ACS Catalysis
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High-Activity Iron Catalysts for the Hydrogenation of Hindered, Unfunctionalized Alkenes

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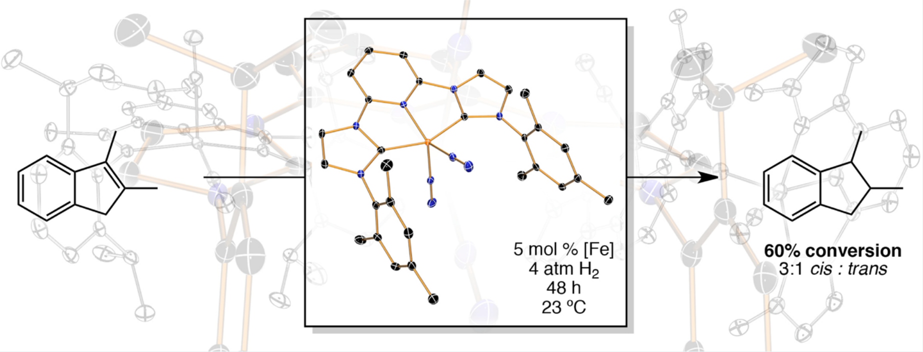
S *Supporting Information*



ABSTRACT: The activity of aryl-substituted bis(imino)pyridine and bis(arylimidazol-2-ylidene)pyridine iron dinitrogen complexes has been evaluated in a series of catalytic olefin hydrogenation reactions. In general, more electron-donating chelates with smaller 2,6-aryl substituents produce more active iron hydrogenation catalysts. Establishment of this structure−activity relationship has produced base metal catalysts that exhibit high turnover frequencies for the hydrogenation of unfunctionalized, tri- and tetrasubstituted alkenes, one of the most challenging substrate classes for homogeneous hydrogenation catalysts.

KEYWORDS: *iron, hydrogenation, catalysis, N-heterocyclic carbene*

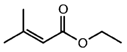
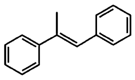
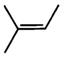
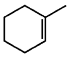
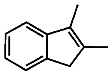
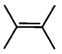
The hydrogenation of alkenes with soluble transition metal complexes, particularly in asymmetric form, has emerged as one of the most powerful and widely applied methods in homogeneous catalysis.[1−4] Precious metal compounds, principally those based on rhodium, iridium, and ruthenium, have dominated the catalyst landscape.[5−9] The high cost, low terrestrial abundance, and environmental impact associated with these rare elements inspires the search for catalysts with less toxic, more cost-effective, earth-abundant metals.[10−13]

Although olefin hydrogenation in the presence of catalytic quantities of $\mathrm{Fe(CO)_5}$ and related derivatives has been known for some time,[14,15] examples of iron catalysts that operate under mild conditions with high activity and a broad substrate scope are rare.[16,17] The aryl-substituted bis(imino)pyridine iron dinitrogen compound $(^{iPr}\mathrm{PDI})\mathrm{Fe(N_2)_2}$ ($^{iPr}\mathrm{PDI}$ = 2,6-$(2,6\text{-}^{i}\mathrm{Pr_2{-}C_6H_3{-}N{=}CMe})_2\mathrm{C_5H_3N}$)[18−20] was reported in 2004 and exhibited high turnover frequencies for the hydrogenation of unfunctionalized olefins at low iron loadings (as low as 0.3 mol %) and ambient temperature. Since this initial discovery, our group has been interested in the functional group tolerance of this catalyst class[21] as well as improving overall performance through rational ligand manipulation. Bis(imino)pyridine ligands are ideally suited for exploration of structure−reactivity relationships because numerous variants are accessible through relatively straightforward synthetic routes.[22]

Various positions are available on the bis(imino)pyridine for substitution. Our laboratory has previously reported that reduction of the size of the 2,6-aryl substituents from isopropyl to ethyl or methyl resulted in dimeric iron dinitrogen complexes, $[(^{R}\mathrm{PDI})\mathrm{Fe(N_2)}]_2(\mu\text{-}\mathrm{N_2})$[23] ($^{R}\mathrm{PDI}$ = 2,6-$(2,6\text{-}\mathrm{R_2{-}C_6H_3{-}N{=}CMe})_2\mathrm{C_5H_3N}$; R = Me, Et), with dramatically improved activity for alkene hydrogenation[23] and hydrosilyation.[24] Substitution of the imine position has also been explored. Introduction of phenyl substituents, as in the case of $(^{iPr}\mathrm{BPDI})\mathrm{Fe(N_2)_2}$ ($^{iPr}\mathrm{BPDI}$ = 2,6-$(2,6\text{-}^{i}\mathrm{Pr_2{-}C_6H_3{-}N{=}CPh})_2\mathrm{C_5H_3N}$), resulted in high turnover frequency for 1-hexene hydrogenation but overall reduced catalyst lifetime due to competing formation of intramolecular η^6-arene complexes.[25] Replacement of the ketamine chelates with aldimine variants complicates isolation of iron dinitrogen compounds; however, evaluation of iron butadiene precatalysts demonstrated reduced turnover frequencies and lifetimes as compared with ketamine-based iron complexes.[26]

Received: June 7, 2012
Revised: July 17, 2012
Published: July 23, 2012

Table 1. Catalytic Hydrogenation of Unfunctionalized Alkenes with Bis(imino)pyridine and Bis(arylimidazol-2-ylidene)pyridine Iron Dinitrogen Complexes

Entry	Substrates	Conversion[a] [%] (Reaction time)					
		(^{iPr}PDI)Fe(N_2)$_2$	**[(^{Me}PDI)Fe(N_2)]$_2$ (μ-N_2)**	**(4-NMe_2-^{iPr}PDI)Fe(N_2)$_2$**	**(^{iPr}CNC)Fe(N_2)$_2$**	**(^{Me}CNC)Fe(N_2)$_2$**	**(^{Mes}CNC)Fe(N_2)$_2$**
1[b]		65 (24 h)	> 95 (1 h)	> 95 (7 h)	> 95 (1 h)	35 (1 h)[e]	35 (1 h)
2[b]		12 (24 h)	4 (24 h)	76[d] (24 h)	89 (12 h)	> 95 (1 h)	> 95 (1 h)
3[c]		32 (24 h)	15 (24 h)	15 (24 h)	> 95 (15 h)	> 95 (1 h)	> 95 (1 h)
4[b]		0 (24 h)	2 (24 h)	3 (24 h)	20 (24 h)	> 95 (12 h)	> 95 (1 h)
5[b]		3 (48 h)	< 1 (48 h)	3 (48 h)	4 (48 h)	68 (48 h) 3:1 *cis* : *trans*	60 (48 h) 3:1 *cis* : *trans*
6[c]		0 (24 h)	0 (24 h)	0 (24 h)[f]	0 (24 h)	0 (24 h)	0 (24 h)

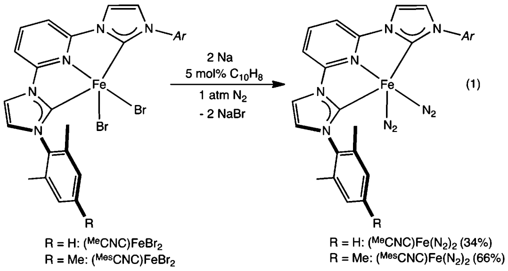
[a] All catalytic reactions carried out with 5 mol % Fe (0.032 mmol based on Fe), 0.633 mmol of substrate, and 0.915 M substrate at 4 atm H_2 and 23 °C. [b] Conversions were determined by GC-FID. [c] Benzene-d_6 used as solvent; conversions were determined by ^{1}H NMR spectroscopy. [d] Quantitative conversion (>95%) observed after 60 h. [e] 45% conversion observed after 24 h. [f] 25% conversion observed after 24 h at 45 °C; significant decomposition of the iron compound was also observed.

The established redox noninnocence and activity[27,28] of bis(imino)pyridine ligands in reduced iron complexes[29,30] suggested that in-plane modifications of the chelate, particularly in the *para*-pyridine position, may have a profound impact on catalytic performance. Our laboratory has recently reported the synthesis of a series of 4-substituted bis(imino)pyridine iron dinitrogen complexes, (4-X-^{iPr}PDI)Fe(N_2)$_2$ (X = ^{t}Bu, Bn, NMe_2) and evaluation of the electronic influences of each group.[31] Although no gross change in electronic structure of the iron compound was observed, more electron-rich iron centers arose from introduction of alkyl or NMe_2 substituents. Here, we describe evaluation of the performance of these compounds in the catalytic hydrogenation of alkenes, begin to establish structure−reactivity relationships, and report that replacement of the imine fragments with *N*-heterocyclic carbenes results in highly active iron precatalysts for the hydrogenation of sterically hindered, unfunctionalized alkenes.

Our group has previously used the hydrogenation of ethyl 3,3-dimethylacrylate to benchmark the catalytic activity of iron catalysts.[21,23] Under standard conditions (5 mol % Fe, 0.915 M substrate, 23 °C, 4 atm H_2)[21] with (^{iPr}PDI)Fe(N_2)$_2$, only 65% conversion to alkane was observed. Completion of the catalytic reaction was impeded by competitive deactivation of the iron compound by C−O bond cleavage of the ester.[32] By contrast, catalysis with [(^{Me}PDI)Fe(N_2)]$_2$(*μ*-N_2) resulted in complete conversion to alkane in under 1 h, highlighting the dramatic impact of aryl group substituent effects.[23] Introduction of a NMe_2 substituent into the 4-position of the chelate while maintaining the steric environment imparted by the 2,6-diisopropyl groups dramatically increases the hydrogenation activity of the iron compound. Complete conversion to alkane was observed with (4-NMe_2-^{iPr}PDI)Fe(N_2)$_2$ in 7 h (Table 1).

The improved hydrogenation activity observed with (4-NMe_2-^{iPr}PDI)Fe(N_2)$_2$ prompted the synthesis of more electron-rich iron dinitrogen compounds. Danopoulos and co-workers have reported a related iron dinitrogen complex, (^{iPr}CNC)Fe(N_2)$_2$ (^{iPr}CNC = 2,6-(2,6-^{i}Pr$_2$-C_6H_3-imidazol-2-ylidene)$_2$−C_5H_3N), where the imine groups of the bis(imino)pyridine have been replaced by *N*-heterocyclic carbenes.[33] As evidenced by the toluene solution infrared stretching frequencies of the N_2 ligands (2104, 2037 cm^{-1}), (^{iPr}CNC)Fe(N_2)$_2$ is more electron-rich than (4-NMe_2-^{iPr}PDI)Fe(N_2)$_2$ (2117, 2055 cm^{-1}), raising the possibility of improved hydrogenation activity. Indeed, (^{iPr}CNC)Fe(N_2)$_2$ promotes the complete (>95% conversion) hydrogenation of ethyl 3,3-dimethylacrylate over the course of 1 h at 23 °C, a significant improvement over two of the bis(imino)pyridine iron catalysts.

The remarkable catalytic hydrogenation activity of (^{iPr}CNC)Fe(N_2)$_2$ prompted synthesis of bis(arylimidazol-2-ylidene)pyridine iron dinitrogen complexes with smaller 2,6-aryl substituents. Using standard synthetic methods to access compounds of this type, reduction of (^{Me}CNC)FeBr$_2$ (^{Me}CNC = 2,6-(2,6-Me_2-C_6H_3-imidazol-2-ylidene)$_2$−C_5H_3N) or (^{Mes}CNC)FeBr$_2$ (^{Mes}CNC = 2,6-(2,4,6-Me_3-C_6H_2-imidazol-2-ylidene)$_2$−C_5H_3N) with 2 equiv of sodium metal in the presence of 5 mol % of naphthalene under an N_2 atmosphere furnished the desired iron bis(dinitrogen) complexes, (^{Me}CNC)Fe(N_2)$_2$ and (^{Mes}CNC)Fe(N_2)$_2$, as dark brown, diamagnetic solids in 34 and 66% yields, respectively (eq 1).



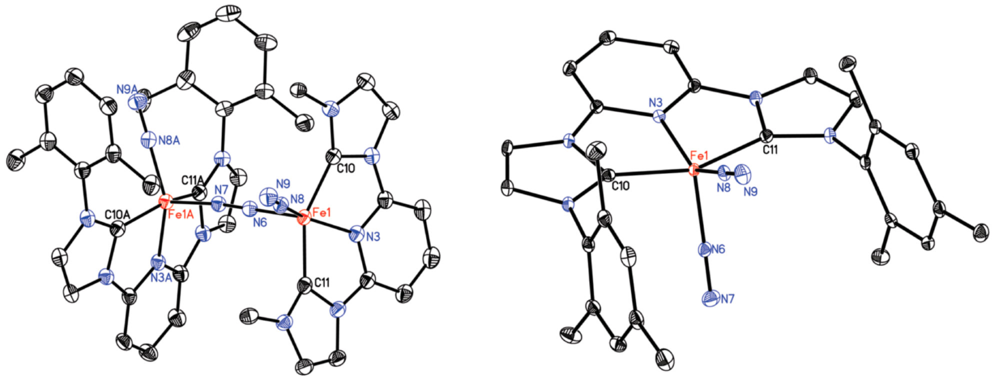


Figure 1. Solid state molecular structures of $[(^{Me}CNC)Fe(N_2)]_2(\mu\text{-}N_2)$ and $(^{Mes}CNC)Fe(N_2)_2$ at 30% probability ellipsoids. Hydrogen atoms and aryl groups on Fe1 of $[(^{Me}CNC)Fe(N_2)]_2(\mu\text{-}N_2)$ were omitted for clarity.

Isolation and characterization of the 2,6-dimethyl-substituted compounds proved challenging because of the limited solubility of these species in hydrocarbon and ethereal solvents and accounts for the higher isolated yield for $(^{Mes}CNC)Fe(N_2)_2$.

Both new iron dinitrogen complexes were characterized by single-crystal X-ray diffraction (Figure 1). The dimethyl-substituted compound, $[(^{Me}CNC)Fe(N_2)]_2(\mu\text{-}N_2)$, is dimeric in the crystal selected for the diffraction experiment. However, infrared data indicated that both monomers and dimers are present in the solid state (KBr). In contrast, the crystal structure of $(^{Mes}CNC)Fe(N_2)_2$ established a monomeric iron compound in the solid state. Solution infrared spectroscopy on both compounds revealed that only monomers are present in toluene solution at 23 °C (see the Supporting Information).

Initial assays of the catalytic hydrogenation activity of $(^{Me}CNC)Fe(N_2)_2$ and $(^{Mes}CNC)Fe(N_2)_2$ were conducted with ethyl 3,3-dimethylacrylate under standard conditions. In both cases, only 35% conversion to the desired alkane was observed after 1 h at 23 °C. To probe whether catalytic deactivation was resulting with the less sterically protected iron dinitrogen compounds, the hydrogenation of ethyl 3,3-dimethylacrylate was repeated in the presence of *trans*-methylstilbene, a substrate that was known to undergo complete conversion with these compounds (vide infra). The competitive hydrogenation was performed for 1 h at 23 °C with $(^{Mes}CNC)Fe(N_2)_2$; only 24% and 6.5% conversion of 3,3-dimethylacrylate and the stilbene were observed, suggesting that the carboxylated alkene is an inhibitor for hydrogenation activity with the more open iron compounds.

To further explore the possibility of inhibition, addition of ethyl 3,3-dimethylacrylate to $(^{R}CNC)Fe(N_2)_2$ compounds was studied in the absence of H_2. No change in the ^1H NMR spectrum was observed upon addition of 1 equiv of ethyl 3,3-dimethylacrylate to $(^{iPr}CNC)Fe(N_2)_2$, indicating no coordination of the substrate to this iron compound.

Performing the analogous experiment with $(^{Mes}CNC)Fe(N_2)_2$ resulted in coordination of the ester, likely through the carbonyl oxygen and possibly the C═C bond. Addition of 4 atm of H_2 to a benzene-d_6 solution of the compound resulted in gradual liberation of the alkane, demonstrating that substrate coordination was reversible and not a source of deactivation by C−O bond cleavage.[32] Thus, the steric protection imparted by the 2,6-isopropyl groups serves to generate a more active hydrogenation catalyst by preventing formation of inactive O-bound iron ester complexes.

The scope and performance of both the bis(imino)pyridine and bis(arylimidazol-2-ylidene)pyridine iron dinitrogen complexes have been studied for unfunctionalized tri- and tetrasubstituted alkenes. This class of substrate remains a significant challenge for precious metal catalysts.[34] Buchwald and co-workers have reported titanocene[35] and zirconocene[36] catalysts for the asymmetric hydrogenation of these substrates, although the complexity of the precatalyst synthesis and the high hydrogen pressures are limitations. The previously reported bis(imino)pyridine iron dinitrogen compounds, $(^{iPr}PDI)Fe(N_2)_2$ and $[(^{Me}PDI)Fe(N_2)]_2(\mu\text{-}N_2)$, exhibit minimal activity for these types of hydrogenations. For example, the hydrogenation of *trans*-methyl stilbene proceeded with only 12 (R = ^{i}Pr) and 4% (R = Me) conversion after 24 h. Similar results were obtained for the hydrogenation of 2-methyl-2-butene, for which 32 (R = ^{i}Pr) and 15% (R = Me) conversion was observed. The higher conversions observed with $(^{iPr}PDI)Fe(N_2)_2$ are believed to be a result of longer catalyst lifetimes during slower substrate hydrogenations. Essentially no activity was observed for the hydrogenations of methylcyclohexene, 2,3-dimethyl-1*H*-indene, or 2,3-dimethyl-2-butene with these two bis(imino)pyridine iron compounds.

Use of the more electron-rich bis(imino)pyridine iron dinitrogen complex, $(4\text{-}NMe_2\text{-}^{iPr}PDI)Fe(N_2)_2$, overcomes some of these limitations. The hydrogenation of *trans*-methyl stilbene proceeded to 76% conversion in 24 h with quantitative (>95%) formation of alkane occurring after 60 h at 23 °C. Unfortunately, little activity was observed for the hydrogenation of methylcyclohexene or tetrasubstituted alkenes.

The bis(arylimidazol-2-ylidene)pyridine iron dinitrogen complexes are also effective for the hydrogenation of unfunctionalized, hindered alkenes. Complete hydrogenation of *trans*-methyl stilbene was accomplished in 24 h with $(^{iPr}CNC)Fe(N_2)_2$. Introduction of smaller aryl rings resulted in even more active hydrogenation catalysts, as complete hydrogenation of *trans*-methyl stilbene was observed in less than 1 h with both $(^{Me}CNC)Fe(N_2)_2$ and $(^{Mes}CNC)Fe(N_2)_2$. The improved activity observed with the less hindered compounds with unfunctionalized olefins also supports the carbonyl functional group inhibiting the hydrogenation activity of ethyl 3,3-dimethylacrylate.

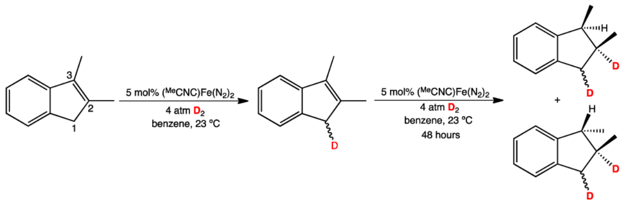
The success in *trans*-methyl stilbene hydrogenation prompted further study of substrate scope with the bis(arylimidazol-2-ylidene)pyridine iron compounds. The more hindered compound, $(^{iPr}CNC)Fe(N_2)_2$, is an effective precatalyst for the hydrogenation of 2-methyl-2-butene reaching quantitative conversion in 15 h. Only modest activity was observed for the hydrogenation of methylcyclohexene, and essentially no turnover was obtained for the hydrogenation of 2,3-dimethyl-1*H*-indene or 2,3-dimethyl-2-butene, identifying both endocyclic tri- and tetrasubstituted alkenes as limitations for this specific catalyst.

To improve substrate scope and activity, hydrogenations with the more open iron dinitrogen compounds, $(^{Me}CNC)Fe(N_2)_2$ and $(^{Mes}CNC)Fe(N_2)_2$, were studied. With $(^{Me}CNC)Fe(N_2)_2$, the hydrogenation of methylcyclohexene was complete in 12 h; with $(^{Mes}CNC)Fe(N_2)_2$, a significantly improved turnover frequency was observed with complete conversion after only 1 h. The difference in hydrogenation activity between the two compounds is attributed to the improved solubility of $(^{Mes}CNC)Fe(N_2)_2$ in hydrocarbon solvents. For hydrogenations with $(^{Me}CNC)Fe(N_2)_2$, the metal complex was not completely dissolved under standard conditions,[23] thereby reducing the concentration of the active iron compound. For less challenging trisubstituted alkenes, such as 2-methyl-2-butene, this complication is less evident because complete conversion to alkane was observed in 1 h with both iron dinitrogen compounds.

The successful hydrogenation of unfunctionalized trisubstituted alkenes prompted exploration of even more challenging tetrasubstituted olefins.[36] Although neither $(^{Me}CNC)Fe(N_2)_2$ nor $(^{Mes}CNC)Fe(N_2)_2$ was active for the hydrogenation of 2,3-dimethyl-2-butene at 23 °C, 68 and 60% conversions were observed with 2,3-dimethyl-1*H*-indene after 48 h. In both cases, a 3:1 ratio of cis/trans diastereomers of the alkane was observed.

To gain insight into the origin of the trans isomer, a deuterium labeling experiment was conducted (Scheme 1).

Scheme 1. Catalytic Deuteration of 2,3-Dimethyl-1*H*-indene with 5 mol % of $(^{Me}CNC)Fe(N_2)_2$ in Benzene and 4 atm of D_2



Exposure of a benzene solution of 2,3-dimethyl-1*H*-indene to D_2 gas in the presence of 5 mol % of $(^{Me}CNC)Fe(N_2)_2$ resulted in catalytic deuteration. The fate of the deuterium atoms was determined using a combination of ^1H, ^2H, and ^{13}C NMR spectroscopies. No isotopic label was detected in the 3-position, as would be expected for the direct hydrogenation (or deuteration) of the tetrasubstituted olefin. Deuterium was instead observed in both the 1- and 2-positions of the alkane product, suggesting olefin isomerization occurs prior to hydrogenation. In addition, analysis of the substrate during turnover revealed deuterium incorporation into the 1-position, consistent with C−H catalytic activation that is competitive with hydrogenation.

In summary, we have discovered that more electron-rich iron dinitrogen complexes are effective for the catalytic hydrogenation of unfunctionalized alkenes. The origin of these profound electronic influences as well as elucidation of mechanistic pathways, including the role of redox activity, is currently under investigation. These results provide important insight for catalyst design efforts for evolution into asymmetric variants.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, including full characterization of all new compounds and crystallographic data for $(^{Me}CNC)Fe(N_2)_2$ and $(^{Mes}CNC)Fe(N_2)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge the U.S. National Science Foundation and the Deutsche Forschungsgemeinschaft for a Cooperative Activities in Chemistry between U.S. and German Investigators grant. Z.R.T. thanks the US-UK Fulbright Commission and AstraZeneca for a fellowship. J.M.D. acknowledges support from the National Institute of General Medical Sciences (Award No. T32GM008500). The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institute of General Medical Sciences or the National Institutes of Health.

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