Carbon−Oxygen Bond Cleavage by Bis(imino)pyridine Iron Compounds: Catalyst Deactivation Pathways and Observation of Acyl C−O Bond Cleavage in Esters

Ryan J. Trovitch, Emil Lobkovsky, Marco W. Bouwkamp, and Paul J. Chirik*

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853

Received June 16, 2008

Investigations into the substrate scope of bis(imino)pyridine iron-catalyzed hydrogenation and [$2\pi + 2\pi$] diene cyclization reactions identified C−O bond cleavage as a principal deactivation pathway. Addition of diallyl or allyl ethyl ether to the bis(imino)pyridine iron dinitrogen complex, (^{iPr}PDI)Fe(N_2)$_2$ (^{iPr}PDI = 2,6-(2,6-^{i}Pr$_2$-C_6H_3N═CMe)$_2$$C_5H_3$N, **1-(N$_2$)$_2$**), under a dinitrogen atmosphere resulted in facile cleavage of the C−O bond and yielded a mixture of the corresponding paramagnetic iron allyl and alkoxide complexes. For ethyl vinyl ether, clean and selective formation of the iron ethoxide was observed with concomitant loss of the vinyl fragment. In situ monitoring of the catalytic hydrogenation of *trans*-methyl cinnamate established ester C−O bond cleavage as a competing process. Stoichiometric reactions between **1-(N$_2$)$_2$** and allyl and vinyl acetate also produced facile C−O oxidative addition. For the latter, a six coordinate diamagnetic bis(imino)pyridine acetatoxy iron vinyl compound was obtained and characterized by X-ray diffraction. Phenyl acetate undergoes exclusive acyl C−O bond cleavage, while alkyl-substituted esters such as ethyl, pentyl, benzyl, isopropyl, cyclohexyl, and *tert*-butyl acetate undergo competing ester and acyl C−O bond cleavage accompanied by iron-promoted decarbonylation. Deuterium labeling studies established that reversible C−H activation and chelate cyclometalation occur prior to, but are not a prerequisite for, carbon−oxygen bond oxidative addition of ethyl acetate. The molecular and electronic structures of the ether and ester C−O bond cleavage products have been established and demonstrate that ligand- rather than metal-based oxidation accompanies substrate activation.

Introduction

Oxidative addition is a fundamental transformation in organometallic chemistry and often constitutes a key bond activation step in many stoichiometric reactions and catalytic processes.[1] This two electron redox event typically requires accessible M^n and M^{n+2} oxidation states and is most common with electron rich (e.g. d^6 and d^8), late transition metal complexes. For first row ions, oxidative addition of alkyl halides is known to involve radical processes[2] and can result in a two electron oxidation at a single metal center[3] or occur as two one electron oxidations involving two metals.[4,5]

As interest grows in replacing toxic and expensive precious metal catalysts with more cost-effective and benign iron compounds,[6,7] so grows the need to understand the elementary steps, such as oxidative addition, that comprise catalytic turnover and irreversible deactivation pathways.[8] Introduction of redox-active ligands, those that can actively participate in reversible electron transfer chemistry with the metal,[9,10] render oxidative transformations more intriguing as formal electron loss may be either metal- or ligand-based. Rationally designing compounds that undergo well-understood electron transfer events coupled to oxidative addition may ultimately prove valuable for discovering base metal catalysts that mimic or surpass the reactivity and selectivity often achieved with their second and third row congeners.

Inspired by seminal reports on $Fe(CO)_5$ promoted hydrogenation catalysis,[11,12] our laboratory has reported the synthesis of aryl-substituted bis(imino)pyridine iron dinitrogen compounds, (^{iPr}PDI)Fe(N_2)$_2$ (^{iPr}PDI = 2,6-(2,6-^{i}Pr$_2$-C_6H_3N═CR)$_2$$C_5H_3$N, R

* Corresponding author. E-mail: pc92@cornell.edu.

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) Rossi, R. A.; Pierini, A. B.; Penenory, A. B. *Chem. Rev.* **2003**, *103*, 71.

(3) San Filippo, J., Jr.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834.

(4) Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry*; Prentice Hall: Upper Saddle River, NJ, 1996; p 175.

(5) Blaser, H.-U.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 1684.

(6) Bolm, C.; Legros, J.; Le Paih, J.; Zani, L. *Chem. Rev.* **2004**, *104*, 6217.

(7) Enthaler, S.; Junge, K.; Beller, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3317.

(8) For seminal studies on the oxidative addition of E-X bonds to phosphine-ligated Fe(0) and related complexes see (a) Klein, H.-F. *Angew. Chem., Int. Ed.* **1980**, *19*, 362. (b) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 6073. (c) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080. (d) Parker, S. F.; Peden, C. H. F.; Barrett, P. H.; Pearson, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1304.

(9) Jørgensen, C. K. *Coord. Chem. Rev.* **1966**, *1*, 164.

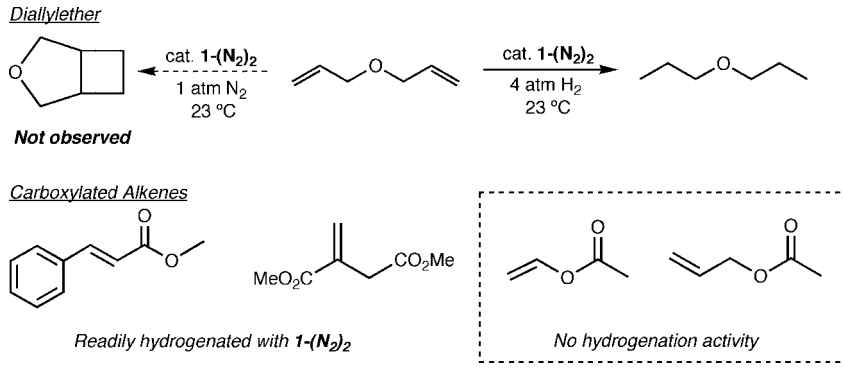
(10) (a) Pierpont, C. G *Coord. Chem. Rev.* **2001**, *219−221*, 415. (b) Ward, M. D.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **2002**, 275. (c) Chaudhuri, P.; Verani, C. N.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2001**, *123*, 2213.

(11) (a) Schroeder, M. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 551. (b) Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345.

(12) Frankel, E. N.; Emken, E. A.; Peters, H. M.; Davison, V. L.; Butterfield, R. O. *J. Org. Chem.* **1964**, *29*, 3292.

10.1021/om8005596 CCC: $40.75
Publication on Web 10/30/2008

Scheme 1



= Me, **1-(N$_2$)$_2$**;[13] R = Ph, **2-(N$_2$)$_2$**),[14] that function as efficient catalysts for the hydrogenation and hydrosilylation of olefins and alkynes at low metal loadings. Subsequently, **1-(N$_2$)$_2$** was also found to promote the catalytic [2π + 2π] cycloisomerization of α, ω-dienes to yield substituted cyclobutanes.[15] Spectroscopic and computational studies on **1-(N$_2$)$_2$**[16] and on related neutral ligand derivatives, (^{iPr}PDI)FeL$_n$ (L = CO, PR$_3$, NH$_2$R, N≡CPh, etc.),[17] have unequivocally established the redox-activity of the bis(imino)pyridine chelate (Figure 1).[18] Thus, **1-(N$_2$)$_2$** is best described as an intermediate spin, d^6 ferrous compound antiferromagnetically coupled to a bis(imino)pyridine diradical dianion.[16]

During the course of our investigations into the substrate scope of catalytic olefin hydrogenation and [2π + 2π] cycloisomerization reactions with **1-(N$_2$)$_2$**,[19] dramatic substituent effects were observed (Scheme 1). Diallyl ether was readily hydrogenated to dipropyl ether in the presence of **1-(N$_2$)$_2$** and 4 atm of dihydrogen. Performing the reaction under a dinitrogen atmosphere, in an attempt to induce [2π + 2π] cycloaddition, produced no turnover. Likewise, *trans*-methyl cinnamate and dimethyl itaconate were both readily hydrogenated to the corresponding acetatoxy-substituted alkane with **1-(N$_2$)$_2$** and 4 atm of H$_2$, while allyl and vinyl acetate exhibited no turnover under the same conditions (Scheme 1).[19]

Here, we describe a systematic investigation into the interaction of various ethers, esters, and carboxylated alkenes with **1-(N$_2$)$_2$**. In addition to identifying important deactivation pathways in catalytic olefin hydrogenation and [2π + 2π] cycloisomerization processes, these studies provide fundamental insight into oxidative addition chemistry at a reducing iron center bearing a redox active ligand[20] and demonstrate rare examples of acyl C−O bond cleavage in alkyl-substituted esters.

Results

Carbon−Oxygen Bond Cleavage in Ethers. The divergent reactivity of diallyl ether in catalytic hydrogenation (facile turnover)[19] versus [2π + 2π] cycloisomerization (no turnover)[15] with **1-(N$_2$)$_2$** prompted further investigation into the substrate−iron interaction. Treatment of a pentane solution of **1-(N$_2$)$_2$** with 0.5 equivalents of diallyl ether at 23 °C furnished two iron products, the bis(imino)pyridine iron allyloxide and the iron allyl, **1-OCH$_2$CH=CH$_2$** and **1-Allyl**, respectively (Scheme 2). Red, paramagnetic **1-Allyl** was also independently synthesized by allylation of **1-Br** with one equivalent of CH$_2$=CHCH$_2$MgBr. While this method yielded **1-Allyl**, the product was contaminated with small yet inseparable amounts of **1-Br** even when excess Grignard reagent was used.

The ^{1}H NMR spectroscopic features of **1-Allyl** are notably different from S = 3/2 bis(imino)pyridine iron alkyls, alkoxides and halides. Typically, these compounds, (^{iPr}PDI)Fe-X (X = Br, **1-Br**; Me, **1-Me**; CH$_2$CMe$_3$, **1-Np**),[21,22] exhibit paramagnetically shifted resonances over a 600 ppm chemical shift range. Importantly, the hydrogen atoms located in the chelate plane appear the most shifted from their diamagnetic reference values. For example, the imine methyl groups of these complexes appear upfield between −160 and −220 ppm, while the *p*-pyridine hydrogen resonances are the most downfield, between 200 and 400 ppm, depending on the identity of the X-type ligand. The *m*-pyridine peak generally appears around 65 ppm and varies only slightly as a function of the X-type ligand. Additionally, the isopropyl methine resonances are shifted significantly upfield, to approximately −110 ppm, likely due to a through space interaction with the metal center. In contrast, the paramagnetically broadened resonances of **1-Allyl** are dispersed over a much narrower chemical shift range (~175 ppm). The imine methyl and *m*-pyridine resonances appear at −26.64 ppm and 47.64 ppm, respectively. The narrower chemical shift range is likely due to an η^3-, rather than η^1-, allyl interaction in benzene solution and a different degree of bis(imino)pyridine chelate reduction. The observed C_{2v} symmetry of the compound is a result of an in-plane rotation of the η^3-allyl or facile η^3-, η^1-interconversion on the NMR time scale.

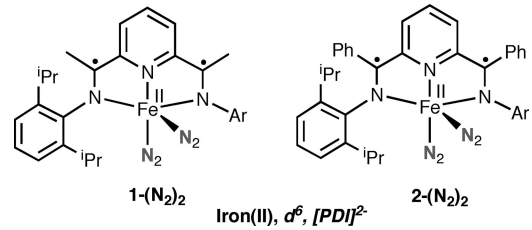
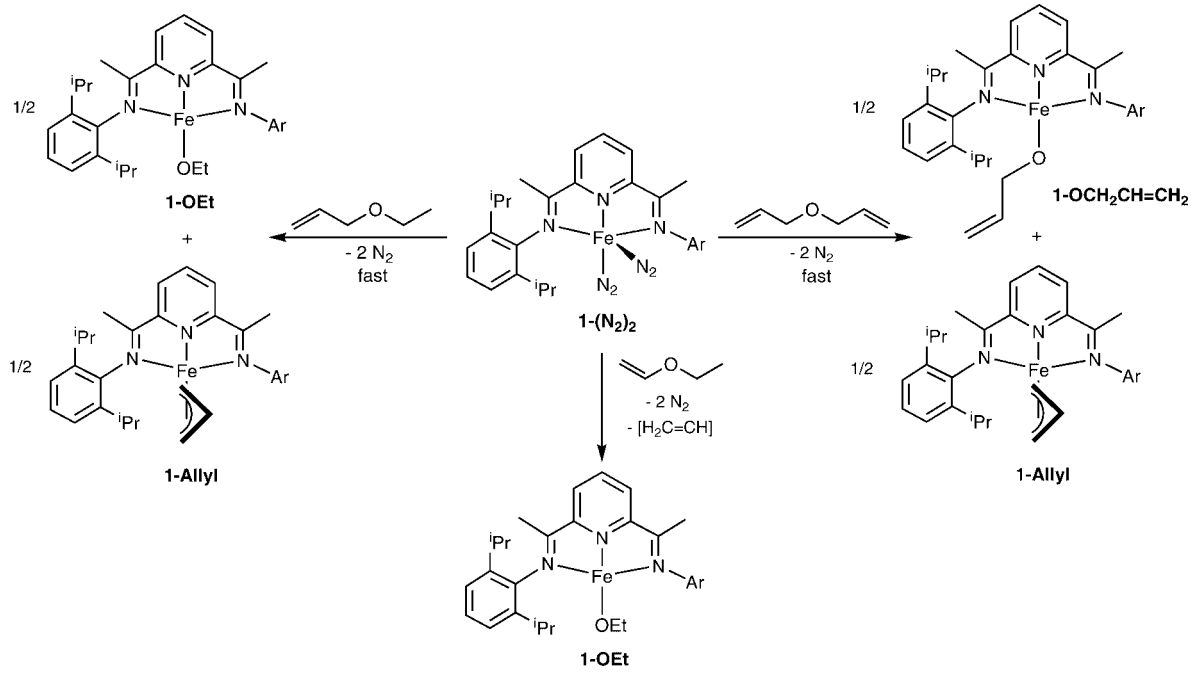


Figure 1. Bis(dinitrogen) iron complexes bearing redox active bis(imino)pyridine ligands.

(13) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 13794.
(14) Archer, A. M.; Bouwkamp, M. W.; Cortez, M.-P.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2006**, *25*, 4269.
(15) Bouwkamp, M. W.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13340.
(16) Bart, S. C.; Chlopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901.
(17) Bart, S. C.; Lobkovsky, E.; Bill, E.; Wieghardt, K.; Chirik, P. J. *Inorg. Chem.* **2007**, *46*, 7055.
(18) (a) Knijnenburg, Q.; Gambarotta, S.; Budzelaar, P. H. M. *Dalton Trans.* **2006**, 5442. (b) Zhu, D.; Budzelaar, P. H. M. *Organometallics* **2008**, *27*, 2699.
(19) Trovitch, R. J.; Lobkovsky, E.; Bill, E.; Chirik, P. J. *Organometallics* **2008**, *27*, 1470.
(20) (a) Bianchini, C.; Giambastiani, G.; Rios, I. G.; Mantovani, G.; Meli, A.; Segarra, A. M. *Coord. Chem. Rev.* **2006**, *250*, 1391. (b) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (c) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849.

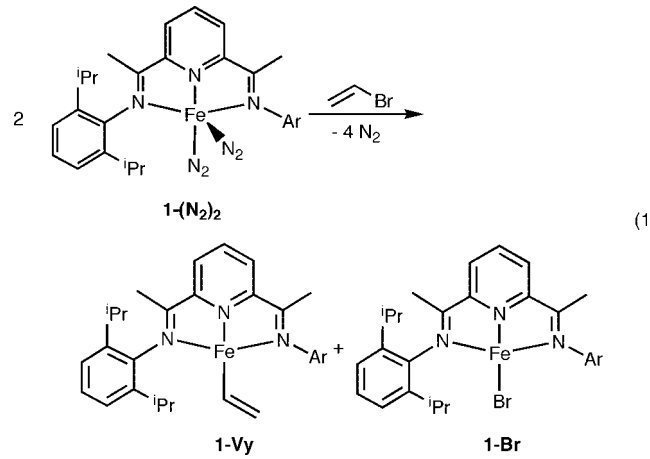
Scheme 2



The observation of facile diallyl ether C−O bond cleavage by **1-$(N_2)_2$** under mild conditions prompted additional studies into the scope of the transformation. Addition of 0.5 equivalents of allyl ethyl ether to a pentane solution of **1-$(N_2)_2$** at 23 °C yielded **1-Allyl** and the bis(imino)pyridine iron ethoxide compound, **1-OEt** (Scheme 2). These two products were formed exclusively, demonstrating selective and quantitative cleavage of the allylic C−O bond. The iron ethoxide complex, **1-OEt**, was independently synthesized by the addition of one equivalent of anhydrous ethanol to **1-$(N_2)_2$**. Other unidentified, ^{1}H NMR-silent paramagnetic iron compounds are also formed from this synthetic route and likely account for the fate of the hydrogen atom. These species were detected by ^{2}H NMR spectroscopy following the addition of CH_3CH_2OD.

Selective C−O bond cleavage was also observed with ethyl vinyl ether. Stirring a pentane solution of **1-$(N_2)_2$** with one equivalent of CH_2=$CHOCH_2CH_3$ for 24 h yielded **1-OEt** as the sole, ^{1}H NMR observable iron product (Scheme 2). To explore whether the putative bis(imino)pyridine iron vinyl complex is sufficiently stable to observe by ^{1}H NMR spectroscopy, an independent synthesis was pursued. Our laboratory has previously reported the oxidative addition of alkyl bromides to **1-$(N_2)_2$** as a convenient method to synthesize four-coordinate bis(imino)pyridine iron alkyls.[21] Extending this approach to sp^2-hybridized alkenyl halides may allow synthesis of the desired vinyl compound.

Addition of 0.5 equivalents of vinyl bromide to **1-$(N_2)_2$** yielded a mixture of the bis(imino)pyridine iron monobromide, **1-Br**,[22] and the desired iron vinyl complex, **1-Vy** (eq 1). Unfortunately, **1-Vy** was formed in low (∼30%) yield. Attempts to synthesize the compound by salt metathesis of **1-Br** with CH_2=$CHMgBr$ were unsuccessful. Under an inert atmosphere in benzene-d_6 at 23 °C, **1-Vy** persists for over 48 h after which time ethane[23] and unidentified iron compounds were observed. The ^{1}H NMR resonances and half-life established from the independent synthesis of **1-Vy** clearly demonstrate that the iron vinyl compound is not a product of ethyl vinyl ether cleavage.



(1)

To probe whether a ^{1}H NMR-silent iron compound accompanied the formation of **1-OEt** and accounted for the missing vinyl fragment, **1-$(N_2)_2$** was treated with 0.5 equivalents of ethyl vinyl ether. Monitoring this experiment by ^{1}H NMR spectroscopy established approximately 50% conversion to **1-OEt** with the balance of the iron remaining as **1-$(N_2)_2$**. While accurate quantitation of the relative amounts of paramagnetic versus diamagnetic iron compounds is complicated by the different relaxation rates of the hydrogens, this experiment demonstrated that no other iron compounds accompany **1-OEt** formation from ethyl vinyl ether cleavage. Because no other organic products (ethane, acetylene, etc.) were observed, the fate of the vinyl fragment remains unknown.

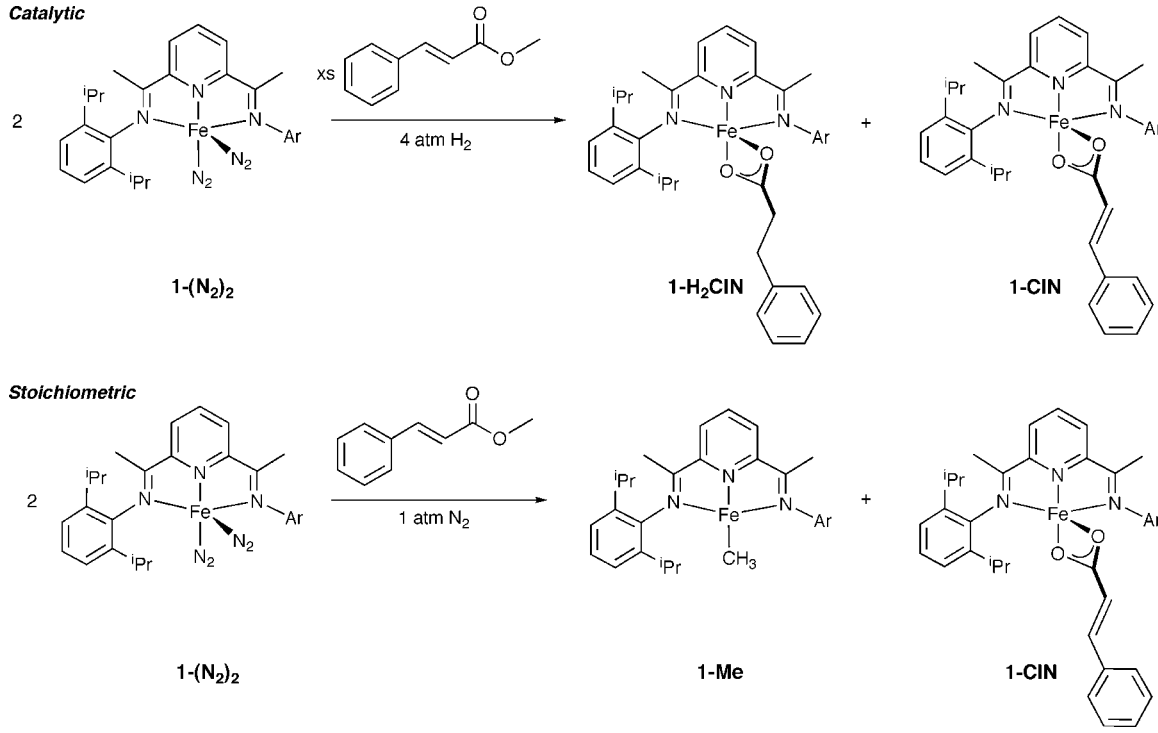
Given the facility with which unsaturated ethers undergo C−O bond cleavage with **1-$(N_2)_2$**, similar chemistry was

(21) Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J *J. Am. Chem. Soc.* **2008**, *130*, 11631.

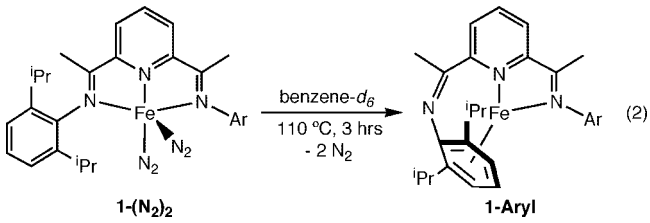
(22) Bouwkamp, M. W.; Bart, S. C.; Hawrelak, E. J.; Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. *Chem. Commun.* **2005**, *27*, 3406.

(23) Thorn, R. P.; Payne, W. A.; Stief, L. J.; Tardy, D. C. *J. Phys. Chem.* **1996**, *100*, 13594.

Scheme 3



explored with saturated compounds. No evidence for C−O bond rupture was obtained upon heating **1-(N$_2$)$_2$** with a large excess of diethyl ether or THF. For the THF experiments, the diamagnetic coordination complex, **1-(THF)$_n$** (n = 1, 2) was observed by ^{1}H NMR spectroscopy analogous to the previously reported compound with the phenylated backbone.[14] Addition of excess anisole to a benzene-d_6 solution of **1-(N$_2$)$_2$** produced no change at 23 °C. Heating this solution in a sealed tube to 110 °C for three hours resulted in clean conversion to a new diamagnetic, C_s symmetric iron compound with arene resonances centered at 4.14 (*para*) and 5.46 (*meta*) ppm. These peaks are diagnostic for an η^6-coordinated aryl group (eq 2).[14] The product has therefore been assigned as **1-Aryl**, similar to the structurally characterized compound previously reported for the bis(imino)pyridine iron complex with a phenyl-substituted backbone.[14] In a control experiment, a benzene-d_6 solution of **1-(N$_2$)$_2$** was heated to 110 °C and yielded **1-Aryl**, demonstrating that the anisole plays little, if any, role in arene coordination.



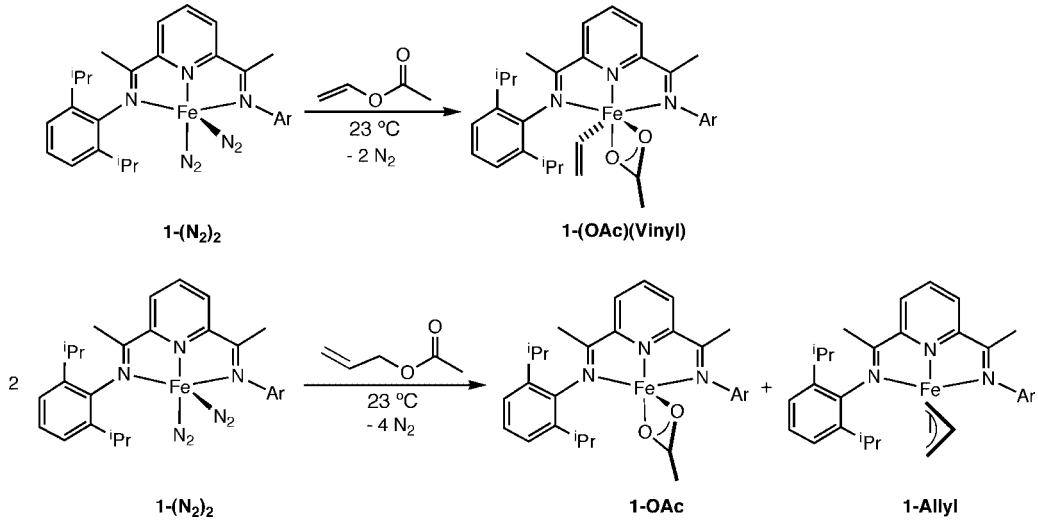
(2)

Carbon−Oxygen Bond Cleavage in Carboxylated Alkenes. As reported previously,[19] **1-(N$_2$)$_2$** is an effective precatalyst for the hydrogenation of various carboxylated alkenes. During the course of exploring the substrate scope in this class of reductions, certain peculiarities were observed. Substrates such as *trans*-methyl cinnamate and dimethylitaconate were readily hydrogenated under 4 atm of H_2 in the presence of **1-(N$_2$)$_2$**, while other compounds such as vinyl and allyl acetate produced no turnover under the same conditions. For the successful catalytic hydrogenations, relatively high catalyst loadings of 5 mol % were required. Pure hydrocarbon substrates such as cyclohexene or 1-hexene can be reduced with superior turnover frequencies using only 0.3 mol % of **1-(N$_2$)$_2$**,[13] suggesting a potential catalyst deactivation pathway with the functionalized substrates.

The possibility of **1-(N$_2$)$_2$** deactivation by C−O bond cleavage prompted a series of additional experiments whereby the fate of the iron compound was directly studied by ^{1}H NMR spectroscopy. Performing the hydrogenation of *trans*-methyl cinnamate with 10 mol % **1-(N$_2$)$_2$** established the formation of two new paramagnetic iron compounds during the course of catalytic turnover. Both compounds gradually accumulated over time and were the exclusive iron products after hours of hydrogenation. A subsequent series of experiments identified these compounds as the bis(imino)pyridine iron cinnamate and hydrocinnamate compounds, **1-CIN** and **1-H$_2$CIN**, respectively, arising from ester C−O bond cleavage (Scheme 3). Both compounds were independently prepared by the addition of the free carboxylic acid to **1-(N$_2$)$_2$**. Isolating each compound and subjecting it to catalytic hydrogenation conditions produced no turnover, demonstrating that C−O bond cleavage is a competing catalyst deactivation pathway. The hydrogenated compound, **1-H$_2$CIN** derives from C−O bond scission of the reduced product formed during catalytic turnover, as attempts to hydrogenate **1-CIN** in the presence of **1-(N$_2$)$_2$** produced no conversion.

Observation of ester C−O bond cleavage under catalytic hydrogenation conditions prompted an additional series of stoichiometric experiments. Addition of one-half of an equivalent of *trans*-methyl cinnamate to a benzene-d_6 solution of **1-(N$_2$)$_2$** at 23 °C under a dinitrogen atmosphere resulted in immediate cleavage of the ester C−O bond to yield an equimolar mixture of the bis(imino)pyridine iron cinnamate complex, **1-CIN**, and the iron methyl compound, **1-Me**[22] (Scheme 3). Exposure of this mixture of products and excess *trans*-methyl cinnamate to 4 atm of H_2 resulted in complete consumption of

Scheme 4



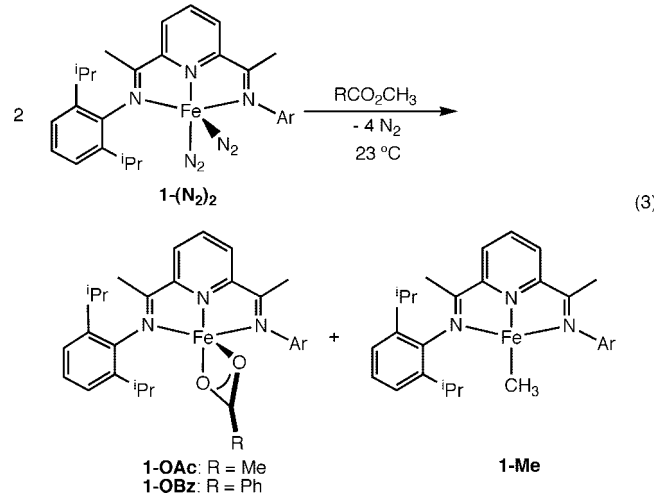
1-Me, forming methane, **1-CIN**, and **1-H_2CIN**, and accounts for the observations made during catalytic turnover.

The observation of H_2 pressure dependent C−O bond cleavage with *trans*-methyl cinnamate prompted a more detailed investigation into the reaction chemistry of vinyl and allyl acetate with **1-$(N_2)_2$**. Recall that these substrates were not hydrogenated using 5−10 mol % of **1-$(N_2)_2$** and 4 atm of dihydrogen, suggesting rapid C−O bond cleavage (Scheme 1).[19] Addition of one equivalent of vinyl acetate to a pentane solution of **1-$(N_2)_2$** followed by recrystallization at −35 °C furnished bright purple crystals identified as **1-(OAc)(Vinyl)** (Scheme 4).

1-(OAc)(Vinyl) is diamagnetic and was readily characterized by multinuclear (^{1}H and ^{13}C) and two-dimensional NMR spectroscopy. The benzene-d_6 ^{1}H NMR spectrum recorded at 23 °C exhibits the number of peaks consistent with overall C_s molecular symmetry with the mirror plane equivalencing the bis(imino)pyridine chelate plane. The β-hydrogens on the vinyl ligand appear as two doublets centered at 4.66 and 1.87 ppm for the *cis* and *trans* (with respect to the iron) hydrogens on the terminal carbon. The methine hydrogen on the carbon directly attached to the metal appears downfield at 10.07 ppm with a $\{^1H\}^{13}C$ NMR resonance for this position observed at 189.91 ppm. These assignments have been confirmed by COSY, HSQC, and HMBC NMR spectroscopy.

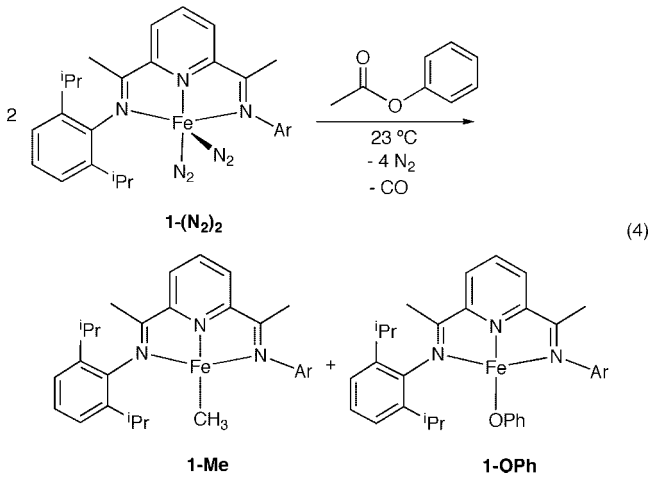
Addition of allyl acetate to **1-$(N_2)_2$** at 23 °C also resulted in rapid cleavage of the ester C−O bond; however, two products, the bis(imino)pyridine iron acetate, **1-OAc**, and allyl complex, **1-Allyl**, were observed (Scheme 4). Small amounts (5−10%) of free propene were also observed when the reaction was conducted in a sealed NMR tube. The alkene likely arises from decomposition of **1-Allyl**, as more propene accumulated over the course of one week at 23 °C and was observed from the cleavage of diallyl ether.

C−O Bond Cleavage in Saturated and Phenyl-Substituted Esters. The possibility of C−O bond cleavage in saturated esters was also explored. Addition of methyl acetate to **1-$(N_2)_2$** at 23 °C resulted in the formation of the iron acetate complex, **1-OAc**, and the iron methyl compound, **1-Me** (eq 3). Careful monitoring of the reaction mixture by ^{1}H NMR spectroscopy revealed that the bis(imino)pyridine iron ester complex, **1-MeOAc**, was formed immediately after mixing. The imine methyl resonance is shifted upfield to −4.88 ppm, while the *m*- and *p*-pyridine resonances appear downfield at 11.67 and 8.63 ppm, respectively. These chemical shifts are diagnostic of temperature independent paramagnetism, whereby an $S = 1$ excited-state mixes into the $S = 0$ ground-state by spin orbit coupling.[16] A similar C−O bond cleavage reaction was observed following the addition of methyl benzoate to **1-$(N_2)_2$**; an equimolar mixture of the bis(imino)pyridine iron benzoate compound, **1-OBz**, and **1-Me**, was identified (eq 3). In this case, the putative bis(imino)pyridine iron methyl benzoate complex, **1-MeOBz**, was not observed by NMR spectroscopy.



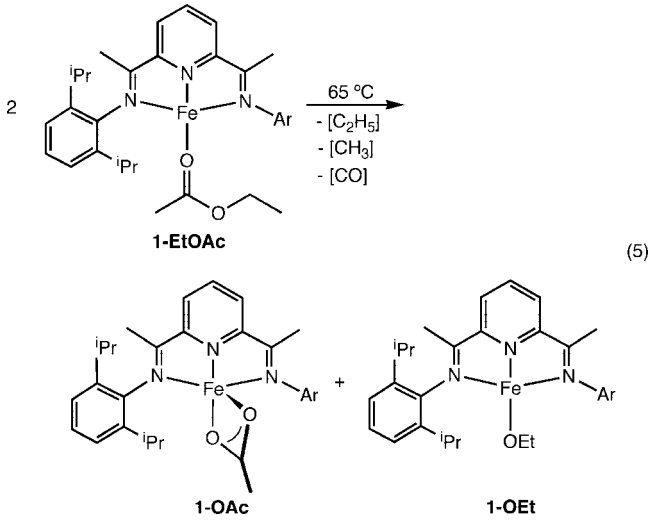
Addition of an isomer of methyl benzoate, phenyl acetate, to **1-$(N_2)_2$** reversed the selectivity of the C−O bond cleavage reaction. Addition of one equivalent of phenyl acetate to a benzene-d_6 solution of **1-$(N_2)_2$** exclusively yielded the products of *acyl* C−O bond cleavage: the iron phenoxide complex, **1-OPh**, and **1-Me** (eq 4). Careful inspection of the diamagnetic region of the ^{1}H NMR spectrum also revealed formation of small quantities **1-$(CO)_2$** accounting for the fate of the carbonyl group.[24]

(24) Yamamoto, A.; Kakino, R.; Shimizu, I. *Helv. Chim. Acta* **2001**, *84*, 2996.
(25) Neese, F. *Inorg. Chim. Acta* **2002**, *337*, 181.
(26) Fernández, I.; Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2008**, *27*, 109.
(27) Furimsky, E. *Appl. Catal., A* **2000**, *199*, 147.
(28) Lin, Y. S.; Yamamoto, A. In *Topics in Organometallic Chemistry*; Murai, S., Ed.; Springer-Verlag: Berlin, Germany, 1999; Vol *3*, p 161.
(29) Trost, B, Verhoven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, A. E., Eds.; Pergamon: Oxford, England, 1982; Vol *8*, p 799.
(30) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385.



(4)

Because acyl bond cleavage, particularly in alkyl esters, is relatively rare,[24] the scope and selectivity of bis(imino)pyridine iron C−O bond cleavage was examined in more detail. Addition of one equivalent of ethyl acetate to a benzene-d_6 solution of **1-(N$_2$)$_2$** at 23 °C immediately yielded the bis(imino)pyridine iron ethyl acetate complex, **1-EtOAc**. Gently warming a benzene-d_6 solution of **1-EtOAc** to 65 °C for 18 h yielded an equimolar mixture of **1-OAc** and **1-OEt** (eq 5).

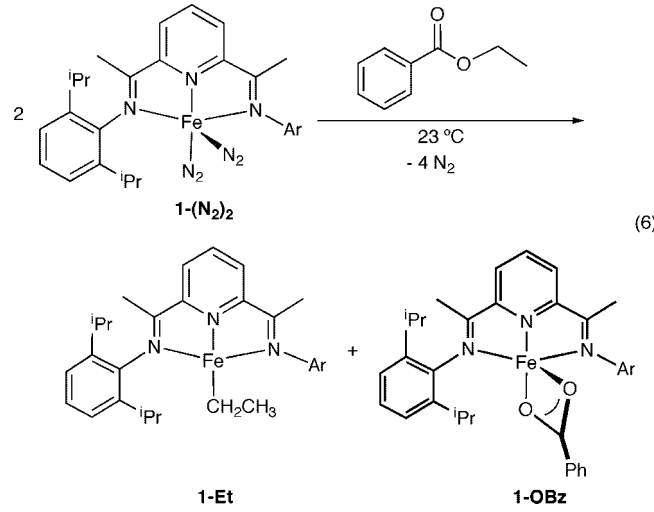


(5)

The formation of the iron acetate and ethoxide compounds signals two competing C−O bond cleavage reactions. **1-OAc** is the product of ester C−O bond cleavage, while **1-OEt** is the persistent product derived from acyl C−O bond rupture. Ester C−O bond cleavage would, in principle, also form the bis(imino)pyridine iron ethyl complex, **1-Et**. This compound was previously synthesized by our laboratory and found to decompose over the course of hours at 23 °C.[21] Under the more forcing conditions required for ethyl acetate cleavage (18 h at 65 °C), **1-Et** would not persist. For acyl C−O bond cleavage, the bis(imino)pyridine iron methyl complex, **1-Me**, is the other expected product. This compound was also not observed, but it too is unstable under the conditions required for ethyl acetate cleavage. Control experiments on isolated samples of pure **1-Me** revealed decomposition to an unidentified mixture of products upon heating to 65 °C. Thus, **1-OAc** and **1-OEt** were the only products thermally robust enough to persist following ethyl acetate cleavage.

In an attempt to observe the putative bis(imino)pyridine iron alkyl products from ethyl acetate cleavage, the reaction was repeated at 23 °C. The expected products, **1-OAc** and **1-OEt**, were observed over the course of one week. No evidence for the formation of either **1-Me** or **1-Et** was obtained by ^{1}H NMR spectroscopy. The inability to observe **1-Et** is a result of the relative fast rate ($t_{1/2}$ ~3 h) of decomposition of the iron alkyl[21] compared to the slower rate ($t_{1/2}$ ~3 days) of the C−O bond cleavage reaction. Because the bis(imino)pyridine iron acyl complex, **1-C(O)Me**, is a likely product following the oxidative addition of the acyl C−O bond of ethyl acetate, attempts were made to evaluate the kinetic stability of such an intermediate. Addition of one atmosphere of carbon monoxide to a benzene-d_6 solution of **1-Me** resulted in immediate formation of **1-(CO)$_2$** along with small quantities of acetone and methane. In a related experiment, addition of 0.5 equivalents of $CH_3C(O)Cl$ to a benzene-d_6 solution of **1-(N$_2$)$_2$** yielded **1-Cl** along with **1-Me**, consistent with decarbonylation from the putative bis(imino)pyridine iron acyl.

As part of our studies into the substrate scope and selectivity of C−O bond cleavage, the chemistry of ethyl benzoate was explored. Addition of one equivalent of this ester to **1-(N$_2$)$_2$** at 23 °C resulted in rapid and exclusive cleavage of the ester C−O bond over the course of two hours to furnish **1-Et** and **1-OBz** (eq 6). No products derived from acyl C−O bond cleavage were detected by ^{1}H NMR spectroscopy. This result demonstrates that when ester C−O bond cleavage is sufficiently facile, the alkyl products can be observed by ^{1}H NMR spectroscopy. Thus, it is likely that **1-Et** is formed from ester C−O bond oxidative addition of ethyl acetate but has a rate of decomposition faster than substrate activation.

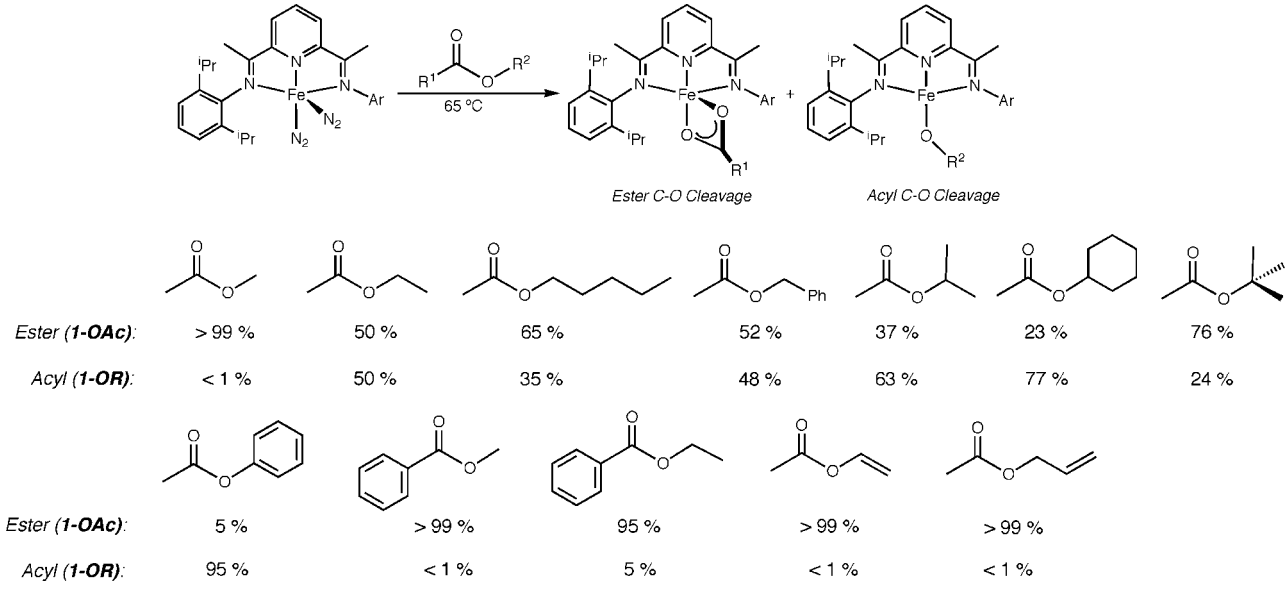


(6)

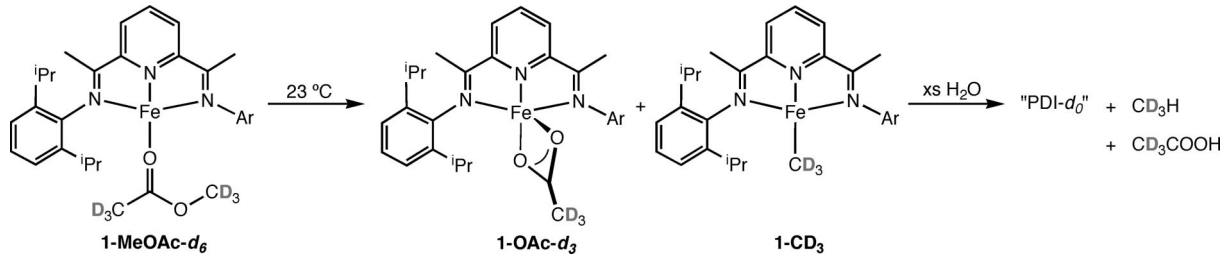
Having demonstrated rare examples of acyl C−O bond cleavage with phenyl and ethyl acetate at ambient temperature, **1-(N$_2$)$_2$** was treated with other alkyl acetates to assay selectivity. The results of these studies are summarized in Scheme 5. Because the reactions were conducted at 65 °C, the corresponding bis(imino)pyridine iron alkyl complexes were not observed. Thus, only the kinetically persistent iron acetate and iron alkoxide compounds were detected by ^{1}H NMR spectroscopy. The ratios of products are approximate because they were determined by integration of paramagnetically broadened and shifted isopropyl methyl resonances.

Observation of acyl C−O bond cleavage in esters suggested that similar chemistry may be possible with formates. Treatment of **1-(N$_2$)$_2$** with one equivalent of either ethyl, isopropyl, or phenyl formate cleanly afforded the desired bis(imino)pyridine iron alkoxide compounds, **1-OEt**, **1-O^{i}Pr**, and **1-OPh**, respectively (eq 7). As with acyl bond cleavage in esters, examination

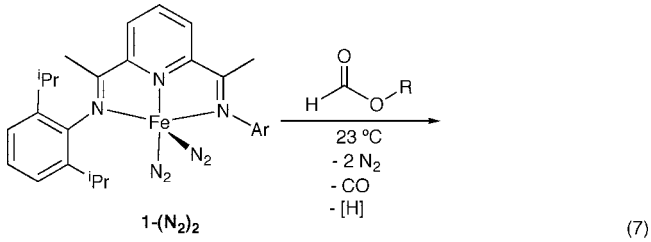
Scheme 5



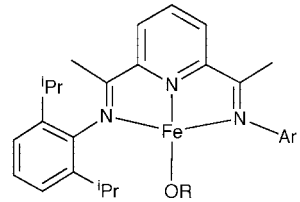
Scheme 6



of the diamagnetic region of the ^{1}H NMR spectrum revealed the formation of small quantities of **1-(CO)$_2$**, consistent with decarbonylation. To provide additional evidence for CO loss, the cleavage of isopropyl formate was conducted with an excess of **1-(N$_2$)$_2$**. Under these conditions, the expected amount of **1-(CO)$_2$** (25%) was detected by ^{1}H NMR spectroscopy.



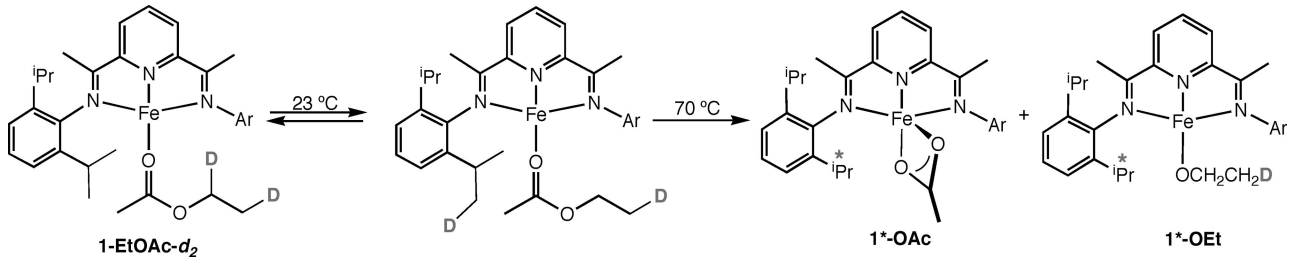
(7)



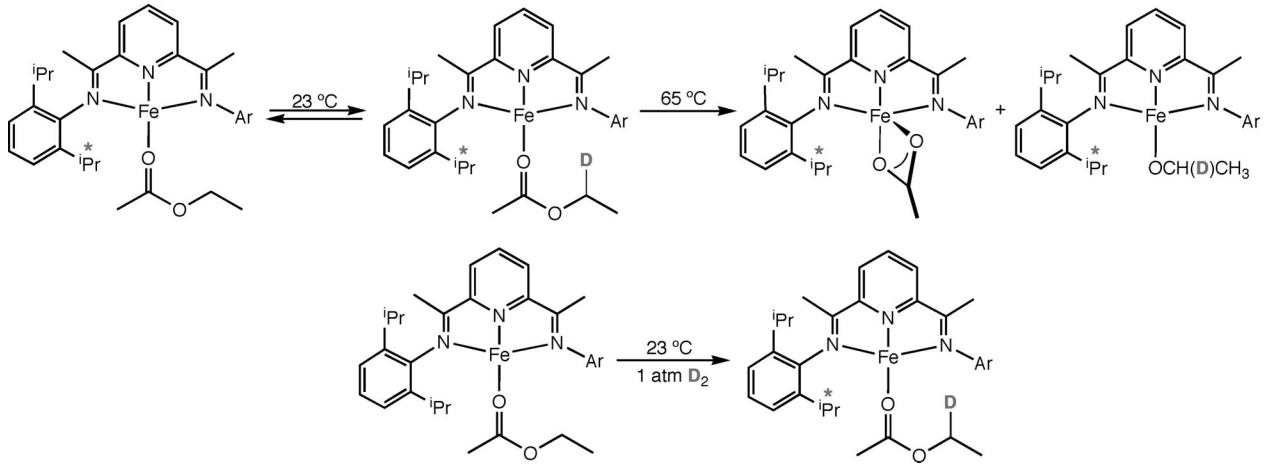
Deuterium Labeling Experiments. A series of deuterium labeling experiments were conducted to probe whether C−H(D) activation was competitive with iron-promoted ester cleavage. Addition of methyl acetate-d_6 to a benzene or benzene-d_6 solution of **1-(N$_2$)$_2$** at 23 °C resulted in observation of **1-MeOAc-d_6**, as judged by ^{1}H and ^{2}H NMR spectroscopy. Over time, **1-MeOAc-d_6** cleanly converted to an approximately equimolar mixture of **1-OAc-d_3** and **1-CD$_3$** (Scheme 6). Because the methyl group of **1-CD$_3$** (or isotopologues) has not been detected by NMR spectroscopy, chemical degradation experiments were used to determine the isotopic composition of the iron methyl group. Hydrolysis of the product mixture and subsequent analysis of the bis(imino)pyridine ligand by ^{2}H NMR spectroscopy established no deuterium incorporation into the isopropyl methyl substituents. Collection of the liberated methane from protonolysis of the iron methyl complex and analysis by ^{1}H NMR spectroscopy clearly demonstrated that CD_3H was the sole isotopologue of methane formed. A converse experiment was also conducted whereby natural abundance methyl acetate was added to the deuterium labeled bis(imino)pyridine iron dinitrogen complex, **1*-(N$_2$)$_2$**, (* denotes deuterium labeling of the isopropyl methyl substituents).[13] In this case, **1*-OAc** and **1*-CH$_3$** were identified as the sole products. Again, the isotopic composition of the iron methyl group was assayed by hydrolysis, and CH_4 was the only methane isotopologue observed by ^{1}H NMR spectroscopy.

Analogous experiments were conducted with isotopologues of ethyl acetate; preparation of 1,2-d_2-ethyl acetate was accomplished by D_2 addition to vinyl acetate in the presence of a catalytic amount of palladium on carbon. Addition of the isotopically labeled ester to **1-(N$_2$)$_2$** immediately furnished the diamagnetic bis(imino)pyridine iron ethyl acetate complex, **1-EtOAc-d_2**. As anticipated, the benzene solution ^{2}H NMR spectrum exhibited two peaks centered at 0.74 and 3.02 ppm for the coordinated ester. Allowing the solution to stand at 23 °C for 20 min revealed isotopic exchange between the isopropyl methyl group of the bis(imino)pyridine chelate and the meth-

Scheme 7



Scheme 8



ylene position (Scheme 7). No evidence was obtained for isotopic exchange involving the methyl group of the ester. Warming the solution to 70 °C for 14 h yielded the bis(imino)pyridine iron acetate and ethoxide compounds (Scheme 7). Analysis of the product mixture by ^{2}H NMR spectroscopy revealed deuterium incorporation in the isopropyl methyl groups of the bis(imino)pyridine ligands in both **1*-OEt** and **1*-OAc** and in the methyl group of the iron ethoxide.

The converse experiment was conducted, whereby the deuterium labeled iron dinitrogen compound, **1*-(N$_2$)$_2$**, was treated with a slight excess of natural abundance ethyl acetate (Scheme 8). Over the course of four hours at 23 °C, deuterium exchange was observed with the methylene position of both the free and coordinated esters. No evidence was obtained for isotopic exchange into the terminal methyl group. Warming the solution to 65 °C resulted in C−O bond cleavage and yielded the expected iron acetate and ethoxide compounds. Analysis of the paramagnetic iron products by ^{2}H NMR spectroscopy established deuterium incorporation into the isopropyl methyl groups of both compounds (Scheme 8). To establish the isotopic composition of the acetate and ethoxide ligands, each bis(imino)pyridine iron compound was treated with water and the organic products: free bis(imino)pyridine, ethanol, and acetic acid were analyzed by ^{2}H NMR spectroscopy. While no deuterium was detected in the acetic acid, the free ethanol exhibited a peak consistent with isotopic incorporation exclusively in the methylene position.

In a related experiment, a benzene solution of **1-EtOAc** was exposed to 4 atm of D_2 gas at 23 °C. Over the course of four hours, isotopic exchange was observed in the isopropyl methyl group of the bis(imino)pyridine chelate of **1-EtOAc** as well as in the methylene position of the ester (Scheme 8). When the reaction is carried out with excess ethyl acetate, the deuteration of the methylene is catalytic, demonstrating rapid C−H activation and ligand exchange prior to C−O bond cleavage. The observation of reversible ester coordination is similar to the behavior observed between **1-(N$_2$)$_2$** and amines or ketones.[19]

X-ray Structures of Selected C−O Bond Cleavage Products. Several of the products of ether and ester C−O bond cleavage were characterized by single crystal X-ray diffraction. The bond lengths of the bis(imino)pyridine ligand determined from high quality X-ray diffraction data are diagnostic for redox activity of the chelate.[18a] While these parameters are undoubtedly useful, it should be noted that a complete and accurate description of the electronic structure is only obtained from a combination of magnetochemistry, structural analysis, and Mössbauer spectroscopy augmented with open shell DFT calculations.[25] The relevant metrical parameters for the bis(imino)pyridine chelates for all structurally characterized compounds in this work are reported in Table 1. Features of each individual structure will be described independently.

A representation of the solid state structure of **1-OCH$_2$-CH=CH$_2$** is presented in Figure 2. An idealized square planar iron center is observed with the sum of the angles around the metal totaling 360°. The metrical parameters of the chelate (Table 1) are consistent with one electron reduction.[16] A benzene-d_6 solution magnetic moment of 4.0 μ_B was determined by Evans method at 23 °C and is consistent with an $S = 3/2$ iron compound. The magnetic data, in combination with the metrical parameters, suggest that **1-OCH$_2$CH=CH$_2$** is best described as a high spin iron(II) compound ($S_{Fe} = 2$) antiferromagnetically coupled to a bis(imino)pyridine radical anion ($S_L = 1/2$). Both electronic and molecular structures of this compound are identical to that previously described for the isoelectronic bis(imino)pyridine iron chloride, **1-Cl**.[16]

The solid state structures of **1-OAc** and **1-OBz** were also determined and are presented in Figure 3. In both cases, the iron is five coordinate with a κ^2-carboxylate, where the O(1)−C(34)−O(2) and iron chelate planes are essentially orthogonal. The central carboxylate carbons, C(34), are nearly

Table 1. Selected Bond Lengths (Å) and Angles (Deg) for Compounds Crystallographically Characterized in This Work

	1-OCH$_2$CH=CH$_2$	1-OAc	1-OBz	1-Allyl	1-(OAc)(Vinyl)
Fe(1)−N(1)	2.1242(17)	2.1085(15)	2.1166(13)	1.9934(11)	1.9540(9)
Fe(1)−N(2)	1.9983(17)	1.9949(17)	1.9842(15)	1.8418(11)	1.7976(9)
Fe(1)−N(3)	2.1467(18)	2.1615(15)	2.1269(15)	2.0017(12)	1.9504(9)
Fe(1)−O(1)	1.8486(16)	2.0837(16)	2.116(13)	2.074(3)[a]	2.0771(9)
Fe(1)−O(2)		2.1271(14)	2.1033(13)	2.151(3)[b]	2.0135(8)
Fe(1)−C(34)		2.430(2)	2.437(2)	2.155(4)	1.9942(14)
N(1)−C(2)	1.312(3)	1.316(2)	1.305(2)	1.3273(18)	1.3127(14)
N(3)−C(8)	1.306(2)	1.302(3)	1.308(2)	1.3369(18)	1.3103(15)
N(2)−C(3)	1.370(2)	1.376(2)	1.372(2)	1.3800(18)	1.3685(13)
N(2)−C(7)	1.374(3)	1.371(2)	1.375(2)	1.3799(18)	1.3655(14)
C(2)−C(3)	1.459(3)	1.444(3)	1.450(3)	1.420(2)	1.4402(16)
C(7)−C(8)	1.460(3)	1.461(3)	1.455(2)	1.410(2)	1.4444(15)
O(1)−C(34)	1.351(3)	1.275(3)	1.272(2)		
O(2)−C(34)		1.256(3)	1.268(2)		
N(1)−Fe(1)−N(2)	75.75(7)	75.94(6)	75.26(6)	79.40(5)	81.00(4)
N(1)−Fe(1)−N(3)	150.80(7)	149.75(7)	150.27(6)	152.10(5)	159.67(4)
N(2)−Fe(1)−N(3)	75.05(7)	75.06(6)	75.99(6)	79.46(5)	81.15(4)

[a] Fe(1)−C(35). [b] Fe(1)−C(36).

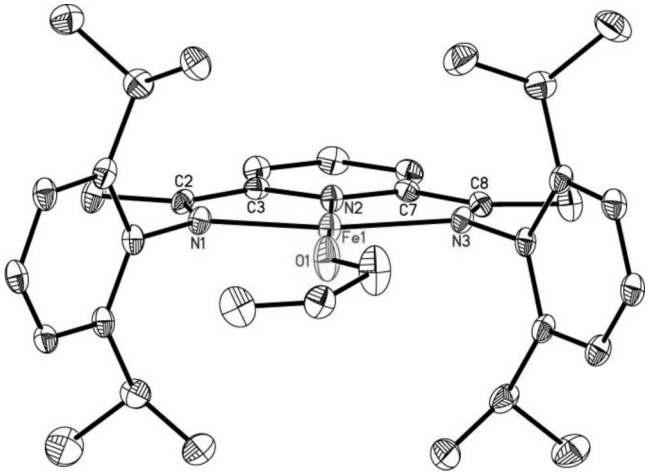


Figure 2. Molecular structure of **1-OCH$_2$CH=CH$_2$** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

symmetrically disposed about the metal. The metrical parameters of the chelate (Table 1) are consistent with one electron reduction.[16] The Fe(1)−O(1) bond lengths of 2.0837(16) and 2.116(13) Å for **1-OAc** and **1-OBz** are elongated from typical iron-alkoxide complexes (vide infra). Similar Fe(1)−O(2) distances of 2.1271(14) and 2.1033(13) Å were observed for **1-OAc** and **1-OBz**, respectively.

One particularly interesting compound is **1-Allyl**. Bis(imino)pyridine iron monoalkyl compounds are relatively rare,[21,22,26] and to our knowledge, an allyl derivative has yet to be prepared. The solid state structure of **1-Allyl** is presented in Figure 4. The allyl ligand is η^3-coordinated with the three carbon plane oriented nearly perpendicular to the iron chelate plane and the methine carbon, C(35), directed toward an imine nitrogen. Notably, this carbon is not in the iron chelate plane, providing a molecule with a more idealized square pyramidal rather than trigonal bipyramidal geometry. The allyl ligand is positionally disordered with nearly equal populations of the rotamer where the methine carbon is directed toward N(1) and the opposite rotamer where it is directed toward N(3). Although successfully modeled, the disorder compromises discussion of the metrical parameters of the allyl ligand. The distortions observed in the bond distances of the bis(imino)pyridine chelate clearly establish redox activity. Somewhat surprising, however, are the $C_{imine}-C_{pyridine}$ distances of 1.420(2) and 1.410(2) Å, contractions consistent with two rather than one electron reduction.[16] Likewise, the $N_{imine}-C_{imine}$ distances are elongated to 1.3273(18) and 1.3369(18) Å, also consistent with a doubly reduced bis(imino)pyridine.

Notably, the iron−nitrogen bond distances in **1-Allyl** are statistically shorter than other previously characterized (^{iPr}PDI)Fe-X complexes. Typically, this class of compounds exhibits an overall $S = 3/2$ ground-state comprising a high spin ($S_{Fe} = 2$) iron center antiferromagnetically coupled to a bis(imino)pyridine radical anion. The contraction of the iron−nitrogen bonds in the solid state structure of **1-Allyl** suggests an intermediate-spin ferric center ($S_{Fe} = 3/2$) that avoids population of the σ^* d_{x2-y2} orbital, antiferromagnetically coupled to a bis(imino)pyridine diradical dianion. More detailed spectroscopic, magnetic, and computational studies are required to fully elucidate the electronic structure of this compound.

The solid state structure of **1-(OAc)(Vinyl)** was also determined by X-ray diffraction (Figure 5) and represents a rare example of a neutral six-coordinate bis(imino)pyridine iron compound.[20a] The N(1)−C(2) and N(3)−C(8) bond lengths (Table 1) of 1.3127(14) and 1.3103(15) Å are comparable to those observed for compounds with single electron reduction of the bis(imino)pyridine chelate.[16] Similarly, the C(2)−C(3) and C(7)−C(8) distances of 1.4402(16) and 1.4444(15) Å are contracted compared to the values of 1.487(3) Å in free ^{iPr}PDI and also support one electron reduction of the bis(imino)pyridine chelate.[16] Two descriptions of the electronic structure accommodate the observed diamagnetic ground state. One possibility is a low spin, d^6 ferrous complex with a neutral bis(imino)pyridine chelate, while the other is a low spin, d^5 ferric compound antiferromagnetically coupled to a ^{iPr}PDI radical anion. While the metrical data seems to favor the latter description, care must be taken in over interpreting crystallographic data as ligand field strength, and other factors may also influence the bond lengths of the coordinated bis(imino)pyridine.

Discussion

Carbon−oxygen bond oxidative addition reactions are of interest because of their potential application in hydrodeoxygenation (HDO) reactions[27] as well as various cross coupling

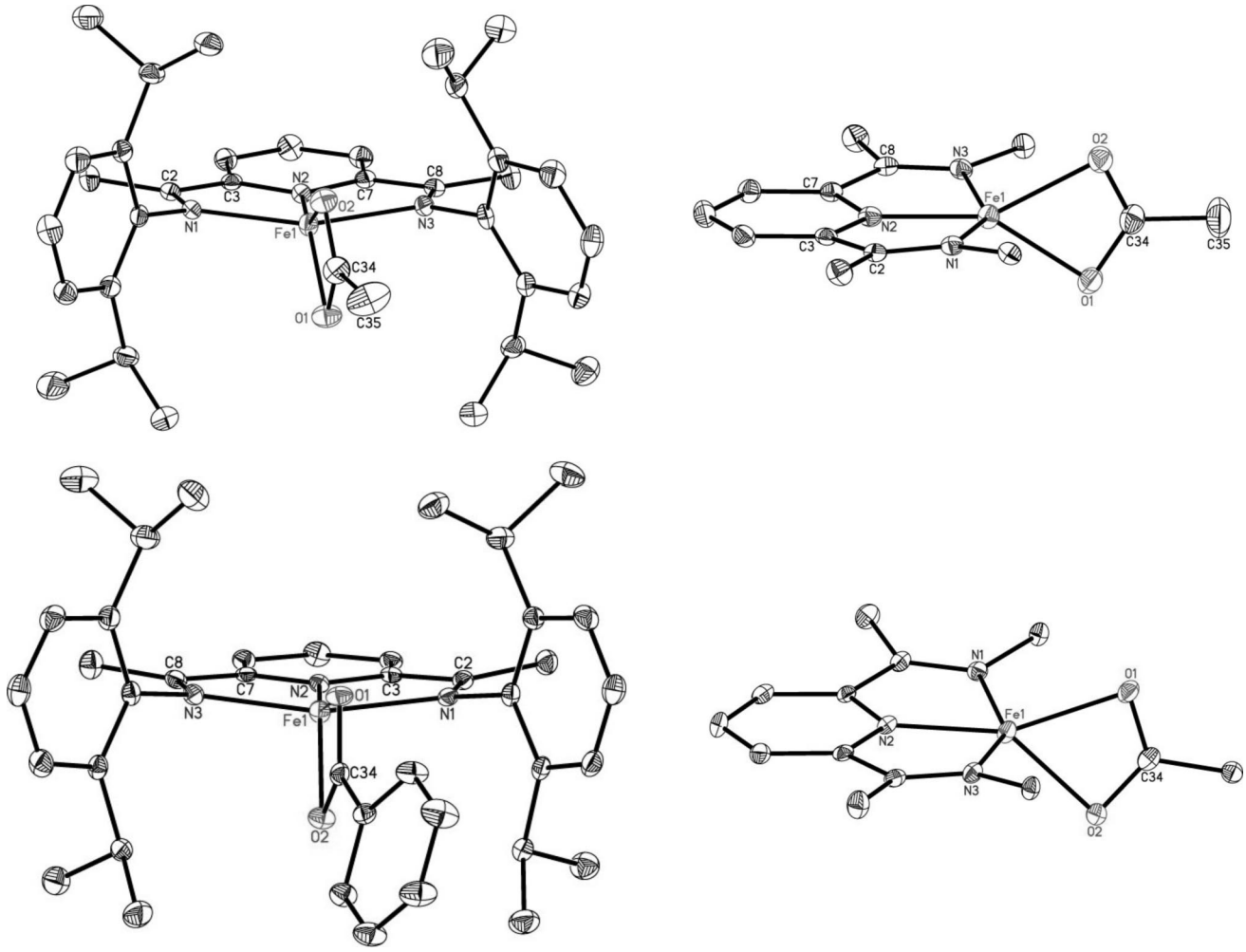


Figure 3. Molecular structure of **1-OAc** (top) and **1-OBz** (bottom) at 30% probability ellipsoids. View of the core of the molecules (right). Hydrogen atoms are omitted for clarity.

methodologies used in organic synthesis.[28] Oxidative addition of allylic ethers, carboxylates, carbonates, and halides has enjoyed special utility in the synthesis of metal allyl complexes, which can undergo subsequent nucleophilic attack[29,30] or cross-coupling chemistry.[31] C−O bond cleavage chemistry is well known for second and third row transition metals including palladium,[24,32] rhodium,[33] iridium,[34] ruthenium,[35] zirconium,[36] molybdenum,[37] and tantalum.[38,39] For first row metal ions, C−O oxidative addition chemistry of both ethers[40,41] and esters[42,43] to Ni(0) has been well-studied and known for some time. Examples with nickel(II) precursors have been reported more recently.[44]

Examples of C−O bond cleavage with well-defined iron compounds are more limited. In a seminal example, Ganem and Small reported the application of ferric chloride to the cleavage of ethereal C−O bonds.[45] A more recent example, described by Plietker and co-workers, applies nitrosylated variants of Collman's reagent[46] for the transesterification of vinyl acetates, phenyl carboxylates, and electron poor esters with various alcohols.[47] Iron acyl complexes that do not undergo decarbonylation are proposed as key intermediates in the catalytic cycle. Direct oxidative addition of carbon−oxygen bonds to electron rich iron(0) compounds has also been reported by Ittel and co-workers. Addition of anisole or methyl benzoate to a transient bis(diphosphine)iron(0) yielded the products of C−O cleavage.[48,49]

(31) Waetzig, S. R.; Rayabharapu, D. K.; Weaver, J. D.; Tunge, J. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 4977.
(32) Tsuji, J. In *Palladium Reagents and Catalysts*; Wiley: Chichester, U. K., 1995; p 290.
(33) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 6531.
(34) Lara, P.; Paneque, M.; Poveda, M. L.; Salazar, V.; Santos, L. L.; Carmona, E. *J. Am. Chem. Soc.* **2006**, *128*, 3512.
(35) Ueno, S.; Mizushima, E.; Chatani, N.; Kakiuchi, F. *J. Am. Chem. Soc.* **2006**, *128*, 16516.
(36) Bradley, C. A.; Veiros, L. F.; Pun, D.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 16600.
(37) Faller, J. W.; Linebarrier, D. *Organometallics* **1988**, *7*, 1670.
(38) Bonanno, J. B.; Henry, T. P.; Neithamer, D. R.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1996**, *118*, 5132.
(39) Kawaguchi, H.; Matsuo, T. *J. Am. Chem. Soc.* **2003**, *125*, 14254.
(40) Yamamoto, T.; Ishizu, J.; Yamamoto, A. *Chem. Lett.* **1979**, 1385.
(41) Eisch, J. J.; Im, K. R. *J. Organomet. Chem.* **1977**, *139*, C45.
(42) Yamamoto, T.; Ishizu, J.; Kohara, T.; Komiya, S.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 3758.
(43) Yamamoto, T.; Ishizu, J.; Yamamoto, A. *J. Am. Chem. Soc.* **1981**, *103*, 6863.
(44) van der Boom, M. E.; Liou, S.-Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Inorg. Chim. Acta* **2004**, *357*, 4015.
(45) Ganem, B.; Small, V. R., Jr. *J. Org. Chem.* **1974**, *39*, 3728.
(46) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.
(47) Magens, S.; Ertelt, M.; Jatsch, A.; Plietker, B. *Org. Lett.* **2008**, *10*, 53.
(48) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742.
(49) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577.

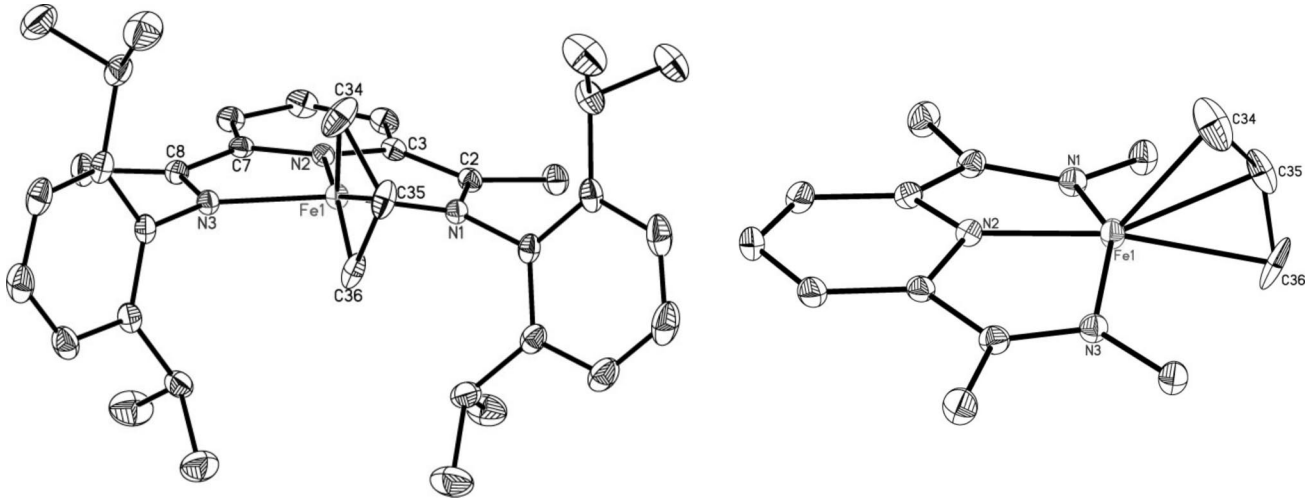


Figure 4. Molecular structure of **1-Allyl** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Core of the molecule presented on the right.

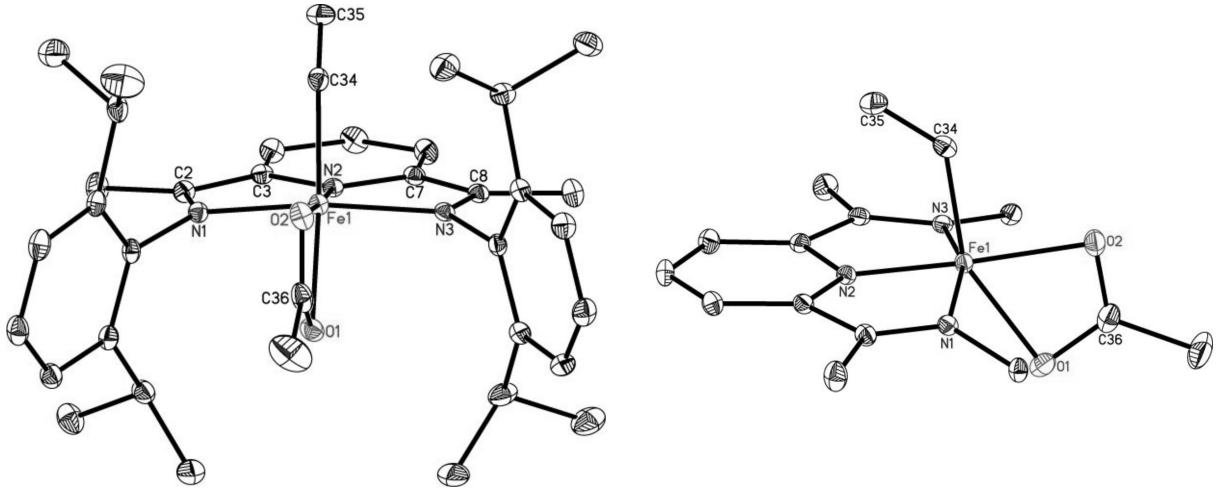
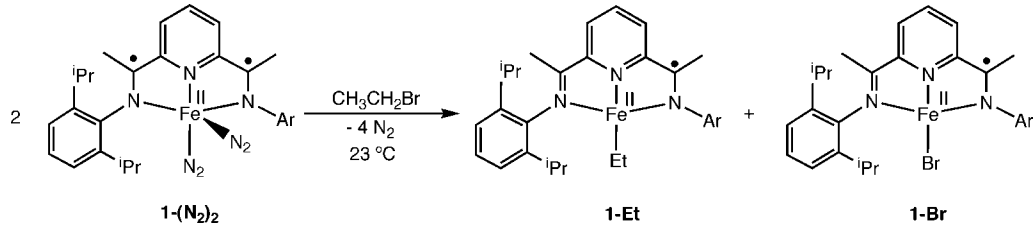


Figure 5. Molecular structure of **1-(OAc)(Vinyl)** at 30% probability ellipsoids (left). Side view of the core of the molecule (right). Hydrogen atoms are omitted for clarity.

Scheme 9



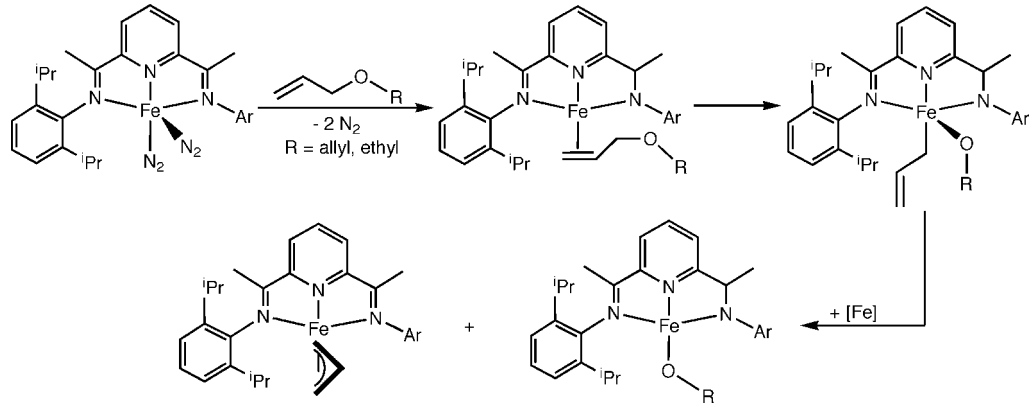
Formal oxidation of the ligand, not the metal

For methyl benzoate addition, exclusive scission of the ester, not the acyl C−O bond, was observed.

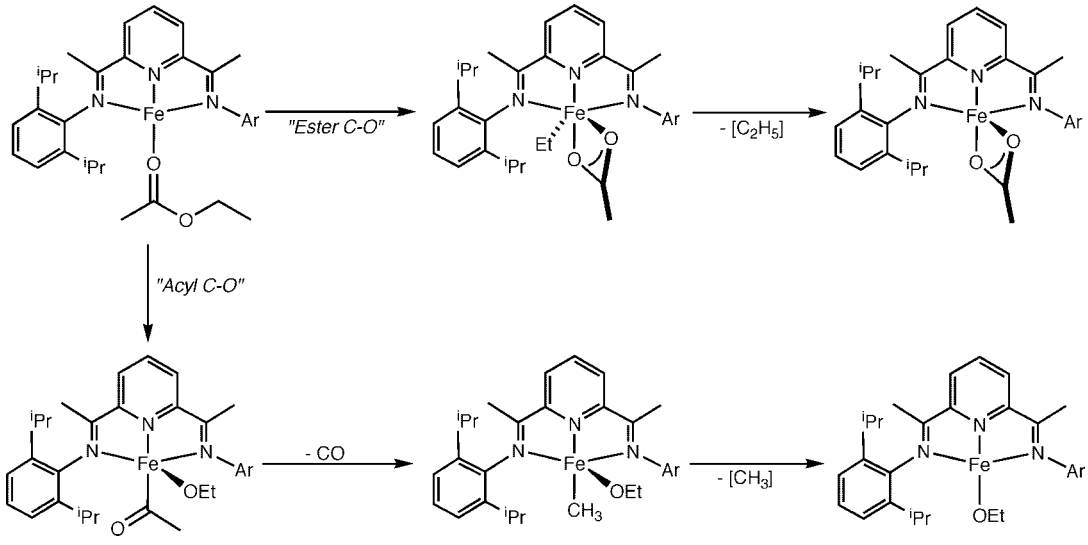
Oxidative Addition in Reduced Bis(imino)pyridine Iron Compounds. Oxidative addition reactions to reduced iron complexes bearing electronically non-innocent bis(imino)pyridine chelates raise the interesting possibility of having ligand- rather than metal-based redox events. Related ligand-based oxidative chemistry has been reported by Heyduk and co-workers with group 4 transition metals.[50] Previous studies from our laboratory have established that oxidative addition of alkyl halides (e.g., CH_3CH_2Br, $(CH_3)_2CHCH_2Br$, etc.) to **1-(N$_2$)$_2$** yields two iron products where formal electron loss occurs at the bis(imino)pyridine chelate and maintains the ferrous oxidation state (Scheme 9).[21] Several examples of C−O bond cleavage reported in this work follow this general reaction paradigm: oxidative addition to yield two iron complexes with formal oxidation of the ligand not the metal.

(50) (a) Blackmore, K. J.; Lal, N.; Ziller, J. W.; Heyduk, A. F. *J. Am. Chem. Soc.* **2008**, *130*, 2728. (b) Ketterer, N. A.; Fan, H.; Blackmore, K. J.; Yang, X.; Ziller, J. W.; Baik, M.-H.; Heyduk, A. F. *J. Am. Chem. Soc.* **2008**, *130*, 4364.

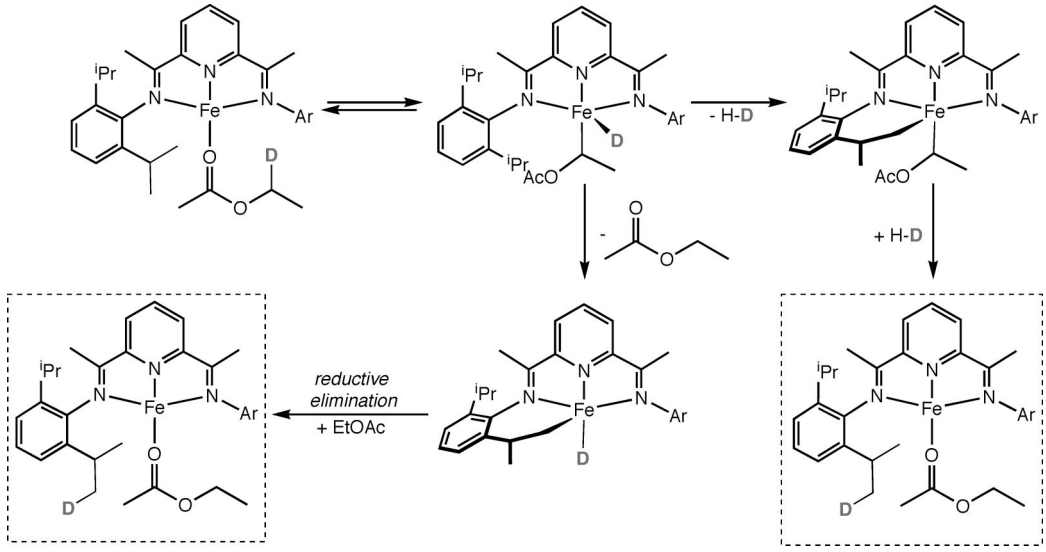
Scheme 10



Scheme 11



Scheme 12



The oxidative addition of vinyl acetate to **1-(N_2)$_2$** provides additional insight into the nature of the bond cleavage event at the reducing iron center. Observation of the six-coordinate **1-(OAc)(Vinyl)** compound suggests that such monometallic oxidative addition products may be intermediates common to all C−O bond cleavage reactions. In cases where this species is not observed, it is likely that Fe−C bond homolysis occurs from the initial five- or six-coordinate oxidative addition product followed by radical capture to yield the observed products. Several observations support this assertion. Attempts to prepare five-coordinate bis(imino)pyridine iron bis(neopentyl) or neopentyl chloride complexes by ligand substitution reactions resulted in the isolation of four-coordinate (^{iPr}PDI)FeX compounds arising from Fe−C bond homolysis.[26] Likewise, oxidative addition of 5-hexenyl-1-bromide to **1-(N_2)$_2$** yielded **1-Br** along with the cyclized iron alkyl product,[21] consistent with

ejection of the 5-hexenyl radical, which is known to undergo rapid cyclization.[51,52] In addition, hydrogenation of the vinyl ligand of **1-(OAc)(Vinyl)** in the presence of palladium on carbon resulted in conversion to **1-OAc**, supporting radical ejection upon conversion to the saturated iron-ethyl intermediate. It should be noted, however, that the difference in bond strengths between sp^2- and sp^3-hybridized C−O bonds may result in a change in mechanism, and in certain cases, radical ejection may occur without prior formation of an iron−carbon bond.

Relative Rates and Selectivity for C−O Cleavage by 1-$(N_2)_2$. When examining the relative rates of C−O bond cleavage within classes of ethers and esters promoted by **1-$(N_2)_2$**, several salient trends emerge. Within the family of ester substrates, benzoate esters generally undergo more rapid cleavage than the corresponding acetates. Specifically, ethyl benzoate (exclusive ester cleavage) converted to products over the course of hours at 23 °C, while ethyl acetate (both acyl and ester cleavage) required nearly a week under the same conditions. This effect is likely electronic in origin as the electron withdrawing phenyl group renders the substrate more electrophilic and prone to oxidative cleavage. It is also possible that differences in one electron reduction potentials account for the observed differences.

Comparison of various substituted acetates also establishes several important trends. The unsaturated esters, vinyl and allyl acetate, undergo extremely rapid C−O bond cleavage; a reaction so fast that no catalytic hydrogenation is observed in the presence of **1-$(N_2)_2$** and 4 atm of H_2. In contrast, C−O bond cleavage in *trans*-methyl cinnamate, while relatively facile under an N_2 atmosphere, is sufficiently slow such that catalytic olefin hydrogenation can be achieved with 5 mol % of **1-$(N_2)_2$** and 4 atm of dihydrogen. Eventually, however, all of the iron is converted to catalytically inactive iron carboxylate compounds, establishing C−O bond activation as the principal catalyst deactivation pathway for this class of substrates.

Carbon−oxygen bond cleavage in various allylated substrates also demonstrates the importance of leaving group effects. For diallyl and allyl ethyl ether, the rate of C−O bond cleavage is sufficiently slow such that iron-catalyzed olefin hydrogenation is observed. As mentioned previously, allyl acetate has not been hydrogenated using our experimental conditions because of the extremely fast rate of C−O bond oxidative addition. This trend is similar to those observed in nickel(0) and palladium(0) chemistry, where allyl acetates undergo more facile oxidative addition than the corresponding allylated ethers.[33,42,43]

It is noteworthy that **1-$(N_2)_2$** promotes *acyl* C−O bond cleavage in alkyl esters. Electron rich Ni(0) compounds[42] undergo selective acyl C−O bond cleavage with phenyl acetate but are unreactive toward alkyl-substituted esters. Aryl acetate cleavage reactions are also known with $(dppe)_2Mo(N_2)_2$ (dppe = 1,2-diphenylphosphinoethane),[53] $(Ph_3P)_3RhH$,[54] (η^5-C_5Me_5)-RhCl(mdmpp-κP, -κO),[55] $(Ph_3P)_3Ru(CO)_2$,[56] and $Ru_3(CO)_{12}$.[57] In one case, an acyl rhodium complex was isolated following C−O oxidative addition.[58] Using pyridine directing groups, a $Ru_3(CO)_{12}$-catalyzed reductive decarbonylation method has also been developed and has been extended to alkyl-substituted substrates.[59]

To our knowledge, acyl C−O bond cleavage in alkyl esters lacking a directing group has not been reported. Thus, the facile C−O bond cleavage of alkyl acetates with **1-$(N_2)_2$** at 65 °C highlights the reducing potential of a formally iron(II) center with electrons stored in the bis(imino)pyridine chelate. For the alkyl acetates presented in Scheme 5, a modest trend in selectivity emerges. The smallest member in the series, methyl acetate, undergoes rapid and selective ester C−O bond cleavage likely due to the steric accessibility of the ester C−O bond. Lengthening the alkyl chain resulted in slower rates as ethyl, pentyl, benzyl, isopropyl, cyclohexyl, and *tert*-butyl acetate all require heating to 65 °C or extended reaction times at 23 °C to reach conversion. With the exception of *tert*-butyl acetate, the selectivity of acyl bond cleavage increases as the steric protection of the ester C−O bond increases. Thus, for alkyl-substituted acetates, it appears that in the absence of overriding steric effects, ester C−O bond cleavage is preferred over acyl. Why *tert*-butyl acetate reverses the kinetic selectivity for C−O bond cleavage is not known.

Mechanistic Considerations. Proposed mechanisms for ether, ester, and acyl C−O bond cleavage are presented in Schemes 10 (ethers) and 11 (ester, acyl) and are inspired by pathways previously reported by Yamamoto for electron rich Ni(0) compounds.[24,40,42,43] Because ether cleavage was only observed with allyl and vinyl-substituted ethers, initial coordination of the alkene of the substrate is proposed.[43] For diallyl and allyl ethyl ethers, S_N2'-type substitution is also plausible and may be preferred accounting for the observed rapid rates of reaction. Oxidative addition of the C−O bond yields a five-coordinate iron allyl alkoxide intermediate, analogous to the six-coordinate iron vinyl acetate complex, **1-(OAc)(Vinyl)**, that was isolated and structurally characterized. Ejection of allyl radical and capture by a reduced iron species, either **1-$(N_2)_2$** or the iron olefin compound, yields the observed products. To have a significant concentration of reduced iron compound available for allyl radical capture, C−O bond cleavage must be the rate-determining step. Circumstantial experimental data support this assertion. Addition of one equivalent of diallyl ether to **1-$(N_2)_2$** yielded an equimolar mixture of **1-Allyl** and **1-$OCH_2CH{=}CH_2$** with unreacted substrate remaining. This suggests that the products do not participate in radical capture. For the case of ethyl vinyl ether cleavage, the olefin compound was observed by ^1H NMR spectroscopy immediately after mixing the reagents; C−O bond cleavage occurred over the course of 24 h at 23 °C. In general, when the C−O bond cleavage reactions are fast, all of the products of radical capture are observed. When these reactions are slow, as in the case of ethyl vinyl ether, the fate of the ejected organic radical fragment has not been determined.

Similar pathways are proposed in Scheme 11 for ester and acyl C−O bond cleavage. Ethyl acetate is presented as a representative substrate because both ester and acyl scissions were observed. For ester C−O bond cleavage, oxidative addition to yield the six-coordinate iron ethyl acetate complex followed by iron−carbon bond homolysis yields the observed **1-OAc** product. A six-coordinate iron intermediate is proposed on the basis of the analogy to isolated **1-(OAc)(Vinyl)**. Ejection of the ethyl radical from this compound seems plausible given the

(51) Lal, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6355.
(52) Williams, G. M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1122.
(53) Tatsumi, T.; Tominaga, H.; Hidai, M.; Uchida, Y. *J. Organomet. Chem.* **1981**, *218*, 177.
(54) Yamamoto, T.; Miyashita, S.; Naito, Y.; Komiya, S.; Ito, T.; Yamamoto, A. *Organometallics* **1982**, *1*, 808.
(55) Yamamoto, Y.; Han, X.-H.; Ma, J.-F. *Angew. Chem., Int. Ed.* **2000**, *39*, 1965.
(56) Hiraki, K.; Kira, S.-I.; Kawano, H. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1583.
(57) Tatamidani, H.; Yokota, K.; Kakiuchi, F.; Chatani, N. *J. Org. Chem.* **2004**, *69*, 5615.
(58) Grotjahn, D. B.; Joubran, C. *Organometallics* **1995**, *14*, 5171.
(59) Chatani, N.; Tatamidani, H.; Ie, Y.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **2001**, *123*, 4849.

previous studies from our laboratory that have demonstrated the propensity of five-coordinate bis(imino)pyridine iron dialkyls to undergo Fe−C homolysis.[26] For acyl C−O bond cleavage, oxidative addition of the C−O bond forms a five-coordinate intermediate analogous to **1-(OAc)(Vinyl)**. Decarbonylation followed by Fe-CH_3 homolysis yields the observed product. Observation of **1-Me** and **1-Cl** following treatment of **1-$(N_2)_2$** with $CH_3C(O)Cl$ provides a precedent of decarbonylation in bis(imino)pyridine iron compounds.

Deuterium labeling studies with ethyl acetate also established a competing C−H activation pathway. A proposed mechanism for this transformation, not required for C−O bond cleavage, is presented in Scheme 12. Recall that this reaction is selective: isotopic exchange occurs only between the isopropyl aryl methyl groups on the bis(imino)pyridine chelate and the methylene position on the ethyl chain adjacent to the oxygen. The process begins with reversible dissociation−coordination of ethyl acetate to facilitate C−H activation of either the methylene position of the ester or cyclometalation of an isopropyl methyl group of the bis(imino)pyridine chelate. Following the formation of the alkyl deuteride, isotopic exchange can occur through cyclometalation, likely by σ-bond metathesis, with either the iron-hydride (deuteride) or alkyl. If the reaction occurs with the iron hydride (deuteride), loss of H-D occurs. Subsequent productive recapture places deuterium in the isopropyl group and hydrogen in the ester, completing isotopic exchange. An alternative σ-bond metathesis pathway involves the reaction of the isopropyl methyl group with the iron alkyl, liberating free ethyl acetate, which following reductive elimination of the iron cyclometalated deuteride and recapture, completes isotopic exchange. Pathways involving formal oxidative addition and formation of iron(IV) intermediates are also possible but are deemed less plausible.

The selective isotopic exchange between the methylene position of the ester and the isopropyl methyl groups of the bis(imino)pyridine chelate raises the question of why this process was not observed with the corresponding iron methyl acetate complex. The lack of a competing C−H activation process for the methyl acetate derivative is accommodated by the relative rates of C−O bond cleavage for the two substrates. Whereas C−O bond cleavage in ethyl acetate occurs over one hour at 65 °C, methyl acetate cleavage occurs within minutes at 23 °C. The lack of deuterium exchange with methyl acetate clearly demonstrates that C−H activation can be competitive with C−O cleavage, but is by no means a prerequisite.

Concluding Remarks

Investigation into the substrate scope of catalytic olefin hydrogenation reactions promoted by the bis(imino)pyridine iron complex, **1-$(N_2)_2$**, established that oxidative addition of carbon−oxygen bonds of ethers and esters is a principal catalyst deactivation pathway. For substrates such as diallyl ether, vinyl ethyl ether, and *trans*-methyl cinnamate, catalytic hydrogenation is competitive with C−O cleavage, and conversion to alkane was observed. For molecules such as allyl and vinyl acetate, C−O cleavage is more rapid than hydrogenation (up to 4 atm of H_2), and no turnover was observed. Exploration of the scope of ester C−O bond cleavage established competing ester and acyl C−O bond cleavage reactions, depending on the specific substrate. Methyl acetate and *trans*-methyl cinnamate underwent exclusive ester C−O bond cleavage, while phenyl acetate yielded products from selective acyl C−O bond scission. In alkyl-substituted esters such as ethyl, pentyl, isopropyl, cyclohexyl, and *tert*-butyl acetate, competing ester and acyl C−O bond cleavage occurred. In both ethers and esters, oxidative addition of the C−O bond to the reduced bis(imino)pyridine iron complex is proposed. In all but one case, vinyl acetate, homolysis of the iron−carbon bond from the product of oxidative addition yields the observed products. Deuterium labeling studies with isotopologues of the iron dinitrogen complex and ethyl acetate establish competing cyclometalation of the 2,6-diisopropyl aryl substituents. Taken together, these studies once again highlight both the chemical and redox-activity of bis(imino)pyridine ligands in reduced iron chemistry.

Experimental Section[60]

Preparation of (^{iPr}PDI)Fe(O_2CMe)($CH{=}CH_2$) (1-(OAc)(Vinyl)). A 20 mL scintillation vial was charged with 0.200 g (0.337 mmol) of **1-$(N_2)_2$** and approximately 10 mL of pentane. A separate solution of 0.029 g (32 μL, 0.337 mmol) of vinyl acetate in ∼5 mL of pentane was slowly added dropwise while stirring, resulting in immediate evolution of N_2 along with a change in color to bright purple. After 2 h, the solution was filtered through Celite, and the solvent was removed *in vacuo* to yield a purple residue. Recrystallization from pentane yielded 0.131 g (62%) of a bright purple solid identified as **1-(OAc)(Vinyl)**. Analysis for $C_{37}H_{49}FeN_3O_2$: Calcd C, 71.26; H, 7.92; N, 6.74. Found: C, 71.11; H, 7.74; N, 6.61. ^{1}H NMR (benzene-d_6): δ = 10.07 (dd, 16.0 Hz, 7.5 Hz, 1H, C*H* = CH_2), 7.43 (d, 7.5 Hz, 2H, *m-pyr*), 7.25 (t, 7.5 Hz, 1H, *p-pyr*), 6.96 (d, 6.0 Hz, 1H, *m-aryl*), 6.95 (d, 6.0 Hz, 1H, *m-aryl*), 4.66 (d, 7.5 Hz, 1H, CH=CH_2), 3.12 (sept., 7.0 Hz, 2H, C*H*$(CH_3)_2$), 1.94 (sept., 7.0 Hz, 2H, C*H*$(CH_3)_2$), 1.87 (d, 16.0 Hz, 1H, CH=CH_2), 1.78 (m, 12H, CH(CH_3)$_2$ and C(CH_3)), 1.23 (d, 7.0 Hz, 6H, CH(CH_3)$_2$), 1.18 (s, 3H, CO_2CH_3), 1.07 (d, 7.0 Hz, 6H, CH(CH_3)$_2$), 0.80 (d, 7.0 Hz, 6H, CH(CH_3)$_2$), *p*-aryl peak not located. ^{13}C{^{1}H} NMR (benzene-d_6): δ = 189.91 (*C*H=CH_2), 181.48 (*C*O_2Me), 163.67 (*C*(CH_3)), 144.44 (*aryl*), 143.20, 142.26, 126.89 (*p-aryl*), 124.28 (*m-aryl*), 123.99 (*m-aryl*), 120.79 (*m-py*), 118.39 (*p-py*), 117.14 (CH=*C*H_2), 28.54 (*C*H$(CH_3)_2$), 28.25 (*C*H$(CH_3)_2$), 25.59 (CH(*C*H_3)$_2$), 25.07 (CH(*C*H_3)$_2$), 24.81 (CH(*C*H_3)$_2$), 24.51 (CH(*C*H_3)$_2$), 22.42 (CO_2*C*H_3), 19.20 (C(*C*H_3)).

Preparation of (^{iPr}PDI)Fe($OCH_2CH{=}CH_2$) (1-$OCH_2CH{=}CH_2$). A 20 mL scintillation vial was charged with 0.050 g (0.084 mmol) of **1-$(N_2)_2$** and approximately 15 mL of pentane. Using a microsyringe, 0.005 g (6 μL, 0.084 mmol) of allyl alcohol was added to 5 mL of pentane, and this mixture was added slowly to the stirring **1-$(N_2)_2$** solution. After one hour, the resulting solution was filtered through Celite, and the solvent was removed in vacuo to yield 0.026 g (52%) of a dark brown solid identified as **1-$OCH_2CH{=}CH_2$**. This complex was additionally observed upon the addition of allyl ether to **1-$(N_2)_2$**. Analysis for $C_{35}H_{48}FeN_3O$: Calcd C, 72.15; H, 8.30; N, 7.21. Found: C, 71.94; H, 8.30; N, 6.99. Magnetic susceptibility: μ_{eff} = 4.0 μ_B (benzene-d_6, 20 °C). ^{1}H NMR (benzene-d_6, 20 °C): δ = 112.09 (190 Hz, 1H), 92.59 (298 Hz, 1H), 73.61 (73 Hz, 2H), 54.76 (52 Hz, 1H), −8.90 (28 Hz, 2H, *m-aryl*), −14.82 (24 Hz, 1H, *p-aryl*), −24.26 (29 Hz, 12H, CH(CH_3)$_2$), −38.47 (149 Hz, 12H, CH(CH_3)$_2$), −118.79 (394 Hz, 4H, C*H*$(CH_3)_2$), −219.87 (131 Hz, 6H, C(CH_3)), one peak not located.

Preparation of (^{iPr}PDI)Fe($CH_2CH{=}CH_2$) (1-Allyl). This compound was directly synthesized by the slow addition of 0.053 g of allylmagnesium bromide (362 μL of a 1.0 M solution in ether, 0.362 mmol) to a cold stirring pentane solution containing 0.175 g (0.283 mmol) of **1-Br**. Approximately 1 mL of 1,4-dioxane was added to the reaction mixture to aid $MgBr_2$ precipitation. After stirring for 1 h, the reddish-brown solution was filtered through Celite, and the solvent was removed in vacuo to yield a reddish-brown solid. This residue was washed 5 times with approximately 2 mL of pentane, and the resulting concentrated pentane solution was chilled to −35 °C for days. Recrystallization yielded 0.035 g (21%) of a brown solid identified as **1-Allyl**. This complex was also observed upon the addition of substoichiometric amounts of allyl ether, ethyl allyl ether, or allyl acetate to **1-$(N_2)_2$**. Analysis for $C_{36}H_{48}FeN_3$:

Calcd C, 74.73; H, 8.36; N, 7.26. Found: C, 74.66; H, 8.49; N, 6.90. Magnetic susceptibility: $\mu_{eff} = 2.4\ \mu_B$ (benzene-d_6, 20 °C). ^{1}H NMR (benzene-d_6, 20 °C): δ = 148.64 (770 Hz, 2H, *allyl*), 98.47 (795 Hz, 1H, *allyl*), 72.80 (619 Hz, 2H, *allyl*), 47.64 (42 Hz, 2H, *m-pyr*), 8.07 (39 Hz, 2H), 2.99 (59 Hz, 4H, C*H*(CH$_3$)$_2$), 0.09 (48 Hz, 12H, CH(C*H*$_3$)$_2$), −0.46 (50 Hz, 12H, CH(C*H*$_3$)$_2$), −26.64 (184 Hz, 6H, C(C*H*$_3$)), two peaks not located.

Preparation of (^{iPr}PDIFe)(CH$_3$O$_2$CCH$_2$CH$_3$) (1-EtOAc). A 20 mL scintillation vial was charged with 0.80 g (0.135 mmol) of **1-(N$_2$)$_2$** and approximately 10 mL of diethyl ether. With stirring, 0.012 g (13 μL, 0.135 mmol) of ethyl acetate was added via microsyringe resulting in immediate evolution of N_2along with a change in color to reddish-brown. After 30 min, the solution was filtered though a Celite fitted frit, and the solvent was removed in vacuo to yield 0.070 g (83%) of a dark brown solid identified as **1-EtOAc**. Analysis for $C_{37}H_{51}FeN_3O_2$: Calcd C, 71.03; H, 8.22; N, 6.72. Found: C, 70.74; H, 7.86; N, 6.97. ^{1}H NMR (toluene-d_8, −60 °C): δ = 11.61 (d, 7.5 Hz, 2H, *m-pyr*), 8.66 (t, 7.0 Hz, 1H, *p-pyr*), 7.50 (t, 8.0 Hz, 2H, *p-aryl*), 7.09 (d, 7.0 Hz, 4H, *m-aryl*), 2.92 (q, 6.0 Hz, 2H, C*H*$_2$CH$_3$), 2.52 (sept., 5.5 Hz, 4H, C*H*(CH$_3$)$_2$), 1.24 (d, 5.5 Hz, 12H, CH(C*H*$_3$)$_2$), 0.81 (t, 6.0 Hz, 3H, CH$_2$C*H*$_3$), 0.58 (s, 3H, COC*H*$_3$), −0.12 (d, 5.5 Hz, 12H, CH(C*H*$_3$)$_2$), −4.67 (s, 6H, C(C*H*$_3$)). ^{13}C {^{1}H} NMR (toluene-d_8, −60 °C): δ = 183.41, 181.65, 163.30, 160.00, 137.62, 136.80 (*p-pyr*), 124.53 (*p-aryl*), 123.69 (*m-aryl*), 103.83 (*m-pyr*), 64.22 (*C*H$_2$CH$_3$), 35.39 (C(*C*H$_3$)), 28.29 (*C*H(CH$_3$)$_2$), 23.73 (CH(*C*H$_3$)$_2$), 22.86 (CH(*C*H$_3$)$_2$), 22.33 (CO*C*H$_3$), 13.79 (CH$_2$*C*H$_3$).

Preparation of (^{iPr}PDI)Fe(CH=CH$_2$) (1-Vy). Using a calibrated gas bulb, 0.021 mmol of vinyl bromide was transferred to a J. Young NMR tube containing 0.025 g (0.042 mmol) of **1-(N$_2$)$_2$** and approximately 0.7 mL of benzene-d_6. Upon standing at ambient temperature for 20 min, analysis of the reaction mixture by ^{1}H NMR spectroscopy revealed the formation of a mixture of **1-Br** and **1-Vy**. ^{1}H NMR (benzene-d_6, 20 °C): δ = 127.07 (221 Hz, 1H, *p-pyr*), 52.84 (45 Hz, 2H, *m-pyr*), −7.37 (32 Hz, 12H, CH(C*H*$_3$)$_2$), −12.74 (136 Hz, 12H, CH(C*H*$_3$)$_2$), −55.29 (271 Hz, 4H, C*H*(CH$_3$)$_2$), −141.77 (506 Hz, 6H, C(C*H*$_3$)), *aryl* and *vinyl* resonances not located.

Preparation of 1-Aryl. To a solution of **1-(N$_2$)$_2$** (0.033 g, 0.056 mmol) in benzene-d_6 (0.7 mL) was added (12 μL, 0.057 mmol) of hexamethyldisiloxane. The dark green solution was transferred to an NMR tube fitted with a J. Young adapter and placed in a 95 °C oil bath for 16 h. The resulting burgundy solution was cooled to room temperature and filtered, and solvent and other volatiles were removed in vacuo, yielding a pink solid identified as **1-Aryl** (0.023 g, 0.044 mmol, 78%). Similaily, **1-Aryl** was effectively prepared in the presence of a stoichiometric amount of anisole, instead of hexamethyldisiloxane, or in the absence of ether. Analysis for $C_{33}H_{43}N_3Fe$: Calcd: C, 73.73; H, 8.06; N, 7.82. Found: C, 73.69; H, 7.81; N, 7.95. ^{1}H NMR (benzene-d_6): δ = 7.37−7.16 (m, 3H, *pyr*), 6.61 (d, $^3J_{HH}$ = 8.0 Hz, 2H, *m-aryl*), 6.56 (t, $^3J_{HH}$ = 8.0 Hz, 1H, *p-aryl*), 5.46 (d, $^3J_{HH}$ = 5.6 Hz, 2H, η^6-*m-aryl*), 4.12 (t, $^3J_{HH}$ = 5.6 Hz, 1H, η^6-*p-aryl*), 3.36−3.22 (m, 4H, C*H*(CH$_3$)$_2$), 2.83 (s, 3H, C(C*H*$_3$)), 1.46 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.39 (s, 3H, C(C*H*$_3$)), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.06 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.97 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} (benzene-d_6): δ = 170.3, 155.6, 147.0, 146.7, 144.2, 143.3, 141.5, 129.1 (*m-aryl*), 125.9, 124.2, 122.4, 116.7 (*p-aryl*), 79.3 (η^6-*m-aryl*), 78.4 (η^6-*p-aryl*), 28.2 (*C*H(CH$_3$)$_2$), 27.6 (*C*H(CH$_3$)$_2$), 27.0 (*C*(CH$_3$)), 24.9 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$), 22.4 (CH(*C*H$_3$)$_2$), 16.3 (*C*(CH$_3$)).

Preparation of (^{iPr}PDI)Fe(O$_2$CCH=CH(Ph)) (1-CIN). A 20 mL scintillation vial was charged with 0.050 g (0.084 mmol) of **1-(N$_2$)$_2$** and approximately 10 mL of pentane. To the solution, 0.013 g (0.084 mmol) of *trans*-cinnamic acid was added, and dinitrogen evolution was observed along with a color change from green to brown. The solution was allowed to stir for 2 h and was then filtered through Celite. The solvent was removed *in vacuo*, and the residue was recrystallized from pentane at −35 °C to afford 0.036 g (62%) of a brown solid identified as **1-CIN**. Analysis for $C_{42}H_{50}FeN_3O$: Calcd C, 75.03; H, 7.50; N, 6.25. Found: C, 75.24; H, 7.90; N, 6.32. ^{1}H NMR (benzene-d_6, 20 °C): δ = −283.51 (336 Hz, 6H, C(C*H*$_3$)), −113.05 (524 Hz, 4H, C*H*(CH$_3$)$_2$), −30.12 (135 Hz, 12H, CH(C*H*$_3$)$_2$), −19.56 (50 Hz, 12H, CH(C*H*$_3$)$_2$), −16.66 (42 Hz, 1H, *p-aryl*), −3.14 (47 Hz, 2H, *m-aryl*), 11.82 (30 Hz, 1H, *p-phenyl*), 19.01 (16 Hz, 2H, *m-phenyl*), 27.99 (45 Hz, 2H, *o-phenyl*), 58.80 (191 Hz, 1H, C*H*(C$_6$H$_5$)), 119.25 (294 Hz, 2H, *m-pyr*), 159.36 (275 Hz, 1H, COC*H*), 372.72 (219 Hz, 1H, *p-pyr*).

Preparation of (^{iPr}PDI)Fe(O$_2$CMe) (1-OAc). Method A: A solution of **1-(EtOAc)** was prepared in a thick-walled glass vessel by adding 21 μL (0.202 mmol) of ethyl acetate to 10 mL of a pentane solution containing 0.120 g (0.202 mmol) of **1-(N$_2$)$_2$**. The vessel was sealed, and the solution was heated to 65 °C in an oil bath for 16 h. The resulting brown solution was filtered though Celite, and the solvent was removed in vacuo to yield a dark brown solid. Recrystallization from pentane yielded 0.044 g (36%) of **1-OAc**. Method B: A thick-walled glass vessel was charged with 0.100 g (0.170 mmol) of **1-(N$_2$)$_2$** and approximately 10 mL of pentane. Upon addition of 0.015 g (16 μL, 0.189 mmol) of methyl acetate, the vessel was sealed, submerged in liquid nitrogen, and evacuated on a high vacuum line. After adding 1 atm of dihydrogen, the solution was thawed and stirred for 4 h at ambient temperature. The volatiles were removed, and the resulting reddish-brown residue was washed through a Celite fitted frit with diethyl ether. The solvent was removed in vacuo, and recrystallization from pentane at −35 °C afforded spectroscopically pure **1-OAc**. Analysis for $C_{35}H_{46}FeN_3O_2$: Calcd C, 70.46; H, 7.77; N, 7.04. Found: C, 70.25; H, 8.04; N, 6.79. ^{1}H NMR (benzene-d_6, 20 °C): δ = −284.76 (280 Hz, 6H, C(C*H*$_3$)), −114.95 (525 Hz, 4H, C*H*(CH$_3$)$_2$), −30.37 (170 Hz, 12H, CH(C*H*$_3$)$_2$), −19.78 (75 Hz, 12H, CH(C*H*$_3$)$_2$), −16.50 (66 Hz, 1H, *p-aryl*), −3.20 (73 Hz, 2H, *m-aryl*), 119.59 (163 Hz, 2H, *m-pyr*), 187.25 (370 Hz, 3H, CO$_2$C*H*$_3$), 372.47 (18 Hz, 1H, *p-pyr*).

Acknowledgment. We thank the Packard Foundation (Fellowship in Science and Engineering to P.J.C.) for financial support. Dr. Bradley Wile is acknowledged for the characterization of **1-Aryl**.

Supporting Information Available: Complete experimental details, crystallographic data for **1-(OAc)(vinyl)**, **1-OBz**, **1-OAc**, **1-Allyl**, and **1-OCH$_2$CH=CH$_2$** in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8005596

(60) General considerations and additional experimental procedures can be found in the Supporting Information.