



Hydrogen Storage Characterization and Optimization Research Effort (HySCORE)

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Pacific Northwest National Laboratory

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Project ID: ST132

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Timeline

Project Start: 10/1/2015

End: Project continuation determined by DOE. Currently scheduled through 9/30/18

Budget PNNL

FY16	\$1005 K
FY17	\$1080 K
FY18	\$ 500 K
Total	\$ 2585 K

Barriers

- **General:**
- A. Cost; B. Weight and Volume; C. Efficiency; E. Refueling Time
- **Reversible Solid-State Material:**
- M. Hydrogen Capacity and Reversibility;
- N. Understanding of Hydrogen Physi- and Chemi- sorption; O. Evaluation Facilities.

Partners/Collaborators

- NREL - Tom Gennett, Phil Parilla
- NIST - Craig Brown, Terry Udovic
- LBNL - Jeff Long, Martin Head-Gordon
- HyMARC - Brandon Wood, Vitalie Stavila
- Hawaii – Craig Jensen
- DICP Chen, T He
- AIST – Q Xu, Y Himeda, H Kawanami
- Erlangen Nuremberg – K Müller

Milestones

- 09/30/2017 Provide analysis and characterization of 2 samples from seedling projects (NMR, TEM or Calorimetric) **complete**
- 12/31/2017 Heats of adsorption of H₂ in sp² and sp³ boron doped carbon. Determine most accurate computational protocol (density functional theory, DFT), benchmarked to published experimental determinations for graphene materials, to calculate energies of H₂ sorption in boron (2 – 8 wt%) doped graphene to understand nature of binding sites. The work will provide an analysis of binding energies of sp² and sp³ hybridized boron. The calculations will be benchmarked against experimental measurements of B doped carbon materials by collaborators at NREL. **complete**
- 03/31/2018 Reaction calorimetry. Rate enhancement of H₂ uptake in Lewis base adducts of borane clusters. Measure the rate of H₂ uptake by solvent free and the THF solvate of Mg(B₃H₈)₂ by reaction calorimetry and follow the appearance of Mg(BH₄)₂ at temperatures between 300 – 450 K. **delayed 50% complete**
- 06/30/2018 Demonstrate that Mg(BH₄)₂ can be regenerated from Mg(B₁₀H₁₀) at T < 150 C and P < 150 bar. **on track**
- 09/30/2018 Provide analysis and characterization of 2 samples from seedling projects (NMR, TEM or Calorimetric) **on track**

We build upon the guidance provided by Hydrogen Storage Centers of Excellence

PNNL leverages unique capabilities to assist material developers:

- Solid-state in-situ high-pressure variable-temperature ^{11}B , ^{13}C , ^{15}N NMR (to identify key intermediates involved in the release and uptake of H_2),
- Solid-state low temperature ^1H and ^2H NMR (5 – 300 K) to investigate physi-sorption of H_2 , ultimate goal to validate $> 2\text{H}_2/\text{metal site}$.
- Variable pressure reaction calorimetry to experimentally determine enthalpy of H_2 addition in solid and liquid hydrogen stores (high pressure cells unique to PNNL)
- TEM and high pressure XRD for materials characterization

Goal of Consortium:

- to assist materials developers to measure (and validate) critical properties and to double energy density from 25 to 50 g H_2/liter .
- to develop and enhance FCTO hydrogen storage **core characterization capabilities**
- to **validate new concepts** for input into predictive models that will accelerate progress of materials developers and improve approaches to onboard H_2 storage

Collaborations

providing access to instrumentation and *sample preparation*



- Argonne - ^{11}B NMR NaBH_4 @graphene
- NREL - ^{11}B NMR MgB_2 and MgBH_4 @ Al_2O_3
- NREL – ^{11}B NMR of B-doped carbons
- NIST – $\text{THF}_x^*\text{Mg}(^{11}\text{BD}_4)_2$ for neutron studies
- LBNL – Low temperature ^2H NMR Mg-dobdc
- Caltech – HR TEM
- SRNL – High pressure XRD
- Geneva - ^{11}B NMR and calorimetry unsolvated $\text{Mg}(\text{B}_3\text{H}_8)_2$.
- DICP - Reaction calorimetry ΔH_{H_2} and validation of claims.
- AIST – High pressure NMR *in-situ* solution phase NMR

Dynamic connection between theory and experiment



- Use theory to guide experiment and interpret complex results
 - Predict key intermediates and products based on thermodynamics (E_{static} , ΔH° and ΔG°)
 - Binding energies of H_2 to B-doped carbon

- Use experiment to benchmark and validate theory
 - NMR to follow evolution of H_2 release pathways (key intermediates and products)
 - Calorimetry to measure enthalpies of H_2 uptake and release

Progress and accomplishments with sorbents, solids, and liquids

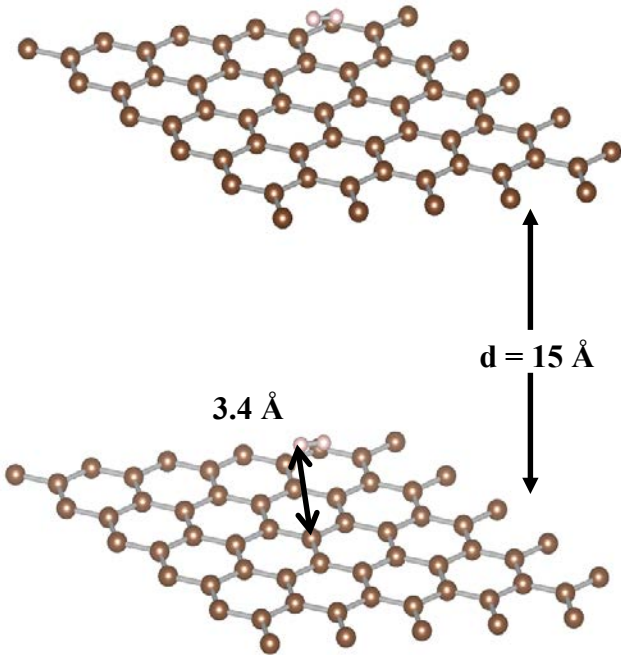


- B-doped carbon (NREL)
 - **Coronene and graphene (theory)** Increase binding energy by ca. 25-100%
 - H₂ attracted to defects – not to B
- Complex hydrides (Hawaii, Geneva)
 - **Mg(BH₄)₂** Lewis base adducts play multiply roles to enhance reactivity
 - phase change/ eutectic mixtures to lower melting point
 - shuttle boranes
 - Catalytic activation of H₂
- Liquid carriers (DICP, AIST)
 - **'PhOH'** – ΔH_{-H_2} ca. 61 - 65 kJ/mol H₂
 - Modify thermodynamics by increasing *electron density* – validate using calorimetry
 - Decrease H₂ release temperature by 65 K



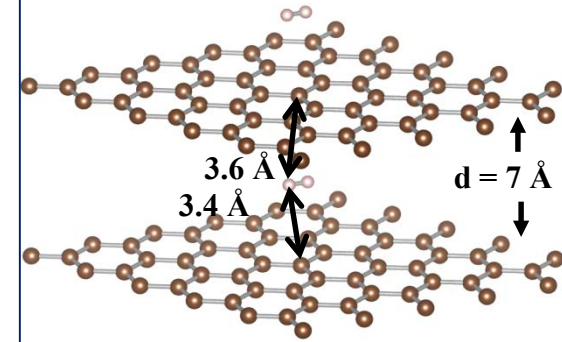
Iffat Nayyar

Graphene C₅₀



binding energy 5.2 kJ/mol

- Approach: compare variety of basis sets, functionals, dispersion corrections to find best agreement with experiment – use graphene as model
- LDA overestimates binding energy. GGA better but can underestimate binding energy. Best agreement for graphene experiment and theory vdW-DF2 with revPBE exchange

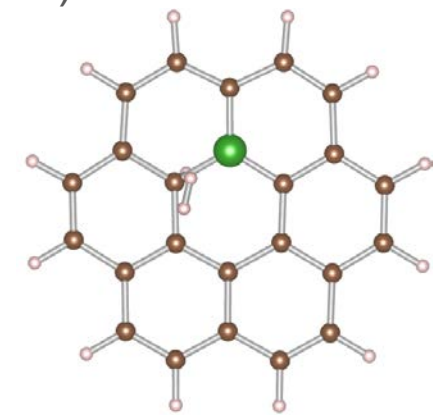
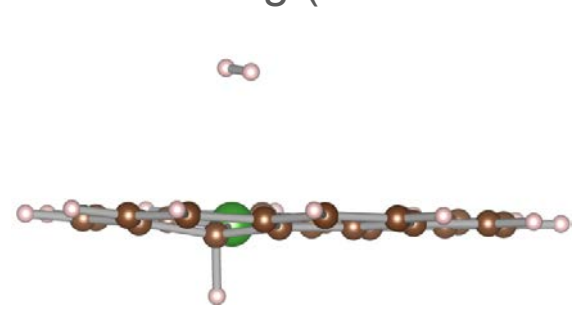


binding energy 10.6 kJ/mol increases when spacing decreases. Use 15 Å in calculations to focus on B-doping effects

literature reports for binding energy of H₂ to B-doped carbon ranges from 5 to >50 kJ/mol. what is real?

- 1st B-doped into coronene increases binding energy (6.2 to 7.6 kJ/mol)
- 2nd B-doped on same ring actually predicted to decrease binding energy (7.6 to 5.6 kJ/mol).
- 2nd H₂ (to single B- doped coronene) slightly reduced binding energy and prefers opposite side
- BN ring binds H₂ more weakly then all carbon ring (6.2 to 5.5 kJ/mol)

System	Nomenclature	Binding Energy (kJ/mol H ₂)
C ₂₄ H ₁₂	C	6.2
B C ₂₃ H ₁₃	B	7.6
N C ₂₃ H ₁₃	N	6.7
B ₂ C ₂₂ H ₁₂	BB ortho	6.6
	BB meta	5.9
	BB para	5.6
B ₂ C ₂₂ H ₁₂	BN ortho	6.8
	BN meta	7.4
	BN para	6.9
B ₃ N ₃ C ₁₆ H ₁₂	BN cyclic	5.5



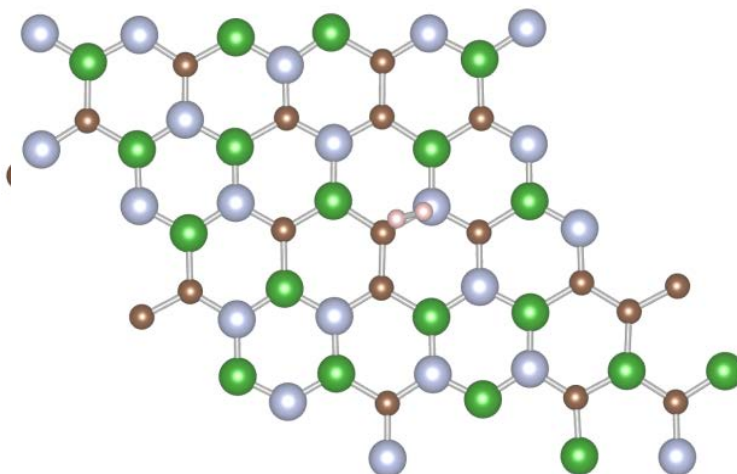
Future work: identify *descriptors* to correlate binding energy, e.g., charge, bond order, symmetry, defects.

Calculated binding energy in B, BN and CBN graphene. *Something unique about CBN*

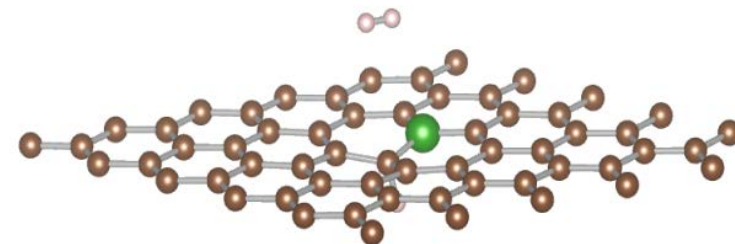


System	Nomenclature	Site of Physisorption	Binding Energy (kJ/mol H ₂)
C ₅₀	C	Top site C	5.2
B C ₄₉ H ₁	B	Top site C <i>ortho</i>	6.6
		Hollow site	5.8
B ₆ C ₄₄ H ₆	nB		
B N C ₄₈	BN <i>meta</i>	Top site C <i>ortho</i>	5.2
B ₃ N ₃ C ₄₄	BN <i>cyclic</i>	Top site N	5.4
B ₁₇ N ₁₇ C ₁₆	CBN	Bridge site C-N	12.5
		Top site N	8.3
		Hollow site	8.3
		Top site B	7.6

CBN graphene E = 12.5 kJ/mol



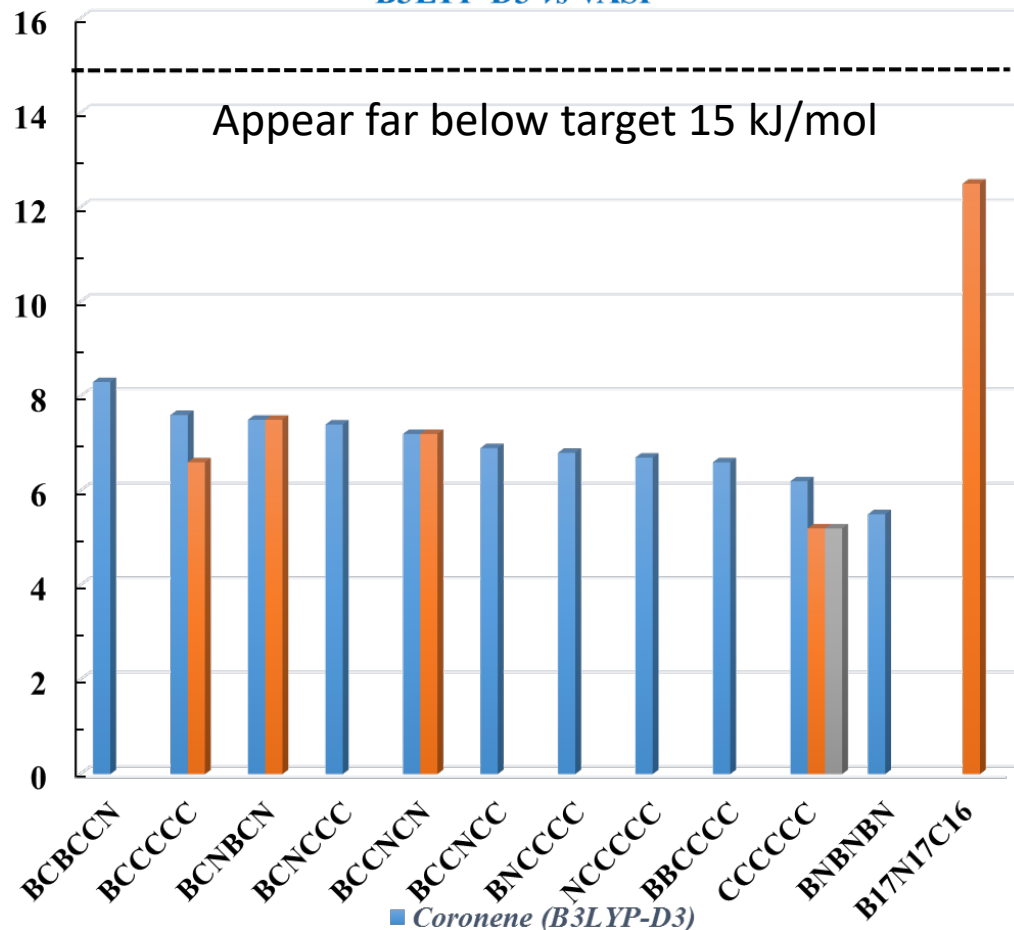
B-doped graphene E = 6.6 kJ/mol



H₂ attracted to defects created in boron doped coronene.
What is best way to generate the most defects in graphene?



Molecular vs Extended Systems
Coronene vs Graphene
B3LYP-D3 vs VASP



► Sorbents

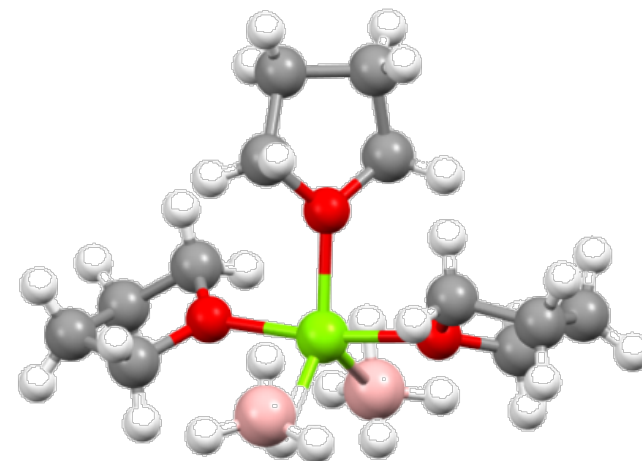
- vdW-DF2 method with revPBE exchange provides best agreement with experiment
 - B-doped carbon increases binding energy of H₂ by 25 %
 - **CBN graphene appears uniquely interesting (E = -12.5 kJ/mol)**
- Peer review paper with NREL describing results
- Potential future work
 - *Deep dive into coronene to look more closely at 'parameters' enabling larger binding energies with H₂*

Solid* phase hydrogen carriers

* solid becomes liquid at 100°C - liquid may have some distinct advantages

► Results

- A simple cycle describing reversible reaction pathway
 - $\text{Nido} + \text{H}_2 \rightleftharpoons \text{Arachno}$
 - $\text{Arachno} + \text{H}^- \rightleftharpoons \text{Hypho}$
 - $\text{Hypho} \rightleftharpoons \text{Nido} + \text{BH}_4^-$
- A mechanism for formation of 'unstable' $\text{Mg}(\text{B}_3\text{H}_8)_2$.
 - $2 \text{B}_2\text{H}_7^- \rightarrow \text{B}_3\text{H}_8^- + \text{BH}_4^-$
- Dual role for THF
 - Phase change
 - Catalyst
 - H_2 activation
 - BH_3 transfer



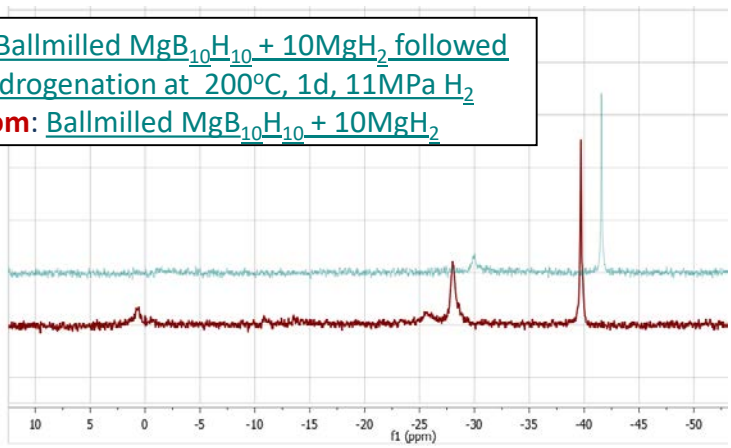


Validated H₂ uptake by closoborane MgB₁₀H₁₀

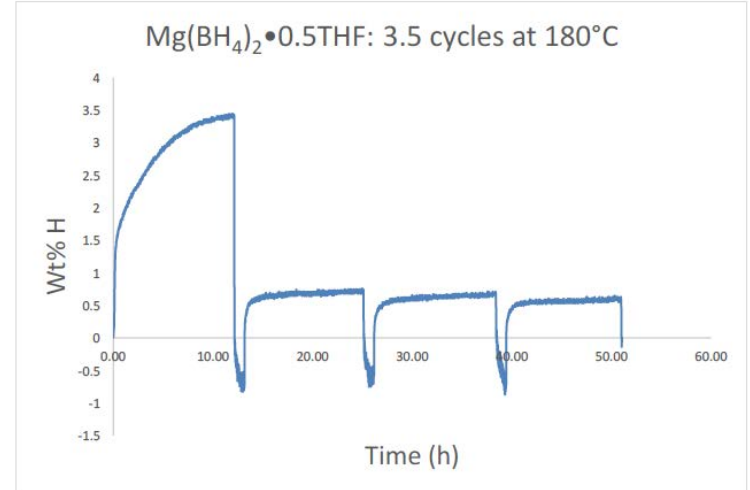
Hawaii, Craig Jensen, Phuong Nguyen, Sunil Shrestha

Following recycle by ¹¹B NMR

Top: Ballmilled MgB₁₀H₁₀ + 10MgH₂ followed by hydrogenation at 200°C, 1d, 11MPa H₂
Bottom: Ballmilled MgB₁₀H₁₀ + 10MgH₂



Following cycling in PCT at 180 °C



Exp. #	Sample	Conditions	Amount/Mol%					
			Species / δ ¹¹ B (ppm)					
			B(OH) ₄ ⁻ (2)	[B ₁₀ H ₁₀] ²⁻ (0 & -30)	[B ₁₂ H ₁₂] ²⁻ (-15)	[BH ₄] ⁻ (-42)	[B ₃ H ₈] ⁻ (-31)	Other
1	Ballmilled-B10 + 10 MgH ₂	5 mins*6 cycles, 1 min break	-	59	-	41	-	-
2	rehyd-ballmilled mixture	11 MPa H ₂ - 200°C - 1d	-	34	-	66	-	-

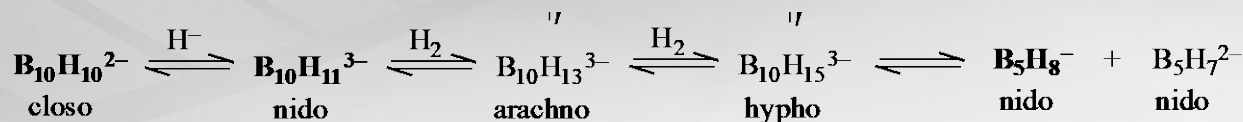


Last year provided base line

Insight into mechanism will help guide rational selection of catalyst



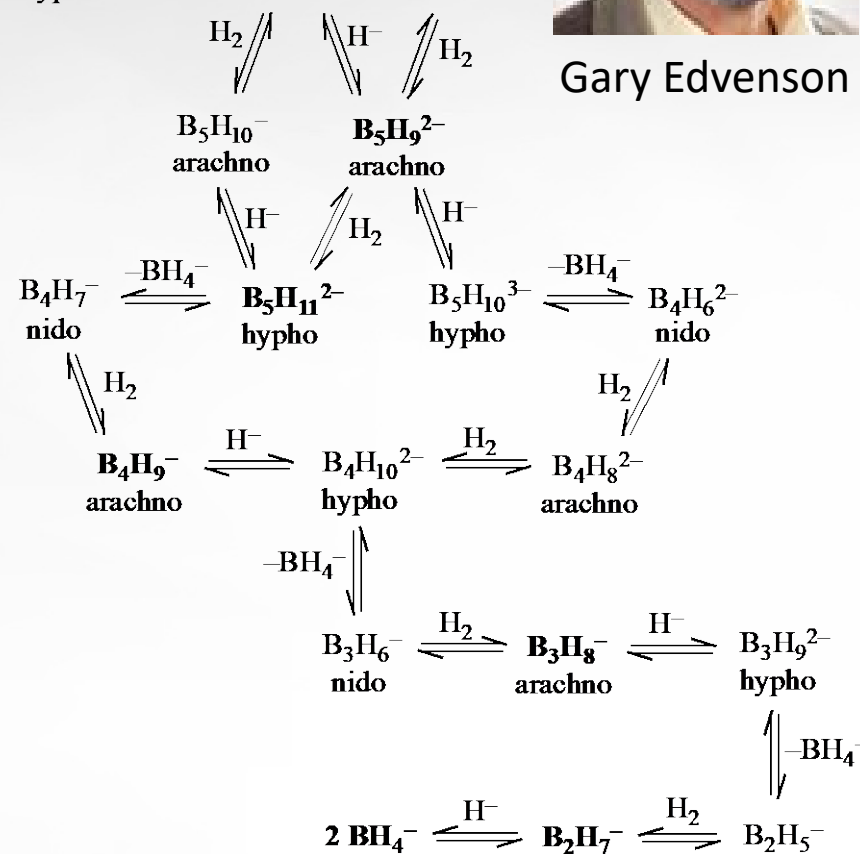
Gary Edverson



Recall only have H_2 and H^- (and THF)

Look for patterns in complex reaction schemes to 'simplify' mechanism

To developed 'rules of thumb' for H_2 uptake and release from $\text{B}_{10}\text{H}_{10}^{2-}$ to BH_4^-

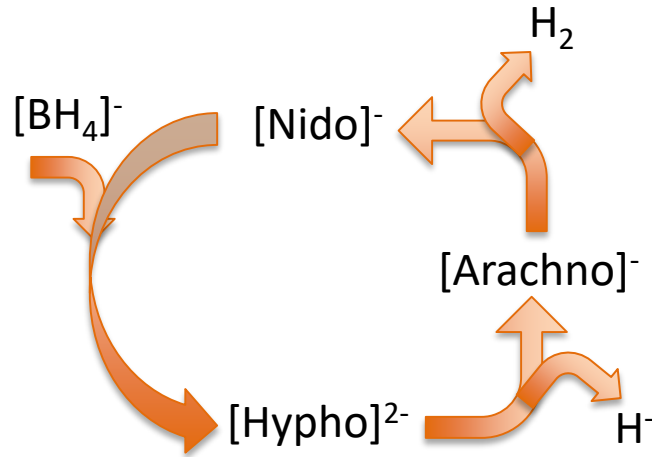


reaction pathway described by simple cycle

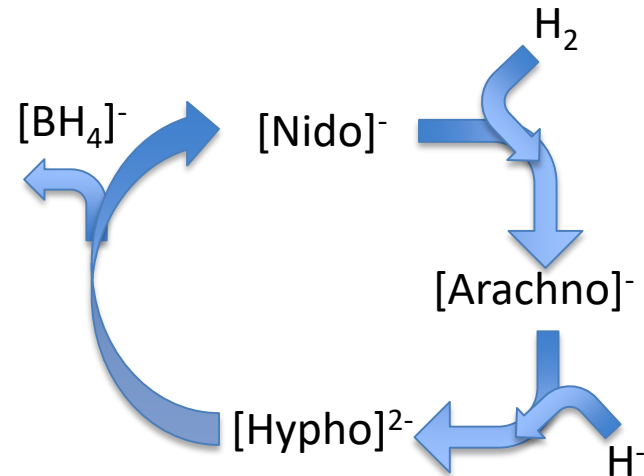
interconversion between nido – arachno and hypho boranes involve, H_2 , H^- and BH_4^- respectively



Hydrogen Release



Regeneration



- **Insight into regeneration?**
 - **If rate limiting step is H_2 activation, then need catalysts to activate H_2 to convert nido to arachno**

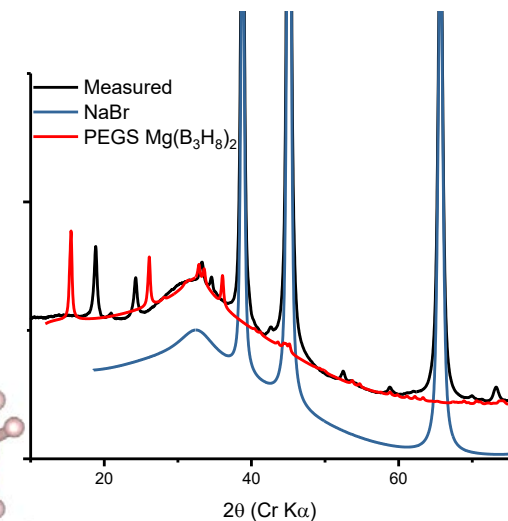
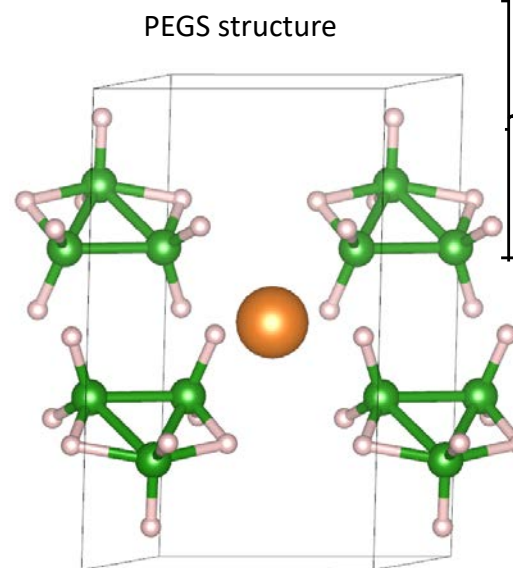
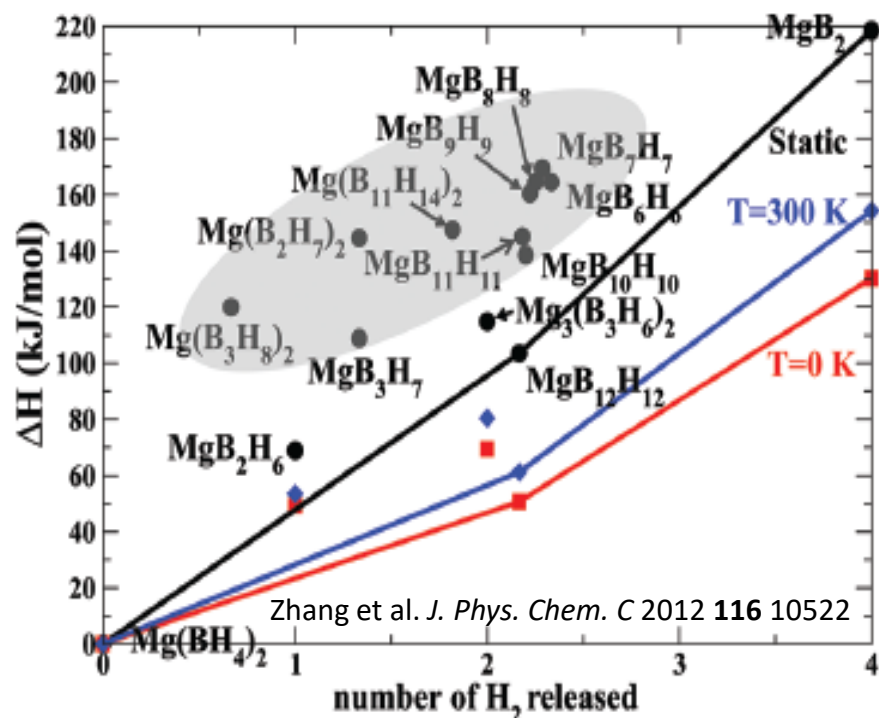
Observation of $\text{Mg}(\text{B}_3\text{H}_8)_2$ is not consistent

with theory. Intermediates in gray balloon should not be observable – if calculated structures (i.e., PEGS) are comparable to experimental structures



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Solvent-free $\text{Mg}(\text{B}_3\text{H}_8)_2$
courtesy Romain Moury and
Hans Hagemann, Geneva

- PEGS structure not consistent with experimental structure
- Need to solve the structure and/or measure ΔH by calorimetry or PCT*
 - *University of Hawaii

Key Accomplishment

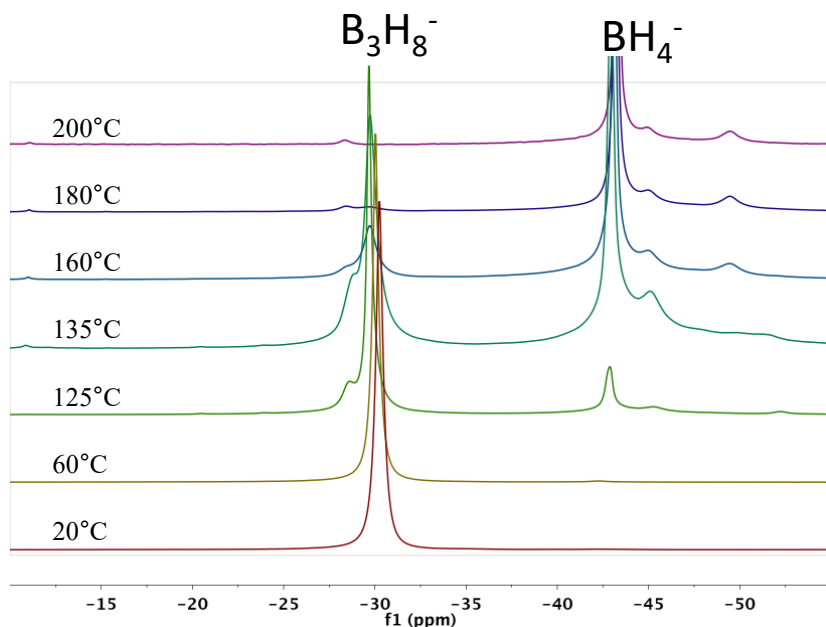
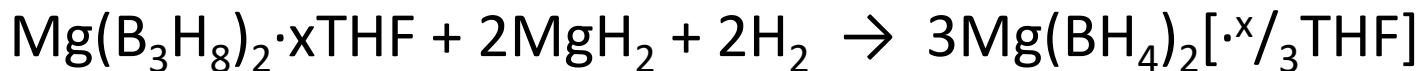
Experimental measurement of ΔH

Use calorimetry to measure H_2 uptake. (THF adduct) – change the sign to get ΔH_{H_2} release ca. $\sim 70 \pm 10$ kJ/mol (not 150 kJ/mol)

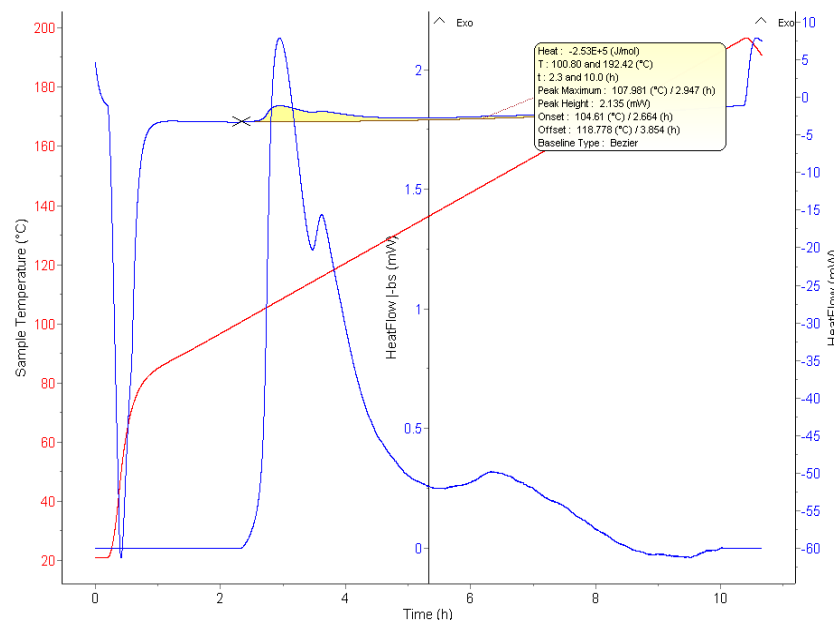
Pacific
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Marina Chong



In-situ high pressure ^{11}B NMR of $\text{Mg}(\text{B}_3\text{H}_8)_2 \cdot x\text{THF} : 2\text{MgH}_2$ (50 bar H_2) shows near quantitative conversion



Calorimetry provides enthalpy for $\text{Mg}(\text{BH}_4)_2 \cdot x\text{THF}$ formation from $\text{Mg}(\text{B}_3\text{H}_8)_2 \cdot x\text{THF} : 2\text{MgH}_2$ (5 bar H_2)

Lewis base additives enhance properties of complex hydrides, e.g., $\text{THF}_x^* \text{Mg}(\text{BH}_4)_2$

- Lewis base adducts lower the mp of the hydride – so kinetics are significantly enhanced in the melt - need to find way to keep it a liquid throughout
- THF adduct ‘stabilizes’ $\text{Mg}(\text{B}_3\text{H}_8)_2$ intermediate – still unstable (70 kJ/mol) – but lower than 150 kJ/mol
- THF may act as a ‘catalyst’ to: (i) stabilize and transfer $\text{BH}_3^* \text{THF}$ intermediates (back-up)
 - $\text{THF}^* \text{Mg}(\text{BH}_4)_2 \rightleftharpoons \text{HMgBH}_4 + \text{THF}^* \text{BH}_3$
 - $2\text{THF}^* \text{BH}_3 + \text{Mg}(\text{BH}_4)_2 \rightleftharpoons \text{THF}_2^* \text{Mg}(\text{B}_2\text{H}_7)_2$
- Disproportion of two BH_4^- species to make a stable and unstable intermediate provides a pathway to make unstable intermediates
- THF adduct directs $\text{Mg}(\text{BH}_4)_2$ to $\text{MgB}_{10}\text{H}_{10}$ – and $\text{MgB}_{10}\text{H}_{10}$ can be reconverted back to $\text{Mg}(\text{BH}_4)_2$ – so long as you keep it in liquid phase (University of Hawaii)
- **Future work: Developing approaches to retain liquid phase complex hydrides to enhance kinetics and enable catalysts**

Accomplishments – validating concepts

Liquid phase hydrogen carriers (LPHCs)

tuning thermodynamics – stabilizing arenes and/or destabilizing cycloalkanes

■ Pez & Cooper

- Increasing conjugation decreases ΔH_{H_2}
- Adding heteroatoms decreases ΔH_{H_2}

■ Clot, Eisenstein & Crabtree

- Heteroatoms destabilize ‘charged’ carrier

■ Jessop

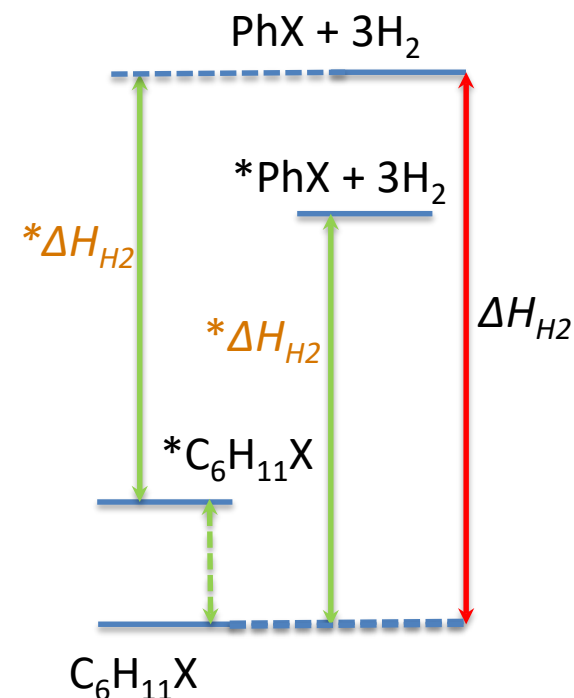
- Electron donating substituents decreases ΔH_{H_2}
- Linear correlation with Hammett $\sigma(p)$ $X-Ph \leftrightarrow X-C_6H_{11}$

■ PNNL

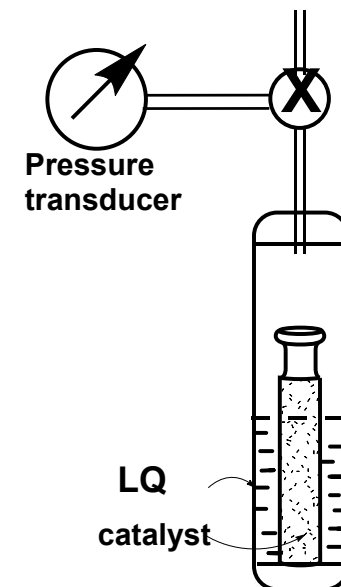
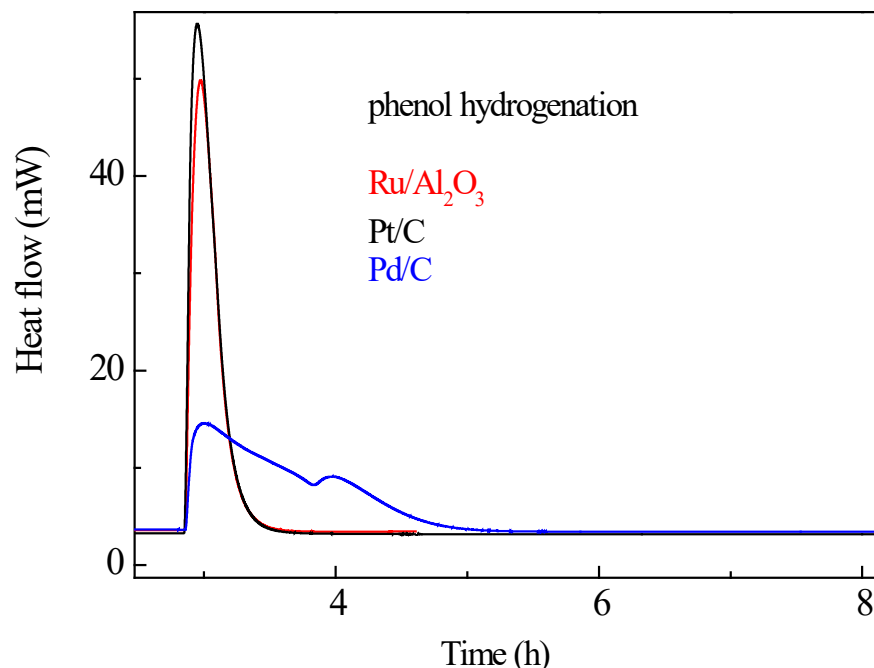
- Tuning ΔH_{H_2} with Lewis base
 - ◆ $H_2 + CO_2 + B: \leftrightarrow [HCO_2^-][BH^+]$

■ DICP

- Electron donating groups decreases ΔH_{H_2}
- $^*\Delta H_{H_2} < \Delta H_{H_2}$



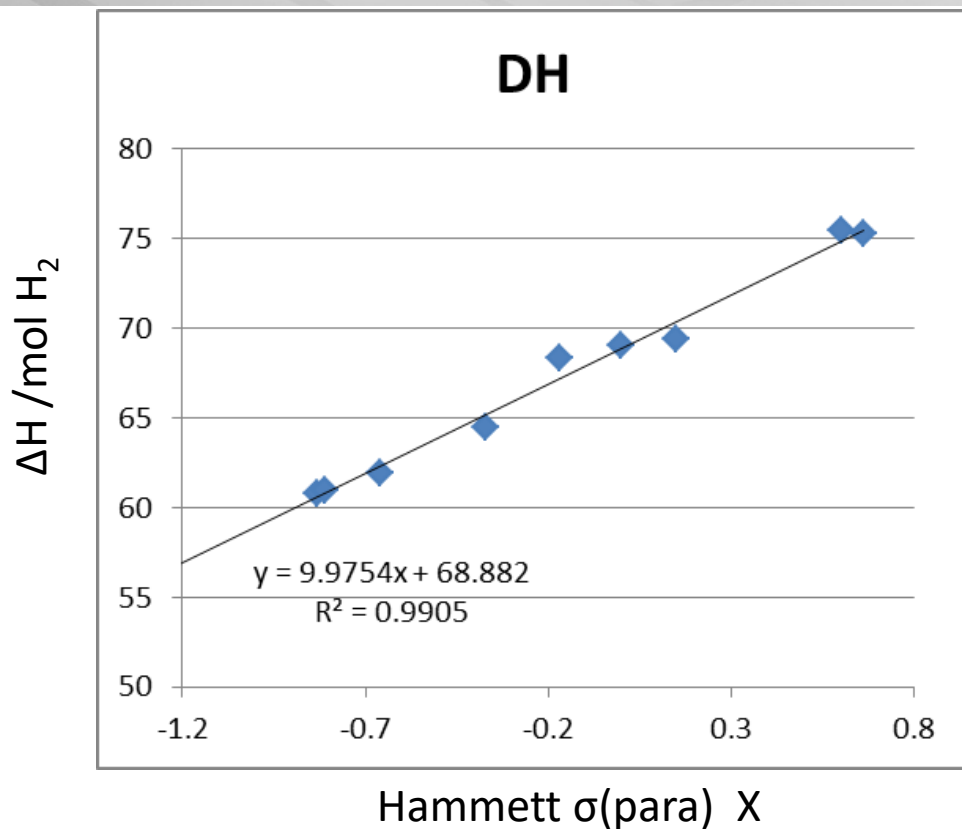
Validating concepts – modifying ΔH with electron donating substituents



$$\Delta H_{H_2}(\text{PhOH}) = -207(10) \text{ kJ/mol}$$
$$\Delta H_{H_2}(\text{PhO}^-) = -182(11) \text{ kJ/mol}$$

Note heat is measured as function of time so we can compare rates of different catalysts (Ru~Pt > Pd)

Predicting the temperature required for H₂ release

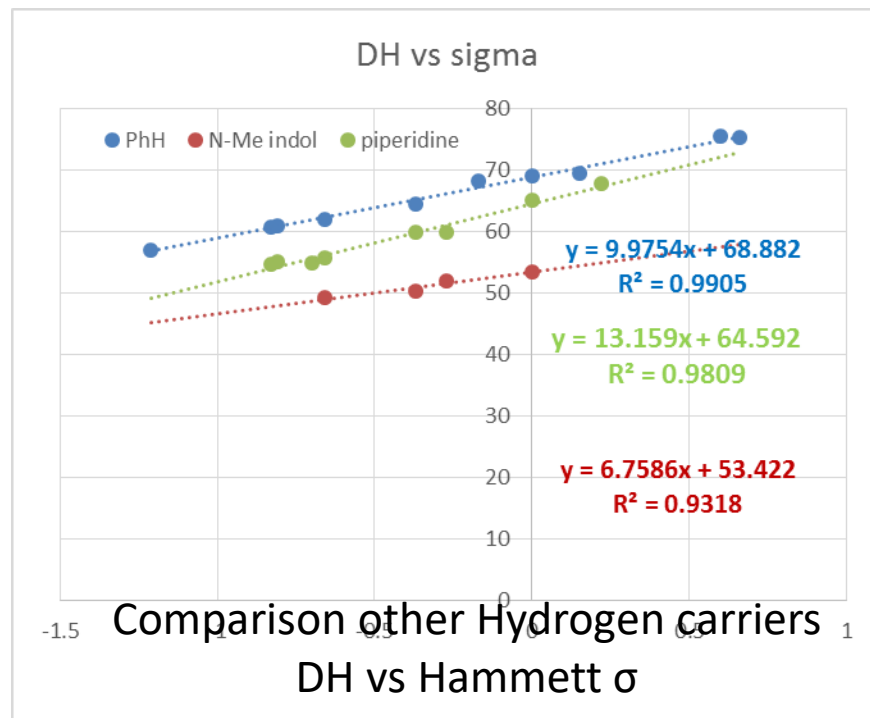


Linear correlation with Hammett parameter*
X-Ph. X = H, Me, OH, NH₂, NMe₂, NH₃⁺, O⁻
*Phil Jessop

- ▶ $\Delta G = \Delta H - T\Delta S$
- ▶ At $\Delta G = 0$; $K_{\text{eq}} = 1$ bar H₂
- ▶ $\Delta H = T\Delta S$
- ▶ T (1 bar H₂) = $\Delta H / \Delta S$
- ▶ Assume $\Delta S \sim 125$ J/K/mol
- ▶ ΔH gives estimated temperature for H₂ release. E.g.,
 - $\Delta H(\text{C}_6\text{H}_6) = 69$ kJ/mol H₂
 $T_{1\text{bar H}_2} \text{ ca. } 280$ °C
 - $\Delta H(\text{C}_6\text{H}_5\text{O}^-) = 61$ kJ/mol H₂
 $T_{1\text{bar H}_2} \text{ ca. } 214$ °C
- ▶ **Ca. 65 °C decrease in temperature for H₂ release**

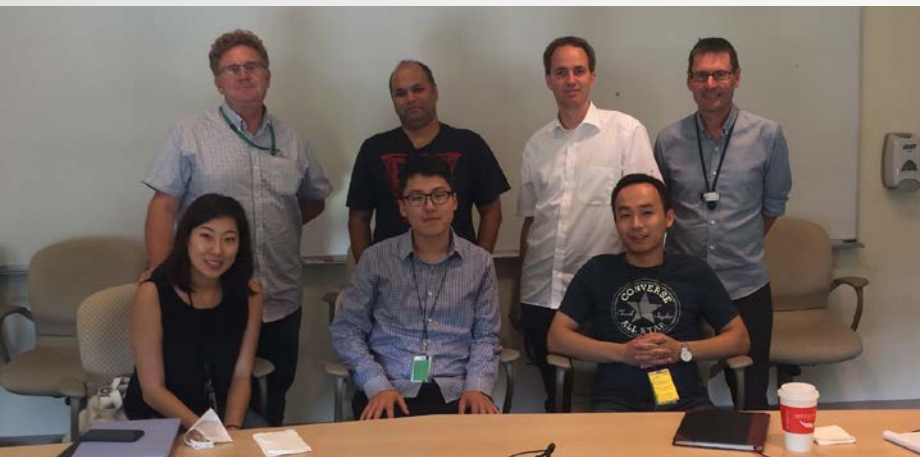
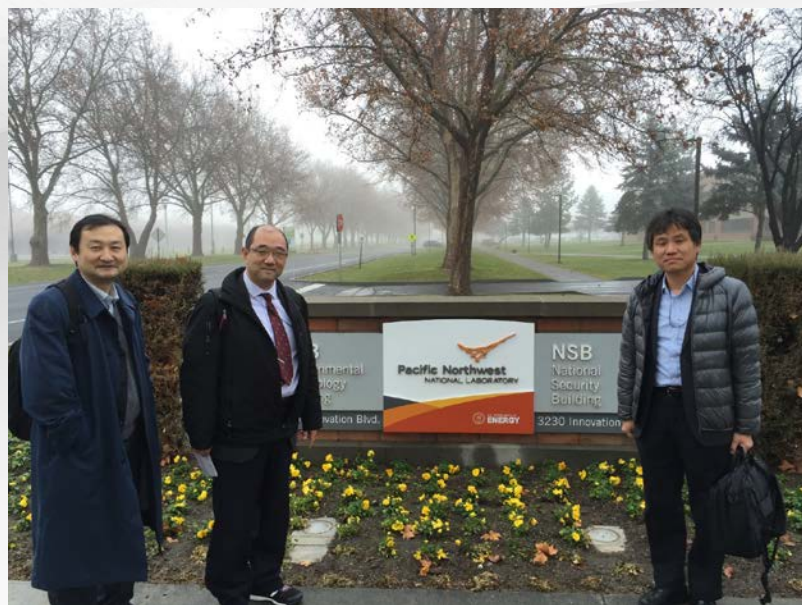
Liquid carriers (transport and off board storage)

- Decrease ΔH_{H_2} - adding negative charge to arene ring results in a lower enthalpy of H_2 adsorption in a predictable way.
 - Provided 'further' validation for correlation between ΔH_{H_2} and Hammett $\sigma(p)$ parameter
- Developing methods to predict enthalpy hydrogenation for families of LPHCs
 - Want both small intercept and larger slope
- Future work
 - Use DFT to calculate ΔH_{H_2} for extremes of Hammett parameters to get slope to predict T for H_2 release from hydrogen storage materials and carriers



Collaborations

- Argonne - ^{11}B NMR NaBH_4 @graphene
- NREL - ^{11}B NMR MgB_2 and MgBH_4 @ Al_2O_3
- NREL – ^{11}B NMR of B-doped carbons
- NIST – $\text{THF}_x^* \text{Mg}(\text{}^{11}\text{B}\text{D}_4)_2$ for neutron studies
- LBNL – Low temperature ^2H NMR Mg -dobdc
- Caltech – HR TEM
- SRNL – High pressure XRD



- Erlangen; K Mueller (H_2CO_2 , HCO_2^-)
- DICP; T He, P Chen (aq. PhOH)
- KIST; CW Yoon, H Jeong (Catalysts)
- Geneva; H Hagemann (unsolvated $\text{Mg}(\text{B}_3\text{H}_8)_2$)
- AIST; Q Xu, Y Himeda, H Kawanami (Catalysis)

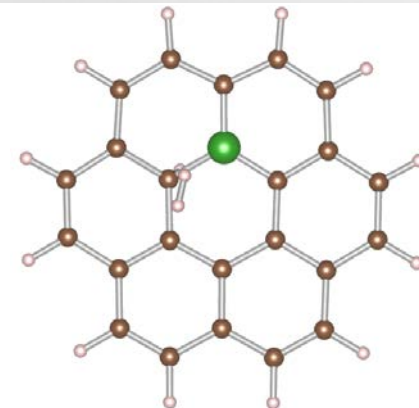
Remaining Challenges and Barriers

- ▶ An approach to maintain liquid phase of complex hydrides throughout the H₂ release (and uptake) cycle
 - Prevent phase separation of less soluble species
 - Identify catalysts to activate H₂ to convert nido to arachno boranes
- ▶ Light weight additives to control reaction pathways in complex hydrides
 - make B₁₀H₁₀⁻, not B₁₂H₁₂⁻
 - make B₃H₆²⁻ to avoid phase separation of MgH₂
- ▶ Identify the physiochemical properties of ‘defects’ in sorbent materials that provide > 12 kJ/mol binding energy
- ▶ Novel approaches to tune thermodynamics of hydrogen carriers to lower ‘operating’ temperature to release H₂ from hydrogen carriers
- ▶ Synthesis of hydrogen carriers without using H₂
- ▶ Understand the correlation between thermodynamics of H₂ release and the ‘kinetic’ Hammett parameter to predict ΔH_{H_2} .

Future work *(subject to funding availability)*

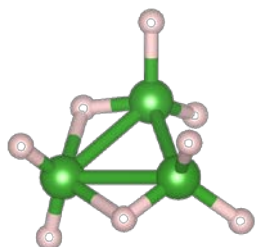
► B-doped C:

- identify *descriptors* to correlate binding energy, e.g., charge, bond order, symmetry, defects.
- Investigate binding energies in **BN doped C**



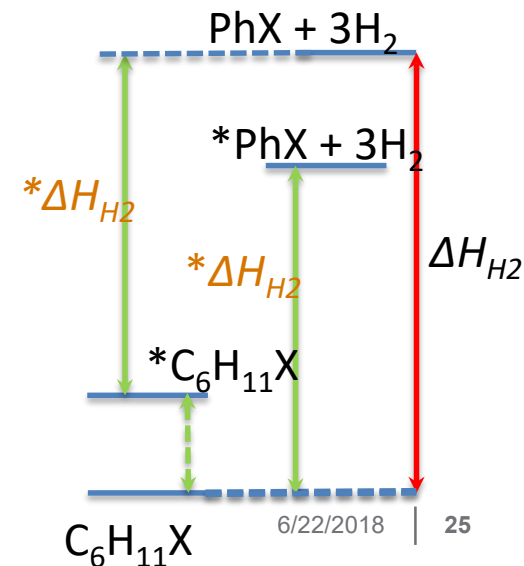
► Complex hydrides

- Investigate approaches to retain liquid phase complex hydrides to enhance kinetics and enable catalysts
- H₂ activation to convert nido to arachno



► Hydrogen carriers

- Use DFT to calculate ΔH_{H_2} for extremes of Hammett parameters to get slope to predict T for H₂ release from hydrogen storage materials and carriers
- *Chemical compression* – exergonic and endothermic, e.g., $H_2CO_2 \rightarrow H_2 + CO_2$





Mandatory summary slide

▶ B-doped C

- 1st B-doped into coronene increases binding energy (6.2 to 7.6 kJ/mol)
- 2nd B-doped on same ring actually predicted to decrease binding energy (7.6 to 5.6 kJ/mol).
- 2nd H₂ (to single B- doped coronene) slightly reduced binding energy and prefers opposite side
- BN ring binds H₂ more weakly than all carbon ring (6.2 to 5.5 kJ/mol)

▶ Complex Hydrides

- Lewis base adducts lower the mp of the hydride – so kinetics are significantly enhanced in the melt - need to find way to keep it a liquid throughout
- THF adduct ‘stabilizes’ Mg(B₃H₈)₂ intermediate – still unstable (70 kJ/mol) – but lower than 150 kJ/mol
- THF may act as a ‘catalyst’ to stabilize and transfer BH₃*THF intermediates
- Disproportion of two BH- species to make a stable and unstable intermediate provides a pathway to make unstable intermediates

▶ Liquid carriers

- adding negative charge to arene ring results in a lower enthalpy of H₂ adsorption in a predictable way.

Acknowledgements



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Hydrogen Materials - Advanced Research Consortium (HyMARC), established as part of the Energy Materials Network under the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office.

- *Pacific Northwest National Laboratory is a multiprogram national laboratory operated by Battelle for the U.S. Department of Energy under Contract DE-AC05-76RL01830.*
- "Hydrogen is a light, odorless gas, which, given enough time, turns into people." - Edward Robert Harrison, astronomer and cosmologist



Technical backup slides

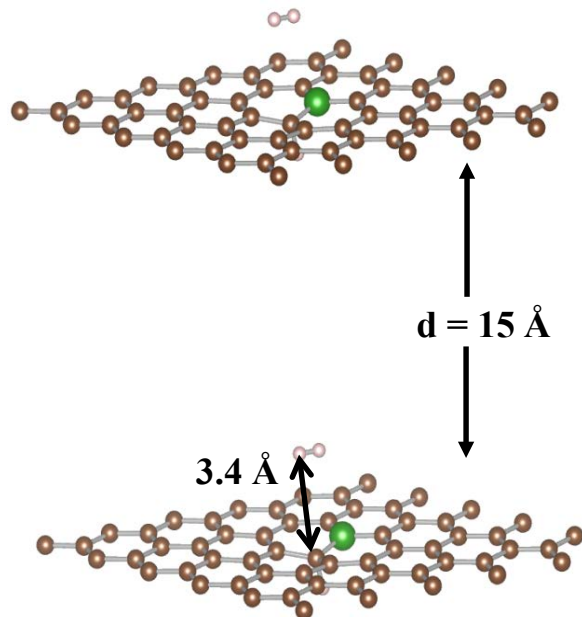


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Effect of B doping in carbon *binding energy* reports over large range 5-20 kJ/mol

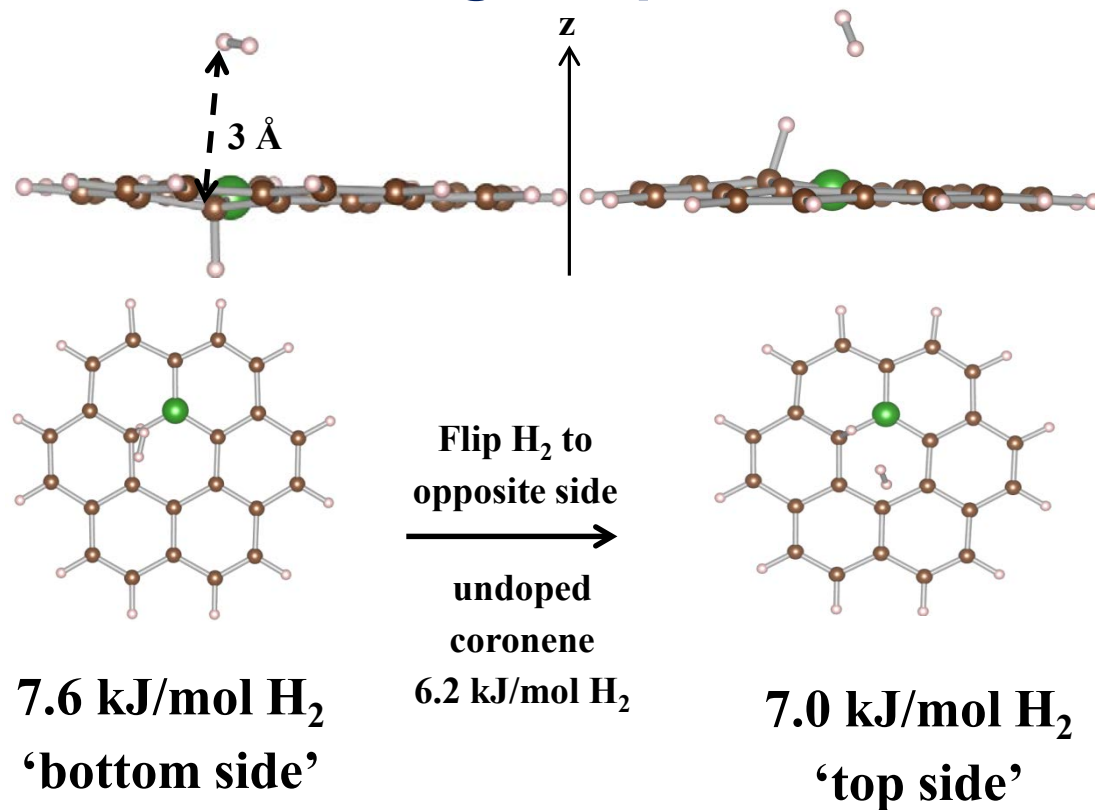


binding energy 6.6 kJ/mol

BC₄₉H ~ 2% B

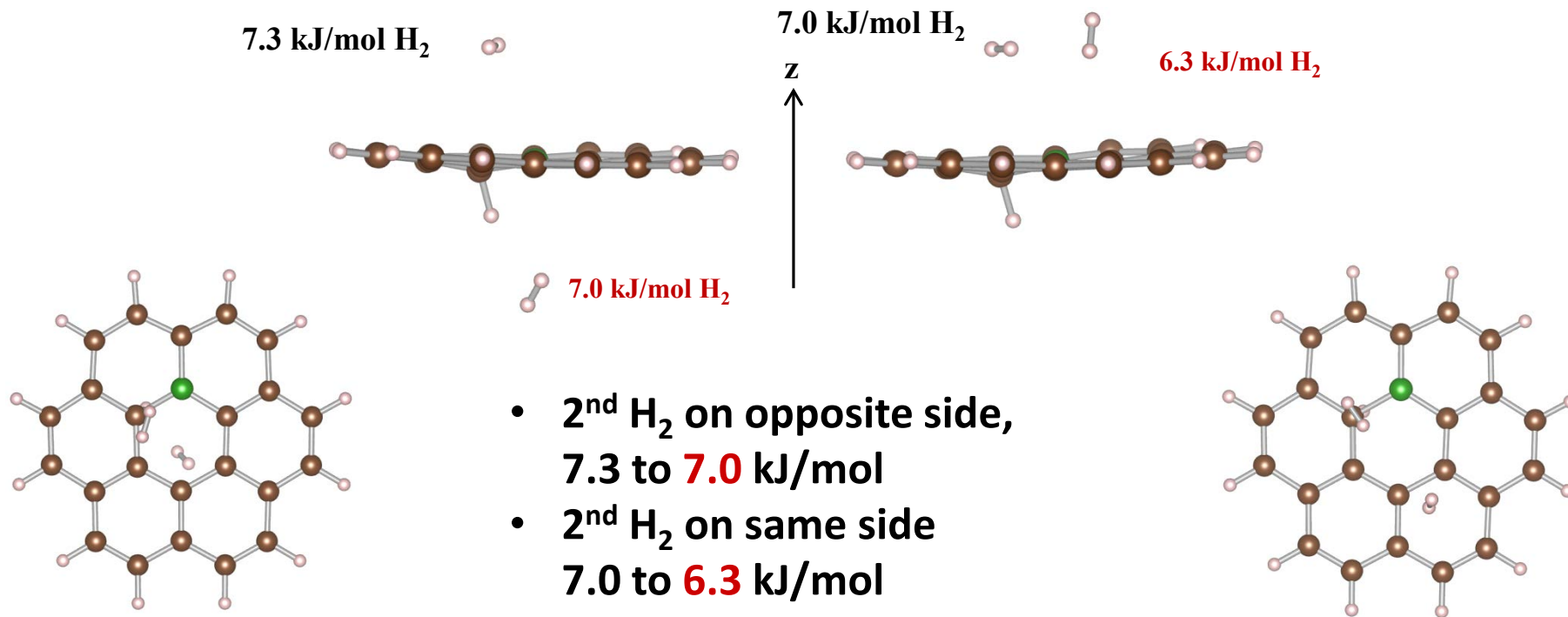
- Binding energy increases 25% with B doped into graphene (5.2 to 6.6 kJ/mol H₂)
- Distance from surface does not significantly change (3.4 Å)
- Notice that H₂ is not directly over the B
- Theory can provide insight into complex phenomena: can we learn what B is doing that increases binding energy?
- Is there a linear correlation between binding energy in coronene and graphene? (easier to do coronene – but need to know it is a good model)

B-doped coronene – which is the preferred side for binding – top or bottom?



- N.B. H₂ molecule prefers site next to B – a defect site
- Only minor difference for binding on bottom side away from 'defect'
- Where does the next H₂ go?
- What is the binding energy of 2nd H₂?

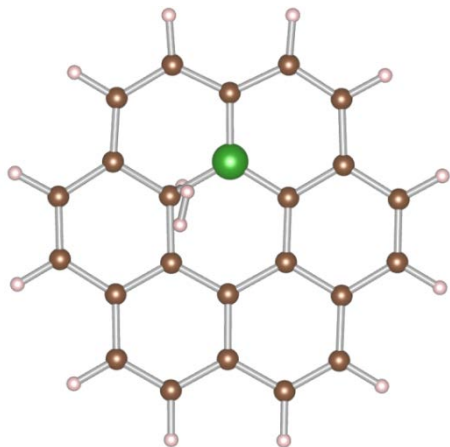
B-doped coronene – fate of 2nd H₂?



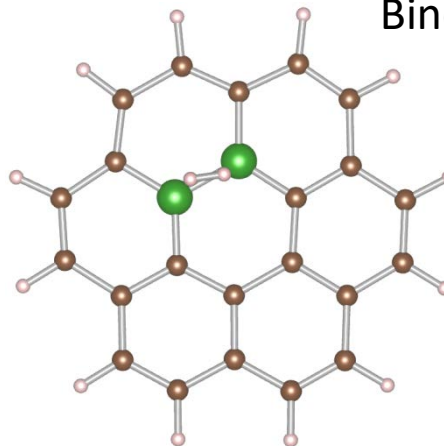
Does increasing B content increase binding energy?

Increase B-doping - decrease binding energy

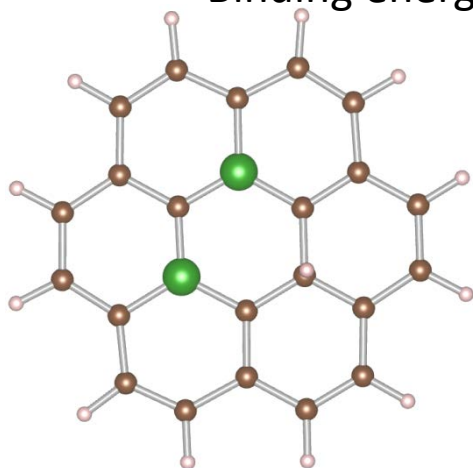
Binding energy 7.6 kJ/mol



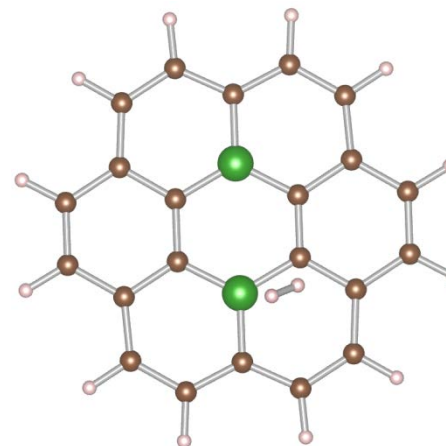
Binding energy 6.6 kJ/mol



Binding energy 5.9 kJ/mol

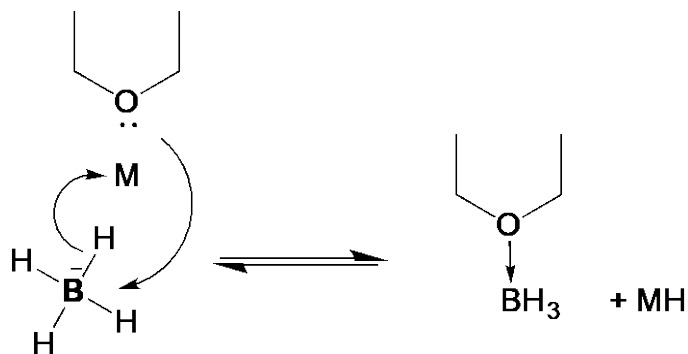


Binding energy 5.6 kJ/mol

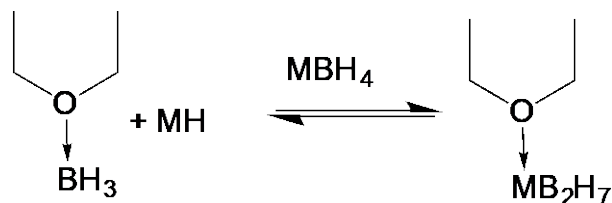


Understanding roles of THF, chemical stabilization of unstable intermediates & physical role in phase change

(PNNL thanks one of last years reviewers for making the suggestion that THF can act as a shuttle)



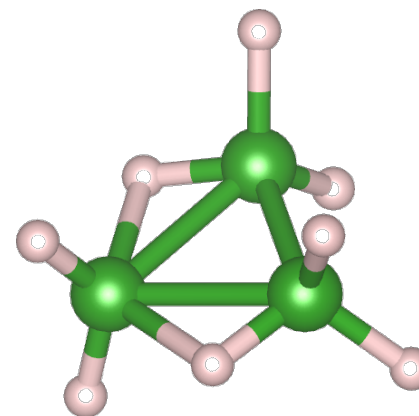
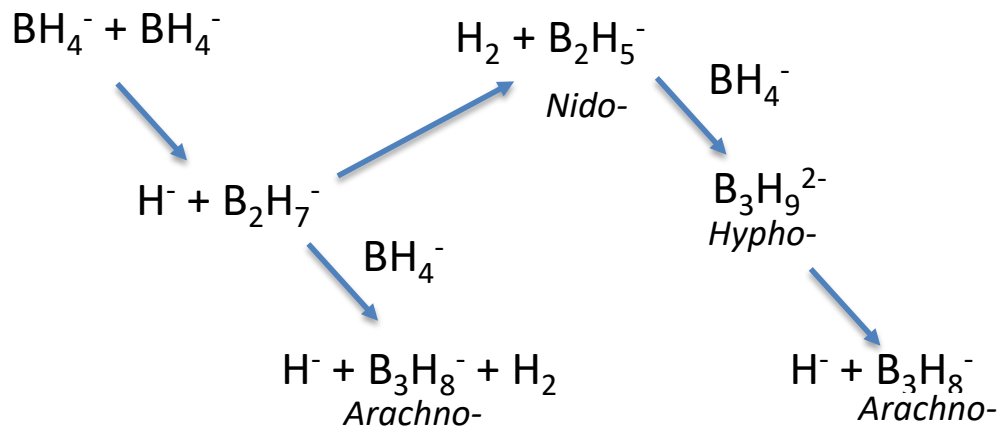
- **Stabilizing intermediates**
THF traps BH_3 , lower energy transition state and prevents diborane formation



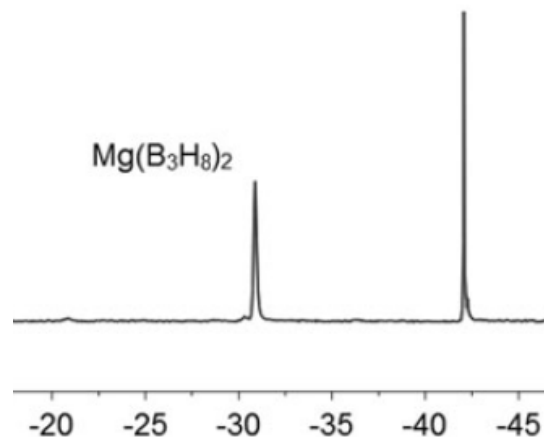
- **THF never makes it to gas phase** *moves back and forth between Mg cation and BH_3*

Cycle consistent with experiment

$Mg(B_3H_8)_2$ – first intermediate detected ($B_2H_7^-$, $B_2H_5^-$, $B_3H_9^-$ 'unstable')



Mg(BH₄)₂

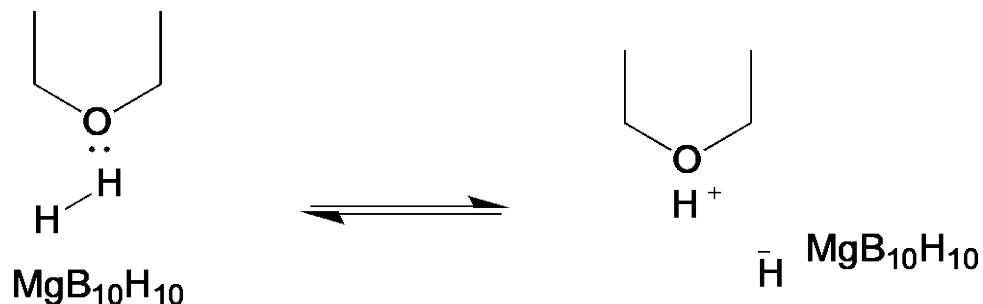


Chong et al. *Chem. Commun.* 2011 **47** 1330

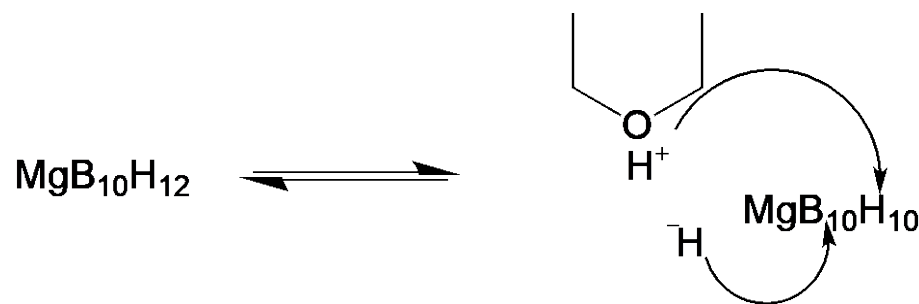
¹¹B NMR of aqueous extract of Mg(BH₄)₂ heated 200°C for 35 days. Mg(B₃H₈)₂ also seen at higher temperatures, e.g. 350°C/6h.



Hypothesis for catalytic role of Lewis base for regeneration: THF helps to activate H_2

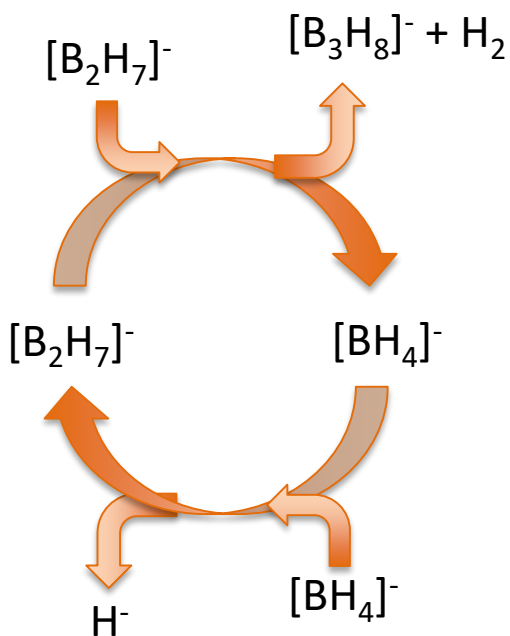


- H_2 activation by electron poor Mg^{2+} and electron rich THF to form HMg^+ and $(THF)H^+$

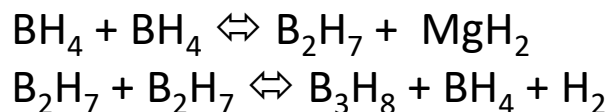


- super acid $(THF)H^+$ protonates B-B bond with synchronous H^- transfer

Mimicking Nature – understanding pathways to generate unstable (higher energy intermediates)

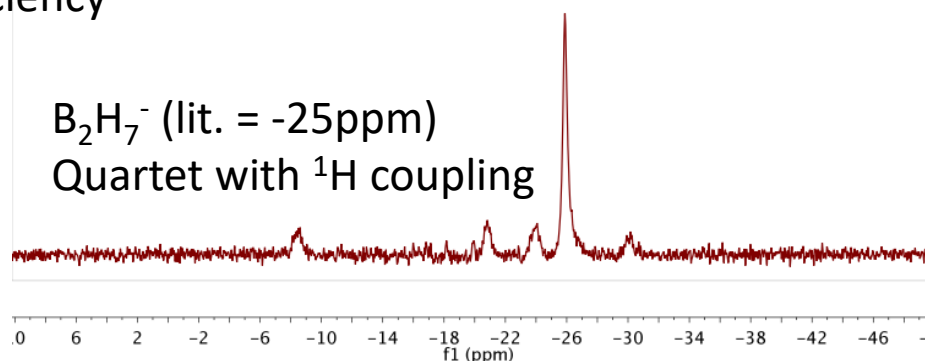


Disproportional (bifurcation mechanism) can lead to the formation of 'unstable' $Mg(B_3H_8)_2$. – coupled with formation of stable intermediates, e.g., $Mg(BH_4)_2$.



This requires you cycle through BH_4 multiply times – two steps forward and one step back - decreases atom efficiency

^{11}B NMR of CD_3CN extract of $Mg(B_3H_8)_2 \cdot THF/4MgH_2$ heated $100^\circ C$ in N_2 , quenched after first exotherm



Add series of calculated energies to compare new pathways: B_2H_7 looks worse than B_3H_8

Reaction	ΔE_{static} (0K) kJ/mol H_2	ΔH_{ZPE} (0K) kJ/mol H_2	ΔH_{ZPE} (300K) kJ/mol H_2	ΔS (300K) J/(mol H_2 K)	ΔG_{ZPE} (300K) kJ/mol H_2
$3Mg(BH_4)_2 \rightarrow Mg(B_3H_8)_2 + 2MgH_2 + 2H_2$	176.3	148.7	147.9	84.9	124.2
$2Mg(BH_4)_2 \rightarrow Mg(B_2H_7)_2 + MgH_2$	214	204	202	-26	208
$2Mg(B_2H_7)_2 \rightarrow Mg(B_3H_8)_2 + Mg(BH_4)_2 + 2H_2$	-38	-56	-52	110	-85
$3Mg(BH_4)_2 \rightarrow Mg_3(B_3H_6)_2 + 6H_2$	53.6	35.3	37.9	94.3	9.7
$Mg(BH_4)_2 \rightarrow Mg(B_2H_6) + H_2$	66	47	49	93	22
$2Mg(B_2H_6) + 4H_2 \rightarrow Mg(B_3H_8)_2 + 3Mg(BH_4)_2 + 2MgH_2$	-10	4	1	-97	30

Liquid carriers – reaction calorimetry provides capability to validate concepts

- ▶ Aqueous phase mixtures of H_2CO_2 provides a potential approach for low pressure delivery and transport of H_2 .
 - Perfect thermodynamics for chemical compression
 - Smart people working on development of catalyst and methods to purify H_2 and recovery to recycle CO_2 .
- ▶ Solid formates, M^+CO_2^- ($\text{M} = \text{Na}, \text{K}$) provide a potential approach to store large quantities of H_2 – “Just add water”
 - Perfect thermodynamics for reversibility and hydrogen comes from H_2O
 - Smart people working on development of catalyst.
- ▶ Aqueous phase mixtures of $\text{PhOH}/\text{M}^+\text{PhO}^-$.
 - Can tune thermodynamics - adding negative charge to arene ring results in a lower enthalpy of H_2 adsorption and corresponding decrease in ‘operating temperature’
 - Developing methods to predict enthalpy hydrogenation for families of LPHCs