Low-Valent α-Diimine Iron Complexes for Catalytic Olefin Hydrogenation

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Received July 25, 2005

A family of low-valent α-diimine iron complexes has been synthesized and their utility in catalytic olefin hydrogenation reactions evaluated. Reduction of the ferrous dichloride complex [ArN=C(Me)C(Me)=NAr]$FeCl_2$ (Ar = 2,6-$(CHMe_2)_2$-C_6H_3) with sodium amalgam in benzene or toluene furnished the iron arene complexes, [ArN=C(Me)C(Me)=NAr]Fe(η^6-C_6H_5R) (R = H, Me). The solid-state structure of the toluene adduct revealed a contracted carbon−carbon backbone, short iron−imine bonds, and elongated imine nitrogen−carbon distances, suggesting significant reduction of the α-diimine ligand. The analogous reduction in alkane solvents afforded the bis(α-diimine) complex $[ArN{=}C(Me)C(Me){=}NAr]_2Fe$, which has also been crystallographically characterized. The arene complexes and the bis(α-diimine) complexes are inactive for catalytic olefin hydrogenation. Performing the reduction in the presence of internal alkynes such as diphenylacetylene and bis(trimethylsilyl)acetylene furnished the alkyne adducts [ArN=C(Me)C(Me)=NAr]Fe(η^2-RC≡CR) (R = Ph, $SiMe_3$). Analogous olefin complexes with 1,5-cyclooctadiene and cycloctene have also been isolated using similar reduction procedures. The olefin adducts provide more active precatalysts than the alkyne compounds for the hydrogenation of 1-hexene. In each case, formation of η^6-arene adducts serves as a major catalyst deactivation pathway.

Introduction

Organometallic and coordination complexes of iron have received considerable interest, due to their utility in biomimetic chemistry[1] as well as in small-molecule[2] and hydrocarbon activation processes.[3] Because of high natural abundance, environmental compatibility, and relatively low cost, iron complexes are emerging as potential surrogates for precious metals in catalytic bond-forming processes.[4] A recent breakthrough in this area was provided in independent reports by Brookhart,[5] Gibson,[6] and others[7] of the catalytic polymerization and oligomerization of ethylene and α-olefins promoted by pyridine(diimine) (PDI) iron dihalides activated with methylalumoxane. Inspired by these findings, we sought to prepare well-defined, single-component iron complexes that could serve as effective catalysts for carbon−hydrogen, carbon−carbon, and carbon−silicon bond construction in small organic molecules.

Previous work from Wrighton and co-workers established that photogenerated $[Fe(CO)_3]$ is an active catalyst for the hydrogenation, hydrosilation, and isomerization of olefins.[8] Similar results were obtained from thermal activation, although temperatures in excess of 200 °C were required for reasonable activity.[9] Seeking access to a similar low-valent iron fragment under mild conditions, our laboratory has been exploring the reduction chemistry of aryl-substituted pyridine(diimine) iron(II) dihalide complexes.[10] Tridentate pyridine(diimines) were chosen as initial supporting ligands due to their ease of synthesis, steric and electronic modularity, and ability to support catalytically active iron complexes.[5−7] Furthermore, this class of ligand is known to engage in redox chemistry with the metal center, delocalizing charge over the conjugated π system of the pyridine-diimine core,[11] making them attractive for

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(1) (a) Evans, D. J.; Pickett, C. J. *Chem. Soc. Rev.* **2003**, *32*, 268. (b) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385.

(2) (a) Vela, J.; Stoian, S.; Flaschenriem, C. J.; Munck, E.; Holland, P. L. *J. Am. Chem. Soc.* **2004**, *126*, 4522. (b) Smith, J. M.; Lachicotte, R. J.; Pittard, K. A.; Cundari, T. R.; Lukat-Rodgers, G.; Rodgers, K. R.; Holland, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 9222. (c) Betley. T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 6252. (d) Komiya, S.; Akita, M.; Yoza, A.; Kasuga, N.; Fukuoka, A.; Kai, Y. *Chem. Commun.* **1993**, 787. (e) Hirano, M.; Akita, M.; Morikita, T.; Kubo, A.; Fukuoka, A.; Komiya, S. *J. Chem. Soc., Dalton Trans.* **1997**, 3453. (f) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 5507.

(3) Perthuisot, C.; Jones, W. D. *New J. Chem.* **1994**, *18*, 621.

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

(5) (a) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (b) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143. (c) Small, B. L.; Brookhart, M. *Macromolecules* **1999**, *32*, 2120.

(6) (a) Smit, T. M.; Tomov, A. K.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2004**, *43*, 6511. (b) O'Reilly, R. K.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *Polyhedron* **2004**, *23*, 2921. (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.

(7) (a) Bianchini, C.; Giambastiani, G.; Guerrero, I. R.; Meli, A.; Passaglair, E.; Gragnoli, T. *Organometallics* **2004**, *23*, 6087. (b) Sun, W. H.; Tang, X. B.; Gao, T. L.; Wu, B.; Zhang, W. J.; Ma, H. W. *Organometallics* **2004**, *23*, 5037. (c) Kim, I.; Han, B. H.; Ha, Y. S.; Ha, C. S.; Park D. W. *Catal. Today* **2004**, *93−95*, 281.

(8) Schroeder, M. A.; Wrighton, M. A. *J. Am. Chem. Soc.* **1976**, *98*, 551.

(9) Harmon, R. E.; Gupta, S. K.; Brown, D. J. *Chem. Rev.* **1973**, *73*, 21.

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

10.1021/om050625b CCC: $30.25

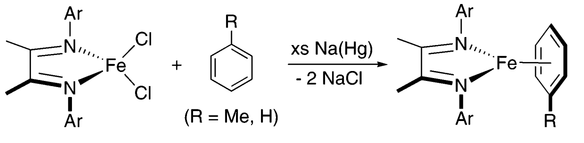
stabilizing low-valent iron species. Indeed, reduction of (^{iPr}PDI)FeBr$_2$ (^{iPr}PDI = ((2,6-CHMe$_2$)$_2$C$_6$H$_3$N=CMe)$_2$-C$_5$H$_3$N) with excess 0.5% sodium amalgam under an atmosphere of N$_2$ furnished an unusual bis(dinitrogen) complex, (^{iPr}PDI)Fe(η^1-N$_2$)$_2$.[10] Both solid-state and solution magnetic susceptibility measurements revealed a paramagnetic ground state with two unpaired electrons, giving the appearance of a high-spin iron(0) d^8 complex. However, a combination of spectroscopic and computational studies support involvement of the conjugated π system of the pyridine(diimine), suggesting a higher oxidation state. After our findings, Danopoulos and coworkers[12] synthesized an iron(0) bis(dinitrogen) complex with an $S = 0$ ground state. In this case, the supporting bis(N-heterocyclic carbene)pyridine ligand is a weaker π acceptor and is less likely to facilitate metal−ligand electron transfer.

Significantly, (^{iPr}PDI)Fe(η^1-N$_2$)$_2$ is an effective catalyst for both the hydrogenation and hydrosilation of olefins and alkynes at 22 °C. Synthetically useful activities are observed at part per million levels of iron and, unlike precious metal catalysts, do not require polar organic solvents for optimal activity.[13,14] These observations prompted investigation into other formally iron(0) platforms with the goal of generating more active catalysts with a wider substrate scope. Specifically, we were interested in generating [L$_2$Fe^0] fragments with the expectation that bidentate "ancillary" ligands would engender more reactive metal centers than their tridentate counterparts by virtue of their lower formal electron count.

α-Diimine ligands, [RN=C(R^1)C(R^1)=NR], seemed ideal for this purpose, offering a low-lying molecular orbital that is antibonding with respect to the imine portion of the molecule but bonding with respect to the carbon−carbon backbone.[15,16] This synergistic interaction may facilitate back-donation from an electron-rich iron center and allow isolation of suitable catalyst precursors. Iron α-diimine complexes have precedent in catalytic bond-forming reactions serving as initiators in atom transfer radical polymerization,[17] catalysts for the dimerization of dienes,[18] and the polymerization of olefins.[19] In this article we describe our initial exploration of reduced α-diimine iron chemistry. Synthesis of a family of α-diimine iron arene, alkyne, and olefin complexes is described and their utility in catalytic hydrogenation reactions evaluated.

Results and Discussion

Reduction of [ArN=C(Me)C(Me)=NAr]FeCl$_2$. Following the method used for the preparation of (^{iPr}PDI)-Fe(η^1-N$_2$)$_2$,[10] a toluene slurry of the four-coordinate iron(II) dichloride complex [ArN=C(Me)C(Me)=NAr]-FeCl$_2$[20] was stirred with an excess of 0.5% sodium amalgam under 1 atm of dinitrogen. Filtration and recrystallization from pentane afforded a bright red-orange diamagnetic powder identified as the iron arene complex [ArN=C(Me)C(Me)=NAr]Fe(η^6-C$_7$H$_8$) (**1**) (eq 1).



(1)

1: R = Me (74 %)
2: R = H (58 %)

The analogous reduction in benzene furnished the corresponding η^6-benzene adduct [ArN=C(Me)C(Me)=NAr]Fe(η^6-C$_6$H$_6$) (**2**). These results highlight the propensity of less congested, formally iron(0) compounds to attain a coordinatively saturated 18-electron configuration. Both **1** and **2** are similar to the α-diimine iron(0) toluene compounds [RN=C(Me)C(Me)=NR]Fe-(η^6-C$_7$H$_8$) (R = ^{t}Bu, Cy, ^{i}Pr, 2,6-Me$_2$-C$_6$H$_3$), prepared previously by displacement of ethylene from (η^6-C$_7$H$_8$)-Fe(η^2-C$_2$H$_4$)$_2$.[18b]

Diamagnetic **1** and **2** were readily characterized by a combination of ^{1}H and ^{13}C NMR spectroscopy. For **1**, the number of resonances expected for a C_{2v}-symmetric ligand environment is observed, indicating rapid rotation of the toluene ring on the time scale of the NMR experiment. The aromatic hydrogens of the coordinated toluene appear at 4.40 (meta), 4.80 (ortho), and 5.69 (para) ppm in benzene-d_6, shifted well upfield from those of free toluene, and are diagnostic of coordination to iron.[18b] Significantly, these resonances are retained in benzene-d_6, demonstrating that arene exchange does not occur rapidly at ambient temperature. The spectroscopic features of both **1** and **2** are in good agreement with previous observations with [ArN=C(Me)C(Me)=NAr]-Fe(η^6-C$_7$H$_8$) compounds, where both fast arene rotation and reluctance to participate in arene exchange reactions were observed.[18b]

Crystals of **1** suitable for X-ray diffraction were obtained from a concentrated pentane solution chilled to −35 °C. Figure 1 depicts the solid-state structure of the molecule, while selected bond distances and angles are reported in Table 1. Also included in Table 1 are the metrical parameters for the tetrahedral ferrous bis(alkyl) complex [ArN=C(Me)C(Me)=NAr]Fe(CH$_2$SiMe$_3$)$_2$ and the formally iron(I) monochloride dimer [(ArN=C(Me)C(Me)=NAr)Fe(μ_2−Cl)]$_2$ (**3**).[20] In the solid-state structure of **1**, the iron atom lies essentially in the plane of the α-diimine ligand with a deviation of only 0.0071(4) Å. As is typically observed with this class of ligand,

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(11) (a) Sugiyama, H.; Korobkov, I.; Gambarotta, S.; Möller, A.; Budzelaar, P. H. M. *Inorg. Chem.* **2004**, *43*, 5771. (b) Enright, D.; Gambarotta, S.; Yap, G. P. A.; Budzelaar, P. H. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3873. (c) Budzelaar, P. H. M.; de Bruin, B.; Gal, A. W.; Wieghardt, K.; van Lenthe, J. H. *Inorg. Chem.* **2001**, *40*, 4649. (d) de Bruin, B.; Bill, E.; Bothe, E.; Weyermüller, T.; Wieghardt, K. *Inorg. Chem.* **2000**, *39*, 2936.

(12) Danopoulos, A. A.; Wright, J. A.; Motherwell, W. B. *Chem. Commun.* **2005**, 784.

(13) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3091.

(14) For a zwitterionic Rh catalyst that displays high activity in nonpolar media see: Betley, T. A.; Peters, J. C. *Angew. Chem., Int. Ed.* **2003**, *42*, 2385.

(15) Uhlig, E. *Pure Appl. Chem.* **1988**, *60*, 1235.

(16) Reinhold, J.; Benedix, R.; Birner, P.; Hennig, H. *Inorg. Chim. Acta* **1978**, *33*, 209.

(17) (a) Gibson, V. C.; O'Reilly, R. K.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Macromolecules* **2003**, *36*, 2591. (b) Gibson, V. C.; O'Reilly, R. K.; Reed, W.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2002**, 1850.

(18) (a) tom Dieck, H.; Stamp, L.; Diercks, R.; Müller, C. *New J. Chem.* **1985**, *9*, 289. (b) Le Floch, P.; Knoch, F.; Kremer, F.; Mathey, F.; Scholz, J.; Scholz, W.; Theile, K.-H.; Zenneck, U. *Eur. J. Inorg. Chem.* **1998**, 119.

(19) Lorber, C.; Choukroun, R.; Costes, J.-P.; Donnadieu, B. *C. R. Chim.* **2002**, *5*, 251.

(20) Bart, S. C.; Hawrelak, E. J.; Schmisseur, A. K.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2004**, *23*, 237.

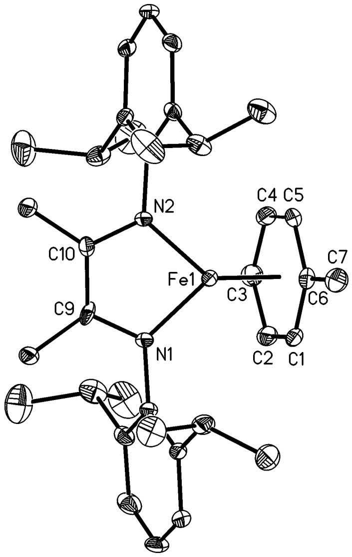


Figure 1. Molecular structure of **1** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 1, (DI)Fe(CH$_2$SiMe$_3$)$_2$, and 3

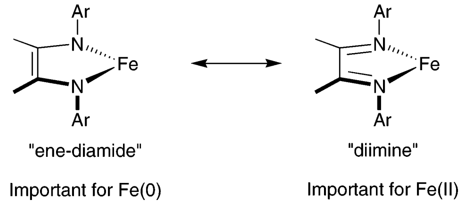
	1	(DI)Fe(CH$_2$SiMe$_3$)$_2$^{a}	**3**^{a}
Fe(1)−N(1)	1.886(2)	2.025(2)	1.979(1)
Fe(1)−N(2)	1.886(2)	2.013(2)	1.979(1)
N(1)−C(9)	1.356(3)	1.329(2)	1.339(2)
N(2)−C(10)	1.361(3)	1.320(3)	1.339(2)
C(9)−C(10)	1.358(4)	1.507(3)	1.420(3)
C(1)−C(2)	1.405(5)		
C(1)−C(6)	1.417(4)		
C(2)−C(3)	1.409(4)		
C(3)−C(4)	1.421(4)		
C(4)−C(5)	1.389(4)		
C(5)−C(6)	1.429(4)		
C(1)−C(2)	1.405(5)		
N(1)−Fe(1)−N(2)	81.23(8)	79.59(9)	80.87(8)
C(9)−N(1)−Fe(1)	114.96(16)	111.81(17)	112.87(10)
N(1)−C(9)−C(10)	115.0(2)	115.4(2)	115.36(9)

[a] Values taken from ref 20 and are for the corresponding bond lengths and angles. DI = [ArN=C(Me)C(Me)=NAr].

the ortho-substituted aryl groups are oriented perpendicular to the iron-α-diimine plane, while the methyl group on the toluene ring is nestled between the isopropyl substituents to avoid unfavorable steric interactions.

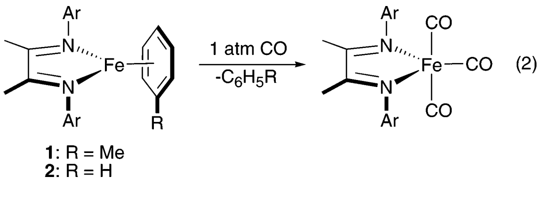
The structural data contained in Table 1 establish the redox flexibility of the α-diimine ligand and its ability to smoothly adjust to the electronic requirements of the metal. In the electron-rich iron toluene complex **1**, relatively short Fe(1)−N(1) and C(9)−C(10) bond distances of 1.886(2) and 1.358(4) Å are observed, respectively. Concomitantly, the imine bonds, N(1)−C(9) and N(2)−C(10), elongate to 1.356(3) and 1.361(3) Å, respectively. In contrast, little perturbation of the carbon−carbon bonds in the toluene ring is observed. These findings are in good agreement with the structural data reported[18b] for the α-diimine ligand in [(C$_6$H$_{11}$)N=C(H)C(H)=N(C$_6$H$_{11}$)]Fe(η^6-C$_7$H$_8$), where the C−C backbone distance was contracted by 0.078 Å and the average C=N distance was elongated by 0.043 Å compared to the free α-diimine. Observation of such pronounced bond alternation in both cases is consistent with π-back-donation from the electron-rich iron center to the LUMO of the α-diimine, suggesting an important contribution from the "ene-diamide" canonical form (Chart 1). In this limit, the arene complexes can be viewed as low spin ferrous compounds similar to (η^5-C$_5$Me$_5$)Fe(acac) (acac = acetylacetonate).[21] Interestingly, the degree of α-diimine ligand reduction observed in **1** is comparable to that reported in the formally d^2 group 4 metallocene complexes (η^5-C$_5$H$_5$)$_2$M(PhNC(Ph)C(Ph)-NPh) (M = Ti, Zr, Hf),[22] highlighting the reducing nature of the iron(0) fragment.

Chart 1



Comparison of the α-diimine bond distances in **1** and [(C$_6$H$_{11}$)N=C(H)C(H)=N(C$_6$H$_{11}$)]Fe(η^6-C$_7$H$_8$) to that in [ArN=C(Me)C(Me)=NAr]Fe(CH$_2$SiMe$_3$)$_2$ revealed longer iron−nitrogen and carbon−carbon backbone bond lengths in the dialkyl complex, suggesting a diminished back-bonding interaction from the more oxidized ferrous center. The monochloride dimer **3** has metrical parameters between these two extremes with Fe−N bond distances of 1.979(1) Å and a backbone carbon−carbon bond length of 1.420(3) Å. This continuum of bond lengths demonstrates the ability of the α-diimine to adjust for the electronic requirements of the metal.

The iron arene complexes **1** and **2** were evaluated for the catalytic hydrogenation of 1-hexene. No hydrogenated product was observed up to temperatures of 80 °C in benzene-d_6 or cyclohexane-d_{12} with 4 atm of dihydrogen. Monitoring the addition of H$_2$ to a benzene-d_6 solution of **1** by ^{1}H NMR spectroscopy indicated no reaction, even after several days. Displacement of the arene can be achieved by addition of 1 atm of carbon monoxide to afford the previously reported iron tricarbonyl complex [ArN=C(Me)C(Me)=NAr]Fe(CO)$_3$ (eq 2).[19,23]



To circumvent the formation of robust arene complexes, the reduction of [ArN=C(Me)C(Me)=NAr]FeCl$_2$ with sodium amalgam was performed in alkane solvent. Aliquots of the reaction mixture were analyzed by ^{1}H NMR spectroscopy and revealed the α-diimine iron chloride dimer **3** as the initial reduction product, followed by formation of small quantities of the bis-

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[21] Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680.

[22] (a) Scholz, J.; Dlikan, M.; Ströhl, D.; Dietrich, A.; Schumann, H.; Theile, K.-H. *Chem. Ber.* **1990**, *123*, 2279. (b) Scholz, J.; Hadi, G. A.; Theile, K.-H.; Görls, H.; Weimann, R.; Schumann, H.; Sieler, J. *J. Organomet. Chem.* **2001**, *626*, 243.

[23] tom Dieck, H.; Bruder, H. *Chem. Commun.* **1977**, 24.

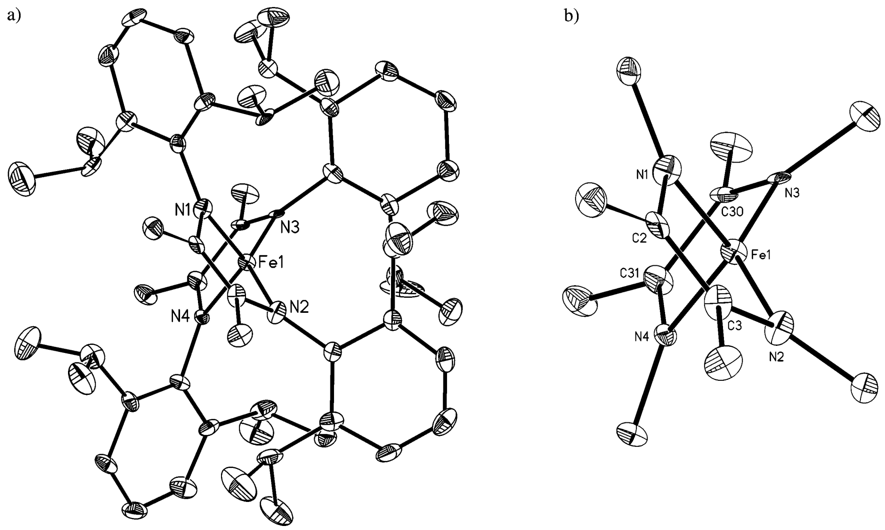
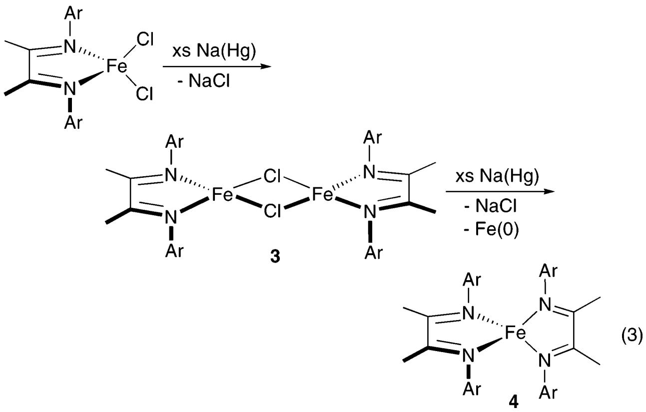


Figure 2. (a) Molecular structure of **4** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. (b) View of the core of the molecule.

(α-diimine) iron complex $[ArN{=}C(Me)C(Me){=}NAr]_2Fe$ (**4**) with deposition of iron metal (eq 3). An improved



procedure for the preparation of **4** has been devised by reducing the α-diimine ferrous dichloride complex with sodium amalgam in the presence of a stoichiometric quantity of $ArN{=}C(Me)C(Me){=}NAr$. These results are analogous to previous observations by tom Dieck and Bruder,[23] who reported the synthesis of several $[RN{=}CHCH{=}NR]_2Fe$ (R = ^iPr, ^tBu, C_6H_{11}, CH^iPr_2) derivatives by reduction of a mixture of $FeCl_2$ and the free ligand. These complexes, when activated with organoaluminum compounds, are active for the selective dimerization of 1,3-dienes.[24]

Red-brown **4** displays paramagnetically broadened ^1H NMR resonances over a relatively narrow chemical shift window. Diastereotopic isopropyl methyl resonances appear at −2.2 and 4.0 ppm, relatively close to their diamagnetic reference values, consistent with the aryl groups being orthogonal to the α-diimine ligand plane. In contrast, the methyl groups on the α-diimine backbone appear as a broad ($\Delta\nu_{1/2} = 41$ Hz) singlet centered at −22.2 ppm, indicative of spin delocalization over the core of the ligand. Although **4** was sufficiently soluble in benzene-d_6 to collect NMR data, reliable solution magnetic data could not be obtained, due to partial solubility of the compound. Solid-state (Gouy balance) magnetic measurements produced a magnetic moment of 2.8 μB, consistent with the spin-only value for two unpaired electrons.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 4

Fe(1)−N(1)	2.013(9)	Fe(1)−N(3)	2.061(8)
Fe(1)−N(2)	1.988(9)	Fe(1)−N(4)	2.077(8)
N(1)−C(2)	1.354(14)	N(3)−C(30)	1.275(12)
N(2)−C(3)	1.431(12)	N(4)−C(31)	1.349(13)
C(2)−C(3)	1.351(14)	C(30)−C(31)	1.472(13)
N(1)−Fe(1)−N(2)	82.7(4)	N(1)−Fe(1)−N(4)	126.25(11)
N(2)−Fe(1)−N(3)	144.33(12)	N(3)−Fe(1)−N(4)	79.6(3)
N(1)−Fe(1)−N(3)	116.4(3)		

Chilling a concentrated pentane solution of **4** to −35 °C produced crystals suitable for X-ray diffraction. The molecular structure of the compound is depicted in Figure 2, and selected metrical parameters are reported in Table 2. In agreement with the magnetic data, a tetrahedral geometry is observed, where the iron atom is displaced by 0.524(16) Å from the core of the α-diimine ligand. Significant variation in the bond distances and angles in the α-diimine core are also observed. For one ligand, a short carbon−carbon backbone distance of 1.351(14) Å is observed for C(2)−C(3), suggesting significant back-donation from the iron center. In agreement with this assertion is the elongated N(2)−C(3) distance of 1.431(12) Å, much longer than the corresponding N(1)−C(2) distance of 1.354(14) Å. Curiously, the Fe(1)−N(2) distance of 1.998(9) Å is longer than those found in **1**, where there is significant electron donation from the iron to the α-diimine ligand.

In contrast, the other α-diimine ligand in **4** contains an elongated carbon−carbon backbone with a C(30)−C(31) distance of 1.472(13) Å. Accordingly, the nitrogen−carbon bond lengths are relatively short with N(3)−C(30) and N(4)−C(31) distances of 1.275(12) and 1.349(13) Å, respectively. The iron−nitrogen bond lengths of 2.061(8) and 2.077(8) Å are comparable to those found in $[ArN{=}C(Me)C(Me){=}NAr]Fe(CH_2SiMe_3)_2$,[20] where there is little back-donation from the iron to the α-diimine. The metrical data, in conjunction with the magnetic susceptibility measurements, suggest that **4** can be viewed as a tetrahedral iron(0) d^8 complex or as

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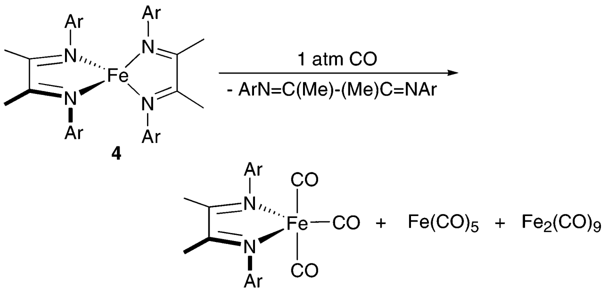
(24) tom Dieck, H.; Dietrich, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 781.

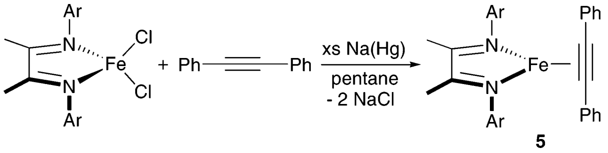
a intermediate-spin iron(II) d^6 complex, where the α-diimine acts as a strong field ligand, engaged in π back-bonding with the iron center.

As was observed with **1**, **4** is not active for the catalytic hydrogenation of 1-hexene and does not react with excess dihydrogen. Replacement of one or both of the α-diimine ligands can be accomplished by exposure of the compound to 1 atm of carbon monoxide. A mixture of [ArN=C(Me)C(Me)=NAr]Fe(CO)$_3$, Fe(CO)$_5$, Fe$_2$(CO)$_9$, and free ligand were observed upon treatment of **4** with CO (eq 4). As with previously reported bis(α-diimine) iron complexes,[23] **4** is catalytically active for the dimerization of 1,3-butadiene to 1,5-cyclooctadiene at 23 °C. Significantly, no trialkylaluminum activator was required for catalytic activity.



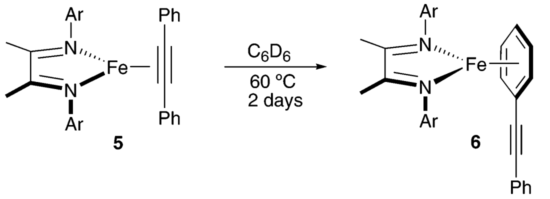
(4)

Isolation of the bis(α-diimine) ligand complex **4** prompted reduction of [ArN=C(Me)C(Me)=NAr]FeCl$_2$ in the presence of other neutral donors. An ideal ligand is one that would allow isolation of an [ArN=C(Me)C(Me)=NAr]FeL$_n$ species but is sufficiently labile to dissociate (or be hydrogenated) to engender catalytically active iron centers. The utility of (^{iPr}PDI)Fe(η^2-PhC≡CPh) in catalytic hydrogenation and hydrosilation reactions[10] suggested that alkynes may be effective in stabilizing α-diimine iron(0) complexes while maintaining sufficient lability to generate catalytically active metal centers. Reduction of a pentane slurry of [ArN=C(Me)C(Me)=NAr]FeCl$_2$ with an excess of 0.5% sodium amalgam in the presence of a stoichiometric quantity of PhC≡CPh furnished the desired α-diimine iron(0) η^2-alkyne complex [ArN=C(Me)C(Me)=NAr]Fe(η^2-PhC≡CPh) (**5**), as a red-brown solid (eq 5). The solid-state magnetic moment of 3.2 μB (Guoy method) is consistent with two unpaired electrons and is in accord with a trigonal iron(0) or tetrahedral iron(II) complex. The ^{1}H NMR spectrum of **5** in benzene-d_6 exhibits nine paramagnetically broadened and shifted resonances over a 300 ppm chemical shift range, in agreement with a C_{2v}-symmetric η^2-alkyne complex.



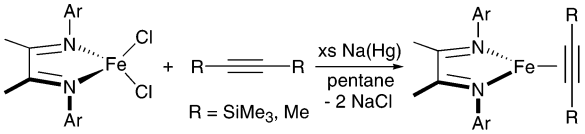
(5)

The observed paramagnetism of **5** is consistent with coordination of one of the π faces of the carbon−carbon triple bond rather than formation of the corresponding arene complex. If the alkyne ligand was η^6 coordinated through one of the phenyl substituents, a closed-shell, diamagnetic compound would be expected. To determine whether the formally 18-electron, η^6-arene isomer was accessible and perhaps thermodynamically favored, the thermal stability of **5** was studied. Gently warming a benzene-d_6 solution of **5** to 60 °C for approximately 48 h furnished a new, diamagnetic iron product, identified as the η^6-diphenylacetylene complex [ArN=C(Me)C(Me)=NAr]Fe(η^6-C$_6$H$_5$C≡CPh) (**6**), arising from migration of the alkyne ligand (eq 6). While detailed kinetic studies have not been performed, competitive formation of **2**-d_6 was not observed, suggesting an intramolecular rearrangement process.



(6)

Due to complications from competitive η^6 coordination in aryl-substituted alkynes, the synthesis of alkyl- or silyl-substituted acetylene complexes was explored (eq 7). Stirring a pentane slurry of [ArN=C(Me)C(Me)=NAr]FeCl$_2$ with an excess of 0.5% sodium amalgam in the presence of a slight excess (~3 equiv) of bis(trimethylsilyl)acetylene furnished [ArN=C(Me)C(Me)=NAr]Fe(η^2-(Me$_3$Si)C≡C(SiMe$_3$)) (**7**). As with **5**, **7** is paramagnetic with a benzene-d_6 solution magnetic moment of 2.9 μB (Evans method, 23 °C). Accordingly, the ^{1}H NMR spectrum displays five broad and featureless signals. Additional characterization has been obtained from combustion analysis and degradation experiments. Treatment of **7** with a benzene−water mixture produced free α-diimine ligand and bis((trimethylsilyl)acetylene) along with insoluble iron products. Performing an analogous reduction of the α-diimine iron dichloride in the presence of 2-butyne furnished an oily compound, tentatively assigned as [ArN=C(Me)C(Me)=NAr]Fe(η^2-MeC≡CMe) (**8**). However, the inability to obtain the compound in the solid state and purify it by recrystallization prevented combustion analysis and determination of a reliable magnetic moment.



(7)

7: R = SiMe$_3$ (54 %)
8: R = Me (88 %)

The solid-state structure of **7** was determined by X-ray diffraction and is presented in Figure 3, while selected metrical parameters are reported in Table 3. The data were modeled such that one isopropyl methyl group on the α-diimine ligand is positionally disordered, and one representation is presented in Figure 3. As is typically observed with hindered α-diimine ligands, the sterically demanding aryl groups are oriented perpendicular to the iron−ligand plane. The alkyne ligand is canted with respect to the iron−diimine plane, forming a dihedral angle of 25.5°. The iron−nitrogen bond lengths of 1.9843(8) and 1.9821(7) Å and the carbon−carbon backbone distance of 1.4139(12) Å are between the limiting "ene-diamide" form of the ligand principally

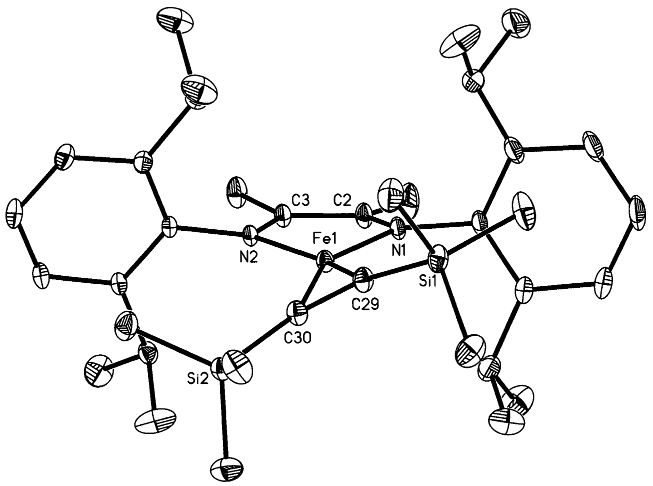


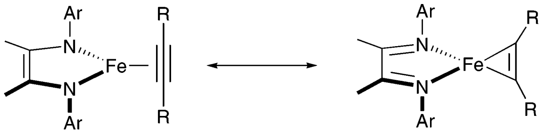
Figure 3. Molecular structure of **7** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 7

Fe(1)−N(1)	1.9843(8)	Fe(1)−C(29)	1.9377(9)
Fe(1)−N(2)	1.9821(7)	Fe(1)−C(30)	1.9486(10)
N(1)−C(2)	1.3423(12)	C(2)−C(3)	1.4139(12)
N(2)−C(3)	1.3393(11)	C(29)−C(30)	1.2956(14)
N(1)−Fe(1)−N(2)	80.83(3)	C(29)−Fe(1)−C(30)	38.94(4)
N(1)−Fe(1)−C(29)	119.39(4)	Fe(1)−C(29)−Si(1)	147.07(6)
N(2)−Fe(1)−C(30)	123.43(4)	Fe(1)−C(30)−Si(2)	144.67(6)
N(2)−Fe(1)−C(29)	158.00(4)	dihedral angle[a]	25.5
N(1)−Fe(1)−C(30)	154.22(4)		

[a] The angle formed between the planes defined by N(1)−Fe(1)−N(2) and C(29)−Fe(1)−C(30).

Chart 2



A

B

observed in **1** and the neutral diimine that is the major canonical form in [ArN=C(Me)C(Me)=NAr]Fe(CH$_2$SiMe$_3$)$_2$. Both the carbon−carbon bond length of 1.2956(14) Å and the Fe(1)−C(29)−Si(1) and Fe(1)−C(30)−Si(2) bond angles of 147.07(6) and 144.67(6)° are consistent with considerable metallacyclopropene character. Thus, the X-ray data suggest that **7** is best described as an iron(II) complex intermediate between an "ene-diamide" acetylene complex (**A**) and an α-diimine compound with a metallacyclopropene ligand (**B**; Chart 2).

The successful synthesis and isolation of the α-diimine iron alkyne complexes prompted exploration of related olefin complexes. Iron complexes containing 1,5-cyclooctadiene were targeted, given the well-documented ability of this diolefin to stabilize catalytically active precursors.[25,26] Stirring [ArN=C(Me)C(Me)=NAr]FeCl$_2$ in the presence of excess 0.5% sodium amalgam and 5 equiv of 1,5-cyclooctadiene furnished dark brown crystals identified as [ArN=C(Me)C(Me)=NAr]Fe(η^2:η^2-1,5-C$_8$H$_{12}$) (**9**) (eq 8).

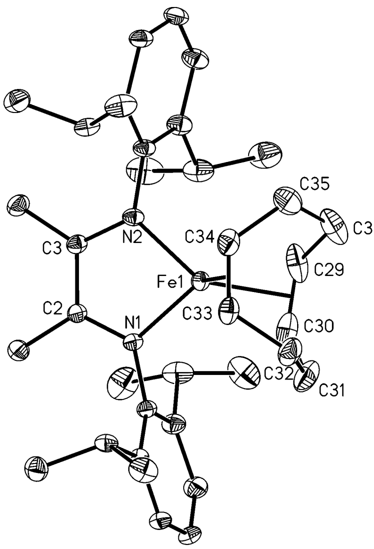
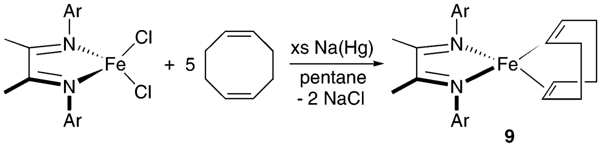


Figure 4. Molecular structure of **9** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for 9

Fe(1)−N(1)	1.9964(18)	Fe(1)−C(30)	2.115(3)
Fe(1)−N(2)	1.9944(18)	Fe(1)−C(33)	2.105(2)
Fe(1)−C(29)	2.096(3)	Fe(1)−C(34)	2.082(2)
N(1)−C(2)	1.344(3)	C(29)−C(30)	1.375(6)
N(2)−C(3)	1.349(3)	C(33)−C(34)	1.397(4)
C(2)−C(3)	1.413(3)		
N(1)−Fe(1)−N(2)	79.59(7)	C(29)−Fe(1)−C(34)	85.46(12)
C(29)−Fe(1)−C(30)	38.12(15)	C(29)−Fe(1)−C(33)	92.71(11)
C(33)−Fe(1)−C(34)	38.96(11)		



9

(8)

The benzene-d_6 ^{1}H NMR spectrum of **9** recorded at 23 °C exhibits six paramagnetically shifted and broadened peaks over a 200 ppm chemical shift range. Accordingly, a solution magnetic moment of 2.8 μ_B was observed at 23 °C in benzene-d_6, consistent with a high-spin, tetrahedral iron(0) center with two unpaired electrons. Significantly, **9** is stable in benzene-d_6 and does not undergo substitution with the arene solvent. Brown crystals of **9** suitable for X-ray diffraction were obtained from a concentrated pentane−ether solution chilled to −35 °C. The molecular structure of the compound is presented in Figure 4, while selected metrical data are reported in Table 4. During the final stages of structure refinement, the R1 value could not be lowered below 7%. A difference Fourier map showed a strong (3.7 e/Å^3) residual peak about 2 Å from Fe(1) along with other weaker peaks. The overall residual peak distribution resembles the data for **9**, suggesting a whole-molecule disorder. The core atoms, Fe, N, and C, were included into the model with a 0.14 occupancy. The resulting *R* factor was reduced in the subsequent

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(25) (a) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397. (b) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2143.

(26) (a) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *Chem. Commun.* **1975**, 449. (b) Krause, J.; Cestaric, G.; Haack, K.-J.; Seevogel, K.; Storm, W.; Pörschke, K.-R. *J. Am. Chem. Soc.* **1999**, *121*, 9807.

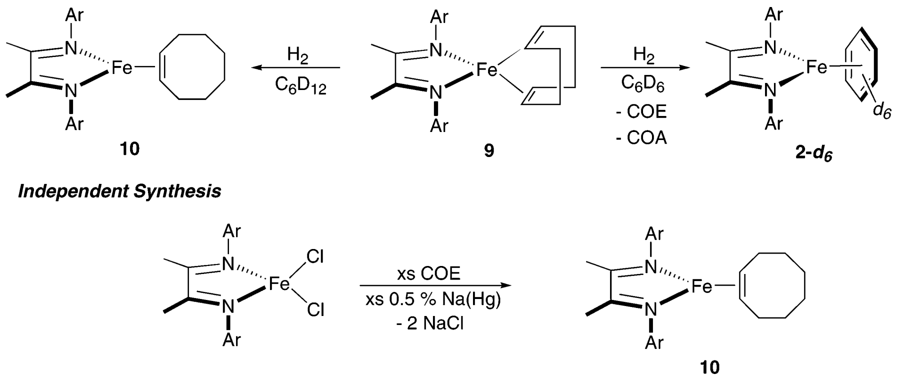


Figure 5. Reactivity of **9** with dihydrogen and synthetic routes to **10**.

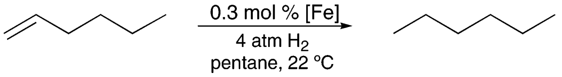
refinement; however, a full second molecule could not be completed. Interestingly, this disorder appears to be a intrinsic property of the material, consistently appearing in multiple crystals grown under different conditions.

The molecular geometry about iron in **9** is best described as pseudo-tetrahedral, with the centroids formed from the midpoints of C(29)−C(30) and C(33)−C(34) occupying two coordination sites above and below the plane of the α-diimine ligand. The C(2)−C(3) bond distance of 1.4139(12) Å is similar to that found in the solid-state structure of **4** and, along with the C=N bond lengths of the imine, suggests partial ligand reduction and some contribution from the "ene-diamide" resonance structure of the nitrogen chelate. Likewise, the C(29)−C(30) and C(33)−C(34) bond distances of 1.375(6) and 1.397(4) Å are only slightly elongated from the typical C=C distance of 1.34 Å.

Exposure of a benzene-d_6 solution of **9** to 1 atm of dihydrogen resulted in rapid conversion to **2**-d_6 with concomitant loss of cyclooctene and cyclooctane (Figure 5). Performing the hydrogenation in cyclohexane-d_{12} rather than aromatic solvent also produced some cyclooctene and cyclooctane along with a new iron compound, assigned as the cyclooctene complex [ArN=C(Me)C(Me)=NAr]Fe(η^2-C_8H_{14}) (**10**). To confirm this assertion, an independent synthesis of **10** was explored by reduction of [ArN=C(Me)C(Me)=NAr]$FeCl_2$ with excess 0.5% sodium amalgam in the presence of 5 equiv of olefin. Excess olefin is employed to suppress formation of **4**. This synthetic procedure furnished a green crystalline material identified as the desired cyclooctene adduct, **10**, on the basis of magnetic data, combustion analysis, NMR spectroscopy, and degradation experiments. As with **9**, the cyclohexane-d_{12} NMR spectrum of **10** displays eight broad and featureless signals over a 100 ppm chemical shift range. Dissolving **10** in benzene-d_6 resulted in olefin loss and formation of **2**-d_6.

The iron alkyne complexes **6** and **7** and the corresponding olefin compounds **9** and **10** were evaluated for the catalytic hydrogenation of 1-hexene. Each catalytic run was conducted with a 1.25 M solution of 1-hexene in pentane containing 0.3 mol % of the desired catalyst with 4 atm of dihydrogen. While the olefin complexes are efficient hydrogenation catalysts at lower H_2 pressures, 4 atm was used to avoid potential complications from rate-determining gas diffusion at higher conversions and to obtain reliable comparisons of turnover frequencies. The time to reach >98% conversion and the turnover frequencies for each catalyst are reported in Table 5.

Table 5. Assay of the Catalytic Hydrogenation Activity of α-Diimine Iron Alkyne Complexes



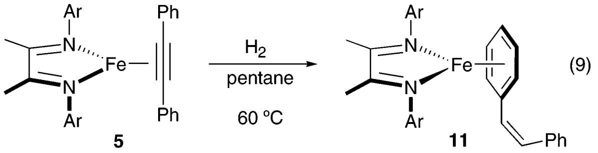
compd	time (min)[a]	tof (mol/h)[b]
(^{iPr}PDI)Fe$(N_2)_2$	12	1800
7[c]	1440[d]	4
9	240	90
10	240	90

[a] Time required to reach >98% conversion as judged by GC. [b] Determination based on time for completion. [c] Hydrogenation carried out at 60 °C. [d] 25% conversion to hexane, 12% internal hexenes observed.

In general, the alkyne complexes are poor precursors for 1-hexene hydrogenation, reaching only partial conversion after 24 h at 60 °C. Significant (~12%) olefin isomerization to a mixture of internal hexenes accompanies the hydrogenation reaction. In contrast, the olefin complexes **9** and **10** are efficient catalysts at 22 °C with turnover frequencies of 90 mol/h. Observation of nearly identical hydrogenation rates with the two olefin complexes suggests that the first hydrogenation in the cyclooctadiene compound **9** is fast and generates **10**, which in turn undergoes subsequent hydrogenation or displacement by substrate to generate the active species. Such an observation has been noted in stoichiometric reactions, where addition of H_2 to **9** furnishes **10** over the course of minutes at ambient temperature. It should be noted that variable induction periods, ranging between minutes and 1 h, have been observed, suggesting that generation of the catalytically active species is not straightforward. Further investigations into the nature of the active species and the scope and mechanism of the catalytic hydrogenation reaction are currently underway in our laboratory. Significantly, both of the olefin precursors offer inferior rates of hydrogenation compared to the bis(dinitrogen) iron complex with the tridentate pyridine(diimine) ligand.

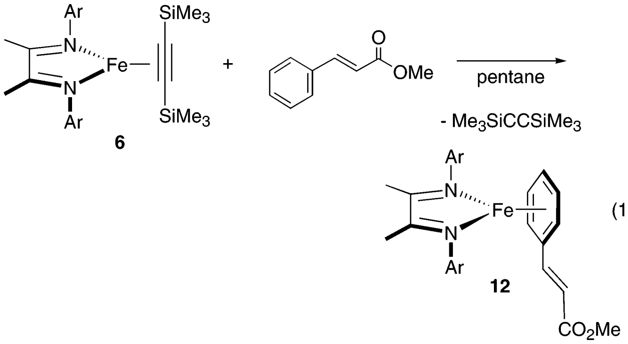
The poor performance of the diphenylacetylene compound **5** suggested complications from competing η^6 coordination during catalytic turnover. To investigate this possibility, a pentane solution of **5** was stirred under 4 atm of H_2 for 16 h at 60 °C in a thick-walled glass vessel. This procedure furnished an orange-red diamagnetic solid identified as the α-diimine iron *cis*-stilbene complex [ArN=C(Me)C(Me)=NAr]Fe(η^6-(C_6H_5)-

HC=CH(C_6H_5)) (**11**), arising from partial hydrogenation of the diphenylacetylene ligand in **6** (eq 9). Similar to the arene complexes **1** and **2**, a C_{2v}-symmetric ligand environment is observed by ^1H and ^{13}C NMR spectroscopy for **11**, consistent with rapid rotation of the arene ligand. In addition, upfield-shifted resonances are observed at 4.48 (meta), 5.07 (ortho), and 5.79 ppm (para), corresponding to the aromatic protons on the coordinated arene. Importantly, **11** does not react with additional H_2 or isomerize to the olefin complex, accounting for the lower activity of **5** in catalytic 1-hexene hydrogenation.



(9)

To further investigate potential complications from arene-containing substrates, the bis(trimethylacetylene) complex **7** was treated with a functionalized aromatic olefin. Addition of 1 equiv of methyl *trans*-cinnamate to a pentane solution of **7** resulted in an immediate color change to red, and a diamagnetic powder identified as the methyl *trans*-cinnamate complex [ArN=C(Me)C(Me)=NAr]Fe(η^6-(C_6H_5)CH=CHCOOCH_3) (**12**) was isolated in excellent yield (eq 10). Interestingly, the substitution reaction can also be performed in benzene-d_6 without complications from formation of **2**. The ^1H NMR spectrum of **12** in benzene-d_6 exhibits the number of peaks expected for a C_{2v} α-diimine ligand environment, in addition to three upfield peaks centered at 4.46, 5.08, and 5.83 for the meta, ortho, and para hydrogen resonances for the coordinated arene. This result demonstrates the strong preference for the α-diimine iron fragment to form coordinatively saturated arene complexes, even in the presence of carbonyl functional groups and aromatic solvent.



(10)

The preference for thermodynamic arene coordination is reinforced by the thermal behavior of **5**. While the η^2-alkyne complex is kinetically preferred from the alkali-metal reduction of the ferrous dihalide in the presence of diphenylacetylene, gently warming the compound produces the thermodynamically favored, coordinatively saturated arene complex. This thermodynamic preference has ramifications on the "functional" group tolerance of α-diimine-based iron hydrogenation catalysts, as substrates with arene substituents inhibit turnover through formation of inactive, 18-electron arene complexes.

Concluding Remarks

The reduction of the α-diimine ferrous dichloride complex [ArN=C(Me)C(Me)=NAr]FeCl_2 under a variety of conditions has been described. In the presence of aromatic organic solvents such as benzene or toluene, robust 18-electron α-diimine iron arene complexes are formed that display metrical parameters consistent with a significant contribution from the "ene-diamide" form of the bidentate nitrogen ligand. Replacing the aromatic reduction medium with an alkane solvent such as pentane furnished the bis(α-diimine) iron complex, which also exhibits significant reduction of the ligand in the solid state. Both the arene complexes and the bis(ligand) adducts are inactive for catalytic olefin hydrogenation. Performing the reduction of the α-diimine ferrous dichloride in the presence of a trapping ligand such as an olefin or alkyne afforded the corresponding adduct of the unsaturate, where both the α-diimine and the organic ligand engage in π back-bonding with the iron center. The olefin compounds are more active than the acetylene precursors for 1-hexene hydrogenation, and both classes of compounds are subject to forming catalytically inactive, coordinatively saturated arene compounds upon exposure to aromatic solvents or substrates.

Experimental Section

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard vacuum-line, Schlenk, and cannula techniques or in an M. Braun inert-atmosphere drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were initially dried and deoxygenated using literature procedures.[27] The M. Braun dryboxes were equipped with cold wells designed for freezing samples in liquid nitrogen. Argon and hydrogen gas were purchased from Airgas Inc. and 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 was purchased from Cambridge Isotope Laboratories and distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves or sodium metal. Chloroform-*d* was purchased from Cambridge Isotope Laboratories and distilled from CaH_2. Diphenylacetylene was purchased from Acros, dried under high vacuum, and recrystallized from pentane before use. Bis(trimethylsilyl)acetylene and 2-butyne were purchased from Acros, dried over 4 Å molecular sieves, and vacuum-transferred immediately before use. Likewise, 1-hexene, 1,5-cyclooctadiene, and cyclooctene were purchased from Acros and dried over LiAlH_4. [ArN=C(Me)C(Me)=NAr]FeCl_2 and **3** were prepared according to the previously reported procedure.[20]

^1H spectra were recorded on Varian Mercury 300 and Inova 400 and 500 spectrometers operating at 299.763, 399.780, and 500.618 MHz, respectively. All chemical shifts are reported relative to SiMe_4 using ^1H (residual) chemical shifts of the solvent as a secondary standard. ^2H NMR spectra were recorded on a Varian Inova 500 spectrometer operating at 76.851 MHz, and the spectra were referenced using an external benzene-d_6, toluene-d_8, or chloroform-*d* standard. For paramagnetic compounds, ^1H NMR data are reported with the chemical shift followed by the peak width at half-height in hertz followed by integration value and, where possible, peak assignment. Unless stated otherwise, magnetic moments were measured at 22 °C by the method originally described by

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[27] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

Evans[28] with stock and experimental solutions containing a known amount of a ferrocene standard.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox and were quickly transferred to the goniometer head of a Siemens SMART CCD area detector system equipped with a molybdenum X-ray tube (λ = 0.710 73 Å). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified, and the data were processed using the Bruker SAINT program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

Preparation of [ArN=C(Me)C(Me)=NAr]Fe(η^6-C_7H_8) (1). A 500 mL round-bottomed flask was charged with 129 g of Hg (643 mmol) and approximately 200 mL of toluene. With stirring, 0.660 g (28.2 mmol) of Na metal was added, and the resulting amalgam was stirred for 30 min. After this time, 3.00 g (5.60 mmol) of [ArN=C(Me)C(Me)=NAr]$FeCl_2$ was added, forming a bright orange-red solution over time. After it was stirred at ambient temperature for 2 days, the reaction mixture was decanted and filtered through Celite and the filtrate collected. The solvent was removed in vacuo and the resulting solid recrystallized from pentane to afford 2.30 g (74%) of deep red crystals identified as **1**. Anal. Calcd for $C_{35}H_{46}FeN_2$: C, 76.06; H, 8.75; N, 5.07. Found: C, 75.93; H, 8.28; N, 4.95. ^1H NMR (C_6D_6): δ 1.01 (m, 6.1 Hz, 18H, CH(CH_3)$_2$), 1.04 (s, 6H, N=C(CH_3)), 1.53 (d, 7.6 Hz, 12H, CH(CH_3)$_2$), 2.30 (s, 3H, $C_6H_5CH_3$), 3.52 (sept, 6.1 Hz, 4H, *CH*(CH_2)$_3$), 4.40 (t, 6.1 Hz, 2H, *m*-$C_6H_5CH_3$), 4.80 (d, 6.10 Hz, 2H, *o*-$C_6H_5CH_3$), 5.69 (t, 6.0 Hz, 1 H, *p*-$C_6H_5CH_3$), 7.27−7.39 (m, 7.63, 6 H, C_6H_3). ^{13}C NMR (C_6D_6): δ 18.51 (*C*H(CH_3)$_2$, 20.26 ($C_6H_5CH_3$), 25.06 (CH(CH_3)$_2$), 25.41 (CH(CH_3)$_2$), 28.23 (N=C(CH_3)), 80.46 (*o*- or *m*−$C_6H_5CH_3$), 80.81 (*o*- or *m*-$C_6H_5CH_3$), 82.10 (*p*-$C_6H_5CH_3$), 97.27 (i-$C_6H_5CH_3$), 123.70 (aryl), 126.17 (aryl), 142.23 (aryl), 143.73 (aryl), 154.36 (N=*C*(CH_3)).

Preparation of [ArN=C(Me)C(Me)=NAr]Fe(η^6-C_6H_6) (2). This molecule was prepared in a manner identical with that for **1** with 0.500 g (0.941 mmol) of [ArN=C(Me)C(Me)=NAr]$FeCl_2$ and 5 equiv of 0.5% Na(Hg) to yield 0.296 g (58%) of **2** as bright red crystals. Anal. Calcd for $C_{34}H_{46}FeN_2$: C, 75.82; H, 8.61; N, 5.20. Found: C, 75.47; H, 8.69; N, 5.22. ^1H NMR (C_6D_6): δ 1.00 (d, 6.8 Hz, 12H, CH(CH_3)$_2$), 1.05 (s, 6H, N=C(CH_3)), 1.47 (d, 6.8 Hz, 12H, CH(CH_3)$_2$), 3.52 (sept, 6.8 Hz, 4H, *CH*(CH_3)$_2$), 5.03 (s, 6H, C_6H_6), 7.25 (d, 7.3 Hz, 4H, *m*-C_6H_3), 7.32−7.35 (m, 2H, *p*-C_6H_3).^{13}C NMR (C_6D_6): δ 17.93 (*C*H(CH_3)$_2$), 24.38 (CH(CH_3)$_2$), 25.05 (CH(CH_3)$_2$), 27.99 (N=C(CH_3)), 81.02 (C_6H_6), 123.33 (aryl), 125.886 (aryl), 141.68 (aryl), 143.79 (aryl), 153.99 (N=*C*(CH_3)).

Preparation of [ArN=C(Me)C(Me)=NAr]$_2$Fe (4). A 100 mL round-bottomed flask was charged with 43.8 g (219 mmol) of mercury and approximately 50 mL of pentane. With stirring, 0.219 g (9.52 mmol) of sodium was added. After 10 min, 1.01 g (1.90 mmol) of [ArN=C(Me)C(Me)=NAr]$FeCl_2$ was added to the flask and the resulting red-green reaction mixture stirred for approximately 24 h. After this time an additional 0.716 g (1.90 mmol) of ArN=C(Me)C(Me)=NAr was added and the reaction mixture stirred for an additional 24 h. The liquid was decanted from the flask and filtered through Celite. The volatiles were removed in vacuo, and the resulting red-brown solid was recrystallized from pentane to afford 1.45 g (94%) of **4**. Anal. Calcd for $C_{56}H_{80}FeN_4$: C, 77.75; H, 9.32; N, 6.48. Found: C, 77.43; H, 9.54; N, 5.99. Magnetic susceptibility (Guoy balance): μ_{eff} = 2.8 μ_B.^1H NMR (C_6D_6) δ −22.2 (41.5, 6 H, N=C(CH_3)), −15.9 (24.72, 4H), −6.0 (15.0, 4H), −3.6 (24.5, 2H, *p*-C_6H_3), −2.2 (28.3, 12 H, CH(CH_3)$_2$), 3.96 (88.0, 6H, CH(CH_3)$_2$).

Preparation of [ArN=C(Me)C(Me)=NAr]Fe(η^2-PhC≡CPh) (5). This molecule was prepared in a manner similar to that for **4** with 1.00 g (1.90 mmol) of [ArN=C(Me)C(Me)=NAr]$FeCl_2$ and 5 equiv of 0.5% Na(Hg) in the presence of 0.335 g (1.90 mmol) of PhC≡CPh. Recrystallization from pentane at −35 °C afforded 0.759 g (63%) of brown crystals identified as **5**. Anal. Calcd for $C_{42}H_{50}FeN_2$: C, 78.98; H, 7.89; N, 4.39. Magnetic susceptibility (Guoy method): μ_{eff} = 3.2 μ_B. Found: C, 79.01; H, 7.76; N, 4.40. ^1H NMR (C_6D_6): δ −281.5 (58.2, 4H), −50.8 (219, 4H), −25.4 (38.4, 4 H), −21.2 (28.4, 6 H, N=C(CH_3)), −18.1 (17.9, 2H), −9.5 (16.8, 4H), −6.5 (17.4, 2H), −0.90 (55.7, 12 H, CH(CH_3)$_2$), 5.4 (12.9, 12 H, CH(CH_3)$_2$).

Characterization of [ArN=C(Me)C(Me)=NAr]Fe(η^6-C_6H_5C≡CPh) (6). ^1H NMR (C_6D_6): δ 0.99 (d, 6.1 Hz, 18H, CH(CH_3)$_2$), 1.10 (s, 6H, N=C(CH_3)), 1.60 (d, 6.1 Hz, 12H, CH(CH_3)$_2$), 3.53 (sept, 6.1 Hz, 4H, *CH*(CH_2)$_3$), 4.41 (t, 6.1 Hz, 2H, m−C_6H_5CCPh (bound)), 5.17 (d, 6.1 Hz, 2H, *o*-C_6H_5CCPh (bound)), 5.86 (t, 6.1 Hz, 1 H, *p*-C_6H_5CCPh (bound)), 6.97−7.35 (m, 5 H, PhCCC$_6H_5$ (free)).

Preparation of [ArN=C(Me)C(Me)=NAr]Fe(η^2-Me_3SiC≡CSiMe$_3$) (7). A 100 mL round-bottomed flask was charged with 64.8 g (324 mmol) of mercury and 50 mL of pentane. Small pieces of sodium (0.324 g, 14.1 mmol) were added with stirring and the resulting amalgam mixed for 20 min. After this time, 1.505 g (2.11 mmol) of [ArN=C(Me)C(Me)=NAr]$FeCl_2$ was added immediately, followed by 1.438 g (8.46 mmol) of bis(trimethylsilyl)acetylene. The resulting reaction mixture was stirred for 48 h and then filtered through Celite and the filtrate collected, and the volatiles were removed in vacuo. The resulting residue was recrystallized from a pentane−diethyl ether mixture to yield 0.957 g (54%) of a red-brown solid identified as **7**. Anal. Calcd for $C_{36}H_{58}N_2Si_2Fe$: C, 62.41; H, 8.44; N, 4.04. Found: C, 62.28; H, 8.51; N, 4.40. Magnetic susceptibility (benzene-d_6): μ_{eff} = 2.9 μ_B. ^1H NMR (benzene-d_6): δ −25.3 (47.0), −17.7 (26.1), −13.3 (21.1), −2.7 (208), 4.1 (14.7).

Preparation of [ArN=C(Me)C(Me)=NAr]Fe(η^2-MeC≡CMe) (8). A thick-walled glass vessel was charged with 13.0 g (65.0 mmol) of mercury and approximately 50 mL of pentane. With stirring, 0.065 g (2.83 mmol) of sodium, cut into small pieces, was added to the flask. After approximately 10 min, 0.300 g (0.564 mmol) of [ArN=C(Me)C(Me)=NAr]$FeCl_2$ was added to the flask. The vessel was transferred to the high-vacuum line, where it was submerged in liquid nitrogen and evacuated. Using a 31.6 mL calibrated gas volume, 331 Torr (0.564 mmol) of 2-butyne was added. The resulting reaction mixture was thawed and stirred for 28 h at ambient temperature, forming a dark brown solution. After this time, the toluene was removed in vacuo and the desired product was extracted into pentane. Recrystallization from pentane at −35 °C yielded 0.255 g (88%) of a dark brown solid identified as **8**. ^1H NMR (benzene-d_6): δ −21.6 (49.0), 0.0 (376).

Preparation of [ArN=C(Me)C(Me)=NAr]Fe(η^2:η^2-1,5-COD) (9). This compound was prepared in a manner similar to that for **7** with 1.124 g (2.11 mmol) of [ArN=C(Me)C(Me)=NAr]$FeCl_2$, 5 equiv of 0.5% Na(Hg), and 0.685 g (6.34 mmol) of 1,5-cyclooctadiene in approximately 20 mL of pentane. Following stirring for 48 h and standard workup, 0.596 g (50%) of **9** was obtained as a brown solid. Anal. Calcd for $C_{36}H_{52}N_2$Fe: C, 76.04; H, 9.22; N, 4.93. Found C, 76.19; H, 9.23; N, 4.96. Magnetic susceptibility (benzene-d_6): μ_{eff} = 2.8 μ_B.^1H NMR (benzene-d_6): δ −61.5 (305.0), 5.9 (25.3), 0.0 (57.6), 1.70 (24.9), 93.0 (525.4), 143.5 (889).

Preparation of [ArN=C(Me)C(Me)=NAr]Fe(η^2-COE) (10). This molecule was prepared in a manner similar to **9** with 8.65 g (43.3 mmol) of mercury, 0.043 g (1.88 mmol) of sodium, 0.200 g (0.376 mmol) of [ArN=C(Me)C(Me)=NAr]$FeCl_2$, and 0.206 g (1.88 mmol) of cyclooctene, yielding 0.127 g (59%) of a brown solid identified as **10**. Anal. Calcd for $C_{36}H_{54}N_2Fe$: C, 75.77; H, 9.54; N, 4.91. Found: C, 75.52; H, 9.78; N, 4.87. Magnetic susceptibility (Guoy method): μ_{eff} =

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[28] Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.

3.1 μ_B. ^{1}H NMR (cyclohexane-d_{12}): δ −75.2 (530.4), −46.7 (657.5), −32.9 (170.0), −17.4 (115.1), −13.2 (30.2), 0.39 (36.1), 11.8 (93.3), 19.5 (74.0).

Preparation of [ArN=C(Me)C(Me)=NAr]Fe(η^6-(C_6H_5)-HC=CH(C_6H_5)) (11). A thick-walled glass vessel was charged with 0.094 g (0.147 mmol) of **5** and approximately 20 mL of pentane. On the high-vacuum line, the vessel was frozen in liquid nitrogen and evacuated and 1 atm of dihydrogen was admitted. The vessel was thawed and the mixture stirred for 16 h at 60 °C. After this time, the brown solution turned bright orange-red. The volatiles were removed in vacuo to yield 0.090 g (96%) of an orange red solid identified as **11**. Purification was accomplished by recrystallization from pentane. ^{1}H NMR (C_6D_6): δ 1.00 (m, 7.63 Hz, 18H, $\mathrm{CH}(\mathit{CH}_3)_2$), 1.01 (s, 6H, $\mathrm{N{=}C}(\mathit{CH}_3)$), 1.47 (d, 6.10 Hz, 12H, $\mathrm{CH}(\mathit{CH}_3)_2$), 3.46 (sept, 6.10 Hz, 4H, $\mathit{CH}(\mathrm{CH}_2)_3$), 4.48 (t, 6.10 Hz, 2H, bound *m*-$\mathrm{C}_6\mathit{H}_5\mathrm{CH_2CH_2C_6H_5}$), 5.07 (d, 6.10 Hz, 2H, bound *o*-$\mathrm{C}_6\mathit{H}_5\mathrm{CH_2CH_2C_6H_5}$), 5.73 (t, 4.58 Hz, 1H, bound *p*-$\mathrm{C}_6\mathit{H}_5\mathrm{CH_2CH_2C_6H_5}$), 6.64 (d, 10.68 Hz, 1H, free *p*-$\mathrm{C_6H_5CH_2CH_2C_6}\mathit{H}_5$), 6.87 (m, 3.06 Hz, 4H, *m*-$\mathrm{C}_6\mathit{H}_3$), 7.11−7.27 (m, 6.10 Hz, 8 H, *p*-$\mathrm{C}_6\mathit{H}_3$, free $\mathrm{C_6H_5}\mathit{CH}_2\mathit{CH}_2\mathrm{C_6H_5}$, free *o- ,m-, and p*-$\mathrm{C_6H_5CH_2CH_2C_6}\mathit{H}_5$). ^{13}C NMR ($C_6D_6$): δ 18.33 ($\mathit{C}\mathrm{H(CH_3)_2}$, 24.82 ($\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$), 25.10 ($\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$), 27.98 ($\mathrm{N{=}C}(\mathit{C}\mathrm{H}_3)$), 80.65 (*o*- or *m*-$\mathrm{C_6H_5CH_2CH_2C_6H_5}$), 81.08 (*o*- or *m*-$\mathit{C}_6\mathrm{H_5CH_2CH_2C_6H_5}$), 81.93 (*p*-$\mathit{C}_6\mathrm{H_5CH_2CH_2C_6H_5}$), 96.06 (i-$\mathit{C}_6\mathrm{H_5CH_2CH_2C_6H_5}$), 123.40 ($\mathit{C}_6\mathrm{H}_3$), 126.00 ($\mathit{C}_6\mathrm{H}_3$), 127.20, 129.56, 130.17, 130.91, 137.21 ($\mathit{C}_6\mathrm{H}_3$), 141.71 ($\mathit{C}_6\mathrm{H}_3$), 144.63 ($\mathit{C}_6\mathrm{H}_3$), 153.70 ($\mathrm{N{=}}\mathit{C}(\mathit{C}\mathrm{H}_3)$).

Preparation of [ArN=C(Me)C(Me)=NAr]Fe(η^6-(C_6H_5)-CH=CHCOOCH$_3$) (12). A 20 mL scintillation vial was charged with 0.100 g (0.157 mmol) of **7** and approximately 10 mL of diethyl ether. Solid methyl *trans*-cinnamate (0.026 g (0.157 mmol)) was added to the vial, immediately forming a red solution. The volatiles were removed in vacuo, and the residue was recrystallized to yield 0.080 g (82%) of a red solid identified as **12**. Anal. Calcd for $C_{38}H_{50}N_2O_2Fe$: C, 73.30; H, 8.09; N, 4.50. Found: C, 72.94; H, 8.27; N, 4.25. ^{1}H NMR (benzene-d_6): δ 0.92 (d, 6.8 Hz, 12H, $\mathrm{CH}(\mathit{CH}_3)_2$), 0.96 (s, 6H, $\mathrm{N{=}C}(\mathit{CH}_3)$), 1.52 (d, 6.8 Hz, 12H, $\mathrm{CH}(\mathit{CH}_3)_2$), 3.50 (q, 6.8 Hz, 4H, $\mathit{CH}(\mathrm{CH}_3)_2$), 3.54 (s, 3H, $\mathrm{C_6H_5CHCHCOOC}\mathit{H}_3$), 4.46 (t, 5.9 Hz, 2H, *m*-$\mathrm{C}_6\mathit{H}_5\mathrm{CHCHCOOCH_3}$), 5.08 (d, 6.4 Hz, 2H, *o*-$\mathrm{C}_6\mathit{H}_5\mathrm{CHCHCOOCH_3}$), 5.83 (t, 5.9 Hz, 1H, *p*-$\mathrm{C}_6\mathit{H}_5\mathrm{CHCHCOOCH_3}$), 6.42 (d, 15.6 Hz, 1H, $\mathrm{C_6H_5CHC}\mathit{H}\mathrm{COOCH_3}$), 7.21 (d, 7.8 Hz, 4H, *m*-aryl), 7.30 (t, 7.8 Hz, 2H, *p*-aryl), 8.18 (d, 15.6 Hz, 1H, $\mathrm{C_6H_5C}\mathit{H}\mathrm{CHCOOCH_3}$). ^{13}C NMR ($C_6D_6$): δ 18.95 ($\mathit{C}\mathrm{H(CH_3)_2}$), 25.12 ($\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$), 25.42 ($\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$), 28.27 ($\mathrm{N{=}C}(\mathit{C}\mathrm{H}_3)$), 51.49, 80.40 (*o-, m-, or p*-$\mathit{C}_6\mathrm{H_5CHCHCOOCH_3}$), 82.45 (*o-, m-,* or *p*-$\mathit{C}_6\mathrm{H_5CHCHCOOCH_3}$), 82.63 (*o-, m-, or p*-$\mathit{C}_6\mathrm{H_5CHCHCOOCH_3}$), 92.55 (ipso-$\mathit{C}_6\mathrm{H_5CHCHCOOCH_3}$), 116.57, 123.93 (aryl), 126.60 (aryl), 141.97 (aryl), 147.03 (aryl), 153.55 ($\mathrm{N{=}}\mathit{C}(\mathrm{CH}_3)$), 197.16, 236.17.

General Hydrogenation Procedure. A thick-walled glass vessel was charged with 0.02 mmol of the desired iron complex, along with approximately 4 mL of pentane and a stir bar. Approximately 4.90 mmol of substrate was added to the vessel. The vessel was submerged in liquid nitrogen and evacuated. One atmosphere of hydrogen was admitted, and the reaction mixture was warmed to ambient temperature and stirred for the appropriate time. The progress of the reaction was assayed periodically by gas chromatography.

Acknowledgment. We thank Cornell University, Research Corp. (Cottrell Scholarship to P.J.C.), and the Packard Foundation for financial support. S.C.B. acknowledges support from the National Institutes of Health as part of the Chemistry and Biology Interface Training Grant at Cornell.

Supporting Information Available: Crystallographic data for **1**, **4**, **7**, and **9**, including full atom labeling schemes and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050625B