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Regulation of Iron-Catalyzed Olefin Hydroboration by Ligand Modifications at a Remote Site

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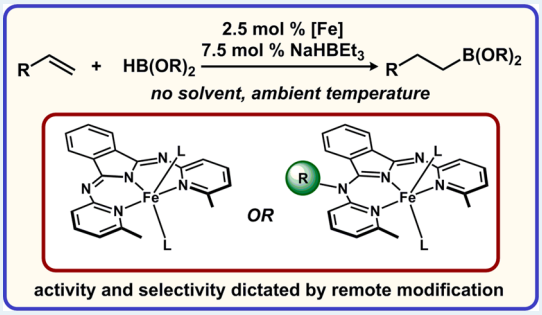
Supporting Information

ABSTRACT: An amide-derived *N,N,N*-Fe(II) complex catalyzes the hydroboration of alkenes at room temperature. Alkylation of a remote site on the ligand backbone was used as a late-stage modification to provide a more electrophilic complex as determined by electrochemical studies. The alkylated variant, compared to the parent complex, catalyzes olefin hydroboration with an increased reaction rate and exhibits distinct regioselectivity for internal alkene hydroboration.

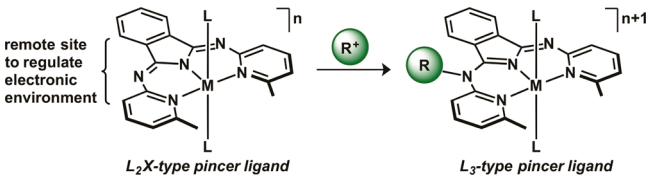


KEYWORDS: *alkylboronates, hydroboration, iron, ligand effects, homogeneous catalysis*

Regulation of catalysis by an applied chemical, electrochemical, or photochemical response is broadly used in biology,[1] yet these principles are not widely adapted in synthetic systems.[2,3] In some cases, modifications at a site far removed from a metal's active site can have dramatic effects on reactivity, substrate turnover, and importantly, can turn reactions on or off.[4] To mimic such functions, metal complexes containing redox active and/or proton-responsive ligands have been shown to work synergistically for selective bond activation and cooperative catalysis.[5,6] Many multifunctional complexes direct reactivity by presenting groups at a site proximal to a metal's primary coordination sphere.[7] Alternatively, a remote site removed from the primary coordination sphere environment can also serve to modify the electronic properties of a metal center without perturbing the primary coordination environment.[6a,8] Our group is working to evaluate how the precise structural, electronic, and cooperative modes of a metal's secondary coordination sphere can be used to regulate reactivity,[6f,9] and herein, we report a system where the ligand's donor properties can be tuned by modifying a remote site (Scheme 1).

We recently reported a series of ruthenium complexes containing an *N,N,N*-bMepi pincer ligand (bMepi = 1,3-bis(6′-methyl-2′-pyridylimino)isoindolate), which are precatalysts for the dehydrogenation of alcohols and amines.[10] The backbone of the isoindoline framework contains imine linkers whose lone pair can be engaged upon protonation.[11] Alternatively, alkylation or binding a Lewis acid to the imine may also be used to confer a more electrophilic metal environment to bias catalytic reactivity.

Scheme 1. Electronic Tunability of a Pincer Ligand via Backbone Alkylation



One class of reactions to test these reactivity concepts are hydrogenation[12] and/or hydrofunctionalization[13] reactions because the rate-limiting steps are largely influenced by electronics at the metal. In particular, transition-metal catalyzed olefin hydroboration is an atom-economical and selective methodology to generate alkyl boronate esters,[14] which are widely used as intermediates in organic synthesis.[15] Although this reaction has classically required expensive Rh or Ir catalysts,[14b,16] a few recent reports have shown that a select few low-valent Fe complexes can also catalyze olefin hydroboration.[17] In this Letter, we report the synthesis and characterization of Fe-bMepi complexes and showcase the ligand's electronic tunability by modifying a remote site within the secondary coordination sphere in order to control activity and selectivity in olefin hydroboration reactions.

The Fe(bMepi)Br complex[18] was synthesized using a similar methodology to that reported for bMepi-ligated Ru complexes recently reported by our laboratory.[10a] Addition of 1.05 equiv of the K(bMepi) to $FeBr_2$ over 17 h in THF solvent afforded the desired complex, Fe(bMepi)Br, as an orange solid in 83% yield (Figure 1). The ^{1}H NMR spectrum features six paramagnetically shifted resonances, which is consistent with

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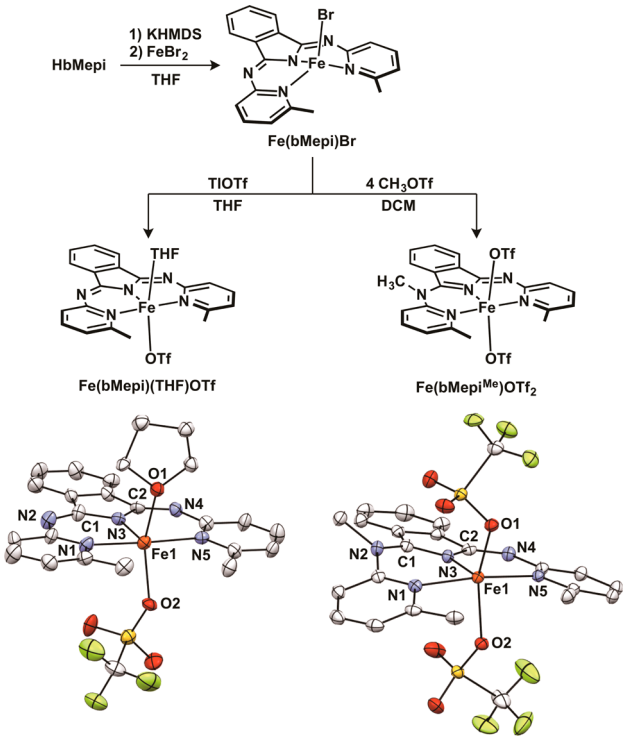


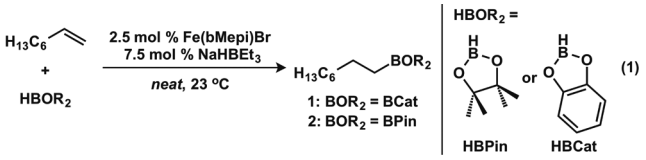
Figure 1. Synthesis of Fe(bMepi)(THF)OTf (left) and Fe(bMepi^{Me})-OTf_2 (right) with thermal ellipsoids depicted at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances for Fe(bMepi)(THF)OTf (Å): N2−C1 1.375(9), C1−N3 1.317(8). For Fe(bMepi^{Me})OTf_2: N2−C1 1.345(3), C1−N3 1.327(3), N3−C2 1.405(3), C2−N4 1.282(3).

symmetric binding of the ligand. Crystals suitable for single-crystal X-ray diffraction were obtained from vapor diffusion of pentane into a THF solution of Fe(bMepi)Br, and the solid-state structure reveals a distorted trigonal monopyramidal geometry around the Fe(II) center ($\tau' = 1.10$).[19] The solution magnetic moment of Fe(bMepi)Br is 5.1 μ_B, as assessed using the Evans method in CD_2Cl_2, which is consistent with a high spin, $S = 2$ molecule. The analogous OTf (OTf = CF_3SO_3) complex, Fe(bMepi)(THF)OTf, was isolated as a brown solid in 84% yield by allowing equimolar amounts of Fe(bMepi)Br and TlOTf to react in THF solvent for 2 h (Figure 1). ^{1}H NMR spectroscopy revealed six paramagnetically shifted resonances (μ_{eff} = 5.1 μ_B), distinct from those observed for Fe(bMepi)Br. A brown crystal of Fe(bMepi)(THF)OTf was subjected to an X-ray diffraction experiment, and the solid-state structure exposed a square-based pyramid geometry around the Fe(II) center ($\tau = 0.06$)[20] with a THF ligand *trans* to the triflate anion (Figure 1).

We next examined the viability of modifying the bMepi pincer scaffold by treatment with an electrophile, which we predicted would induce a change from an L_2X-type to an L_3-type ligand. When Fe(bMepi)Br was subjected to a Brønsted acid such as HOTf, a mixture of products was obtained, which is likely due to multiple reversible protonation events. In contrast, the addition of 4 equiv of MeOTf to a suspension of Fe(bMepi)Br in CH_2Cl_2 resulted in the clean conversion to Fe(bMepi^{Me})OTf_2 after 21 h, isolated in 86% yield as brown crystalline plates (Figure 1). The solid-state structure reveals a distorted square-based pyramid geometry about Fe ($\tau = 0.21$)[20] with an asymmetric neutral bMepiMe ligand meridionally coordinated with two *trans* triflate ligands. The asymmetry of the bMepi^{Me} ligand is retained in solution, confirmed by 13 distinct paramagnetically shifted resonances in the ^{1}H NMR spectrum, and the solution magnetic moment of 5.1 μ_B is consistent with a high spin $S = 2$ Fe(II) complex.

The electronic differences at the iron center imposed by bMepi and bMepi^{Me} were assessed by electrochemical studies. Differential pulse voltammetry was used to evaluate the reduction potentials cathodic of the open-circuit potential for the three Fe complexes at a Pt electrode in 0.1 M [^{n}Bu$_4$N]PF_6 in THF. The potentials for the first reduction event of Fe(bMepi)Br and Fe(bMepi)(THF)OTf are within 60 mV (−1.26 and −1.20 V vs SCE, respectively; Figure S1), which is consistent with similar ligand donor strength of Br^- and OTf^- ligands.[21] In contrast, Fe(bMepi^{Me})OTf_2 exhibits a reductive wave anodically shifted by 390 mV (−0.81 V vs SCE; Figure S2) from Fe(bMepi)(THF)OTf, suggesting that the bMepi^{Me} ligand furnishes a more stable reduced species.[22]

As quantified by electrochemical experiments, Fe(bMepi^{Me})-OTf_2 features a metal center that is more electrophilic than Fe(bMepi)(THF)OTf and thus easier to reduce. The difference in electrophilicity might be exploited by a catalytic hydrofunctionalization reaction whose rate-determining steps are perturbed by electronics at a metal site.[8a] We initiated studies by examining the hydroboration of 1-octene, a transformation most commonly performed with Rh or Ir complexes.[14b,16,23] When a vial containing Fe(bMepi)Br (2.5 mol %) in neat 1-octene (1.0 mmol) was charged with 2.0 mmol of catecholborane (HBCat) or pinacolborane (HBPin), $NaHBEt_3$ (7.5 mol %) and stirred at 23 °C for 20 h, the anti-Markovnikov hydroboration product (**1** and **2**) was isolated in 99% and 90% yield, respectively.[24]



In situ examination of the reaction mixture revealed no branched or dehydrogenative borylation products, determined by GC-MS, and control experiments showed that Fe(bMepi)Br and $NaHBEt_3$ were both required for catalysis.

In order to evaluate the catalytic competence of the electronically distinct iron complexes, as well as the generality of the hydroboration reaction, the reaction products of hydroboration mediated by both Fe(bMepi)(THF)OTf and Fe(bMepi^{Me})OTf_2 systems were assessed. Hydroboration reactivity with acyclic and cyclic olefins was investigated, and both were converted to the boronate ester as the sole product (Table 1). For instance, when either Fe(bMepi)(THF)OTf or Fe(bMepi^{Me})OTf_2 were used, the hydroboration of 1-octene afforded the corresponding anti-Markovnikov product **2** in high yields (88% and 91%, respectively). Furthermore, cyclooctyl boronate ester (**3**) was formed from cyclooctene (COE) in high isolated yields, 84% and 90% for Fe(bMepi)(THF)OTf and Fe(bMepi^{Me})OTf_2, respectively.[25]

Guided by the high selectivity for anti-Markovnikov hydroboration of aliphatic olefins, we examined whether regioselective hydroboration was possible with styrene, an activated alkene that has proven challenging for rhodium and iron catalysts.[14b,17b] When the hydroboration of styrene was performed with Fe(bMepi)(THF)OTf, the anti-Markovnikov hydroboration product was generated in 75% yield; however,

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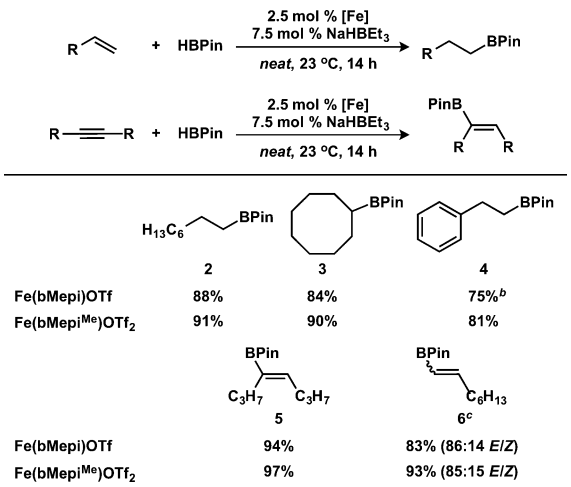
Table 1. Hydroboration of Unsaturated Hydrocarbons Catalyzed by Fe(bMepi)(THF)OTf or Fe(bMepi^{Me})OTf$_2$[a]



	2	3	4
Fe(bMepi)OTf	88%	84%	75%[b]
Fe(bMepi^{Me})OTf$_2$	91%	90%	81%

	5	6[c]
Fe(bMepi)OTf	94%	83% (86:14 *E*/*Z*)
Fe(bMepi^{Me})OTf$_2$	97%	93% (85:15 *E*/*Z*)

[a]Reaction conditions: substrate (1.0 mmol), HBPin (2.0 mmol), [Fe] (2.5 mol %), and $NaHBEt_3$ (7.5 mol %) were stirred at 23 °C for 14 h in a sealed vial under N_2. [b]Side products (11%) including dehydrogenative borylation and hydrogenation products were observed by ^{1}H NMR spectroscopy. [c]A mixture of products. Isolated yields are reported.

dehydrogenative borylation and hydrogenation products were also detected by ^{1}H NMR spectroscopy.[26] In contrast, **4** was obtained in 81% isolated yield as the *exclusive* product when using Fe(bMepi^{Me})OTf$_2$ under the same reaction conditions.

The hydroboration of internal and terminal alkynes also afforded high conversions of the corresponding vinyl boronate esters with stereoselectivity dependent on the substrate. For example, the conversion of 1-octyne to **6** proceeded with a regioselectivity of 86:14 and 85:15 *E*/*Z* for Fe(bMepi)(THF)OTf and Fe(bMepi^{Me})OTF$_2$ precatalysts, respectively. In contrast, when 4-octyne was used as the substrate, a single regioisomer (**5**) was formed in high yields (94% and 97%) when using either precatalyst.

In addition to the reaction regioselectivity, we evaluated the effect of the metal−ligand electronic environment on reaction rate. The rates of 1-octene hydroboration catalyzed by Fe(bMepi)Br, Fe(bMepi)(THF)OTf, and Fe(bMepi^{Me})OTf$_2$ were obtained by using the method of initial rates. The reaction rates for Fe(bMepi)Br (5.2(3) × 10^{-4} M/s) and Fe(bMepi)(THF)OTf (5.2(4) × 10^{-4} M/s) were identical, which is consistent with the similar reduction potentials, vide supra. Electron-deficient metal complexes can accelerate certain organometallic transformations including reductive elimination,[8a] which is a key step in catalytic hydroboration reactions. The reaction rate was significantly increased (>4×) when Fe(bMepi^{Me})OTf$_2$ (2.2(3) × 10^{-3} M/s; Figure S5) was used instead of Fe(bMepi)X (X = Br, OTf). Furthermore, an identical reaction rate (5.4(4) × 10^{-4} M/s) was obtained for Fe(bMepi)(THF)OTf when sodium naphthalenide was used as the reductant, which suggests that the alkylation state affects an elementary step within the catalytic cycle, rather than reduction to a low valent state. The enhancement of catalytic rates demonstrates the dramatic impact that may be realized through simple electronic modifications of a ligand's secondary coordination environment.

The synthesis of branched alkyl boronate esters using HBPin from acyclic internal olefins remains a limitation of metal-catalyzed hydroboration reactions,[14b,27] and only one iron catalyst has been reported for this transformation.[17c] During catalysis, chain walking is often fast and reversible, relative to C−B bond formation at the terminal position of an aliphatic acyclic substrate, which affords linear boronate esters.[17c,28] On the basis of the reaction rate enhancement observed for the hydroboration of 1-octene, we hypothesized that the hydroboration of an acyclic internal olefin catalyzed by Fe(bMepi^{Me})OTf$_2$ should yield branched hydroboration products due to acceleration of the rate-limiting reductive elimination step (Figure 2). Indeed, when *cis*-4-octene was subjected to

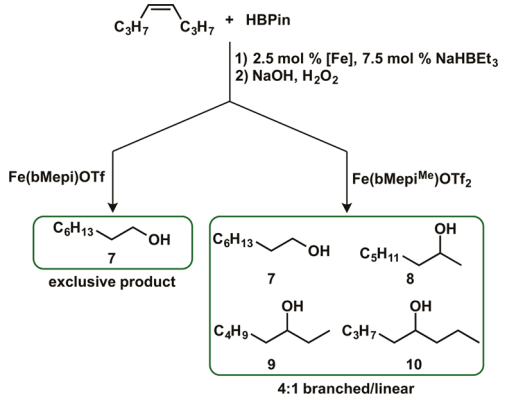


Figure 2. Selectivity of internal alkene hydroboration.

Fe(bMepi^{Me})OTf$_2$, a mixture of **7**, **8**, **9**, and **10** was isolated in a 4:1 ratio of branched to linear hydroboration products. In contrast, only the linear product (**7**) was obtained in when using Fe(bMepi)(THF)OTf. Hence, in addition to enhanced reaction rates, the regioselectivity of olefin hydroboration was also affected by tuning the electrophilicity of iron complexes from a remote site in the secondary coordination sphere.

Iron nanoparticles, formed from molecular Fe(II) precatalysts, have been implicated as the catalytically active species in several Fe-mediated reductive reactions.[29] Because catalyst structure/function reoptimization is predicated on the knowledge (or assumption) of active catalyst structure, the elucidation of catalyst nuclearity is critical. In contrast to irreproducible kinetic data often associated with heterogeneous catalysts, reproducible kinetic data has been observed from reactions catalyzed by homogeneous catalysts as well as nanoparticles.[30] We probed the active catalyst identity of Fe(bMepi^{Me})OTf$_2$ promoted 1-octene hydroboration to interrogate the nature of the observed catalysis. Although classic mercury poisoning experiments are an ineffective method of catalyst identification with iron catalysis,[29,31] substoichiometric ligand poisoning experiments are a simple and effective means of assessing whether a given precatalyst forms a catalyst of higher nuclearity.[32] Complete poisoning of catalysis was observed with 2 equiv of PMe_3 (Figure S6). In contrast, in the presence of 0.1 and 0.5 equiv of PMe_3, the product distribution remained unchanged. These results are inconsistent with a heterogeneous or nanoparticle system where low surface area aggregates are typically poisoned by ≪1 equiv ligand poison. Finally, in the absence of any poisoning reagent, nonsigmoidal reaction profiles and a lack of induction period are consistent with a homogeneous iron complex as the active catalytic species.

In conclusion, this work demonstrates the application of using a catalyst's secondary coordination environment to

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facilitate facile electronic modifications that can change reaction activity and selectivity. We have developed Fe-bMepi complexes capable of catalyzing the hydroboration of olefins and alkynes at room temperature. Although prior reports demonstrated iron-catalyzed olefin hydroboration, our systems are unique because they feature control over activity and regioselectivity by modifications at a remote site on the ligand backbone, which serve to tune the ligand's electronic environment. Of particular note, higher reaction rate and distinct regioselectivity were observed for olefin hydroboration when using the more electrophilic Fe(bMepi^{Me})OTf$_2$ complex. Because modification of the catalyst occurred at the last step, this late-stage functionalization strategy may be exploited as a general, highly modular protocol that may be adapted to other catalysts. Future efforts will further explore the impact of secondary coordination sphere interactions on transition-metal complexes as a means for improving the activity, stability, and selectivity of metal-based catalytic systems.

■ ASSOCIATED CONTENT

Supporting Information

The following files are available free of charge on the ACS Publications website at DOI: 10.1021/cs501820w.

Chemical characterization (CIF)

Experimental procedures and data (PDF)

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Notes

The authors declare no competing financial interest.

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