Synthesis of Bis(imino)pyridine Iron Di- and Monoalkyl Complexes: Stability Differences between $FeCH_2SiMe_3$ and $FeCH_2CMe_3$ Derivatives

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The scope of aryl-substituted bis(imino)pyridine iron dihalide alkylation and arylation reactions has been explored with $LiCH_2SiMe_3$, $LiCH_2CMe_3$, and LiPh. Dialkylation was only observed when the 2,6-diisopropylaryl-substituted iron complex was treated with 2 equiv of $LiCH_2SiMe_3$. In all other cases, reductive alkylation to form four-coordinate bis(imino)pyridine iron monoalkyl complexes occurred. One of these products, (^{Et}PDI)$FeCH_2CMe_3$ [^{Et}PDI = 2,6-(2,6-$Et_2C_6H_3N$=CMe$)_2C_6H_3N$)], has been crystallographically characterized and shown to exhibit a distorted square planar geometry arising from the steric disposition of the alkyl group. Five-coordinate bis(imino)pyridine iron aryl"ate" complexes bearing weakly activated dinitrogen ligands were isolated from treatment of the corresponding dihalide with 3 equiv of aryllithium. The tolyl derivative was characterized by X-ray diffraction, and a distorted square pyramidal structure was established where the dinitrogen ligand completes the idealized basal plane. Ligand substitution reactions where the terdentate bis(imino)pyridine is used to displace pyridine from $py_2Fe(R)X$ (R = CH_2SiMe_3, CH_2CMe_3; X = Cl, CH_2SiMe_3, CH_2CMe_3) further demonstrated the relative stability of five-coordinate $FeCH_2SiMe_3$ versus $FeCH_2CMe_3$ complexes. For the neopentyl compounds, ejection of a neopentyl radical or alkylation of the *p*-pyridine position of the chelate was observed.

Introduction

The advent of highly active bis(imino)pyridine iron and cobalt complexes[1] for ethylene polymerization and α-olefin oligomerization was a landmark discovery in the era of "post-metallocene" polymerization catalysis.[2,3] Iron dihalide precatalysts are noteworthy in their ability to oligomerize α-olefins with nearly ideal Schultz−Flory distributions (without "chain walking").[2] The resulting hydrocarbons are produced with activities rivaling existing catalysts and are of extremely high purity. Both the iron and cobalt compounds are compatible with other early and late metal based catalysts, allowing for tandem processes that result in the synthesis of new polymer architectures (e.g., branched polyethylenes, reactor-blended materials with controlled molecular weight distributions, etc.).[3–6] These advantages, coupled with the reduced environmental impact of iron as compared to existing nickel and chromium oligomerization catalysts,[7] make expanding the utility of this catalyst class a worthwhile pursuit.

While numerous modifications have been made to the bis(imino)pyridine ligand architecture,[8,9] limitations such as a short catalyst lifetime and the formation of low-molecular-weight products persist. Attempts to rationally design catalyst precursors to overcome these challenges are complicated by the paucity of information regarding the nature of the propagating species. Open questions include the oxidation and spin state of the iron center during chain growth and the involvement, both electronically and chemically, of the bis(imino)pyridine ligand.[10,11]

In principle, treatment of a bis(imino)pyridine dialkyl complex with the appropriate borane or borate reagent could generate a single-component polymerization catalyst and provide insight into the nature of the active species. For many years, synthesis of the requisite bis(imino)pyridine iron dialkyl was a major obstacle to exploring this approach. Recently, several research groups have independently discovered reliable routes to this desirable class of compounds. Our laboratory reported that the addition of 2 equiv of $LiCH_2SiMe_3$ to (^{iPr}PDI)$FeCl_2$ (**1-Cl$_2$**;

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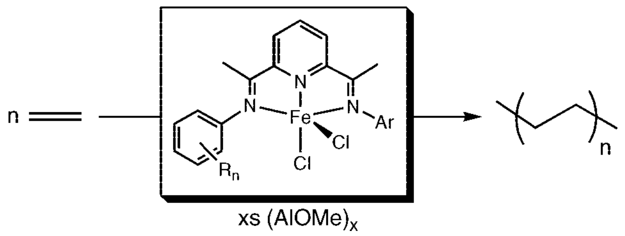


Figure 1. Bis(imino)pyridine iron complexes for ethylene polymerization.

^{iPr}PDI = 2,6-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CMe)$_2$C$_5$H$_3$N) yielded the corresponding dialkyl complex **1-(CH$_2$SiMe$_3$)$_2$**.[12] Shortly thereafter, Gambarotta and co-workers described a more detailed investigation of this reaction and discovered that alkylation of the bis(imino)pyridine chelate can be observed under certain experimental conditions.[13] In a method distinct from the others, Cámpora and co-workers have also described an elegant synthesis of bis(imino)pyridine iron dialkyl complexes by the addition of the free chelate, ^{iPr}PDI, to (pyridine)$_2$Fe(CH$_2$SiMe$_3$)$_2$.[14]

With the desired iron dialkyl compounds in hand, our laboratory reported that treatment of **1-(CH$_2$SiMe$_3$)$_2$** with the neutral borane B(C$_6$F$_5$)$_3$ resulted in silicon methide rather than iron alkyl abstraction and the formation of the bis(imino)pyridine iron alkyl cation, [(^{iPr}PDI)Fe(CH$_2$SiMe$_2$CH$_2$SiMe$_3$)][MeB(C$_6$F$_5$)$_3$].[15] Exposure of this compound to 1 atm of ethylene produced linear polyethylene with a narrow polydispersity and molecular weights comparable to those of traditional methyl aluminoxane (MAO)-activated precatalysts. Subsequently, Gambarotta and co-workers reported bis(imino)pyridine ligand alkylation,[16] transmetalation to aluminum,[17] and the formation of "ate" complexes[18] during various activation procedures, suggesting that a more complex activation process is likely operative with MAO.

In this contribution, we describe our continuing synthetic efforts in bis(imino)pyridine dialkyl chemistry. Particular attention has been devoted to understanding the influence of the organolithium reagent in the course of the alkylation reaction. Ligand substitution reactions have also been used to evaluate the relative stability of five-coordinate FeCH$_2$SiMe$_3$ and FeCH$_2$CMe$_3$ complexes.

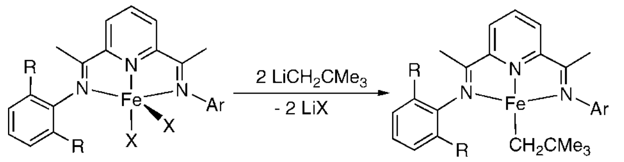
Results and Discussion

Alkylation of Bis(imino)pyridine Iron Dihalide Complexes. Previous reports in the literature indicate that the alkylation of bis(imino)pyridine iron dihalide compounds is sensitive to both the organolithium reagent and the aryl substituents on the bis(imino)pyridine chelate. For example, treatment of **1-Cl$_2$** with 2 equiv of LiCH$_2$SiMe$_3$ furnished the corresponding dialkyl, **1-(CH$_2$SiMe$_3$)$_2$**, while the addition of 2 equiv of methyllithium resulted in reductive alkylation to yield the monoalkyl complex, **1-Me** (Figure 2).[12]

The steric environment imparted by the aryl substituents also impacts the outcome of the alkylation reaction. Changing the 2,6-diisopropylaryl groups to 2,6-diethyl substituents resulted in a mixture of the dialkylated product, **2-(CH$_2$SiMe$_3$)$_2$**, and the product of reductive alkylation, **2-CH$_2$SiMe$_3$** (Figure 2).[12] The monoalkyl derivative was also independently prepared by alkylation of **2-Cl** with LiCH$_2$SiMe$_3$.[12] In our initial communication,[12] we incorrectly reported that **1-Cl** does not react with LiCH$_2$SiMe$_3$. We have subsequently discovered that the synthesis of **1-CH$_2$SiMe$_3$** proceeds in a straightforward manner by the addition of the alkyllithium reagent to either **1-Cl** or **1-Br** in diethyl ether. The similar ^{1}H NMR features of **1-Cl** and **1-CH$_2$SiMe$_3$** were likely the cause of our initial error. A comparison of representative spectra is reported in the Supporting Information.

The differences in the outcome of the dialkylation reactions prompted a more systematic study of the chemistry of the bis(imino)pyridine iron dihalide complexes, **1-Cl$_2$** and **1-Br$_2$**, with organolithium reagents. Because treatment of **1-(CH$_2$SiMe$_3$)$_2$** with B(C$_6$F$_5$)$_3$ resulted in silicon methide rather than iron alkyl abstraction,[15] we have targeted the preparation of the bis(neopentyl) analogue. The preparation of the corresponding bis(imino)pyridine iron neopentyl cation may also allow evaluation of the role of β-methyl elimination as a chain-transfer pathway in iron polymerization catalysis.[19]

The addition of 2 equiv of LiCH$_2$CMe$_3$ to a diethyl ether slurry of either **1-Cl$_2$** or **1-Br$_2$**, followed by filtration and recrystallization from pentane at −35 °C, furnished the bis(imino)pyridine iron mono(neopentyl) complex, **1-Np**, arising from reductive alkylation (eq 1). In an independent experiment, the addition of 1 equiv of LiCH$_2$CMe$_3$ to the bis(imino)pyridine iron monobromide, **1-Br**, also yielded **1-Np**, suggesting that the first 1 equiv of the alkyllithium serves to reduce **1-Br$_2$** to **1-Br** and the second results in alkylation. A similar reduction of **1-Cl$_2$** to **1-Cl** with 1 equiv of LiCH$_2$SiMe$_3$ or LiMe has also been reported.[12] For the reductive alkylation of **1-Br$_2$** with 2 equiv of LiCH$_2$CMe$_3$, both Me$_3$CCH$_2$CH$_2$CMe$_3$ and small amounts of neopentane were detected when the reaction was carried out in a sealed NMR tube. The iron mono(neopentyl) complex, **1-Np**, was isolated as a paramagnetic, dark-green solid. A benzene-d_6 solution magnetic moment of 4.0 μ_B was measured at 23 °C and is consistent with three unpaired electrons, similar to **1-Me**.[12] Despite the paramagnetism, the ^{1}H NMR spectra of **1-Np** and other alkyl derivatives reported in this work are informative and have been partially assigned. Diagnostic signals are reported in Table 1.



1-Cl$_2$: X = Cl; R = ^{i}Pr
1-Br$_2$: X = Br; R = ^{i}Pr
2-Cl$_2$: X = Cl; R = Et

1-Np: R = ^{i}Pr
2-Np: R = Et

(1)

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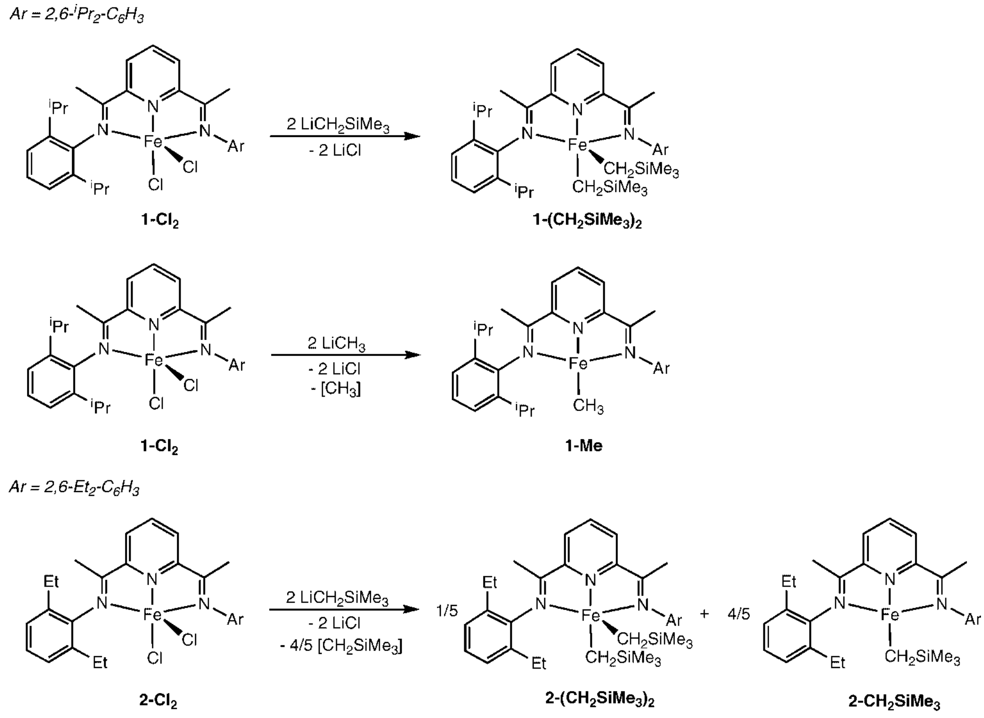


Figure 2. Alkylation of aryl-substituted bis(imino)pyridine iron compounds.

Table 1. ^{1}H NMR Chemical Shifts (in ppm) of Diagnostic Resonances for Bis(imino)pyridine Iron Mono- and Dialkyl Complexes in Benzene-d_6 at 293 K

	1-					2-		
	CH_2CMe_3	CH_2SiMe_3	Me	Ph	$(CH_2SIMe_3)_2$	CH_2CMe_3	CH_2SIMe_3	$(CH_2SiMe_3)_2$
$C(CH_3)$(imine)	−199.95	−206.76	−163.8	−153.70	−151.43	−192.59	−195.92	−150.37
m-pyr	63.80	66.93	58.9	64.37	64.57	67.38	68.78	59.83
p-pyr	374.05	*a*	216.5	216.59	238.45	347.84	345.04	285.53

[a] Not located.

Using the ^{1}H NMR spectrum of **1-Np** as a representative example, several salient features common to bis(imino)pyridine iron alkyl complexes are highlighted. In general, the in-plane hydrogens on the chelate exhibit relatively large deviations from their diamagnetic reference values. In benzene-d_6, the imine methyl groups for **1-Np** appear significantly upfield at −199.5 ppm. Likewise, the *m*- and *p*-pyridine hydrogens are observed downfield at 63.8 and 374.1 ppm, respectively (Table 1). For the orthogonal aryl groups, the chemical shift dispersion is less pronounced with the diasterotopic isopropyl methyls appearing at −19.56 and −33.94 ppm. A full description of all observed ^{1}H NMR resonances for each compound is reported in the Experimental Section.

A similar sequence of transformations was used to prepare **2-Np**. Treatment of **2-Br** or **2-Br$_2$** with 1 or 2 equiv of $LiCH_2CMe_3$, respectively, yielded the bis(imino)pyridine iron neopentyl compound. As with **1-Np**, **2-Np** was isolated as a dark-green, microcrystalline solid with a benzene-d_6 solution magnetic moment (23 °C) of 4.2 μ_B, consistent with an $S = {}^3/_2$ ground state. The ^{1}H NMR spectroscopic features of **2-Np** at 23 °C in benzene-d_6 are similar to those observed for **1-Np** (Table 1).

The solid-state structure of **2-Np** was also determined by X-ray diffraction. A representation of the molecular structure is presented in Figure 3, while selected metrical parameters are reported in Table 2. Modeling of the data suffered from complications because of rotational disorder in the methyl groups of the neopentyl ligand and the absence of long-range order. During the course of our investigations, crystals of **2-CH$_2$SiMe$_3$** suitable for X-ray diffraction were obtained. This molecule was previously reported and was synthesized by straightforward alkylation of **2-Br** with $LiCH_2SiMe_3$.[12] A representation of the molecular structure is also presented in Figure 3, and selected metrical parameters are reported in Table 2.

The overall molecular geometries of **2-Np** and **2-CH$_2$SiMe$_3$** are best described as distorted square planar, where the nitrogen atoms of the chelate and the iron centers define the plane and the Fe1−C30 vectors deviate. The distortions observed in **2-Np** and **2-CH$_2$SiMe$_3$** are likely a result of the steric pressure between the large [CMe$_3$] and [SiMe$_3$] substituents and the orthogonal ethyl aryl groups. By way of comparison, **1-Me** is nearly perfectly square planar.

Because the metrical parameters of **2-CH$_2$SiMe$_3$** are more reliable as a result of higher data quality and the absence of disorder, these will be discussed in detail. The imine N−C distances of 1.3177(17) and 1.3188(17) Å along with the $C_{imine}-C_{ipso}$ distances of 1.4397(16) and 1.4388(19) Å are indicative of one-electron chelate reduction.[10c,11] These data, in combination with the solution magnetic moment, suggest that this class of compound is best described as having a high-spin ferrous center ($S_{Fe} = 2$) antiferromagnetically coupled to a bis(imino)pyridine radical anion ($S_L = {}^1/_2$).[11]

The disparate behavior between alkylations with $LiCH_2SiMe_3$ and those with $LiCH_2CMe_3$ and $LiCH_3$ prompted an investigation into the synthesis of bis(imino)pyridine iron aryl compounds. Would aryllithium reagents result in diarylation or reductive arylation? Treatment of **1-Br$_2$** with 2 equiv of phenyllithium in either toluene or diethyl ether resulted in

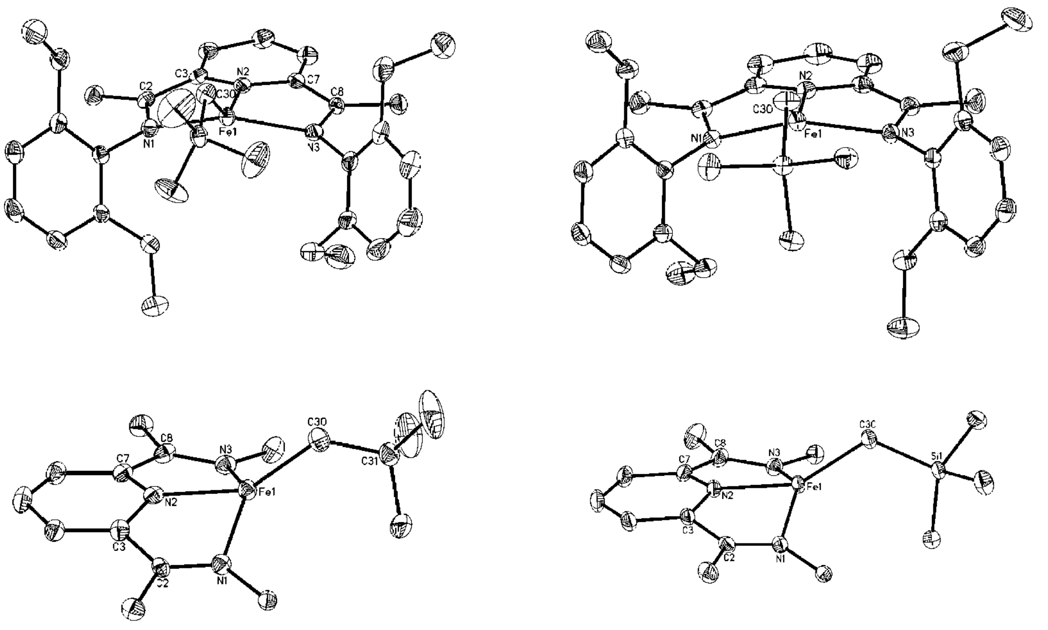
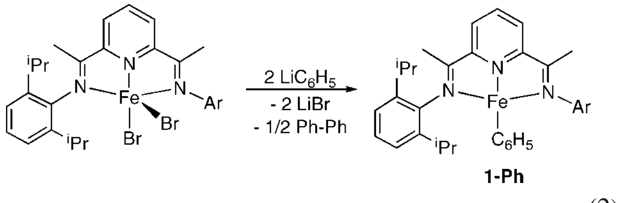


Figure 3. Molecular structures of **2-Np** (left) and **2-CH$_2$SiMe$_3$** (right) at 30% probability ellipsoids. Views of the cores of the molecules are shown below. Hydrogen atoms were omitted for clarity.

Table 2. Selected Metrical Parameters for 2-Np and 2-CH$_2$SiMe$_3$

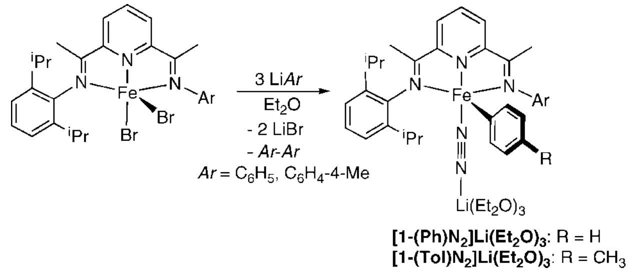
	2-Np	2-CH$_2$SiMe$_3$
Fe1−N1	2.158(3)	2.1100(9)
Fe1−N2	1.986(3)	1.9958(10)
Fe1−N3	2.126(3)	2.1187(10)
N1−C2	1.314(4)	1.3177(17)
N3−C8	1.329(4)	1.3188(17)
C2−C3	1.446(5)	1.4397(16)
C7−C8	1.428(5)	1.4388(19)
N2−C3	1.390(4)	1.3610(16)
N2−C7	1.366(4)	1.3587(15)
Fe1−C30	2.036(4)	2.0343(14)
N2−Fe1−C30	142.24(14)	147.40(5)
N2−Fe1−N1	75.08(10)	75.61(4)
N2−Fe1−N3	75.19(10)	75.62(4)
N1−Fe1−N3	136.68(11)	138.05(4)
C31/Si1−C30−Fe1	123.0(2)	117.33(8)

reductive arylation to furnish the bis(imino)pyridine iron phenyl complex, **1-Ph**, as a dark-green paramagnetic solid (eq 2). A stoichiometric quantity of biphenyl was also identified as a byproduct of the reaction and likely arises from the one electron reduction of the starting iron complex. A solution magnetic moment of 4.2 μ_B was measured for **1-Ph** in benzene-d_6 at 23 °C and is in agreement with those measured for **1-Me**[12] and **1-Np** and is also consistent with three unpaired electrons. Accordingly, the ^{1}H NMR spectrum in benzene-d_6 at 23 °C exhibits diagnostic resonances with large isotropic shifts for the in-plane hydrogens (Table 1).



(2)

Treatment of **1-Ph** with an additional 1 equiv of phenyllithium resulted in reduction and the formation of the bis(imino)pyridine iron phenyl "ate" complex, **[1-(Ph)N$_2$]Li(Et$_2$O)$_3$**, as a red solid (eq 3). Similar reactivity has been previously reported by Scott et al. for the corresponding iron methyl derivative, **1-Me**, where the addition of excess MeLi formed the corresponding iron methyl anion, **[Li(THF)$_4$][1-Me]**.[18] One notable difference between **[Li(THF)$_4$][1-Me]** and **[1-(Ph)N$_2$]Li(Et$_2$O)$_3$** is the coordination of dinitrogen in the latter molecule. A strong N≡N band was observed in the solution IR spectrum centered at 2069 cm^{-1}, consistent with weak activation of dinitrogen. A benzene-d_6 solution magnetic moment of 2.9 μ_B was measured at 23 °C, indicative of an $S = 1$ complex arising from the one-electron reduction of **1-Ph**. Because X-ray-quality crystals of **[1-(Ph)N$_2$]Li(Et$_2$O)$_3$** proved difficult to obtain, the tolyl variant was prepared by treatment of **1-Br$_2$** with 3 equiv of the aryllithium (eq 3). Using this procedure, **[1-(Tol)N$_2$]Li(Et$_2$O)$_3$** was isolated as a red paramagnetic solid with a measured benzene-d_6 solution magnetic moment of 2.7 μ_B, consistent with two unpaired electrons and an $S = 1$ complex. Assuming a similar electronic structure, such a moment is expected from the one-electron reduction of an $S = {}^3/_2$ monophenyl compound. Analogous to **[1-(Ph)N$_2$]Li(Et$_2$O)$_3$**, **[1-(Tol)N$_2$]Li(Et$_2$O)$_3$** exhibits a strong N≡N stretch centered at 2068 cm^{-1} in the solid state (KBr) IR spectrum. Unlike other bis(imino)pyridine iron alkyl derivatives prepared in this work, both **[1-(Ph)N$_2$]Li(Et$_2$O)$_3$** and **[1-(Tol)N$_2$]Li(Et$_2$O)$_3$** do not exhibit clearly observable peaks in the benzene-d_6 ^{1}H NMR spectrum at 23 °C.



(3)

The solid-state structure of **[1-(Tol)N$_2$]Li(Et$_2$O)$_3$** was determined by X-ray diffraction and is presented in Figure 4. Selected metrical parameters are reported in Table 3. In agreement with

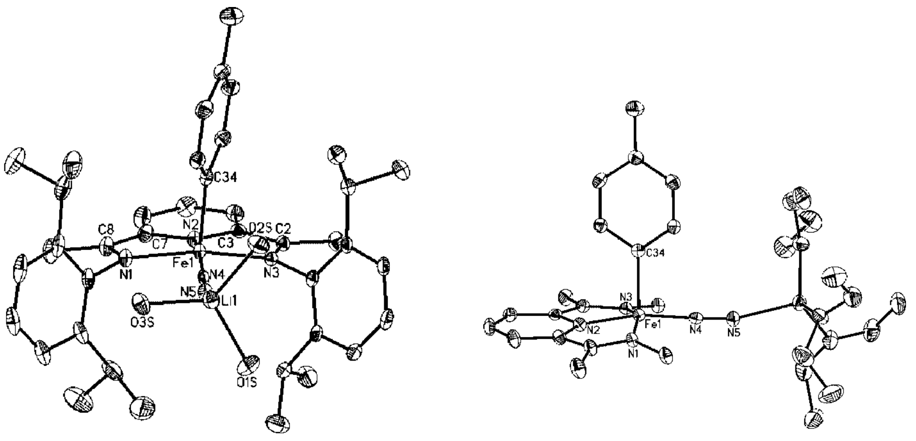


Figure 4. Molecular structure (left) of **[1-(Tol)N$_2$]Li(Et$_2$O)$_3$** at 30% probability ellipsoids, with diethyl ether carbons and all hydrogen atoms omitted for clarity. View of the core (right).

Table 3. Selected Metrical Parameters for [1-(Tol)N$_2$]Li(Et$_2$O)$_3$

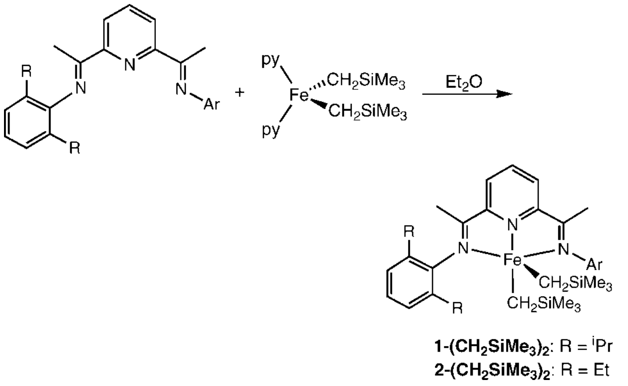
	[1-(Tol)N$_2$]Li(Et$_2$O)$_3$
Fe1−N1	1.9269(19)
Fe1−N2	1.837(2)
Fe1−N3	1.9269(19)
Fe1−N4	1.752(2)
N1−C8	1.356(3)
N3−C2	1.354(3)
C2−C3	1.407(3)
C7−C8	1.402(4)
N2−C3	1.382(3)
N2−C7	1.380(3)
Fe1−C34	2.005(2)
N4−N5	1.138(3)
N5−Li1	2.092(5)
N2−Fe1−N4	167.25(9)
N2−Fe1−N1	79.89(8)
N2−Fe1−N3	79.55(8)
N1−Fe1−N3	154.89(8)
N4−N5−Li1	164.8(2)

the IR data, dinitrogen coordination is observed where the dinitrogen ligand occupies one of the basal positions of an idealized square pyramid. Notably, lithium coordination occurs at the terminal nitrogen atom, but as evidenced by the N4−N5 distance of 1.138(3) Å, the iron center is not sufficiently reducing to activate the N≡N bond. The coordination sphere of the lithium atom is completed by three molecules of diethyl ether. Retention of the diethyl ether in bulk samples of this compound and **[1-(Ph)N$_2$]Li(Et$_2$O)$_3$** has been confirmed by combustion analyses and degradation experiments.

The metrical parameters of the bis(imino)pyridine ligand are consistent with two-electron reduction. Thus, reduction of **1-Ph** (and presumably **1-Tol**) to yield **[1-(Ph)N$_2$]Li(Et$_2$O)$_3$** (and **[1-(Tol)N$_2$]Li(Et$_2$O)$_3$**) occurs at the ligand rather than the iron center. Similar ligand-based reductions have been reported previously, notably the reduction of **1-X$_2$** to **1-X** (X = Cl, Br), where the bis(imino)pyridine is reduced from its neutral form to the radical anion and the iron maintains the ferrous oxidation state.[11] The two-electron reduction of the bis(imino)pyridine in **[1-(Tol)N$_2$]Li(Et$_2$O)$_3$** likely accounts for the weak activation of the dinitrogen ligand.

Addition of Bis(imino)pyridine Ligands to (Pyridine)$_2$-FeR$_2$ Complexes. Because of the complications associated with alkylation of bis(imino)pyridine iron dihalide compounds with organolithium reagents, alternative methods for the synthesis of the bis(neopentyl) and bis(aryl) compounds were explored. Cámpora and co-workers have reported a straightforward method for the preparation of bis(imino)pyridine iron dialkyl complexes by substitution of the pyridine ligands in py$_2$Fe(CH$_2$SiMe$_3$)$_2$ by the free chelate.[14]

Inspired by this synthetic route, we sought to extend this method to include **1-(CH$_2$SiMe$_3$)$_2$** and **2-(CH$_2$SiMe$_3$)$_2$**. Recall that attempts to prepare the latter compound by dialkylation of **2-Cl$_2$** with 2 equiv of LiCH$_2$SiMe$_3$ resulted in a mixture of **2-(CH$_2$SiMe$_3$)$_2$** and **2-CH$_2$SiMe$_3$**, where the dialkyl was the minor component.[12] The addition of either ^{iPr}PDI or ^{Et}PDI to a pentane solution of (py)$_2$Fe(CH$_2$SiMe$_3$)$_2$ furnished the corresponding bis(imino)pyridine iron dialkyl compounds, **1-(CH$_2$SiMe$_3$)$_2$** and **2-(CH$_2$SiMe$_3$)$_2$**, as bright purple, crystalline solids in 68 and 79% yields, respectively (eq 4). This method has proven quite robust, reproducible, and operationally simple. In a typical experiment, a pentane slurry of py$_4$FeCl$_2$ was treated with 2 equiv of LiCH$_2$SiMe$_3$, stirred for 1 h, and added to a pentane solution of the chelate. Good to excellent yields of **1-(CH$_2$SiMe$_3$)$_2$** and **2-(CH$_2$SiMe$_3$)$_2$** were obtained, and an excess of pyridine was not required to isolate analytically pure compounds.



(4)

During the course of these studies, X-ray-quality crystals of **2-(CH$_2$SiMe$_3$)$_2$** were obtained. A representation of the solid-state structure is presented in Figure 5, and selected metrical parameters are reported in Table 4. Also included in Table 4 are the values for **1-(CH$_2$SiMe$_3$)$_2$**. Not surprisingly, the metrical parameters for the two compounds are statistically indistinguishable, demonstrating little structural impact of modest modifications in the *o*-aryl substituents.

The successful application of py$_2$Fe(CH$_2$SiMe$_3$)$_2$ to the preparation of **1-(CH$_2$SiMe$_3$)$_2$**, **2-(CH$_2$SiMe$_3$)$_2$**, and other bis-

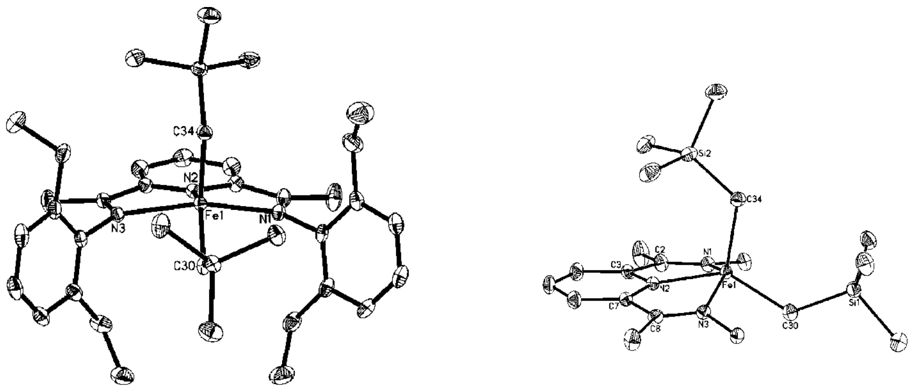
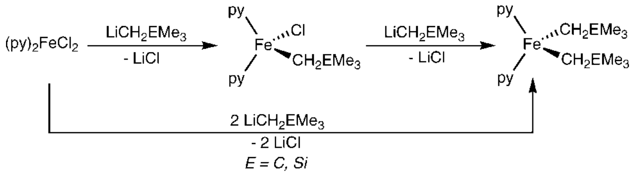


Figure 5. Molecular structure of **2-(CH_2SiMe_3)$_2$** at 30% probability ellipsoids (left) and the core of the molecule (right). Hydrogen atoms were omitted for clarity.

Table 4. Selected Metrical Parameters for 2-(CH_2SiMe_3)$_2$ and 1-(CH_2SiMe_3)$_2$

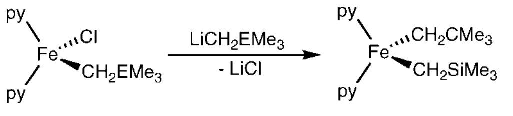
	2-(CH_2SiMe_3)$_2$	1-(CH_2SiMe_3)$_2$
Fe1−N1	2.2115(13)	2.2030(19)
Fe1−N2	2.0073(18)	2.0133(19)
Fe1−N3	2.2138(13)	2.263(2)
Fe1−C30	2.0537(18)	2.062(3)
Fe1−C34	2.0718(13)	2.054(3)
N1−C2	1.301(2)	1.302(3)
N3−C8	1.306(2)	1.301(3)
C2−C3	1.446(2)	1.448(3)
C7−C8	1.445(2)	1.454(3)
N2−C3	1.370(2)	
N2−C7	1.367(2)	
N2−Fe1−N1	73.63(5)	74.03(7)
N2−Fe1−N3	73.81(5)	72.88(7)
N1−Fe1−N3	142.26(5)	141.07(7)
C30−Fe1−C34	113.83(7)	112.00(11)

(imino)pyridine iron dialkyl derivatives[14] prompted investigation of related bis(neopentyl) chemistry. To our knowledge, the requisite dialkyl precursor, $py_2Fe(CH_2CMe_3)_2$, has not been reported. Treatment of py_4FeCl_2 with 1 equiv of $LiCH_2CMe_3$ furnished the ferrous monoalkyl monochloride compound, $py_2Fe(CH_2CMe_3)Cl$, isolated as an orange solid (eq 5). Subsequent addition of a second 1 equiv of $LiCH_2CMe_3$ to $py_2Fe(CH_2CMe_3)Cl$ furnished a purple solid identified as the desired bis(neopentyl) ferrous complex, $(py)_2Fe(CH_2CMe_3)_2$ (eq 5). This compound was also prepared directly from py_4FeCl_2 with 2 equiv of $LiCH_2CMe_3$.



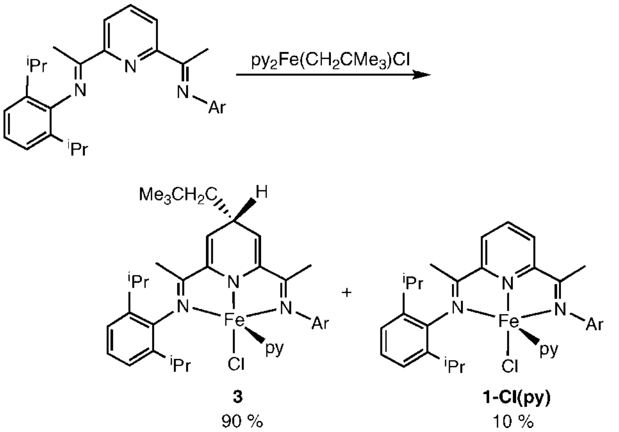
(5)

The isolation of $py_2Fe(CH_2CMe_3)Cl$ prompted the synthesis of the corresponding neosilyl derivative as well as mixed dialkyl compounds. The monoalkyl, $py_2Fe(CH_2SiMe_3)Cl$, was prepared analogously to $py_2Fe(CH_2CMe_3)Cl$ by treatment of py_4FeCl_2 with 1 equiv of $LiCH_2SiMe_3$ and isolated as a red oil. The mixed iron dialkyl compound, $py_2Fe(CH_2CMe_3)(CH_2SiMe_3)$, was isolated as a purple oil and was synthesized by treatment of either $py_2Fe(CH_2CMe_3)Cl$ with $LiCH_2SiMe_3$ or $py_2Fe(CH_2SiMe_3)Cl$ with $LiCH_2CMe_3$ (eq 6). Despite each complex containing a high-spin, $S = 2$ ferrous ion,[14] the ^{1}H NMR spectrum of each of these compounds is informative and useful for characterization. Representative spectra of each compound are presented in Figure 6. Each compound exhibits a downfield-shifted peak assigned to the *o*-pyridine hydrogens while the *meta* and *para* peaks appear closer to their diamagnetic reference values. For all cases studied, the methylene hydrogens adjacent to the iron center have not been located.



(6)

With a family of bis(pyridine) ferrous alkyl starting materials in hand, substitution of the pyridine by bis(imino)pyridine chelates was explored. The addition of ^{iPr}PDI to a pentane solution of $py_2Fe(CH_2CMe_3)Cl$ yielded a 9:1 mixture of two paramagnetic iron products (eq 7). The major product, **3**, was identified as the iron monochloride pyridine complex where the neopentyl group has migrated to the *para* position of the pyridine ring in the chelate. Similar reactivity was reported by Cámpora and co-workers by the treatment of $MnR_2(THF)$ (R = CH_2CMe_2Ph, CH_2Ph, $CH_2CH{=}CH_2$) with ^{iPr}PDI.[20] In the iron chemistry, the minor product, accounting for approximately 10% of the mixture, is the bis(imino)pyridine iron monochloride pyridine compound, **1-Cl(py)**, where the ^{iPr}PDI chelate has not been substituted. This compound was independently prepared by adding a slight excess of pyridine to **1-Cl**. From this synthetic



(7)

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(20) Cámpora, J.; Pérez, C. M.; Rodríguez-Delgado, A.; Naz, A. M.; Palma, P.; Álvarez, E. *Organometallics* **2007**, *26*, 1104.

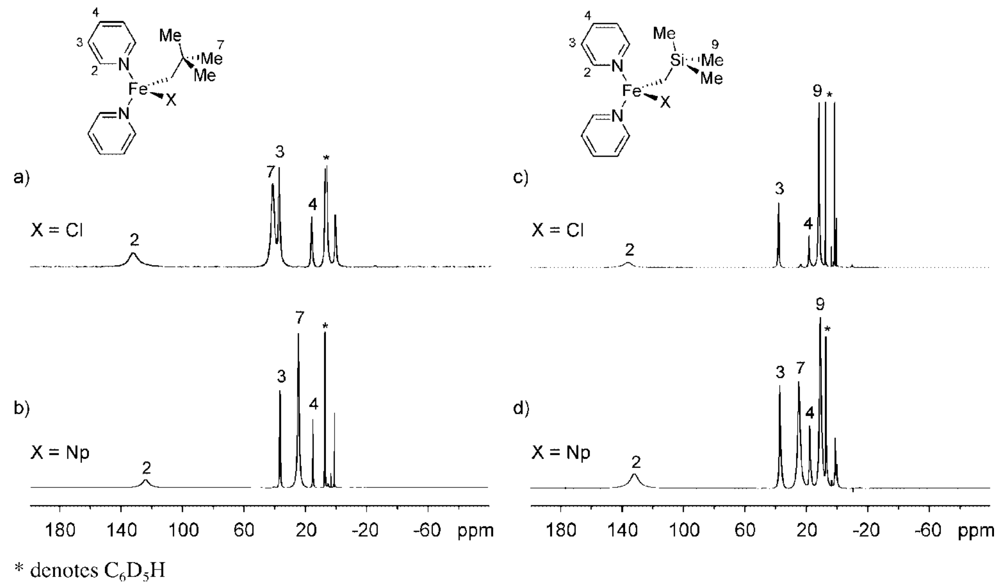


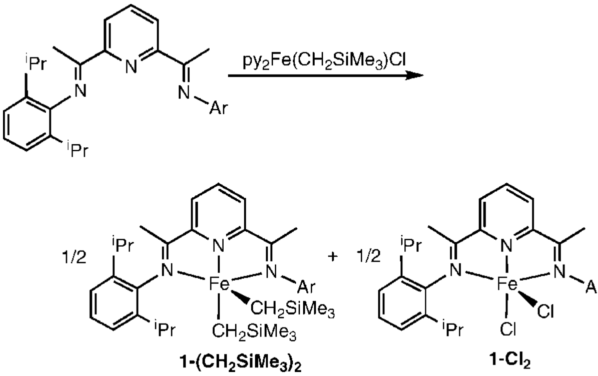
Figure 6. Representative ^{1}H NMR spectra of bis(pyridine) ferrous alkyl compounds in benzene-d_6 at 23 °C.

method, **1-Cl(py)** was fully characterized by ^{1}H NMR spectroscopy and X-ray diffraction (see the Supporting Information).

Confirmation of the ligand modification in **3** was obtained by aerobic hydrolysis of the reaction mixture and analysis of the organic products by mass spectrometry. A parent ion peak at 551.3 amu was observed, corresponding to the mass of the bis(imino)pyridine ligand with a neopentyl substituent. The ^{1}H NMR spectrum in benzene-d_6 of the substituted free ligand also confirms substitution in the *p*-pyridine position. The hydrogens of the *m*-pyridine, which typically appear as a doublet centered at 8.50 ppm, appear as a singlet at 8.53 ppm.

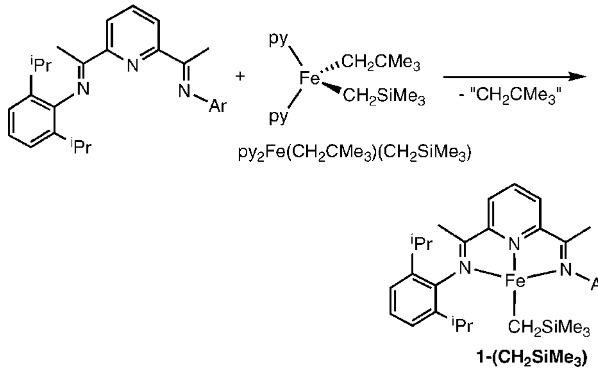
Similar ligand substitution reactivity was observed upon the addition of ^{iPr}PDI to py$_2$Fe(CH$_2$CMe$_3$)$_2$. In this case, a purple product, tentatively identified as the iron neopentyl pyridine compound, was formed. However, the reaction produced several other products. Notably, aerobic hydrolysis furnished the free bis(imino)pyridine ligand with a neopentyl substituent in the *p*-pyridine position, as evidenced by ^{1}H NMR spectroscopy and mass spectrometry.

Further insight into the relative stability of bis(imino)pyridine iron dialkyl complexes was gained from studying the reactivity of py$_2$Fe(CH$_2$SiMe$_3$)Cl and py$_2$Fe(CH$_2$CMe$_3$)(CH$_2$SiMe$_3$) with ^{iPr}PDI. The addition of 1 equiv of chelate to py$_2$Fe(CH$_2$SiMe$_3$)Cl cleanly yielded a mixture of the bis(imino)pyridine iron dialkyl, **1-(CH$_2$SiMe$_3$)$_2$**, and the corresponding ferrous dichloride, **1-Cl$_2$**,[1] arising from ligand redistribution (eq 8). The observation of **1-(CH$_2$SiMe$_3$)$_2$** and **1-Cl$_2$** from this synthetic procedure demonstrates the relative instability of the putative bis(imino)pyridine iron alkyl chloride complex, **1-(CH$_2$SiMe$_3$)Cl**. While by no means conclusive, the inability to observe this species may indicate that the dialkylation of **1-Cl$_2$** may proceed via the initial formation of **1-(CH$_2$SiMe$_3$)Cl** followed by rapid ligand redistribution.



(8)

The addition of ^{iPr}PDI to the mixed ferrous dialkyl, py$_2$Fe(CH$_2$CMe$_3$)(CH$_2$SiMe$_3$), resulted in clean and near-quantitative formation of the bis(imino)pyridine iron monoalkyl complex, **1-CH$_2$SiMe$_3$**, with loss of the neopentyl fragment (eq 9). This result clearly establishes the preference for Fe-CH$_2$SiMe$_3$ over Fe-CH$_2$CMe$_3$ bond formation offers insight into the inability to synthesize (^{iPr}PDI)Fe(CH$_2$CMe$_3$)$_2$. If formed, this compound likely would eject [CH$_2$CMe$_3$], demonstrating that isolation of **1-Np** from treatment of **1-Cl$_2$** with LiCH$_2$CMe$_3$ is not solely a consequence of the alkyllithium reagent.



(9)

Hydrogenation and Thermal Stability of Bis(imino)pyridine Iron Alkyl Complexes. Preliminary reactivity studies were carried out with the bis(imino)pyridine iron alkyl complexes. Given their ease of synthesis, we are particularly interested in using these compounds as catalytic precursors and synthons for neutral ligand derivatives.[21] Mild thermolysis of **1-(CH$_2$SiMe$_3$)$_2$** or **2-(CH$_2$SiMe$_3$)$_2$** at 45 °C in benzene-d_6 resulted in decomposition to an intractable mixture of products. Repeating the

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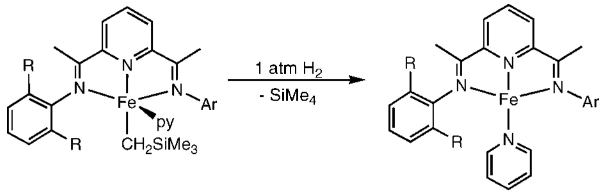
(21) Bart, S. C.; Lobkovsky, E.; Bill, E.; Wieghardt, K.; Chirik, P. J. *Inorg. Chem.* **2007**, *46*, 7055.

experiments in the presence of a slight excess of pyridine cleanly yielded the iron alkyl pyridine compounds **1-(CH_2SiMe_3)py** and **2-(CH_2SiMe_3)py**. Both molecules were independently synthesized by the addition of pyridine to the corresponding iron monoalkyl. Notably, the qualitative rate of conversion is the same in the presence and absence of pyridine, suggesting that the added ligand merely traps the monoalkyl formed from iron−carbon bond homolysis, thereby preventing further decomposition.

Exposure of benzene-d_6 solutions of either **1-(CH_2SiMe_3)$_2$** or **2-(CH_2SiMe_3)$_2$** to 1 atm of dihydrogen also produced a complex mixture of products from which $SiMe_4$ was identified (^{1}H NMR). In contrast, the addition of 1 atm of H_2 to either **1-(CH_2SiMe_3)py** or **2-(CH_2SiMe_3)py** in benzene-d_6 resulted in clean hydrogenolysis of the iron−carbon bond to yield the bis(imino)pyridine iron pyridine compounds (eq 10). An independent synthesis of **1-py** was accomplished by the addition of pyridine to **1-(N_2)$_2$**. Because our laboratory has yet to find a synthetic route to **2-(N_2)$_2$**, the hydrogenation of **2-(CH_2SiMe_3)py** to **2-py** represents a unique method to access compounds of this type. The benzene-d_6 ^{1}H NMR spectrum of **2-py** is diagnostic of a compound exhibiting temperature-independent paramagnetism.[11] The imine methyl group, which normally appears in the vicinity of 2 ppm, is shifted upfield to −5.08 ppm, while the *m*- and *p*-hydrogens of the chelate are shifted downfield to 11.21 and 9.12 ppm, respectively. The resonances for the orthogonal aryl substituents and the pyridine ligand are observed close to their diamagnetic reference values.



1-(CH_2SiMe_3): R = ^{i}Pr
2-(CH_2SiMe_3): R = Et

1-py: R = ^{i}Pr
2-py: R = Et

(10)

Concluding Remarks

Exploration of the alkylation and arylation chemistry of aryl-substituted bis(imino)pyridine iron complexes with alkyl- and aryllithium reagents demonstrates the unique chemistry associated with $LiCH_2SiMe_3$. Only with this reagent and 2,6-diisopropyl aryl groups on the iron complex has dialkylation been observed. Treatment of the bis(imino)pyridine iron dihalide complexes with methyl-, neopentyl-, or phenyllithium resulted in exclusive formation of the iron monoalkyl (or aryl) complex, arising from reductive alkylation. Further probes into the origin of this behavior by treatment of py_2FeR_2 (R = CH_2SiMe_3, CH_2CMe_3) with free bis(imino)pyridine ligands demonstrate the inherent instability of the iron bis(neopentyl) compounds. In lieu of the desired dialkyl, ejection of the alkyl radical or migration of the neopentyl group to the *p*-pyridine position of the ligand was observed.

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.[22] Hydrogen and deuterium gases were passed through a column containing manganese oxide supported on vermiculite and 4 Å molecular sieves before admission to the high-vacuum line. Benzene-d_6 and toluene-d_8 were purchased from Cambridge Isotope Laboratories and dried over 4 Å molecular sieves or titanocene, respectively. Both PhLi and $LiCH_2SiMe_3$ solutions were purchased from Aldrich. **1-Br_2**, **1-Br**,[12] **1-(CH_2SiMe_3)$_2$**,[12] **1-Cl**,[12] **2-Cl**,[12] **2-CH_2SiMe_3**,[12] ^{iPr}PDI,[1] $LiCH_2CMe_3$,[23] py_4FeCl_2[24] and $py_2Fe(CH_2SiMe_3)_2$[14] were prepared according to literature procedures.

^{1}H NMR spectra were recorded on Varian Mercury 300 and Inova 400 and 500 spectrometers operating at 299.76, 399.78, and 500.62 MHz, respectively. All ^{1}H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ using ^{1}H (residual) and ^{13}C NMR chemical shifts of the solvent as a secondary standard. Solution magnetic moments were determined by the Evans method[25] using a ferrocene standard and are the average value of at least two independent measurements. ^{1}H NMR multiplicity and coupling constants are reported where applicable. Peak width at half-height is given for paramagnetically broadened resonances. 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 = 0.710 73 Å). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of the 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.

Preparation of (^{iPr}PDI)$FeCH_2CMe_3$ (1-Np). A 250 mL round-bottomed flask was charged with 0.100 g (0.175 mmol) of **1-Cl** and approximately 100 mL of diethyl ether. The resulting solution was placed in a liquid-nitrogen-chilled cold well for approximately 20 min. A second diethyl ether solution containing 0.014 g (0.175 mmol) of neopentyllithium in 15 mL of solvent was prepared and added dropwise to the cold stirring solution of **1-Cl**. The solution changed color slightly over the course of 2 h from bright green to brownish green. At this time, the solution was filtered through a Celite-fitted frit and the solvent was removed in vacuo to yield 0.090 g (85%) of a dark-olive-colored powder identified as **1-Np**. Anal. Calcd for $C_{38}H_{54}N_3Fe$: C, 74.98; H, 8.94; N, 6.90. Found: C, 74.63; H, 9.19; N, 6.47. Magnetic susceptibility (benzene-d_6, 293 K): μ_{eff} 4.0 μ_B. ^{1}H NMR (benzene-d_6, 293 K): δ 374.05 (169 Hz, 1H, *p*-pyr), 86.68 (367 Hz, 9H, $C(CH_3)_3$), 63.80 (67 Hz, *m*-pyr), −11.27 (23 Hz, 4H, *m*-aryl), −16.21 (20 Hz, 2H, *p*-aryl), −19.56 (29 Hz, 12H, $CH(CH_3)_2$), −33.94 (87 Hz, 12H, $CH(CH_3)_2$), −118.94 (371 Hz, 4H, $CH(CH_3)_2$), −199.95 (143 Hz, 6H, $C(CH_3)$); the $FeCH_2C(CH_3)_3$ resonance was not located.

Preparation of (^{Et}PDI)$FeCH_2CMe_3$ (2-Np). This complex was prepared in a manner similar to that of **1-Np** with 0.250 g (0.484 mmol) of **2-Cl** and 0.045 g (0.484 mmol) of neopentyllithium to yield 0.143 g (54%) of a dark-green powder identified as **2-Np**. Anal. Calcd for $C_{34}H_{46}N_3Fe$: C, 73.90; H, 8.39; N, 7.60. Found: C, 73.84; H, 8.03; N, 7.28. Magnetic susceptibility (benzene-d_6, 293 K): μ_{eff} 4.2 μ_B. ^{1}H NMR (benzene-d_6, 293 K): δ 347.84 (235 Hz, 1H, *p*-pyr), 91.06 (443 Hz, 9H, $C(CH_3)_3$), 67.38 (87 Hz, 2H, *m*-pyr), −11.90 (37 Hz, 4H, *m*-aryl), −16.09 (31 Hz, 2H, *p*-aryl), −27.70 (68 Hz, 12H, CH_2CH_3), −66.10 (257 Hz, 2H, CH_2CH_3), −82.35

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(22) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(23) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.

(24) Baudisch, O.; Hartung, W. H. *Inorg. Synth.* **1939**, *1*, 184.

(25) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.

(308 Hz, 2H, CH_2CH$_3$), −192.59 (62 Hz, 6H, C(CH_3)); the FeCH_2C(CH$_3$)$_3$ resonance was not located.

Preparation of (^{iPr}PDI)FeC$_6$H$_5$ (1-Ph). A 20 mL scintillation vial was charged with 0.400 g (0.57 mmol) of **1-Br$_2$**, and a slurry formed with diethyl ether. The mixture was chilled in a −35 °C freezer for approximately 30 min, after which time a solution of phenyllithium (0.64 mL, 1.8 M in di-*n*-dibutyl ether) was added dropwise. The blue slurry immediately became a dark-green solution. The resulting reaction mixture was stirred for 30 min, and the volatiles were removed in vacuo. The solid residue was dissolved in approximately 5 mL of pentane, filtered through Celite, and cooled at −35 °C overnight to afford 0.136 g (39%) of **1-Ph** as a green crystalline solid. Anal. Calcd for C$_{39}$H$_{48}$FeN$_3$: C, 76.21; H, 7.87; N, 6.84. Found: C, 75.97; H, 7.49; N, 6.94. Magnetic susceptibility (benzene-d_6, 293 K): μ_{eff} 4.2 μ_B. ^{1}H NMR (benzene-d_6, 293 K): δ 216.59 (130 Hz, 1H, *p*-pyr), 64.37 (464 Hz, 2H, *m*-pyr), 50.80 (56 Hz, 4H, *m*-Ph), 50.11 (61 Hz, 4H, *o*-Ph), 11.21 (70 Hz, 1H, *p*-Ph), −3.40 (19 Hz, 4H, *m*-aryl), −12.01 (21 Hz, 12H, CHCH_{32}), −18.63 (68 Hz, 12H, CH(CH_3)$_2$), −79.87 (477 Hz, 4H, CH(CH$_3$)$_2$), −153.70 (73 Hz, 6H, C(CH_3).

Preparation of [(^{iPr}PDI)Fe(C$_6$H$_4$-*p*-CH$_3$)N$_2$]Li(Et$_2$O)$_3$ ([(1-Tol)N$_2$]Li(Et$_2$O)$_3$). A 20 mL scintillation vial was charged with 0.100 g (0.17 mmol) of **1-(N$_2$)$_2$**, and approximately 10 mL of diethyl ether was added to form a green solution. The solution was cooled at −35 °C for approximately 30 min, after which time a diethyl ether solution of *p*-tolyllithium (0.033 g, 0.34 mmol) was added dropwise. The green solution immediately turned to a dark-red solution. The resulting reaction mixture was stirred for 30 min, and the volatiles were removed in vacuo. The resulting solid was dissolved in approximately 1–2 mL of diethyl ether, filtered through Celite, and cooled at −35 °C overnight, yielding 0.065 g (43%) of red crystals identified as **[1-(Tol)N$_2$]Li(Et$_2$O)$_3$**. Anal. Calcd for C$_{52}$H$_{80}$FeLiN$_5$O$_3$: C, 70.49; H, 9.10; N, 7.90. Found: C, 69.99; H, 9.16; N, 7.84. Magnetic susceptibility (benzene-d_6, 293 K): μ_{eff} 2.7 μ_B. IR (pentane): ν_{N_2} 2068 cm^{-1}.

Preparation of [(^{iPr}PDI)Fe(C$_6$H$_5$)N$_2$]Li(Et$_2$O)$_3$ ([1-(Ph)N$_2$]Li(Et$_2$O)$_3$). This molecule was prepared in a manner similar to that of **[1-(Tol)N$_2$]Li(Et$_2$O)$_3$** (vide infra) with 0.400 g (0.57 mmol) of **1-Br$_2$** and 0.98 mL of 1.8 M phenyllithium in di-*n*-butyl ether, yielding 0.235 g (47%) of **[1-(Ph)N$_2$]Li(Et$_2$O)$_3$** as a red crystalline solid. Anal. Calcd for C$_{51}$H$_{78}$FeLiN$_5$O$_3$: C, 70.25; H, 9.02; N, 8.03. Found: C, 70.55; H, 8.99; N, 7.70. Magnetic susceptibility (benzene-d_6, 293 K): μ_{eff} 2.9 μ_B. IR (pentane): ν_{N_2} 2069 cm^{-1}.

Alternative Procedure for the Preparation of (^{iPr}PDI)Fe(CH$_2$SiMe$_3$)$_2$ (1-(CH$_2$SiMe$_3$)$_2$). A 20 mL scintillation vial was charged with 0.200 g (0.45 mmol) of (py)$_4$FeCl$_2$ and 2 mL of pentane, forming a slurry. The mixture was cooled at −35 °C for approximately 30 min, after which time a pentane solution of LiCH$_2$SiMe$_3$ (0.084 g, 0.90 mmol) was added dropwise. The yellow slurry turned dark purple and was stirred for 1–2 h at ambient temperature. After this time, the reaction mixture was filtered through Celite and the filtrate transferred to a new vial. This solution was then chilled at −35 °C for approximately 30 min, after which time a pentane solution of the ^{iPr}PDI ligand (0.217 g, 0.45 mmo1) was added dropwise. The purple solution turned immediately dark violet and was stirred for 1–2 h at ambient temperature. After this time, the reaction mixture was filtered through Celite and the volatiles from the filtrate were removed in vacuo. The resulting solid was dissolved in approximately 2–4 mL of pentane and cooled at −35 °C overnight to afford 0.217 g (68%) of **1-(CH$_2$SiMe$_3$)$_2$** as a light-violet crystalline solid. The product has spectroscopic properties identical with those of authentic **1-(CH$_2$SiMe$_3$)$_2$** prepared by previously reported procedures.[12]

Improved Procedure for the Preparation of (^{Et}PDI)Fe(CH$_2$SiMe$_3$)$_2$ (2-(CH$_2$SiMe$_3$)$_2$). A procedure similar to that for **1-(CH$_2$SiMe$_3$)$_2$** was used with 0.200 g (0.45 mmol) of py$_4$FeCl$_2$ and 0.192 g (0.45 mmol) of ^{Et}PDI, yielding 0.233 g (79%) of deep-purple crystals identified as **2-(CH$_2$SiMe$_3$)$_2$**. Anal. Calcd for C$_{37}$H$_{57}$FeN$_3$Si$_2$: C, 67.76; H, 8.76; N, 6.41. Found: C, 67.89; H, 8.49; N: 6.37. Magnetic susceptibility (benzene-d_6, 293 K): μ_{eff} 5.3 μ_B. ^{1}H NMR (benzene-d_6, 298 K): δ 285.58 (405 Hz, 1H, *p*-pyr), 59.81 (173 Hz, 2H, *m*-pyr), 26.16 (326 Hz, 4H, CH_2CH$_3$), 21.83 (2960 Hz, 4H, CH_2CH$_3$), 11.98 (434 Hz, 18H, Si(CH_3)$_3$), 0.15 (218 Hz, 12H, CH$_2$CH_3), −16.72 (69 Hz, 4H, *m*-aryl), −150.31 (563 Hz, 6H, C(CH_3)); two peaks were not located.

Preparation of (^{iPr}PDI)Fe(CH$_2$Si(CH$_3$)$_3$) (1-CH$_2$SiMe$_3$). A 20 mL scintillation vial was charged with 0.100 g (0.162 mmol) of **1-Br** (or 0.093 g of **1-Cl**) and diethyl ether, forming a slurry. The solution was cooled at −35 °C for approximately 30 min, after which time a diethyl ether solution of LiCH$_2$SiMe$_3$ (0.015 g, 0.16 mmol) was added dropwise. The blue slurry immediately turned to a soluble dark-green solution. The resulting reaction mixture was stirred for 30 min, and the volatiles were removed in vacuo. The resulting solid was dissolved in approximately 2–3 mL of pentane, filtered through Celite, and cooled at −35 °C overnight to yield 0.079 g (78%) of compound **1-CH$_2$SiMe$_3$** as a green crystalline solid. Anal. Calcd for C$_{37}$H$_{54}$FeN$_3$Si: C, 71.13; H, 8.71; N, 6.73. Found: C, 70.81; H, 8.47; N, 6.44. Magnetic susceptibility (benzene-d_6, 293 K): μ_{eff} 3.8 μ_B. ^{1}H NMR (benzene-d_6, 298 K): δ 66.93 (96 Hz, 2H, *m*-pyr), 48.80 (169 Hz, 9H, C(CH_3)$_3$), −11.22 (31 Hz, 1H, *m*-aryl), −17.87 (23 Hz, 2H, *p*-aryl), −18.90 (40 Hz, 12H, CH(CH_3)$_2$), −32.46 (107 Hz, 12H, CH(CH_3)$_2$), −109.04 (531 Hz, 4H, CH(CH$_3$)$_2$), −206.76 (150 Hz, 6H, C(CH_3)); *p*-pyr and FeCH_2C(CH$_3$)$_3$ resonances were not located.

Preparation of (py)$_2$Fe(CH$_2$SiMe$_3$)Cl. A 20 mL scintillation vial was charged with 0.200 g (0.45 mmol) of (py)$_4$FeCl$_2$ and pentane, forming a slurry. The mixture was cooled at −35 °C for approximately 30 min, after which time a pentane solution of LiCH$_2$SiMe$_3$ (0.042 g, 0.45 mmo1) was added dropwise. The yellow slurry turned dark red and was stirred for 1–2 h at room temperature. The resulting reaction mixture was filtered through Celite, and the volatiles were removed in vacuo to afford 0.131 g (86%) of a red oil identified as (py)$_2$Fe(CH$_2$SiMe$_3$)Cl. ^{1}H NMR (benzene-d_6, 298 K): δ 136.17 (2226 Hz, 4H, *o*-pyr), 37.69 (215 Hz, 4H, *m*-pyr), 17.82. (230 Hz, 2H, *p*-pyr), 11.32 (223 Hz, 9H, Si(CH_3)$_3$); the FeCH_2Si(CH$_3$)$_3$ resonance was not located.

Preparation of (py)$_2$Fe(CH$_2$CMe$_3$)Cl. This compound was prepared in a manner similar to that of (py)$_2$Fe(CH$_2$SiMe$_3$)Cl with 0.200 g (0.45 mmol) of (py)$_4$FeCl$_2$ and 0.035 g (0.45 mmo1) of LiCH$_2$CMe$_3$, yielding 0.102 g (71%) of an orange crystalline solid identified as (py)$_2$Fe(CH$_2$CMe$_3$)Cl. ^{1}H NMR (benzene-d_6, 298 K): δ 132.63 (2055 Hz, 4H, *o*-pyr), 41.76 (938 Hz, 9H, C(CH_3)$_3$), 37.63 (456 Hz, 4H, *m*-pyr), 16.38 (364 Hz, 2H, *p*-pyr); the FeCH_2C(CH$_3$)$_3$ resonance was not located.

Preparation of (py)$_2$Fe(CH$_2$CMe$_3$)$_2$. A 20 mL scintillation vial was charged with 0.200 g (0.45 mmol) of (py)$_4$FeCl$_2$ and approximately 2 mL of pentane, forming a slurry. The solution was cooled at −35 °C for approximately 30 min, after which time a pentane solution of LiCH$_2$CMe$_3$ (0.071 mg, 0.91 mmol) was added dropwise. The yellow slurry turned dark purple and was stirred for 1–2 h at ambient temperature. The resulting reaction mixture was filtered through Celite, and the volatiles were removed in vacuo. The residue was dissolved in approximately 1–2 mL of pentane and cooled at −35 °C overnight to afford 0.095 g (59%) of (py)$_2$Fe(CH$_2$CMe$_3$)$_2$ as a purple crystalline solid. ^{1}H NMR (benzene-d_6, 298 K): δ 124.56 (1735 Hz, 4H, *o*-pyr), 36.50 (166 Hz, 4H, *m*-pyr), 24.53 (428 Hz, 18H, C(CH_3)$_3$), 15.03 (118 Hz, 2H, *p*-pyr); the FeCH_2C(CH$_3$)$_3$ resonance was not located.

Preparation of (py)$_2$Fe(CH$_2$CMe$_3$)(CH$_2$SiMe$_3$). A 20 mL scintillation vial was charged with 0.200 g (0.62 mmol) of (py)$_2$Fe(CH$_2$CMe$_3$)Cl and approximately 5 mL of diethyl ether. The solution was cooled at −35 °C for approximately 30 min, after which time a diethyl ether solution of LiCH$_2$SiMe$_3$ (0.058 g, 0.62 mmo1) was added dropwise. The orange solution turned dark red and was stirred for 1–2 h at ambient temperature. The resulting reaction mixture was filtered through Celite, and the volatiles were removed in vacuo to afford 0.192 mg (83%) of a red oil identified as $(py)_2Fe(CH_2CMe_3)(CH_2SiMe_3)$ ^{1}H NMR (benzene-d_6, 298 K): δ 131.98 (2369 Hz, 4H, *o*-pyr), 37.10 (363 Hz, 4H, *m*-pyr), 24.76 (727 Hz, 9H, C(CH_3)$_3$), 17.62 (299 Hz, 2H, *p*-pyr), 10.82 (557 Hz, 9H, Si(CH_3)$_3$); the FeCH_2Si(CH$_3$)$_3$ and FeCH_2C(CH$_3$)$_3$ resonances were not located.

Preparation of (^{iPr}PDI)Fe(NC$_5$H$_5$) (1-py). A J. Young NMR tube was charged with 20 mg (0.032 mmol) of **1-CH$_2$SiMe$_3$**, approximately 0.5 mL of benzene-d_6, and 0.3 mL of pyridine. The tube was immersed in a liquid-nitrogen bath and evacuated on the high-vacuum line. One atmosphere of H$_2$ was added at –196 K. The contents of the tube was thawed and shaken overnight, yielding a purple solution of a compound identified as **1-py**. This compound was also independently prepared by treating **1-(N$_2$)$_2$** with pyridine.[21] ^{1}H NMR (benzene-d_6, 298 K): δ 11.64 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *m*-pyr-PDI), 9.25 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *p*-pyr-PDI), 7.61 (t, 2H, $^3J_{HH}$ = 7.6 Hz, *m*-aryl), 7.20 (d, 4H, $^3J_{HH}$ = 7.6 Hz, *p*-aryl), 6.78 (t, 1H, $^3J_{HH}$ = 7.6 Hz, *p*-pyr), 6.14 (t, 2H, $^3J_{HH}$ = 7.6 Hz, *m*-pyr), 5.72 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *o*-pyr), 2.34 (sept, 4H, $^3J_{HH}$ = 6.5 Hz, C*H*(Me)$_2$), 1.46 (d, 12H, $^3J_{HH}$ = 6.5 Hz, CH(*Me*)$_2$), 0.09 (d, 12H, $^3J_{HH}$ = 6.5 Hz, CH(*Me*)$_2$), −5.05 (s, 6H, C(*Me*)). ^{13}C{^{1}H} NMR (benzene-d_6, 298 K): δ 22.9 (CH(CH_3)$_2$), 24.5 (CH(CH_3)$_2$), 28.7 (C*H*(CH$_3$)$_2$), 37.6 (C(CH_3)), 104.1 (*p*-aryl), 123.8 (*m*-aryl), 124.5, 125.3, 127.5, 137.6 (C$_{ipso}$−aryl), 138.5, 147.9, 163.7 (C$_{ipso}$−aryl), 166.1 (C$_{ipso}$−pyr), 184.2 (C$_{imine}$).

Observation of (^{Et}PDI)Fe(NC$_5$H$_5$) (2-py). A J. Young NMR tube was charged with 20 mg (0.035 mmol) of **2-CH$_2$SiMe$_3$**, approximately 0.5 mL of benzene-d_6, and pyridine (3 μL, 0.037 mmol). The tube was immersed in a liquid-nitrogen bath and evacuated on the high-vacuum line prior to the addition of 1 atm of hydrogen. The solution was shaken overnight, affording a purple solution of a compound identified as **2-py**. Removing the excess of pyridine is necessary in order to observe sharp lines in the spectra. ^{1}H NMR (benzene-d_6, 298 K): δ 11.21 (bs, 2H, *m*-pyr-PDI), 9.12 (bs, 1H, *p*-pyr-PDI), 7.41 (bs, 2H, *p*-aryl), 7.04 (bs, 4H, *m*-aryl), 6.71 (bs, 1H, *p*-pyr), 5.76 (bs, 2H, *m*-pyr), 4.66 (bs, 2H, *o*-pyr), 2.14 (m, 4H, CH_2CH$_3$), 1.45 (m, 4H, CH_2CH$_3$), 0.74 (bs, 12H, CH$_2$CH_3), −5.08 (s, 6H, C(*Me*)).

Addition of ^{iPr}PDI to py$_2$Fe(CH$_2$CMe$_3$)Cl. A 20 mL scintillation vial was charged with 40 g (0.124 mmol) of py$_2$Fe(CH$_2$CMe$_3$)Cl dissolved in approximately 5 mL of pentane and cooled at −35 °C for 30 min. The ^{iPr}PDI ligand (60 mg, 0.124 mol) dissolved in pentane and precooled at the same temperature was added with stirring. Immediately upon addition, a dark-brown solution formed, which was filtered after 1–2 h through a pad of Celite to remove any particulates. The solvent was removed in vacuo, and the resulting brown oil was recrystallized from pentane at −35 °C to afford an about 9:1 mixture of **3** and **1-Cl(py)**. ^{1}H NMR of **3** (major product, benzene-d_6, 298 K): δ 36.05 (356 Hz), 15.47 (297 Hz), 6.06 (163 Hz), −2.84 (2737 Hz), −3.25 (2761 Hz), −12.71 (188 Hz), −32.36 (295 Hz); several peaks were not located. ^{1}H NMR of **1-Cl(py)** (minor product, benzene-d_6, 298 K): δ 328.18 (104 Hz, 1H, *p*-pyr-PDI), 120.75 (4670 Hz, 2H, pyr), 97.84 (181 Hz, 2H, *m*-pyr-PDI), 40.10 (275 Hz, 1H, pyr), 24.20 (211 Hz, 2H, pyr), −1.34 (768 Hz, 12H, CH(CH_3)$_2$), −6.58 (1437 Hz, 12H, CH(CH_3)$_2$), −8.85 (31 Hz, 2H, *m*-aryl), −10.11 (93 Hz, 1H, *p*-aryl), −240.46 (594 Hz, 6H, C(CH_3)); one peak was not located. Aerobic hydrolysis of the reaction mixture yielded a mixture of ^{i}PrPDI and *p*-neopentyl-substituted PDI. ^{1}H NMR of neopentyl-substituted ligand (benzene-d_6): δ 8.53 (s, 2H, *m*-pyr), 7.24–7.16 (m, 6H, *m*- and *p*-aryl), 2.96 (sept, $^3J_{HH}$ = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 2.35 (s, 6H, C(CH_3)), 2.25 (s, 2H, CH_2C(CH$_3$)$_3$), 1.22 (d, $^3J_{HH}$ = 7.0 Hz, 4H, CH(CH_3)$_2$), 1.18 (d, $^3J_{HH}$ = 7.0 Hz, 4H, CH(CH_3)$_2$), 0.78 (s, 9H, CH$_2$C(CH_3)$_3$). LRMS (*m*/*z*): 551 (26), 536 (53), 281 (33), 207 (100).

Addition of ^{iPr}PDI to py$_2$Fe(CH$_2$CMe$_3$)$_2$. A 20 mL scintillation vial was charged with 40 g (0.112 mmol) of py$_2$Fe(CH$_2$CMe$_3$)$_2$ dissolved in approximately 5 mL of pentane and cooled at −35 °C for 30 min. The ^{iPr}PDI ligand (54 mg, 0.112 mmol) dissolved in pentane and precooled at the same temperature was added with stirring. Immediately upon addition, a dark-brown solution formed, which was filtered after 1–2 h through a pad of Celite to remove any particulates. The solvent was removed in vacuo, and the resulting brown oil was recrystallized from pentane at −35 °C. The resulting solid was hydrolyzed in air and filtered, and the organic products were analyzed by ^{1}H NMR spectropscopy and mass spectrometry.

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Supporting Information Available: Crystallographic data for **2-Np**, **2-CH$_2$SiMe$_3$**, **[1-(Tol)N$_2$]Li(Et$_2$O)$_3$**, **2-(CH$_2$SiMe$_3$)$_2$**, and **1-Cl(py)** in CIF format and a comparison of representative ^{1}H NMR spectra of **1-Cl** and **1-CH$_2$SiMe$_3$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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