Title: A New Mode of Chemical Reactivity for Metal–Free Hydrogen Activation by Lewis Acidic Boranes

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201900861
Angew. Chem. 10.1002/ange.201900861

Link to VoR: http://dx.doi.org/10.1002/anie.201900861
http://dx.doi.org/10.1002/ange.201900861
**A New Mode of Chemical Reactivity for Metal-Free Hydrogen Activation by Lewis Acidic Boranes**


**Abstract:** We herein explore whether tris(aryl)borane Lewis acids are capable of cleaving H₂ outside of the usual Lewis acid/base chemistry described by the concept of “frustrated Lewis pairs” (FLPs). Instead of a Lewis base we use a chemical reductant to generate stable radical anions of two highly-hindered boranes: tris(3,5-dinitromesityl)borane and tris(mesityl)borane. NMR spectroscopic characterization reveals that the corresponding borane radical anions activate (cleave) dihydrogen, whilst EPR spectroscopic characterization, supported by computational analysis, reveals the intermediates along the hydrogen activation pathway for the first time. This radical–based, redox pathway involves homolytic cleavage of H₂, in contrast to conventional models of FLP chemistry which invoke a heterolytic cleavage pathway. This represents a new mode of chemical reactivity for hydrogen activation by borane Lewis acids.

The chemistry of Lewis acidic boranes reacting with H₂ is now almost exclusively described by the Lewis acid/base conceptual framework of “frustrated Lewis pairs” (FLPs),[1,1] introduced by Douglas Stephan in 2006.[2] While some precise mechanistic details are still debated,[3] in general the ability of FLPs to cleave H₂ relies on the cooperative action of the two reactive centers that are sterically encumbered (“frustrated”) within an encounter complex of the Lewis acid–base pair. The Lewis acid, which is most often an organoborane, provides a vacant acceptor orbital, and the Lewis base, typically a phosphine or amine, provides a donor orbital with which to cleave the strong H–H bond.[4] Activation of H₂ by borane–based FLPs is therefore widely thought to involve heterolytic bond cleavage, and to be controlled by the relative strengths of the Lewis acidic/Lewis basic components and the degree of steric encumbrance between them.[1b–e, 5] This contrasts with the transition-metal–based complexes and biological systems that have dominated hydrogenation catalysis for the previous 150 years.[6] In these complexes, the metal center provides both vacant and filled acceptor/donor orbitals at a single reactive site; the chemistry is, to a large extent, operating under redox control of the metal center, and homolytic H₂ bond cleavage is common.

The heterolytic mechanism proposed for FLP activation of H₂ is found generally to be in good agreement with observed trends in reactivity, and it has been supported by a number of computational studies.[4] Nevertheless, definitive experimental proof has remained elusive (perhaps unavoidably so). As such it is interesting to consider that observed patterns of FLP reactivity could also be consistent with alternative H₂ activation pathways. In particular, these trends could also be consistent with plausible radical mechanisms, in which initial single-electron transfer (SET) from the Lewis base to the Lewis acid would transiently generate highly reactive radical pairs capable of activating H₂. For example, while the thermodynamic and kinetic ability of an FLP to activate H₂ is well known to correlate with the hydride ion affinity of the Lewis acid (consistent with heterolytic bond cleavage), these parameters both also correlate well with the one-electron reduction potential of the Lewis acid (consistent with SET). Indeed, recent studies have implied that for some families of borane Lewis acids, reduction potentials may even be a better indicator of reactivity towards H₂ than hydride ion affinities.[7]

There is also a growing body of evidence for the occurrence of radical mechanisms when small molecules such as NO, PH₂SnH, and peroxides are used as the substrates of FLP reactions.[8] To date, however, these “frustrated radical pair” (FRP) mechanisms have not been observed with H₂. Indeed, no FLP is known to cleave H₂ via a radical mechanism. Our previous work studying the electrochemistry of FLP components, together with the recent evidence for radical pathways in FLPs and FRPs reported by others, raises an obvious question that this article sets out to answer: can boranes react with H₂ outside of an FLP chemical framework, if they are allowed to operate via a hitherto unknown redox controlled, radical reaction pathway instead?

To test our hypothesis we carefully selected two boranes as models: tris(3,5-dinitromesityl)borane, 1, and tris(mesityl)borane, 2 (Scheme 1). Both boranes have essentially identical steric shielding of the central boron atom by the six ortho methyl groups on the mesityl rings, leading to the formation of long–lived borane radical anions upon reduction.[9, 10] Neither borane is currently known to be active for H₂ activation within an FLP. The addition of six electron-withdrawing nitro groups in 1 shifts the reduction...
potential in a positive direction to $-1.57$ V vs. $\text{Cp}_2\text{Fe}^{0/+}$ (see Supporting Information), making 1 as electrophilic and comparably facile to reduce as the archetypal electron deficient borane $\text{B}(\text{C}_6\text{H}_5)_3$ used in FLP chemistry ($-1.52$ V vs. $\text{Cp}_2\text{Fe}^{0/+}$). The NO$_2$ groups in 1 also provide useful electron paramagnetic resonance spectroscopic markers for the characterization of reaction intermediates.

The very negative redox potential of 2 necessitates the use of a stronger reducing agent. When a solution of 2 in THF-$d_8$ is reduced over sodium metal and heated in the presence of H$_2$, the appearance of a doublet in the $^{11}$B NMR spectrum at $-14.5$ ppm ($\delta_{\text{B,prot}} = 78$ Hz), and a corresponding 1:1:1:1 quartet in the $^1$H NMR spectrum at 3.75 ppm ($\delta_{\text{H,prot}} = 77$ Hz) is observed, characteristic of the formation of [Na][2-H] (Figure 1b).

The experiments described above clearly indicate that the borane radical anions 1$^-$ and 2$^-$ can cleave H$_2$ in the absence of any exogenous Lewis base. These reactions are, however, slow in comparison to typical FLP H$_2$ activation reactions. In the case of the model borane 1 this is disadvantageous, since it enables the reaction to be monitored in real time and observe reaction intermediates along the H$_2$ cleavage pathway using EPR spectroscopy.

Solutions of 1 dissolved in either CD$_2$Cl$_2$ or THF-$d_8$ were chemically reduced using $\text{Cp}^*\text{Co}(\text{a})$ or 2 in THF-$d_8$. Inset: The corresponding $^{13}$C NMR spectra recorded at the start and end of the experiments showing the conversion of the parent borane starting material to the borohydride product under reduction and exposure to H$_2$.
and the EPR spectra resulting from exposure to H₂ were recorded (Figures 2a–d). Simulation of the EPR spectra yields the isotropic hyperfine coupling constants for the various ¹H, ¹⁴N, and ¹⁸B nuclei, given in Table 1. These data, supported by DFT calculations (performed for the identifiable intermediates of both 1 and 2 and detailed in the Supplementary Information), enable us to observe and characterize the structures of the intermediates and gain valuable insights into the reaction mechanism (given schematically in Figure 3) and the corresponding energetic profile by which organoborane radicals cleave H₂ homolytically (Figure 4).

Upon reduction of 1 under N₂, the EPR spectrum shown in Figure 2a is observed, which is characteristic of ¹⁻ with hyperfine coupling of the unpaired electron spin density to the boron nucleus as well as to the methyl and nitro substituents on the aromatic rings (Table 1).⁴¹⁰ The initiation step is calculated to be exothermic for both compounds (−56.7 kcal mol⁻¹ for 1 and 2, respectively) and reflects the relative LUMO energy and reduction potential of each borane.

Figure 2b shows the resulting spectrum recorded upon first exposing the reaction to H₂ and before heating. An immediate change is evident with the appearance of a sharp 1:1:1 three-line signal superimposed on the original signal of the ¹⁻ parent. After heating the reaction for a further 10 minutes this three-line signal dominates the EPR spectral response (Figure 2c) for the next 48 hours. The only change to the system is the addition of H₂ and computational modelling of the possible interactions between ¹⁻ and H₂ reveal two propagation pathways. Propagation (1a) produces the diamagnetic borohydride product, and is endothermic (+30.8 kcal mol⁻¹ for 1 and 2) albeit to a lesser extent than homolytic H₂ splitting itself (+107.1 kcal mol⁻¹ at this level of theory). The alternative pathway, Propagation (1b) avoids the release of free H⁻ atom radicals and is slightly exothermic (−6.1 and −1.4 kcal mol⁻¹ for 1 and 2). This reaction produces a radical species consistent with that observed in Figures 2b–c. Computation reveals the structure of this intermediate to be [Ar₂B(H)–Ar(H)]⁻ with hydride attached at a four-coordinate boron centre, and H⁻ carried on one of the aromatic rings (denoted as [1–H₂]⁻ with specific reference to borane 1). DFT models indicate that there is little energetic discrimination for the H⁻ to be attached to one or other carbon positions around the aromatic ring. Spin density calculations (see Data S1) confirm, however, that the isomer with the H⁻ predominantly located at a meta carbon on the ring, ipso to one of the nitro groups, is consistent with the observed EPR spectra (Figures 2b–c). Here the unpaired electron is coupled only to one of the nitrogen nuclei in the nitro groups of the aryl ring system and is not coupled to the boron nucleus at all (Table 1).

After 48 hours of heating, the EPR spectrum changes once again (Figure 2d) to reveal a 1:2:2:2:1 five-line hyperfine coupling pattern of a new persistent paramagnetic species. This does not fit the expected coupling pattern from two nitro groups which would give rise to a 1:2:3:2:1 splitting pattern. Instead, it arises from near coincident hyperfine coupling with both an additional single hydrogen atom and the boron nucleus (similar to DFT calculations of a hydrogen–boron adduct).¹⁷ This then, is a neutral [1–H⁻]⁻ intermediate resulting from cleavage of the H₂ molecule.

Insert Table 1 here (see below)

Initiation
Ar₂B + e⁻ → [Ar₂B]⁻

Propagation
Step (1a): [Ar₂B]⁻ + H₂ → [Ar₂B(H)]⁻ + H⁺
Step (1b): [Ar₂B]⁻ + H₂ → [Ar₂B(H)–Ar(H)]⁻
Step (2a): Ar₂B + H⁺ → [Ar₂B–Ar(H)]⁺
Step (2b): [Ar₂B(H)–Ar(H)]⁻ + Ar₂B → [Ar₂B–H⁺] + [Ar₂B–H⁻]

Termination
Step (3a): [Ar₂B(H)–Ar(H)]⁻ + [Ar₂B]⁻ → 2 [Ar₂B–H⁻]
Step (3b): [Ar₂B–Ar(H)]⁺ + [Ar₂B]⁻ → [Ar₂B–H⁻] + Ar₂B

Overall reaction
Ar₂B + reductant + 1/2 H₂ → [reductant] Ar₂B–H

Figure 3. The proposed radical chain–propagation mechanism for the homolytic cleavage of H₂ upon reduction of organoborane Lewis acids. Inset: the chemical structures corresponding to the [Ar₂B(H)–Ar(H)]⁻ and [Ar₂B–Ar(H)]⁺ intermediates (substituents on the aryl rings have been omitted for clarity).

Once again there are two possible pathways that result in the formation of the [1–H⁻]⁻ intermediate: Propagation (2a) and Propagation (2b). Propagation (2a) is exothermic by −37.1 kcal mol⁻¹ and −30.8 kcal mol⁻¹ for 1 and 2, respectively. Interestingly, computation suggests that if [1–H⁻]⁻ is formed with the hydrogen atom at boron, as one might expect, the hydrogen...
atom immediately hops from the boron atom onto the aromatic ring system, until it arrives at the para carbon atom which is the most stable isomer in the case of 1 (whereas the meta position is most stable in 2, see Table S1). This is supported by what is observed experimentally by the EPR monitoring of hydrogen splitting by 1 where the magnitude of the resulting H• atom hyperfine coupling fits well with coupling to spin density on the ring system in the para position located between the two nitro groups (Figure 2d).

If the parent borane is present in excess of the radical anion (Propagation (2b)), the hydrogen atom produced in step (1a) (considered as [ArB(H)–Ar(H)]•) may be transferred, and the borohydride product and the neutral [ArB–H]• radical intermediate is formed. Using the values calculated for propagation steps 1a and 2a, step 2b is energetically neutral. In the system reported herein, it is unlikely that the parent borane is present in excess of the radical anion initially, but as the reaction proceeds through step 3b and the consumption of the [ArB–H]• radical progresses, this stabilization may become more relevant towards the end of the reaction. This situation may also have relevance to potential radical–FLP hydrogen cleavage mechanisms, where the parent borane is most likely present in excess of any potential radical anion intermediates throughout.

The final step in the reaction, which cannot be observed by EPR, is the formation of the diamagnetic [1–H]• product, which is detected by 11B and 1H NMR analysis of the reaction mixture at the end of the experiment. Aside from the obvious recombination of 2H• to form H2 (the reverse of step 1), there are two termination pathways: Termination (3a) (−39.5 and −49.6 kcal mol−1 for 1 and 2, respectively), and Termination–Propagation (3b) (−39.3 and −48.2 kcal mol−1 for 1 and 2, respectively). Step 3a may also be written as [ArB]•− + H•→[ArB–H]• for consistency with the rest of the scheme, or as a termolecular reaction: 2[ArB]•− + H2→2[ArB–H]•. Step 3b yields both the terminal borohydride product and regenerates the parent neutral borane for further reaction in propagation step 2a. Note that whilst it would appear from Figures 2c–d that the EPR spectra are dominated by the [1–H2]•• and [1–H•]• species, respectively, simulation of the spectral data reveals that these spectra are each superimposed over the parent 1•• radical anion species. As the reaction proceeds with heating the weighting between the systems changes (1•• : [1–H2]•• = 98.5 : 1.5 in Figure 2b; 73.0 : 27.0 in Figure 2c, and 1•• : [1–H•]• = 63.0 : 37.0 in Figure 2d. The rate of consumption of 1•• as measured by EPR (Figures 2a–d) correlates with the rate of conversion to borohydride as measured by NMR spectroscopy (Figure 1a).

In summary, using two model boranes which produce stable radical anions upon one-electron reduction, we have successfully demonstrated homolytic dihydrogen cleavage in the absence of a Lewis base. This represents a new mode of chemical reactivity by Lewis acidic boranes towards H2 that opens up new borane and potentially other main group chemistries beyond the framework of conventional FLPs. The reaction between the model borane radical anions and H2 is slow, and the intermediates are sufficiently stabilized so that, for the first time, we can observe several distinct intermediates along the homolytic dihydrogen cleavage pathway using EPR spectroscopy and can model the energetics of the reaction pathway computationally. We are currently exploring the application of boryl radical H2 as a convenient route to more active borane hydride species, which may have application in catalysis and energy materials.

Acknowledgements

The research leading to these results has received funding from the European Research Council under the ERC Grant Agreement no. 307061 (PIHOMER). GGW and AEA thank the Royal Society for financial support via University Research Fellowships (UF/130336 and UF/160395 respectively). FM thanks the Royal Society for support via a Wolfson Research Merit Award. AM acknowledges the faculties of Science and Medicine at the UEA for funding a PhD studentship. JCS acknowledges the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (NWO/CW) for a VIDI grant (723.012.101). We acknowledge the use of the EPSRC funded National Chemical Database Service hosted by the Royal Society of Chemistry, and the EPSRC UK National Mass Spectrometry Facility (NMSF) at the University of Swansea. We thank the EPSRC UK National and the EPSRC UK National Mass Spectrometry Facility (NMSF) at the University of Swansea.
Crystallography Service at the University of Southampton for the collection of the crystallographic data.

Keywords: Lewis acids • boranes • radicals • EPR • dihydrogen


## Table 1. EPR spectral parameters obtained by simulation of the experimental spectra recorded in Figures 2A–D.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Simulated Spectra</th>
<th>Figure 2a</th>
<th>Figure 2b</th>
<th>Figure 2c</th>
<th>Figure 2d</th>
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<td></td>
<td></td>
<td>[1−]− [1−{H₂}]&quot;</td>
<td>[1−]− [1−{H₂}]&quot;</td>
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