Cationic Pyridine(diimine) Iron Tethered Alkene Complexes: Synthetic Models For Elusive Intermediates In Iron-Catalyzed Ethylene Polymerization

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Received March 23, 2016; E-mail: pchirik@princeton.edu

Cationic bis(imino)pyridine iron alkene complexes, key intermediates in the polymerization and oligomerization of ethylene, have been targeted to understand important physical properties such as spin state of the metal and the role of the redox-active supporting ligand. The allyl derivative, (PDI)Fe(η3-C3H5) was synthesized but proved unstable toward one electron oxidation with ferrocenium reagents. Tethered alkoxide-alkene complexes were explored as more well behaved alternatives and (PDI)Fe(OC(Ph)2CH2(η3-CHCH2) was synthesized, crystallographically characterized and determined to be a high spin Fe(II) complex with a bis(imino)pyridine radical anion. One electron oxidation with [Cp2Fe][BArF24] (BArF24 = C6H3-3,5-(CF3)2) generated the desired cationic iron complex, [(PDI)Fe(OC(Ph)2(η3-C3H5))][BArF24]. The solid-state structure confirmed alkene coordination and provided the metrical parameters used to establish a neutral bis(imino)pyridine chelate. The observation of a high spin Fe(II) complex demonstrates that the iron does not change spin state upon olefin coordination.

1. Introduction

Aryl-substituted pyridine(diimine) iron and cobalt dihalide complexes, when activated with excess methylaluminoxane (MAO) in presence of ethylene, exhibit high activity for the production of linear polyethylene. Alteration of the tridentate ligand from pyridine(diimine) to modified α-diimines with pendant phosphine donors (PNN) resulted in efficient iron and cobalt catalysts for ethylene oligomerization. The results are notable as deviation from the pyridine(diimine) scaffold usually results in catalysts with diminished performance.

Considerable effort has been devoted to understanding the identity and nature of the propagating species in olefin polymerization, including the spin state of the first row transition metal and the role of the potentially redox-active chelate. Our group has reported the synthesis of cationic bis(imino)pyridine iron and cobalt alkyl complexes that serve as single component catalysts for the polymerization of ethylene (Figure 1). In each case examined, neutral pyridine(diimine) chelates were observed suggesting that redox chemistry with the supporting ligand is not a necessary component for catalytic performance. More recently, we have discovered that addition of the neutral, Lewis acidic borane, B(C6F5)3 to both bis(imino)pyridine and PNN-supported iron butadiene complexes resulted in C-B bond formation to yield the corresponding borate betaine and provided the metrical parameters used to establish a neutral bis(imino)pyridine chelate. The observation of a high spin Fe(II) complex engaged in antiferromagnetic coupling to both chelate (S = ½) and allyl (S = ½) radical anions.

These observations suggested that while the pyridine(diimine) chelate adopted its neutral form in cationic iron alkyl complexes, the electronic structure may change upon olefin coordination. To probe this effe, we targeted the synthesis of...
cationic pyridine(diimine) iron alkene complexes, recognizing that the high reactivity of these complexes may make complex isolation challenging. Here we describe the synthesis of the first examples of pyridine(diimine) iron complexes bearing tethered alkoxide-alkene ligands to gain insight to the role of olefin coordination on electronic structure.

2. Results and Discussion

A cationic pyridine(diimine) iron allyl complex was initially targeted as an example of an iron-alkene derivative. We reasoned that the possibility of $\eta^3$ coordination of the hydrocarbyl ligand may sufficiently stabilize the compound to allow characterization and electronic structure determination. Our laboratory previously reported the synthesis of the neutral analog, ($iPDI$)Fe($C_3H_5$), however insufficient spectroscopic data was available to definitively assign the electronic structure. We then prepared the 2,6-dimethyl aryl variant, ($MePDI$)Fe($\eta^3$-$C_3H_5$) in 68% isolated yield by straightforward addition of a 1.0 M solution of allylmagnesium bromide in diethyl ether to a cold, stirring pentane solution of ($MePDI$)FeCl (eq 1).

Similar to the 2,6-diisopropylsubstituted variant, the benzene-$d_6$ $^1H$ NMR spectrum of ($MePDI$)Fe($\eta^3$-$C_3H_5$) exhibits the expected number of paramagnetically broadened and shifted resonances for a $C_2v$ symmetric compound over a 175 ppm range, a result of either an $\eta^3$-allyl or an interconversion between $\eta^1$ and $\eta^3$ hapticity on the timescale of the experiment. Solution magnetic measurements (method of Evans, benzene-$d_6$ 23 ºC) established an average magnetic susceptibility of 2.0(1) $u_B$ consistent with a doublet ground state. The X-band EPR spectrum (Figure 2, left) recorded at 10 K in toluene glass exhibited a rhombic signal which was readily simulated using an $S = \frac{1}{2}$ spin Hamiltonian formalism. The zero-field $^{57}$Fe Mössbauer spectrum recorded at 80 K (Figure 2, right) exhibits a quadrupole doublet with an isomer shift of $\delta = 0.45$ mm s$^{-1}$ and $\Delta E_Q = 1.52$ mm s$^{-1}$.

The solid-state structure of ($MePDI$)Fe($\eta^3$-$C_3H_5$) was determined by X-ray diffraction and is presented in Figure 3. An $\eta^1$-allyl ligand is observed with the three carbon plane oriented nearly perpendicular to the iron chelate plane with the central carbon slightly displaced. The metrical parameters of the pyridine(diimine) are between the values typically associated with one- and two-electron reduction, however, the iron-nitrogen distances of 1.974(2) Å, 1.8525(18) Å, and 2.0353(19) Å are most consistent with a high-spin Fe(II) center.

![Fig. 3 Solid state structure of ($MePDI$)Fe($\eta^3$-$C_3H_5$) at 30% probability ellipsoids. Hydrogen atoms (except on the allyl fragment) have been removed for clarity.](image)

<table>
<thead>
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<th>Table 1</th>
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![Fig. 2 $^{57}$Fe Mossbauer (left) and 10K EPR spectra (right) of ($MePDI$)Fe($\eta^3$-$C_3H_5$). Mossbauer parameters: $\delta = 0.45$ mm s$^{-1}$ and $\Delta E_Q = 1.52$ mm s$^{-1}$. X-band EPR spectrum of ($MePDI$)Fe($\eta^3$-$C_3H_5$) recorded in toluene glass at 10K. Microwave frequency = 9.374 GHz, power = 0.05 mW, modulation amplitude = 10 G. Spectroscopic parameters; $g_x = 2.57$, $g_y = 2.07$, $g_z = 1.96$, $g_{strain} = 0.10$, 0.00, 0.00.](image)
Full molecule DFT calculations using the B3LYP functional were carried out to gain insight into the electronic structure of \((^{\text{Me-PDI}})\text{Fe}(\eta^3\text{-C}_3\text{H}_5)\). A broken symmetry (2,1) solution was lowest in energy and reproduced the experimentally determined bond distances. The computed metrical parameters slightly overestimates the metal-ligand bond distances, as is commonly observed with the B3LYP functional. The DFT computed \(^{57}\text{Fe}\) Mössbauer parameters of \(\delta = 0.55 \text{ mm s}^{-1}\) and \(\Delta E_Q = 1.31 \text{ mm s}^{-1}\) are in good agreement with the experimental values of \(\delta = 0.45 \text{ mm s}^{-1}\) and \(\Delta E_Q = 1.52 \text{ mm s}^{-1}\). The combined experimental and computational data support an electronic structure description of an intermediate spin Fe(II) complex \((S_{\text{Fe}} = 1)\) engaged in antiferromagnetic coupling with a bis(imino)pyridine radical anion. A spin density plot corresponding to this electronic structure description is presented in Figure 4.

**Fig. 4** Spin density plot obtained from a Mulliken population analysis for \((^{\text{Me-PDI}})\text{Fe}(\eta^3\text{-C}_3\text{H}_5)\) (red, positive spin density; yellow, negative spin density).

Following isolation and electronic structure characterization of \((^{\text{Me-PDI}})\text{Fe}(\eta^3\text{-C}_3\text{H}_5)\), chemical one electron oxidation was explored as a route to the corresponding cationic iron complex. Treatment of a benzene-\(d_6\) or toluene solution of the compound with \([\text{Cp}_2\text{Fe}]\text{[BARF}2\text{]}\) generated an unidentified mixture of products as judged by \(^{57}\text{Fe}\) Mössbauer spectroscopy. Monitoring the oxidation reaction by \(^1\text{H}\) NMR spectroscopy revealed loss of approximately 50% of the allyl group as propane. In addition, hydrolysis of the isolated product following oxidation revealed very little \(\text{C}_3\) hydrocarbons such as propane or propylene, also consistent with loss of the allyl fragment upon oxidation (equation 2).

The inability to synthesize the cationic bis(imino)pyridine iron complexes inspired exploration of alternative routes to alkene compounds. In metalocene chemistry, Jordan and coworkers previously reported the synthesis of zirconocene alkoxide complexes with tethered alkene as models for elusive and reactive \(\text{Cp}_2\text{Zr(X)(olefin)}^+\) complexes.\(^{30-32}\) These compounds were synthesized by alcoholysis of \(\text{Cp}_2\text{Zr(}n\text{-CH}_3\text{)}\) to yield \(\text{Cp}_2\text{Zr(OR)(CH}_3\text{)}\) complexes, followed by alkyl abstraction with a Lewis acid to generate the desired \(\text{Cp}_2\text{Zr(X)(olefin)}^+\) products. For the synthesis of bis(imino)pyridine iron derivatives, insertion of an organic carbonyl compound into the iron allyl complex was targeted given precedent for iron allyl transfer.\(^{33-35}\)

Addition of one equivalent of benzophenone to a diethyl ether solution of \((^{\text{Me-PDI}})\text{Fe}(\eta^3\text{-C}_3\text{H}_5)\) followed by filtration and recrystallization yielded red-brown crystals identified as \((^{\text{Me-PDI}})\text{Fe(OC(Ph)\text{2CH}_2(\eta^2\text{-CHCH}_2)}\) in 64% yield (eq 3).

The benzene-\(d_6\) \(^1\text{H}\) NMR exhibits the number of resonances expected for a paramagnetic, \(C_2\) symmetric compound, consistent with dynamics associated with alkene ligand in solution. This could either mean the alkene is not coordinated or rapidly changing \(\pi\)-faces on the timescale of the NMR measurement. Solution magnetic data established an average magnetic susceptibility of 3.9(1) \(\mu_B\) at 23 °C in benzene-\(d_6\) consistent with an overall \(S = 3/2\) ground state.

The X-band EPR spectrum of \((^{\text{Me-PDI}})\text{Fe(OC(Ph)\text{2CH}_2(\eta^2\text{-CHCH}_2)}\), recorded in toluene glass at 10 K, exhibits a rhombic signal as expected for an \(S=3/2\) complex. The data were readily simulated using an \(S=3/2\) spin Hamiltonian formalism, large zero-field splitting parameters and a rhombicity of \(E/D = 0.236\). Small amounts of an unknown side product (<5%) were also observed in the spectrum. The complex was also studied by zero-field \(^{57}\text{Fe}\) Mössbauer spectroscopy and an isomer shift of \(\delta = 0.76 \text{ mm s}^{-1}\) and a quadrupole splitting of \(\Delta E_Q =0.93 \text{ mm s}^{-1}\) were obtained, values consistent with a high spin Fe(II) center.
The solid-state structure of \((\text{MePDI})\text{Fe(OC(Ph)2CH2(η²-CHCH2))}\) was determined by X-ray diffraction and is presented in Figure 6. An idealized square pyramidal geometry was observed about the iron center with \(η^2\) coordination of the alkene supported by the Fe-C(26) and Fe-C(27) bond distances of 2.222(3) and 2.220(2) Å, respectively. The distortions to the chelate are modest but are most consistent with a mono-reduced ligand as evidenced by the N-imine-C-imine distances of 1.303(3) and 1.308(3) Å and the C-imine-C-ipso bond lengths of 1.460(3) and 1.449(4) Å. The elongated Fe-N-imine distances of 2.236(2) and 2.234(2) Å are diagnostic for a high spin iron compound and are consistent with the magnetic and \(^{57}\text{Fe}\) Mössbauer data.

Full molecule DFT calculations on \((\text{MePDI})\text{Fe(OC(Ph)2(η²-C3H5))}\) were performed and a broken symmetry (4,1) solution was favored. As illustrated by the spin density plot presented in Figure 7, this solution corresponds to a high spin Fe(II) center antiferromagnetically coupled to bis(imino)pyridine radical anion. The most reliable computational data was obtained when the iron-nitrogen and iron-carbon bond lengths were constrained to values experimentally obtained values (Table 2) and the energy differences between the constrained and unconstrained solutions were small, approximately 2.5 kcal/mol.

To further understand the origins of the effect of intramolecular alkene coordination, the saturated analog \((\text{MePDI})\text{Fe(OC(Ph)2(C3H5))}\) was prepared and by straightforward salt metathesis chemistry and isolated as brown crystals in 79% yield (eq 4). A representation of the molecular structure obtained from X-ray crystallography is shown in Figure 8 and establishes a distorted square planar geometry about the iron. The propyl group is directed away from the metal center with no evidence for interaction with...
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the iron. The distortions to the chelate support a mono-
reduced chelate as evidenced by the N\textsubscript{imine}-C\textsubscript{imine} distances of 1.3188(18) and 1.3205(17) Å and the C\textsubscript{imine}-C\textsubscript{ipso} bond lengths of 1.451(2) and 1.449(2) Å. The elongated Fe-N\textsubscript{imine} distances of 2.1883(12) and 2.1920(12) Å are diagnostic for a high spin iron compound and are in good agreement with the measured magnetic susceptibility of 4.0(1) μ\textsubscript{B} (23 °C in benzene-d\textsubscript{6}).

Table 3 Computed and Experimental Bond Distances (Å) and Angles (deg) for (MePDI)Fe(OC(Ph)\textsubscript{2}(C\textsubscript{3}H\textsubscript{7})).

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The iron alkoxide complex, (MePDI)Fe(OC(Ph)\textsubscript{2}(C\textsubscript{3}H\textsubscript{7})), was also studied by \textsuperscript{57}Fe Mössbauer spectroscopy for comparison to the iron alkoxide bearing the tethered alkene. The solid state spectrum recorded at 10 K exhibits a well resolved doublet with an isomer shift of δ = 0.74 mm s\textsuperscript{-1} and a quadrupole splitting of ΔE\textsubscript{Q}=1.14 mm s\textsuperscript{-1} (Figure 10, left). These values are remarkably similar to those obtained for crystalline samples of (MePDI)Fe(OC(Ph)(η\textsuperscript{2}-C\textsubscript{3}H\textsubscript{5})) (δ = 0.76 mm s\textsuperscript{-1} ΔE\textsubscript{Q}=0.93 mm s\textsuperscript{-1}). The X-band EPR spectrum of (MePDI)Fe(OC(Ph)(η\textsuperscript{2}-C\textsubscript{3}H\textsubscript{5})) (Figure 10, right) was recorded in toluene glass at 10 K and exhibits a rhombic signal with large g anisotropy. The spectrum contains a feature at g = 7.8, well above the traditional value expected for an S = 3/2 complex, and significantly different from the signal observed for (MePDI)Fe(OC(Ph)(η\textsuperscript{1}-C\textsubscript{3}H\textsubscript{5})). This type of large g anisotropy has been observed previously in planar, four coordinate Co(II) complexes\textsuperscript{36-39} and is a result of strong spin orbit coupling from a nearly degenerate set of d orbitals which gives rise to a large orbital contribution to the electronic g values. The absence of large g anisotropy observed with the unsaturated congener (MePDI)Fe(OC(Ph)(η\textsuperscript{2}-C\textsubscript{3}H\textsubscript{5})) strongly suggests that the molecule is five coordinate and the olefin is bound to the metal center.

Fig. 8 Solid state structure of (MePDI)Fe(OC(Ph)\textsubscript{2}(C\textsubscript{3}H\textsubscript{7})) at 30% probability ellipsoids. Hydrogen atoms and imine aryl groups have been removed for clarity.

Table 3 Computed and Experimental Bond Distances (Å) and Angles (deg) for (MePDI)Fe(OC(Ph)\textsubscript{2}(C\textsubscript{3}H\textsubscript{7})).

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Full molecule DFT calculations for (MePDI)Fe(OC(Ph)\textsubscript{2}(C\textsubscript{3}H\textsubscript{7})) favored a broken symmetry(4,1) solution corresponding to a high-spin Fe(II) ion engaged in antiferomagnetically coupling with a bis(imino)pyridine radical. As observed with other compounds in this work, the iron-nitrogen bond lengths were over estimated by the unrestricted calculation. Repeating the computational study with experimentally defined Fe-N bond constraints produced an identical ground state electronic description and the energy difference between the calculations was too small to distinguish. A DFT computed spin-density plot from the constrained calculations is shown in Figure 10. The electronic structure description for (MePDI)Fe(OC(Ph)\textsubscript{2}(C\textsubscript{3}H\textsubscript{7})) is nearly identical to that obtained for (MePDI)Fe(OC(Ph)(η\textsuperscript{2}-C\textsubscript{3}H\textsubscript{5})), and the calculated \textsuperscript{57}Fe Mössbauer parameters are in good agreement for both the isomer shift isomer shift (calculated values for; saturated: δ = 0.65 mm s\textsuperscript{-1} unsaturated: δ = 0.65 mm s\textsuperscript{-1} and quadrupole splitting (calculated values for; saturated: ΔE\textsubscript{Q}=0.84 mm s\textsuperscript{-1} unsaturated: ΔE\textsubscript{Q}=1.29 mm s\textsuperscript{-1}).
parameters. This electronic structure description is analogous to that previously reported for (iPrPDI)FeCH2SiMe322,40 and suggests that iron alkoxides are reasonable electronic approximations for alkyl complexes.

![Spin density plot obtained from a Mulliken population analysis for (MePDI)Fe(OC(Ph)2(C3H7))](image)

One electron oxidation of the bis(imino)pyridine iron alkoxide bearing the tethered alkene was explored with the goal of preparing the corresponding cationic derivative (equation 5). Addition of one equivalent of [Cp2Fe][BArF24] to an ambient temperature toluene solution of (MePDI)Fe(OC(Ph)2CH2(h2-CHCH2) resulted in precipitation of a red-brown solid. The insolubility of the product prohibited NMR measurements. An average solid-state magnetic moment of 4.9(1) μB was measured at 23 ºC and was consistent with an S = 2 iron complex. Zero-field 57Fe Mössbauer parameters of δ = 0.91 mm s⁻¹ and ΔEq = 2.71 mm s⁻¹ were measured at 80 K and are also consistent with formation of a high spin Fe(II) ion (Figure 12).

![Zero-field 57Fe Mössbauer spectrum of [(MePDI)Fe(OC(Ph)2CH2(h2-CHCH2)][BArF24] recorded at 80 K.](image)

Single crystals of [(MePDI)Fe(OC(Ph)2CH2(h2-CHCH2)][BArF24] were obtained from a concentrated fluorobenzene solution stored at -35 ºC. A representation of the molecular structure is shown in Figure 12 and an idealized square pyramid about the iron is observed with the tethered alkene coordinated in the apical position. The oxygen of the alkoxide and the bis(imino)pyridine chelate define the basal plane. There are no close contacts between the [BArF24]⁻ anion and the iron alkoxide cation. The iron-carbon distances to the terminal and internal carbons of the olefin are 2.403(4) and 2.336(4) Å, respectively, and are significantly lengthened compared to the neutral compound. Interestingly, the coordination geometry of the alkene changes upon oxidation. In the cationic complex, the C=C bond is parallel to the Npyridine-Fe-O plane, which is distinct from its alignment parallel to the Nimine-Fe-Nimine plane in the neutral derivative. The metrical parameters of the bis(imino)pyridine are most consistent with a neutral chelate as evidenced by the Nmax-Cmax distances of 1.286(4) and 1.280(4) Å and the Cmax-Cmin bond lengths of 1.489(5) and 1.485(5) Å. The elongated Fe-Nmax distances of 2.214(3) and 2.282(3) Å are diagnostic for a high spin iron compound and are in good agreement with the solid state magnetic data.

![Representation of the solid state molecular structure of [(MePDI)Fe(OC(Ph)2CH2(h2-CHCH2)][BArF24] at 30 % probability ellipsoids. Hydrogen atoms and the [BArF24]⁻ counterion have been omitted for clarity.](image)
Table 4 Computed and Experimental Bond Distances (Å) and Angles (deg) for \([\text{MePDI})\text{Fe(OC(Ph)}_2\text{CH}_2(\eta^2\text{-CHCH}_2)]\text{[BArF}_2\text{]}\).

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DFT calculations on the \(S = 2\) \([\text{MePDI})\text{Fe(OC(Ph)}_2\text{CH}_2(\eta^2\text{-CHCH}_2)]^+\) complex successfully reproduced the experimentally determined bond distances and angles including the rotation of the olefin with respect to the ligand plane. A qualitative molecular orbital diagram and a spin density plot derived from these results are shown in Figure 13. This solution clearly established a high spin iron(II) center with a neutral bis(imino)pyridine ligand. From this electronic structure description, computed \(^{57}\text{Fe}\) Mössbauer parameters of \(\delta = 0.90 \text{ mm s}^{-1}\) and \(\Delta E_Q = 1.78 \text{ mm s}^{-1}\) were obtained and are in good agreement with the experimentally determined values (\(\delta = 0.91 \text{ mm s}^{-1}\) and \(\Delta E_Q = 2.71 \text{ mm s}^{-1}\)). The electronic structure of \([\text{MePDI})\text{Fe(OC(Ph)}_2\text{CH}_2(\eta^2\text{-CHCH}_2)]\text{[BArF}_2\text{]}\) is analogous to that of the previously studied iron alkyl cation complex \([\text{MePDI})\text{Fe(CH}_2\text{CMe}_3]^+\) and demonstrates that olefin coordination very likely does not change the redox state of the supporting ligand.

### 3. Conclusions

The combined synthetic, spectroscopic, and computational data obtained in this study establish a comprehensive understanding of the electronic structure of bis(imino)pyridine iron alkoxide complexes with and without coordinated alkene ligands. Analogous to observations with bis(imino)pyridine iron alkyl complexes, the neutral five-coordinate compound is best described as a high spin Fe(II) ion antiferromagnetically coupled to a bis(imino)pyridine radical anion, avoiding formation of the rare Fe(I) alkyl species. One-electron oxidation of the five-coordinate neutral iron alkoxide complex is ligand based; both the experimental and computational data support a high spin Fe(II) complex with neutral bis(imino)pyridine chelate. These data in combination with our previous studies suggest that ligand participation in the electronic structure does not occur upon coordination of olefin.

### 4. Experimental Section

**General Considerations.** All air- and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures. Allylmagnesium Bromide (1.0M in toluene, Aldrich) was used without further purification. Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves.

\(^1\text{H}\) NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 399.860 MHz. All chemical shifts are reported relative to SiMe\(_4\) using \(^1\text{H}\) (residual) chemical shifts of the solvent as a secondary standard. All \(^1\text{H}\) NMR coupling constants are reported in Hz. \(^13\text{C}\) NMR spectra were recorded on a Bruker 500 spectrometer operating at 125.71 MHz. \(^13\text{C}\) chemical shifts are reported relative to SiMe\(_4\) using chemical shifts of the solvent as a secondary standard where applicable. \(^31\text{P}\) NMR spectra were collected on a Bruker 300 AVANCE spectrometer operating at 299.763 MHz and
were referenced to 85 % H3PO4 as an external standard. For all paramagnetic compounds, peak width at half height is reported in Hertz. Infrared spectra were recorded on a Thermo-Nicolet iS10 FT-IR spectrometer calibrated with a polystyrene standard. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ. Continuous wave (CW) EPR spectra were recorded at 10 K on an X-band Bruker EMXPlus spectrometer equipped with an EMX standard resonator and a Bruker PremiumX microwave bridge. The spectra were simulated using EasySpin for MATLAB®. Solid-state magnetic moments were determined using a Johnson Matthey Magnetic Susceptibility Balance, collected at 295 K, unless otherwise noted. Solution magnetic moments were determined by the method of Evans at 295 K, except when otherwise noted. The geometric optimization of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of DFT. 54-56 This hybrid functional often gives better results for transition metal compounds than pure gradient-corrected functionals, especially with regard to metal–ligand covalency. 57 The all-electron Gaussian basis sets were those developed by Ahlrichs. 46-50 Triple-ζ quality basis sets def2-TZVP with one set of polarization functions on the metals and on the atoms directly coordinated to the metal center were used. For the carbon and hydrogen atoms, slightly smaller polarized split-valence def2-SV(P) basis sets were used, that were of double-ζ quality in the valence region and contained a polarizing set of d-functions on the non-hydrogen atoms. Auxiliary basis sets were chosen to match the orbital basis. 51-53 The RIJCOSX54-56 approximation was used to accelerate the calculations. Computational results using the broken-symmetry (BS) approach by Ginsberg 57 and Noodleman et al. 58 were computed for comparison with unrestricted high spin models. Because several broken symmetry solutions to the spin-unrestricted Kohn–Sham equations may be obtained, the general notation BS(m,n) 59 has been adopted, where m (n) denotes the number of spin-up (spin-down) electrons at the two interacting fragments. Canonical and corresponding orbitals, 60 as well as spin density plots were generated with the program Chimera.

Preparation of (4PDI)Fe(η1-C,H). A 20 mL scintillation vial was charged with 0.300 g (4PDI)FeCl (0.65 mmol) and approximately 10 mL of diethyl ether. In a separate vial, 651 µL (0.65 mmol) of a 1M solution of C,H,MgBr was diluted with approximately 5 mL of diethyl ether. Both vials were chilled to -35 C. Dropwise addition of the C,H,MgBr solution to a stirred solution of the monochloride furnished a brown-red solution that was stirred for approximately 10 minutes after which time the volatiles were removed in vacuo. The product was extracted from the solid residue with pentane and filtered through celite. The filtrate was collected and concentrated and stored at -35 °C yielding 0.206 g (68 %) of a dark red-brown solid identified as (4PDI)Fe(η1-C,H). Magnetic Susceptibility (benzene-d6, 293 K): µeff = 1.98 µB. 1H NMR (300 MHz, benzene-d6, 23 °C); δ = -38.01 (Δν1/2 = 1001 Hz, 6H, C(CH3)), -9.58 (Δν1/2 = 190 Hz, 12H, Aryl CH3), 8.60 (Δν1/2 = 760 Hz, 1H, Allyl CH), 52.41 (Δν1/2 = 72 Hz, 2H, m-py), 73.72 (Δν1/2 = 1085 Hz, 4H, Allyl CH2), 90.74 (Δν1/2 = 924.34 Hz, 4H, Aryl CH), 106.84 (Δν1/2 = 1220 Hz, 1H, p-py), 132.62 (Δν1/2 = 838 Hz, 2H, Aryl CH) ppm.

Preparation of (4PDI)Fe(OC(Ph)2CH2(η1-C,H)). A 20 mL scintillation vial was charged with 0.200 g (4PDI)FeCl (0.43 mmol) and approximately 10 mL of diethyl ether. In a separate vial, 0.078 g of benzophenone (0.43 mmol) was dissolved in approximately 5 mL of diethyl ether and filtered through celite. The filtrate was collected and concentrated and stored at -35 °C yielding 0.178 g (64 %) of a dark red-brown solid identified as (4PDI)Fe(OC(Ph)2CH2(η1-C,H)). Analysis for C41H42FeN3O: Calc. C, 75.92; H, 6.53; N, 6.48. Found C, 75.64; H, 6.50; N, 6.32. Magnetic Susceptibility (benzene-d6, 293 K): µeff = 3.9 (1) µB. 1H NMR (300 MHz, benzene-d6, 23 °C); δ = -214.14 (Δν1/2 = 550 Hz, 6H, C(CH3)), -87.66 (Δν1/2 = 1586 Hz, 1H, OC(Ph)2(CH2CH2CH2)), -9.60 (Δν1/2 = 49 Hz, 2H, p-Aryl CH),
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and the reaction mixture was allowed to stir for about 15 minutes. After the reaction was complete, the pentane solution was filtered through celite, and the resulting filtrate was concentrated and chilled to -35 °C to yield 111 mg (79%) of the product.

ν₁,1-diphenylbutan-1-ol (1.99 mmol) dissolved in 7 mL of pentane was added to the vial with additional pentane yielding 0.314 g (67%) of a red solid to stirring powders. The slurry was stirred for 15 minutes and about 5 minutes. Approximately 5 mL of toluene was added to the alcohol to yield a red solution and a grey precipitate. The slurry was filtered and the solid was washed further with pentane. The solid was collected to yield 378 mg (82%) of the expected lithium alkoxide.

Preparation of (⁶⁸PDI)Fe[OC(PH)(C₃H₅)][BF₄]₂. A 20 mL scintillation vial was charged with 100 mg (MePDI)Fe-Cl (0.21 mmol), 50 mg of lithium 1,1-diphenylbutan-1-olate (0.21 mmol) and a stir bar. Pentane was added to the vial and the reaction mixture was allowed to stir for about 15 minutes. After the reaction was complete, the pentane solution was filtered through celite, and the resulting filtrate was concentrated and chilled to -35 °C to yield 111 mg (79%) of (⁶⁸PDI)Fe[OC(PH)(C₃H₅)][BF₄]₂.

Preparation of [(⁶⁸PDI)FeOC(Ph)(C₃H₅)][BF₄]₂. A 20 mL scintillation vial was charged with a stir bar, 0.200 g ([⁶⁸PDI]FeOC(Ph)(C₃H₅)][BF₄]₂ (0.30 mmol) and 0.307 g of [Cp₂Fe][BF₄]₂ (0.29 mmol). The two powders were mixed in the solid state with slow stirring for about 5 minutes. Approximately 5 mL of toluene was added to stirring powders. The slurry was stirred for 15 minutes and a color change to red was observed. Approximately 10 mL of pentane was added to the solution to precipitate the product. The product was collected on a glass frit and washed with additional pentane yielding 0.314 g (67%) of a red solid identified as [(⁶⁸PDI)FeOC(Ph)(C₃H₅)][BF₄]₂.

Preparation of lithium 1,1-diphenylbutan-1-olate. A 20 mL scintillation vial was charged with a stir bar and 450 mg 1,1-diphenylbutan-1-ol (1.99 mmol) dissolved in 7 mL of cold hexane. A separate vial was charged with 1.014 g of 1.6 M n-BuLi solution (2.38 mmol) diluted with about 5 mL of cold hexane. While stirring, the n-BuLi was added dropwise to the alcohol to yield a red solution and a grey precipitate. The slurry was filtered and the solid was washed further with pentane. The solid was collected to yield 378 mg (82%) of the expected lithium alkoxide.

Preparation of [(⁶⁸PDI)FeOC(Ph)(C₃H₅)][BF₄]₂. A 20 mL scintillation vial was charged with 100 mg (MePDI)Fe-Cl (0.21 mmol), 50 mg of lithium 1,1-diphenylbutan-1-olate (0.21 mmol) and a stir bar. Pentane was added to the vial and the reaction mixture was allowed to stir for about 15 minutes. After the reaction was complete, the pentane solution was filtered through celite, and the resulting filtrate was concentrated and chilled to -35 °C to yield 111 mg (79%) of (⁶⁸PDI)Fe[OC(PH)(C₃H₅)][BF₄]₂.

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