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Bis(imino)pyridine Iron Alkyls Containing β-Hydrogens: Synthesis, Evaluation of Kinetic Stability, and Decomposition Pathways Involving Chelate Participation

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Abstract: Bis(imino)pyridine iron alkyl complexes bearing β-hydrogens, (^{iPr}PDI)FeR ((^{iPr}PDI = 2,6-(2,6-$^{i}Pr_2-C_6H_3N{=}CMe)_2C_5H_3N$; R = Et, ^{n}Bu, ^{i}Bu, $CH_2{}^{cyclo}C_5H_9$; **1-R**), were synthesized either by direct alkylation of (^{iPr}PDI)FeCl (**1-Cl**) with the appropriate Grignard reagent or more typically by oxidative addition of the appropriate alkyl bromide to the iron bis(dinitrogen) complex, (^{iPr}PDI)Fe$(N_2)_2$ (**1-$(N_2)_2$**). In the latter method, the formal oxidative addition reaction produced (^{iPr}PDI)FeBr (**1-Br**), along with the desired iron alkyl, **1-R**. Elucidation of the electronic structure of **1-Br** and related **1-R** derivatives by magnetic measurements, structural studies and NMR spectroscopy established high spin ferrous compounds antiferromagnetically coupled to chelate radical anions. Thus, the formal oxidative process is bis(imino)pyridine ligand-based (one electron is formally removed from each chelate, not the iron) during oxidative addition. The kinetic stability of each **1-R** compound was assayed in benzene-d_6 solution and found to produce a mixture of the corresponding alkane and alkene. The kinetic stability of the iron alkyl complexes was inversely correlated with the number of β-hydrogens present. For example, the iron ethyl complex, **1-Et**, underwent clean loss of ethane over the course of three hours, whereas the corresponding **1-^{i}Bu** compound had a half-life of over 12 h under identical conditions. The mechanism of the decomposition was studied with a series of deuterium labeling experiments and support a pathway involving initial β-hydrogen elimination followed by cyclometalation of an isopropyl methyl group, demonstrating an overall transfer hydrogenation pathway. The relevance of such pathways to chain transfer in bis(imino)pyridine iron catalyzed olefin polymerization reactions is also presented.

Introduction

When activated with methylalumoxane (MAO), aryl-substituted bis(imino)pyridine iron and cobalt dihalide compounds exhibit productivities for ethylene polymerization that rival the most efficient group 4 metallocene catalysts.[1−3] Accordingly, this class of compounds has attracted considerable attention from both academic and industrial laboratories.[4] Systematic evaluation of aryl substituent effects has established structure−reactivity relationships that allow tuning of the polymerization activity by straightforward manipulation of ligand architecture.[5] For example, bis(imino)pyridine iron dihalide precatalysts bearing two large 2,6-substituents on the aryl ring are known to produce linear polyethylene whereas those with only a single *ortho* aryl substituent are selective for α-olefin production with near ideal Schultz-Flory distributions.[1,2,6−8]

Despite the tremendous successes with bis(imino)pyridine iron catalysts, short catalyst lifetimes and formation of large amounts of 1-butene during ethylene oligomerization to α-olefins have been identified as potential obstacles to commercialization.[7] Ideally, new catalyst discovery would be guided by well-understood mechanistic principles - an approach that has proven invaluable in group 4 metallocene catalyst development and implementation.[9] For example, an understanding of counterion effects, the nature of the transition structure and the influence of cyclopentadienyl substituents has resulted in the genesis of improved catalysts with remarkable selectivities, productivities, and lifetimes.[10]

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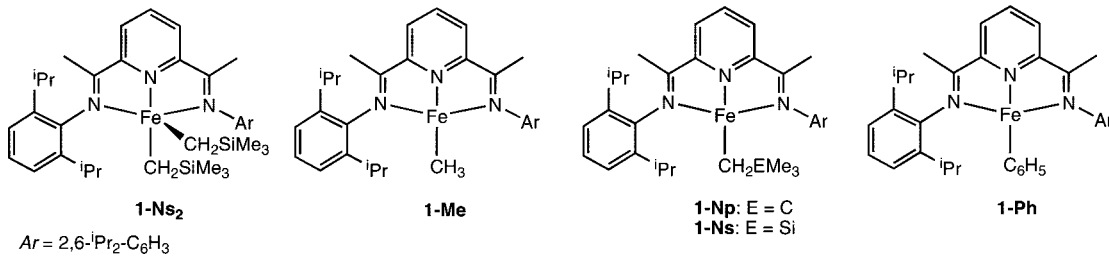

Figure 1. Neutral bis(imino)pyridine iron alkyls stabilized from β-hydrogen elimination.

In contrast, few mechanistic details are known for bis(imino)pyridine iron catalyzed polymerizations. The mode of propagation and the oxidation state of the active species remain matters of controversy. Initial theoretical studies assumed formation of cationic monoalkyl iron(II) compounds upon activation with methylalumoxane (MAO),[11,12] which have been experimentally supported by both NMR spectroscopy[13] and ESI mass spectrometry.[14] Alternatively, Mössbauer spectroscopic and EPR studies suggested that the iron(II) precatalysts are oxidized to iron(III) upon treatment with MAO.[15] Studies into the MAO-activation of bis(imino)pyridine iron dihalides by optical spectroscopy revealed gross spectral changes and a decrease of the *d-d* transitions as a function of time, temperature, and activator concentration and were interpreted as an iron centered spin transition.[16] Both the paramagnetism of the iron center and well-established redox and chemical participation of the bis(imino)pyridine ligand complicate characterization of the active species.[17,18]

In principle, these ambiguities could be resolved by preparation of well-defined, single component bis(imino)pyridine iron catalysts. Bis(imino)pyridine iron alkyl cations are worthy targets as these compounds may allow study of fundamental transformations related to chain initiation, growth and termination. For many years, however, the requisite bis(imino)pyridine iron dialkyl species remained elusive.[19] In 2005, our laboratory reported that treatment of (^{iPr}PDI)FeCl$_2$ (**1-Cl$_2$**; ^{iPr}PDI = 2,6-(2,6-^{i}Pr$_2$−C$_6$H$_3$N = CMe)$_2$C$_5$H$_3$N) with 2 equiv of LiCH$_2$SiMe$_3$ followed by recrystallization from cold pentane furnished the desired iron dialkyl complex, (^{iPr}PDI)Fe(CH$_2$SiMe$_3$)$_2$ (**1-Ns$_2$**).[20] Shortly thereafter, Gambarrotta and co-workers described a more detailed investigation into this reaction and provided evidence for chemical participation of the bis(imino)pyridine chelate.[21] Cámpora and co-workers later described a more versatile synthetic method whereby addition of free bis(imino)pyridine to (pyridine)$_2$Fe(CH$_2$SiMe$_3$)$_2$ furnished the corresponding iron dialkyls in high yield.[22] Our laboratory has since expanded this procedure to explore the relative stability of (^{iPr}PDI)Fe-CH$_2$SiMe$_3$ and (^{iPr}PDI)Fe-CH$_2$CMe$_3$ complexes.[23]

With synthetic routes to **1-Ns$_2$** in hand, the bis(imino)pyridine iron alkyl cations, [(^{iPr}PDI)Fe-R]$^+$X$^-$ (R = CH$_2$SiMe$_3$, X$^-$ = BPh$_4^-$; CH$_2$SiMe$_2$CH$_2$SiMe$_3$, X$^-$ = MeB(C$_6$F$_5$)$_3$−), were synthesized and shown to be active for ethylene polymerization.[24] Although these results demonstrate the catalytic competency of a formally iron(II) alkyl cation as the propagating species, they by no means demonstrate that such a compound is formed from MAO-activation of a bis(imino)pyridine iron dihalide. In fact, studies by Budzelaar,[25] Gambarotta,[21,26,27] and Kissin[28] with bis(imino)pyridine ferrous dihalide-aluminum alkyl mixtures establish that ligand alkylation and transmetalation to aluminum are likely during polymerization and that certain iron ethylene polymerization catalysts may be multicentered.

Despite these complexities, preparation of well-defined bis(imino)pyridine iron alkyl compounds may provide insight into fundamental transformations related to catalytic olefin oligomerization and polymerization and allow a deeper understanding of empirically established structure−reactivity relationships. In addition, these compounds also allow evaluation of the chemical and electronic participation of the bis(imino)pyridine chelate and its role during catalysis. To date, the only bis(imino)pyridine iron alkyls that have been synthesized are those protected from β-hydrogen elimination, thereby limiting the study of this potentially important chain transfer reaction. Examples of known iron alkyls with ^{iPr}PDI as the bis(imino)pyridine chelate are presented in Figure 1.

Although these compounds have proven useful to determine the stability of the iron−carbon bond and as synthons to certain iron alkyl cations, the lack of β-hydrogens limits relevance to the propagating species during olefin polymerization. In addition, preliminary studies with [(^{iPr}PDI)Fe-CH$_2$SiMe$_3$]$^+$ complexes indicate slow initiation relative to propagation.[24] Seeking to expand the number of well-defined, single component iron precatalysts and better mimic the potential propagating species, we sought to prepare bis(imino)pyridine iron alkyl complexes

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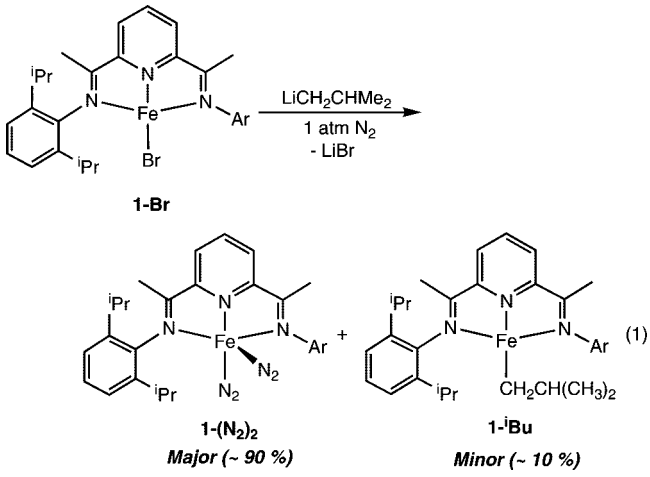
bearing β-hydrogens. Here we describe the results of these efforts and report the synthesis, characterization, and thermal stability of a family of bis(imino)pyridine iron alkyl complexes. Studies into the oxidative addition of alkyl bromides establish ligand rather than iron centered electron loss. The mechanism of iron alkyl complex decomposition has also been studied and found to undergo transfer dehydrogenation of the bis(imino)pyridine chelate.

Results and Discussion

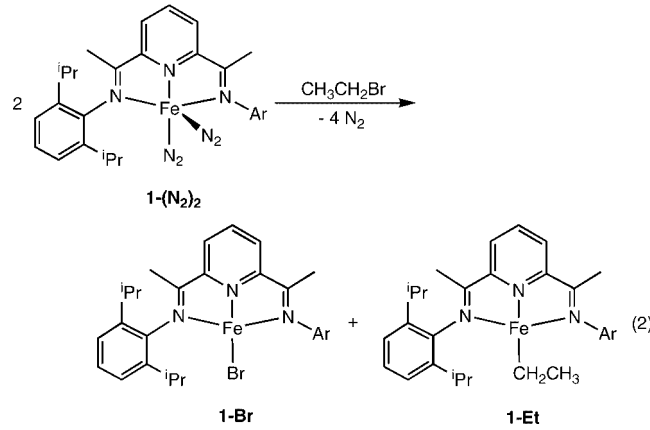
Synthesis of Neutral Bis(imino)pyridine Iron Alkyls Bearing β-Hydrogens: Oxidative Addition of Alkyl Halides to 1-$(N_2)_2$. The bis(imino)pyridine iron isobutyl complex, (^{iPr}PDI)-$FeCH_2CHMe_2$ (**1-^{i}Bu**), was the initial synthetic target of an iron alkyl complex bearing β-hydrogens. Because the synthesis of β-H stabilized bis(imino)pyridine iron alkyls (Figure 1) was accomplished by straightforward salt metathesis of **1-Br** with the appropriate alkyl lithium reagent (e.g., $LiCH_3$, $LiCH_2SiMe_3$, $LiCH_2CMe_3$), this route was initially explored. Stirring a diethyl ether solution of **1-Br** with one equivalent of ^{i}BuLi under a dinitrogen atmosphere for less than 30 min furnished only a small amount (~10%) of a paramagnetic compound identified as **1-^{i}Bu** (*vide infra*). Examination of the diamagnetic region of the ^{1}H NMR spectrum revealed the major iron product as the bis(dinitrogen) complex, **1-$(N_2)_2$**, formed from reduction of **1-Br** (eq 1).[29] Other minor, unidentified paramagnetic iron products were also observed using this procedure.



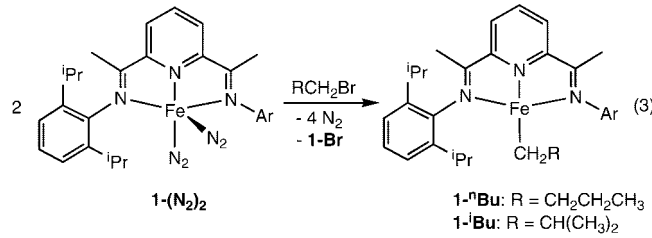
Alternative salt metathetical methods using less reducing Grignard reagents were also explored as potential synthetic routes to **1-^{i}Bu**. Addition of ^{i}BuMgCl to a diethyl ether solution of **1-Cl** furnished the desired iron monoalkyl in greater yield and purity than the corresponding lithiation. Only small (~ 10%) quantities of **1-$(N_2)_2$** were obtained using this procedure. However, the kinetic instability of the compound (*vide infra*) complicated isolation of **1-^{i}Bu** on a preparative scale.

Because other bis(imino)pyridine iron alkyls may be shorter lived than **1-^{i}Bu**, a more reliable synthetic method that obviated the complications of work up, titration of Grignard reagents and possibility for competing reduction reactions was targeted. Oxidative addition of alkyl halides to **1-$(N_2)_2$** was explored as a possible synthetic route to bis(imino)pyridine iron alkyls bearing β-hydrogens. This approach is also of interest because of the unusual electronic structure of **1-$(N_2)_2$**. Previous spectroscopic, structural and computational studies have established this formally iron(0) compound is better described as an intermediate spin ferrous complex with a bis(imino)pyridine diradical dianion.[30] Thus, oxidative transformations are of interest, as formal electron loss could be either metal or ligand based.[31]

Our studies into the oxidative addition of alkyl halides to **1-$(N_2)_2$** began with ethyl bromide. Preparation of a neutral bis(imino)pyridine iron ethyl complex was of interest given the utility of this class of compounds in ethylene polymerization. Treatment of a benzene-d_6 solution of **1-$(N_2)_2$** with 0.5 equivalents of CH_3CH_2Br resulted in immediate formation of two new paramagnetic products. The first was readily identified as the previously reported bis(imino)pyridine iron bromide, **1-Br**,[20] while the second compound was assigned as the desired iron ethyl species, **1-Et** (eq 2). The latter compound was characterized using a combination of ^{1}H NMR spectroscopy as well as degradation studies. Full details of the spectral assignment and the relative stability of each iron alkyl prepared in this study are reported in a later section.



The spectroscopic identification of **1-Et** following addition of ethyl bromide to **1-$(N_2)_2$** suggested that alkyl halide addition was an effective method for the synthesis of bis(imino)pyridine iron alkyl complexes bearing β-hydrogens. Addition of one equivalent of either *n*-butyl or isobutyl bromide to a benzene-d_6 solution of two equivalents of **1-$(N_2)_2$** yielded **1-Br** in both cases and the bis(imino)pyridine iron *n*-butyl and isobutyl compounds, **1-^{n}Bu** and **1-^{i}Bu**, respectively (eq 3).



Vacuum transfer of the volatiles immediately following each of the aforementioned alkyl bromide addition reactions and

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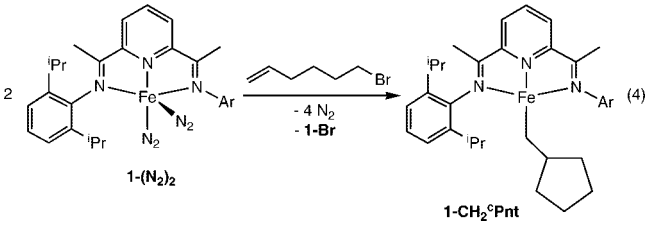
analysis by ^{1}H NMR spectroscopy demonstrated formation of small amounts (25% for *n*-BuBr, 12% for *i*-BuBr) of alkane along with trace amounts of alkene immediately following mixing of the reagents. Addition of more than 0.5 equivalents of alkyl bromide to **1-(N$_2$)$_2$** furnished a detectable quantity of **1-Br$_2$** along with other unidentified products. Again, analysis of the volatile components by ^{1}H NMR spectroscopy following vacuum transfer established formation of the corresponding alkane. Because these results suggested the intermediacy of radicals during the formal oxidative addition event, the addition of 6-bromo-1-hexene to **1-(N$_2$)$_2$** was studied as the free 5-hexenyl radical is known to cyclize at a rate of approximately 10^5 sec^{-1}.[32] This probe has been used previously by Schwartz to assay radical chain involvement in the addition of R-X to [(η^5-C$_5$H$_5$)$_2$Zr].[33]Treatment of a benzene-d_6 solution of **1-(N$_2$)$_2$** with 0.5 equivalents of 6-bromo-1-hexene yielded **1-Br** along with the bis(imino)pyridine iron methylcyclopentyl complex, **1-CH$_2$^{c}Pnt**, as the sole iron alkyl product (eq 4). Analysis of the volatile components immediately following addition yielded 27% organic compounds (86% methylene cyclopentane, 14% methyl cyclopentane) likely arising from ejection of alkyl radical. It is also possible that **1-CH$_2$^{c}Pnt** arises from alkylation of the metal followed by olefin insertion.



The oxidative addition of secondary and tertiary alkyl bromides to **1-(N$_2$)$_2$** was also explored. Addition of one equivalent of 2-bromobutane to a benzene-d_6 solution of two equivalents of **1-(N$_2$)$_2$** furnished **1-Br** along with small quantities (~5%) of the bis(imino)pyridine iron *n*-butyl complex, **1-^{n}Bu**. Analysis of the volatile products of the reaction mixture by ^{1}H NMR spectroscopy established formation of *cis*- (4%) and *trans*-2-butene (12%) as the sole alkene products along with butane (84%). The results implicate fast and irreversible β-hydrogen elimination from secondary iron alkyls along with radical formation (*vide infra*). In an analogous experiment, addition of *tert*-butyl bromide to a benzene-d_6 solution of **1-(N$_2$)$_2$** yielded **1-Br** along with **1-^{i}Bu**. Collection and examination of the volatiles from this reaction (before significant decomposition of the iron alkyl, *vide infra*) by ^{1}H NMR spectroscopy revealed that a near equimolar ratio of isobutene and isobutane accompanies oxidative addition, consistent with involvement of *tert*-butyl radical.

Spectroscopic Characterization of Bis(imino)pyridine Iron Alkyl Complexes. As will be discussed in the next section, each of the bis(imino)pyridine iron alkyl complexes bearing β-hydrogens is kinetically unstable and must be handled carefully—and sometimes quickly—in solution under an inert atmosphere. As a result, characterization of these compounds has relied primarily on ^{1}H and ^{2}H NMR spectroscopy and degradation studies. Because each iron alkyl is paramagnetic, the ^{1}H NMR spectral assignments are not immediately obvious. To circumvent this complication, the ^{1}H NMR spectrum of **1-Br** was examined in detail, as this compound is a product common to all of the oxidative addition reactions. In addition, **1-Br** is indefinitely stable if handled under an inert atmosphere, and serves as a model of comparison for the transient iron alkyl complexes. The electronic structure of **1-Br** and isoelectronic **1-R** derivatives are also of interest to determine whether ligand or metal oxidation occurs upon addition of alkyl halides.

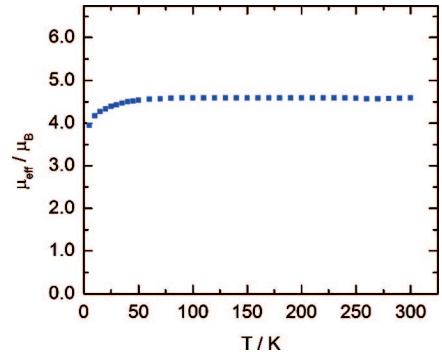


Figure 2. Solid state magnetic susceptibility data for **1-Br**.

Our laboratory has previously investigated the electronic structure of the related bis(imino)pyridine iron monochloride, **1-Cl**, by Mössbauer spectroscopy, structural studies, magnetic measurements, and DFT calculations.[30] The experimental and computational data were consistent with a high spin ferrous center, antiferromagnetically coupled to a monoreduced bis(imino)pyridine anion. Related experiments with **1-Br** support a similar description. For example, variable temperature SQUID magnetization data establish the $S = {}^3/_2$ ground-state and simple paramagnetic behavior for the compound. A plot of effective magnetic moment versus temperature (Figure 2) exhibits μ_{eff} values ranging from 3.9 to 4.5 μ_B (5−300 K) and is consistent with three unpaired electrons and a modest orbital contribution arising from the square planar iron center. Separate runs were conducted on three independently prepared samples to establish reproducibility (see Figure S1, Supporting Information).

The metrical parameters determined from high quality X-ray crystal structures have proven useful for characterizing the degree of ligand reduction and involvement in the electronic structure.[17,18,30] Because repeated attempts to obtain X-ray quality crystals of four-coordinate **1-Cl** and **1-Br** have been unsuccessful, the solid state structure of **1-Br(THF)** was determined. X-ray quality crystals were obtained from a concentrated pentane solution of the iron compound in the presence of a small amount of THF. A representation of the molecular structure is presented in Figure 3 and selected metrical parameters are reported in Table 1. The overall molecular geometry is best described as idealized square pyramidal with the THF ligand occupying the apical position. The THF ligand and one chelate isopropyl group are positionally disordered and were successfully modeled. Because of the disorder, the Fe−O bond distance should be treated cautiously. The imine C=N bond distances of 1.299(4) and 1.306(4) Å and the C$_{imine}$−C$_{ipso}$ distances of 1.446(5) and 1.433(5) Å are consistent with one electron chelate reduction.[17,18,30] To confirm that coordination of the THF molecule did not alter the magnetic properties of the

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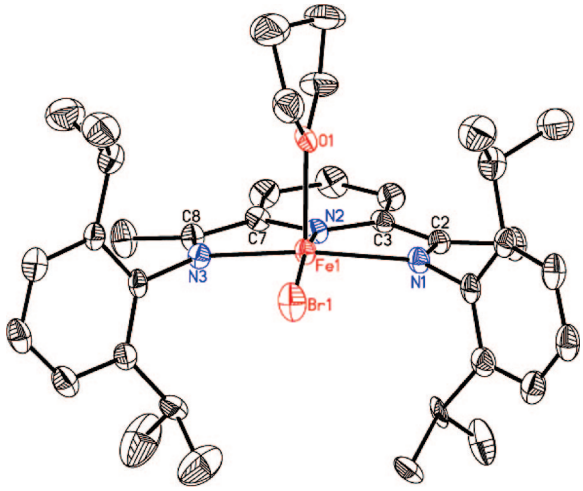


Figure 3. Solid state structure of **1-Br(THF)** at 30% probability ellipsoids. Hydrogen atoms and disordered positions omitted for clarity.

Table 1. Selected Metrical Parameters for **1-Br(THF)**

	distance (Å)		angle (deg)
Fe(1)−Br(1)	2.4165(6)	N(1)−Fe(1)−N(3)	146.93(11)
Fe(1)−N(1)	2.172(3)	N(1)−Fe(1)−N(2)	74.59(11)
Fe(1)−N(2)	2.008(3)	N(2)−Fe(1)−N(3)	74.93(11)
Fe(1)−N(3)	2.150(3)	N(1)−Fe(1)−O(1)	96.33(11)
Fe(1)−O(1)	2.166(5)	N(2)−Fe(1)−O(1)	92.64(15)
N(1)−C(2)	1.299(4)	N(3)−Fe(1)−O(1)	97.58(16)
N(3)−C(8)	1.306(4)	N(1)−Fe(1)−Br(1)	103.69(7)
C(2)−C(3)	1.446(5)	N(2)−Fe(1)−Br(1)	167.89(9)
C(7)−C(8)	1.433(5)	N(3)−Fe(1)−Br(1)	103.39(8)
N(2)−C(3)	1.361(5)		
N(2)−C(7)	1.358(4)		

five-coordinate versus the four-coordinate compound, the solid state magnetic susceptibility of **1-Br(THF)** was determined. A magnetic moment of 4.5 μ_B was measured at 23 °C by Gouy balance, in excellent agreement with the SQUID data at the same temperature for **1-Br**. Thus, the metrical parameters, in combination with the solid state magnetic susceptibility data, support a monoreduced bis(imino)pyridine chelate ($S_{PDI} = {}^1/_2$) antiferromagnetically coupled to a high spin iron center ($S_{Fe} = 2$).[30]

With a firm description of the electronic structure of **1-Br** in hand, the ^{1}H NMR spectrum of the compound was examined in more detail. Despite the paramagnetism, the ^{1}H NMR spectrum is readily assigned and exhibits diagnostic resonances that can be used to identify this and the related bis(imino)pyridine iron alkyl compounds. A representative benzene-d_6 solution ^{1}H NMR spectrum, recorded at 23 °C, is presented in Figure 4. Selected ligand resonances have been tabulated in Table 2. As expected, the hydrogens in the bis(imino)pyridine chelate plane exhibit the largest isotropic shifts, while those orthogonal to the plane of the ligand are closer to their diamagnetic reference values. The temperature dependence of the isotropic shifts was examined and found to vary linearly with the reciprocal of absolute temperature. Representative plots establishing Curie behavior for selected resonances are presented in Figure S2 of the Supporting Information. As expected, the resonances in the plane of the chelate—such as the imine methyl and the *meta* pyridine hydrogens—exhibit the steepest slopes while those orthogonal to the chelate exhibit a relatively shallow temperature dependence.

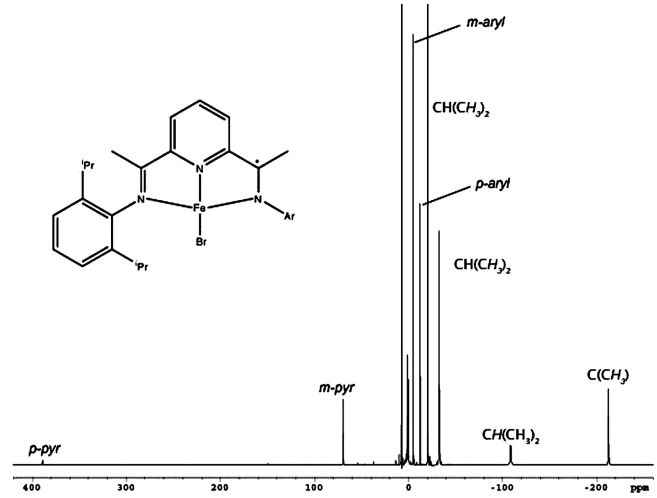


Figure 4. ^{1}H NMR spectrum of **1-Br** in benzene-d_6 at 23 °C.

Table 2. Selected ^{1}H NMR Resonances for **1-Br** as a Function of Added THF[a]

equiv of THF	*p*-pyr	*m*-pyr	C*H*(CH$_3$)$_2$	N=C(C*H*$_3$)
0	388.94	69.22	−108.71	−212.74
10	351.87	69.27	−54.96	−223.06

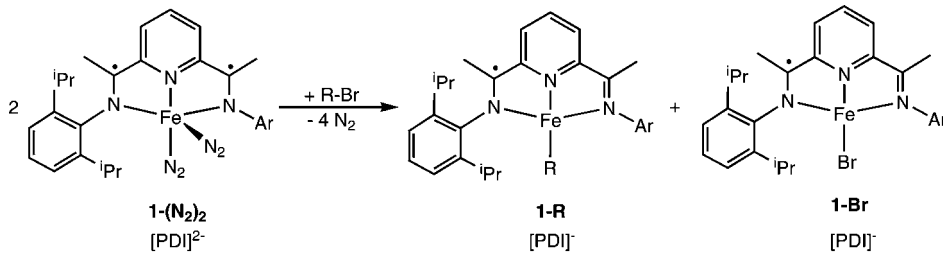
[a] All values reported in ppm in benzene-d_6 at 23 °C.

Because **1-Br(THF)**, not **1-Br**, was crystallographically characterized, the influence of the added base on the ^{1}H NMR spectral features of the compound was examined. Addition of 10 equiv of THF to a 0.035 M benzene-d_6 solution of **1-Br** resulted in dramatic changes to the isotropic shifts of certain bis(imino)pyridine protons (Table 2). Particularly notable is the substantial upfield shifts, by 37 and 10.3 ppm of the *para*-pyridine and imine methyl hydrogens, respectively. The isopropyl methine resonance shifts downfield by over 50 ppm whereas the *meta*-pyridine hydrogen is largely unaffected. Removal of the THF resulted in regeneration the original shifts assigned to four coordinate **1-Br**.

The electronic structure of **1-Br**, in combination with the previously reported magnetic and structural data for the isolable iron alkyls **1-Me**[20] and **1-Ns**,[23] provides additional insight on the oxidative addition of alkyl bromides to **1-(N$_2$)$_2$**. The iron alkyls have an identical electronic structure to **1-Br** - overall $S = {}^3/_2$ ground states arising from high spin ($S_{Fe} = 2$) ferrous centers antiferromagnetically coupled to bis(imino)pyridine radical anions. Thus, oxidative addition of alkyl bromides to **1-(N$_2$)$_2$** is formally *ligand*, rather than metal, based. The two electron reduced bis(imino)pyridine chelate in **1-(N$_2$)$_2$** is oxidized by one electron to produce two new iron products where the iron(II) oxidation state is preserved (Scheme 1).[34] Notably, a spin change from intermediate to high spin occurs at the iron center upon chelate oxidation. These findings are as expected from the principle of microscopic reversibility - the reduction of **1-Br** to yield **1-(N$_2$)$_2$** and related neutral ligand complexes occurs at the chelate with a spin change at iron(II).[30]

The complete assignment of the ^{1}H NMR spectrum of **1-Br** has proven valuable for the spectroscopic characterization of the kinetically unstable bis(imino)pyridine iron alkyl complexes bearing β-hydrogens. Selected assignments for each iron alkyl complex prepared in this work along with the previously reported iron methyl[20] and neosilyl[23] complexes, are given in Table 3. A representative benzene-d_6

Scheme 1



Oxidation occurs at the ligand, not the metal.

Table 3. Selected ^{1}H NMR Resonances for Bis(imino)pyridine Compounds Reported in This Work[a]

complex	*p*-pyr	*m*-pyr	C*H*(CH$_3$)$_2$	N=C(C*H*$_3$)	alkyl
1-Br	388.94	69.22	−108.71	−212.74	N/A
1-OTf	392.79	94.92	−143.50	−242.75	N/A
1-Me[20]	216.5	58.9	−72.6	−163.8	*Not Located*
1-Ns[23]	369.28	66.93	−109.04	−206.76	48.80 (SiMe$_3$)
1-Et	263.35	63.75	−89.75	−172.74	149.69 (C*H*$_3$)
1-CH$_2$^{c}Pnt	338.91	67.37	−120.43	−182.34	197.22 (C*H*), 85.67, 52.53, 46.28, 34.62
1-^{i}Bu	350.03	66.30	−123.36	−185.63	200.42 (C*H*), 73.34 (iPr C*H*$_3$)
1-^{n}Bu	284.47	64.78	−99.21	−175.37	142.49, 60.05, 36.92

[a] All values reported in ppm in benzene-d_6 at 23 °C.

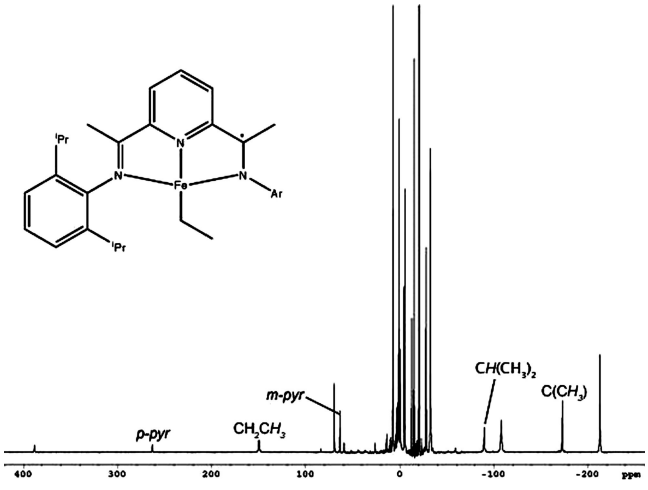
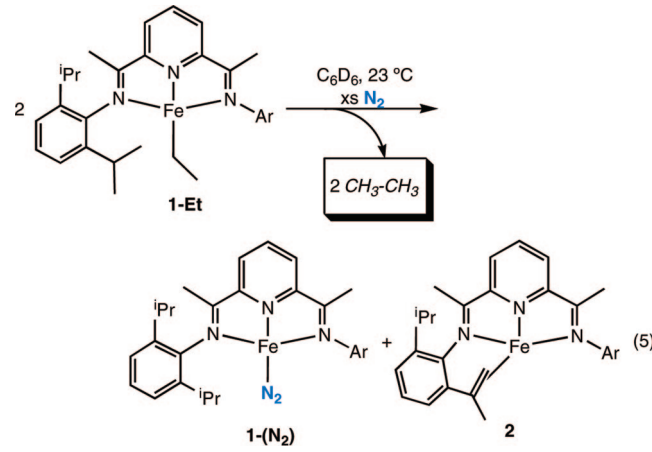


Figure 5. ^{1}H NMR spectrum of **1-Et** (labeled resonances) along with **1-Br** (unlabeled) in benzene-d_6 at 23 °C.

^{1}H NMR spectrum of **1-Et** recorded at 23 °C is presented in Figure 5. As the spectroscopic properties of each alkyl are similar, only **1-Et** will be discussed in detail. Complete assignments and other representative spectra are reported in the Supporting Information. For **1-Et**, the imine methyl group appears the most upfield at −172.74 ppm while the *p*-pyridine hydrogen is the most downfield at 263.35 ppm. Other diagnostic resonances with large isotropic shifts are the *m*-pyridine hydrogens located at 63.75 ppm and the isopropyl methine centered at −89.75 ppm. Unfortunately, the hydrogens on the carbon attached directly to the iron have not been located by ^{1}H NMR spectroscopy for any iron alkyl compound prepared in this study.

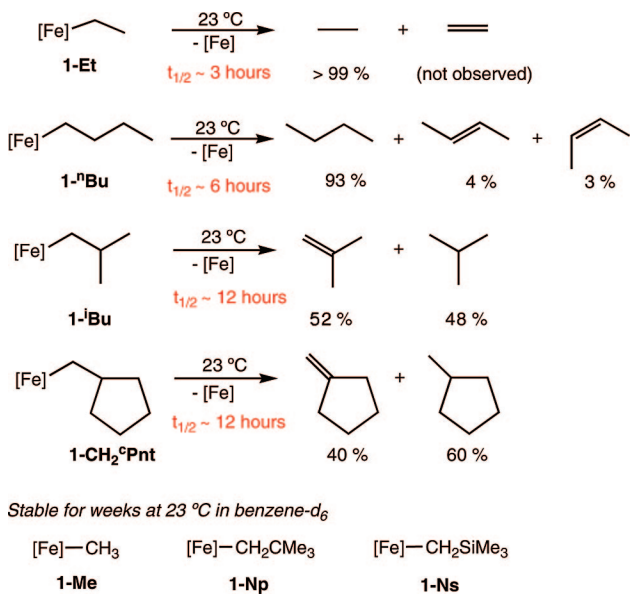
Kinetic Stability of Neutral Bis(imino)pyridine Iron Alkyls. With a family of neutral bis(imino)pyridine iron alkyls with β-hydrogens in hand, the relative stability of each compound was assayed in benzene-d_6 solution at 23 °C. After 18 h, **1-Et** undergoes exclusive loss of ethane and formation of two new iron products (eq 5).



One of the iron products was identified as the previously reported bis(imino)pyridine dinitrogen complex, **1-(N$_2$)** (or **1-(N$_2$)$_2$**, depending on the amount of N$_2$ present).[29] The second iron compound was detected after hydrolysis of the organometallic products and analysis of the free chelate by ^{1}H NMR spectroscopy as well as by D$_2$ addition experiments.[35] In addition to signature resonances for free ^{iPr}PDI, multiplets were observed in the alkene region, indicative of dehydrogenated bis(imino)pyridine ligand. These data, in addition to hydrogenation studies, establish the second iron product as the NMR-silent intramolecular olefin complex, **2**. This molecule was previously observed and characterized following the decomposition of a bis(imino)pyridine iron diazoalkane complex.[35] Thus, the decomposition of **1-Et** can be viewed as a transfer dehydrogenation from the ligand to the iron alkyl, liberating ethane and forming an equimolar mixture of **1-N$_2$** and **2**. In the present case, the liberated ethane was quantified with a Toepler pump and 92% of the expected gas was collected.

The thermal stability and half-lives of the other bis(imino)pyridine iron alkyls prepared in this study were also assayed at 23 °C in benzene-d_6. The organic products released following disappearance of the iron alkyl vary and are reported in Scheme 2. In addition, the half-life for each reaction is also reported in the scheme. In each case, a mixture of iron products, **1-(N$_2$)$_n$**

Scheme 2



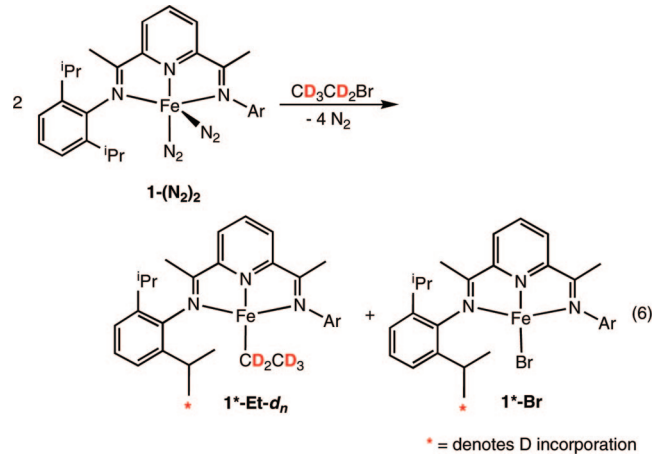
and **2**, was observed and is denoted as "[Fe]" for simplicity. The iron *n*-butyl compound, **1-^{n}Bu**, has a significantly longer half-life than **1-Et** but produces predominantly butane with small amounts of 2-butene. No 1-butene was detected by ^{1}H NMR spectroscopy from these experiments.

Bis(imino)pyridine iron alkyls bearing only one β-hydrogen, **1-^{i}Bu** and **1-CH$_2$^{c}Pnt**, were longer lived than either **1-Et** or **1-^{n}Bu** and produced significantly higher fractions of olefins upon disappearance of the iron alkyl, demonstrating a reduced propensity for transfer hydrogenation with more sterically demanding alkyls. The relatively long lifetime of **1-^{i}Bu** versus **1-^{n}Bu** and **1-Et**, established that stability of the iron alkyls decreased as the number of β-hydrogens increase.

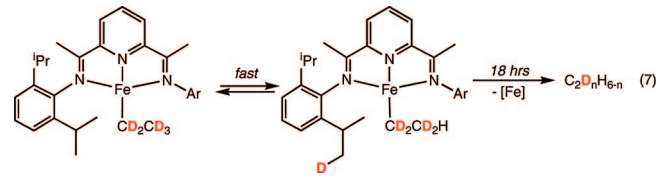
The loss of alkane from the compounds presented in Scheme 2 prompted reinvestigation of the thermal stability of **1-Me**, **1-Ns**, and **1-Np**. It is possible that iron−carbon bond homolysis,[36] not β-hydrogen elimination, is responsible for the kinetic instability of the iron-alkyls prepared in this work. Allowing benzene-d_6 solutions of **1-Me**, **1-Ns**, or **1-Np** to stand at 23 °C produced no detectable change by ^{1}H NMR spectroscopy. Because the differences in iron−carbon bond strengths for **1-Et**, **1-^{n}Bu**, **1-^{i}Bu**, and **1-Np** are expected to be similar,[37] the relative stability of the compounds is a result of the presence or absence of β-hydrogens. In fact, if iron bond homolysis were indeed operative, the more hindered **1-Np** may be expected to be the least, not most, kinetically persistent.

Deuterium Labeling Studies and Proposed Mechanism for Alkane Loss. The loss of alkane and formation of **2** from the bis(imino)pyridine iron alkyl complexes prompted more detailed studies into the mechanism of thermal decomposition for these compounds. Understanding these pathways may provide insight into chain transfer processes related to bis(imino)pyridine iron-catalyzed olefin oligomerizations and polymerizations. Previous studies with MAO-activated metal dihalides indicate that chain transfer by β-hydrogen elimination is more important for cobalt than iron catalysts,[1,3,38] although in single component iron cases, β-hydrogen elimination was indeed dominant.

A series of deuterium labeling experiments were conducted to verify the origin of the hydrogen atoms in the alkane products. Treatment of a benzene solution of **1-(N$_2$)$_2$** with 0.5 equivalents of CD_3CD_2Br yielded a mixture of **1*-Et** and **1*-Br** as judged by ^{2}H NMR spectroscopy (eq 6). The "*" designates deuterium incorporation into an isopropyl methyl group. Analysis of the mixture by ^{2}H NMR spectroscopy within 15 min of alkyl halide addition revealed peaks centered at 36.4 and 149.7 ppm, corresponding to the Fe−CD_2CD_3 and Fe-CD_2CD_3 deuterons, respectively. The resonance for the methylene positions was only observed by ^{2}H NMR spectroscopy; no corresponding peak has been located in the ^{1}H NMR spectrum of natural abundance **1-Et**. Observation of ^{2}H but not ^{1}H NMR peaks is due to better resolution of deuterium spectra for paramagnetic compounds; a phenomenon that is a result of the difference in magnetogyric ratios of the two nuclei.[39] Interestingly, the ^{2}H NMR spectrum of the product mixture also contained four additional peaks corresponding to deuterium labeling of the isopropyl methyl groups of *both* **1-Br** and **1-Et**.



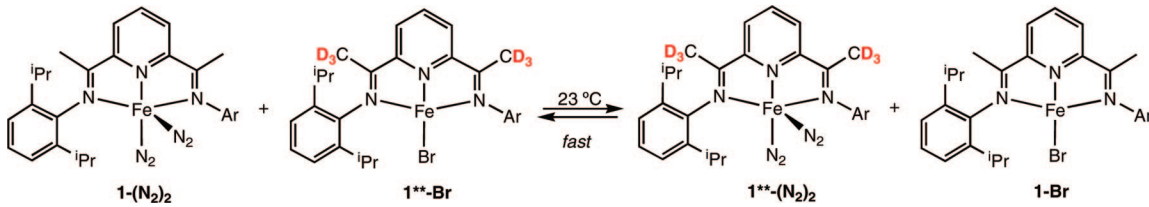
Monitoring the stability of **1*-Et** by ^{2}H NMR spectroscopy at 23 °C in benzene-d_6 revealed smooth disappearance of the resonances for the ethyl chain over the course of 3.5 h. Throughout this experiment, the peaks for the isopropyl methyl positions of **1*-Et** remain, demonstrating deuterium depletion from the ethyl chain *before* alkane loss (eq 7).



After 18 h at 23 °C, no ^{2}H NMR signals assigned to **1*-Et** remained, consistent with the lifetime measured previously for natural abundance **1-Et** determined by ^{1}H NMR spectroscopy. Because of the complexities associated with isotopic scrambling

(36) Lau, W.; Huffman, J. C.; Kochi, J. K. *Organometallics* **1982**, *1*, 155.
(37) Vela, J.; Vaddadi, S.; Cundari, T. R.; Smith, J. M.; Gregory, E. A.; Lachicotte, R. J.; Flaschenreim, C. J.; Holland, P. L. *Organometallics* **2004**, *23*, 5226.
(38) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Stromberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728.
(39) Holm, R. H.; Hawkins, C. J. In *NMR of Paramagnetic Molecules: Principles and Applications*; La Mar, G. N., Horrocks, W. D., Holm, R. H., Eds.; Academic Press: New York, 1973; p 287.

Scheme 3



into the ligand, kinetic isotope effects for the loss of ethane from isotopologues of **1-Et** were not determined.

Evidence for isotopic exchange within the ethyl chain prior to ethane loss was also obtained from ^{1}H NMR spectroscopy. A ^{1}H NMR resonance was observed at 149.7 ppm approximately 20 min following addition of CD_3CD_2Br to **1-(N$_2$)$_2$**. It is likely that hydrogens are also incorporated into the iron methylene position, however, the inability to observe a signal for this position by ^{1}H NMR spectroscopy prohibits obtaining definitive experimental evidence. These experiments definitively establish "chain walking"—reversible β-hydrogen elimination followed by olefin rotation (or loss) and reinsertion—prior to cyclometalation and reductive elimination of ethane.

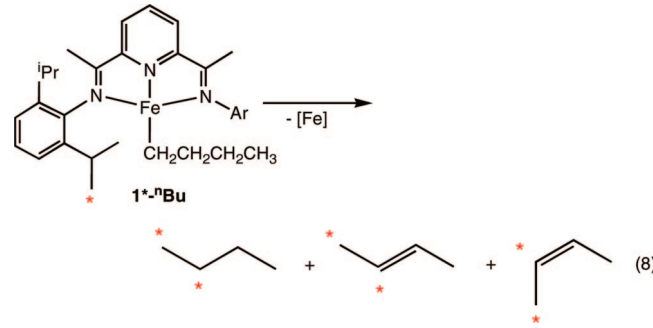
A benzene solution of **1-(N$_2$)$_2$** was also treated with 0.5 equivalents of CH_3CD_2Br. After 30 min at 23 °C, the ^{2}H NMR spectrum of the product mixture established formation of **1*-Br** along with **1*-Et-*d*$_n$**. At this time interval, the alkyl region of the ^{2}H NMR spectrum contained a prominent peak at 38 ppm for the Fe−C*D*$_2$CH$_3$ position and a very small peak, barely above the detection limit of the experiment (≤5%), at 145 ppm, suggesting that only a minimal amount of deuterium was present in the β-methyl group. Continued monitoring of the compound by ^{2}H NMR spectroscopy over the course of 18 h revealed disappearance of the ethyl complex with continued observation of the peaks for **1*-Br**.

The incorporation of deuterium into the isopropyl methyl groups of both the iron alkyl and the iron bromide compounds clearly establishes chemical participation of the bis(imino)pyridine chelate. Additional experiments were carried out to determine the origin of the deuterium in **1*-Br**. Because it is known that the isopropyl methyl groups of **1-(N$_2$)$_2$** are rapidly deuterated upon exposure to four atm of D_2 gas, an analogous experiment was conducted with isolated **1-Br**. No deuterium incorporation was observed over the course of 24 h at 23 °C, demonstrating that isopropyl methyl group cyclometalation is not operative in this compound.

One possibility for the formation of **1*-Br** involves ligand exchange from **1*-R**. Because **1*-Br** was observed immediately following addition of bromoethane to **1-(N$_2$)$_2$**, the product iron alkyl must undergo rapid β-hydrogen (deuterium) elimination and cyclometalation to form **1*-(N$_2$)**, which then would participate in ligand exchange. Crossover experiments were conducted to evaluate this possibility (Scheme 3). The imine methyl groups of the bis(imino)pyridine ligand were deuterium labeled to track the chelate compounds by ^{1}H and ^{2}H NMR spectroscopy. The compounds with deuterium labeled imine methyl groups are designated by "**". Thus, **1**-Br** was prepared in a straightforward manner from $NaBEt_3H$ reduction of **1**-Br$_2$**.[20]

Preparation of a benzene solution containing an equimolar mixture of **1**-Br** and **1-(N$_2$)$_2$** at 23 °C resulted in immediate formation of **1**-(N$_2$)$_2$** as judged by ^{2}H NMR spectroscopy (Scheme 3). Performing a similar experiment with **1**-Br** and **1-Np** produced no evidence for formation of **1**-Np**, suggesting that ligand exchange does not occur between iron halide and persistent iron alkyl complexes. Thus, observation of **1*-Br** from addition of either CD_3CD_2Br or CH_3CD_2Br to **1-(N$_2$)$_2$** is likely due to rapid cyclometalation and isotopic exchange from the iron alkyl followed by ligand exchange to form **1*-Br**. The ligand undergoing exchange could either be the iron-bromide or the bis(imino)pyridine chelate. Although our experiments do not distinguish these two possibilities (or a combination of the two), we tentatively favor the bromide exchange process. Recall that **1-(N$_2$)$_n$** (n = 1, 2) is formed from the thermal decomposition of **1-Et** and thus ligand exchange can occur throughout the process of ethylene dissociation and ethane formation.

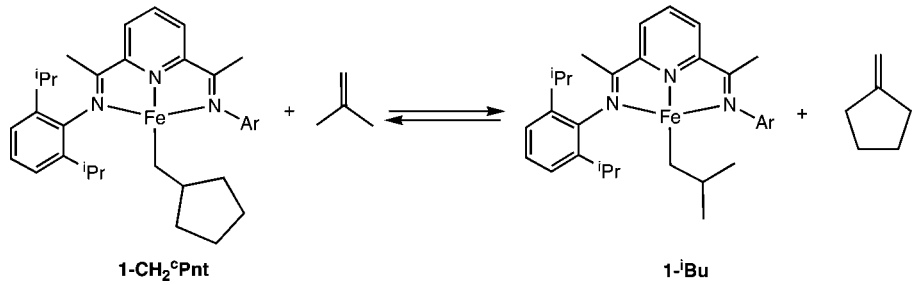
Deuterium labeling experiments were also carried out with **1-^{n}Bu** to assay the possibility of alkyl chain walking and confirm bis(imino)pyridine participation. The deuterium labeled iron dinitrogen complex, **1*-(N$_2$)$_2$**, was prepared by addition of excess D_2 gas to **1-(N$_2$)$_2$**.[29] Addition of 0.5 equivalents of $CH_3CH_2CH_2CH_2Br$ to a benzene solution of **1*-(N$_2$)$_2$** resulted in rapid formation of **1*-Br** along with **1*-^{n}Bu**. Monitoring the disappearance of **1*-^{n}Bu** by ^{2}H NMR spectroscopy established deuterium incorporation into all positions of the butane and 2-butenes (eq 8). Thus, alkyl isomerization (e.g., chain walking) is operative concomitant with alkane and alkene loss and chelate cyclometalation.



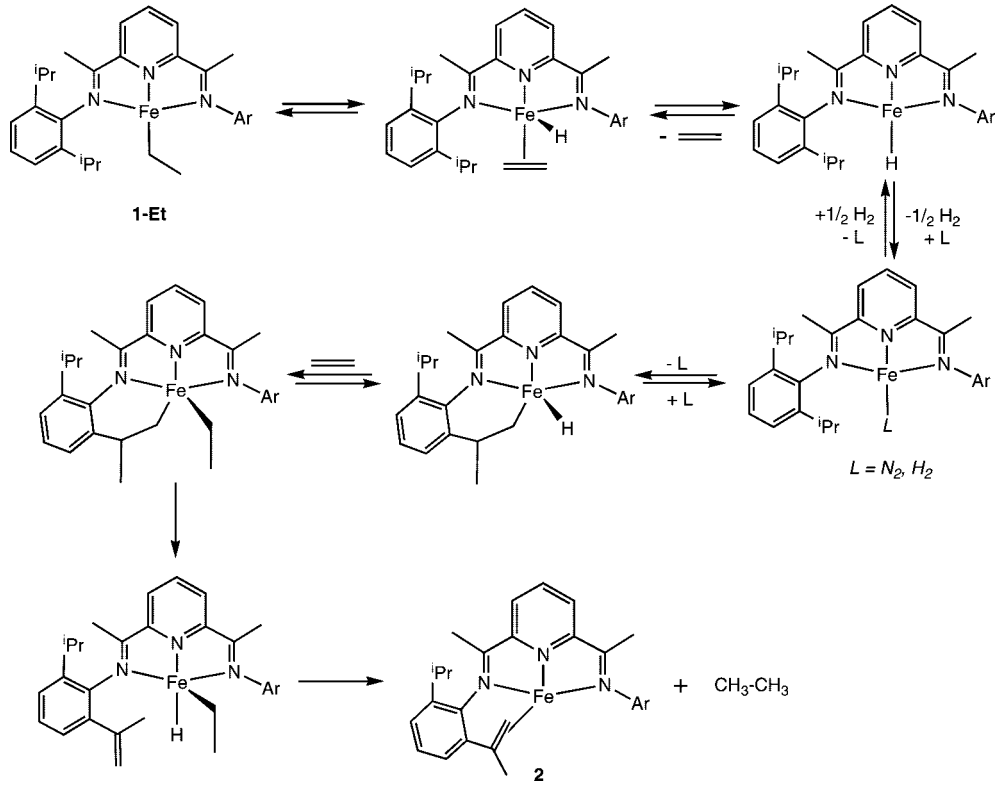
The oxidative addition of CD_3OTf to **1-(N$_2$)$_2$** was also studied as a control experiment to verify that the β-carbon position was the source of the deuterium during competing cyclometalation. Treatment of **1-(N$_2$)$_2$** with 0.5 equivalents of CD_3OTf cleanly furnished the deuterated isotopologue of the previously reported iron methyl complex, **1-CD$_3$**,[20] along with the bis(imino)pyridine iron triflate, **1-OTf**. The latter complex was independently prepared by addition of Me_3SiOTf to **1-(N$_2$)$_2$** and has been fully characterized and has diagnostic ^{1}H NMR shifts, similar to **1-Br** (Table 3). Importantly, analysis of the product mixture by ^{2}H NMR spectroscopy provided no evidence for deuterium incorporation into the isopropyl methyl groups of either **1-CD$_3$** or **1-OTf**, confirming the β-position as the source of isotopic exchange.

In addition to deuterium labeling experiments, olefins were added to **1-(N$_2$)$_2$** to further assay cyclometalation and the transfer hydrogenation step. Addition of one equivalent of 1-hexene to a benzene-d_6 solution of **1-(N$_2$)$_2$** at 23 °C resulted in clean and quantitative formation of **2** and hexane over the course of five days (eq 9). The iron-olefin compound, **2**, and ethane were also

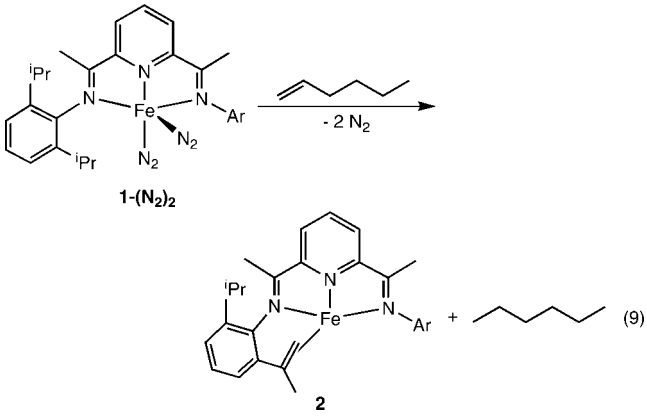
Scheme 4



Scheme 5



obtained following treatment of **1-$(N_2)_2$** with excess ethylene. However, an unidentified red precipitate was also formed. Despite this complication, these experiments clearly establish the role of the chelate isopropyl methyl groups in transfer hydrogenation of the iron alkyl.



(9)

To further substantiate the claim of facile β-hydrogen elimination and olefin dissociation prior to alkane formation, olefin for iron alkyl exchange studies were also conducted. Addition of one equivalent of isobutene to a benzene-d_6 solution of **1-CH_2^{c}Pnt** resulted in a near equimolar mixture of **1-^{i}Bu** and **1-CH_2^{c}Pnt** along with the corresponding free olefins (Scheme 4). Similar exchange reactions were observed in related bis(imino)pyridine cobalt complexes where treatment of (PDI)CoR (R = ^{n}Pr, ^{n}Bu) with ethylene yielded the corresponding cobalt ethyl and free olefins.[40]

Based on all of the experimental data, a mechanism for alkane loss from bis(imino)pyridine iron alkyl complexes is presented in Scheme 5, using **1-Et** as a representative example. β-hydrogen elimination from the iron alkyl forms the bis(imino)pyridine iron olefin hydride compound. Olefin dissociation and reinsertion (or olefin rotation) is fast relative to subsequent steps, as isotopic exchange between the β-CH_3 and α-CH_2 positions is faster than liberation of alkane. If ethylene loss occurs, a putative bis(imino)pyridine iron hydride is formed, which is known to undergo rapid loss of H_2 to form either the iron dihydrogen or N_2 complex, depending on the relative concentration of the respective gases.[29] Formal oxidative addition of an isopropyl methyl C−H bond affords the bis(imino)pyridine cyclometalated hydride. A similar species has been implicated in H/D exchange

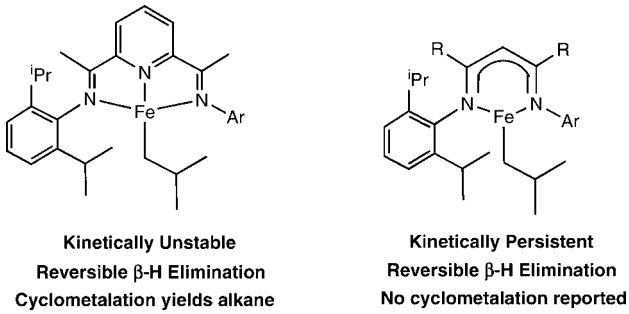


Figure 6. Kinetic stability of bis(imino)pyridine versus β-diketiminate ferrous alkyl complexes.

in the preparation of **1*-(N$_2$)$_2$** from D_2 gas.[29] Insertion of ethylene into the iron hydride bond yields the cyclometalated ethyl compound, which can undergo reversible or productive β-hydrogen elimination to furnish ethane and **2**.

It is interesting to compare the relative stability of the bis(imino)pyridine iron alkyl compounds studied in this work to the three coordinate β-diketiminate (BDI) iron alkyls reported by Holland and co-workers (Figure 6).[37] Because the **1-R** series of compounds are best described as containing high spin ferrous ions antiferromagnetically coupled to bis(imino)pyridine chelate radical anions, both classes of molecules contain a high spin ($S_{Fe} = 2$) iron coordinated to a monoanionic ligand. Furthermore, both ligand environments possess orthogonal 2,6-diisopropyl aryl substituents and to a first approximation (ignoring differences in chelate bite angles), have similar steric environments.

In a comprehensive study of iron(II) alkyl stability, Holland and co-workers prepared a broad spectrum of (BDI)Fe-R compounds bearing β-hydrogens, including secondary and tertiary iron alkyls. Isomerization of the iron alkyl and olefin for alkyl exchange reactions were observed, demonstrating that reversible β-hydrogen elimination is operative. Irreversible formation or decomposition of these compounds by alkane loss was not reported. Why then are the bis(imino)pyridine iron alkyls not kinetically persistent while the β-diketiminate compounds are?

The difference in reactivity may be traced to the competing cyclometalation in the bis(imino)pyridine compounds. The instability of the putative product of β-hydrogen elimination, **1-H**, to H_2 loss and formation of formally low-valent [(^{iPr}PDI)Fe] compounds that undergo C−H activation provide a pathway to irreversible alkane formation and hence decomposition of the iron alkyl. No analogous compound or pathway has been reported in the β-diketiminate chemistry and hence kinetically persistent iron alkyls result. It should be noted that in the bis(imino)pyridine examples, chain walking via β-hydrogen elimination, olefin dissociation (or rotation) followed by reinsertion is operative followed by a slower cyclometalation-insertion sequence.

Concluding Remarks. Neutral bis(imino)pyridine iron alkyl complexes bearing β-hydrogens have been synthesized either by salt metathesis reactions or by oxidative addition of an appropriate alkyl bromide to **1-(N$_2$)$_2$**. In the latter reactions, studies into the electronic structures of the **1-R** and **1-Br** products establish that formal electron loss occurs from the bis(imino)pyridine ligand, not the metal. Evaluation of the kinetic stability of the iron alkyl species revealed decomposition by transfer hydrogenation of an isopropyl methyl substituent on the chelate aryl rings. The ability to access reduced iron compounds, stabilized by a redox active bis(imino)pyridine chelate, promotes C−H bond oxidative addition leading to cyclometalation and irreversible formation of alkane. These studies demonstrate the viability of this processes as a chain termination pathway in bis(imino)pyridine iron catalyzed olefin polymerization reactions. Experiments designed to evaluate this possibility are currently under investigation.

Experimental Section[41]

Characterization of (^{iPr}PDI)Fe(CH$_2$CH$_3$) (1-Et). Using a calibrated gas bulb, 0.021 mmol of either bromoethane or bromoethane-d_5 was transferred to a J. Young Tube containing 0.025 mg (0.042 mmol) of **1-(N$_2$)$_2$** and approximately 0.7 mL of benzene-d_6. Upon sitting at room temperature for 20 min, the reaction mixture was found to contain **1-Br** and **1-Et** (or **1-Et-*d*$_5$**) by ^{1}H NMR spectroscopy. ^{1}H NMR (benzene-d_6, 293 K): δ = 263.35 (221 Hz, 1H, *p-pyr*), 149.69 (555 Hz, 3H, CH$_2$C*H*$_3$), 63.75 (103 Hz, 2H, *m-pyr*), −4.50 (100 Hz, 4H, *m-aryl*), −15.14 (64 Hz, 12H, CH(C*H*$_3$)$_2$), −27.88 (123 Hz, 12H, CH(C*H*$_3$)$_2$), −89.75 (308 Hz, 4H, C*H*(CH$_3$)$_2$), −172.74 (214 Hz, 6H, C(C*H*$_3$)), Fe−C*H*$_2$ and *p-aryl* resonance not located. Degradation of **1-Et** was monitored over the course of 24 h at ambient temperature. Transfer of the volatiles and analysis by ^{1}H NMR spectroscopy confirmed a 15% yield of solely ethane (based on bromoethane) as judged by integration against 1 μL of cyclohexane. A second degradation experiment yielded 92% of the ethane expected by Toepler pump analysis.

Characterization of (^{iPr}PDI)Fe(CH$_2$CHMe$_2$) (1-^{i}Bu). In a manner similar to bromoethane, gas bulb addition of 0.017 mmol of 1-bromo-2-methylpropane to 0.020 g of **1-(N$_2$)$_2$** yielded a mixture of **1-Br** and **1-^{i}Bu** in benzene-d_6, as judged by ^{1}H NMR spectroscopy. This complex was additionally observed by ^{1}H NMR spectroscopy, along with **1-Br**, from the addition of 0.002 g (2 μL, 0.017 mmol) of 2-bromo-2-methylpropane to 0.020 g (0.034 mmol) of **1-(N$_2$)$_2$** in benzene-d_6. A third method of preparation was achieved through the addition of 0.008 g (32 μL of a 2.0 M solution in ether, 0.065 mmol) of isobutylmagnesium chloride to a J. Young tube containing 0.025 g (0.044 mmol) of **1-Cl** in benzene-d_6. ^{1}H NMR (benzene-d_6, 293 K): δ = 350.03 (583 Hz, 1H, *p-pyr*), 200.42 (7533 Hz, 1H, FeCH$_2$C*H*(CH$_3$)$_2$), 73.34 (301 Hz, 6H, ^{i}Pr C*H*$_3$), 66.30 (85 Hz, 2H, *m-pyr*), −9.19 (42 Hz, 4H, *m-aryl*), −13.38 (38 Hz, 2H, *p-aryl*), −19.74 (54 Hz, 12H, CH(C*H*$_3$)$_2$), −31.10 (118 Hz, 12H, CH(C*H*$_3$)$_2$), −123.36 (336 Hz, 4H, C*H*(CH$_3$)$_2$), −185.63 (209 Hz, 6H, C(C*H*$_3$)), two peaks not located. As judged by ^{1}H NMR spectroscopy, a 55% yield of the organic degradation products (52% 2-methylpropene, 48% 2-methylpropane) was achieved upon vacuum transfer of the volatiles after 1 week and integration against 1 μL of cyclohexane.

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Supporting Information Available: Complete experimental procedures, selected NMR spectroscopic data for bis(imino)pyridine iron alkyls, magnetic data and crystallographic data for **1-Br(THF)**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(41) Representative procedures for one specific class of compounds are reported. Full details on all of the remaining compounds, including general considerations, are described in the Supporting Information.