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[(NHC)Fe(CO)$_4$] Efficient Pre-catalyst for Selective Hydroboration of Alkenes

Jianxia Zheng, Jean-Baptiste Sortais,* and Christophe Darcel*[a]

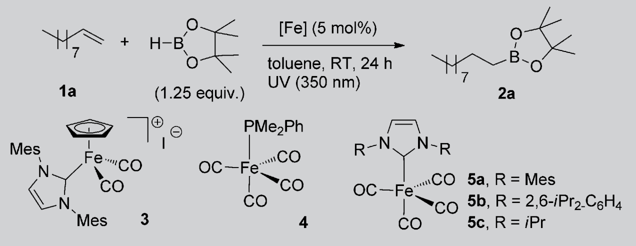
[(IMes)Fe(CO)$_4$] [IMes = 1,3-bis(2,4,6-trimethylphenyl) imidazol-2-ylidene] complex was found to be an efficient pre-catalyst for the hydroboration of functional alkenes in the presence of pinacolborane at room temperature. Notably, UV irradiation (350 nm) is important to promote this catalytic transformation. Interestingly, high chemo- and regioselectivities were observed as only anti-Markovnikov boronate derivatives were obtained and various functional groups can be tolerated.

Organometallic-catalyzed hydroelementation processes using transition metal complexes represent nowadays an efficient and greener approach for the introduction of heteroelements such as boron,[1] phosphorus,[2] and silicon[3] into unsaturated carbon-based structures. More precisely, in the field of transition metal catalyzed hydroboration, organoboronates have emerged as a significant class of organic reagents, owing to their good stability toward atmospheric oxidation, associated with their widespread use as synthons in selective transformations for carbon–carbon or carbon–heteroatom bond formation.[4] To perform such transformations, rhodium is usually the metal of choice.[5] On another hand, iron is an earth-abundant element and, therefore, is a sustainable, economical alternative source for developing new catalytic process. Iron has emerged as a powerful surrogate in transition metal catalysis,[6] in particular in hydrosilylation reactions.[7] By contrast, to promote hydroboration, borylation, and diborylation, iron complexes have been scarcely used. In a stoichiometric version, Hartwig[8] reported a pioneering activation of arenes leading to arylcatecholborane using the complex [CpFe(Bcat)(CO)$_2$] as the promoter. (cat = catechol) Then, Ritter described in 2010 the first iron catalyzed hydroboration of 1,3-dienes in the presence of pinacolborane (HBpin, pin = $O_2C_2Me_4$), using a catalyst generated from a well-defined [(iminopyridine)FeCl$_2$] complex in the presence of magnesium.[9] In 2011, Enthaler succeeded in hydroboration of alkynes using [Fe$_2$(CO)$_9$] complex as the catalyst yielding vinylboronate derivatives with high stereoselectivity.[10] Recently, Huang[11] and Chirik[12] reported in situ generated pincer iron catalysts, bis-*tert*-butylphosphino-methyl-2,2′-bypyridine iron(0) and bis(imino)pyridine iron dinitrogen, respectively, for efficient hydroboration of terminal and disubstituted alkenes.[13]

In the continuation of our investigation on iron-catalyzed transformations,[14] we report that the [(IMes)Fe(CO)$_4$] complex[15] catalyzed the hydroboration of olefins in the presence of pinacolborane at room temperature under UV irradiation at $\lambda = 350$ nm.

We started by investigating the hydroboration of 1-decene (**1a**) as the model substrate in the presence of pinacolborane (1.25 equiv) using several well defined known iron complexes as the catalyst (5 mol%) (Table 1). We have first selected [Fe(cod)(CO)$_3$] (cod = 1,5-cycloocta-diene) and [Fe(PBO)(CO)$_3$] (PBO = *trans*-4-phenylbut-3-en-2-one), which have shown excellent activities and selectivities for the hydrosilylation of carboxylic acids.[16] Unfortunately, either under thermal conditions (50 °C) or UV irradiation ($\lambda = 350$ nm at room temperature) after 24 h, disappointing yields of the hydroboration product

Table 1. Optimization of iron-catalyzed hydroboration of 1-decene with pinacolborane.[a]



Entry	Catalyst [mol %]	Conditions	Conv.[b] [%]	Yield **2a**[b] [%]
1	[Fe(cod)(CO)$_3$] (5)	RT, UV	97[d]	30
2	[Fe(cod)(CO)$_3$] (5)	50 °C[c]	97[d]	25
3	[Fe(PBO)(CO)$_3$] (5)	50 °C[c]	73	<5
4	[Fe$_2$(CO)$_9$] (5)	RT, UV	97[d]	30
5	**3** (5)	RT, UV	0	0
6	**4** (5)	RT, UV	97[d]	75
7	**5a** (5)	RT, UV	97[d]	80
8	**5a** (2.5)	RT, UV	97[d]	80
9	**5a** (5)	RT, UV[e]	97[d]	25
10	**5a** (5)	RT, UV[f]	97	94 (78[g])
11	**5b** (5)	RT, UV	97[d]	55
12	**5c** (5)	RT, UV	92[d]	40

[a] 1-decene (0.25 mmol), pinacolborane (0.313 mmol, 1.25 equiv), iron complex (0.013 mmol, 5 mol%), toluene (1 mL) under UV irradiation ($\lambda = 350$ nm) at RT for 24 h. [b] Conversion of the alkene and yield of borylated derivative **2a**, determined by ^{1}H NMR spectroscopy. [c] Reaction performed without UV irradiation at 50 °C. [d] The observed by-products are resulting from the isomerization of the terminal C=C bond. [e] Reaction performed in THF. [f] Reaction performed in neat conditions. [g] Isolated yield.

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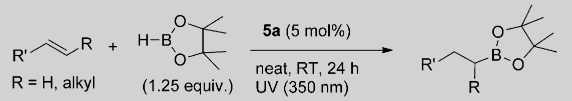
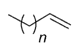
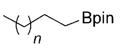
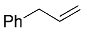
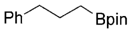
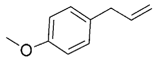
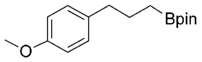
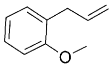
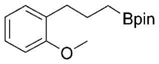
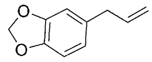
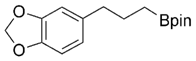
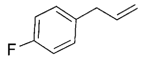
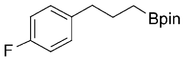
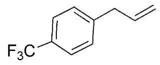
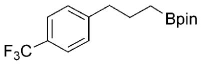
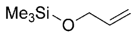
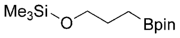
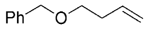
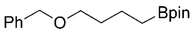
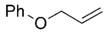
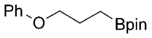
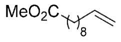
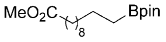
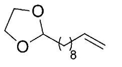
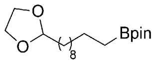
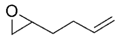
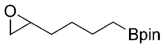
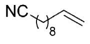
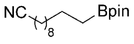
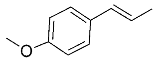
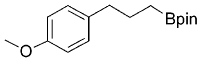
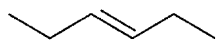
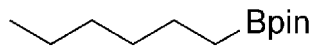
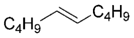
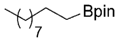
2a were observed with these catalysts even at full conversion, owing to the isomerization of the terminal alkene into a mixture of decenes (entries 1–3). Such isomerization of alkenes was not surprising as it has been already reported for iron carbonyl catalysts, such as [Fe(cod)$(CO)_3$][17] or $[Fe(CO)_5]$[18] under UV irradiation. The complex $[CpFe(CO)_2(IMes)][I]$ **3** acts as an efficient pre-catalyst for the hydrosilylation of aldehydes, ketones and amides.[14] However, under UV irradiation at room temperature for 24 h, no conversion occurred (entry 5). On the other hand, [(NHC)$Fe(CO)_4$] complexes were found to be active precatalyst for chemo-selective hydrosilylation of esters to aldehydes.[15a] First of all, with the complex bearing a phosphine, $[(PhMe_2P)Fe(CO)_4]$, the reactivity and the regioselectivity were enhanced as full conversion was obtained with the anti-Markovnikov boronate **2a** in 75% yield (entry 6). More significantly, the use of [(NHC)$Fe(CO)_4$] complexes as the pre-catalysts (5 mol%) in toluene gave higher yields than with the other complexes. [(IPr)$Fe(CO)_4$] **5b** and [(*i*Pr_2NHC)$Fe(CO)_4$] **5c** gave similar results: 55 and 40% of **2a**, respectively, in mixture with isomerized decenes (entries 11 and 12). Finally, the complex [(IMes)$Fe(CO)_4$] **5a** was found to be the best catalyst to perform the hydroboration of 1-decene with a full conversion and leading to the anti-Markovnikov boronate ester **2a** as the major product in 80% yield (entry 7). Notably, working with 2.5 mol% of **5a** as the catalyst led to similar result, whereas performing the reaction in THF instead of toluene had a deleterious effect as only 25% of **2a** was obtained under similar conditions (entries 8 and 9). Interestingly, in neat conditions, full conversion was observed and the boronate ester **2a** was obtained as the sole product in 74% isolated yield (entry 10).

With these optimized conditions in hand (5 mol% of **5a**, 1 equiv of alkene, 1.25 equiv of pinacolborane at room temperature for 24 h under UV irradiation at $\lambda = 350$ nm), we then studied the scope and limitations of this transformation with a special interest for functional group tolerance (Table 2). Firstly, non-functional linear terminal alkenes such as 1-hexene, 1-octene, and 3-phenyl-1-propene were selectively hydroborated and the corresponding anti-Markovnikov alkylboronate esters were isolated with 65-80% yields (Table 2, entries 1–4). Functionalized aryl substituted terminal olefins with fluoride, trifluoromethyl, methoxy or acetal can be also successfully hydroborated yielding the corresponding boronates with 43–72% yields (Entries 5–9). The olefins bearing ether moieties can be also hydroborated using pinacolborane: 3-trimethylsiloxy-1-propene and 3-benzyloxy-1-propene led to the derivatives **2j** and **2k** with satisfactory yields (58 and 62%, respectively (entries 10 and 11). Surprisingly, 3-phenoxy-1-propene, even if the conversion was full, the borylated compound **2l** was isolated with only 26% yield (entry 12). Interestingly, ester moiety can be tolerated under such conditions, the resulting compound **2m** being isolated with a moderate 52% yield (entry 13). It must be pointed out that in all the cases, the dehydrogenative borylation reaction led to less than 5% of side-product detected in the crude mixture.

α-Olefins containing an epoxide, an acetal, or a cyano group on the lateral chain are also hydroborated, but the corresponding boronate esters are isolated with lower yields (21–37%), mainly due to isomerization processes without hydroboration (entries 14–16).[19] Hydroboration of internal alkenes using [(IMes)$Fe(CO)_4$] as the catalyst (5 mol%) with pinacolborane is also possible. Starting from 1-(*p*-methoxyphenyl)prop-2-ene, 50% conversion was reached after 24 h at room temperature under UV irradiation ($\lambda = 350$ nm) leading to the 3-phenylpropylboronate ester **2e**, with 35% isolated yield, resulting from

Table 2. Scope of [(IMes)$Fe(CO)_4$]-catalyzed hydroboration of alkenes with pinacolborane.[a]

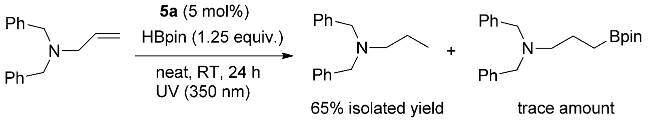


Entry	Alkene	Product		Conv[b] [%]	Yield[c] [%]
1			$n=7$, **2a**	97	80
2			$n=5$, **2b**	95	78
3			$n=3$, **2c**	95	66
4			**2d**	97	65
5			**2e**	97	71
6			**2f**	97	64
7			**2g**	97	72
8			**2h**	97	70
9			**2i**	97	43
10			**2j**	97	58
11			**2k**	97	62
12			**2l**	97	26[d]
13			**2m**	97	52
14			**2n**	97	37[e]
15			**2o**	97	32
16			**2p**	90	21[e]
17			**2e**	50	35
18			**2c**	97	50
19			**2a**	93	73

[a] alkene (0.5 mmol), pinacolborane (0.625 mmol, 1.25 equiv), [(IMes)$Fe(CO)_4$] **5a** (11.8 mg, 0.025 mmol, 5 mol%), under UV irradiation ($\lambda = 350$ nm) at room temperature for 24 h. [b] conversion determined by ^{1}H NMR spectroscopy. [c] Isolated yield after flash chromatography on silica. [d] Mixture of uncharacterized products and **2l** were observed. [e] Main of the by-products results from the isomerization of the olefins.

a tandem iron-catalyzed isomerization/hydroboration of the obtained terminal olefin. Similarly, using internal alkenes such as (3*E*)-hexene and (5*E*)-decene, 1-hexylboronate and 1-decylboronate esters **2c** and **2a** are obtained in 80 and 73 %, respectively (entries 18 and 19).

By contrast, when reacting 3-(dibenzylamino)prop-1-ene, the product resulting from the full reduction of the alkene, namely, dibenzylpropylamine was obtained in 65 % isolated yield, with low trace amount of hydroborated compound, which enlightens that hydroboration of vinyl-functionalized compounds seems to be difficult. (Scheme 1) We also note that under our conditions, the hydroboration of trisubstituted alkene such as 2-methylbut-2-ene was not observed.[20]



Scheme 1.

NMR studies were conducted to obtain insights into the mechanism of this iron-catalyzed hydroboration reaction. Similarly with the case of reaction with hydrosilane,[15a] the reaction of [(IMes)Fe(CO)$_4$] with 5 equiv of pinacolborane or catecholborane in C_6D_6 under UV irradiation at $\lambda = 350$ nm, for 3 h at room temperature, even if the conversion did not exceed 10 %, led to the formation of a new species which was identified in ^{1}H NMR as a singlet at $\delta = -9.04$ ppm and -8.91 ppm, respectively,[21,24] and in ^{11}B NMR with broad signals at $\delta = 47.8$ ppm and 50.2 ppm, respectively.[8a,22] These results imply that [(IMes)Fe(CO)$_3$(H)(BR$_2$)] [BR$_2$ = Bcat or Bpin) intermediates result from the oxidative addition of the B–H bond of the hydroboronate on to unsaturated [(IMes)Fe(CO)$_3$] species.[15a,23] Such data should indicate that in a first step the UV-assisted decoordination of a CO ligand was followed by the oxidative addition of the H-B(OR)$_2$ reagent leading to a plausible iron(hydride)-(boryl) intermediate.[25]

In conclusion, we have shown that [(IMes)Fe(CO)$_4$] complex can be an effective catalyst for hydroboration of alkenes at room temperature under UV irradiation at $\lambda = 350$ nm. Notably, the catalyst is well-suitable for the hydroboration of terminal alkenes leading to anti-Markovnikov boronate esters. In the case of internal olefins, a tandem isomerization/hydroboration permits to obtain the linear anti-Markovnikov products. More interestingly, the reaction can tolerate various functional groups such as ether, ester, silylether, epoxide, acetal, and nitrile, even if in some cases, yields are moderate.

Experimental Section

General procedure for the iron-catalyzed hydroboration reactions: A 10 mL oven dried Schlenk tube containing a stirring bar, was charged with [(IMes)Fe(CO)$_4$] (11.8 mg, 0.025 mmol). After purging with argon (argon-vacuum three cycles), alkene was added followed by HBpin (90 µL, 0.625 mmol). The reaction mixture was stirred at the room temperature for 5 min and then irradiated under UV ($\lambda = 350$ nm) for 24 h. At the end of the reaction, the crude reaction mixture was filtered through a plug of silica gel with CH_2Cl_2 as the eluent and the filtrate was evaporated and was then analyzed by ^{1}H NMR spectroscopy to determine the conversion. The residue was purified by column chromatography on silica using ethyl acetate-pentane mixture to achieve the desired product.

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Keywords: alkenes · alkylboronates · hydroboration · iron · pinacolborane

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