Organometallic Catalysis

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Iron-Catalyzed, Atom-Economical, Chemo- and Regioselective Alkene Hydroboration with Pinacolborane**

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Dedicated to Professor Maurice Brookhart on the occasion of his 70th birthday

Alkylboronic acid derivatives are now widely used as intermediates in organic synthesis.[1] For example, Suzuki–Miyaura reactions can efficiently couple C(sp^3) organoboron species with aryl and alkyl halides.[2] An advantage of alkylboronic acid derivatives over other common C(sp^3) organometallic nuclophiles is their unique stability: many of them can be readily isolated, purified, and even stored in air.[1a] There are several methods for the preparation of alkylboronic acid derivatives. One commonly used method involves the conversion of an alkylhalide into a lithium or Grignard reagent, followed by the reaction of the organometallic reagent with boron compounds.[3] However, the synthetic value of this method is limited, owing to poor functional-group compatibility and the formation of waste inorganic salts. Recently, Hartwig et al. have developed a Rh-catalyzed direct borylation of alkanes with B_2Pin_2 to form alkylboronate esters, albeit under relatively harsh reaction conditions.[4] More recently, Liu, Marder, Steel, and coworkers reported a convenient approach for the synthesis of alkylboronate esters through Cu-catalyzed borylation of alkyl halides.[5] However, the method requires the use of an excess of B_2Pin_2 as the borylation reagent, and waste inorganic salts were also generated.

Alternatively, alkylboronic acid derivatives can be prepared by Rh- or Ir-catalyzed alkene hydroborations.[1b,6] Although dialkylboranes add readily to alkenes, dialkoxyboranes react sluggishly with alkenes in the absence of catalyst. Metal-catalyzed alkene hydroboration is a synthetically useful method, because the reaction is highly atom economical and typically occurs under mild conditions. For example, the Wilkinson catalyst has been extensively used for the hydroboration of a wide range of alkenes.[6h–o] Unfortunately, side reactions such as dehydrogenative borylation and alkene hydrogenation, can compete with alkene hydroboration.[1b,6n,7] Another drawback is the low regioselectivity in the hydroboration of vinylarenes, especially with pinacolborane.[6g,j,k] Moreover, the catalytic performance of the Wilkinson complex is extremely sensitive to impurities and the reaction should be handled with extra care.[6l–n] In many cases relatively high loadings of expensive Rh and Ir catalysts were necessary for good conversion.[6g,l,n]

The low abundance, high cost, and environmental concerns over precious metals has motivated the investigation of earth-abundant and inexpensive base-metal alternatives in recent years.[8] Well-defined iron complexes have received tremendous attention over the past decade in the field of homogeneous catalysis.[9] Recently, Ritter et al. presented an iminopyridine iron catalyst for selective 1,4-hydroboration of 1,3-dienes.[10] However, to date the hydroboration of widely available and commercially relevant alkenes using iron catalyst has remained unknown. Herein, we report the synthesis of an electron-rich iron pincer complex and its application to the first example of iron-catalyzed alkene hydroborations. This system exhibits unprecedented high efficiency for selective α-olefin hydroborations using pinacolborane.

We commenced our studies by examining the known iron complexes for catalytic hydroboration of 4-methyl-1-pentene **1a** (2 equiv) with pinacolborane (HBPin). The results are summarized in Table 1. The Ritter complex (iminopyridine)-$FeCl_2$ **3** acts as a catalyst precursor for 1,3-diene hydroboration.[10] However, complex **3** (5 mol%), upon addition of $NaBHEt_3$ (15 mol%), did not effect α-olefin hydroboration (entry 1).[11] The reaction using $FeCl_2$ alone (5 mol%) or a combination of $FeCl_2$/2,2′-bipyridine (5 mol% each) in the presence of $NaBHEt_3$ also gave no hydroboration product (entries 2 and 3). Furthermore, iron complex **4**, which contains a bidentate PN ligand (see Table 1), was prepared (see Supporting Information). The reaction using **4** (5 mol%) as the precatalyst in THF at 25 °C gave the anti-Markovnikov hydroboration product **2a** in 5% yield after one hour (entry 4). Iron complexes of tridentate terpyridine and bis(imino)pyridine ligands have been successfully applied to alkene hydrogenation[12] and hydrosilylation.[12,13] Encouragingly, the reactions using (terpy)$FeCl_2$ **5** (5 mol%) and (^{iPr}PDI)$FeCl_2$ **6** (5 mol%) afforded **2a** in 9 and 61% yields, respectively (entries 5 and 6).

The above data suggest that the use of a tridentate ligands is essential for iron-catalyzed alkene hydroboration. We envisioned that catalyst development for this transformation would benefit from the use of a tridentate electron-donating phosphine ligand. Such a ligand would induce a less electrophilic iron center and may allow easy access to an olefin-ligated Fe^{II} boryl hydride species, which is a potential key intermediate in catalytic alkene hydroboration.[14] To this end,

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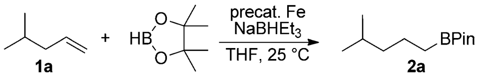
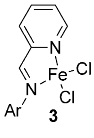
Table 1: Iron-catalyzed hydroboration of **1a** with HBPin.[a]



Entry	Precat.[b]	$NaBHEt_3$ [mol %]	*t* [min]	Yield [%][c]
1	**3**	15	60	<2
2	$FeCl_2$	15	60	<2
3	$FeCl_2$/bpy	15	60	<2
4	**4**	15	60	5
5	**5**	15	60	9
6	**6**	15	60	61
7	**7**	15	60	>99
8	**7**[d]	0.75	10	99
9	none	15	60	0
10	**7**	0	60	0
11	$[Rh(PPh_3)_3Cl]$	0	60	68[e]
12	$[\{Ir(cod)Cl\}_2]$/dppe	0	60	75

[a] Reaction conditions: HBPin (0.5 mmol) and **1a** (1 mmol) in THF (2 mL) at 25 °C. [b] Unless otherwise specified, 5 mol% of precatalyst was used. [c] Unless otherwise specified, yields of **2a** were determined by GC analysis using an internal standard. [d] 0.25 mol% of precatalyst was used. [e] Dehydrogenative borylation product (18%) was also observed. Yield was determined by ^1H NMR spectroscopy using an internal standard. Bpy = bipyridine, cod = 1,5-cyclooctadiene, dppe = 1,2-bis(diphenylphosphino)ethane.



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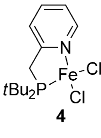

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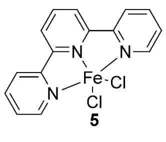

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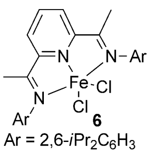

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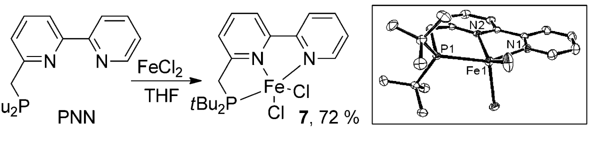
Ar = 2,6-$iPr_2C_6H_3$

we sought to develop an electron-rich iron complex with good thermostability by using a bipyridyl-based phosphine ligand (PNN).



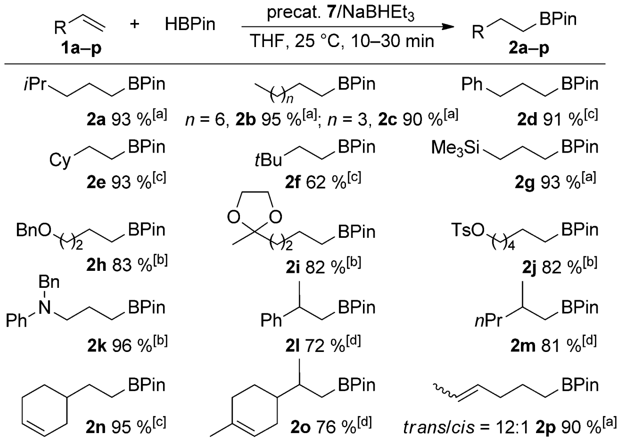
(1)

Treatment of the Milstein PNN ligand bearing phosphino-*tert*-butyl groups[15] with $FeCl_2$ in THF afforded iron pincer complex **7** in 72% yield [Eq. (1)]. The complex was characterized by ^1H NMR spectroscopy, elemental analysis, and single crystal X-ray diffraction. The solid structure of **7** reveals a distorted square pyramidal geometry around the metal center (see the Supporting Information).

Complex **7** was then tested as the precatalyst for alkene hydroboration. Gratifyingly, the reaction of **1a** with HBPin catalyzed by **7** (5 mol%) upon addition of $NaBHEt_3$ (15 mol%) in THF at 25 °C gave the anti-Markovnikov hydroboration product **2a** in quantitative yield in one hour (Table 1, entry 7). The system is so active that the amount of the precatalyst could be reduced to 0.25 mol% and the reaction still afforded 99% of **2a** in 10 min (entry 8). No branched or dehydrogenative borylation products were detected by GC/MS and ^1H NMR analysis. A control experiment without the precatalyst **7**, but with $NaBHEt_3$, gave no product **2a** (entry 9). The addition of $NaBHEt_3$ was necessary for catalysis (entry 10).

As a comparison, hydroboration of **1a** with the Wilkinson catalyst, $[Rh(PPh_3)_3Cl]$ (5 mol%), gave **2a** in only 68% yield after one hour (entry 11).[6g,k,16] Notably, the dehydrogenative borylation product (18%) was also detected by ^1H NMR and GC/MS analysis. Finally, a combination of $[\{Ir(cod)Cl\}_2]$/dppe (5 mol% of Ir and dppe; cod = 1,5-cyclooctadiene, dppe = 1,2-bis(diphenylphosphino)ethane) gave **2a** in 75% yield after one hour (entry 12).[6g] These results indicate that the PNN iron pincer complex is more efficient than the well-known Rh and Ir catalysts for α-olefin hydroboration with HBPin.

To evaluate the scope of the iron-catalyzed alkene hydroboration, the reactions of a variety of alkenes with HBPin were carried out using complex **7** as the precatalyst (Scheme 1). All reactions were selective for anti-Markovnikov hydroboration. The alkylboronate ester products are moisture- and air-stable, and can be readily purified by flash chromatography. Hydroborations of simple acyclic α-olefins **1a–c** (2 equiv)[17] with HBPin occurred within 10 min and formed products **2a–c** in 90–95% yields of isolated products. The substrates γ-phenylpropene (**2d**, 91%) and cyclohexylethene (**2e**, 93%) underwent hydroboration in useful yields. The hydroboration of the sterically demanding *tert*-butylethene afforded the product **2f** in relatively low yield (62%). The iron catalytic system is compatible with alkenes bearing various functional groups. Hydroborations of **1g–k** with HBPin afforded alkylpinacolboronates containing silyl (**2g**, 93%), ether (**2h**, 83%), acetal (**2i**, 82%), tosylate (**2j**, 82%), and amine (**2k**, 96%) functional groups. Furthermore, 1,1-disubstituted α-olefins, such as α-methylstyrene **1l** and 2-



Scheme 1. Iron-catalyzed hydroboration of alkenes (**1a–p**) with HBPin. Yields shown are of isolated products. Reaction conditions: HBPin (0.5 mmol) and alkenes **1a–p** (1 mmol) in THF (2 mL) at 25 °C. [a] With **7** (0.25 mol%) and $NaBHEt_3$ (0.75 mol%), 10 min. [b] With **7** (1 mol%) and $NaBHEt_3$ (3 mol%), 30 min. [c] With **7** (2 mol%) and $NaBHEt_3$ (6 mol%), 30 min. [d] With **7** (5 mol%) and $NaBHEt_3$ (15 mol%), 30 min. Bn = benzyl, Cy = cyclohexyl, Pin = pinacol, Ts = *p*-toluenesulfonyl.

methyl-1-pentene **1m**, were hydroborated to give **2l** and **2m** in 72 and 81 % isolated yields, respectively.

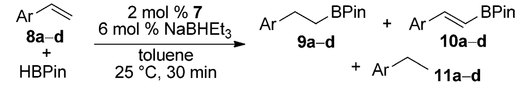
Notably, the PNN iron pincer system is inactive for hydroboration of internal alkenes, such as *trans*-3-octene and cyclooctene. The sensitivity of this catalytic system to steric effects enables the chemoselective hydroboration of a terminal alkene within a molecule containing multiple C=C bonds. For example, the hydroboration of the terminal olefin proceeded without hydroboration of the internal olefin in 4-vinyl-cyclohexene **1n**, to produce 95 % yield of isolated **2n**. The selective hydroboration of 1,1-disubstituted olefin in (±)-limonene afforded 76 % yield of isolated **2o**. Moreover, the reaction of 1,4-hexadiene **1p** (*trans*/*cis* = 12:1) gave 90 % yield of isolated **2p** (*trans*/*cis* = 12:1) without hydroboration or isomerization of the disubstituted olefin.

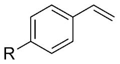
The iron-catalyzed chemoselective hydroboration of an α-olefin relative to 1,2-disubstituted olefin is remarkable. As a comparison, $[Rh(PPh_3)_3Cl]$-catalyzed (5 mol %) hydroboration of **1n** afforded six hydroboration products after one hour, including **2n** (51 %) and the products arising from internal olefin hydroboration (14 % total by-product yield; see the Supporting Information for product distributions). Furthermore, hydroboration of 1,4-hexadiene **1p** (*trans*/*cis* = 12:1) catalyzed by $[Rh(PPh_3)_3Cl]$ (5 mol %) gave *trans*-**2p** in only 5 % yield after one hour (10 % conversion of HBPin), together with multiple other hydroboration products. After 15 h, at least six hydroboration products, including *trans*-**2p** (51 %), were detected by GC/MS (see the Supporting Information). We attribute the poor chemoselectivity of the Rh-catalyzed alkene hydroboration to facile internal olefin hydroboration and olefin isomerization.

In contrast to the exclusive formation of hydroboration products in the reactions of alkene substrates **1a–p**, iron-catalyzed hydroboration of styrene **8a** (2 equiv) with HBPin in THF not only formed the linear hydroboration product **9a** (34 % yield), but also the dehydrogenative borylation product **10a** in 65 % yield after 30 min. Ethylbenzene **11a** (21 % yield relative to HBPin) formed by styrene hydrogenation was also obtained. It should be noted that dehydrogenative boration is a common side reaction accompanying metal-catalyzed vinylarene hydroboration with HBPin.[6k,7a,18]

The selectivity of iron-catalyzed styrene hydroboraion appeared to be solvent sensitive. With toluene as the solvent, the yield of the hydroboration product **9a** (51 %) was somewhat improved versus the reaction in THF (34 %), but the reaction still gave a moderate amount of **10a** (45 %) and **11a** (20 %) (Table 2). Similarly, reactions of 4-methylstyrene (**8b**), 4-methoxystyrene (**8c**), and 4-flourostyrene (**8d**) with HBPin in toluene gave a mixture of linear hydroboration products **9b–d**, dehydrogenative borylation products **10b–d**, and hydrogenation products **11b–d** (Table 2). No side product resulting from dehydrogenative borylation was detected when using acetonitrile as the solvent, although the reaction of styrene with HBPin gave the hydroboration product **9a** in only 5 % yield after 30 min.[19]

Table 2: Iron-catalyzed hydroboration of vinylarenes (**8a–d**) with HBPin.[a]

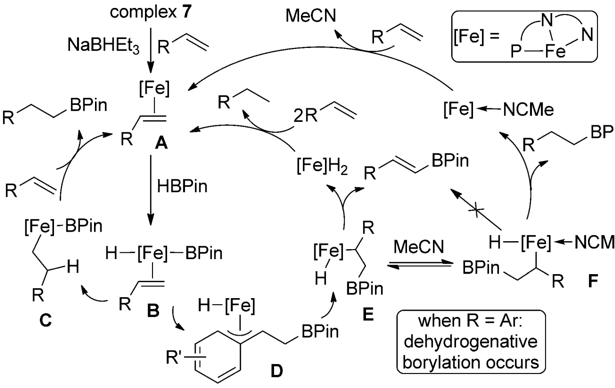


Entry		**9/10/11**[b] (no MeCN)	**9/10/11**[b] (20 mol % MeCN)	**9/10/11**[b] (40 mol % MeCN)
1	H, **8a**	51:45:20	86:–:–	78:–:–
2	Me, **8b**	52:41:21	95:–:–	83:–:–
3	MeO, **8c**	51:43:29	80:5:–	88:–:–
4	F, **8d**	39:55:17	82:10:–	81:–:–

[a] Reaction conditions: HBPin (0.5 mmol) and **8a–8d** (1 mmol) in toluene (2 mL) with complex **7** (2 mol %) and $NaBHEt_3$ (6 mol %) at 25 °C for 30 min. [b] Data shown are yields [%] relative to HBPin, and were determined by ^1H NMR spectroscopy using an internal standard.

We speculated that acetonitrile plays a role in inhibiting both the alkene hydroboration and dehydrogenative borylation processes, but the suppressing effect of acetonitrile on the latter is more significant. Indeed, in the presence of acetonitrile (20 mol %), reactions of styrene and 4-methylstyrene with HBPin in toluene exclusively formed linear boronate esters **9a** (86 %) and **9b** (95 %) after 30 min (Table 2, entries 1 and 2), whereas reactions of 4-methoxylstyrene and 4-fluorostyrene gave linear boronate esters as the major products (80 and 82 %, respectively) with the formation of a small amount of vinylboronate esters (5 and 10 %). To our delight, doubling the amount of acetonitrile (40 mol % relative to HBPin) resulted in the exclusive formation of the addition products **9c** (88 %) and **9d** (81 %; Table 2, entries 3 and 4).

On the basis of our preliminary data and precedent regarding related iron-catalyzed alkene addition processes, we propose the mechanism of iron-catalyzed alkene hydroborations shown in Scheme 2. Following the coordination of alkene to the iron center, oxidative addition of HBPin to **A** forms the formal 18 electron Fe^{II} boryl hydride species **B**, which is similar to those believed to be involved in alkene hydrogenation and hydrosilylation, and in 1,3-diene hydroboration and hydrosilylation catalyzed by iron complexes.[14] Terminal alkenes, except for vinylarenes, undergo selective 1,2-insertion into the Fe–H bond to form linear alkyl complex **C**.[6l,o] Reductive elimination then generates the anti-Markovnikov product.



Scheme 2. Proposed mechanism for the iron-catalyzed alkene hydroboration and dehydrogenative borylation reactions.

For vinylarenes without an α substituent, however, dehydrogenative borylation presumably proceeds by insertion of vinylarene into the Fe–B bond rather than the Fe–H bond in complex **B**;[6n,7b] this may be facilitated by the formation of η^3-benzyl Fe$^{\mathrm{II}}$ species **D** (Scheme 2).[20] The 18 electron complex **D** then undergoes an η^3–η^1 rearrangement to form η^1-benzyl Fe$^{\mathrm{II}}$ complex **E**, in which β-hydride elimination occurs to generate the vinylboronate ester. Both η^3-benzyl[21] and η^1-benzyl Fe complexes[21a,22] have been reported, and Wrighton et al. have demonstrated that the 18 electron Fe$^{\mathrm{II}}$ η^3-benzyl species could be in equilibrium with the 16 electron Fe$^{\mathrm{II}}$ η^1-benzyl species.[21a] For α-methylstyrene **1l**, the formation of the η^1-benzyl Fe$^{\mathrm{II}}$ complex **E** is presumably difficult owing to steric hindrance. Thus, the reaction of α-methylstyrene is unlikely to form vinylboronate, which is consistent with our experimental data (Scheme 1, **2l**). The observation that acetonitrile inhibits the dehydrogenative borylation process can be rationalized by the formation of a coordination-saturated species **F** through binding of the cyano group to the Fe center in **E**. Complex **F** lacks a vacant site for β-hydride elimination and thus would not give vinylboronate ester.

In summary, we have developed the first iron-catalyzed alkene hydroboration using an electron-rich PNN iron pincer complex as the precatalyst. The new iron system is far more efficient than known noble metal systems for catalytic α-olefin hydroborations with pinacolborane, and can be used to synthesize alkylboronate esters that would be difficult to access by other methods. Featuring a cost-effective and environmentally benign iron catalyst, 100% atom efficiency, mild reaction conditions, simple product isolation, and good functional group compatibility, this is a practical method for preparing synthetically important alkylboronic acid derivatives.

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[17] Reaction using only 1-nonene (1.05 equiv) with **7** (0.5 mol%) and $\mathrm{NaBHEt_3}$ (1 mol%) gave 83% yield of isolated **2b**.

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