Olefin hydroboration catalyzed by an iron-borane complex†

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The well-defined iron(0) complex \([i^3\text{Pr DPB Ph }]\text{Fe}_2-\mu-1,2-\text{N}_2\] (A) reacts with HBpin to afford the complex \([i^3\text{H}_2-\text{H}_2\text{DPB}]\text{Fe}(\mu^3-\text{H}_2\text{Bpin})\] (B) via oxidative addition of the \(\text{H–B}\) bond. Complex A is an effective precatalyst for the hydroboration of a range of olefins in synthetically useful yields (typically >80%) under neat conditions.

Reduction of unsaturated carbon-carbon and carbon-heteroatom bonds by hydrofunctionalization is of paramount importance to the synthesis of pharmaceuticals and agrochemicals. Amongst the hydrofunctionalization reactions, hydroboration has proven to be a powerful reaction in the generation of value-added reagents for organic synthesis. This is in part due to the wide availability of boranes coupled with their high reactivity and selectivity towards unsaturated substrates. To date, many catalytic systems have been reported for hydroboration, with a large proportion being based on transition metals. However, it is Earth-abundant catalysts which are taking centre stage, exhibiting high levels of activity in the hydroboration of unsaturated \(\text{C–C}\) bonds. Of these metals, iron has proved to be popular in novel catalytic systems.

Arguably, the most common approach for iron-catalyzed olefin hydroboration is via the use of a neutral ligand in the presence of \(\text{Fe(II)}\) salts, and a catalytic amount of an activator, namely Grignard reagents or hydride additives. However, there are a limited number of reports which use molecular-defined low valent iron pre-catalysts. The Chirik group have reported that a bis(imino)pyridine iron dinitrogen complex (Fe1) was efficient for the hydroboration of terminal and disubstituted olefins with 1 mol% catalyst loading under neat conditions (Scheme 1a). The group of Darcel reported an efficient NHC-iron complex (Fe2) which facilitated the hydroboration of functionalized terminal olefins using HBpin with 5 mol% catalyst loading under photochemical conditions (Scheme 1b).

Metal-borane complexes are emerging as promising systems for cooperative catalysis. It has been recently demonstrated that late-first-row transition metal-borane complexes can readily facilitate well-defined two-electron chemistry. To date, catalysis using these systems is limited to a handful of examples, such as olefin hydrogenation (using Ni), and hydrosilylation of aldehydes and ketones (Co, Fe and Ni) all proceeding via addition of \(\text{E–H } (\text{E = H or Ph}_2\text{SiH})\) across the metal-borane interaction leading to the formation of a borohydrido-hydride species.

Motivated by this bifunctional reactivity and its untapped potential for realizing well-defined two-electron catalytic processes with iron, we sought to broaden the scope of catalytic transformations facilitated by iron-borane complexes, namely \([[(\text{i}^3\text{PrDPB})\text{Fe}]_2-\mu-1,2-\text{N}_2\] (A), which was first developed by Peters. Herein, we report the activation of the \(\text{B–H}\) bond in HBpin across the \(\text{Fe–B}\) core in complex A, and subsequent application in olefin hydroboration (Scheme 1c).

Scheme 1  
(a) and (b) Previous studies using well-defined iron complexes as catalysts for olefin hydroboration; (c) this work. DIPP = 2,6-diisopropylphenyl and Mes = 2,4,6-trimethylphenyl.
Firstly, a stoichiometric reaction between complex A and HBpin was conducted. Treatment of A with an excess of HBpin (6 equivalents) at 50 °C in benzene-\(d_6\) for 24 h afforded diamagnetic (\(S = 0\)) complex B in 85% isolated yield (Scheme 2a). When 20 equivalents of HBpin were added no rate enhancement was observed, with the same yield obtained after 24 hours. Complex B could be purified by silica gel column chromatography eluting with hexanes and exhibits good air-stability, with no decomposition observed after 7 days. The \(^1\)H NMR spectrum of complex B features two upfield proton resonances (\(\delta = -16.71\) ppm and \(-20.68\) ppm) corresponding to iron-hydride signals, which integrate in a 1:1 ratio with respect to each other (Fig. 1a). The hydride signal at \(-16.71\) ppm is comparable with reports by Wang and Song for \(\eta^3\)-H\(_2\)Bpin complexes.\(^15\) The \(^{31}\)P NMR spectrum displays a broad triplet at 98.1 ppm with \(J_{PH} = 17.8\) Hz. The \({}^{11}\)B NMR spectrum displays two resonances at \(\delta = 36.3\) ppm and \(47.9\) ppm, diagnostic of two chemically inequivalent boron centres. From \(^1\)H-\(^{11}\)B correlation spectroscopy, the proton resonance at \(\delta = -16.71\) ppm interacts exclusively with the boron resonance at \(\delta = 47.9\) ppm, whereas the resonance at \(\delta = -20.68\) ppm interacts exclusively with the boron resonance at \(\delta = 36.3\) ppm, indicating two discrete borohydride-type fragments. The \(^{13}\)B NMR resonance at \(\delta = 47.9\) ppm is in good agreement with that reported by Lin and Peters for a \(\eta^1\)-H\(_2\)BR\(_2\) hydroborate complex\(^16\) and the \(\delta = 36.3\) resonance is in good agreement with a recently reported \(\eta^3\)-H\(_2\)Bpin complex.\(^15\) Isotopic labelling studies using DBpin showed the corresponding deuterides in the \(^1\)H NMR spectrum at the same positions as hydride resonances in the \(^1\)H NMR spectrum. The infrared spectrum of complex B contains a broad and intense stretch at ca. 1900 cm\(^{-1}\) corresponding to a Fe–H–B fragment. As expected, when using DBpin, this stretching frequency is sensitive to the isotopic labelling (\(v_{Fe-D-B}\) ca. 1300 cm\(^{-1}\), see ESI†).\(^14\)

The solid-state structure of complex B was confirmed by single-crystal X-ray diffraction from crystals obtained by slow-evaporation from diethyl ether (Scheme 2b). Complex B adopts a distorted octahedral geometry with a P–Fe–P bond angle of 170.32°. The Fe–B1 distance of 2.082(2) Å and Fe–B2 distance of 2.037(2) Å lie within the reported range for Fe(II) hydridoborates.\(^15,17–20\) The B1–H distances in complex B are both 1.30 Å, whereas the B2–H bonds are slightly longer at 1.35 Å and 1.36 Å. Both sets of values are comparable with reported hydridoborate species of \(\eta^3\)-H\(_2\)Bpin and \(\eta^1\)-H\(_2\)BR\(_2\) fragments.\(^15,16\)

Complex B could presumably form via initial oxidative addition of HBpin by complex A, followed by reductive elimination of PhBpin (observed by NMR spectroscopy) to generate an iron(0) species. Analogous transformations have been reported with rhodium complexes bearing the same ligand framework.\(^21\) Oxidative addition of another equivalent of HBpin to the new Fe(0) species, followed by metathesis of the iron-boryl bond with HBpin, furnishes an iron(η)-hydride species. Finally, HBpin is captured and bonded to the Fe–H unit in the \(\eta^3\)-H\(_2\)Bpin mode, leading to complex B, an 18-valence electron complex. Further investigations into the formation of complex B are currently ongoing within our laboratory.

The stoichiometric treatment of complex B with vinyltrimethylsilane (1d) led to the formation of the desired alkylboronate ester 2d in 38% yield (Scheme 2c). When employed as a pre-catalyst (5 mol%), complex B gave none of the desired product. Using complex A as the catalyst (5 mol%), the intermolecular hydroboration of 1d with 1.1 equivalents of HBpin proceeded smoothly, giving the anti-Markownikov hydroboration product 2d in 83% yield, suggesting that complex A could be a suitable pre-catalyst for olefin hydroboration (Scheme 2d).

To examine the feasibility of A as a potential pre-catalyst for hydroboration, vinyltrimethylsilane (1d) was selected as the model substrate with HBpin as the terminal reductant. After
systematic evaluation of various reaction parameters (see ESI† for full optimization), the desired hydroboration product 2d was obtained in 98% yield (Table 1, entry 1), with 5 mol% complex A as the pre-catalyst, 1.1 equivalents of HBpin at 50 °C under neat conditions (Table 1, entry 1). With reduced catalyst loading the reaction took place, albeit with much lower yield (entry 2). In the absence of the iron catalyst, no reaction was observed (entry 3). Solvent effects were also explored. The solvent-free reaction gave superior yields, however non-polar solvents such as benzene or methylecyclohexane lead to a good yield of 2d whereas reactions in Lewis basic solvents such as diethyl ether led to lower yields (entries 4–6). Performing the reaction for shorter durations or lower temperatures lowered the product yield (entries 7 and 8). Finally, the reaction also proceeded when higher equivalents of HBpin were used, with little effect on the yield (entry 9).

With optimized conditions in hand (5 mol% of A, 1.0 equiv. of olefin, 1.1 equiv. of pinacolborane at 50 °C under neat conditions for 15 hours), we then turned our attention to the scope and limitations of this transformation (Scheme 3). Firstly, simple aliphatic terminal olefins such as 1-hexene, 1-octene and vinyl-cyclohexane were selectively hydroborated, furnishing the anti-Markovnikov alkylboronate esters (2a–c) in 83–96% yield. Simple vinyl silanes bearing either alkyl, aryl or alkoxy substituents (or a combination thereof) also underwent smooth hydroboration to the anti-Markovnikov products in good to excellent yields (2d–j). Styrene and a range of functionalized styrenes bearing electron donating groups such as methyl, methoxy or dimethylamino were successfully hydroborated to the corresponding alkylboronates in 76–97% yield (2k–q). Electron-deficient styrenes bearing fluorides or trifluoromethyl substituents were also well-tolerated (2r–t); however, when other halide (chloride or bromide) substituted styrenes were used, an intractable mixture of products was formed. Simple olefins bearing heterocycles, such as thiophene, could also be hydroborated in 78% yield (2u). From these results, it is evident that electronic effects of the substituents on the aryl ring have a slight effect, with more electron rich olefins undergoing hydroboration in slightly higher yields (2o vs. 2k vs. 2l). The effect of steric hindrance had little effect on the outcome of the reaction, although ortho-substituted styrenes delivered the olefin in slightly diminished yields when compared to the meta/para substituted styrenes (2l vs. 2m vs. 2n). Olefins bearing an epoxide on the lateral chain or 1,1-disubstituted olefins either gave an inseparable mixture or showed no reactivity with pinacolborane under optimized conditions.

Table 1 Selected reaction optimization with substrate 1d

<table>
<thead>
<tr>
<th>Entry</th>
<th>Deviation from standard conditions</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>2 mol% catalyst</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>Without complex A</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>Benzene as solvent</td>
<td>83</td>
</tr>
<tr>
<td>5</td>
<td>Methylcyclohexane as solvent</td>
<td>81</td>
</tr>
<tr>
<td>6</td>
<td>Diethyl ether as solvent</td>
<td>68</td>
</tr>
<tr>
<td>7</td>
<td>6 hours reaction time</td>
<td>45</td>
</tr>
<tr>
<td>8</td>
<td>Room temperature</td>
<td>9</td>
</tr>
<tr>
<td>9</td>
<td>1.5 equivalents of HBpin</td>
<td>95</td>
</tr>
</tbody>
</table>

a Conditions: 1d (0.205 mmol), HBpin (0.225 mmol), complex A (5 mol%) at 50 °C for 15 h. "isolated yields.

Scheme 3 Scope of olefin hydroboration.
the catalytic reaction, and indicates that the olefin insertion step is reversible and proceeds without selectivity.

In conclusion, complex A reacts with excess HBpin to generate \([\eta^3-H_2Dpb]Fe(\eta^3-H_2Bpin)\) (complex B) which has been characterised by multinuclear NMR, IR spectroscopy and single crystal X-ray diffraction. Complex A was also found to be a competent pre-catalyst for the hydroboration of a range of olefins leading to the anti-Markovnikov alkylboronates in good yields. We posit that the cooperative nature of the system herein is crucial for reactivity of the DPB-iron complexes, and this is something that we are exploring in our laboratory.

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Conflicts of interest

There are no conflicts to declare.

Notes and references


