

An Electrochemical Study of Frustrated Lewis Pairs: A Metal-free Route to Hydrogen Oxidation

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ABSTRACT: Frustrated Lewis pairs have found many applications in the heterolytic activation of H₂ and subsequent hydrogenation of small molecules through delivery of the resulting proton and hydride equivalents. Herein, we describe how H₂ can be pre-activated using classical frustrated Lewis pair chemistry and combined with *in situ* non-aqueous electrochemical oxidation of the resulting borohydride. Our approach allows hydrogen to be cleanly converted into two protons and two electrons *in situ*, and reduces the potential (the required energetic driving force) for non-aqueous H₂ oxidation by 610 mV (117.7 kJ mol⁻¹). This significant energy reduction opens up routes to the development of non-aqueous hydrogen energy technology.

INTRODUCTION

H₂ is attractive as a “clean” fuel source, leading to a vast body of literature concerned with fuel cell technology.^{1,2} In the absence of an appropriate electrocatalyst (defined as a system which reduces the overpotential – the required energetic driving force – and/or increases the rate of electron transfer), the non-aqueous oxidation of H₂ to liberate two protons and two electrons is slow, requiring large overpotentials (often in excess of 1000 mV vs. Cp₂Fe^{0/+} at carbon electrodes) and producing broad, ill-defined oxidation waves. Conventional, predominantly aqueous, fuel cells surmount this problem by using precious metals such as Pt as a catalytic electrode material.³⁻⁵ Since Pt electrodes are often used for both half-reactions of the fuel cell (H₂ oxidation and O₂ reduction), the high costs of these metals and limited availability present significant problems for large-scale use. Of course, this is true for a multitude of catalyzed processes, and as a result, huge efforts have been made to find inexpensive and abundant alternatives to precious metals.⁶

The majority of molecular electrocatalysts for H₂ oxidation or production have taken inspiration from the hydrogenase enzymes that are found in Nature.⁷⁻⁹ The active site of hydrogenase enzymes feature a coordinatively unsaturated [FeFe] or [NiFe] metal center with pendant Lewis base groups in close proximity. These enzymes are able to overcome the high energy cost that is required to heterolytically cleave H₂ (318.0 kJ mol⁻¹ in MeCN)^{10,11} by virtue of the strong hydricity of the metal center and the strong proton acceptor ability of the pendant base. Several groups, notably DuBois and coworkers, have reported bio-inspired molecular electrocatalysts for H₂ oxidation using nickel,¹²⁻¹⁴ and iron¹⁵⁻¹⁷ metals that mimic the role of hydrogenases. Rauchfuss and coworkers took an alternative approach to H₂ oxidation electrocatalysis, using unsaturated iridium complexes with redox-active non-innocent amidophenolate ligands.^{18,19} They were able to induce Lewis acidity on the metal center through a ligand-centered oxidation, allowing the formation of a H₂ adduct that is susceptible to deprotonation by a weakly-coordinating base. All of these approaches still use metal-

containing catalysts, and there are a greater number of literature reports that focus on biomimetic electrocatalysts for the reverse process – H₂ production *via* proton reduction – than for H₂ oxidation.⁹ The greatest challenges in developing H₂ energy technologies still remain – to find systems that are catalytic in terms of hydrogen bond cleavage, that operate at low overpotentials (i.e. that are “electrocatalytic”), that are metal free and/or employ inexpensive, readily available electrode materials such as carbon, and that are facile and economic to synthesize.

In this report we build on our recent studies of the electrochemistry of electron deficient Lewis acid boranes,^{20–22} and introduce a new approach that combines classical frustrated Lewis pair (FLP) chemistry to “pre-activate” H₂ with non-aqueous electrochemical oxidation of the resulting borohydride. To the best of our knowledge, this is the first time that FLPs have been directly used for the *electrochemical* activation of small molecules. Aqueous-phase borohydride ([BH₄][−]) electrooxidation has been reviewed extensively because of its potential for fuel cell applications;^{3–5} however, in this respect the field has so far been devoid of non-aqueous applications. Since the pioneering work of Stephan’s group in 2006,²³ research involving FLP chemistry has grown rapidly. The “unquenched” reactivity, arising from a suitable combination of a sterically bulky Lewis acid and a Lewis base, has been shown to heterolytically cleave H₂, resulting in a hydride adduct of the Lewis acid and a protonated Lewis base.^{6,23–28} Boranes are typically – but not exclusively – employed as the Lewis acid component.^{26,27,29–35} Following the heterolytic cleavage of H₂, using an FLP system, the majority of literature reports focus on delivering the resulting hydride *via* heterolytic B–H bond cleavage to activate/reduce other small molecules such as imines, enamines, nitriles,^{36,37} and even CO₂.^{38,39} The only prior report that indirectly combines electrochemistry with FLP systems, that we are aware of, is by Stephan and co-workers, who used mono- and bis-ferrocenylphosphines in an FLP system, to observe the quasi-reversible oxidation of the ferrocene redox “label” and the reduction of the proton on the phosphonium moiety.⁴⁰

We begin by exploring the electrochemical properties of Stephan’s paradigm ^tBu₃P/B(C₆F₅)₃ FLP system²⁹ and seek to use this approach to demonstrate the conversion of H₂ into two protons and two electrons (Fig. 1a). After elucidating the kinetic and mechanistic electrochemical behavior of this classical FLP system, we report that our approach reduces the oxidation potential of H₂ in non-aqueous solvents by 610 mV (117.7 kJ mol^{−1}) on carbon electrodes – a significant and large reduction in the required energetic driving force (Fig. 1b). This new route to H₂ oxidation is metal-free, operating on inexpensive, ubiquitous, carbon electrodes. Whilst this initial finding proffers a significant enabling step towards economically viable energy technologies, we can also identify some areas for improvement in this pioneering study of a classical FLP system. Fortunately, FLPs are versatile and inherently

tunable systems, with evermore-improved H₂-activating FLPs reported apace. It is envisaged that the introduction of our innovative electrochemical frustrated Lewis pair approach, herein, will open up new avenues to researchers for further development in small molecule activation and clean energy technologies.

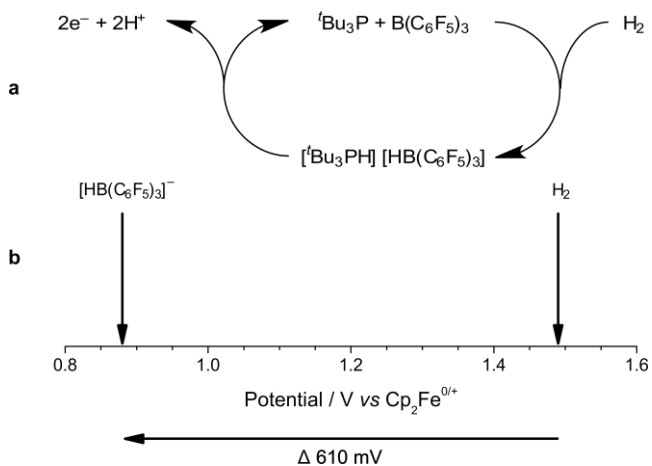


Figure 1. Proposed electrooxidation of the H₂-activated ^tBu₃P/B(C₆F₅)₃ frustrated Lewis pair (FLP) results in (a) the generation of two protons and two electrons, and (b) an effective diminution in the potential required for H₂ oxidation by 610 mV (117.7 kJ mol^{−1}) in CH₂Cl₂.

RESULTS AND DISCUSSION

Initial Electrochemical Studies. An authentic sample of [ⁿBu₄N][HB(C₆F₅)₃] ([ⁿBu₄N]**1**), containing the hydridic component (**1**[−]) of the FLP H₂-cleavage step, was prepared and its structure established by X-ray crystallography and spectroscopic methods (see Supplementary Information sections S1.2, S2 and S3). The authentic borohydride sample allowed a detailed electrochemical study into the redox behaviour of **1**[−] to be undertaken. The direct voltammetric oxidation of [ⁿBu₄N]**1**, at varying concentrations, was performed at a macrodisk glassy carbon electrode (GCE) using cyclic voltammetry (Fig. 2-3).

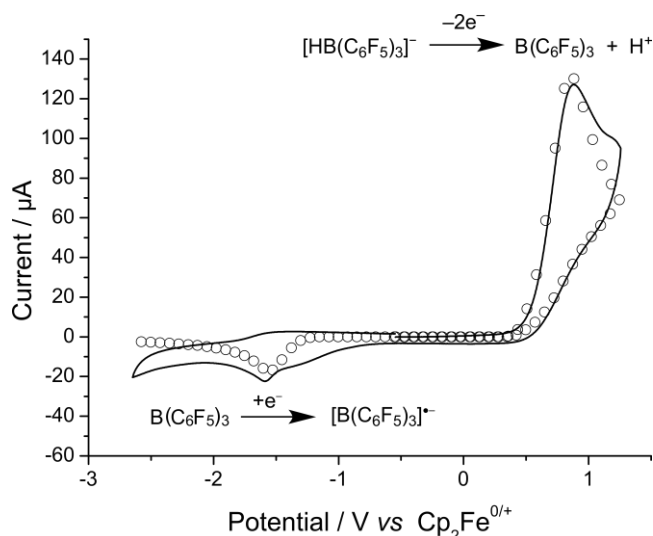


Figure 2. Cyclic voltammograms of a 4.9 mM solution of $[\text{tBu}_4\text{N}]\mathbf{1}$ in CH_2Cl_2 recorded at voltage scan rates of 1000 mVs^{-1} over the full scan range on a glassy carbon electrode (GCE). Solid lines are experimental data; open circles are best fit simulated data. The oxidation wave corresponds to the oxidation of $\mathbf{1}^-$ whilst the reduction wave corresponds to reduction of regenerated $\text{B}(\text{C}_6\text{F}_5)_3$.^{21,22}

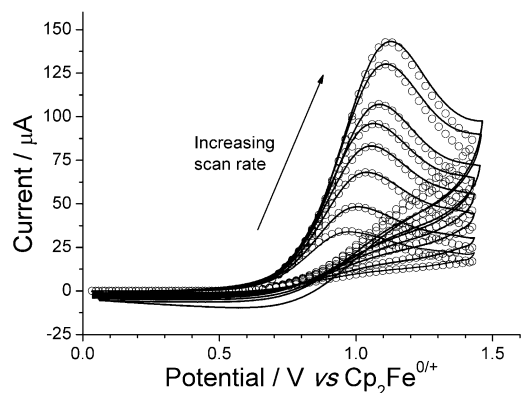


Figure 3. Cyclic voltammograms of a 4.9 mM solution of $[\text{tBu}_4\text{N}]\mathbf{1}$ in CH_2Cl_2 recorded at voltage scan rates of 50, 100, 200, 300, 400, 500, 750, and 1000 mVs^{-1} on a glassy carbon electrode (GCE). Solid lines are experimental data; open circles are best fit simulated data (see text).

A weakly coordinating electrolyte system comprising $0.05 \text{ M } [\text{tBu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ in CH_2Cl_2 was selected for all electrochemical studies minimize the decomposition of $\text{B}(\text{C}_6\text{F}_5)_3$.^{20,41} On sweeping the potential anodically at a scan rate of 100 mV s^{-1} , an oxidative wave was initially observed with a peak potential of (E_p) $+0.88 \pm 0.01 \text{ V vs Cp}_2\text{Fe}^{0/+}$, and no corresponding (quasi-reversible) reduction peak was observed upon reversing the scan direction. However, a small irreversible reduction wave was observed at $-1.59 \text{ V vs Cp}_2\text{Fe}^{0/+}$ (Fig. 2) that we assign to the reduction of some catalytically regenerated parent Lewis acid, $\text{B}(\text{C}_6\text{F}_5)_3$ from our previous studies.^{21,22} The small size of this reduction wave is likely as a result of subsequent protonoly-

sis of the parent $\text{B}(\text{C}_6\text{F}_5)_3$ (see below). The observed voltammetry can be explained by the mechanism proposed in Fig. 4, which is supported by a good fit between simulation and experiment (Fig. 2-3) and detailed chemical and density functional theory (DFT) studies described below. The globally optimized parameters describing the oxidation of $\mathbf{1}^-$ were obtained from digital simulation of the CVs and are given in Table 1, whilst the parameters describing the reduction of $\text{B}(\text{C}_6\text{F}_5)_3$ are taken from our previous work.²¹

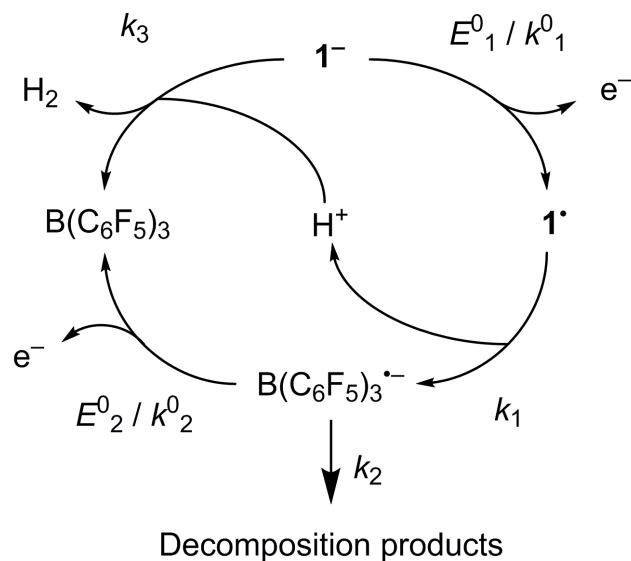


Figure 4. Proposed mechanism and associated thermodynamic and kinetic parameters used in simulation of the voltammetric oxidation of $\mathbf{1}^-$ at a GCE. (standard reduction potential, E^o / V ; standard electron transfer rate constant, $k^o / \text{cm s}^{-1}$; chemical rate constant, k / s^{-1}).

Table 1. Globally optimized best-fit thermodynamic and kinetic parameters obtained from digital simulation of voltammetric data for [ⁿBu₄N]1 at a GCE, following the mechanism proposed in Fig. 4

Redox Process	Redox Parameters		
	E° / V vs Cp ₂ Fe ^{0/+}	k° / 10 ⁻³ cm s ⁻¹	Charge transfer coefficient α
$1^- \rightleftharpoons 1^\bullet + e^-$	+1.13±0.05	13±2	0.74±0.1
$B(C_6F_5)_3^- \rightleftharpoons B(C_6F_5)_3 + e^-$	-1.79±0.01 ^a	1.3±0.3 ^a	0.50±0.05 ^a
Chemical Step			
	Rate Constant k		
$1^\bullet \longrightarrow B(C_6F_5)_3^- + H^+$	$k_1 > 1 \times 10^{13} \text{ s}^{-1}$		
$B(C_6F_5)_3^- \longrightarrow \text{Decomposition products}$	$k_2 > 6.1 \text{ s}^{-1a}$		
$1^- + H^+ \longrightarrow B(C_6F_5)_3 + H_2$	$k_3 = 1.50 \pm 0.25 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$		

^a Parameters taken from our previous studies of B(C₆F₅)₃.²¹

Stoichiometric Reactions. When [ⁿBu₄N]1 is subjected to chemical oxidation using a stoichiometric amount of the single-electron oxidant [NO][PF₆] in CH₂Cl₂, effervescence is observed. Analysis of the reaction mixture headspace using gas chromatography with a thermal conductivity detector (GC-TCD) revealed that H₂ gas was evolved.

Two mechanisms for H₂ production are possible: i) the reaction of electrogenerated H⁺ with the parent 1⁻, as we propose (Fig. 4), or ii) by a reaction between transient [(C₆F₅)₃BH][•] (1[•]) intermediates acting as H⁺ donors. In order to exclude the possibility of the latter pathway, we conducted a control experiment using an authentic H⁺-donor, ⁿBu₃SnH, which was mixed with 4-bromobenzophenone in equimolar quantities in a sealed NMR tube and allowed to react under UV light. ¹H-NMR characterization of the products revealed the formation of benzophenone *via* the radical dehalogenation of 4-bromobenzophenone by H[•]. However, when [ⁿBu₄N]1 is stoichiometrically oxidized in the presence of [NO][PF₆] and an equimolar amount of 4-bromobenzophenone, the latter is recovered in quantitative yield by NMR; no benzophenone is detected in the reaction mixture. Furthermore, effervescence is observed when 1 and a stoichiometric amount of Jutzi's strong oxonium acid, [H(OEt₂)₂][B(C₆F₅)₄],⁴² are combined in CH₂Cl₂. H₂ gas is once again detected in the reaction headspace, supporting the proposed proton-mediated H₂ evolution mechanism.

Note that in either case ¹¹B NMR characterization of the product mixture reveals a number of peaks in the range -0.5 to -7.0 ppm consistent with our previous characterization of the complex products of B(C₆F₅)₃⁻ decomposition (such as [(C₆F₅)₃BCl]⁻, [(C₆F₅)₂BCl₂]⁻, [(C₆F₅)₂BHCl]⁻, and [(C₆F₅)₃BH]⁻ and F⁻ abstraction products from the [PF₆]⁻ anion in the former case – see reference 21 for details).²¹

Conclusively, when a sample of deuterated [ⁿBu₄N][DB(C₆F₅)₃] ([ⁿBu₄N]1^D) is subjected to bulk electrolytic oxidation at a glassy carbon electrode in the presence of ^tBu₃P, an intense triplet resonance is seen in the ³¹P{¹H} NMR spectrum at 59.6 ppm (*J* = 65.8 Hz), which corresponds to [^tBu₃P-D]⁺. Since the only possible source of D⁺ is from the oxidation of 1^{D•}, this strongly supports the proposed mechanism in Fig. 4, wherein B-D/B-H bond cleavage in 1^{D•} results in the formation of a deuterium/proton, respectively. Further support for the proposed mechanism is obtained from DFT computational calculations (Supporting Information Section S5). The calculated bond energies for parent 1⁻ and 1[•] reveal that bond scission is significantly enhanced upon electrooxidation.

In situ electrochemical studies during the heterolytic cleavage of H₂ by a frustrated Lewis pair. With a detailed understanding of the redox chemistry of 1⁻ we proceeded towards *in situ* electrochemical studies of the archetypal ^tBu₃P/B(C₆F₅)₃ system during the FLP cleavage of H₂. The kinetics of heterolytic H₂ cleavage by this FLP

system are much slower than the rate of electrooxidation when monitored using ^{11}B , ^{19}F and ^{31}P NMR spectroscopy (see Supporting Information Figs. S8-10). The heterolytic cleavage of H_2 by the FLP was complete after 12 hours, but even within 1 hour evidence of H_2 cleavage by the FLP could be observed in the NMR spectra. Fig. 5 shows the resulting voltammetry recorded after a 1:1 solution of ${}^t\text{Bu}_3\text{P}:\text{B}(\text{C}_6\text{F}_5)_3$ (containing ferrocene as an internal reference) was sparged with H_2 gas for 1 hour.

Reassuringly, we observe the characteristic oxidation wave of $\mathbf{1}^-$, which is identical to that of $[\text{}^n\text{Bu}_4\text{N}]\mathbf{1}$. Confirmation of this was shown by a proportional increase in the oxidation current at $+0.88\text{ V}$ vs $\text{Cp}_2\text{Fe}^{0/+}$ when the solution was spiked with an authentic sample of $[\text{}^n\text{Bu}_4\text{N}]\mathbf{1}$ (Fig. 5). H_2 is itself oxidized sluggishly, with a broad, ill-defined wave at *ca.* $+1.49\text{ V}$ vs. $\text{Cp}_2\text{Fe}^{0/+}$ in CH_2Cl_2 on a glassy carbon electrode (See Fig. S13). Hence, by employing combined electrochemical FLP approach the oxidation of H_2 now occurs with a *ca.* 610 mV (117.7 kJ mol^{-1}) diminution in the required driving force. Note that $[\text{}^t\text{Bu}_3\text{PH}]^+$ is not redox active at the potentials studied. However, some oxidation of unreacted ${}^t\text{Bu}_3\text{P}$ is apparent as a small oxidation wave at $+0.44\text{ V}$ vs $\text{Cp}_2\text{Fe}^{0/+}$.

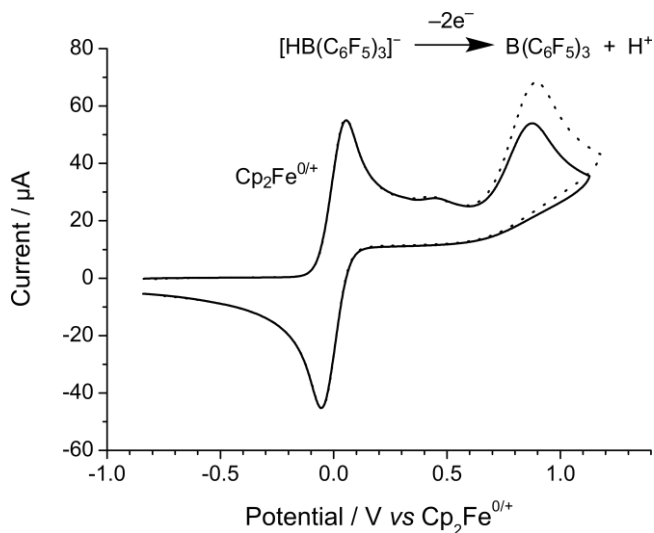


Figure 5. Cyclic voltammogram of a 5 mM solution of ${}^t\text{Bu}_3\text{P}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ in CH_2Cl_2 solution, at a GCE, after being exposed to a 1 hour sparge with H_2 (black line). Addition of authentic $[\text{}^n\text{Bu}_4\text{N}]\mathbf{1}$ (dotted line) to the sample confirms that the observed oxidation wave corresponds to the H_2 -activated product. The cyclic voltammograms were taken in the presence of a Cp_2Fe internal reference at a voltage scan rate of 100 mV s^{-1} .

To investigate whether or not this electrochemical FLP system can be recycled, *i.e.* is catalytic in the Lewis acid, the following experiments were performed: a CH_2Cl_2 solution containing a 5 mM 1:1 mixture of $\text{B}(\text{C}_6\text{F}_5)_3: {}^t\text{Bu}_3\text{P}$ and 0.1 M $[\text{}^n\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ electrolyte was sealed under an atmosphere of H_2 for 12 hours at room temperature to ensure that the FLP heterolytic cleavage of H_2 was complete. This solution was then subjected to bulk electroly-

sis using a glassy carbon felt electrode until all of the $\mathbf{1}^-$ had been oxidized. The solution was again sealed under H_2 with the addition of another equimolar amount of ${}^t\text{Bu}_3\text{P}$, for a further 12 hours and the electrolysis repeated. Disappointingly, upon a second and third electrolytic cycle no evidence for the regeneration of the parent borane, $\text{B}(\text{C}_6\text{F}_5)_3$ and subsequent re-formation of $\mathbf{1}^-$ could be observed, consistent with the ^{11}B NMR characterization of the products of chemical oxidation of $\mathbf{1}^-$ and the fact that we only observe a small reductive peak corresponding to $\text{B}(\text{C}_6\text{F}_5)_3$ upon cyclic voltammetric oxidation of $[\text{}^n\text{Bu}_4\text{N}]\mathbf{1}$, described above. Clearly, the $\text{B}(\text{C}_6\text{F}_5)_3^{\cdot-}$ intermediate produced upon oxidation undergoes significant side reactions with the solvent, and any $\text{B}(\text{C}_6\text{F}_5)_3$ generated is susceptible to protonolysis by the H^+ which is liberated alongside the formation of $\text{B}(\text{C}_6\text{F}_5)_3^{\cdot-}$. Note that “buffering” the electrolyte using excess phosphine Lewis base to prevent unwanted protonolysis reactions is not possible in this system as the Lewis base is itself redox active at similar potentials to $\mathbf{1}^-$.

Given that this is the first study of the electrochemistry of FLPs towards H_2 activation, and choosing the archetypal $\text{B}(\text{C}_6\text{F}_5)_3/ {}^t\text{Bu}_3\text{P}$ seems a logical starting point for these investigations, it is perhaps not surprising that this system is not optimal. However, these findings *are* important as they demonstrate that the electrochemical FLP approach has genuine promise for metal-free H_2 oxidation at significantly lower oxidative potentials, with obvious synthetic and energy applications. This study also allows us to immediately identify areas for future improvement in electrochemical FLP systems: i) competing protonation of $\mathbf{1}^-$ regenerates H_2 and reduces the overall efficiency of the process (although the H_2 may be subsequently recycled in future systems), but protonolysis also leads to unwanted decomposition of the Lewis acidic borane. Lewis acids that are resistant to protonolysis are required; ii) The $\text{B}(\text{C}_6\text{F}_5)_3^{\cdot-}$ radical anion intermediate generated during oxidation of the parent borohydride is susceptible to reaction with the solvent, again preventing the system from being recycled. Steric and/or electronic protection of any radical anion intermediates is required; iii) the kinetics of H_2 splitting by the FLP are rate determining vs rapid electron transfer in this classical FLP system. Fortunately, improved combinations of novel Lewis acids and bases continue to develop rapidly in conventional FLP chemistry. The inherent “tuneability” of FLP properties thus offers enormous potential for the further development of electrochemical FLP systems, and promising candidates that may overcome all of these obstacles are currently under investigation.

CONCLUSIONS

We have characterized the complex non-aqueous redox chemistry of $\mathbf{1}^-$ for the first time. By combining FLP pre-activation of H_2 with electrochemical oxidation of the resultant Lewis acid hydride we have reduced the potential that is required for non-aqueous H_2 oxidation by 610

mV (117.7 kJ mol⁻¹) at readily available carbon electrodes. This is a *significant* energy reduction without the use of metals (precious or otherwise), which opens up hitherto unexplored routes to the development of economically viable H₂-based energy technologies and H₂-activation chemistries. We have also demonstrated that our electrochemical FLP approach is possible with *in situ* H₂ activation using a classical FLP system. Our work has identified specific areas for future development to further extend the scope and possibilities of this electrochemical FLP chemistry. Patent protection for the intellectual property described herein has been sought.

EXPERIMENTAL DETAILS

General Considerations. Commercially available reagents were purchased from Sigma-Aldrich (Gillingham, UK) and used without further purification unless stated otherwise. All synthetic reactions and manipulations were performed under a rigorously dry N₂ atmosphere (BOC Gases) using standard Schlenk-line techniques on a dual manifold vacuum/inert gas line or either a Saffron or MBraun glovebox. All glassware was flame-dried under vacuum before use. Anhydrous solvents were dried *via* distillation over appropriate drying agents. All solvents were sparged with nitrogen gas to remove any trace of dissolved oxygen and stored in ampules over activated 4 Å molecular sieves. ⁿBu₄NCl and NOPF₆ were purchased from Alfa Aesar. ⁿBu₄NCl was recrystallized from acetone prior to use. H₂ gas (99.995 %) was purchased from BOC gases and passed through drying columns containing P₄O₁₀ and 4 Å molecular sieves. D₂ gas was generated *in situ* from the reaction of Na with degassed D₂O (99.9 %, Cambridge Isotope Laboratories Inc.); it was passed through a drying column containing P₄O₁₀. Deuterated NMR solvents ([D₆]DMSO, 99.9 %; CDCl₃, 99.8 %; C₆D₆, 99.5 %) were purchased from Cambridge Isotope Laboratories Inc. and were dried over P₄O₁₀, degassed using a triple freeze-pump-thaw cycle and stored over activated 4 Å molecular sieves. B(C₆F₅)₃,⁴³ [ⁿBu₄N][B(C₆F₅)₄],^{44,45} [H(OEt)₂][B(C₆F₅)₄]⁴² and ⁴Bu₃P⁴⁶ were prepared according to literature methods. [TMP-D][D-B(C₆F₅)₃] was prepared using an adapted literature method,⁴⁷ which is detailed in the Supplementary Information. Synthesis and characterization of compounds [ⁿBu₄N]1 and [ⁿBu₄N]1^D are detailed in the Supplementary Information.

NMR spectra were recorded using either a Bruker Avance DPX-300 MHz or Bruker Avance DPX-500 MHz spectrometer. Chemical shifts are reported in ppm and are referenced relative to appropriate standards: ¹⁹F (CFCl₃); ¹¹B (Et₂O·BF₃); ³¹P (85% H₃PO₄). IR spectra were recorded using a PerkinElmer μ-ATR Spectrum II spectrometer. Sample headspace analysis was performed using a PerkinElmer Clarus 580 gas chromatograph coupled with a thermal conductivity detector (GC-TCD). Retention time for H₂ gas was calibrated using a standard sample. Electrochemical measurements were performed in CH₂Cl₂ containing 0.05–0.10 M [ⁿBu₄N][B(C₆F₅)₄] as a

weakly coordinating electrolyte salt using either a PGSTAT 302N or PGSTAT 30 computer-controlled potentiostat (Autolab, Utrecht, The Netherlands) in an inert atmosphere three-electrode cell that was designed in-house (see Supporting Information for further details). Digital simulation of voltammetric data was performed using the commercially available DigiElch™ Pro software package (v.7). Diffraction intensities of [ⁿBu₄N]1 were recorded using a AFC12 Kappa 3 CCD diffractometer (at the EPSRC UK National Crystallography Service) equipped with Mo-Kα radiation and confocal mirrors monochromator (for further details see the Supplementary Information).

ASSOCIATED CONTENT

Supporting Information. Synthetic details, NMR characterization, X-ray crystallography, electrochemistry, and DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ABBREVIATIONS

CV, cyclic voltammogram; FLP, frustrated Lewis pair; TMP, 2,2,6,6-tetramethylpiperidine, DFT, density functional theory.

REFERENCES

- (1) Dunn, S. *Int. J. Hydrogen Energ.* **2002**, *27*, 235–264.
- (2) Turner, J.; Sverdrup, G.; Mann, M. K.; Maness, P.-C.; Kroposki, B.; Ghirardi, M.; Evans, R. J.; Blake, D. *Int. J. Energ. Res.* **2008**, *32*, 379–407.
- (3) Santos, D. M. F.; Sequeira, C. A. C. *Renew. Sust. Energ. Rev.* **2011**, *15*, 3980–4001.
- (4) Merino-Jiménez, I.; Ponce de León, C.; Shah, A. A.; Walsh, F. C. *J. Power Sources* **2012**, *219*, 339–357.
- (5) Ma, J.; Choudhury, N. A.; Sahai, Y. *Renew. Sust. Energ. Rev.* **2010**, *14*, 183–199.
- (6) *Catalysis Without Precious Metals*; Bullock, R. M., Ed.; Wiley, 2010.
- (7) Vignais, P. M.; Billoud, B. *Chem. Rev.* **2007**, *107*, 4206–4272.
- (8) Tard, C.; Pickett, C. J. *Chem. Rev.* **2009**, *109*, 2245–2274.
- (9) DuBois, D. L.; Bullock, R. M. *Eur. J. Inorg. Chem.* **2011**, *2011*, 1017–1027.
- (10) Curtis, C. J.; Miedaner, A.; Ellis, W. W.; DuBois, D. L. *J. Am. Chem. Soc.* **2002**, *124*, 1918–1925.

- (11) Wayner, D. D.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287–294.
- (12) Yang, J. Y.; Bullock, R. M.; Shaw, W. J.; Twamley, B.; Fraze, K.; Rakowski DuBois, M.; DuBois, D. L. *J. Am. Chem. Soc.* **2009**, *131*, 5935–5945.
- (13) Goff, A. L.; Artero, V.; Jusselme, B.; Tran, P. D.; Guillet, N.; Métayé, R.; Fihri, A.; Palacin, S.; Fontecave, M. *Science* **2009**, *326*, 1384–1387.
- (14) Yang, J. Y.; Chen, S.; Dougherty, W. G.; Kassel, W. S.; Bullock, R. M.; DuBois, D. L.; Raugei, S.; Rousseau, R.; Dupuis, M.; Rakowski DuBois, M. *Chem. Commun.* **2010**, *46*, 8618–8620.
- (15) Camara, J. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2011**, *133*, 8098–8101.
- (16) Camara, J. M.; Rauchfuss, T. B. *Nat. Chem.* **2012**, *4*, 26–30.
- (17) Liu, T.; DuBois, D. L.; Bullock, R. M. *Nat. Chem.* **2013**, *5*, 228–233.
- (18) Ringenberg, M. R.; Kokatam, S. L.; Heiden, Z. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2008**, *130*, 788–789.
- (19) Ringenberg, M. R.; Nilges, M. J.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **2010**, *29*, 1956–1965.
- (20) Ashley, A. E.; Herrington, T. J.; Wildgoose, G. G.; Zaher, H.; Thompson, A. L.; Rees, N. H.; Kraemer, T.; O'Hare, D. *J. Am. Chem. Soc.* **2011**, *133*, 14727–14740.
- (21) Lawrence, E. J.; Oganessian, V. S.; Wildgoose, G. G.; Ashley, A. E. *Dalton Trans.* **2013**, *42*, 782–789.
- (22) Cummings, S. A.; Iimura, M.; Harlan, C. J.; Kwaan, R. J.; Trieu, I. V.; Norton, J. R.; Bridgewater, B. M.; Jaekle, F.; Sundararaman, A.; Tilset, M. *Organometallics* **2006**, *25*, 1565–1568.
- (23) Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124–1126.
- (24) Stephan, D. W. *Org. Biomol. Chem.* **2012**, *10*, 5740–5746.
- (25) Stephan, D. W. *Org. Biomol. Chem.* **2008**, *6*, 1535.
- (26) Stephan, D. W. *Dalton Trans.* **2009**, 3129.
- (27) Stephan, D. W.; Erker, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76.
- (28) Erker, G. *Dalton Trans.* **2011**, *40*, 7475–7483.
- (29) Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129*, 1880–1881.
- (30) Jiang, C.; Blacque, O.; Fox, T.; Berke, H. *Dalton Trans.* **2011**, *40*, 1091.
- (31) Lu, Z.; Cheng, Z.; Chen, Z.; Weng, L.; Li, Z. H.; Wang, H. *Angew. Chem. Int. Ed.* **2011**, *50*, 12227–12231.
- (32) Herrington, T. J.; Thom, A. J. W.; White, A. J. P.; Ashley, A. E. *Dalton Trans.* **2012**, *41*, 9019.
- (33) Voss, T.; Mahdi, T.; Otten, E.; Fröhlich, R.; Kehr, G.; Stephan, D. W.; Erker, G. *Organometallics* **2012**, *31*, 2367–2378.
- (34) Binding, S. C.; Zaher, H.; Chadwick, F. M.; O'Hare, D. *Dalton Trans.* **2012**, *41*, 9061–9066.
- (35) Travis, A. L.; Binding, S. C.; Zaher, H.; Arnold, T. A. Q.; Buffet, J.-C.; O'Hare, D. *Dalton Trans.* **2013**, *42*, 2431.
- (36) Chase, P. A.; Jurca, T.; Stephan, D. W. *Chem. Commun.* **2008**, 1701.
- (37) Stephan, D. W.; Greenberg, S.; Graham, T. W.; Chase, P.; Hastie, J. J.; Geier, S. J.; Farrell, J. M.; Brown, C. C.; Heiden, Z. M.; Welch, G. C.; Ullrich, M. *Inorg. Chem.* **2011**, *50*, 12338–12348.
- (38) Tran, S. D.; Tronic, T. A.; Kaminsky, W.; Michael Heineke, D.; Mayer, J. M. *Inorg. Chim. Acta* **2011**, *369*, 126–132.
- (39) Ashley, A. E.; Thompson, A. L.; O'Hare, D. *Angew. Chem. Int. Ed.* **2009**, *48*, 9839–9843.
- (40) Ramos, A.; Lough, A. J.; Stephan, D. W. *Chem. Commun.* **2009**, 1118–1120.
- (41) Geiger, W. E.; Barrière, F. *Acc. Chem. Res.* **2010**, *43*, 1030–1039.
- (42) Jutzi, P.; Müller, C.; Stammli, A.; Stammli, H.-G. *Organometallics* **2000**, *19*, 1442–1444.
- (43) Lancaster, S. J. *ChemSpider SyntheticPages* **2003**. DOI: 10.1039/SP215.
- (44) Martin, E.; Hughes, D. L.; Lancaster, S. J. *Inorg. Chim. Acta* **2010**, *363*, 275–278.
- (45) LeSuer, R. J.; Buttolph, C.; Geiger, W. E. *Anal. Chem.* **2004**, *76*, 6395–6401.
- (46) Srivastava, R. C. *J. Chem. Res. (S)* **1985**, 330–331.
- (47) Sumerin, V.; Schulz, F.; Nieger, M.; Leskelä, M.; Repo, T.; Rieger, B. *Angew. Chem. Int. Ed.* **2008**, *47*, 6001–6003.
- (48) Gale, P. A.; Coles, S. *Chem. Sci.* **2012**, 683.

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