readily identified by solution infrared spectroscopy. The values of the symmetric and asymmetric N≡N bands recorded in toluene solution are reported in Table 1. One exception is [(^{Me}BPDI)Fe(N$_2$)]$_2$(μ_2-N$_2$) where the reported values are from a solid state (KBr) spectrum because of the complications of competing THF coordination at 23 °C. Toluene solution values were obtained by in situ infrared spectroscopy below 10 °C in the presence of 1 atm of N$_2$. In all cases no stretches were identified that could be assigned to the bridging N$_2$ ligand, which may be a result of a centrosymmetric structure in solution. Recently, Berry reported the observation of the bridging N$_2$ stretch in [(^{Ar}PDI)Ru]$_2$(μ_2-N$_2$) compounds.[24]

The relatively high frequencies of the N≡N bands suggest little activation of the dinitrogen ligands by the iron center. Within the series, there is little variation, the most notable being the values for [(^{Me}BPDI)Fe(N$_2$)]$_2$(μ_2-N$_2$) compared to the other compounds. As has been established previously,[25,31] introduction of phenyl substituents into the imine backbone results in a more electron poor iron center. As a result, higher frequency N≡N bands are observed. It is therefore not surprising that [(^{Me}BPDI)Fe(N$_2$)]$_2$(μ_2-N$_2$) has the highest affinity

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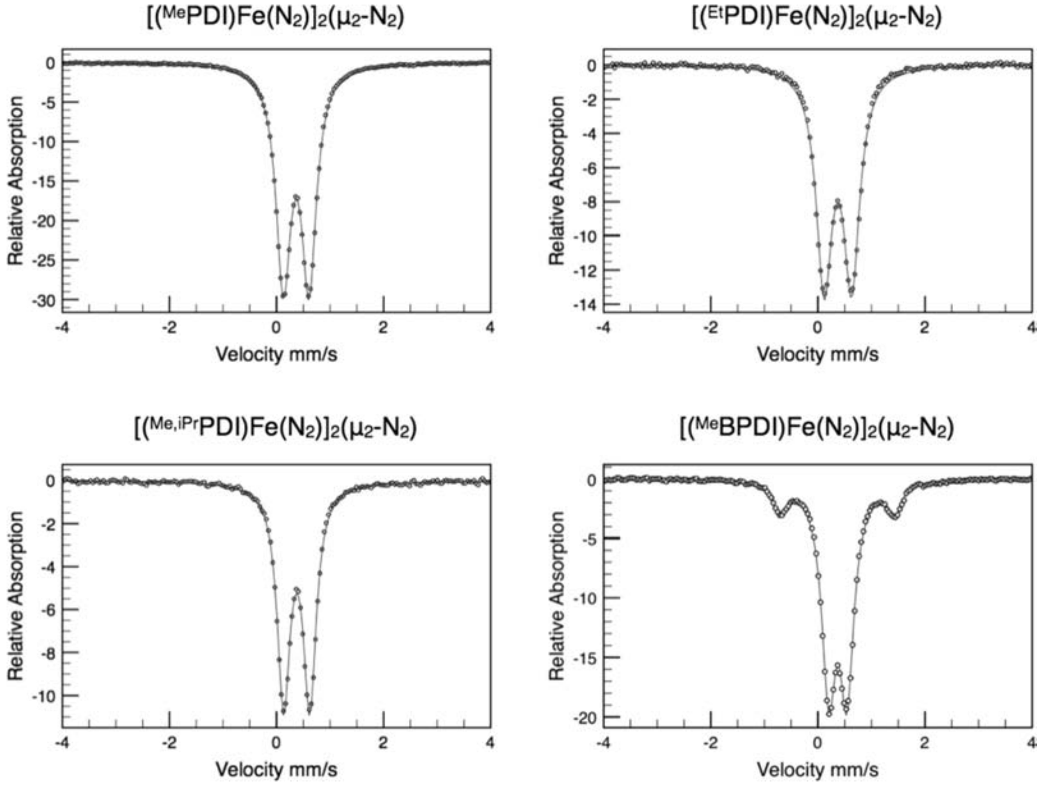

Figure 2. Representative zero-field ^{57}Fe Mössbauer spectra of the bis(imino)pyridine iron dinitrogen compounds described in this work. The data were collected at 80 K.

for THF, likely because of the increased electrophilicity of the iron center from the electron withdrawing bis(imino)pyridine.

Each of the diamagnetic, dimeric dinitrogen compounds was also studied by NMR spectroscopy. The benzene-d_6 ^{1}H NMR spectra of [(^{Et}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$), [(^{Me,iPr}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$), and [(^{Me}BPDI)Fe(N$_2$)]$_2$(μ_2-N$_2$) are broad and featureless at 23 °C. This behavior precluded assignment of the number of isomers present for [(^{Me,iPr}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$). The ethylated derivative, [(^{Et}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$), was studied by variable temperature NMR spectroscopy in benzene-d_6 (20 to 80 °C) or toluene-d_8 (−80 to 20 °C). Upon warming, many of the ligand resonances sharpened, although not to the point where coupling was observed. At low temperatures, the number of peaks increased, particularly the number of bis(imino)pyridine methyl groups, indicating inequivalency within the dimer; however, the spectra remained quite broad and otherwise difficult to assign. The ^{15}N NMR spectrum of [(^{Et}PDI)Fe(^{15}N$_2$)]$_2$(μ_2-^{15}N$_2$), prepared by addition of ^{15}N$_2$ gas to the natural abundance compound, was recorded in toluene-d_8 at −80 °C. Three broad peaks centered at −324.1, −331.5, and −356.7 ppm were observed, consistent with two terminal and one bridging dinitrogen ligand. The peak broadness observed at this temperature suggests that exchange processes are still operative, and the lack of coupling information precludes assignments of the peaks. This phenomenon has been observed previously in phosphine-ligated iron dinitrogen compounds.[32] No improvements in the quality of the spectra were observed if the data were collected under vacuum, suggesting an intramolecular exchange process occurs both between bridging and terminal dinitrogen ligands.

For the methylated complex, [(^{Me}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$), a sharper, more informative ^{1}H NMR spectrum was obtained at 20 °C. The number of peaks consistent with a C_{2v} symmetric molecule was observed, again indicating a rapid fluxional process and interchange of the terminal and bridging N$_2$ ligands on the NMR time scale. Notably, the imine methyl group was observed at 1.78 ppm, in contrast to the downfield value of 13.61 ppm observed for (^{iPr}PDI)Fe(N$_2$).[5]

The bis(imino)pyridine iron dinitrogen complexes prepared in this study were also characterized by zero-field ^{57}Fe Mössbauer spectroscopy at 80 K. Representative spectra are presented in Figure 2, and the experimentally determined parameters are reported in Table 2. The previously reported isomer shift and quadrupole splitting[5] for (^{iPr}PDI)Fe(N$_2$)$_2$ as well as for the THF compounds, (^{Et}PDI)Fe(THF) and (^{Me}BPDI)Fe(THF)$_2$, are also included for comparison. The spectrum of (^{Et}PDI)-Fe(THF) is presented in Figure 3 as a representative example while the spectrum of (^{Me}BPDI)Fe(THF)$_2$ is reported in the Supporting Information. During the course of this investigation, the zero-field Mössbauer spectrum of (^{iPr}BPDI)Fe(N$_2$)$_2$ was also recorded, and the experimentally determined parameters are reported in Table 2

The Mössbauer data for [(^{Et}PDI)Fe(N$_2$)]$_2$(μ_2-N$_2$) and (^{Et}PDI)Fe(THF) clearly establish that the former compound is not contaminated with the latter and also demonstrates the reduced affinity of the methyl-substituted

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[32] Field, L. D.; Hazari, N.; Li, H. L.; Luck, I. J. *Magn. Reson. Chem.* **2003**, *41*, 709.

Table 2. Zero-Field ^{57}Fe Mössbauer Parameters for the Bis(imino)pyridine Iron Dinitrogen and THF Complexes

compound	δ (mm/s)	ΔE_Q (mm/s)
$(^{iPr}PDI)Fe(N_2)_2$	0.39	0.53
$(^{iPr}PDI)Fe(N_2)$	0.38	1.72
$[(^{Et}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$	0.37	0.51
$[(^{Et}PDI)Fe]_2(\mu_2\text{-}N_2)$	0.33	1.50
$(^{Et}PDI)Fe(THF)^a$	0.39	2.04
$[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$	0.37	0.49
$[(^{Me,iPr}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$	0.38	0.49
$(^{iPr}BPDI)Fe(N_2)_2$	0.43	0.41
$(^{iPr}BPDI)Fe(N_2)$	0.43	1.91
$[(^{Me}BPDI)Fe(N_2)]_2(\mu_2\text{-}N_2)^b$	0.37	0.34
$(^{Me}BPDI)Fe(THF)_2{}^a$	0.35	2.17

[a] Both samples of $(^{Et}PDI)Fe(THF)$ and $(^{Me}BPDI)Fe(THF)_2$ were independently synthesized for analysis. [b] Contains 88% dinitrogen compound and 12% $(^{Me}BPDI)Fe(THF)_2$.

bis(imino)pyridine-ligated compound for THF as compared to $[(^{Me}BPDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$. Spectroscopic studies and degradation experiments with carbon monoxide also support these conclusions. It should also be recognized that $(^{Et}PDI)Fe(THF)$ coordinates one equivalent of THF while $(^{Me}BPDI)Fe(THF)_2$ is isolated with two. Both $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ and $[(^{Me,iPr}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ were isolated following recrystallization solely as dimers with two terminal dinitrogen ligands

The Mössbauer parameters of the iron dinitrogen complexes fall into two distinct classes that are diagnostic for the two different types of N_2 compounds that are present. Five-coordinate, (^{Ar}PDI) iron bis(dinitrogen) complexes have isomer shifts (δ) between 0.37 and 0.39 mm/sec and small quadrupole splittings (ΔE_Q) between 0.49 and 0.53 mm/sec. The corresponding four-coordinate mono(dinitrogen) compounds have slightly lower isomer shifts and larger quadrupole splittings. In both classes, the isomer shifts are consistent with intermediate spin iron(II) complexes with doubly reduced, bis(imino)pyridine chelates as described previously.[15b,33] The differences in the values of the quadrupole splittings are likely due to a change in electric field gradient arising from different ordering, and hence population, of the cloverleaf d-orbitals and d_{z^2} between the two coordination numbers. It should be recognized that additional spectroscopic and computational studies are required to support this assertion. The Mössbauer data for the two THF compounds, $(^{Et}PDI)Fe(THF)$ and $(^{Me}BPDI)Fe(THF)_2$, are also consistent with intermediate spin ferrous compounds with dianionic bis(imino)pyridine chelates as observed with other neutral ligand compounds of this type.[33]

Two compounds, $[(^{Et}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ and $[(^{Me}BPDI)Fe(N_2)_2](\mu_2\text{-}N_2)$, were also characterized by X-ray diffraction and obtained from pentane solution −35 °C and contain two terminal dinitrogen ligands. The molecular structure of $[(^{Et}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ is presented in Figure 4 while that of $[(^{Me}BPDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ is shown in Figure 5. Selected metrical parameters are reported in Tables 3 and 4. The data for the monomeric analogues, $(^{iPr}PDI)Fe(N_2)_2$ and $(^{iPr}BPDI)Fe(N_2)_2$, are included in the appropriate table for comparison.

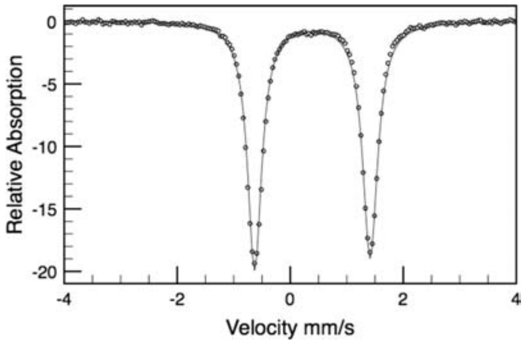

Figure 3. Zero-field ^{57}Fe Mössbauer spectrum of $(^{Et}PDI)Fe(THF)$.

The molecular geometry of each iron monomer in $[(^{Et}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ is best described as an idealized square pyramid with the bridging dinitrogen ligand occupying the apical position on one iron center and a basal position on the other. The monomeric subunits in $[(^{Me}BPDI)Fe(N_2)_2](\mu_2\text{-}N_2)$ are also idealized square pyramidal; however, in this case the bridging N_2 ligand is apical for both iron centers. These different arrangements change the relative orientation of the planes of the bis(imino)pyridine chelates with respect to each other. In $[(^{Et}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ an "edge to face" arrangement is present while in $[(^{Me}BPDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$, a "face to face" structure with S_4 molecular symmetry is observed.

The metrical parameters of bis(imino)pyridines are well-known to be diagnostic of redox-activity.[15] While the $N_{imine}-C_{imine}$ distances, with one exception, are statistically indistinguishable between $[(^{Et}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ and monomeric $(^{iPr}PDI)Fe(N_2)_2$,[5] the $C_{imine}-C_{pyridine}$ distances are more contracted in the dimeric compound. Overall the distortions are within the range for a two electron reduced chelate and consistent with the Mössbauer isomer shift, which established an intermediate spin ferrous center.[33] Examining the metrical parameters for $[(^{Me}BPDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ and the previously reported $(^{iPr}BPDI)Fe(N_2)_2$[25] also establishes two electron ligand reduction. For the dimer, elongated $N_{imine}-C_{imine}$ distances of 1.341(2) and 1.340(2) Å are well within the accepted range for an intermediate spin bis(imino)pyridine ferrous compound. One of the $C_{imine}-C_{pyridine}$ distances is significantly contracted to 1.419(3) Å and is consistent with two electron reduction. The other $C_{imine}-C_{pyridine}$ distance is slightly longer at 1.437(2) Å but is also indicative of a doubly reduced, dianionic bis(imino)pyridine.

Catalytic Hydrogenation of Ethyl-3-Methylbut-2-Enoate. Each of the new bis(imino)pyridine iron dinitrogen complexes synthesized in this study was evaluated for the catalytic hydrogenation of ethyl-3-methylbut-2-enoate. Standard conditions employed a 0.92 M solution of substrate in benzene-d_6, 5 mol % of iron (2.5% of the dimer), and four atmospheres of dihydrogen. When possible, each reaction was run to >95% conversion as judged by ^{1}H NMR spectroscopy. As presented in Table 5, the imino aryl substituents on the bis(imino)pyridine chelate have a significant influence on the catalytic hydrogenation

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(33) Bart, S. C.; Lobkovsky, E.; Bill, E.; Wieghardt, K.; Chirik, P. J. *Inorg. Chem.* **2007**, *46*, 7055.

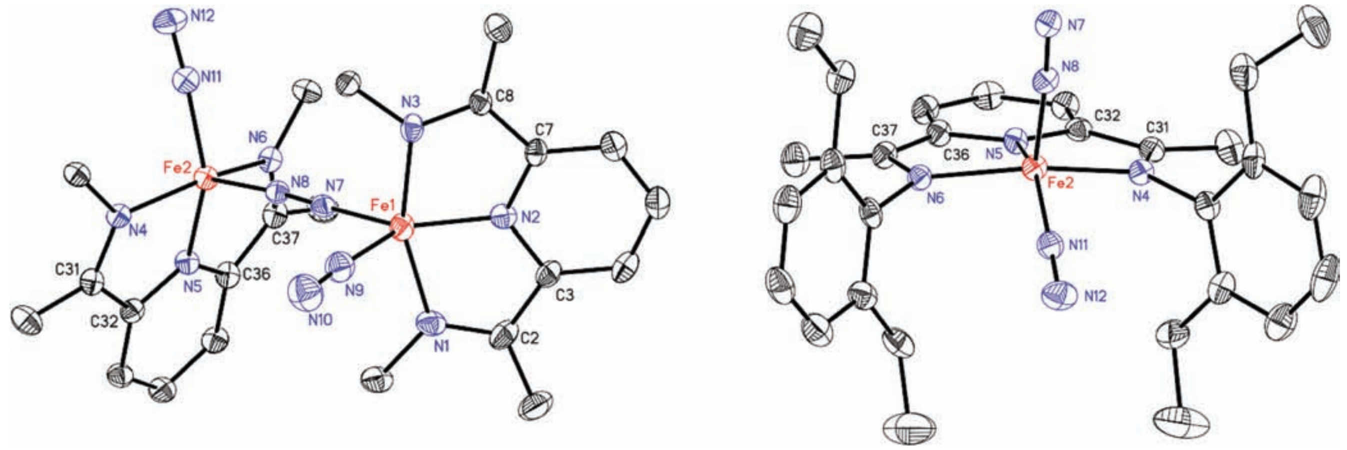

Figure 4. Solid state structure of $[(^{Et}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ at 30% probability ellipsoids. A truncated version of the dimer is presented on the left, a full view of the monomeric unit on the right.

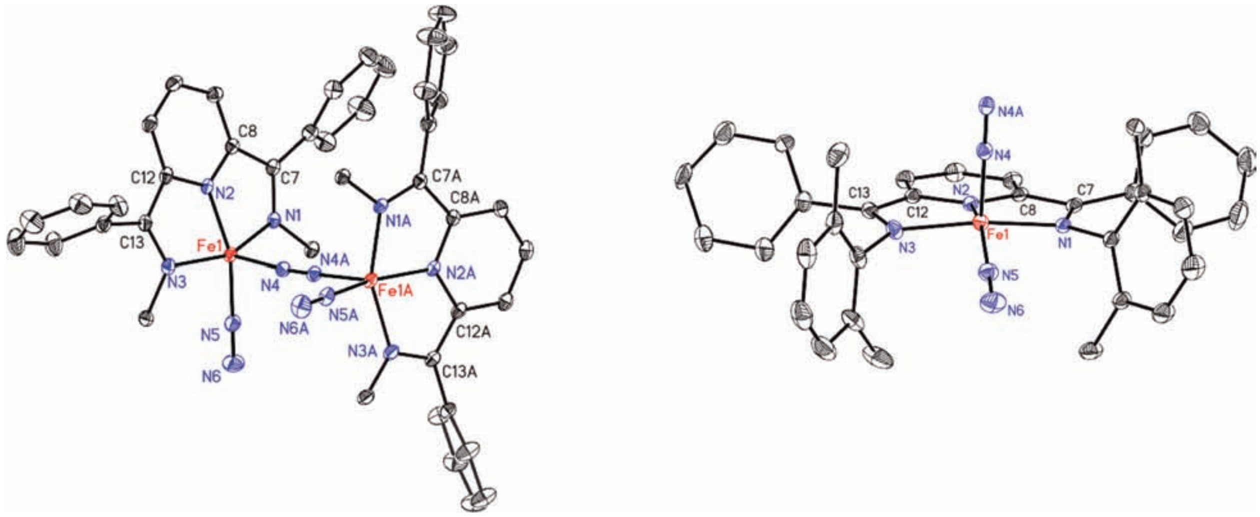

Figure 5. Solid state structure of $[(^{Me}BPDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ at 30% probability ellipsoids. A truncated version of the dimer is presented on the left, a full view of the monomeric unit on the right.

activity of the iron dinitrogen complex and widen the substrate scope for this class of molecules. The originally reported compound, $(^{iPr}PDI)Fe(N_2)_2$, reached only 60% conversion to product after 72 h. At longer reaction times no appreciable additional conversion was observed as the iron complex also undergoes competitive deactivation by irreversible C−O bond cleavage.[6,34] In contrast, replacing one of the isopropyl groups with a methyl substituent as in the case of *rac*/*meso*-$[(^{Me,iPr}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$, resulted in complete conversion in just 5 h. Similar improvements were observed when $[(^{Et}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ and $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ were used as the catalyst precursors, and the time to reach $>95\%$ was 10 and 1.5 h, respectively. The turnover frequencies observed for $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ establish this precursor as one of the most active iron hydrogenation catalysts known.

The phenylated iron pre-catalyst, $[(^{Me}BPDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$, was also active for the hydrogenation of ethyl-3-methylbut-2-enoate, albeit with reduced turnover frequency and number as compared to the methylated (imine backbone) series of dinitrogen compounds. Analysis of the iron compound by ^{1}H NMR spectroscopy following hydrogenation established the formation of the unsaturated and saturated bis(imino)pyridine iron ester complexes (vide infra) with little evidence for formation of η^6-arene complexes. However, a significant amount of unidentified paramagnetic compounds were also observed and are likely derived from C−O bond cleavage chemistry.[34] Because this material is often contaminated with the THF compound, the catalytic hydrogenations were repeated in the presence of 2−5 equiv of THF, and no significant change in the hydrogenation performance was observed. The isopropyl-substituted variant, $(^{iPr}BPDI)Fe(N_2)_2$, was also screened for catalytic hydrogenation activity. No turnover was observed after stirring ethyl-3-methylbut-2-enoate with 4 atm of dihydrogen for days at 23 °C.

Why then are both $[(^{Me}BPDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ and $(^{iPr}BPDI)Fe(N_2)_2$ such poor pre-catalysts for catalytic ethyl-3-methylbut-2-enoate hydrogenation as compared to $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$? To answer this question, a series of stoichiometric experiments and NMR studies were carried out. For $(^{iPr}BPDI)Fe(N_2)_2$, recovering the

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(34) Trovitch, R. J.; Lobkovsky, E.; Bouwkamp, M. W.; Chirik, P. J. *Organometallics* **2008**, *27*, 6264.

Table 3. Metrical Parameters for $[(^{Et}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$[a]

	$[(^{Et}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$	$(^{iPr}PDI)Fe(N_2)_2$
Fe(1)−N(1)	1.929(3)	1.9473(16)
Fe(1)−N(2)	1.818(3)	1.8362(14)
Fe(1)−N(3)	1.926(3)	1.9452(16)
Fe(1)−N(7)	1.873(3)	1.8800(19)
Fe(1)−N(9)	1.849(3)	1.8341(16)
Fe(2)−N(4)	1.923(3)	
Fe(2)−N(5)	1.834(2)	
Fe(2)−N(6)	1.932(3)	
Fe(2)−N(8)	1.879(3)	
Fe(2)−N(11)	1.837(3)	
N(1)−C(2)	1.328(4)	1.333(2)
N(3)−C(8)	1.318(4)	1.332(2)
N(4)−C(31)	1.328(4)	
N(6)−C(37)	1.331(4)	
C(2)−C(3)	1.410(5)	1.427(2)
C(7)−C(8)	1.406(4)	1.428(3)
C(31)−C(32)	1.423(4)	
C(36)−C(37)	1.400(4)	
N(1)−Fe(1)−N(2)	79.64(12)	79.90(6)
N(1)−Fe(1)−N(7)	98.86(12)	97.41(7)
N(2)−Fe(1)−N(3)	79.41(11)	79.49(6)
N(3)−Fe(1)−N(7)	97.15(11)	96.65(7)
N(2)−Fe(1)−N(7)	135.96(12)	159.09(8)
N(2)−Fe(1)−N(9)	130.21(13)	102.89(7)
N(7)−Fe(1)−N(9)	93.82(13)	98.02(8)
N(4)−Fe(2)−N(5)	79.52(11)	
N(4)−Fe(2)−N(11)	95.28(11)	
N(5)−Fe(2)−N(6)	79.62(11)	
N(6)−Fe(2)−N(11)	95.96(12)	
N(5)−Fe(2)−N(11)	149.01(12)	
N(5)−Fe(2)−N(8)	114.04(11)	
N(8)−Fe(2)−N(11)	96.95(12)	

[a] The values for $(^{iPr}PDI)Fe(N_2)_2$ are included for comparison. Data taken from reference 5.

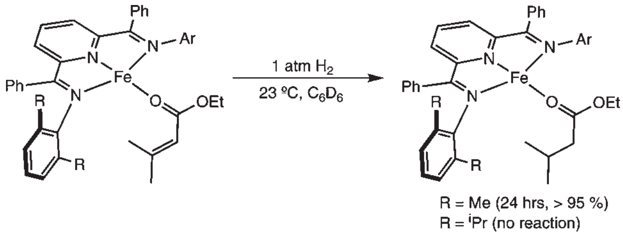
Table 4. Metrical Parameters for $(^{R}BPDI)$ Iron Dinitrogen Complexes (R = ^{i}Pr, Me)[a]

	$[(^{Me}BPDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$	$(^{iPr}BPDI)Fe(N_2)_2$
Fe(1)−N(1)	1.9320(13)	1.927(4)
Fe(1)−N(2)	1.8385(13)	1.842(4)
Fe(1)−N(3)	1.9284(13)	1.935(5)
Fe(1)−N(4)	1.8800(13)	1.865(5)
Fe(1)−N(5)	1.8536(14)	1.841(5)
N(4)-N(4A)	1.123(3)	1.107(5)
N(5)−N(6)	1.102(2)	1.106(6)
N(1)−C(7)	1.340(2)	1.344(7)
N(2)−C(8)	1.369(2)	1.376(7)
N(2)−C(12)	1.3811(18)	1.379(6)
N(3)−C(13)	1.341(2)	1.355(7)
C(7)−C(8)	1.437(2)	1.429(8)
C(12)−C(13)	1.419(3)	1.430(7)
Fe(1)−N(4)−N(4A)	174.96(12)	170.4(5)
Fe(1)−N(5)−N(6)	179.16(15)	178.5(5)
N(4)−Fe(1)−N(5)	93.85(6)	99.0(2)
N(1)−Fe(1)−N(5)	97.80(6)	96.6(2)
N(3)−Fe(1)−N(5)	95.78(6)	97.2(2)
N(1)−Fe(1)−N(2)	79.84(5)	79.3(2)
N(2)−Fe(1)−N(3)	80.11(6)	80.9(2)

[a] Data for R = ^{i}Pr taken from reference 26.

iron species following attempted catalytic hydrogenation and analysis by ^{1}H NMR spectroscopy again indicated little deactivation by formation of η^6-arene compounds. Instead, the diamagnetic ester complex, $(^{iPr}BPDI)Fe(OC(OEt)(CH{=}CMe_2))$, was cleanly observed. This compound, along with $(^{Me}BPDI)Fe(OC(OEt)(CH{=}CMe_2))$, was independently prepared by addition of ethyl-3-methylbut-2-enoate to the corresponding dinitrogen compounds. Both ester complexes exhibit typical NMR spectral features for neutral ligand derivatives of bis(imino)pyridine iron (see Experimental Section).[33,34]

Because formation of η^6-arene complexes is not the origin of catalyst deactivation in either case, both iron ester complexes were studied in stoichiometric hydrogenation reactions (eq 4). Exposure of a benzene-d_6 solution of $(^{Me}BPDI)Fe(OC(OEt)(CH{=}CMe_2))$ to 4 atm of H_2 at 23 °C resulted in smooth and complete (> 95%) conversion to the corresponding saturated ester complex over the course of 24 h. No other paramagnetic products were observed during the reaction. Repeating this procedure with $(^{iPr}BPDI)Fe(OC(OEt)(CH{=}CMe_2))$ produced no change over the course of hours demonstrating that the iron ester complex is not an initiator of hydrogenation catalysis.



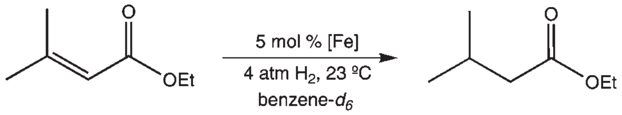
(4)

The differences in hydrogenation activity of $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ and $[(^{Me}BPDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ and $(^{iPr}BPDI)Fe(N_2)_2$ may be traced to the affinity of the latter compounds for coordination of the carbonyl oxygen of the ester substrates. This behavior arises from a more electrophilic iron center imparted by the electron withdrawing phenylated bis(imino)pyridine chelates. The more congested isopropyl-substituted compound, $[(^{iPr}BPDI)Fe]$, has a more sterically protected iron center that prohibits coordination of the π-face of the hindered trisubstituted alkene, favoring formation of the carbonyl adduct and preventing catalytic turnover. Making the iron center more accessible, as in the case of $[(^{Me}BPDI)Fe]$, allows competitive coordination of the alkene relative to the O-bound ester compound. However, hydrogenation is still sufficiently slow such that C−O bond cleavage pathways that result in catalyst decomposition become competitive. It is possible that higher dihydrogen pressures would minimize or completely suppress this pathway.

Concluding Remarks

The synthesis of new, dimeric aryl-substituted bis(imino)pyridine iron dinitrogen complexes has been accomplished by reduction of the corresponding iron dihalide precursor with in situ generated sodium naphthalenide. This reduction protocol contrasts the outcome with sodium amalgam, where often catalytically inactive iron bis(chelate) complexes were isolated. The metrical parameters determined by X-ray diffraction, infrared stretching frequencies, the zero-field ^{57}Fe Mössbauer parameters, and observed diamagnetism are consistent with a ferrous center with a bis(imino)pyridine dianion. Evaluation of the performance of each of the new compounds for the catalytic hydrogenation of

Table 5. Comparison of Various Aryl-Substituted Bis(imino)pyridine Iron Dinitrogen Complexes in the Catalytic Hydrogenation of Ethyl-3-methylbut-2-enoate



compound	time (hrs)[a]
$(^{iPr}PDI)Fe(N_2)_2$	50% (24 h)[b]
$[(^{Me,iPr}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$	5
$[(^{Et}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$	10
$[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$	1.5
$(^{iPr}BPDI)Fe(N_2)_2$	0% (24 h)
$[(^{Me}BPDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$	21% (24 h)[c]

[a] Time required to reach > 95% conversion as judged by ^1H NMR spectroscopy. Conditions: 5.0 mol % [Fe], 0.92 M substrate in benzene-d_6 solution, 4 atm H_2, 23 °C. [b] Maximum 60% conversion due to catalyst deactivation. [c] 45% observed after 72 h.

ethyl-3-methylbut-2-enoate demonstrates the importance of the 2,6-disubstituted aryl groups; the compound bearing 2,6-dimethyl aryl rings is one of the most active iron olefin hydrogenation catalysts reported to date. However, bis(imino)pyridines with phenyl substituents in the imine backbone create more electrophilic iron centers which in turn are more subject to contamination by THF complexes and exhibit a greater affinity for carbonyl coordination thereby reducing hydrogenation efficiency of carboxylated alkenes.

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.[35] Benzene-d_6 was purchased from Cambridge Isotope Laboratories, distilled from Na metal, and dried over 4 Å molecular sieves. The complexes: $(^{Et}PDI)FeBr_2$,[27] $(^{Me,iPr}PDI)FeBr_2$,[36] and $(^{Me}BPDI)FeCl_2$[37] were prepared according to literature procedures. $(^{Me}PDI)FeBr_2$ was prepared according to the published procedure for the corresponding iron dichloride compound using $FeBr_2$.[12b]

^1H 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 ^1H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ using the ^1H (residual) and ^{13}C chemical shifts of the solvent as a secondary standard. ^{15}N NMR spectra were recorded on a Varian 500 spectrometer operating at 50.663 MHz, and chemical shifts were externally referenced to liquid ammonia. 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.

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 Lorentzian peaks). The minimum experimental line widths were 0.23 mm s^{-1}. The temperature of the sample was controlled by a Janis Research Co. CCS-850 He/N_2 cryostat within an accuracy of ±0.3 K. Isomer shifts were determined relative to α-iron at 298 K.

In situ solution infrared spectra were recorded with a Mettler Toledo ReactIR iC10 equipped with a DS Series 9.5 mm × 1.5 m AgX fiber conduit with a silicon probe tip on a 0.005 M solution of the compound in toluene. The spectra were acquired at 30 s intervals with a resolution of eight using a toluene background taken at 22 °C. The solution was cooled using an acetone/dry ice bath, and the temperature was monitored using an external, low-temperature thermometer. Data was analyzed using the iC IR 4.0 software.

Preparation of $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$. A 100 mL round-bottom flask was charged with 1.00 g $(^{Me}PDI)FeBr_2$ (1.71 mmol), 0.081 g sodium metal (3.50 mmol, 2.1 equiv) and 0.011 g of naphthalene (0.085 mmol, 0.05 equiv). To the flask was added approximately 20 mL of THF, and the resulting reaction mixture was stirred for 3−4 h. During this time, the solution changed color from blue to green to red-brown. After reduction was complete (indicated by the formation of the red solution), the THF was removed in vacuo. The resulting solid was dissolved in diethyl ether and filtered through Celite. The filtrate was collected and concentrated and stored at −35 °C yielding 0.550 g (69%) of a dark brown solid identified as $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$. Analysis for $C_{50}H_{54}N_{12}Fe$: Calcd C, 64.25; H, 5.82; N, 17.98. Found C, 63.87; H, 6.19; N, 17.80. ^1H NMR (benzene-d_6, 20 °C): δ = 1.35 (bs, 24H, Ar CH_3), 1.78 (bs, 12H, C(CH_3)), 6.92 (bs, 12H, *m*- and *p-Ar*), 7.52 (bs, 2H, *p-py*), 8.10 (bs, 4H, *m-py*). ^{13}C NMR (benzene-d_6, 20 °C): δ = 16.17 (*Ar* CH_3), 19.50 (C(CH_3)), 115.92 (*m*- or *p*- *py*), 125.35 (*m*- or *p*- *Ar*), 130.93 (*m*- or *p*- *Ar*), 148.76 (*m*- or *p*- *py*), 153.05, 3 peaks not located. ^{15}N NMR (toluene-d_8, −80 °C) δ = −355.5 (bs), −334.2 (bs), −322.4 (bs). IR(toluene): $\nu(N_2)$ = 2102, 2085 cm^{-1}.

Preparation of $[(^{Et}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$. The compound was prepared in a similar manner to $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ with 1.00 g (1.56 mmol) $(^{Et}PDI)FeBr_2$, 0.073 g (3.20 mmol) sodium metal, and 0.010 g (0.078 mmol) of naphthalene. Following recrystallization from diethyl ether at −35 °C, 0.500 g (61% yield) of $[(^{Et}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ were isolated as dark green needles. Crystals suitable for X-ray analysis were grown from a pentane/ether solution. Analysis for $C_{58}H_{70}N_{12}Fe_2$: Calcd C, 66.54; H, 6.74; N, 16.05. Found C, 66.27; H, 7.10; N, 15.65. ^1H NMR (benzene-d_6, 20 °C): δ = 0.72 (bs, 24H, CH_2CH_3), 1.65 (bs, 28H, C(CH_3)) and CH_2CH_3), 7.04 (bm, 12H, *m*- and *p-Ar*), 7.64 (bs, 2H, *p-py*), 8.16 (bs, 4H, *m-py*). ^{13}C NMR (benzene-d_6, 20 °C): δ = 14.79 (CH_2CH_3), 18.07 (C(CH_3)), 24.68 (CH_2CH_3), 117.04 (*m*- or *p*- *py*), 125.77 (*m*- or *p*- *Ar*), 126.19 (*m*- or *p*- *Ar*), 135.94 (*m*- or *p*- *py*), 4 peaks not located. ^{15}N NMR (toluene-d_8, −80 °C) δ = −356.7 (bs), −331.5 (bs), −324.1 (bs). IR (toluene): $\nu(N_2)$ = 2101, 2086 cm^{-1}.

Preparation of $(^{Et}PDI)Fe(THF)$. A 20 mL scintillation vial was charged with 0.100 g (0.096 mmol) of $[(^{Et}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$, approximately 7 mL of pentane, and approximately 3 mL

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of THF. The resulting red-brown solution was stirred for 10 min. The solution was filtered through Celite, and all volatiles removed to yield 0.100 g (95%) of a red-brown powder identified as (^{Et}PDI)Fe(THF). Analysis for $C_{33}H_{41}N_3O_1Fe$: Calcd C, 71.86; H, 7.49; N, 7.62. Found C, 71.58; H, 7.48; N, 7.51. ^{1}H NMR (benzene-d_6, 23 °C) δ, -6.32 (s, 6H, C(CH_3)), 0.70 (t, 7.6 Hz, 12H, CH_2CH_3), 1.02 (bs, 4H, THF CH_2), 1.52 (q, 7.6 Hz, 4H, CH_2CH_3), 1.90 (q, 7.6 Hz, 4H, CH_2CH_3), 2.40 (bs, 4H, THF OCH_2), 7.12 (d, 7.6 Hz, 2H, *m-Ar*), 7.61 (t, 7.6 Hz, 2H, *p-Ar*), 8.89 (t, 7.6 Hz, 1H, *p-py*), 12.36 (d, 7.6 Hz, 2H, *m-py*). ^{13}C NMR (benzene-d_6, 23 °C) δ = 13.87 (CH_2CH_3), 24.01 (CH_2CH_3), 25.83 (CH_2CH_3), 26.94 (THF CH_2), 68.85 (THF OCH_2), 102.80 (*m-py*), 124.33 (*p-Ar*), 125.97 (*m-Ar*), 131.60 (*p-py*), quaternary carbons not located.

Preparation of [(^{Me,iPr}PDI)Fe(N_2)]$_2$(μ_2-N_2). The compound was prepared in a similar manner to [(^{Me}PDI)Fe(N_2)]$_2$(μ_2-N_2) with 1.00 g (1.56 mmol) of (^{Me,iPr}PDI)FeBr_2, 0.073 g (3.20 mmol) sodium metal, and 0.10 g (0.078 mmol) of naphthalene. Following recrystallization from diethyl ether at -35 °C, 0.304 g (37%) of [(^{Me,iPr}PDI)Fe(N_2)]$_2$(μ-N_2) was isolated as a dark solid. ^{1}H NMR (benzene-d_6, 20 °C): δ = 0.71 (bs, 24H, CH(CH_3)$_2$), 0.80 − 2.50 (bm, 28H, C(CH_3) and *Ar*-CH_3 and CH(CH_3)$_2$), 6.50 − 7.30 (bm, 12H, *m-* and *p- Ar*), 7.50 (bs, 2H, *p-py*), 8.00 (bs, 4H, *m-py*). ^{13}C NMR (benzene-d_6, 20 °C): δ = 23.48, 25.61, 27.98, 30.58, 118.19, 123.84, 125.93, 129.61, 141.75, 151.21. IR (toluene): $\nu(N_2)$ = 2099, 2084 cm^{-1}.

Alternate Preparation of [(^{Me,iPr}PDI)Fe(N_2)]$_2$(μ_2-N_2). A 250 mL round-bottom was charged with 43.02 g (214.4 mmol) of mercury and approximately 70 mL of toluene. With stirring, 0.215 g (9.36 mmol) of sodium metal was added to the flask, and the resulting mixture stirred for 10 min. To this was added 1.00 g (1.56 mmol) of (^{MeiPr}PDI)FeBr_2, and the resulting reaction mixture was stirred for 16 h. After this time, the dark solution was filtered through Celite, and the toluene removed in vacuo. Recrystallization from diethyl ether at -35 °C afforded 0.350 g (43%) of a dark red solid identified as [(^{Me,iPr}PDI)Fe(N_2)]$_2$(μ-N_2).

Preparation of *rac/meso*-(^{Me,iPr}PDI)Fe(CO)$_2$. A thick walled glass vessel was charged with 0.100 g (0.096 mmol) of [(^{Me,iPr}PDI)Fe(N_2)]$_2$(μ_2-N_2) and approximately 20 mL of diethyl ether. The vessel was brought out of the drybox, submerged in liquid nitrogen, and evacuated on the high vacuum line. Four atmospheres of carbon monoxide were added, and the vessel and the contents warmed to room temperature after which the solution turned from brown to green. The reaction mixture was stirred for 1 h. The vessel was then degassed and brought back into the drybox. The solution was filtered through Celite, concentrated and stored at -35 °C yielding 0.42 (41%) of a green solid identified as the major isomer of (^{Me,iPr}PDI)Fe(CO)^2. Analysis for $C_{31}H_{35}N_3O_2Fe$: Calcd C, 69.28; H, 6.56; N, 7.82. Found C, 69.10; H, 6.65; N, 7.95. ^{1}H NMR (benzene-d_6, 23 °C) δ = 0.87 (d, 6.8 Hz, 6H, CH(CH_3)$_2$), 1.41 (d, 6.8 Hz, 6H, CH(CH_3)$_2$), 1.94 (s, 6H, C(CH_3) or *Ar* CH_3), 2.02 (s, 6H, C(CH_3) or *Ar* CH_3), 2.98 (sept, 6.8 Hz, 2H, CH(CH_3)$_2$), 6.94 (d, 7.6 Hz, 2H, *m-Ar*), 7.03 (t, 7.6 Hz, 2H, *p-Ar*), 7.13 (d, 7.6 Hz, 2H, *m-Ar*), 7.15 (t, 7.6 Hz, 1H, *p-py*), 7.68 (d, 7.6 Hz, 2H, *m-py*). ^{13}C NMR (benzene-d_6, 23 °C) δ = 15.82 (C(CH_3) or *Ar* CH_3), 18.91 (C(CH_3) or *Ar* CH_3), 23.94 (CH(CH_3)$_2$), 25.64 (CH(CH_3)$_2$), 28.10 (CH(CH_3)$_2$), 117.36 (*p-py*), 121.41 (*m-py*), 124.45 (*m-Ar*), 126.69 (*p-Ar*), 128.51 (*m-Ar*), 129.61, 141.07, 145.75, 151.88, 155.53, 212.96, 215.99 (quaternary carbons). IR(pentane, 23 °C) ν(CO) = 1915, 1973 cm^{-1}.

Minor isomer (obtained only as a mixture with the major): ^{1}H NMR (benzene-d_6, 23 °C) δ = 0.89 (d, 6.8 Hz, 6H, CH(CH_3)$_2$), 1.39 (d, 6.8 Hz, 6H, CH(CH_3)$_2$), 1.94 (s, 6H, C(CH_3) or *Ar* CH_3), 2.02 (s, 6H, C(CH_3) or *Ar* CH_3), 2.91 (sept, 6.8 Hz, 2H, CH(CH_3)$_2$), 6.96 (d, 7.6 Hz, 2H, *m-Ar*), 7.07 (t, 7.6 Hz, 2H, *p-Ar*), 7.13 (d, 7.6 Hz, 2H, *m-Ar*), 7.15 (t, 7.6 Hz, 1H, *p-py*), 7.67 (d, 7.6 Hz, 2H, *m-py*). ^{13}C NMR (benzene-d_6, 23 °C) δ = 15.85 (C(CH_3) or *Ar* CH_3), 18.98 (C(CH_3) or *Ar* CH_3), 24.36 (CH(CH_3)$_2$), 25.45 (CH(CH_3)$_2$), 27.97 (CH(CH_3)$_2$), 117.48 (*p-py*), 121.42 (*m-py*), 124.58 (*m-Ar*), 126.65 (*p-Ar*), 129.84 (*m-Ar*), 129.61, 140.75, 145.78, 151.88, 155.49, 214.58 (quaternary carbons). IR(pentane, 23 °C) ν(CO) = 1896, 1967 cm^{-1}.

Preparation of [(^{Me}BPDI)Fe(N_2)]$_2$(μ_2-N_2). A scintillation vial was charged with 0.750 g of (^{Me}BPDI)FeCl_2 (1.21 mmol), 0.058 g of sodium metal (2.5 mmol, 2.1 equiv), and 0.008 g of naphthalene (0.06 mmol, 0.05 equiv). To the vial was added 5 mL THF, and the resulting mixture was stirred for 1.5 h. During this time, the solution turned from blue-green to brown. After reduction was complete (signaled by the formation of the brown solution), the THF was removed in vacuo. The dark residue was taken up in diethyl ether to yield a dark orange-brown mixture and was filtered through a plug of Celite. Removal of the solvent in vacuo and recrystallization of the residue from ether at -35 °C afforded 0.321 g (45%)of a brown solid identified as [(^{Me}BPDI)Fe(N_2)]$_2$(μ-N_2). Crystals suitable for X-ray diffraction were grown from a dilute diethyl ether solution. ^{1}H NMR (benzene-d_6, 20 °C): δ = 1.17 (bs, 12H, aryl CH_3), 6.57−7.48 (bm, 19H, *aryl-*, *phenyl-*, and *py*-H). ^{13}C NMR (benzene-d_6, 20 °C): δ = 23.2 (b, CH_3), 108.2, 112.9, 124.9, 126.1, 128.6, 131.9, 134.1, 134.7, 136.7, 147.9 (b), 151.1 (b), 158.2 (b). IR (KBr): $\nu(N_2)$ = 2104, 2094 cm^{-1}. IR (toluene, 10 °C): $\nu(N_2)$ = 2120, 2109 cm^{-1}.

Allowing a benzene solution of [(^{Me}**BPDI)Fe(N_2)]$_2$(μ_2-N_2**) to stand at 22 °C for 48 h furnished a 1.4:1 mixture of [(κ^2-^{Me}**BPDI)Fe(η^6-Phenyl**) and [(κ^2-^{Me}**BPDI)Fe(η^6-Aryl**), respectively.

Preparation of (^{Me}BPDI)Fe(THF)$_2$. A 100 mL round-bottom flask was charged with 0.100 g of [(^{Me}BPDI)Fe(N_2)]$_2$(μ_2-N_2) (0.090 mmol) and a needle valve attached. On a high vacuum line, the vessel was evacuated, and 20 mL of THF was added by vacuum transfer. After stirring for 20 min, the solvent was removed in vacuo to afford 0.072 g (61%) of a dark solid identified as (^{Me}BPDI)Fe(THF)$_2$. ^{1}H NMR (benzene-d_6, 20 °C): δ = 0.90 (11 Hz, 12H, CH_3), 1.45 (41 Hz, 8H, THF), 3.26 (24 Hz, 8H, THF), 6.77 (21 Hz, 4H, *m*-phenyl), 6.89 (19 Hz, 4H, *m*-aryl), 7.44 (19 Hz, 2H, *p*-Ar), 8.67 (26 Hz, 3H, *p*-pyr and *p*-aryl), 9.88 (18 Hz, 4H, *o*-phenyl), 15.30 (18 Hz, 2H, *m*-pyr). ^{1}H NMR (THF-d_8, 20 °C): δ = 0.95 (41 Hz, 12H, CH_3), 6.78 (60 Hz, 4H, *m*-phenyl), 6.98 (62 Hz, 4H, *m*-aryl), 7.45 (23 Hz, 2H, *p*-aryl), 8.55 (21 Hz, 1H, *p*-pyr), 8.84 (49 Hz, 2H, *p*-phenyl), 9.71 (47 Hz, 4H, *o*-phenyl), 15.24 (48 Hz, 2H, *m*-pyr). ^{13}C NMR THF-d_8, 20 °C): δ = 22.7 (b, CH_3), 107.1, 111.8, 118.0 (b), 124.4 (b), 125.8 (b), 128.4 (b), 131.9 (b), 132.9 (b), 136.7.

Characterization of [(κ^2-^{Me}BPDI)Fe](η^6-Phenyl). ^{1}H NMR (benzene-d_6, 20 °C): δ = 2.25 (s, 6H, CH_3), 2.32 (s, 6H, CH_3), 3.69 (t, 6 Hz, 1H, *p*-Ph), 5.01 (dd, 2 Hz and 6 Hz, 2H, *m*-Ph), 5.59 (d, 4.1 Hz, 2H, *o*-Ph), 6.45 (dd, 8 Hz and 8 Hz, 1H, *p*-py), 6.83−7.02 (m, 11H, *m-* and *p*-aryl, and *o-*, *m-*, *p*-phenyl), 7.05 (d, 8 Hz, 1H, *m*-py), 7.60 (d, 8 Hz, 1H, *m*-py). ^{13}C NMR (benzene-d_6, 20 °C): δ = 18.9 (CH_3), 19.2 (CH_3), 19.5 (CH_3), 80.8 (*p*-Ph), 83.4 (*o*-Ph), 84.7 (*m*-Ph), 89.5 (quaternary-Ph), 108.9, 122.2, 123.2, 123.5, 124.0, 124.5, 126.1, 126.5, 129.3, 129.7, 130.8, 131.1, 134.1, 136.4, 143.5, 148.3, 149.4, 165.7, 168.5.

Characterization of [(κ^2-^{Me}BPDI)Fe](η^6-Aryl). ^{1}H NMR (benzene-d_6, 20 °C): δ = 2.12 (s, 6H, CH_3), 2.22 (s, 6H, CH_3), 4.09 (t, 6 Hz, 1H, *p*-Ar), 5.21 (d, 6 Hz, 2H, *m*-Ar), 6.43 (dd, 8 Hz and 8 Hz, 1H, *p*-pyr), 6.79−6.94 (m, 10H, *p*-py and phenyl), 7.28−7.34 (m, 2H, *p*-Ar and *p-* Ph), 7.41 (d, 8 Hz, 1H, *m*-pyr), 7.81 (d, 7 Hz, 2H, *m*-Ar). ^{13}C NMR (benzene-d_6, 20 °C): δ = 17.1 (CH_3), 17.3 (CH_3), 17.5 (CH_3), 19.2 (CH_3), 81.1, 86.3, 87.8, 108.2, 112.1, 124.9, 126.1, 127.0, 128.1, 129.0, 129.2, 129.3, 130.7, 131.9, 136.8, 162.6.

Characterization of (^{Me}BPDI)Fe(ethyl 3,3-dimethylacrylate). A scintillation vial was charged with 0.10 g of [(^{Me}BPDI)Fe(N_2)]$_2$(μ_2-N_2) (0.085 mmol) and 5 mL of diethyl ether. To this mixture was added 0.022 g of ethyl 3,3-dimethylacrylate

(0.17 mmol, 2 equiv), which elicited a color change from brown to black. After 0.5 h, the solvent was removed in vacuo, and the crude solid was recrystallized from pentane to afford 0.088 g (77%) of a black solid identified as (${}^{\text{Me}}$BPDI)Fe(ethyl 3,3-dimethylacrylate). ^{1}H NMR (benzene-*d*$_6$, 20 °C): δ = 0.43 (s, 3H, olefin-C*H*$_3$), 0.73 (s, 1H, olefin-C*H*), 0.78 (t, 7 Hz, 3H, OCH$_2$C*H*$_3$), 1.10 (s, 3H, olefin-C*H*$_3$), 1.51 (s, 12H, aryl-C*H*$_3$), 3.31 (q, 7 Hz, 2H, OC*H*$_2$CH$_3$), 6.83 (d, 7 Hz, 4H, *m*-aryl), 6.94 (t, 8 Hz, 4H, *m*-phenyl), 7.27 (t, 7 Hz, 2H, *p*-aryl), 8.18 (t, 8 Hz, 1H, *p*-pyr), 8.20 (t, 8 Hz, 2H, *p*-phenyl), 9.43 (d, 7 Hz, 4H, *o*-phenyl), 11.75 (d, 8 Hz, 2H *m*-pyr). ^{13}C NMR (benzene-*d*$_6$, 20 °C): δ = 21.3, 27.8, 32.3, 62.3, 76.5, 104.6, 108.1, 121.2, 122.8, 124.0, 126.7, 131.0, 131.9, 135.5, 140.3, 158.9, 167.3, 167.4, 169.5, 185.2.

Characterization of (${}^{\text{Me}}$BPDI)Fe(ethyl 3-methylbutanoate). A thick walled vessel was charged with a solution of 0.040 g (0.059 mmol) of (${}^{\text{Me}}$BPDI)Fe(ethyl 3,3-dimethylacrylate) in 5 mL of toluene. On the high-vacuum line, 4 atm of H_2 was added, and the resulting solution was allowed to stir for 24 h eliciting a color change from black to brown. Removal of excess H_2 and solvent yielded 0.029 g (72%) of a brown solid identified as (${}^{\text{Me}}$BPDI)Fe(ethyl 3-methylbutanoate). ^{1}H NMR (benzene-*d*$_6$, 20 °C): δ = 0.05 (d, 7 Hz, 2H, C*H*$_2$), 0.24 (d, 6 Hz, 3H, CH(C*H*$_3$)$_2$), 0.86 (m, 1H, C*H*(CH$_3$)$_2$), 1.12 (t, 7 Hz, 3H, OCH$_2$C*H*$_3$), 1.50 (s, 12H, aryl-C*H*$_3$), 2.71 (q, 7 Hz, 2H, OC*H*$_2$CH$_3$), 6.84 (d, 7 Hz, 4H, *m*-aryl), 6.93 (t, 8 Hz, 4H, *m*-phenyl), 7.33 (t, 7 Hz, 2H, *p*-aryl), 8.15 (t, 8 Hz, 1H, *p*-pyr), 8.20 (t, 8 Hz, 2H, *p*-phenyl), 9.37 (d, 8 Hz, 4H, *o*-phenyl), 11.86 (d, 8 Hz, 2H, *m*-pyr). ^{13}C NMR (benzene-*d*$_6$, 20 °C): δ = 21.4, 32.4, 40.9, 47.8, 55.5, 56.7, 104.3, 107.2, 120.9, 123.0, 126.7, 128.7, 131.0, 141.0, 159.5, 163.2, 167.5, 167.8, 186.3.^{1}H NMR (benzene-*d*$_6$, 20 °C): δ = 0.05 (d, 7 Hz, 2H, C*H*$_2$), 0.24 (d, 6 Hz, 3H, CH(C*H*$_3$)$_2$), 0.86 (m, 1H, C*H*(CH$_3$)$_2$), 1.12 (t, 7 Hz, 3H, OCH$_2$C*H*$_3$), 1.50 (s, 12H, aryl-C*H*$_3$), 2.71 (q, 7 Hz, 2H, OC*H*$_2$CH$_3$), 6.84 (d, 7 Hz, 4H, *m*-aryl), 6.93 (t, 8 Hz, 4H, *m*-phenyl), 7.33 (t, 7 Hz, 2H, *p*-aryl), 8.15 (t, 8 Hz, 1H, *p*-pyr), 8.20 (t, 8 Hz, 2H, *p*-phenyl), 9.37 (d, 8 Hz, 4H, *o*-phenyl), 11.86 (d, 8 Hz, 2H, *m*-pyr).

Characterization of (${}^{\text{iPr}}$BPDI)Fe(ethyl 3,3-dimethylacrylate). A scintillation vial was charged with 0.060 g of (${}^{\text{iPr}}$BPDI)Fe(N_2)$_2$ (0.083 mmol) and approximately 5 mL of diethyl ether. To this mixture was added 0.013 g (0.10 mmol, 1.2 equiv) of ethyl 3,3-dimethylacrylate resulting in a color change from brown to dark purple. After 0.5 h, the solvent was removed in vacuo, and the remaining solid was recrystallized from pentane to afford 0.058 g (88%) of a dark purple solid identified as (${}^{\text{iPr}}$BPDI)Fe(ethyl 3,3-dimethylacrylate). ^{1}H NMR (benzene-*d*$_6$, 20 °C): δ = $-$0.22 (d, 6 Hz, 12H, CH(C*H*$_3$)$_2$), 0.97 (t, 7 Hz, 3H, OCH$_2$C*H*$_3$), 1.01 (d, 7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.12 (s, 3H, olefin-C*H*$_3$), 1.60 (s, 3H, olefin-C*H*$_3$), 2.07 (sep, 7 Hz, 4 H, C*H*(CH$_3$)$_2$), 3.34 (q, 7 Hz, 2H, OC*H*$_2$CH$_3$), 3.92 (s, 1H, olefin C*H*), 6.86 (t, 8 Hz, 4H, *m*-phenyl), 7.07 (d, 8 Hz, 4H, *m*-aryl), 7.48 (t, 8 Hz, 2H, *p*-aryl), 8.31 (t, 8 Hz, 1H, *p*-pyr), 8.47 (t, 8 Hz, 2H, *p*-phenyl), 9.53 (d, 8 Hz, 4H, *o*-phenyl), 12.70 (d, 8 Hz, 2H, *m*-pyr). ^{13}C NMR (benzene-*d*$_6$, 20 °C): δ = 13.6, 23.3, 24.1, 30.1, 63.6, 104.6, 108.6, 116.5, 120.6, 121.1, 123.1, 123.9, 124.2, 124.4, 128.1, 129.0, 131.5, 136.6, 160.6, 167.8, 168.1, 188.0.

General Procedure for Catalytic Olefin Hydrogenation. In a typical experiment, a thick walled glass vessel was charged with a solution containing 0.016 mmol of the desired iron compound in 0.65 g (7.72 mmol) of benzene-*d*$_6$ and a magnetic stir bar. The vessel was placed in a liquid nitrogen cooled cold well for 20 min. Once the solution was frozen, 0.081 g (0.63 mmol) of ethyl 3,3-dimethylacrylate was layered on the reaction mixture. The vessel was taken out of the drybox and transferred to a high vacuum line while continuously submerged in liquid nitrogen. Following evacuation of the dinitrogen atmosphere, 1 atm of dihydrogen was admitted at 80 K. The solution was then thawed and stirred and ambient temperature. After the desired reaction time, the vessel was vented of dihydrogen and exposed to air. Decomposed iron compound was removed by filtration through Celite, and the filtrate collected into an NMR tube. Conversions were determined by integrating the olefinic methyl resonances of the substrate against the isopropyl methyl groups of the product.

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Supporting Information Available: Additional Mössbauer and NMR data and crystallographic details for (${}^{\text{Et}}$PDI)FeN$_2$ and [(${}^{\text{Me}}$BPDI)Fe(N_2)]$_2$(μ_2-N_2) in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.