Check for updates

Olefin hydroboration catalyzed by an iron-borane complex†

Laura A. Grose and Darren Willcox ⓘ *

The well-defined iron(0) complex [(^{iPr}DPB^{Ph})Fe$_2$-(μ-1,2-N$_2$)] (A) reacts with HBpin to afford the complex [(η^3-H$_2$^{iPr}DPB)Fe(η^3-H$_2$Bpin)] (B) *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%) 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.[1] Amongst the hydrofunctionalization reactions, hydroboration has proven to be a powerful reaction in the generation of value-added reagents for organic synthesis.[2] 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.[2,3] However, it is Earth-abundant catalysts which are taking centre stage, exhibiting high levels of activity in the hydroboration of unsaturated C–C bonds.[4–8] Of these metals, iron has proved to be popular in novel catalytic systems.[9,10]

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.[11] 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).[12] 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).[13]

Department of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, UK. E-mail: darren.willcox@manchester.ac.uk

† Electronic supplementary information (ESI) available: Synthesis and spectral characterisation. CCDC 2260204. See DOI: https://doi.org/10.1039/d3cc00494e

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 Ph$_2$SiH) across the metal-borane interaction leading to the formation of a borohydrido-hydride species.[14]

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 [{(^{iPr}DPB^{Ph})Fe}$_2$(μ-1,2-N$_2$)] (**A**), which was first developed by Peters.[14f] Herein, we report the activation of the B–H bond in HBpin across the Fe–B core in complex **A**, and subsequent application in olefin hydroboration (Scheme 1c).
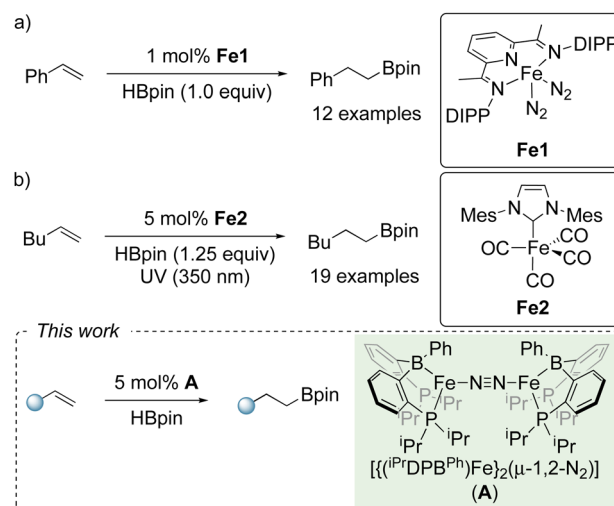
Scheme 1 (a) and (b) Previous studies using well-defined iron complexes as catalysts for olefin hydroboration; (c) this work. DIPP = 2,6-diisopropylphenyl and Mes = 2,4,6-trimethylphenyl.

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 η^3-H$_2$Bpin complexes.[15] The ^{31}P NMR spectrum displays a broad triplet at 98.1 ppm with $^2J_{PH} = 17.8$ Hz. The ^{11}B NMR spectrum displays two resonances at $\delta = 36.3$ ppm and $\delta = 47.9$ ppm, diagnostic of two chemically inequivalent boron centres. From ^{1}H-^{11}B correlation spectroscopy, the proton resonance at $\delta = -16.71$ ppm interacts only 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 ^{11}B NMR resonance at $\delta = 47.9$ ppm is in good agreement with that reported by Lin and Peters for a η^3-H$_2$BR$_2$ hydroborate complex,[16] and the $\delta = 36.3$ resonance is in good agreement with
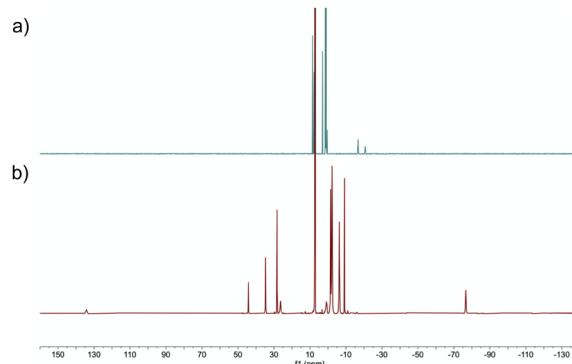

Fig. 1 ^{1}H NMR spectra of (a) complex **B** and (b) complex **A**.

a recently reported η^3-H$_2$Bpin complex.[15b] Isotopic labelling studies using DBpin showed the corresponding deuterides in the ^{2}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 (ν_{Fe-D-B} *ca.* 1300 cm^{-1}, see ESI†).[14f]
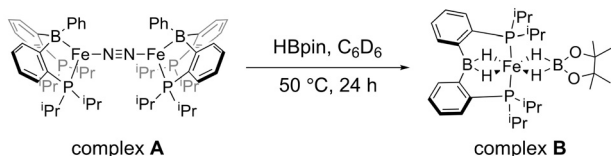
The solid-state structure of complex **B** was confirmed by single-crystal X-ray diffraction from crystals obtained by slow-evaporation from diethyl ether (Scheme 2b). Complex **B** adopts a distorted octahedral geometry with a P–Fe–P bond angle of 170.32°. The Fe–B1 distance of 2.082(2) Å and Fe–B2 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 η^3-H$_2$Bpin and η^3-H$_2$BR$_2$ fragments.[15a,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(II)-hydride species. Finally, HBpin is captured and bonded to the Fe–H unit in the η^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-Markovnikov 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
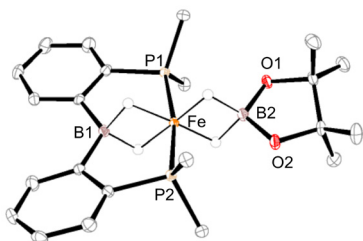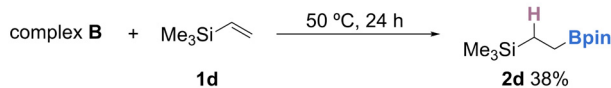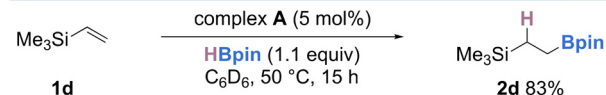

Scheme 2 (a) Stoichiometric reaction of complex **A** with HBpin. (b) solid state structure of complex **B** with selected atomic labelling; methyl groups and hydrogen atoms not bonded to Fe omitted for clarity, ellipsoids drawn at the 50% probability level. (c) stoichiometric reaction of **B** with olefin and (d) initial catalytic reaction.

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 methylcyclohexane 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.* **2t**). The effect of steric hindrance

Scheme 3 Scope of olefin hydroboration.

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.

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

To gain mechanistic insight into the catalytic hydroboration reaction using complex **A**, a deuterium labelling experiment was performed with DBpin. Using our optimized conditions for catalytic hydroboration of vinyltrimethylsilane, deuterium was incorporated into the desired alkylboronate ester product with a roughly 0.67 (D_{b}, $\delta = 0.85$ ppm) to 1 (D_{a}, $\delta = 0.68$ ppm) distribution of deuterium at the terminal and internal positions (Scheme 5). This observation is in accord with the presence of a borane-derived iron hydride/deuteride intermediate over the duration of

Table 1 Selected reaction optimization with substrate 1d[a]

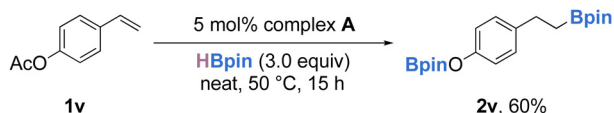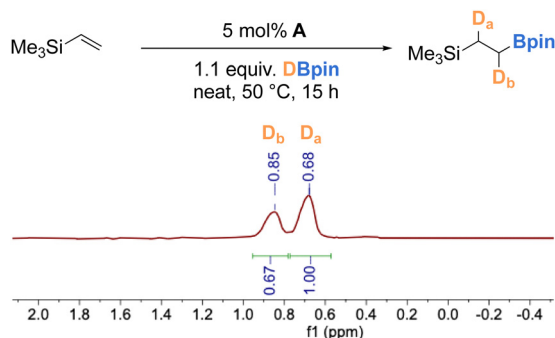| Entry	Deviation from standanrd conditions	Yield[b] (%)
1	None	98
2	2 mol% catalyst	19
3	Without complex **A**	0
4	Benzene as solvent	83
5	Methylcyclohexane as solvent	81
6	Diethyl ether as solvent	68
7	6 hours reaction time	45
8	Room temperature	9
9	1.5 equivalents of HBpin	95

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

Scheme 4 Hydroboration of p-acetoxystyrene.

Scheme 5 Deuterium labelling study to gain mechanistic insight into the catalytic reaction.

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 $[(\eta^3\text{-}H_2{}^{iPr}DPB)Fe(\eta^3\text{-}H_2Bpin)]$ (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.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 (a) *Hydrofunctionalization*, ed. V. P. Ananikov and M. Tanaka, Springer, Berlin, 2011; (b) J. Seyden-Penne, *Re-ductions by Alumino and Borohydrides in Organic Synthesis*, Wiley-VCH, New York, 2nd edn, 1997; (c) *Modern Reduction Methods*, ed. P. G. Andersson and I. J. Munslow, Wiley-VCH, Weinheim, 2008.
2 S. J. Geier, C. M. Vogels, J. A. Melanson and S. A. Westcott, *Chem. Soc. Rev.*, 2022, **51**, 8877–8922.
3 C. M. Vogels and S. A. Westcott, *Curr. Org. Chem.*, 2005, **9**, 687–699.
4 (a) *Catalysis without Precious Metals*, ed. Bullock, R. M., Wiley-VCH, Weinheim, 2010; (b) *Non-Noble Metal Catalysis: Molecular Approaches and Reactions*, ed. R. J. Klein-Gebbink, and M.-E. Moret, Wiley-VCH, Weinheim, 2019.
5 S. R. Tamang and M. Findlater, *Molecules*, 2019, **24**, 3194.
6 J. V. Obligacion and P. J. Chirik, *Nat. Rev. Chem.*, 2018, **2**, 15–34.
7 H. Yoshida, *ACS Catal.*, 2016, **6**, 1799–1811.
8 J. Chen, J. Guo and Z. Lu, *Chin. J. Chem.*, 2018, **36**, 1075–1109.
9 D. Wei and C. Darcel, *Chem. Rev.*, 2019, **119**, 2550–2610.
10 M. L. Shegavi and S. K. Bose, *Catal. Sci. Technol.*, 2019, **9**, 3307–3336.
11 (a) L. Zhang, D. Peng, X. Leng and Z. Huang, *Angew. Chem.*, 2013, **125**, 3764–3768; (b) M. D. Greenhalgh and S. P. Thomas, *Chem. Commun.*, 2013, **49**, 11230–11232; (c) R. Gilbert-Wilson, W.-Y. Chu and T. B. Rauchfuss, *Inorg. Chem.*, 2015, **54**, 5596–5603; (d) K.-N. T. Tseng, J. W. Kampf and N. K. Szymczak, *ACS Catal.*, 2015, **5**, 411–415; (e) M. Espinal-Viguri, C. R. Woof and R. L. Webster, *Chem. – Eur. J.*, 2016, **22**, 11605–11608; (f) T. Ogawa, A. J. Ruddy, O. L. Sydora, M. Stradiotto and L. Turculet, *Organometallics*, 2017, **36**, 417–423; (g) X. Chen, Z. Cheng and Z. Lu, *Org. Lett.*, 2017, **19**, 969–971; (h) A. J. MacNair, C. R. Millet, G. S. Nichol, A. Ironmonger and S. P. Thomas, *ACS Catal.*, 2016, **6**, 7217–7221; (i) J. Chen, T. Xi and Z. Lu, *Org. Lett.*, 2014, **16**, 6452–6455.
12 J. V. Obligacíon and P. J. Chirik, *Org. Lett.*, 2013, **15**, 2680–2683.
13 J. Zheng, J.-B. Sortais and C. Darcel, *ChemCatChem*, 2014, **6**, 763–766.
14 (a) W. Hill Harman and J. C. Peters, *J. Am. Chem. Soc.*, 2012, **134**, 5080–5082; (b) S. N. MacMillan, W. Hill Harman and J. C. Peters, *Chem. Sci.*, 2014, **5**, 590–597; (c) M. A. Nesbit, D. L. M. Suess and J. C. Peters, *Organometallics*, 2015, **34**, 4741–4752; (d) H. Fong, M.-E. Moret, Y. Lee and J. C. Peters, *Organometallics*, 2013, **10**, 3053–3062; (e) H. Fong and J. C. Peters, *Inorg. Chem.*, 2015, **11**, 5124–5134; (f) D. L. M. Suess and J. C. Peters, *J. Am. Chem. Soc.*, 2013, **135**, 4938–4941; (g) D. L. M. Suess and J. C. Peters, *J. Am. Chem. Soc.*, 2013, **135**, 12580–12583.
15 (a) R. Sun, W. H. Deng, B. Yu, Y. Lu, X. Zhai, R. Z. Liao, C.-H. Tung and W. Wang, *Organometallics*, 2022, **41**, 2504–2512; (b) Q. Liang, H. A. G. Mayerstein and D. Song, *Organometallics*, 2023, **42**(9), 816–824.
16 T.-Z. Lin and J. C. Peters, *J. Am. Chem. Soc.*, 2013, **135**, 15310–15313.
17 M. P. Mehn, S. D. Brown, T. K. Paine, W. W. Brennessel, C. J. Cramer, J. C. Peters and J. L. Que, *Dalton Trans.*, 2006, 1347–1351.
18 C. A. Ghilardi, P. Innocenti, S. Midollini and A. Orlandini, *J. Chem. Soc., Dalton Trans.*, 1985, 605–609.
19 R. Langer, M. A. Iron, L. Konstantinovski, Y. Diskin-Posner, G. Leitus, Y. Ben-David and D. Milstein, *Chem. – Eur. J.*, 2012, **18**, 7196–7209.
20 Y. Ohki, T. Hatanaka and K. Tatsumi, *J. Am. Chem. Soc.*, 2008, **130**, 17174–17186.
21 W.-C. Shih, W. Gu, M. C. MacInnis, D. E. Herbert and O. V. Ozerov, *Organometallics*, 2017, **36**, 1718–1726.