The well-defined iron(0) complex \([[(\text{DPB})\text{Fe}_2(\mu-1,2-N_3)]\) (A) reacts with HBPin affords the complex \([(\text{DPB})\text{Fe}(\mu-H)\text{Fe}(\mu-B)\text{Pin}]_2\) via oxidative addition of the H-B bond. Complex A is an effective pre-catalyst for the hydroboration of a range of olefins in synthetically useful yields (typically >80%).

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 the generation of value-added reagents from organic synthesis. This is in part due to the wide availability of boranes and transition metals. However, it is Earth-abundant catalysts which are taking center stage, exhibiting high levels of activity in the hydroboration unsaturated C–C bonds. Of these, iron has proved to be a popular catalytic system.

Arguably, the most common approach for iron-catalyzed olefin hydroboration is via the use of a neutral ligand in the presence of 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 precatalysts. Notably, the Chirik group 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 E–H (E = H or Ph₂SiH) across the metal-borane interaction leading to the formation of a borohydrido-hydride species.

Interested 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 \([(\text{DPB})\text{Fe}_2(\mu-1,2-N_3)]\) (A).

**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.
Herein, we report the activation of the B–H bond in HBPin across the Fe–B core and subsequent application in olefin hydroboration (Scheme 1c).

First, a stoichiometric reaction between complex A and HBpin was conducted. Treatment of A with an excess of HBPin (6 equiv) at 50 °C in benzene–d6 for 24 hours afforded complex B in 85% isolated yield (Scheme 2a). The 1H NMR spectra of complex B features two upfield proton resonances corresponding to an iron-hydride signal. The broad resonance at -20.68 ppm corresponds to a bridging hydride, whereas the resonance at -16.71 ppm is a sharp singlet and as expected, these peaks integrate to a 1:1 ratio. The 31P{1H} NMR spectra displays a singlet at 98.1 ppm with no J_Hp coupling being resolved at room temperature, which is similar to a borohydrido-iron complex previously reported by Peters. Interestingly, the 11B{1H} NMR displays three resonances, two of which are sharpened, one which is slightly broad. All are relatively upfield, indicative of increased electron density at the boron center. Infra-red spectroscopy of Complex B shows a broad stretching frequency around 2000 cm⁻¹, indicative of the formation of a bridging hydride between the ligand boron and iron centers and a stretching frequency around 1000 cm⁻¹ which is indicative of an iron-boryl group. This spectroscopic data implies that complex B has the general formula [µ-HFe(BPin)]₂. The formation of this complex can be attributed to complex A undergoing an initial oxidative addition to generate the 14 electron [µ-HFe(BPin)]₂ species, and while this complex could be an important intermediate in the catalytic hydroboration reaction, the complex is too reactive to be isolated. This 14 electron complex, in the absence of any other reactant, has the possibility to react with a further equivalent of HBpin present in solution to furnish the 16 electron Fe(IV) complex B. Previously, the groups of Nakazawa and Akita have reported that thermal or photochemical reactions of CpFe(CO)₃R (R = Me, CH₂CH₂Ph) with R₂EH (E = Si, Ge, Sn) affords hydridooiron(IV) complexes bearing two group 14 ligands. To gain more information on stoichiometric reaction of complex A with HBPin, we further explored the effect of varying the amount of HBPin on the reaction via 1H NMR spectroscopy.

Increasing the amount of HBpin from 1 to 6 equivalents leads to a decrease in the characteristic signals (134 ppm and -76 ppm) of complex A, this is coupled with a concomitant increase in the 1H resonances at -16.71 and -20.68 ppm associated with complex B (Fig 1a). When this stoichiometric reaction was monitored as a function of time, (Figure 1b) using 6 equivalents of pinacolborane, it could be seen that after 2 hours, the formation of B is negligible, however characteristic signals for B starts to grow in around 6h with complete consumption of complex A seen after 12 hours reaction time. The stoichiometric treatment of complex B with vinyltrimethylsilane (1d) led to the formation of the desired alkylboronate ester 2d in 38% yield suggesting that this complex could be part of an active catalyst system. Using complex A as the catalyst (5 mol% of Fe), the intermolecular hydroboration of 1d with 1.1 equivalents of HBpin proceeded smoothly, giving the anti-Markovnikov hydroboration product 2d in 83% yield, suggesting that complex A could be a suitable pre-catalyst for olefin hydroboration (Scheme 2c).
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 SI for full optimization), the desired hydroboration product 2d was obtained in 98% yield (Table 1, entry 1), with 5 mol% complex A as the precatalyst, 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, running the reaction neat was superior to using solvents, however non-polar solvents such as benzene or methylcyclohexane lead to a good yield of 2d whereas the reaction in Lewis basic solvents, such as diethyl ether led to lower yield (entry 4).

With the optimized conditions in hand (5 mol% of A, 1.0 equiv of olein, 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. Firstly, simple aliphatic terminal olefins such as 1-hexene, 1-octene and vinylcyclohexane 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-0). 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).

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>19</td>
</tr>
<tr>
<td>3</td>
<td>w/o complex A</td>
<td>0</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>

**Scheme 3.** Scope of olefin hydroboration.

From these results, it is evident that electronic effects of the substituents on the aryl ring has a slight effect, with more electron rich olefins undergoing hydroboration in slightly higher yields (2o vs 2k vs 2t). The effect of steric hindrance had little effect on the outcome of the reaction, although, ortho-substituted styrenes did deliver the olefin in slightly diminished yields when compared to the meta/para substituted styrenes (2l vs 2m vs 2n). Unfortunately, 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 our optimized conditions.

**Scheme 4.** Hydroboration of p-acetoxystyrene.
Hydroboration of $p$-acetoxy styrene (1v) with 1 equivalent of HBpin led to a mixture of products containing the desired hydroboration product but also ester reduction was observed. However, running the reaction with an excess of HBpin (3 equivalents) led to the clean formation of 2v in 60% yield.

In conclusion, complex A undergoes B-H bond insertion to generate a new borohydride-Fe-boryl species (complex B) which has been studied by multinuclear NMR and IR spectroscopy. 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.

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Conflicts of interest
There are no conflicts to declare.

Notes and references