Metal-Free Dihydrogen Oxidation by a Borenium Cation: A Combined Electrochemical-Frustrated Lewis Pair Approach

Elliot J. Lawrence,[a] Thomas J. Herrington,[b] Andrew E. Ashley*[b] and Gregory G. Wildgoose*[a]

Abstract: *In order to use H_2 as a clean source of electricity, prohibitively rare and expensive precious metal electrocatalysts, such as Pt, are often used to overcome the large oxidative voltage required to convert H_2 into $2H^+$ and $2e^-$. Herein, we report a new, metal-free, approach to catalyze the oxidation of H_2 that combines the ability of frustrated Lewis pairs (FLPs) to heterolytically cleave H_2 with the in situ electrochemical oxidation of the resulting borohydride. The use of a N-heterocyclic carbene (NHC)-stabilized borenium cation, $[(I^iPr_2)(BC_8H_{14})]^+$ ($I^iPr_2 = C_3H_2(N^iPr)_2$), as the Lewis acidic component of the FLP is shown to decrease the voltage required for H_2 oxidation by 910 mV at inexpensive carbon electrodes – a significant energetic saving equivalent to 175.6 kJ mol^{-1}. The NHC-borenium Lewis acid also offers improved catalyst recyclability and chemical stability compared to $B(C_6F_5)_3$, the paradigm Lewis acid originally used to pioneer our combined electrochemical-frustrated Lewis pair approach.*

In the global effort to develop carbon-neutral, alternative energy economies, H_2 is often regarded as an attractive, clean fuel for the generation of electricity. However, in the absence of a suitable electrocatalyst, the electrochemical oxidation of H_2 to generate $2H^+$ and $2e^-$ requires a large oxidative voltage – the energetic "driving force" – in order to overcome the sluggish kinetics of this electrochemical process.[1] Conventional electrocatalyst materials typically use Pt or Pt-group metals (e.g. Pd, Ru, Rh) to significantly lower the voltage required for H_2 oxidation reactions to occur. However, the high cost and relative scarcity of these precious metals pose a significant economic barrier to their widespread use in a H_2-based energy economy.

Recently, we reported a new, metal-free approach to H_2 oxidation that combines the ability of frustrated Lewis pairs (FLPs) to activate H_2 with in situ electrochemistry, in order to convert H_2 into $2H^+$ and $2e^-$ at cheap and abundant carbon electrodes.[2] The chemical activation of H_2 using FLPs was first introduced by Stephan et al. in 2006.[3] They found that H_2 may be heterolytically cleaved by a suitable combination of a sterically encumbered Lewis acid/base pair.[3–5] Our initial approach was to couple the FLP activation of H_2 using, $^tBu_3P/B(C_6F_5)_3$, with the in situ electrochemical oxidation of the resulting $[HB(C_6F_5)_3]^-$ intermediate. This "combined electrochemical-frustrated Lewis pair approach" decreased the

voltage required to oxidize H_2 at a carbon electrode by 610 mV. However, a detailed mechanistic study of this particular system revealed several undesirable side reactions that prevented the electrocatalytic system from turning over.[2]
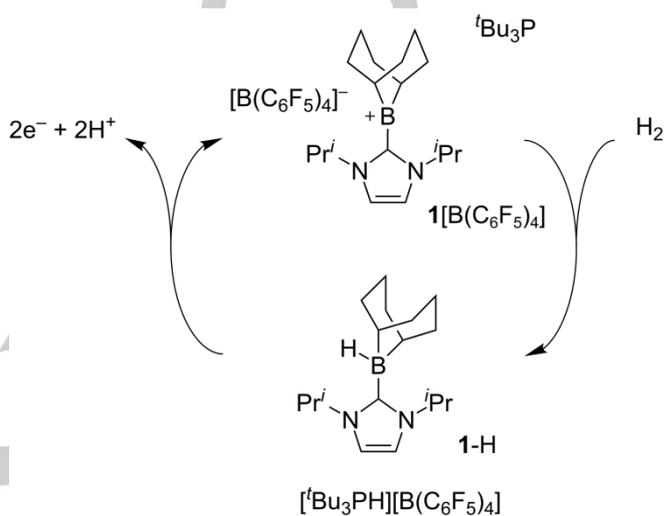
Scheme 1. Electrooxidation of the H_2-activated $^tBu_3P/\mathbf{1}[B(C_6F_5)_4]$ frustrated Lewis pair (FLP) results in the electrochemical generation of two protons and two electrons.

In this report we extend our "combined electrochemical-FLP approach" beyond simple arylborane Lewis acid catalysts, to the *N*-heterocyclic carbene (NHC) stabilized borenium cation $[(I^iPr_2)(BC_8H_{14})]^+$, ($\mathbf{1}^+$ in Scheme 1; $I^iPr_2 = C_3H_2(N^iPr)_2$). The ability of $\mathbf{1}^+$ to activate H_2, when combined with Lewis base $^tBu_3P$, has previously been reported and the lack of electron-withdrawing groups in $\mathbf{1}^+$ imparts considerable hydridic character to the neutral NHC-borane adducts, even in comparison with *anionic* borohydrides such as $[HB(C_6F_5)_3]^-$.[6,7] Indeed, $B(C_6F_5)_3$ is capable of abstracting H^- from $\mathbf{1}$-H to give the salt $\mathbf{1}[HB(C_6F_5)_3]$.[6] In addition, the bond dissociation energy of the B–H bond is weakened by the coordination of a carbene ligand.[8,9] As we demonstrate herein, these properties combine to improve the chemical stability of borenium Lewis acid catalysts towards unwanted side reactions (e.g. reaction with the solvent) and further decrease the voltage required to oxidize H_2 at a carbon electrode by 910 mV (equivalent to 175.6 kJ mol^{-1}).

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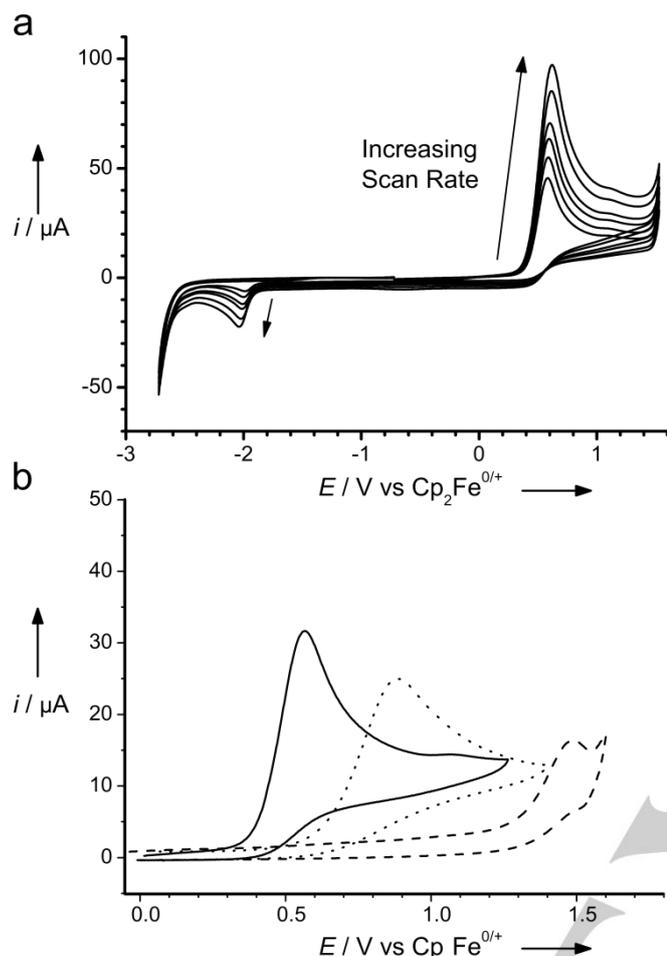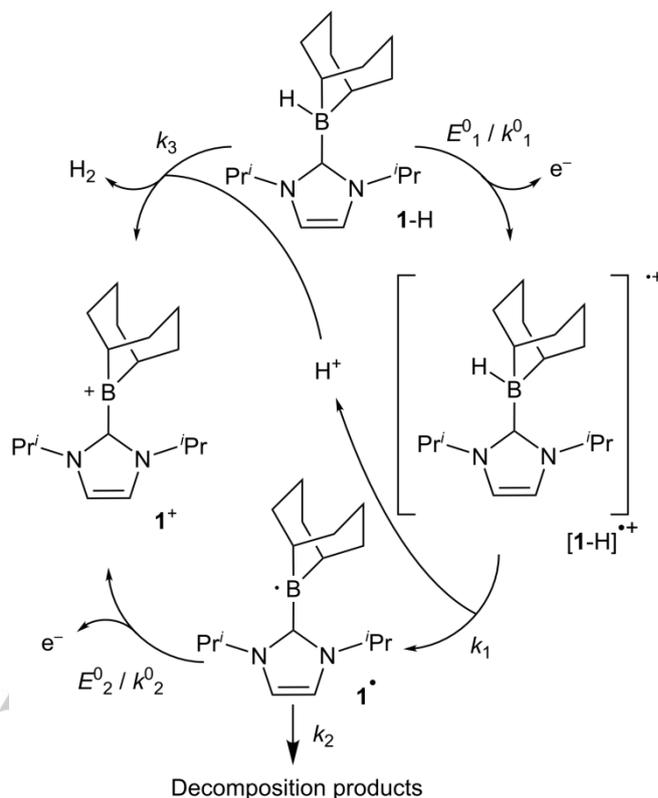   E-mail: a.ashley@imperial.ac.uk

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Figure 1. a) Overlaid cyclic voltammograms showing the complete potential window for **1**-H (2.0 mM, CH$_2$Cl$_2$) over the voltage scan rate range 200-1000 mV s^{-1}. b) Cyclic voltammograms comparing the oxidation potentials of **1**-H (solid line, 2.0 mM), [HB(C$_6$F$_5$)$_3$]$^-$ (dotted line, 2.0 mM), H$_2$ (dashed line, 2.0 mM) in CH$_2$Cl$_2$ at voltage scan rates of 100 mV s^{-1}.

Scheme 2. The proposed mechanism and associated thermodynamic and kinetic parameters used in digital simulation of the voltammetric oxidation of **1**-H at a GCE.

1-H was prepared according to the method of Farrell et. al.[6] and its redox properties were explored using cyclic voltammetry. A single oxidation wave was observed at +0.58 ± 0.01 V vs Cp$_2$Fe$^{0/+}$ (Figure 1) with no corresponding reduction wave at scan rates up to 5 Vs^{-1}. The observed voltammetric behavior of **1**-H is very similar to that of [HB(C$_6$F$_5$)$_3$]$^{-[2]}$ (Figure 1b) and therefore we propose the mechanism shown in Scheme 2 to account for the observed voltammetry: upon the application of an oxidizing potential **1**-H undergoes a one-electron oxidation to form a transient [**1**-H]$^{•+}$ species. This then undergoes rapid dissociation in solution to give H$^+$ and a neutral radical, **1**$^•$. Since the applied potential is very positive of the formal potential for the **1**$^+$/**1**$^•$ couple (see below), this radical undergoes a second one-electron oxidation to generate **1**$^+$. This second oxidation occurs in competition with side reactions: i) the decomposition of **1**$^•$ by the solvent; ii) the reaction between electrogenerated H$^+$, and a second incoming molecule of **1**-H to regenerate **1**$^+$ and H$_2$ (see below).

On the reverse scan (Figure 1a) a smaller, irreversible reduction wave was observed at −1.97 ± 0.01 V vs Cp$_2$Fe$^{0/+}$. This corresponds to the one-electron reduction of electrogenerated **1**$^+$, and was confirmed independently by performing cyclic voltammetry on an authentic sample of [**1**][B(C$_6$F$_5$)$_4$] (SI Figure 1). It is worth noting that the reduction of **1**$^+$ occurs 150 mV more negative than that of the archetypal Lewis acid B(C$_6$F$_5$)$_3$.[10] This suggests that **1**$^+$ is significantly less electrophilic than B(C$_6$F$_5$)$_3$, and accounts for the increased hydricity (and lower oxidation potential) of **1**-H compared to [HB(C$_6$F$_5$)$_3$]$^-$. The reduction of **1**$^+$ to form **1**$^•$ is irreversible at all scan rates up to 5 Vs^{-1}. This is due to the rapid decomposition of **1**$^•$ in solution to form a mixture of various redox-inactive, four-coordinate borates. This presumably occurs in an analogous manner to the solvent-specific decomposition of the boron-centered radical anion, [B(C$_6$F$_5$)$_3$]$^{•-}$,[10] since one would expect the unpaired electron in **1**$^•$ to be localized in a B–C π-bonding orbital with notable polarization towards the boron atom – similar to the previously reported NHC-boryl radical, [(C$_3$H$_2$(NMe)$_2$)BMes$_2$]$^{•}$.[11–13] However, the reduction wave (and hence the concentration) of electrogenerated **1**$^+$ arising from the oxidation of **1**-H is much larger than that observed in the B(C$_6$F$_5$)$_3$/[HB(C$_6$F$_5$)$_3$]$^-$ system.[2]

Treatment of **1**-H with one equivalent of Jutzi's strong acid, [H(OEt$_2$)$_2$][B(C$_6$F$_5$)$_4$],[14] resulted in the quantitative conversion of **1**-H to **1**[B(C$_6$F$_5$)$_4$]. This confirms the protolytic side-reaction between electrogenerated H$^+$ and **1**-H. This is in stark contrast to

the corresponding reaction of $[HB(C_6F_5)_3]^-$ with H^+, where neither the free Lewis acid, $B(C_6F_5)_3$, nor the etherate adduct, $Et_2O\cdot B(C_6F_5)_3$, were found to be present.[2] This result, together with the observation of significant amounts of electrogenerated **1**$^+$ in the voltammetry of **1**-H, suggests that Lewis acid **1**$^+$ has a markedly improved stability towards H^+ compared to $B(C_6F_5)_3$.

Digital simulation of the cyclic voltammetric data for the oxidation of **1**-H was undertaken in order to extract pertinent mechanistic, thermodynamic and kinetic parameters (See SI for further details). The experimental and simulated cyclic voltammograms were found to be in very good agreement (Figure 2) when simulated according to the mechanism proposed in Scheme 2.
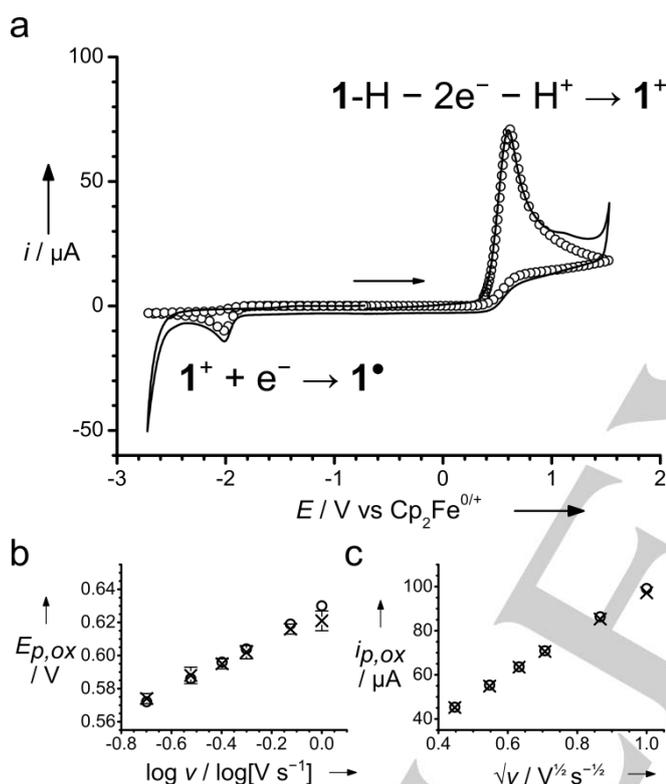

Figure 2. a) Simulated (circles) and experimental (line) cyclic voltammograms showing the full potential window for **1**-H (2.0 mM, CH_2Cl_2) at a voltage scan rate (v) of 500 mV s^{-1}. Comparisons between experimental and simulated data showing the quality of fitting for: b) the oxidative peak potential ($E_{p,\ ox}$) vs the logarithm of voltage scan rate (v); c) the oxidative peak current ($i_{p,\ ox}$) vs the square root of voltage scan rate (v).

Comparing the results of our digital simulations for the **1**-H/**1**$^+$ system to the $[HB(C_6F_5)_3]^-/B(C_6F_5)_3$ system reported previously,[2] three observations are apparent: i) the rate of oxidation of **1**-H is ca. forty times greater than for $[HB(C_6F_5)_3]^-$, leading to larger oxidative currents (see Figure 1b); ii) The oxidation of **1**-H occurs at *ca.* 300 mV lower potential than for $[HB(C_6F_5)_3]^-$, corresponding to a *significantly* large net decrease in the potential required to oxidize H_2 at a glassy carbon electrode of 910 mV (see Figure 1b.); iii) the rate of unwanted protonation of **1**-H by electrogenerated H^+ to generate **1**$^+$ and H_2 (k_3) is 3×10^5 times slower than in the $[HB(C_6F_5)_3]^-$ system. Indeed, simulation reveals that only 30-40% of **1**$^+$ that is reduced

at the electrode surface is generated via this undesirable protolytic H_2 regeneration process, with the majority of **1**$^+$ being generated through the two-electron oxidation of **1**-H. This, combined with the greater chemical stability of **1**$^+$ towards unsolvated H^+, demonstrates a significant improvement over the previous $[HB(C_6F_5)_3]^-/B(C_6F_5)_3$ system.[2]

Encouraged by these findings, we next investigated the application of **1**$^+$ towards in situ H_2 oxidation using a combined electrochemical-FLP approach and, importantly, whether this system could then be subsequently cycled. H_2 was admitted to a 1:1 solution of $[\mathbf{1}][B(C_6F_5)_4]$:$^tBu_3P$ in CH_2Cl_2 containing $[^nBu_4N][B(C_6F_5)_4]$ electrolyte. The reaction mixture was then left to stir in a sealed flask overnight to allow H_2 cleavage by the FLP to go to completion. The resulting solution containing **1**-H (as identified from an initial cyclic voltammogram of the solution) and $[^tBu_3PH][B(C_6F_5)_4]$ was then subjected to bulk electrolysis, holding the electrode at the oxidation potential of **1**-H until complete conversion was achieved. Afterwards, an aliquot of $^tBu_3P$ (equimolar to the original quantity of $[\mathbf{1}][B(C_6F_5)_4]$) was added to the solution, and the reaction mixture was again sealed under H_2 overnight. This cycle of bulk electrolysis and subsequent "recharging" under H_2 was repeated a total of three times (see SI Figure 3). The total charge passed (equivalent to the concentration of **1**-H) in the second cycle of electrolysis was 75% that of the first cycle, clearly indicating that the system is capable of turning over more than a single cycle. However, upon the third cycle of electrolysis the current and charge passed had dropped to below 5% of the initial cycle. Closer investigation revealed that the capacitive charging current had diminished considerably and cyclic voltammetry of the solution provided evidence of electrode fouling due to the presence of a broad, ill-defined, surface bound oxidation wave over the range 0.2-0.8 V vs $Cp_2Fe^{0/+}$. This most likely results from oxidative polymerization of the phosphine Lewis base, which, assuming that 100% of **1**-H could be regenerated in each step, was subsequently present in excess. Although the oxidation potential of $^tBu_3P$ occurs at slightly more positive potentials than that of **1**-H, the oxidation of free $^tBu_3P$ may still occur to an extent. Whilst it is not yet clear whether improved turnover of the system may have been possible in the absence of fouling, the fact that **1**-H can be recycled even once is an improvement over the initial $[HB(C_6F_5)_3]^-/B(C_6F_5)_3$ system, where all previous recycling attempts failed. Note that whilst our system is electrocatalytic in the Lewis acid component, it is stoichiometric in the Lewis base $^tBu_3P$. This is because this study is only concerned with the *anodic* half-cell reaction, H_2 oxidation. If our system were to be utilized as part of a complete electrochemical cell reaction (e.g. a fuel cell) then clearly it requires coupling to a suitable *cathodic* half-cell reaction, that is capable of consuming the protons generated, and closing the catalytic cycle.

In conclusion, this report has successfully demonstrated the use of an NHC-stabilised borenium cation, **1**$^+$, in the electrocatalytic oxidation of H_2 using a combined electrochemical-frustrated Lewis pair approach. Using borenium cations as Lewis acid components of the FLP has several advantages over the initial $B(C_6F_5)_3$-based system reported previously:[2] the oxidative voltage (driving energy) required to

oxidise H_2 at a carbon electrode is *very significantly* decreased by almost one Volt (910 mV, *ca.* 175.6 kJ mol^{-1}), the rate of H_2 oxidation is faster producing larger currents, and the NHC-stabilized borenium Lewis acid catalyst is more resistant to unwanted protolytic side-reactions. These factors combine to make the NHC-stabilized borenium system somewhat "rechargeable" – allowing the in situ regeneration of **1**-H from **1**$^+$ in the presence of $^tBu_3P$ and H_2, with 75% efficiency after the first cycle.

However, our approach is still in its infancy and several challenges remain. The rate of H_2 cleavage by the FLP remains the rate-determining step, and the neutral radical intermediate, **1**$^·$, is still susceptible to decomposition in the solvent. Both of these factors may limit the "turnover" or recycling of this system, which would render it truly electrocatalytic. However, the advantage of FLP systems is that they are inherently "tunable" with new, improved combinations of Lewis acids and bases reported apace. The structural and electronic factors that affect the ability of a variety of different synthetically accessible borenium cations to effect the FLP-activation of H_2 is complex,[15,16] and is still being developed. Thus, the incorporation of other borenium Lewis acid catalysts that may proffer improved electrochemical–frustrated Lewis pair systems remains to be explored.

Acknowledgements

[1]   A. J. Bard, L. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, **2001**.
[2]   E. J. Lawrence, V. S. Oganesyan, D. L. Hughes, A. E. Ashley, G. G. Wildgoose, *J. Am. Chem. Soc.* **2014**, *136*, 6031–6036.
[3]   G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126.
[4]   D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76.
[5]   G. Erker, *Comptes Rendus Chim.* **2011**, *14*, 831–841.
[6]   J. M. Farrell, J. A. Hatnean, D. W. Stephan, *J. Am. Chem. Soc.* **2012**, *134*, 15728–15731.
[7]   P. Eisenberger, A. M. Bailey, C. M. Crudden, *J. Am. Chem. Soc.* **2012**, *134*, 17384–17387.
[8]   P. R. Rablen, *J. Am. Chem. Soc.* **1997**, *119*, 8350–8360.
[9]   S.-H. Ueng, M. Makhlouf Brahmi, E. Derat, L. Fensterbank, E. Lacôte, M. Malacria, D. P. Curran, *J. Am. Chem. Soc.* **2008**, *130*, 10082–10083.
[10]   E. J. Lawrence, V. S. Oganesyan, G. G. Wildgoose, A. E. Ashley, *Dalton Trans.* **2013**, *42*, 782–789.
[11]   T. Matsumoto, F. P. Gabbaï, *Organometallics* **2009**, *28*, 4252–4253.
[12]   T. Matsumoto, F. P. Gabbaï, *Organometallics* **2009**, *28*, 4898–4898.
[13]   C.-W. Chiu, F. P. Gabbaï, *Angew. Chem. Int. Ed.* **2007**, *46*, 1723–1725.
[14]   P. Jutzi, C. Müller, A. Stammler, H.-G. Stammler, *Organometallics* **2000**, *19*, 1442–1444.
[15]   E. R. Clark, A. Del Grosso, M. J. Ingleson, *Chem. – Eur. J.* **2013**, *19*, 2462–2466.
[16]   E. R. Clark, M. J. Ingleson, *Organometallics* **2013**, *32*, 6712–6717.

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COMMUNICATION

The potential required for non-aqueous H_2 oxidation at a carbon electrode can be significantly reduced by using a borenium cation in a combined electrochemical-frustrated Lewis pair approach. This system exhibits faster electrode kinetics, increased stability to electrogenerated protons, and improved catalyst recycling over our previously reported system based on the borane Lewis acid, $B(C_6F_5)_3$.
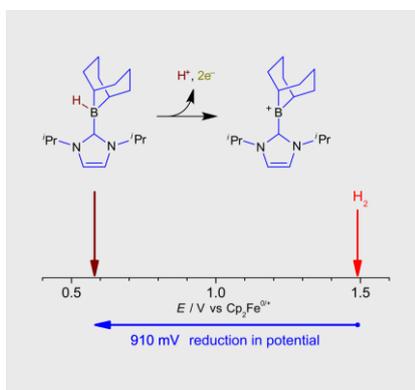
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