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Highly Selective Bis(imino)pyridine Iron-Catalyzed Alkene Hydroboration

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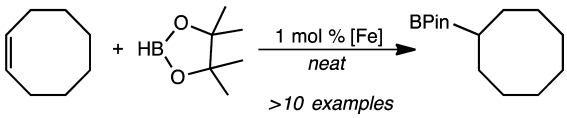
ABSTRACT



Bis(imino)pyridine iron dinitrogen complexes have been shown to promote the anti-Markovnikov catalytic hydroboration of terminal, internal, and geminal alkenes with high activity and selectivity. The isolated iron dinitrogen compounds offer distinct advantages in substrate scope and overall performance over known precious metal catalysts and previously reported in situ generated iron species.

Transition metal catalyzed hydroboration has emerged as an atom-economical and selective route for the synthesis of alkylboronic acids.[1] Alkylboranes are valuable targets due to their diverse range of applications in organic synthesis,[2] principally as the nucleophilic partner in metal-catalyzed Suzuki–Miyaura cross-coupling reactions.[3] Historically, precious metal catalysts, specifically organometallic rhodium and iridium complexes,[4,5] have been the most commonly employed for homogeneous hydroboration. In certain instances, a broad alkene scope and high selectivity have been reported.[5]

Because of the potential high cost, low terrestrial abundance, and performance limitations associated with precious metal catalysts, there has been renewed interest in the discovery of catalysts based on earth-abundant, first row transition metals.[6] Often times the unique electronic structures available to these metals in conjunction with smaller atomic radii compared to heavier elements offer the possibility for distinct reactivity. Cu-catalyzed hydroboration of *trans*-β-substituted styrenes and related arenes have been reported by Yun et al.[7] Using a Cu(I) source, chiral bidentate phosphines, and NaO^{t}Bu, alkylboronic esters were isolated in high yield and enantiopurity. This method has recently been extended to the asymmetric synthesis of 1,1-diborylalkanes.[7c]

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Base metal-catalyzed alkene hydroboration has recently been extended to iron. Ritter described in situ activation of (imino)pyridine iron dichloride complexes for the selective 1,4-hydroboration of various conjugated dienes with pinacolborane (HBPin).[8] During the preparation of this manuscript, Huang et al.[9] reported an evaluation of various iron(II) dichloride complexes activated with $NaBEt_3H$ for the hydroboration of 4-methyl-1-pentene with HBPin. Tridentate chelates such as terpyridine and the aryl-substituted bis(imino)pyridine, ^{iPr}PDI [2,6-(2,6-$^{i}Pr_2$-C_6H_3-N=CMe)$_2C_5H_3N$], produced encouraging yields of 9% and 61%, respectively, of the anti-Markovnikov boronate ester. Quantitative conversion to product was observed with an iron dichloride complex with an electron-rich bipyridyl-phosphine ligand, (^{tBu}PNN)$FeCl_2$, a pincer originally described by Milstein.[10] With both iron precursors, improved activity and selectivity as compared to precious metal catalysts were observed. Examination of the substrate scope established that terminal olefins with remote alkyl, tertiary amine, silyl, and alkoxy substituents were tolerated by the catalyst mixture. No hydroboration activity was observed with internal olefins such as *trans* 3-octene and cyclooctene, representing limitations with this generation of catalyst.

Previous studies from our laboratory have demonstrated that the bis(imino)pyridine iron dinitrogen complexes, (^{iPr}PDI)$Fe(N_2)_2$ and [(^{Mes}PDI)$Fe(N_2)]_2(\mu_2$-$N_2)$ (^{Mes}PDI = 2,6-(2,4,6-Me_3-C_6H_2-N=CMe)$_2C_5H_3N$)), are highly active catalysts for the hydrogenation[11] and hydrosilylation[12] of alkenes (Figure 1). Catalytic hydrosilylation proceeded with high anti-Markovnikov selectivity, and with internal olefins, addition of $PhSiH_3$ to *trans*-2-hexene furnished exclusively terminally silylated products.[11c,12] In general, the more sterically protected iron precursor, (^{iPr}PDI)$Fe(N_2)_2$, is more selective yet less active than the less hindered compound, [(^{Mes}PDI)$Fe(N_2)]_2(\mu_2$-$N_2)$. These results inspired the exploration of bis(imino)pyridine iron-catalyzed hydroborations, and here we describe highly selective catalysts for the anti-Markovnikov synthesis of alkylboronates. The reactions proceed with high activity without the need for organic solvent and expand the substrate scope of iron-catalyzed hydroboration. Advantages of the isolated iron precatalysts as compared to in situ generated species are also reported.

To compare the performance of (^{iPr}PDI)$Fe(N_2)_2$ and [(^{Mes}PDI)$Fe(N_2)]_2(\mu_2$-$N_2)$ to $NaBEt_3H$-activated (^{iPr}PDI)-$FeCl_2$ and (^{tBu}PNN)$FeCl_2$ methods, the hydroboration of 4-methyl-1-pentene with HBPin was examined. The conditions used were identical to those described by Huang et al. and employed a 2:1 ratio of alkene to HBPin.[9] To complete the series of in situ activated bis(imino)pyridine iron compounds,[13] catalytic hydroboration was also conducted with (^{Mes}PDI)$FeCl_2$ activated with $NaBEt_3H$. A modest 47% isolated yield of the anti-Markovnikov boronate ester was obtained. Other unidentified boron products also accompanied the catalytic hydroboration.

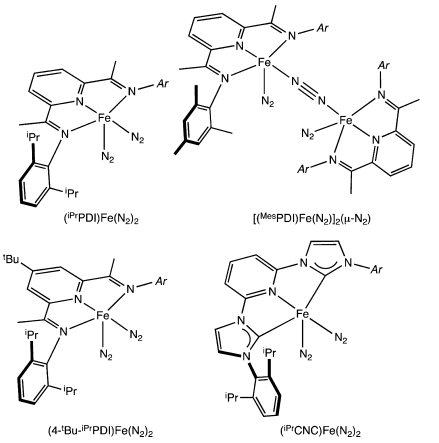

Figure 1. Bis(imino)pyridine iron dinitrogen compounds studied for catalytic alkene hydroboration.

The data reported in Table 1 establish that the isolated bis(imino)pyridine iron dinitrogen complexes proved superior to in situ activation of iron dichloride compounds with $NaBEt_3H$. This effect was previously reported by our laboratory in the context of iron-catalyzed [2 + 2] cycloaddition chemistry.[13] For example, using isolated (^{iPr}PDI)$Fe(N_2)_2$, an isolated yield of 87% of the boronate ester (entry 1) was obtained as compared to 61% using the in situ method[9] (entry 8). Comparable yields were obtained with [(^{Mes}PDI)$Fe(N_2)]_2(\mu_2$-$N_2)$ (entry 3) and (4-^{t}Bu-^{iPr}PDI)$Fe(N_2)_2$ (entry 5). With the isolated bis(imino)pyridine iron dinitrogen compounds, both THF and benzene solution reactions were explored. The identity of the solvent had little effect on the yields and selectivity of the catalytic hydroboration reactions with these precursors.

An iron dinitrogen complex, (^{iPr}CNC)$Fe(N_2)_2$ (^{iPr}CNC = 2,6-(2,6-$^{i}Pr_2$-C_6H_3-imidazole-2-ylidene)$_2$-C_5H_3N), where the imine methyl groups have been replaced by aryl-substituted *N*-heterocyclic carbenes, was also examined for catalytic hydroboration activity. This compound, originally reported by Danopoulos et al.,[14] exhibits improved activity over (^{iPr}PDI)$Fe(N_2)_2$ in catalytic alkene hydrogenation.[11a] For the catalytic hydroboration of 4-methyl-1-pentene in THF (entry 6), a 69% isolated yield of the boron-containing products was obtained. In this mixture, 30% of the products derived from dehydrogenative borylation while the remaining 70% of the material was the desired anti-Markovnikov

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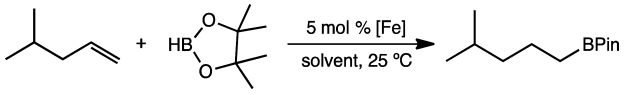
Table 1. Evaluation of Iron Precatalysts for Alkene Hydroboration



entry	[Fe][a]	solvent	yield [%][b]
1	(^{iPr}PDI)Fe(N_2)$_2$	THF	87
2	(^{iPr}PDI)Fe(N_2)$_2$	C_6H_6	86
3	[(^{Mes}PDI)Fe(N_2)]$_2$(μ_2-N_2)	THF	82
4	[(^{Mes}PDI)Fe(N_2)]$_2$(μ_2-N_2)	C_6H_6	78
5	(4-^{t}Bu-^{iPr}PDI)Fe(N_2)$_2$	THF	76
6	(^{iPr}CNC)Fe(N_2)$_2$	THF	69[d]
7	(^{iPr}CNC)Fe(N_2)$_2$	C_6H_6	81
8	(^{iPr}PDI)FeCl_2/NaBEt_3H[c]	THF	61
9	(^{Mes}PDI)FeCl_2/NaBEt_3H	THF	47
10	(^{tBu}PNN)FeCl_2/NaBEt_3H[c]	THF	>99

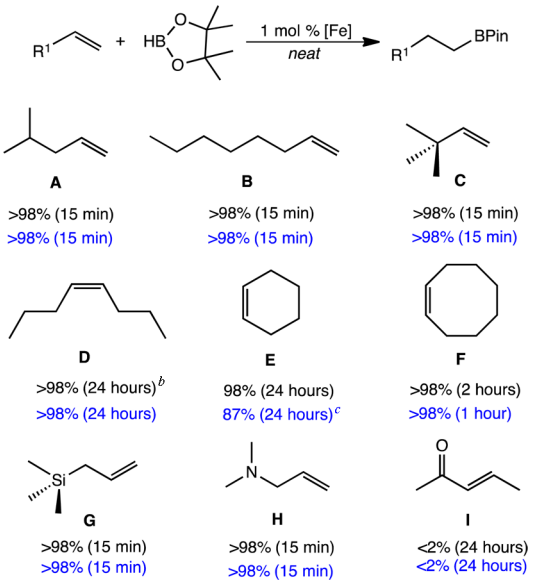
[a] Conditions: 0.5 mmol of HBPin, 1.0 mmol of 4-methyl-1-pentene, and 0.025 mmol of [Fe] compound in 2 mL of the specified solvent as reported in ref 9. [b] Isolated yield. [c] Data from ref 9. [d] Contains 30% of products derived from dehydrogenative borylation.

boronate ester. Notably, performing the catalytic reaction in benzene (entry 7) increased the isolated yield of boronate ester to 81% with no evidence for products derived from dehydrogenative borylation.

The results in Table 1 establish the benefits of the isolated bis(imino)pyridine iron dinitrogen precatalysts as compared to the in situ activation method. Accordingly, the scope of catalytic alkene hydroboration with both (^{iPr}PDI)Fe(N_2)$_2$ and [(^{Mes}PDI)Fe(N_2)]$_2$(μ_2-N_2) was further explored. Each reaction was conducted in a neat, equimolar mixture of alkene and HBpin with 1 mol % of the iron compound at 25 °C. A 1:1 stoichiometric ratio of olefin to borane contrasts the conditions reported by Huang[9] where excess alkene was used. Neat conditions were chosen to minimize waste and facilitate product isolation and because of previous studies in iron-catalyzed hydrosilylation, where highest activity and selectivity were achieved in the absence of solvent.[12b] As shown in Scheme 1, unactivated, unfunctionalized 1-alkenes **A**−**C** undergo facile bis(imino)pyridine iron-catalyzed hydroboration. With both iron precursors, complete (>98%) conversion to product was observed in 15 min. Similarly, isolated yields >90% were routinely obtained for this class of olefins. Introduction of a silyl (**G**) or a dimethyl amino-substituent (**H**) had little effect on the activity or selectivity of the iron catalysts, but we note no productive hydroboration was observed with enone (**I**).

The bis(imino)pyridine iron dinitrogen complexes also proved active for the catalytic hydroboration of internal alkenes. For *cis*-4-octene (**D**), (^{iPr}PDI)Fe(N_2)$_2$ reached >98% conversion in 24 h and furnished a mixture of 1- and 4-octylboronate products in a 5:1 ratio. Quantification of the ratio of products was accomplished by oxidation of the boronate ester with H_2O_2 followed by analysis of the resulting alcohols by ^{13}C NMR spectroscopy. With [(^{Mes}PDI)Fe(N_2)]$_2$(μ_2-N_2), selective and exclusive formation of the

Scheme 1. Iron-Catalyzed Hydroboration of Alkenes (**A**-**I**) with HBPin[a]



[a] Reaction conditions 1.2 mmol of HBPin, 1.2 mmol of alkene, 0.012 mmol (1 mol %) of [Fe] at 25 °C. Time given to reach the reported percent conversion. Values in black are for (^{iPr}PDI)Fe(N_2)$_2$; those in blue are for [(^{Mes}PDI)Fe(N_2)]$_2$(μ_2-N_2). [b] A 5:1 mixture of 1- and 4-octyl boronates were obtained. [c] Mixture of products obtained; see text.

1-octylboronate ester was observed after 24 h. This reactivity trend is in contrast to that reported previously in iron-catalyzed hydrogenation and hydrosilylation, where (^{iPr}PDI)Fe(N_2)$_2$ tends to be the more selective iron precursor.[11,12]

The cyclic olefins, cyclohexene (**E**) and cyclooctene (**F**), also readily undergo bis(imino)pyridine iron-catalyzed hydroboration. Complete conversion (>98%) to the cyclooctyl boronate ester was observed in 2 and 1 h with (^{iPr}PDI)Fe(N_2)$_2$ and [(^{Mes}PDI)Fe(N_2)]$_2$(μ_2-N_2), respectively. Hydroboration of cyclohexene (**E**) also proceeded to complete conversion in the presence of (^{iPr}PDI)Fe(N_2)$_2$ over the course of 24 h. With [(^{Mes}PDI)Fe(N_2)]$_2$(μ_2-N_2), the conversion was reduced to 87% over the same time course and products of hydroboration (59%), dehydrogenative borylation (24%), and hydrogenation (4%) were identified.

The selective anti-Markovnikov hydroboration of styrene has proven challenging for both precious and base metal catalysts.[9,15] In addition to poor regioselectivity, most catalysts also promote dehydrogenative borylation, which is accompanied by hydrogenation of the substrate to ethylbenzene. We do note that an iridium-catalyzed variant that proceeds with high activity and selectivity has been reported.[15e] In the presence of 1% (^{iPr}PDI)Fe(N_2)$_2$,

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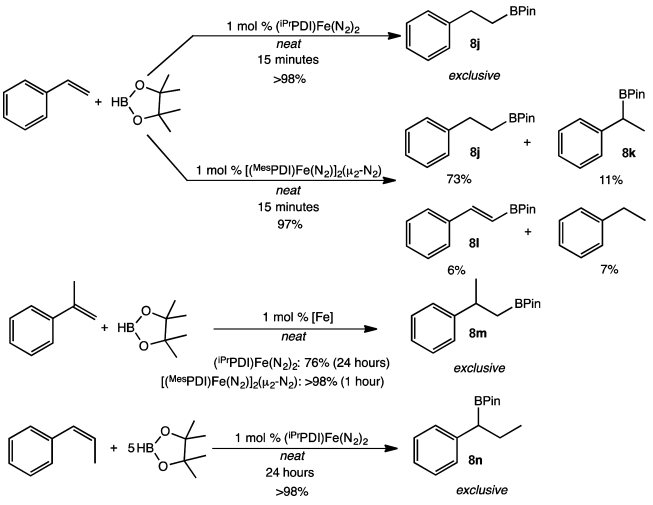
exclusive and quantitative formation of the anti-Markovnikov borylation product was observed after 15 min using neat conditions (Scheme 2). This result highlights one of the unique benefits of the bis(imino)pyridine iron catalyst, as no net dehydrogenative borylation was observed. With $[(^{Mes}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$, complete conversion was observed in 15 min although the selectivity was reduced. The anti-Markovnikov boronate ester, $PhCH_2CH_2BPin$, was the major product constituting 73% of the mixture. The minor products were identified as the phenylethyl boronate ester from Markovnikov hydroboration (11%), the styrenyl boronate ester from anti-Markovnikov dehydrogenative borylation (6%), and ethylbenzene (7%). These selectivities were unchanged if the hydroboration are conducted with 1 mol % iron precursor in benzene solution.

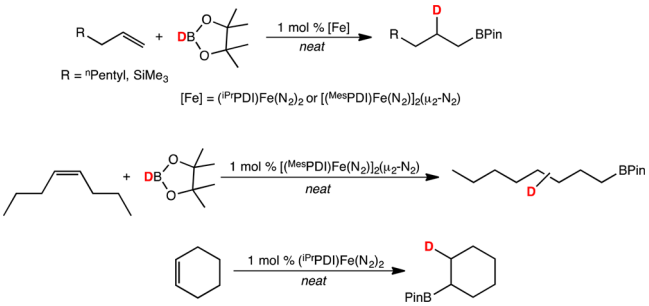
Scheme 2. Bis(imino)pyridine Iron-Catalyzed Hydroboration of Styrene Derivatives



The catalytic hydroborations of α- and *cis*-β-methyl styrene were also examined with $(^{iPr}PDI)Fe(N_2)_2$. For the geminal olefin, 76% conversion to exclusively the anti-Markovnikov product was observed after 24 h. In the case of *cis*-β-methyl styrene, complete (>98%) conversion was achieved after 24 h but required 5 equiv of HBPin. Notably, the 1-phenylpropyl boronate ester was formed exclusively as judged by NMR spectroscopy and GC-MS. The longer reaction times and requirement for excess borane highlight the reduced reactivity of the more substituted bis(imino)pyridine iron dinitrogen complex with hindered olefins. Perhaps more significantly, however, is the exclusive regioselectivity observed in both cases. In general, $(^{iPr}PDI)Fe(N_2)_2$-catalyzed hydroborations of various styrene derivatives are among the most regioselective in transition metal catalyzed reactions of this type.

Deuterium labeling studies were conducted to gain additional insight into the course of bis(imino)pyridine iron-catalyzed hydroboration. The results of these studies are presented in Scheme 3. Addition of DBPin to 1-octene in the presence of 1 mol % of either $(^{iPr}PDI)Fe(N_2)_2$ or

Scheme 3. Isotopic Labelling Studies for Bis(imino)pyridine Iron-Catalyzed Hydro(deutero)boration



$[(^{Mes}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ furnished the anti-Markovnikov octyl boronate ester with deuterium exclusively in the 2-position of the hydrocarbyl chain. The position of the deuterium was established by ^2H and quantitative ^{13}C NMR spectroscopy and demonstrates the chain running processes (alkyl isomerization) do not compete with B−H addition for terminal olefins. For 4-octene, deuteroboration in the presence of $[(^{Mes}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ placed deuterium in every position of the octyl chain as judged by ^2H NMR spectroscopy with the majority of the deuterium located on the C2−C5 carbons. This result demonstrates, along with the selectivity of the reaction, that chain running is fast and reversible relative to C−B bond formation at the terminal position. With cyclohexene and DBPin, exclusive 1,2-addition of the borane was observed in the presence of $(^{iPr}PDI)Fe(N_2)_2$, demonstrating that chain running is not competitive with catalytic turnover.

In summary, isolated bis(imino)pyridine iron dinitrogen complexes have been demonstrated to be highly active and selective precatalysts for hydroboration of a range of olefins. These precursors offer distinct advantages in substrate scope and selectivity over previously reported precious and base metal catalysts. Furthermore, the iron compounds reported herein are effective in the absence of organic solvents, thereby minimizing waste and facilitating product isolation. While the mechanism of these reactions is currently under scrutiny in our laboratory, our results clearly establish that well-defined iron precursors offer unique advantages in homogeneous catalysis.

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Supporting Information Available. Detailed experimental procedures and NMR spectra for all hydroboration products. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.