Functional Group Tolerance and Substrate Scope in Bis(imino)pyridine Iron Catalyzed Alkene Hydrogenation

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The functional group tolerance and substrate scope for bis(imino)pyridine iron catalyzed olefin hydrogenation have been examined. Allyl amines, $R_2NCH_2CH{=}CH_2$ (R = H, Me), are hydrogenated in the presence of (^{iPr}PDI)Fe(N_2)$_2$ (^{iPr}PDI = 2,6-(2,6-$^{i}Pr_2$-$C_6H_3N{=}CMe)_2C_5H_3N$, **1-(N_2)$_2$**) and the observed turnover frequencies increase with steric protection of the nitrogen donor. Likewise, ether-substituted olefins such as ethyl vinyl ether, ethyl allyl ether, and allyl ether are hydrogenated with turnover frequencies indistinguishable from the analogous α-olefins. For carbonyl-substituted alkenes, the hydrogenation activity is exquisitely sensitive to the position and type of the functional group. Esters such as dimethyl itaconate and *trans*-methyl cinnamate are effectively hydrogenated at 23 °C while ketones such as 5-hexen-2-one require heating to 65 °C for efficient turnover. In contrast, conjugated α,β-unsaturated ketones induce decomposition of the iron compound. Stoichiometric experiments were conducted to probe the iron substrate interaction and to gauge the coordination affinity of the functional group relative to the alkene. In addition, several new bis(imino)pyridine iron amine and ketone complexes were synthesized and the molecular and electronic structures probed by NMR spectroscopy, Mössbauer spectroscopy, and in one case, X-ray diffraction.

Introduction

Interest continues to grow in developing inexpensive and environmentally responsible iron catalysts as alternatives to more widely used precious metals.[1] Given the indispensability of olefin and alkyne hydrogenation in fine and commodity chemical synthesis,[2] these transformations are important targets for more environmentally benign catalytic methods. While impressive levels of activity, specificity, and selectivity have been achieved with ruthenium, rhodium, and iridium hydrogenation catalysts,[3] the high cost of the metal–ligand combinations as well as stringent requirements on acceptable levels of trace metal impurities in the resulting alkane inspire the search for alternatives. Effective, highly enantioselective, metal-free organocatalytic transfer hydrogenations have recently been described,[4] although these reactions often rely on carbonyl-containing substrates for interaction with the iminium catalyst.[5] Thus, general methods for olefin and alkyne hydrogenation, especially for unactivated substrates, are likely to continue to rely on transition metal catalysts.

Seminal studies in iron-catalyzed olefin hydrogenation utilized $Fe(CO)_5$ as the precursor to the active species. The $Fe(CO)_5$-promoted hydrogenation of methyl linoleate occurred under thermal conditions, although temperatures in excess of 180 °C and dihydrogen pressures of 400 psi were required for effective turnover.[6] Subsequently, Wrighton and co-workers described a photocatalytic method for the hydrogenation of simple, unactivated olefins such as 1-hexene at ambient temperature and 1 atm of dihydrogen pressure.[7] Seeking to mimic the proposed [$Fe(CO)_3$] active species[8] under mild thermal conditions, our laboratory has been exploring reduced bis(imino)pyridine iron compounds.[9] Concurrent with our efforts, Daida and Peters reported a family of tris(phosphino)borate iron(II) alkyl complexes that serve as catalyst precursors for the catalytic hydrogenation of simple unactivated olefins with modest turnover frequencies at 50 °C.[10] In more recent work, Casey and Guan have reported a bifunctional, Shvo-type[11] iron catalyst for the hydrogenation of ketones.[12]

The aryl-substituted bis(imino)pyridine iron bis(dinitrogen) complex, (^{iPr}PDI)Fe(N_2)$_2$ (^{iPr}PDI = 2,6-(2,6-$^{i}Pr_2$-$C_6H_3N{=}CMe)_2$-C_5H_3N, **1-(N_2)$_2$**), has been shown to be an effective precursor

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

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

(3) (a) Knowles, W. S. *Adv. Synth. Catal.* **2003**, *345*, 3. (b) Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008.

(4) (a) Tuttle, J. B.; Ouellet, S. G.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2006**, *128*, 12662. (b) Ouellet, S. G.; Tuttle, J. B.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2005**, *127*, 32. (c) Mayer, S.; List, B. *Angew. Chem., Int. Ed.* **2006**, *45*, 4193.

(5) For an example of imine reduction see: Rueping, M.; Antonchick, A. P.; Theismann, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 3683.

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

(7) (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.

(8) Kismartoni, L. C.; Weitz, E.; Cedeno, D. L. *Organometallics* **2005**, *24*, 4714.

(9) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 13794.

(10) Daida, E. J.; Peters, J. C. *Inorg. Chem.* **2004**, *43*, 7474.

(11) (a) Casey, C. P.; Johnson, J. B. *J. Am. Chem. Soc.* **2005**, *127*, 1883. (b) Casey, C. P.; Bikhanova, G. A.; Guzei, I. A. *J. Am. Chem. Soc.* **2006**, *128*, 2286. (c) Shvo, Y.; Czarkie, D.; Rahamim, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7400.

(12) Guan, H.; Casey, C. P. *J. Am. Chem. Soc.* **2007**, *129*, 5816.

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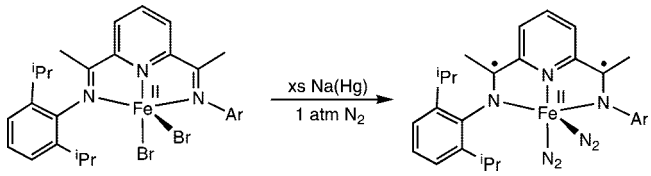


Figure 1. Synthesis and electronic structure of **1-$(N_2)_2$**.

for the catalytic hydrogenation and hydrosilylation of olefins and alkynes[9] and for the $[2\pi + 2\pi]$ cycloisomerization of α,ω-dienes.[13] In catalytic hydrogenation reactions, efficient turnover was observed with unactivated olefins at low catalyst loadings, typically 0.3 mol %, and levels as low as 40 ppm were also effective. More detailed investigations into the electronic structure of **1-$(N_2)_2$** and related neutral ligand derivatives[14] by Mössbauer, infrared and NMR spectroscopy, and DFT calculations established a two-electron-reduced bis(imino)pyridine chelate and a ferrous center (Figure 1).[15]

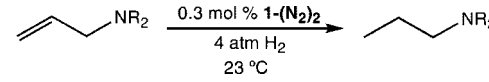
Relatively weak field, σ-donating ligands such as amines, dinitrogen, and tetrahydrothiophene produce intermediate spin ($S_{Fe} = 1$) ferrous centers that are antiferromagnetically coupled to triplet ($S_L = 1$) chelate dianions.[14,15] For amines and N_2, a triplet excited state arising from the singlet ($S_L = 0$) chelate diradical mixes with the ground state resulting in temperature independent paramagnetism.[14,15] These contributions are minimized with stronger field ligands such as phosphines.[14] The strongest field donors such as carbon monoxide and *tert*-butylisocyanide produce low-spin iron(II), d^6 compounds also with doubly reduced bis(imino)pyridines.[14,15] Both Mössbauer spectroscopy and computational studies demonstrate that contributions from an iron(0) canonical form with a high degree of covalency are also important.

If iron-catalyzed olefin hydrogenation is to enjoy the utility of well-established rhodium and ruthenium compounds, precatalysts that exhibit good functional group tolerance and a wide substrate scope must be developed.[16] Inspired by recent targets identified by the pharmaceutical industry,[16,17] the hydrogenation of a range of substituted alkenes catalyzed by **1-$(N_2)_2$** was studied. Here we describe the initial results of those efforts, report a broad substrate scope for iron-catalyzed olefin hydrogenation, and probe iron−substrate interactions by NMR and Mössbauer spectroscopy.

Results and Discussion

Amino Olefins. The first class of substrates examined were substituted allyl amines. Interest in these molecules derives from the importance of amines in numerous pharmaceutical processes and final products.[18] Our studies commenced with the catalytic hydrogenation of a series of commercially available allyl amines, $R_2NCH_2CH{=}CH_2$ (R = H, Me), as representative examples. Standard conditions employing 0.3 mol % of **1-$(N_2)_2$** in a 0.915 M solution of the desired substrate in benzene-d_6 with four atmospheres of dihydrogen were used for each catalytic experiment.[19] Efficient turnover was also observed in toluene and pentane solution. The progress of the reaction was monitored by ^{1}H NMR spectroscopy and the experimentally determined turnover frequencies and conversions are reported in Table 1.

Table 1. Catalytic hydrogenation of amino-substituted olefins and 4-methyl-1-pentene with 1-$(N_2)_2$

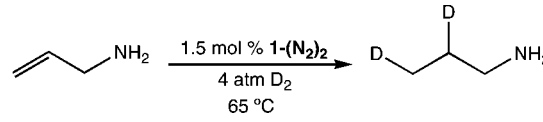


Substrate	Time (min)	% Conversion[a]	TOF (hr^{-1})	K_{eq} (M^{-1})[b]
	1440	20	3	> 100
	60	95	320	15
	15	95	1270	< 0.01
	15	95	1270	< 0.01

[a] Determined by ^{1}H NMR spectroscopy. [b] Estimated from ^{1}H NMR spectroscopy at 23 °C.

In general, the turnover frequencies for allyl group hydrogenation increased with increased nitrogen substitution. The slowest member of the series was allyl amine, which reached only 20% conversion after 24 h. Increased methylation of the nitrogen also increased the turnover frequency such that *N*,*N*-dimethylallylamine was hydrogenated at a rate indistinguishable from that of the analogous hydrocarbon, 4-methyl-1-pentene (Table 1).

Catalytic deuteration experiments were also conducted to gauge competition from chain running processes. Addition of four atmospheres of deuterium gas to *N*,*N*-dimethylallylamine in the presence of 1.5 mol % of **1-$(N_2)_2$** yielded the corresponding propyl amine with deuterium incorporation exclusively in the 2 and 3 positions, providing no evidence for chain running at this D_2 pressure (eq 1). This experiment was conducted at 65 °C to ensure facile conversion to the desired product. No deuterium incorporation was observed in the N−H positions, suggesting that oxidative addition of the amine is not competitive during catalytic turnover.

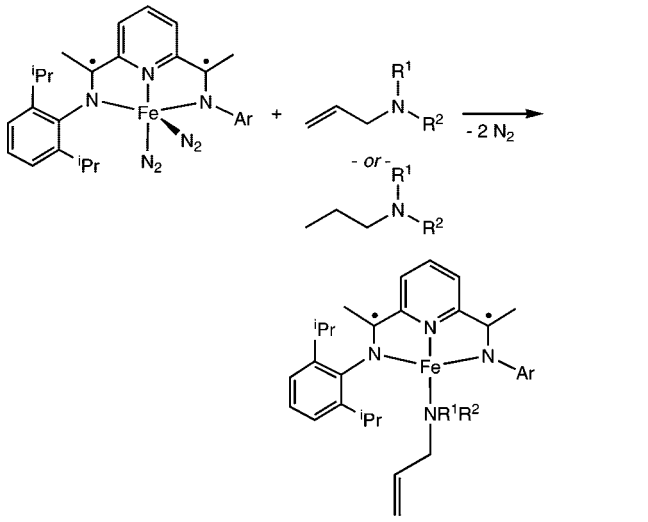


(1)

A series of stoichiometric reactions between **1-$(N_2)_2$** and the amines presented in Table 1 was carried out to gain additional insight into the interaction between the substrate and the iron center. Addition of 1 equiv of allylamine to **1-$(N_2)_2$** resulted in liberation of dinitrogen gas and yielded a brown solid identified as **1-$NH_2CH_2CH{=}CH_2$** (eq 2). Analogous products, **1-$NH_2CH_2CH_2CH_3$** and **1-NH(Me)$CH_2CH{=}CH_2$**, were isolated by using a similar procedure with propylamine and *N*-methylallylamine, respectively. Experiments with *N*,*N*-dimethylallylamine and 4-methyl-1-pentene produced no change in the benzene-d_6 ^{1}H NMR spectra of **1-$(N_2)_2$**. These observa-

(13) Bouwkamp, M. W.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13340.
(14) Bart, S. C.; Bill, E.; Lobkovsky, E.; Wieghardt, K.; Chirik, P. J. *Inorg. Chem.* **2007**, *46*, 7055.
(15) 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.
(16) Shimizu, H.; Nagasaki, I.; Matsumura, K.; Sayo, N.; Saito, T. *Acc. Chem. Res.* **2007**, *40,* 1385.
(17) Johnson, N. B.; Lennon, I. C.; Moran, P. H.; Ramsden, J. A. *Acc. Chem. Res.* **2007**, *40,* 1291.
(18) Janvier, P.; Sun, X.; Bienaymé, H.; Zhu, J. *J. Am. Chem. Soc.* **2002**, *124*, 2560.
(19) All catalytic hydrogenation reactions were conducted in benzene-d_6 or toluene as the solvent. Pentane may also be used and in some cases has been shown to produce higher activity. See: Archer, A. M.; Bouwkamp, M. W.; Cortez, M. P.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2006**, *25*, 4269.

tions suggest that both amine and olefin coordination are minimal for these substrates at 23 °C and 1 atm of N_2.



1-$NH_2CH_2CH{=}CH_2$: $R^1 = R^2 = H$
1-$NH_2CH_2CH_2CH_3$: $R^1 = R^2 = H$
1-$NH(Me)CH_2CH{=}CH_2$: $R^1 = Me$, $R^2 = H$
$R^1 = R^2 = Me$; No reaction

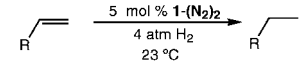
(2)

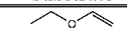
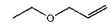
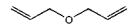
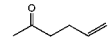
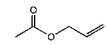
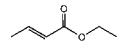
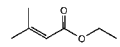
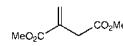
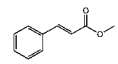
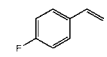
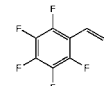
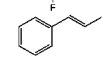
Equilibrium constants (Table 1) for amine coordination to **1-$(N_2)_2$** were also examined as a function of nitrogen substituent and alkyl chain. Addition of 1 equiv of propylamine to **1-$NH_2CH_2CH{=}CH_2$** furnished a 2:1 mixture of the saturated and unsaturated amine complexes. An identical ratio of products was obtained when the converse experiment was conducted, whereby allyl amine was added to **1-$NH_2CH_2CH_2CH_3$**. Finally, addition of 1 equiv of both propyl and allyl amine to **1-$(N_2)_2$** yielded the same product distribution. This series of experiments established that the coordination of the saturated amine is slightly favored ($K_{eq} = 2.0$) at 23 °C.

To gauge the preferences of **1-$NH_2CH_2CH{=}CH_2$** versus **1-$NH(Me)CH_2CH{=}CH_2$** coordination, **1-$(N_2)_2$** was treated with an excess of each olefin (in equimolar quantities) and an 85:15 ratio, favoring the allyl amine compound, was formed. From these data, the equilibrium constant for coordination of *N*-methylallylamine to **1-$(N_2)_2$** was estimated as 15 M^{-1} at 23 °C. Exchange between free and coordinated allylamine was also observed by EXSY spectroscopy at 23 °C with a mixing time of 200 ms, demonstrating that $H_2NCH_2CH{=}CH_2$ is a labile ligand.

Previously, our laboratory has reported the synthesis and characterization of **1-DMAP**[15] and **1-$NH_2{}^tBu$**[14] and established diamagnetic ground states for both compounds with contributions from temperature independent paramagnetism arising from mixing of an $S = 1$ excited state via spin–orbit coupling. The ^1H NMR spectroscopic and magnetic data for amine compounds prepared in this work, **1-$NH_2CH_2CH{=}CH_2$** and **1-$NH(Me)CH_2CH{=}CH_2$**, are consistent with a similar electronic structure. For **1-$NH(Me)CH_2CH{=}CH_2$**, the number of ^1H and ^{13}C resonances observed is consistent with a molecule of C_{2v} symmetry, establishing fast iron−nitrogen (and possibly N−C) bond rotation on the time scale of the experiment. Variable-temperature ^1H NMR experiments in toluene-d_8 established a coalescence temperature of −25 °C for the imine methyl groups corresponding to a barrier of rotation of 11.2 kcal/mol. At 23 °C, the in-plane methyl groups appear at −6.55 ppm and the *m*-pyridine peak is located at 12.62 ppm in the benzene-d_6 ^1H NMR spectrum. The ^{13}C resonance of the former substituent was observed as a broadened peak at 39.17 ppm. Broadening of this peak and the chemical shifts of the other resonances are consistent with diradical character for the delocalized π-system in the plane of the iron center and are also consistent with the results of DFT calculations and spectroscopic data reported for **1-DMAP**.[15]

Table 2. Catalytic Hydrogenation of Oxygen-Substituted and Halogenated Olefins with 1-$(N_2)_2$



Substrate	Time (min)	% Conversion[a]	TOF (hr^{-1})
	5	> 99	> 240
	5	> 99	> 240
	5	> 99	> 480
	60[b]	93	19
	900[b]	0	0
	900	3	0.04
	900	0	0
	5	> 99	>240
	1440	50	0.4
	360[c]	> 99	> 3.3
	5	> 99	> 240
	240	87	4.4
	5	>99	> 240
	5	>99	> 240
	5	> 99	> 240

[a] All catalytic reactions carried out with 5 mol % **1-$(N_2)_2$**. Progress of the reaction and turnover determined by ^1H NMR spectroscopy. [b] Catalytic reaction conducted at 65 °C. [c] Data from ref 9; *trans*-β-methylstyrene is included for comparison.

Oxygen-Substituted Alkenes. Alkenes bearing various oxygen-containing functional groups were also explored in catalytic hydrogenation reactions promoted by **1-$(N_2)_2$**. The substrates examined, conversions, and corresponding turnover frequencies are reported in Table 2. Each catalytic reaction was conducted with 5 mol % **1-$(N_2)_2$** in benzene-d_6 at 23 °C with 4 atm of H_2 mimicking the conditions used previously for the hydrogenation of dimethyl itaconate.[9] To prevent side reactions,[20] solutions containing the iron compound were frozen at liquid nitrogen temperature and the substrate and H_2 gas were added before thawing. Conversions were determined by ^1H NMR spectroscopy.

(20) At low hydrogen pressures, many oxygenated substrates undergo competing C–O bond cleavage: Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. to be published.

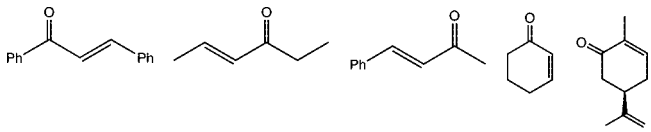


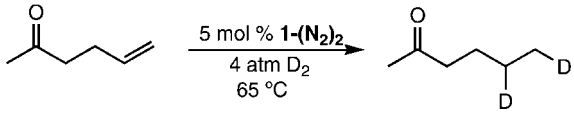
Figure 2. α,β-Unsaturated ketones that induce decomposition of **1-(N_2)$_2$** under catalytic hydrogenation conditions.

The catalytic hydrogenation reactions exhibited remarkable sensitivity to the nature and position of the oxygenated functional group. Introduction of ether functionality has little impact on the hydrogenation turnover frequencies. Ethyl vinyl ether, allyl ethyl ether, and allyl ether hydrogenated at rates indistinguishable from pure hydrocarbon α-olefins.[9] In contrast, carbonyl substitution had a dramatic impact on catalytic activity. The ketone, 5-hexen-2-one, required heating to 65 °C for reasonable turnover while (+)-dihydrocarvone was not hydrogenated even after heating for 15 h (65 °C). The lack of hydrogenation of the latter substrate is likely due to the inability of the *gem*-disubstituted olefin to effectively compete with ketone coordination.

Carboxylated alkenes produced varied hydrogenation activities. Specifically, *trans*-methyl cinnamate exhibited a turnover frequency indistinguishable from that of *trans*-β-methylstyrene, while vinyl acetate and allyl acetate produced no turnover. Previous work from our laboratory has also demonstrated that dimethyl itaconate was effectively hydrogenated in the presence of **1-(N_2)$_2$**.[9] Importantly, internal and trisubstituted olefins were rapidly hydrogenated upon introduction of an ethyl-substituted ester. In contrast, attempts to hydrogenate related sterically hindered, unactivated tri- and tetrasubstituted olefins such as 2-methyl-2-butene and 2,3-dimethyl-2-butene produced only minimal turnover under similar conditions.

Flourinated olefins are also well tolerated by the iron catalyst. Both 4-flourostyrene and pentaflurostyrene were hydrogenated at rates similar to those observed with styrene[9] and *trans*-β-methylstyrene, demonstrating little interaction or decomposition of the iron from introduction of the halogen substituents.

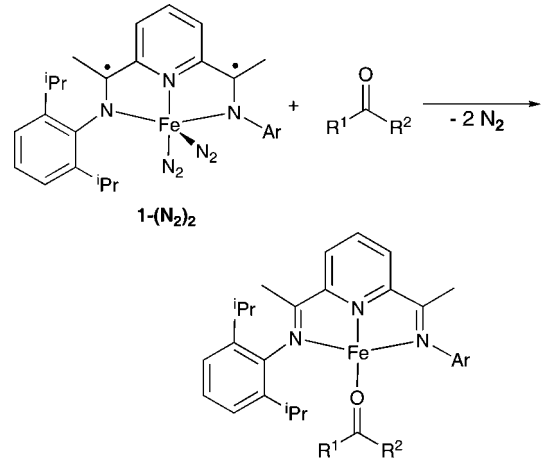
The possibility of chain running during iron-catalyzed olefin hydrogenation was probed by the addition of deuterium gas to 5-hexen-2-one. Monitoring the experiment by ^{2}H NMR spectroscopy established incorporation of the isotopic label in only the 5 and 6 positions of product, demonstrating that chain running was not operative under the conditions employed.



(3)

Attempts to extend the scope of bis(imino)pyridine iron-catalyzed olefin hydrogenation to α,β-unsaturated ketones have been unsuccessful (Figure 2). No hydrogenation of the alkene in *trans*-chalcone, *trans*-4-hexen-3-one, *trans*-4-phenyl-3-buten-2-one, 2-cyclohexenone, or carvone was observed with 10 mol % of **1-(N_2)$_2$** and 4 atm of dihydrogen. These substrates induced rapid decomposition of the iron compound at 23 °C, precluding examination of the hydrogenation reactions.

Stoichiometric Experiments. The remarkable sensitivity exhibited by **1-(N_2)$_2$** to the type and position of oxygen-containing functional groups prompted a more thorough investigation into the iron−substrate interaction. Initial studies were conducted with commercially available ketones to gain insight into their coordination chemistry, and the molecular and electronic structure of the resulting complexes. Addition of 1 equiv of acetophenone to **1-(N_2)$_2$** furnished a dark green, diamagnetic powder identified as the iron acetophenone complex, (^{iPr}PDI)FeOC(Ph)Me (**1-OC(Ph)Me**). By using a similar procedure, bis(imino)pyridine iron compounds of benzophenone, 5-hexen-2-one, 2-hexanone, benzylacetone, and (+)-dihydrocarvone were also isolated (eq 4).

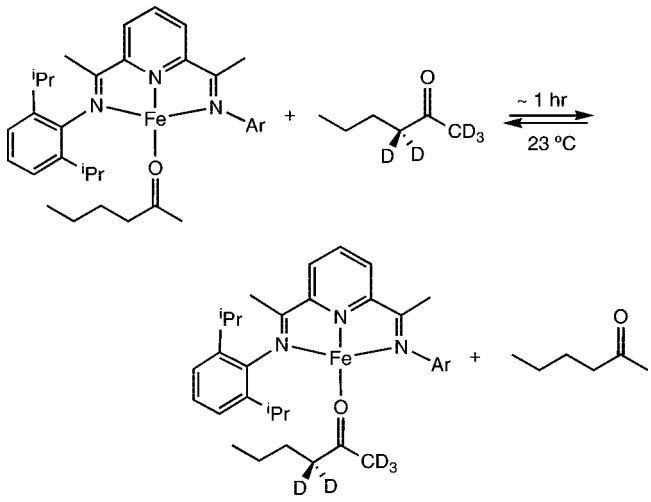


1-OC(Ph)Me: R^1 = Ph, R^2 = Me
1-OCPh$_2$: R^1 = Ph, R^2 = Ph
1-OC(Me)(3-butenyl): R^1 = Me, R^2 = $(CH_2)_2CH{=}CH_2$
1-OC(Me)(^{n}Bu): R^1 = Me, R^2 = ^{n}Bu
1-OC(Me)(PhEt): R^1 = Me, R^2 = $(CH_2)_2$Ph
1-DHC: DHC = dihydrocarvone

(4)

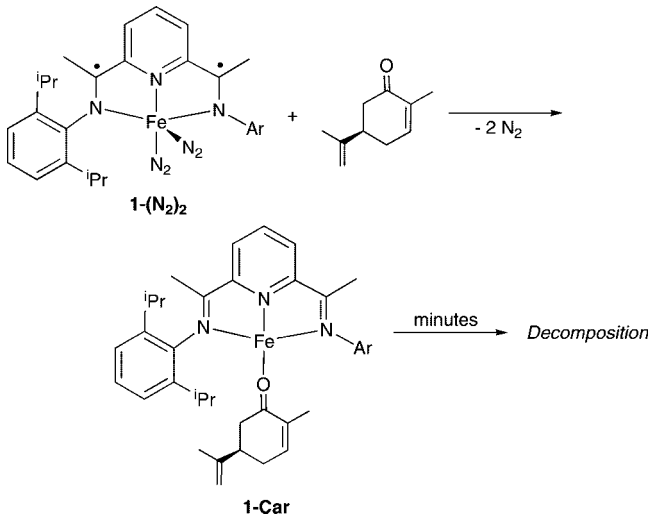
Each ketone studied formed an isolable bis(imino)pyridine iron carbonyl complex that exhibits spectroscopic features consistent with temperature independent paramagnetism.[15] The 5-hexen-2-one compound, **1-OC(Me)(3-butenyl)**, exhibits no evidence for coordination of the alkene at −60 °C as judged by ^{1}H NMR spectrscopy. As with the iron amine compounds, exchange studies were conducted to assay when carbonyl coordination was labile and reversible. Addition of 2-hexanone-*1,1,1,3,3-d*$_5$ to a benzene-*d*$_6$ solution of **1-OC(Me)(^{n}Bu)** resulted in slow exchange over the course of 1 h at 23 °C (eq 5), contrasting amine exchange that occurs on the NMR time scale. A similar rate of exchange was observed upon addition of the partially deuteratated 2-hexanone to **1-OC(Me)(3-butenyl)**. These studies establish that the relative coordination affinity of the carbonyl group compared to the olefin is greater than that in the corresponding amine cases where rapid hydrogenation was observed at 23 °C and lower catalyst loadings.

The lack of catalytic turnover observed upon attempted hydrogenation of α,β-unsaturated ketones was also probed in a series of stoichiometric experiments. Treatment of **1-(N_2)$_2$** with each of the enones presented in Figure 2 resulted in almost immediate decomposition of the iron compound and formation of free ^{iPr}PDI ligand. Identical results were obtained when the addition reaction was conducted under a dihydrogen atmosphere. One exception is (−)-(*R*)-carvone, where a bis(imino)pyridine iron ketone compound, **1-Car**, exhibiting features consistent with temperature independent paramagnetism was observed by ^{1}H NMR spectroscopy (eq 6). However, **1-Car** decomposed to a complex mixture of paramagnetic products over the course of approximately 5 min at 23 °C. These rapid decomposition reactions account for the inability to hydrogenate this class of substrate and are likely a result of the relatively low one-electron-reduction potential of α,β-unsaturated ketones as



(5)

compared to the corresponding carbonyl-substituted alkenes lacking conjugation.[21] Importantly, α,β-unsaturated esters are well tolerated by the iron catalyst and are also sufficiently reducing to prevent catalyst decomposition.



(6)

In all but one case, benzophenone (vide infra), the benzene-d_6 ^{1}H NMR spectra of the bis(imino)pyridine iron ketone complexes exhibit features consistent with temperature independent paramagnetism, arising from mixing of an $S = 1$ excited state with the diamagnetic ground state via spin–orbit coupling.[14] Diagnostic chemical shifts for each compound are reported in Table 3. The imine methyl resonances are shifted upfield of the diamagnetic reference values (free ^{iPr}PDI ligand) and appear upfield of 0 ppm. Likewise, the *m*- and *p*-pyridine peaks are shifted downfield relative to those of the free ligand (Table 3).

Asymmetrically substituted ketones exhibited the number of bis(imino)pyridine resonances at 23 °C consistent with C_{2v} symmetry, likely arising from rapid rotation about the Fe−O bond on the NMR time scale. Cooling a toluene-d_8 solution of **1-OC(Ph)Me** to −70 °C slowed the dynamic process and broadened the peaks although the static limit and hence estimation of the kinetic barrier was not achieved. The iron

(21) For example, the one electron reduction potential of trans-4-phenyl-3-buten-2-one in acetonitrile is −2.01 V while that of the corresponding saturated compound, methyl-3-phenylpropionate, does not occur before reduction of the solvent. Value referenced to ferrocene/ferrocenium.

Table 3. Benzene-d_6 ^{1}H NMR Chemical Shifts of the Imine Methyl Groups and *m*- and *p*-Pyridine Resonances for Bis(imino)pyridine Iron Ketone Compounds Exhibiting Temperature Independent Paramagnetism

	δ (ppm)		
compd	N=CMe	*m*-pyridine	*p*-pyridine
^{i}PrPDI	2.27	8.50	7.28
1-OC(Ph)Me	−2.23	10.05	8.68
1-OCPh$_2$[a]	−18.05	13.83	36.94
1-OC(Me)(3-butenyl)	−2.87	10.49	8.51
1-OC(Me)(^{n}Bu)	−3.07	10.59	8.51
1-OC(Me)(PhEt)	−3.04	10.53	8.53
1-DHC	−2.88, −3.39	10.84, 10.47	8.56, 8.46

[a] Values at 23 °C.

complex prepared from (+)-dihydrocarvone, **1-DHC**, was isolated as a mixture of isomers. Subsequent recrystallization from pentane resulted in isolation of predominantly (~6:1) one diastereomer. For **1-OC(Me)(3-butenyl)**, it is possible that the pendant olefin coordinates to the iron center to form a chelate; however, the ^{1}H NMR shifts of the alkene protons are not significantly perturbed from those of the free olefin and suggest little or no interaction with the metal center.[22]

One notable compound is **1-OCPh$_2$**. The ^{1}H NMR spectrum exhibits features suggestive of a somewhat different electronic structure than those of the other ketone compounds. In benzene-d_6 at 23 °C, resonances are observed over a 55 ppm chemical shift window, much broader than the usual 15–20 ppm range. The imine methyl groups appear substantially upfield at −18.05 ppm while the *p*-pyridine appears downfield at 36.94 ppm. Notably, the resonances for the orthogonal aryl substituents are broadened and are not sufficiently resolved to exhibit typical $^3J_{H\text{-}H}$ couplings. All of the peaks are temperature dependent and move toward the diamagnetic region of the spectrum upon cooling in toluene-d_8 to −80 °C. The peaks remain broad and featureless at low temperatures. This behavior contrasts typical bis(imino)pyridine iron neutral ligand compounds which exhibit ^{1}H NMR spectra with expected $^3J_{H\text{-}H}$ couplings and chemical shifts that are temperature independent.[14,15]

The solid state structure of **1-OCPh$_2$** was determined by X-ray diffraction and is depicted in Figure 3. Selected bond distances and angles are presented in Table 4. The geometry of the iron is best described as idealized square planar with the angles around the metal summing to 360°. The phenyl rings of the benzophenone are nearly orthogonal to the iron chelate plane but are canted with respect to each other. This arrangement is likely to avoid unfavorable interactions with the sterically demanding imine aryl groups.

The metrical parameters for the bis(imino)pyridine ligand in **1-OCPh$_2$** (Table 4) are consistent with two-electron chelate reduction.[14,15] The imine N=C bonds are elongated to 1.342(2) Å while the C(2)−C(3) and C(7)−C(8) bonds are contracted to 1.414(3) and 1.411(3) Å, respectively. Distortions of this type are consistent with population of the π-system that is antibonding with respect to the imine and bonding with respect to the C_{pyr}−C_{imine} bonds.[15] The carbonyl bond distance, O(1)−C(34), of 1.262(4) Å is slightly elongated compared to the value of 1.23(1) Å determined for free benzophenone.[23]

One notable feature of the structure is the short Fe−O bond length of 1.7924(3) Å. This value is considerably contracted

(22) (a) Casey, C. P.; Lee, T. Y.; Tunge, J. A.; Carpenetti, D. W. *J. Am. Chem. Soc.* **2001**, *123*, 10762. (b) Carpentier, J. F.; Wu, Z.; Lee, C. W.; Stromberg, S.; Christopher, J. N.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 7750.

(23) Fleischer, E. B.; Sung, N.; Hawkinson, S. *J. Phys. Chem.* **1968**, *72*, 4311.

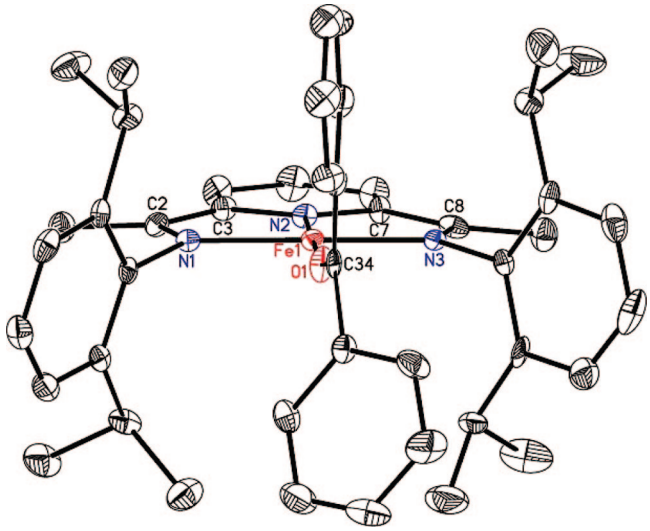


Figure 3. Molecular structure of **1-OCPh$_2$** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 4. Selected bond distances (Å) and angles (deg) for 1-OCPh$_2$

N(1)−C(2)	1.342(2)
N(3)−C(8)	1.342(2)
C(2)−C(3)	1.414(3)
C(7)−C(8)	1.411(3)
O(1)−C(34)	1.262(2)
Fe(1)−N(1)	1.9113(14)
Fe(1)−N(2)	1.8226(15)
Fe(1)−N(3)	1.9225(14)
Fe(1)−O(1)	1.7924(3)
Fe(1)−O(1)−C(34)	167.05(11)
N(1)−Fe(1)−N(2)	80.72(6)
N(2)−Fe(1)−O(1)	179.15(6)
sum of angles about Fe(1)	360

from the distances found in related iron alkoxide ($d_{Fe\text{-}O} \sim 1.85$ Å) and carboxylate complexes ($d_{Fe\text{-}O} \sim 2.10$ Å) and is suggestive of multiple bond character. By way of comparison, Holland and co-workers reported an Fe−O distance of 1.8076(16) Å in the iron(II) β-diiminate iron alkoxide complex, L^{Me}FeOCHPh$_2$,[24] while Aldridge and co-workers reported an Fe−O distance of 1.982(3) Å and a carbonyl C−O distance of 1.256(5) Å in (η^5-C$_5$Me$_5$)Fe(CO)$_2$(OCPh$_2$)]$^+$.[25] In fact, the short Fe−O distance observed in 1-OCPh$_2$ is reminiscent of iron−oxygen bond distances of 1.77 Å in μ-oxo diferrous[26] and ferric compounds[27] and suggests significant contribution from an iron(III) center with a C(34)-centered radical. This view of the electronic structure also accounts for the peak broadening observed by ^{1}H NMR spectroscopy.

Both the reduction potential and infrared carbonyl stretching frequency of benzophenone compared to acetophenone support a more thermodynamically favorable one-electron reduction of the diaryl ketone. In acetonitrile solution, the reduction potential of benzophenone is −2.24 V while the value for acetophenone is shifted to −2.46 V (versus Cp$_2$Fe$^+$/Cp$_2$Fe). Similarly, the pentane solution C=O stretch for benzophenone is 1671 cm^{-1} while that for acetophenone is 1696 cm^{-1}.

(24) Vela, J.; Vaddadi, S.; Cundari, T. R.; Smith, J. M.; Gregory, E. A.; Lachicotte, R. J.; Flaschenriem, C. J.; Holland, P. L. *Organometallics* **2004**, *23*, 5226.
(25) Coombs, D. L.; Aldridge, S.; Rossin, A.; Jones, C.; Willock, D. J. *Organometallics* **2004**, *23*, 2911.
(26) Eckert, N. A.; Stoian, S.; Smith, J. M.; Bominaar, E. L.; Münck, E.; Holland, P. L. *J. Am. Chem. Soc.* **2005**, *127*, 9344.
(27) Tshuva, E. Y.; Lippard, S. J. *Chem. Rev.* **2004**, *104*, 987.

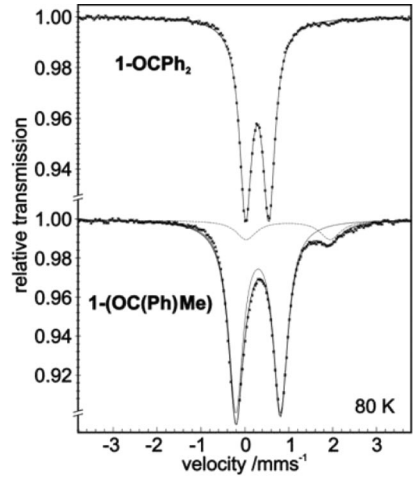


Figure 4. Zero-field Mössbauer spectra of **1-OCPh$_2$** and **1-OC(Ph)Me** recorded at 80 K.

Mössbauer Spectroscopy. The electronic structures of representative bis(imino)pyridine iron ketone compounds were also studied by Mössbauer spectroscopy. Zero-field spectra of **1-OC(Ph)Me** and **1-OCPh$_2$** were recorded at 80 K (Figure 4). The experimentally determined isomer shift (δ) of 0.31 mm·s^{-1} for **1-OC(Ph)Me** is consistent with an intermediate spin iron(II) center and similar to values observed with other four-coordinate bis(imino)pyridine iron compounds with neutral ligands.[14,15] Despite different NMR spectroscopic properties, the iron benzophenone compound, **1-OCPh$_2$**, exhibits a similar isomer shift of 0.28 mm·s^{-1}, also consistent with an intermediate spin, d^6 ferrous ion. On the basis of the X-ray diffraction and Mössbauer data, **1-OCPh$_2$** appears to have a similar electronic structure to other bis(imino)pyridine iron ketone compounds. As stated previously, the unique ^{1}H NMR spectrum of the compound is likely a result of radical character on the carbonyl carbon and a contribution from an iron(III) center rather than a gross change in electronic structure.

Therefore, the electronic structures for the amine and ketone compounds prepared in this work are similar to those of other bis(imino)pyridine neutral ligand derivatives.[14] The observed $S = 0$ ground states are readily accommodated by an intermediate spin ferrous ion antiferromagnetically coupled to a chelate dianion. Mixing via spin–orbit coupling of an energetically similar $S = 1$ excited state accounts for the unusual NMR chemical shifts reported in Table 3.

Concluding Remarks

In summary, the bis(imino)pyridine iron bis(dinitrogen) complex, **1-(N$_2$)$_2$**, is a precatalyst for the hydrogenation of olefins in the presence of unprotected amines, various carbonyls, and fluorinated hydrocarbons. More detailed investigations into the iron−substrate interaction established formation of bis(imino)-pyridine iron−substrate complexes where the coordination affinity of the functional group (e.g., amines, carbonyls) was inversely proportional to the turnover frequency. These studies also demonstrated that α,β-unsaturated ketones induce rapid decomposition of the iron compound, likely due to a relatively low one-electron redox potential. In contrast, α,β-unsaturated esters are readily tolerated by the iron catalyst resulting in efficient hydrogenation turnover.

Experimental Section

General Considerations. All air- and moisture-sensitive manipulations were carried out with standard vacuum line, Schlenk,

and cannula techniques or in an MBraun inert atmosphere dry box containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were initially dried and deoxygenated by using literature procedures.[28] Hydrogen and deuterium gas were passed through a column containing manganese oxide supported on vermiculite and 4 Å molecular sieves before admission to the high-vacuum line. Benzene-d_6 and toluene-d_8 were purchased from Cambridge Isotope Laboratories and dried over 4 Å molecular sieves or titanocene, respectively. **1-(N$_2$)$_2$** and **1-Br** were prepared according to literature procedures.[9,29] *N*-Allylmethylamine, *N*,*N*-dimethylallylamine, propylamine, 2-hexanone, 5-hexen-2-one, 4-hexen-3-one, acetophenone, vinyl acetate, allyl acetate, (+)-dihydrocarvone as a mixture of isomers, *trans*-ethyl crotonate, ethyl 3,3-dimethylacrylate, and 4-fluorostyrene were all purchased from Aldrich and dried over calcium hydride for at least 24 h before being used. Allylamine and (−)-carvone were purchased from Acros and purified in a similar manner. 2-Cyclohexen-1-one was purchased from Fisher Scientific and dried as described above.

Ethyl vinyl ether and allyl ether were purchased from Aldrich and dried over calcium hydride for 24 h. Allyl ethyl ether was purchased from Acros and dried over calcium hydride for 24 h before use. 2,3,4,5,6-Pentafluorostyrene was purchased from Matrix Scientific and was dried in a similar fashion. 4-Methyl-1-pentene was vacuum transferred from lithium aluminum hydride after drying overnight. Benzylacetone and *trans*-β-methylstyrene were purchased from Aldrich and dried over molecular sieves before use. *trans*-Methyl cinnamate and *trans*-chalcone were purchased from Aldrich and dried under vacuum for 16 h. After drying, *trans*-chalcone was recrystallized from a concentrated ethereal solution at −35 °C. Benzophenone was purchased from Fisher Scientific and dried under vacuum for 24 h. *trans*-4-Phenyl-3-buten-2-one was purchased from Acros and dried in vacuo for approximately 1 h before use. 2-Hexanone-*1*,*1*,*1*,*3*,*3*-d_5 was prepared by stirring a solution of 2-hexanone in D_2O in the presence of D_2SO_4 and dried with $MgSO_4$ following extraction with ether.

^{1}H NMR spectra were recorded on Varian Mercury 300 and Inova 400 and 500 spectrometers operating at 299.76, 399.78, and 500.62 MHz, respectively. All spectra were obtained at 23 °C unless stated otherwise. ^{2}H NMR spectra were recorded at 20 °C on the Inova 400 and 500 spectrometers operating at 61.37 and 76.85 MHz, respectively. ^{13}C NMR spectra were recorded on the same spectrometers operating at 101.535 or 125.893 MHz, respectively. All ^{1}H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ with ^{1}H (residual) and ^{13}C chemical shifts of the solvent as a secondary standard. For complexes exhibiting temperature independent magnetism, many assignments were made based on COSY, HSQC, and HMBC NMR experiments. Solution magnetic moments were determined by Evans method[30] with a ferrocene standard and are the average value of at least two independent measurements. ^{1}H NMR multiplicity and coupling constants are reported where applicable. The peak width at half-height is given for paramagnetically broadened resonances. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop, and then quickly transferred to the goniometer head of a Bruker X8 APEX2 diffractometer equipped with a molybdenum X-ray tube (λ = 0.71073 Å). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified and the data were processed by using the Bruker SAINT+ program and corrected for absorption with SADABS. The structures were solved by using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

Mössbauer data were collected on an alternating constant-acceleration spectrometer. The minimum experimental line width was 0.24 mm s^{-1} (full width at half-height). A constant sample temperature was maintained with an Oxford Instruments Variox or an Oxford Instruments Mössbauer-Spectromag 2000 cyrostat. Reported isomer shifts (δ) are referenced to iron metal at 293 K.

General Procedure for the Catalytic Hydrogenation of Amino-Substituted Olefins. A stock solution containing 0.026 g (0.044 mmol) of **1-(N$_2$)$_2$** and 15.00 g (178.3 mmol) of benzene-d_6 was prepared and stored at −35 °C. Upon thawing to ambient temperature, 0.65 g of the resulting solution was charged into a thick-walled glass vessel. With a microsyringe, 0.633 mmol of the desired substrate was added and the vessels were quickly sealed. After being submerged in liquid nitrogen, the frozen solutions were treated with 4 atm of dihydrogen. The timer was started when the solutions began to stir upon thawing. The catalytic reactions were quenched by again submerging the bomb in liquid nitrogen, evacuating the remaining dihydrogen, and transferring the volatile components of the resulting solution to a J. Young tube for analysis by ^{1}H NMR spectroscopy. Conversions were measured by integrating the residual olefin resonances against their saturated counterparts.

Catalytic Deuteration of Allylamine. A J. Young tube was charged with 0.012 g (0.020 mmol) of **1-(N$_2$)$_2$** and approximately 0.65 g of benzene. With a microsyringe, 0.076 g (100 μL, 1.33 mmol) of allylamine was added to the tube. This solution was then submerged in liquid nitrogen, the tube was evacuated, and 4 atm of deuterium was added. The tube was placed in a 65 °C bath for approximately 1 week before the solution was analyzed by ^{2}H NMR spectroscopy.

Catalytic Hydrogenation of Oxygen-Substituted Olefins. For each independent trial, a thick-walled glass vessel was charged with a solution containing 0.019 g (0.032 mmol) of **1-(N$_2$)$_2$** in 0.65 g (7.72 mmol) of benzene-d_6. After standing in a liquid nitrogen chilled cold well for approximately 20 min, 0.633 mmol of the desired substrate was added to the vessel. Immediately after addition, the vessel was submerged in liquid nitrogen to prevent reaction of the substrate and catalyst. On the high-vacuum line, 4 atm of dihydrogen was added and the solution was warmed to ambient temperature or 65 °C. At the desired reaction time, the vessel was opened to air and the catalyst solution was filtered through a glass frit into an NMR tube. Conversions were determined by integrating the remaining ^{1}H NMR olefin resonances against their saturated analogues.

Catalytic Deuteration of 5-Hexen-2-one. This reaction was conducted in a manner similar to that of the oxygenated olefins with an identical catalyst loading in benzene solution with 4 atm of deuterium gas. The reaction was opened to air after 90 min at 65 °C and the solution was filtered through a glass frit into an NMR tube. Deuterium incorporation was determined by ^{2}H NMR spectroscopy.

Preparation of (^{iPr}PDI)Fe(NH$_2$CH$_2$CH=CH$_2$) (1-NH$_2$CH$_2$-CH=CH$_2$). A 20-mL scintillation vial was charged with 0.100 g (0.168 mmol) of **1-(N$_2$)$_2$** and approximately 10 mL of pentane. With a microsyringe, 0.010 g (13 μL, 0.168 mmol) of allylamine was added to the stirring solution. Upon addition of the amine, dinitrogen evolution was observed and a reddish-brown solution formed. After 20 min, the solution was filtered though a frit and the solvent was removed in vacuo to yield 0.077 g (77%) of a dark brown solid identified as **1-NH$_2$CH$_2$CH=CH$_2$**. Anal. Calcd for $C_{36}H_{50}FeN_4$: C, 72.71; H, 8.48; N, 9.42. Found: C, 72.63; H, 8.77; N, 8.99. ^{1}H NMR (benzene-d_6) δ 12.05 (d, 7.5 Hz, 2H, *m-pyr*), 8.77 (t, 7.5 Hz, 1H, *p-pyr*), 7.63 (t, 8.0 Hz, 2H, *p-aryl*), 7.24 (d, 8.0 Hz, 4H, *m-aryl*), 5.35 (m, 1H, CH$_2$CH=CH$_2$), 4.90 (t, 7.5 Hz, 2H, N*H*$_2$CH$_2$), 4.76 (d, 10.5 Hz, 1H, CH$_2$CH=C*H*$_2$), 4.70 (d, 17.0 Hz, 1H, CH$_2$CH=C*H*$_2$), 2.78 (sept., 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 1.63 (m, 2H,

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

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

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

NH_2CH_2), 1.24 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), −0.34 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), −6.09 (s, 6H, $C(CH_3)$). $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 189.45, 165.16, 164.61 (quaternary carbons), 140.00 (*p-pyr*), 137.26 ($CH_2CH{=}CH_2$), 136.57, 125.25 (*p-aryl*), 124.43 (*m-aryl*), 116.86 103.09 (*m-pyr*), ($CH_2CH{=}CH_2$), 44.81 (NH_2CH_2), 39.17 (br s $C(CH_3)$), 28.53 ($CH(CH_3)_2$), 24.23 ($CH(CH_3)_2$), 23.15 ($CH(CH_3)_2$).

Preparation of (iPrPDI)Fe(NH(Me)CH$_2$CH=CH$_2$) (1-NH(Me)-CH$_2$CH=CH$_2$)). This molecule was prepared in a manner similar to **1-NH$_2$CH$_2$CH=CH$_2$** with 0.042 g (0.071 mmol) of **1-(N$_2$)$_2$** and 0.005 g (7 μL, 0.071 mmol) of *N*-allylmethylamine to yield 0.023 g (53%) of a dark brown solid identified as **1-NH(Me)CH$_2$-CH=CH$_2$**. Anal. Calcd for $C_{37}H_{52}N_4Fe$: C, 73.01; H, 8.61; N, 9.20. Found: C, 72.79; H, 8.25; N, 8.96. ^1H NMR (benzene-d_6) δ 12.62 (d, 8.0 Hz, 2H, *m-pyr*), 8.82 (t, 8.0 Hz, 1H, *p-pyr*), 8.28 (m, 1H, $NH(CH_3)$), 7.68 (t, 8.0 Hz, 2H, *p-aryl*), 7.24 (d, 8.0 Hz, 4H, *m-aryl*), 4.99 (m, 1H, $CH_2CH{=}CH_2$), 4.92 (d, 10.5 Hz, 1H, $CH_2CH{=}CH_2$), 4.75 (d, 17.0 Hz, 1H, $CH_2CH{=}CH_2$), 2.16 (m, 2H, $NH(CH_2)$), 1.22 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), 1.02 (d, 7.0 Hz, 3H, $NH(CH_3)$), 0.25 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), −6.55 (s, 6H, $C(CH_3)$), one peak not located. $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 192.79, 165.77, 142.46, 137.04, 134.06, 125.50 (*p-aryl*), 124.54 (*m-aryl*), 123.91, 121.22, 103.07 (*m-pyr*), 52.36 ($NHCH_2$), 40.93 (br s $C(CH_3)$), 34.31 ($NHCH_3$), 28.55 ($CH(CH_3)_2$), 24.76 ($CH(CH_3)_2$), 23.22 ($CH(CH_3)_2$).

Preparation of (iPrPDI)Fe(NH$_2$CH$_2$CH$_2$CH$_3$) (1-NH$_2$CH$_2$CH$_2$CH$_3$). This molecule was prepared in a manner similar to **1-NH$_2$-CH$_2$CH=CH$_2$** with 0.100 g (0.168 mmol) of **1-(N$_2$)$_2$** and 0.010 g (14 μL, 0.168 mmol) of allylamine to yield 0.075 g (75%) of a dark orange solid identified as **1-NH$_2$CH$_2$CH$_2$CH$_3$**. Anal. Calcd for $C_{36}H_{52}N_4Fe$: C, 72.47; H, 8.78; N, 9.39. Found: C, 72.25; H, 8.35; N, 9.00. ^1H NMR (benzene-d_6) δ 12.12 (d, 7.5 Hz, 2H, *m-pyr*), 8.75 (t, 7.5 Hz, 1H, *p-pyr*), 7.63 (t, 8.0 Hz, 2H, *p-aryl*), 7.24 (d, 8.0 Hz, 4H, *m-aryl*), 4.83 (t, 7.5 Hz, 2H, NH_2CH_2), 2.72 (sept., 7.0 Hz, 4H, $CH(CH_3)_2$), 1.25 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), 0.91 (m, 2H, NH_2CH_2), 0.83 (m, 2H, CH_2CH_3), 0.41 (t, 7.0 Hz, 3H, CH_2CH_3), −0.26 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), −6.09 (s, 6H, $C(CH_3)$). $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 189.77, 165.29, 164.41, 140.20, 136.38 (*p-pyr*), 125.15 (*p-aryl*), 124.31 (*m-aryl*), 102.95 (*m-pyr*), 43.68 (NH_2CH_2), 38.82 (br s $C(CH_3)$), 28.48 ($CH(CH_3)_2$), 26.53 (CH_2CH_3), 24.30 ($CH(CH_3)_2$), 23.14 ($CH(CH_3)_2$), 10.80 (CH_2CH_3).

Preparation of (iPrPDI)Fe(OC(Me)(nBu)) (1-OC(Me)(nBu)). A 20-mL scintillation vial was charged with 0.100 g (0.168 mmol) of **1-(N$_2$)$_2$** and approximately 10 mL of pentane. While stirring, 0.017 g (21 μL, 0.168 mmol) of 2-hexanone was added by microsyringe and the solution immediately began to evolve N_2 and turn brown. After 20 min, the solution was filtered though a frit and the solvent was removed in vacuo to yield 0.085 g (79%) of a dark brown solid identified as **1-OC(Me)(*n*-Bu)**. Anal. Calcd for $C_{39}H_{55}FeN_3O$: C, 73.45; H, 8.69; N, 6.59. Found: C, 73.25; H, 8.30; N, 6.46. ^1H NMR (benzene-d_6) δ 10.59 (d, 7.5 Hz, 2H, *m-pyr*), 8.51 (t, 7.5 Hz, 1H, *p-pyr*), 7.46 (t, 8.0 Hz, 2H, *p-aryl*), 7.16 (d, 8.0 Hz, 4H, *m-aryl*), 2.82 (sept., 7.0 Hz, 4H, $CH(CH_3)_2$), 1.21 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), 1.14 (m, 2H, *butyl*), 0.93 (m, 2H, *butyl*), 0.85 (m, 2H, *butyl*), 0.71 (m, 3H, CH_2CH_3), 0.29 (s, 3H, $CO(CH_3)$), 0.22 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), −3.07 (s, 6H, $C(CH_3)$). $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 172.82, 160.82, 155.87, 139.11, 132.07 (*p-pyr*), 124.83 (*p-aryl*), 123.51 (*m-aryl*), 104.68 (*m-pyr*), 47.98, 31.84 ($COCH_3$), 31.41 (br s $C(CH_3)$), 28.43 ($CH(CH_3)_2$), 25.87 (*butyl*), 24.32 ($CH(CH_3)_2$), 23.37 ($CH(CH_3)_2$), 23.35 (*butyl*), 14.16 (CH_2CH_3), one peak not located.

Preparation of (iPrPDI)Fe(OC(Me)(3-butenyl)) (1-OC(Me)(3-butenyl)). This compound was prepared in a similar manner to **1-OC(Me)(nBu)** with 0.100 g (0.168 mmol) of **1-(N$_2$)$_2$** and 0.016 g (20 μL, 0.168 mmol) of 5-hexen-2-one yielding 0.041 g (38%) of a dark brown solid identified as **1-OC(Me)(3-butenyl)**. Anal. Calcd for $C_{39}H_{53}FeN_3O$: C, 73.69; H, 8.40; N, 6.61. Found: C, 73.43; H, 8.43; N, 6.41. ^1H NMR (toluene-d_8, 20 °C) δ 10.49 (br s, 7.5 Hz, 2H, *m-pyr*), 7.42 (t, 8.0 Hz, 2H, *p-aryl*), 7.14 (d, 8.0 Hz, 4H, *m-aryl*), 5.29 (br s, 1H, $CH_2CH{=}CH_2$), 4.83 (br s 2H, $CH_2CH{=}CH_2$), 2.78 (sept., 7.0 Hz, 4H, $CH(CH_3)_2$), 1.44 (br s, 2H, CH_2), 1.20 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), 0.98 (br s, 2H, CH_2), 0.20 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), −2.87 (br s, 6H, $C(CH_3)$). ^1H NMR (toluene-d_8, −60 °C) δ 10.45 (d, 7.5 Hz, 2H, *m-pyr*), 8.55 (t, 7.5 Hz, 1H, *p-pyr*), 7.44 (t, 8.0 Hz, 2H, *p-aryl*), 7.12 (d, 8.0 Hz, 4H, *m-aryl*), 5.30 (m, 1H, $CH_2CH{=}CH_2$), 4.89 (d, 11.0 Hz, 1H, $CH_2CH{=}CH_2$), 4.85 (d, 17.5 Hz, 1H, $CH_2CH{=}CH_2$), 2.74 (sept., 7.0 Hz, 4H, $CH(CH_3)_2$), 1.32 (m, 2H, CH_2), 1.22 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), 0.97 (m, 2H, CH_2), 0.22 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), 0.18 (s, 3H, $CO(CH_3)$), −2.78 (s, 6H, $C(CH_3)$). $^{13}C\{^1H\}$ NMR (toluene-d_8, −60 °C) δ 205.11 (*C*=O), 171.01, 160.02, 155.51, 139.06, 137.62 ($CH_2CH{=}CH_2$), 137.12, 131.25 (*p-pyr*), 124.90 (*p-aryl*), 123.53 (*m-aryl*), 115.97 ($CH_2CH{=}CH_2$), 105.09 (*m-pyr*), 46.96 ($CH_2CH{=}CH_2$), 31.62 ($COCH_3$), 30.78 (br s $C(CH_3)$), 28.36 ($CH(CH_3)_2$), 27.51 ($COCH_2$), 24.24 ($CH(CH_3)_2$), 23.30 ($CH(CH_3)_2$).

Preparation of (iPrPDI)Fe(OC(Ph)Me) (1-OC(Ph)Me). This compound was prepared in a similar manner to **1-OC(Me)(nBu)** with 0.100 g (0.168 mmol) of **1-(N$_2$)$_2$** and 0.020 g (20 μL, 0.168 mmol) of acetophenone to yield 0.092 g (83%) of a dark green solid identified as **1-OC(Ph)Me**. Anal. Calcd for $C_{41}H_{51}FeN_3O$: C, 74.87; H, 7.82; N, 6.39. Found: C, 75.02; H, 7.41; N, 6.46. ^1H NMR (benzene-d_6) δ 10.05 (d, 7.5 Hz, 2H, *m-pyr*), 8.80 (t, 7.5 Hz, 1H, *p-pyr*), 7.44 (br s, 1H, *p-phenyl*), 7.42 (t, 8.0 Hz, 2H, *p-aryl*), 7.15 (d, 8.0 Hz, 4H, *m-aryl*), 7.13 (br s, 2H, *o-phenyl*), 6.69 (br s, 2H, *m-phenyl*), 2.70 (sept., 7.0 Hz, 4H, $CH(CH_3)_2$), 1.19 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), 0.15 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), −0.52 (br s, 3H, $COCH_3$), −2.33 (s, 6H, $C(CH_3)$). ^1H NMR (toluene-d_8, −80 °C) δ 9.96 (d, 7.5 Hz, 2H, *m-pyr*), 8.68 (t, 7.5 Hz, 1H, *p-pyr*), 7.43 (t, 7.5 Hz, 2H, *p-aryl*), 7.26 (t, 7.5 Hz, 1H, *p-phenyl*), 6.83 (d, 7.0 Hz, 2H, *o-phenyl*), 6.69 (m, 2H, *m-phenyl*), 3.09 (br s, 2H, $CH(CH_3)_2$), 2.27 (br s, 2H, $CH(CH_3)_2$), 1.28 (br m, 6H, $CH(CH_3)_2$), 1.18 (br m, 6H, $CH(CH_3)_2$), 0.33 (br s, 6H, $CH(CH_3)_2$), −0.04 (br s, 6H, $CH(CH_3)_2$), −0.11 (s, 3H, $COCH_3$), −2.01 (s, 6H, $C(CH_3)$), *m-aryl* peak not located. $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 166.42, 159.33, 154.74, 139.82, 125.56 (*p-aryl*), 124.01 (*m-aryl*), 107.43 (*m-pyr*), 30.37 (br s $C(CH_3)$), 28.25 ($CH(CH_3)_2$), 24.47 ($CH(CH_3)_2$), 23.14 ($CH(CH_3)_2$), *p-pyr* and *acetophenone* peaks not located.

Preparation of (iPrPDI)Fe(OCPh$_2$) (1-OCPh$_2$). This compound was prepared in a manner similar to **1-OC(Me)(nBu)** with 0.100 g (0.168 mmol) of **1-(N$_2$)$_2$** and 0.031 g (0.168 mmol) of benzophenone to yield 0.082 g (68%) of a dark green solid identified as **1-OCPh$_2$**. Anal. Calcd for $C_{41}H_{51}FeN_3O$: C, 76.76; H, 7.42; N, 5.84. Found: C, 76.52; H, 7.69; N, 5.62. Magnetic susceptibility: $\mu_{eff} = 1.2\ \mu_B$ (benzene-d_6). ^1H NMR (benzene-d_6) δ 36.94 (37 Hz, 1H, *p-pyr*), 29.23 (239 Hz, 1H, *phenyl*), 26.66 (290 Hz, 2H, *phenyl*), 13.83 (14 Hz, 2H, *m-pyr*), 5.95 (d, 7.5 Hz, 4H, *m-aryl*), 5.52 (t, 7.5 Hz, 2H, *p-aryl*), −0.65 (7 Hz, 12H, $CH(CH_3)_2$), −1.95 (11 Hz, 12H, $CH(CH_3)_2$), −5.22 (49 Hz, 4H, $CH(CH_3)_2$), −18.05 (25 Hz, 6H, $C(CH_3)$), one *phenyl* peak not located.

Preparation of (iPrPDI)Fe(OC(Me)(PhEt)) (1-OC(Me)(PhEt)). This compound was prepared in a manner similar to **1-OC(Me)(nBu)** with 0.100 g (0.168 mmol) of **1-(N$_2$)$_2$** and 0.025 g (26 μL, 0.168 mmol) of 4-phenyl-2-butanone. The resulting residual solid was recrystallized from pentane at −35 °C to yield 0.030 g (26%) of a dark brown solid identified as **1-OC(Me)(PhEt)**. Anal. Calcd for $C_{43}H_{55}FeN_3O$: C, 75.31; H, 8.08; N, 6.13. Found: C, 74.99; H, 7.86; N, 5.81. ^1H NMR (benzene-d_6) δ 10.53 (d, 7.5 Hz, 2H, *m-pyr*), 8.52 (t, 7.5 Hz, 1H, *p-pyr*), 7.46 (t, 8.0 Hz, 2H, *p-aryl*), 7.17 (d, 8.0 Hz, 4H, *m-aryl*), 7.11 (d, 7.5 Hz, 2H, *phenyl*), 7.02 (t, 7.5 Hz, 1H, *phenyl*), 6.90 (d, 7.5 Hz, 2H, phenyl), 2.82 (sept., 7.0 Hz, 4H, $CH(CH_3)_2$), 2.07 (m, 2H, CH_2), 1.33 (m, 2H, CH_2), 1.20 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), 0.21 (d, 7.0 Hz, 12H, $CH(CH_3)_2$), 0.17 (s, 3H, $CO(CH_3)$), −3.04 (s, 6H, $C(CH_3)$). $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 204.77 (*C*=O), 172.32, 160.75, 155.98, 139.29, 131.94,

129.14, 129.03, 127.01, 126.63, 124.98 (*p-aryl*), 123.64 (*m-aryl*), 104.87 (*m-pyr*), 49.32 (*C*H_2), 32.58 (CO*C*H_3), 31.31 (br s C(*C*H_3)), 29.17 (*C*H_2), 28.44 (*C*H(CH$_3$)$_2$), 24.30 (CH(*C*H_3)$_2$), 23.39 (CH(*C*H_3)$_2$).

Preparation of (^{iPr}PDI)Fe(DHC) (1-DHC). This compound was prepared in a manner similar to **1-OC(Me)(^{n}Bu)** with 0.100 g (0.168 mmol) of **1-(N$_2$)$_2$** and 0.025 g (28 μL, 0.168 mmol) of (+)-dihydrocarvone as a mixture of isomers. After filtration, the solvent was removed in vacuo and recrystallized from pentane to yield 0.087 g (75%) of a dark purple solid identified as **1-DHC** as a mixture of two diastereomers. Anal. Calcd for $C_{43}H_{59}FeN_3O$: C, 74.87; H, 8.62; N, 6.09. Found: C, 74.80; H, 8.58; N, 5.83. ^{1}H NMR (major diastereomer, benzene-d_6) δ 10.47 (d, 7.5 Hz, 2H, *m-pyr*), 8.46 (t, 7.5 Hz, 1H, *p-pyr*), 7.42 (t, 8.0 Hz, 2H, *p-aryl*), 7.19 (d, 8.0 Hz, 4H, *m-aryl*), 4.63 (s, 1H, *C*═C*H*$_2$), 4.52 (s, 1H, *C*═C*H*$_2$), 3.18 (sept., 7.0 Hz, 2H, C*H*(CH$_3$)$_2$), 2.59 (sept., 7.0 Hz, 2H, C*H*(CH$_3$)$_2$), 1.83 (m, 2H, *DHC*), 1.50 (s, 3H, DHC CC*H*$_3$), 1.21 (d, 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.15 (d, 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 0.90–1.07 (m, 6H, *DHC*), 0.56 (d, 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 0.40 (d, 7.0 Hz, DHC CHC*H*$_3$), 0.13 (d, 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), −2.89 (s, 6H, C(C*H*$_3$)). ^{1}H NMR (minor diastereomer, benzene-d_6) δ 10.84 (d, 7.5 Hz, 2H, *m-pyr*), 8.56 (t, 7.5 Hz, 1H, *p-pyr*), 7.50 (t, 8.0 Hz, 2H, *p-aryl*), 7.20 (d, 8.0 Hz, 4H, *m-aryl*), 4.56 (s, 1H, *C*═C*H*$_2$), 4.45 (s, 1H, *C*═C*H*$_2$), 2.82 (sept., 7.0 Hz, 2H, C*H*(CH$_3$)$_2$), 2.50 (m, 2H, *DHC*), 1.43 (s, 3H, DHC CC*H*$_3$), 1.22 (d, 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.19 (d, 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 0.90–1.07 (m, 6H, *DHC*), 0.36 (d, 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 0.29 (d, 7.0 Hz, DHC CHC*H*$_3$), 0.18 (d, 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), −3.39 (s, 6H, C(C*H*$_3$)), one peak not located. ^{13}C{^{1}H} NMR (major diastereomer, benzene-d_6) δ 210.52 (*C*═O), 171.21, 161.20, 155.18, 147.94, 139.70, 139.10, 130.96 (*p-pyr*), 124.54 (*p-aryl*), 123.74 (*m-aryl*), 123.47 (*m-aryl*), 110.38 (*C*═*C*H$_2$), 104.31 (*m-pyr*), 46.96 (DHC), 46.16 (DHC), 43.66 (DHC), 30.39 (br s C(*C*H$_3$)), 28.38 (*C*H(CH$_3$)$_2$), 27.99 (*C*H(CH$_3$)$_2$), 24.29 (CH(*C*H$_3$)$_2$), 23.69 (CH(*C*H$_3$)$_2$), 23.39 (CH(*C*H$_3$)$_2$), 22.48 (CH(*C*H$_3$)$_2$), 20.08 (DHC C*C*H$_3$), 13.53 (DHC CH*C*H$_3$), one peak not located.

Observation of (^{iPr}PDI)Fe(Car) (1-Car). With a microsyringe, 0.005 g (5.25 μL, 0.034 mmol) of (−)-carvone was added to a solution of **1-(N$_2$)$_2$** in approximately 0.70 g of benzene-d_6. The resulting bright green solution was quickly filtered through Celite into a J. Young tube and submerged in liquid nitrogen to prevent decomposition. The ^{1}H NMR spectrum of this complex was recorded immediately after thawing. The solution turned dark brown during the course of spectral acquisition. ^{1}H NMR (benzene-d_6) δ 10.37 (d, 7.5 Hz, 2H, *m-pyr*), 8.62 (t, 7.5 Hz, 1H, *p-pyr*), 7.47 (t, 8.0 Hz, 2H, *p-aryl*), 7.26 (d, 8.0 Hz, 4H, *m-aryl*), 6.41 (s, 1H, C═C*H*CH$_2$), 4.64 (s, 1H, C═C*H*$_2$), 4.56 (s, 1H, C═C*H*$_2$), 2.93 (sept., 7.0 Hz, 2H, C*H*(CH$_3$)$_2$), 2.61 (m, 2H, C*H*(CH$_3$)$_2$ or carvone C*H*$_2$), 2.22 (m, 1H, *carvone*), 1.41 (s, 3H, carvone C*H*$_3$), 1.30 (s, 3H, carvone C*H*$_3$), 1.16–1.25 (m, 12H, CH(C*H*$_3$)$_2$), 0.48 (d, 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 0.09 (d, 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), −0.78 (dd, 16 Hz, 1H, COC*H*$_2$), −2.59 (s, 6H, C(C*H*$_3$)), two peaks not located.

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Supporting Information Available: Crystallographic data for **1-OCPh$_2$** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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