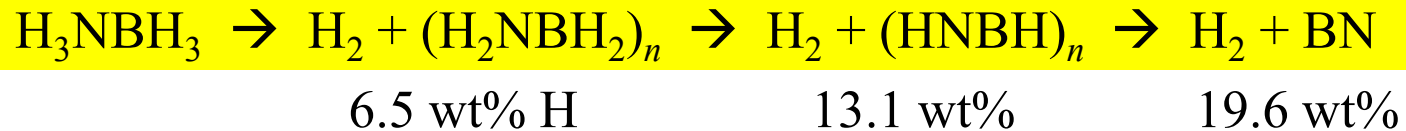


1) Background

Ammonia-Borane: a Promising Material for Hydrogen Storage



- High storage capacity has drawn attention to hydrogen release methods and mechanisms:
 - Catalyzed hydrolysis
 - Solid thermolysis
 - Catalyzed solid thermolysis
- Solution thermolysis in ethers and ionic liquids
 - Catalyzed solution thermolysis

Cf. A. Staubitz et al. Chem. Rev. 2010, 110, 4079-4124.

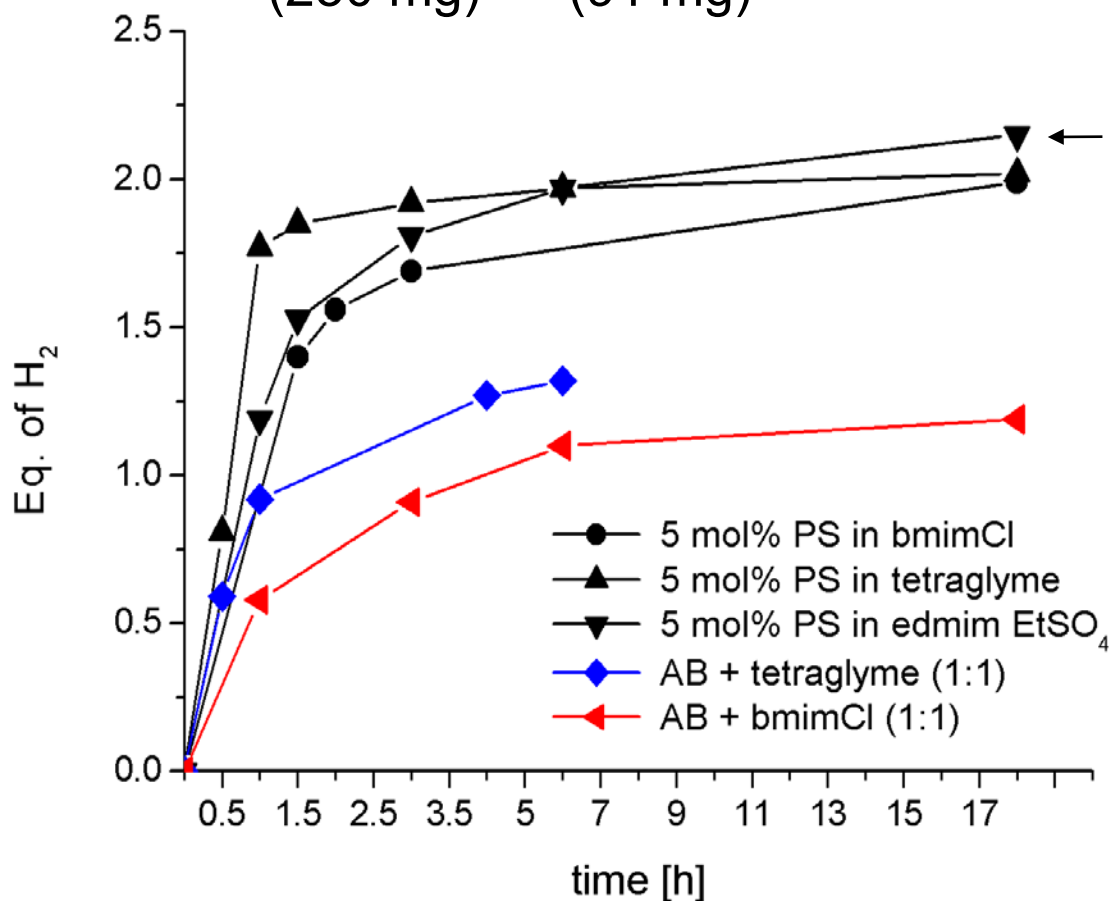
This presentation does not contain any proprietary or confidential information



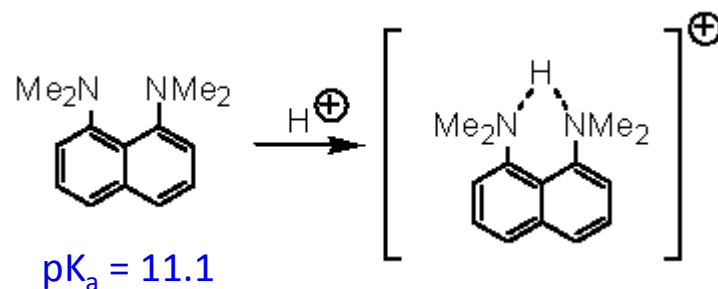
2) Base-Promoted AB dehydrogenation

Enhanced AB H₂-Release with Proton Sponge in Ionic Liquids or Tetraglyme with Reduced Foaming

NH₃BH₃ + 5 mol % PS at 85 °C in Ionic Liquids or Tetraglyme
(250 mg) (91 mg) (250 mg)

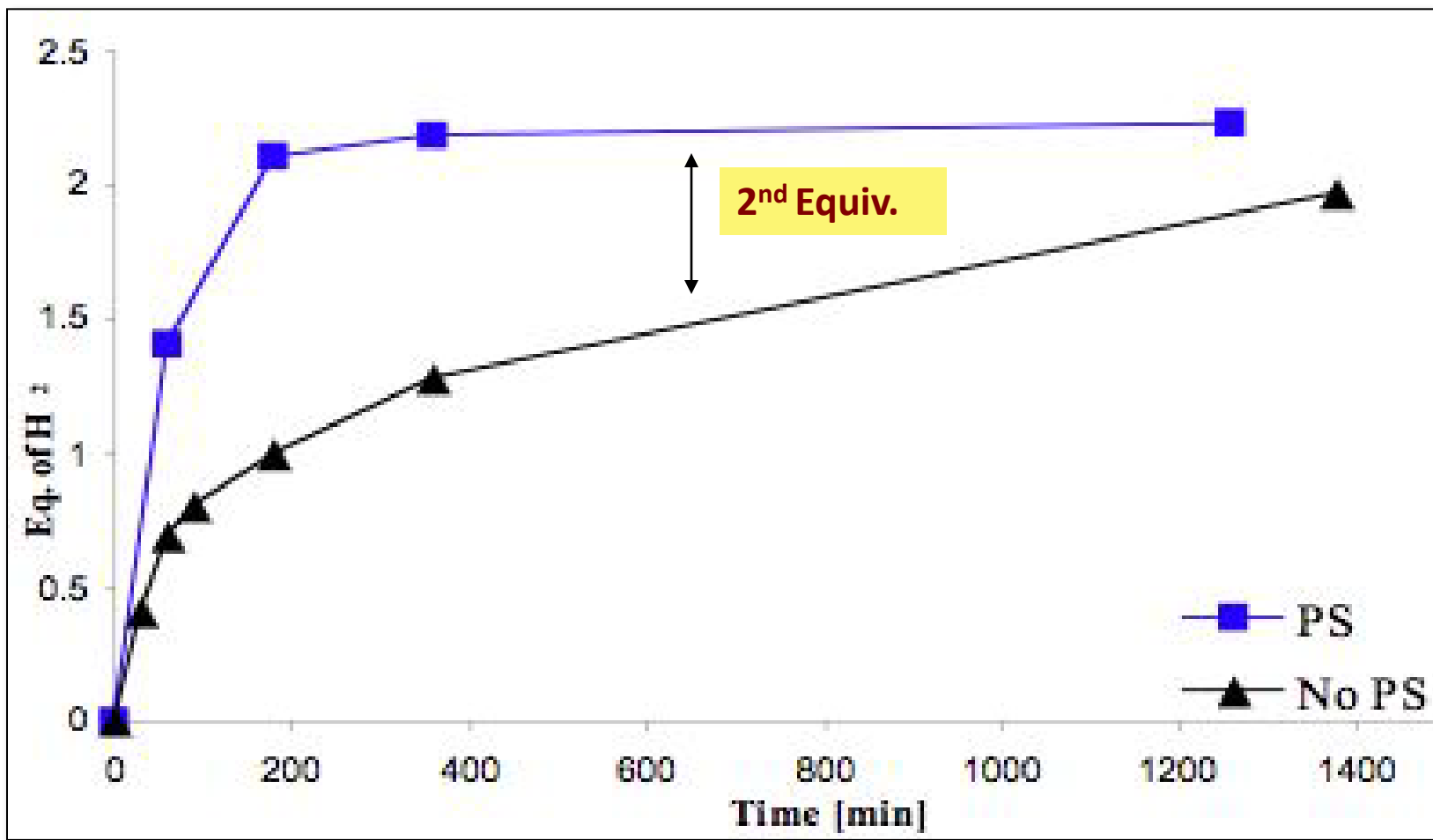


← 5.60 mat. wt. % H₂



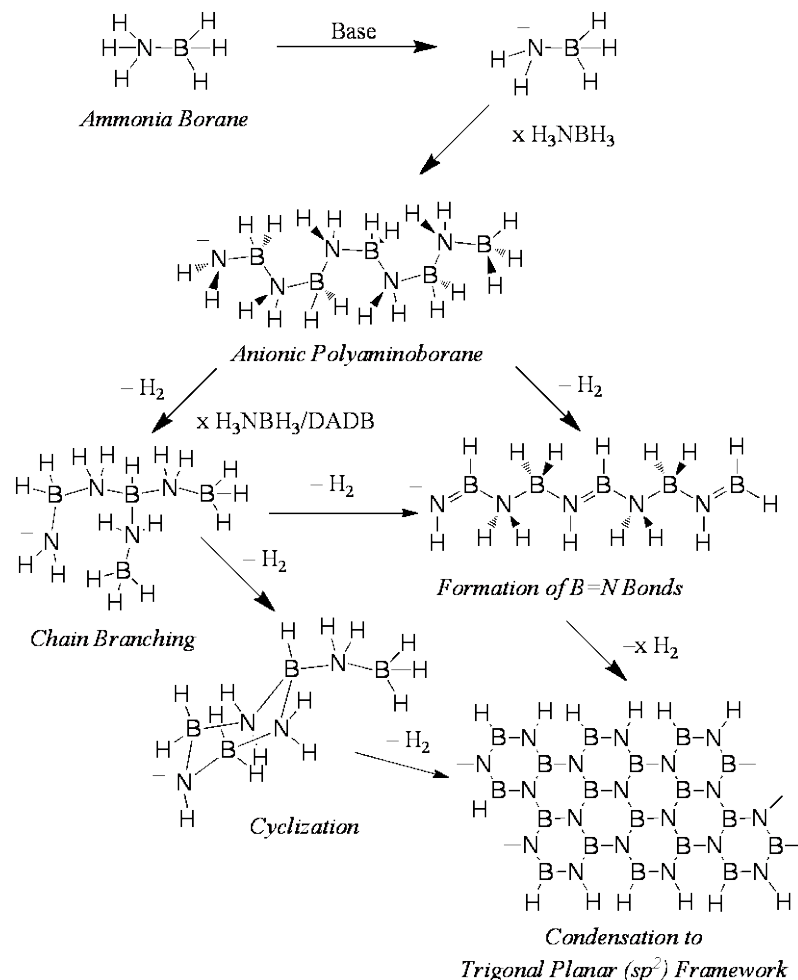
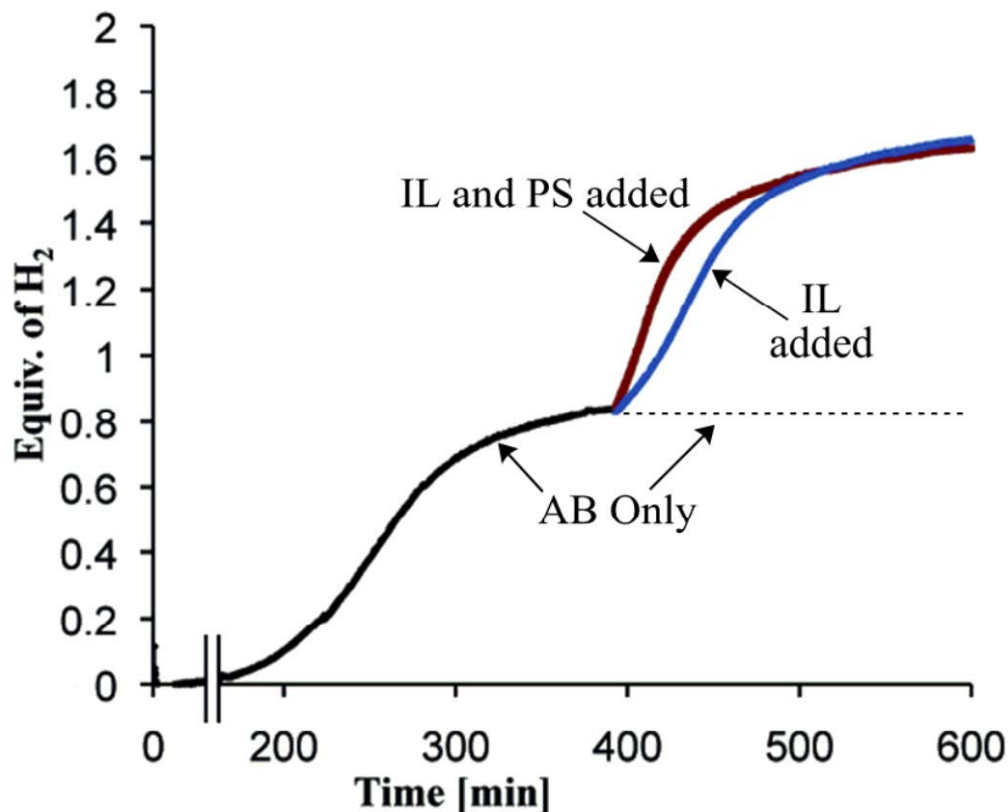
Himmelberger, D.; Yoon, C. W.;
Bluhm, M. E.; Carroll, P. J.;
Sneddon, L. G. *J. Am. Chem. Soc.*
2009, *131*, 14101.

Proton Sponge Increases Release Rate of Second Equivalent of H₂ from AB

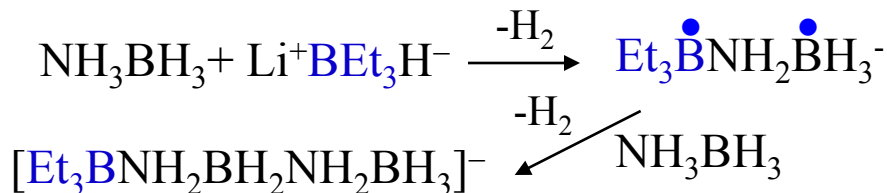


AB with 5 mol% PS
in bmimCl at 85°C

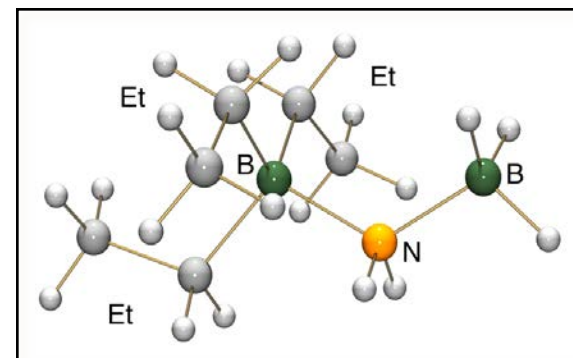
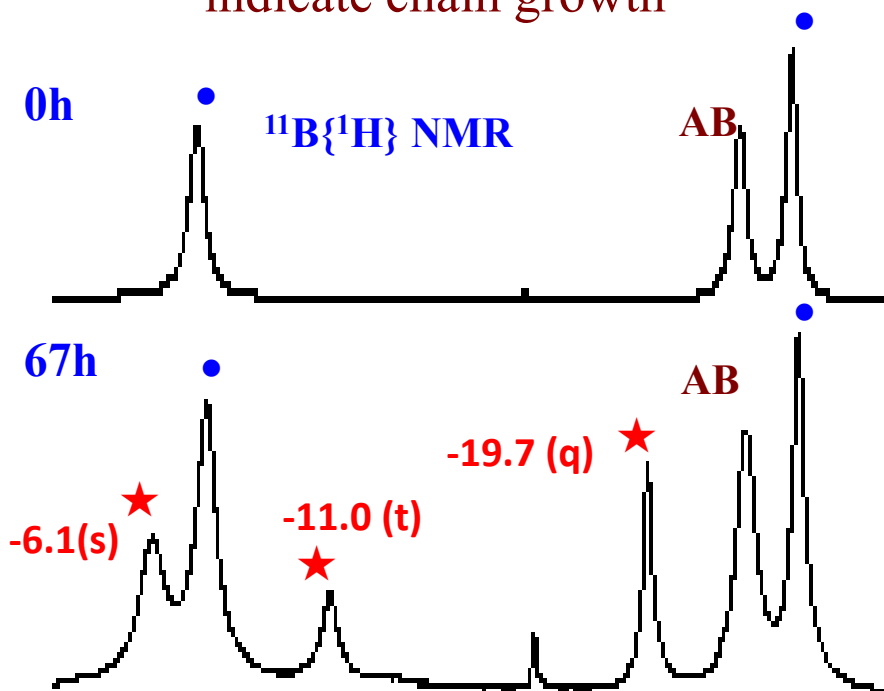
Proton Sponge Induces Loss of a Second H₂-Equivalent from Thermally Dehydrogenated AB



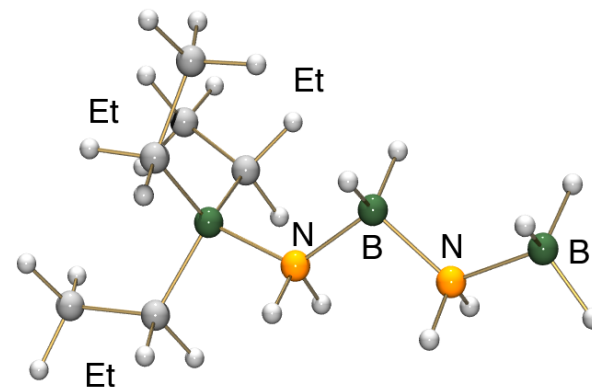
Model Studies: $\text{AB}/[\text{Et}_3\text{BNH}_2\text{BH}_3]^-$ Reactions Show Chain Growth



Mass spec and GIAO/NMR studies indicate chain growth



X-ray structure $\text{Et}_3\text{BNH}_2\text{BH}_3^-$

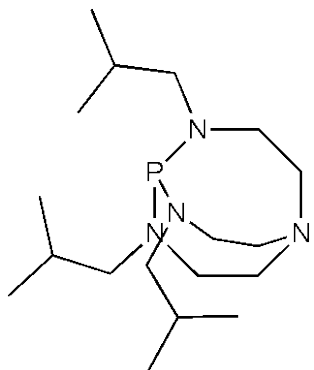


DFT optimized structure of $[\text{Et}_3\text{BNH}_2\text{BH}_2\text{NH}_2\text{BH}_3]^-$

GIAO calculated ^{11}B chem. shifts: -8.2, -12.0, -23.5 ppm



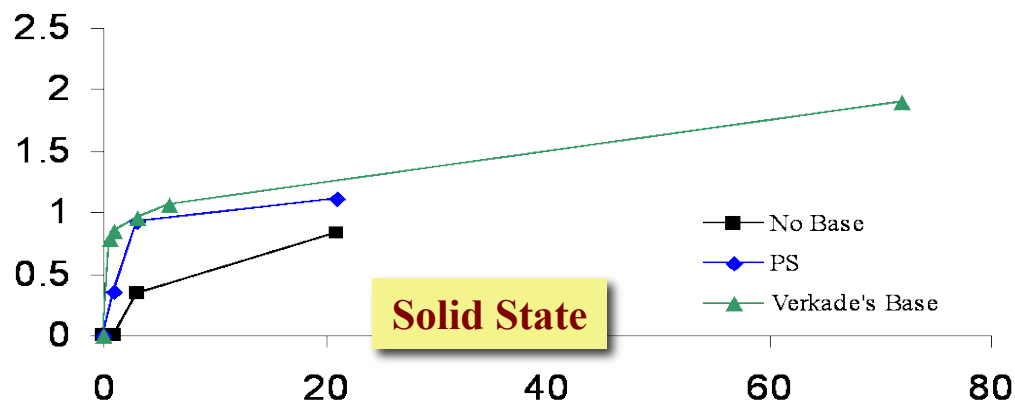
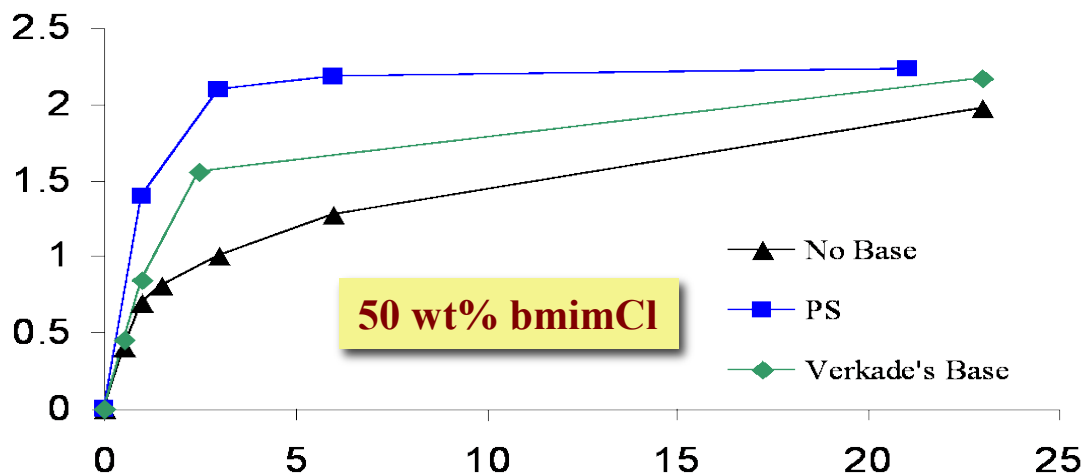
Verkade's Base Also Activates AB H₂-Release



Verkade's Base

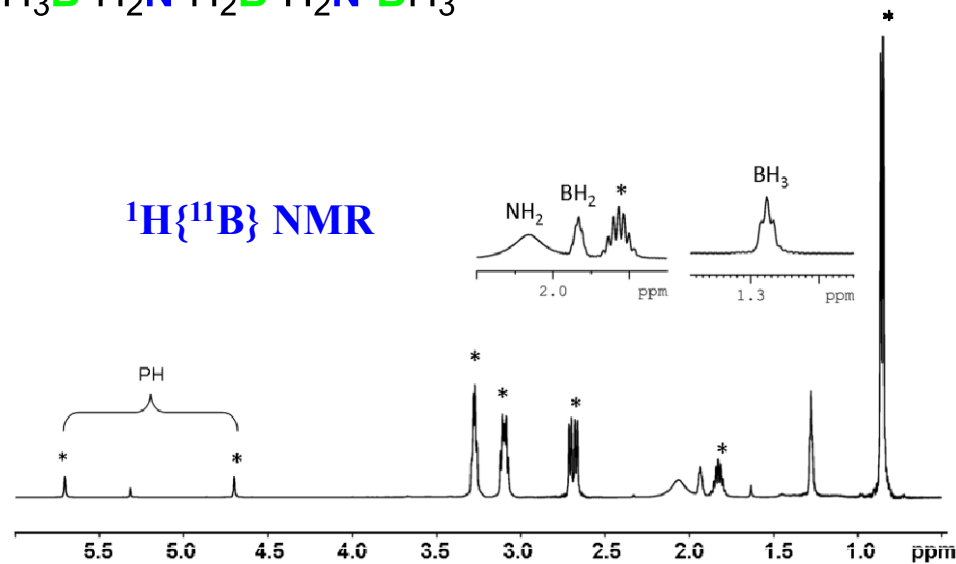
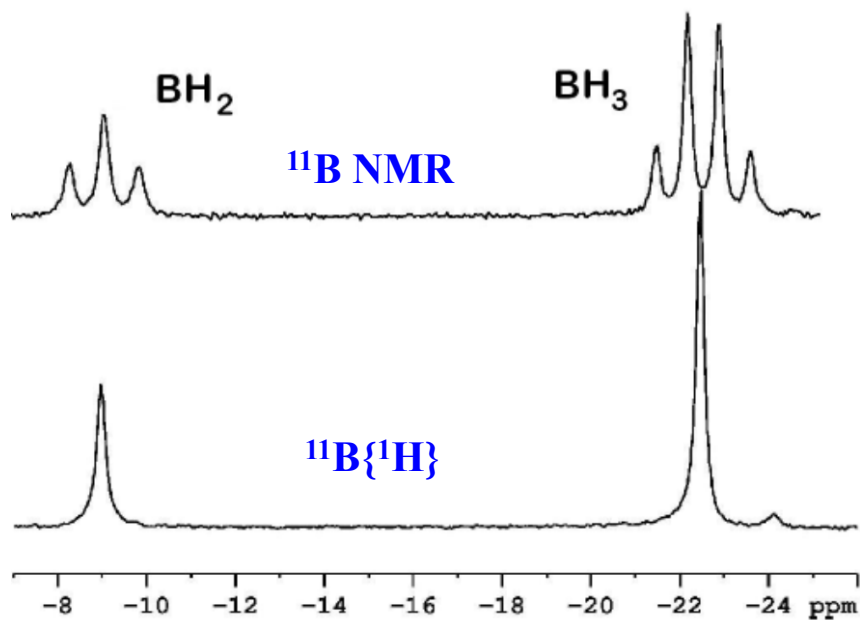
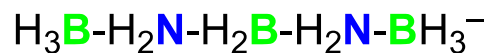
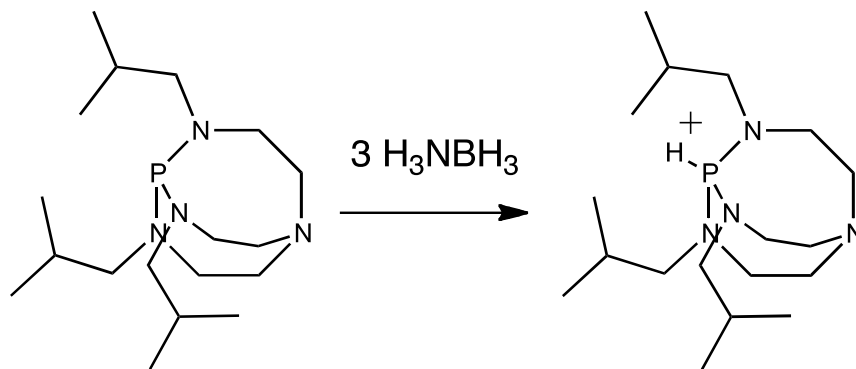
Ewing, W. C.; Marchione, A.; Himmelberger, D. W.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **2011**, *133*, 17093.

Equiv. of H₂

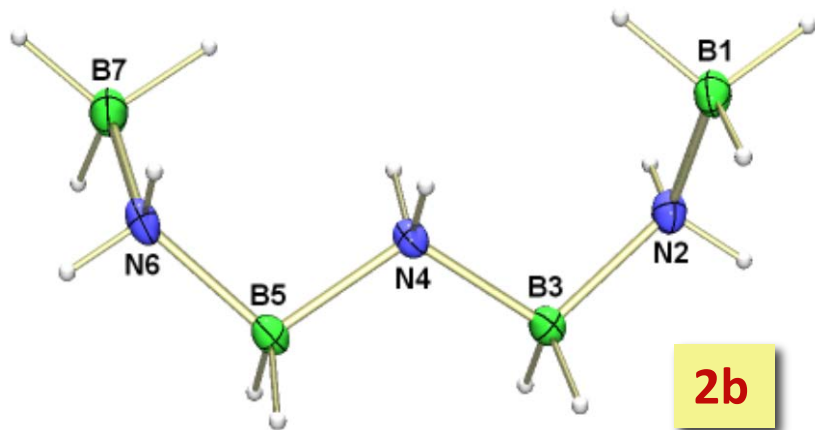
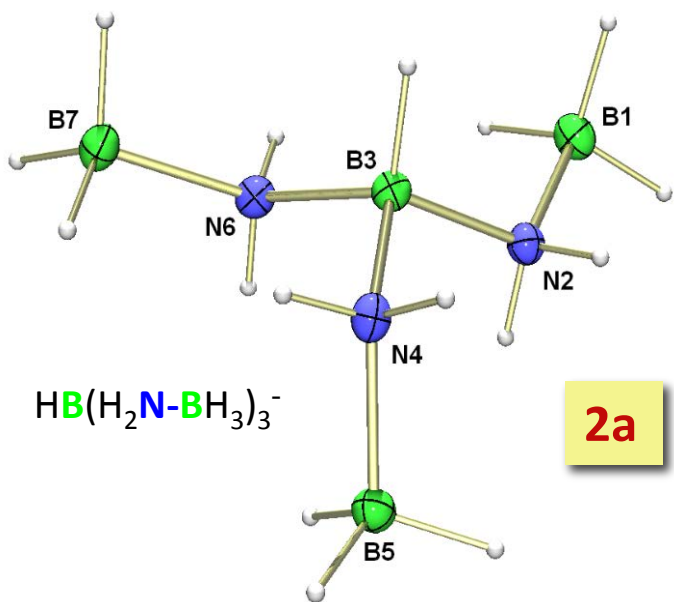


h

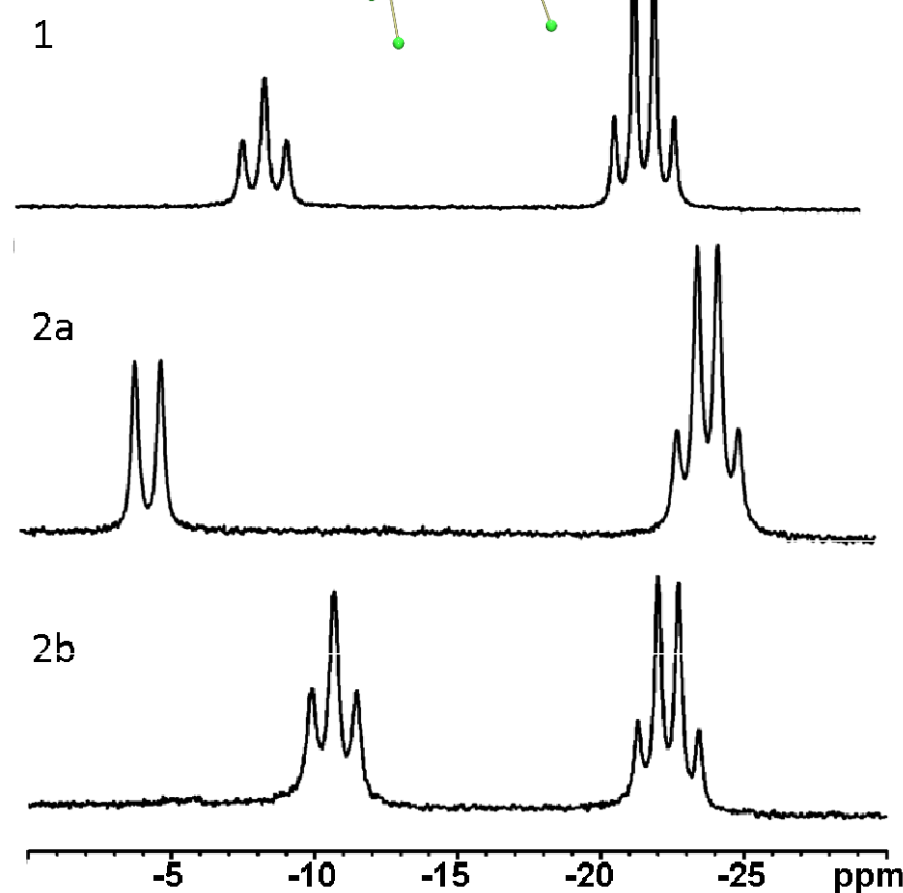
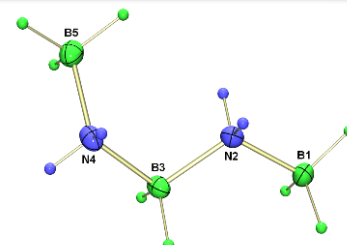
Verkade's Base / AB Reactions Allow Isolation of Chain Growth Products!



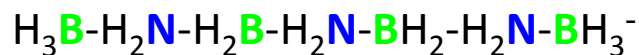
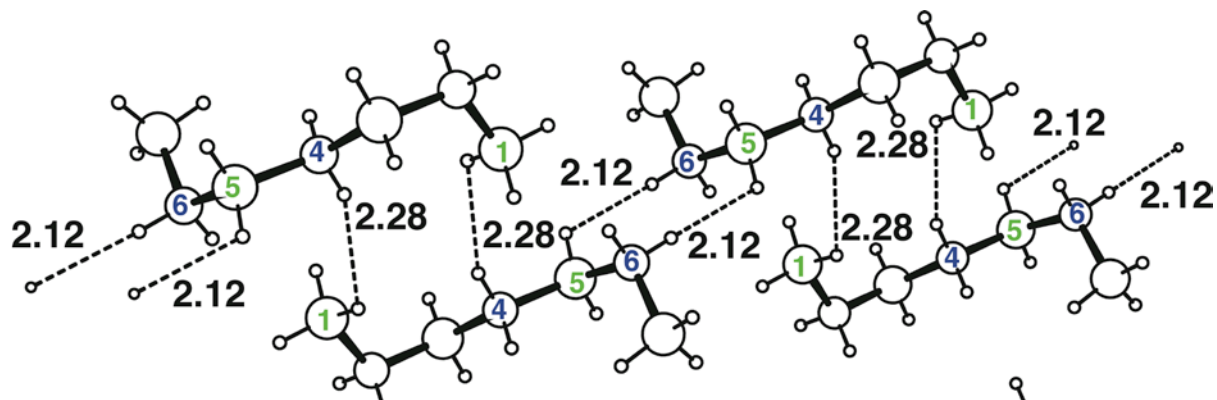
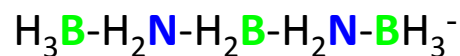
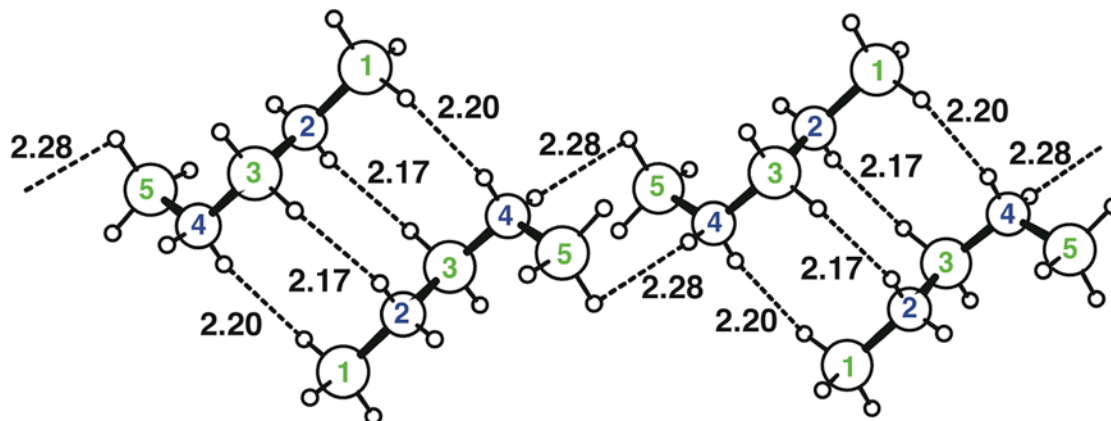
Crystallographic Studies Confirm Formation of Isomeric Chain Growth Products



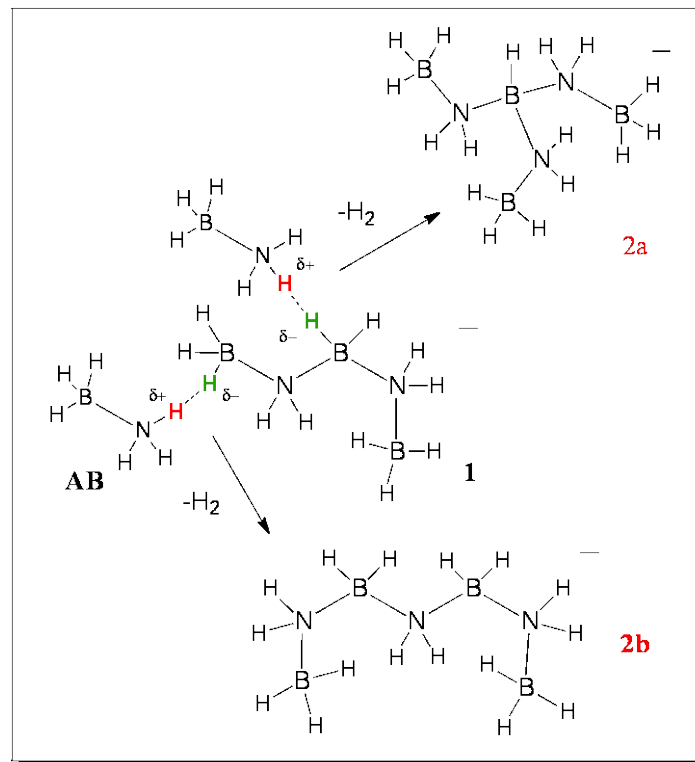
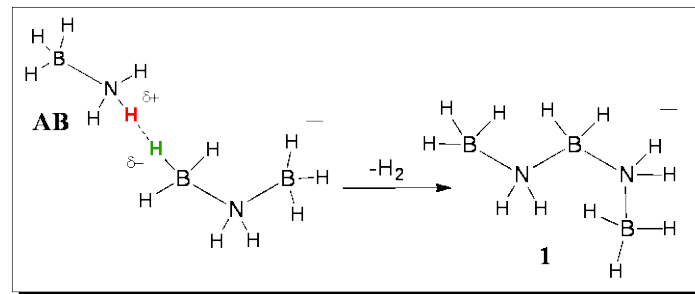
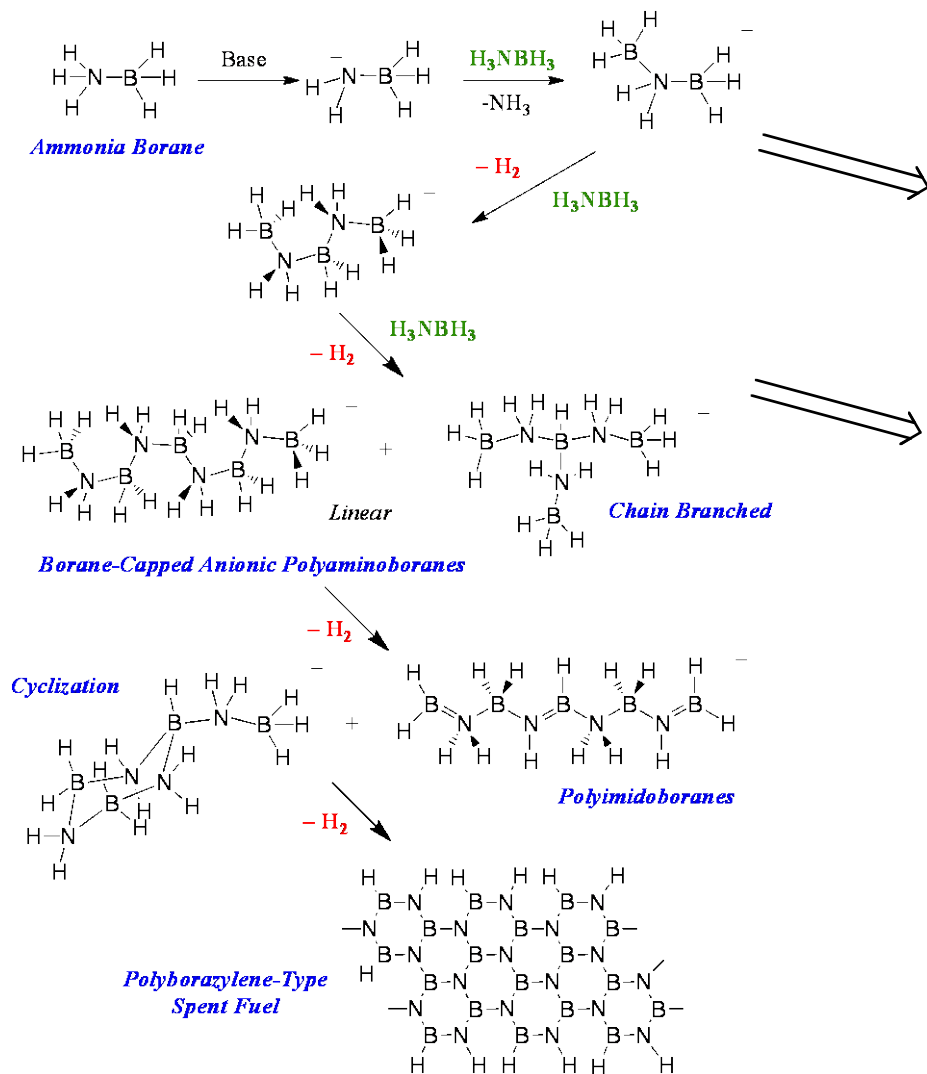
^{11}B NMR



Anions Show Extensive N-H...H-B Hydrogen-Bonding in the Solid State



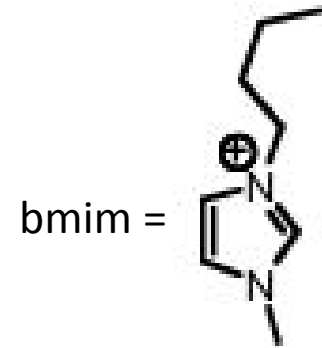
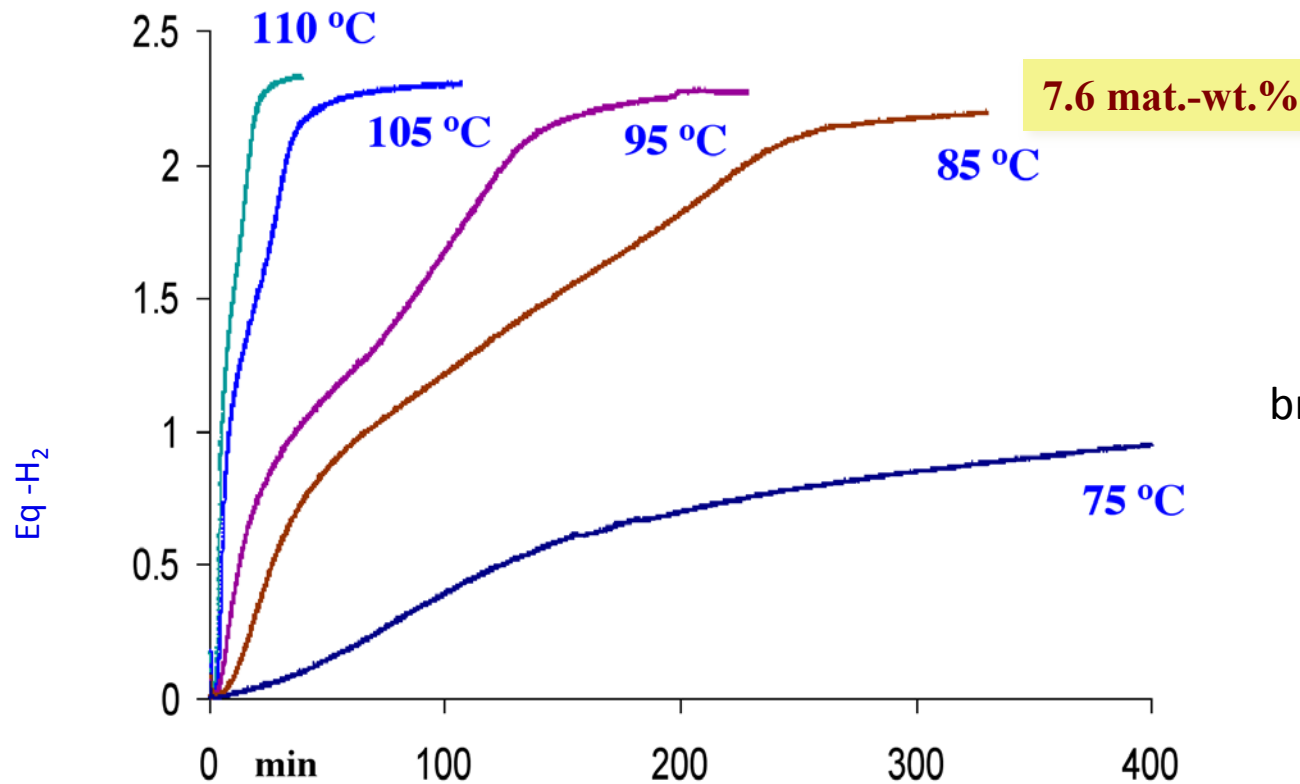
Anionic H₂-Release/Chain-Growth Reactions Facilitated by N-H...H-B Bonding



3) Activated AB Dehydrogenation in Ionic Liquids

Significantly Faster Rates for AB H₂-Release In Ionic Liquids with Only Small Temperature Increases

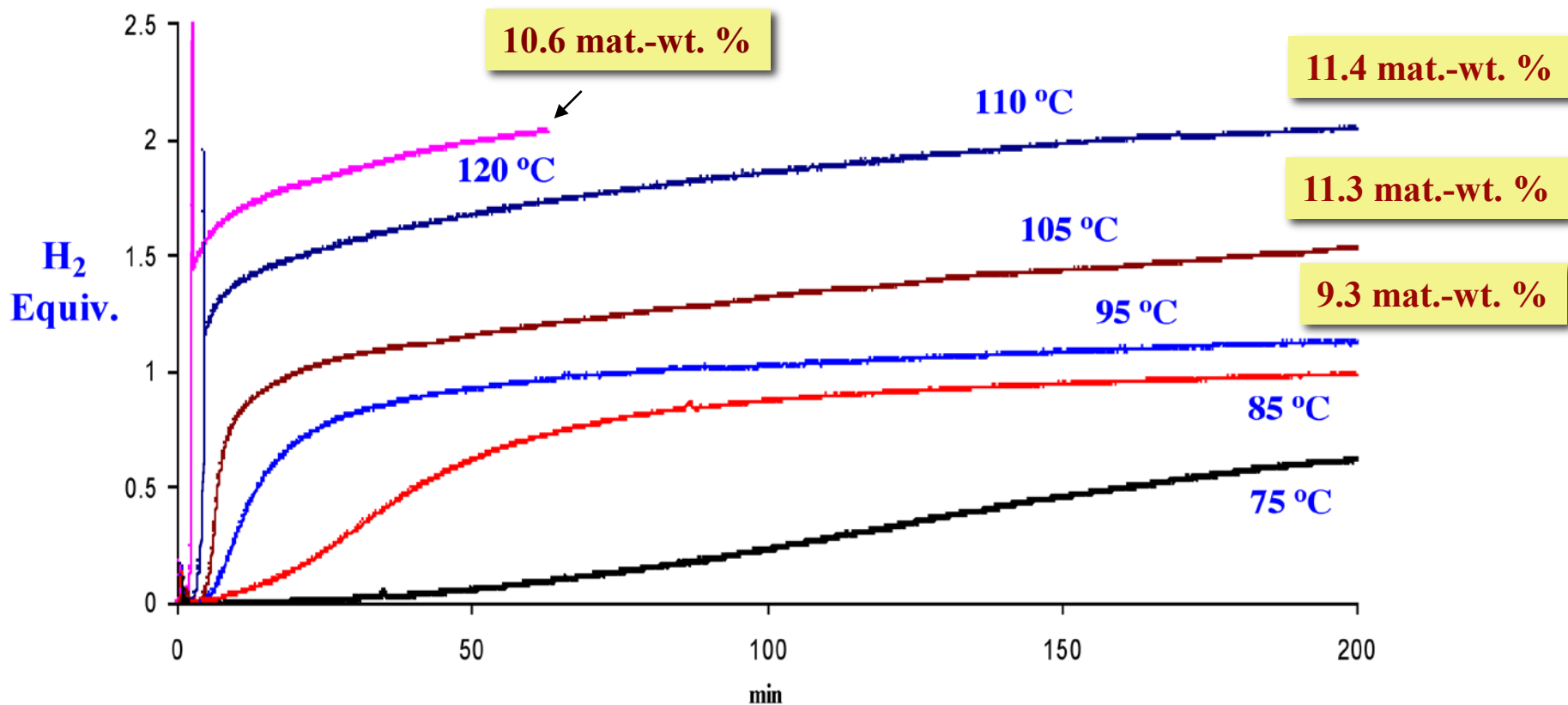
AB H₂-Release versus Temperature for 50 wt. % bmimCl/AB



Conclusion: Fast H₂-Release at higher temperatures, but need to increase mat.-wt. % by decreasing % ionic liquid

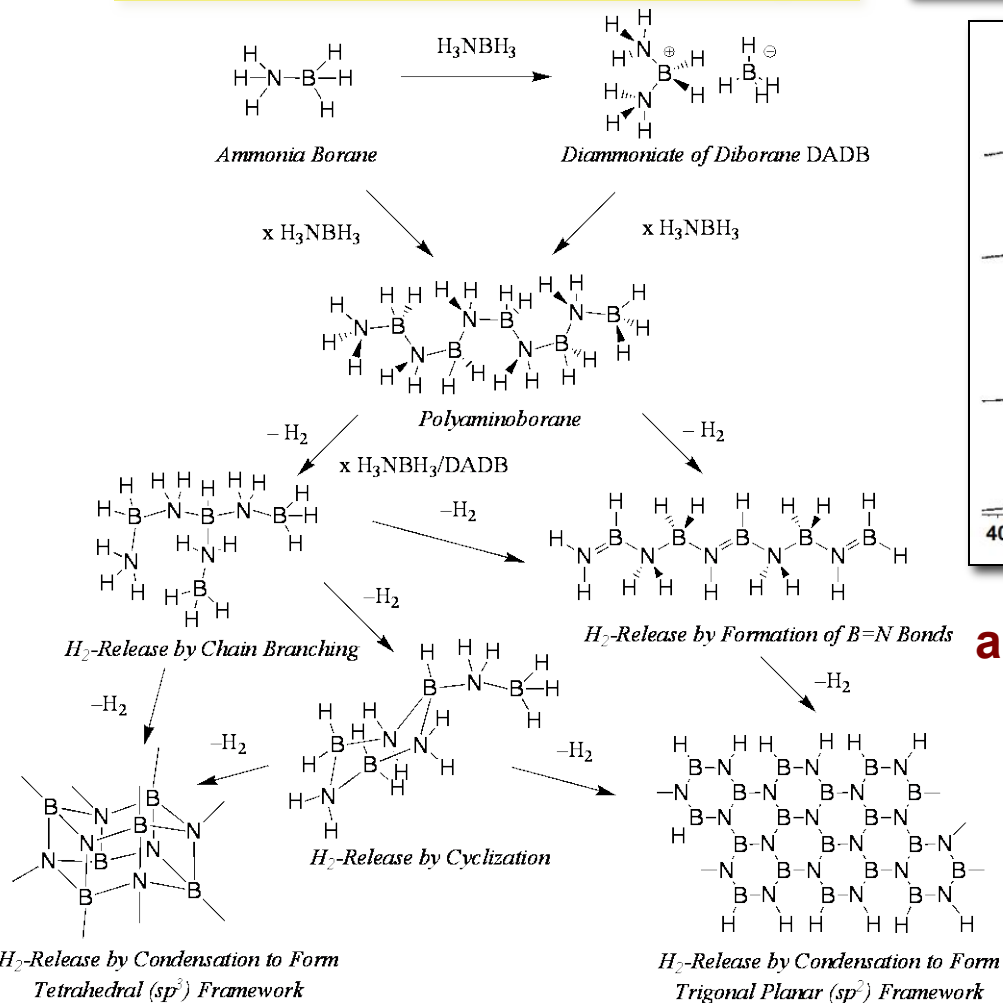
Fast Rate and 11.4 mat.-wt. % H₂-Release Demonstrated for 20 wt. % IL/AB at 110 °C

AB H₂-Release versus Temperature in 20 wt. % bmimCl



NMR Studies Identify Initial and Final Release Products

Possible Mechanistic Steps

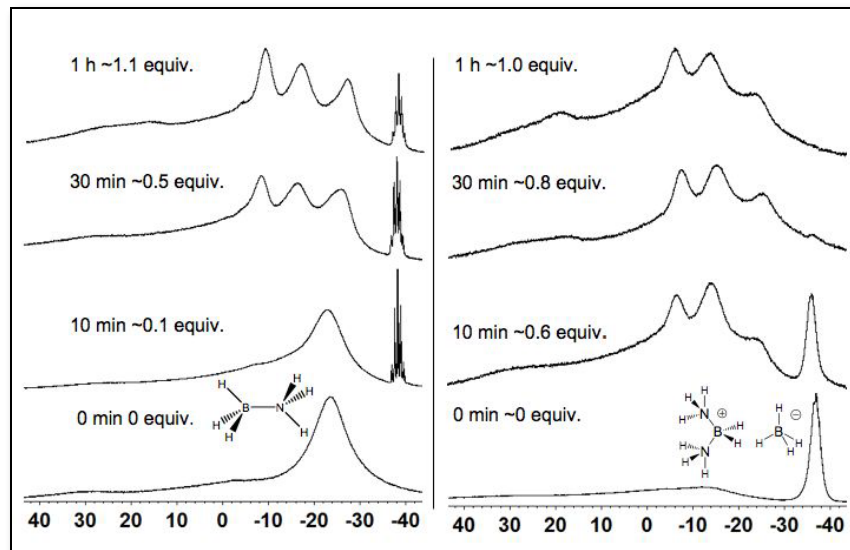


Himmelberger, D.; Alden, A.; Bluhm, M. E.; Sneddon, L. G.
Inorg. Chem. **2009**, *48*, 9883-9889



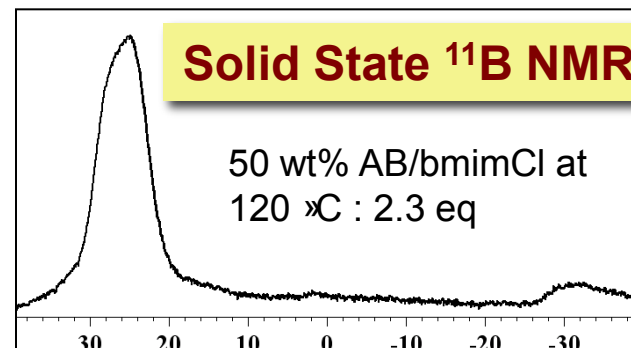
Solution ¹¹B NMR

10 wt% AB and DADB in bmimOTf at 85 °C



Conclusion: Both DADB formation and decomposition is enhanced in ILs

Solid State ¹¹B NMR

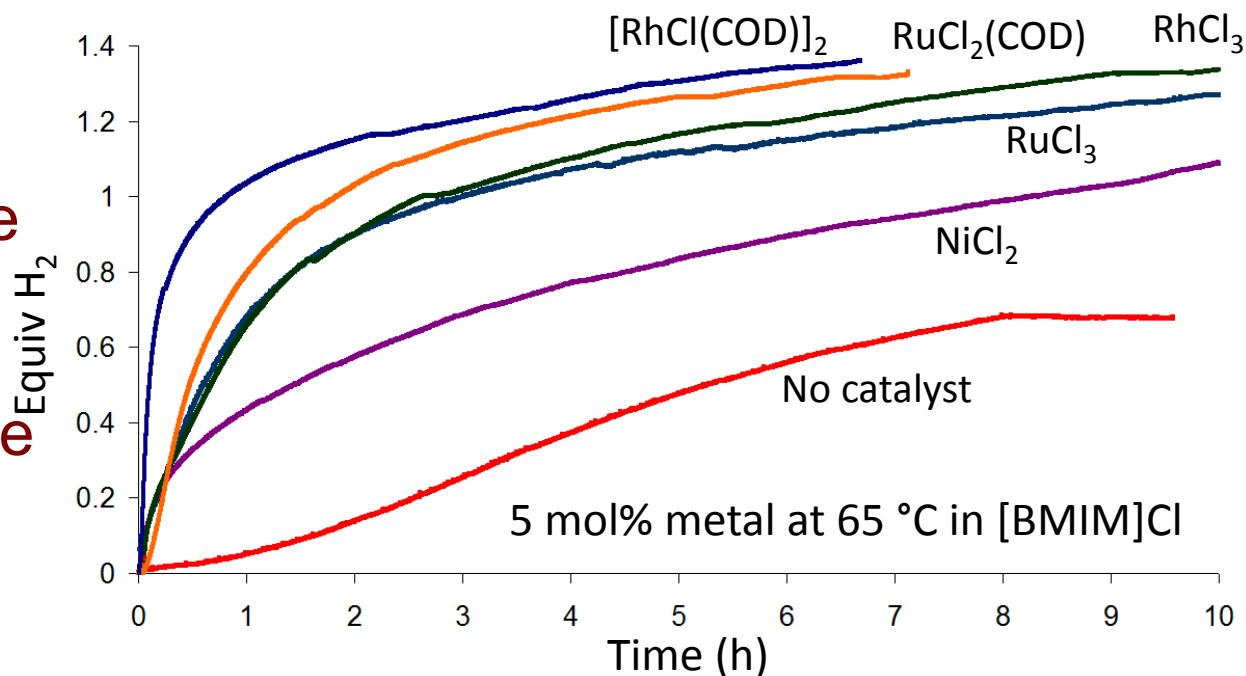


Conclusion: Final spent fuel product has sp²-type framework

Why Use Metal Catalysts for AB Dehydrogenation in Ionic Liquids?

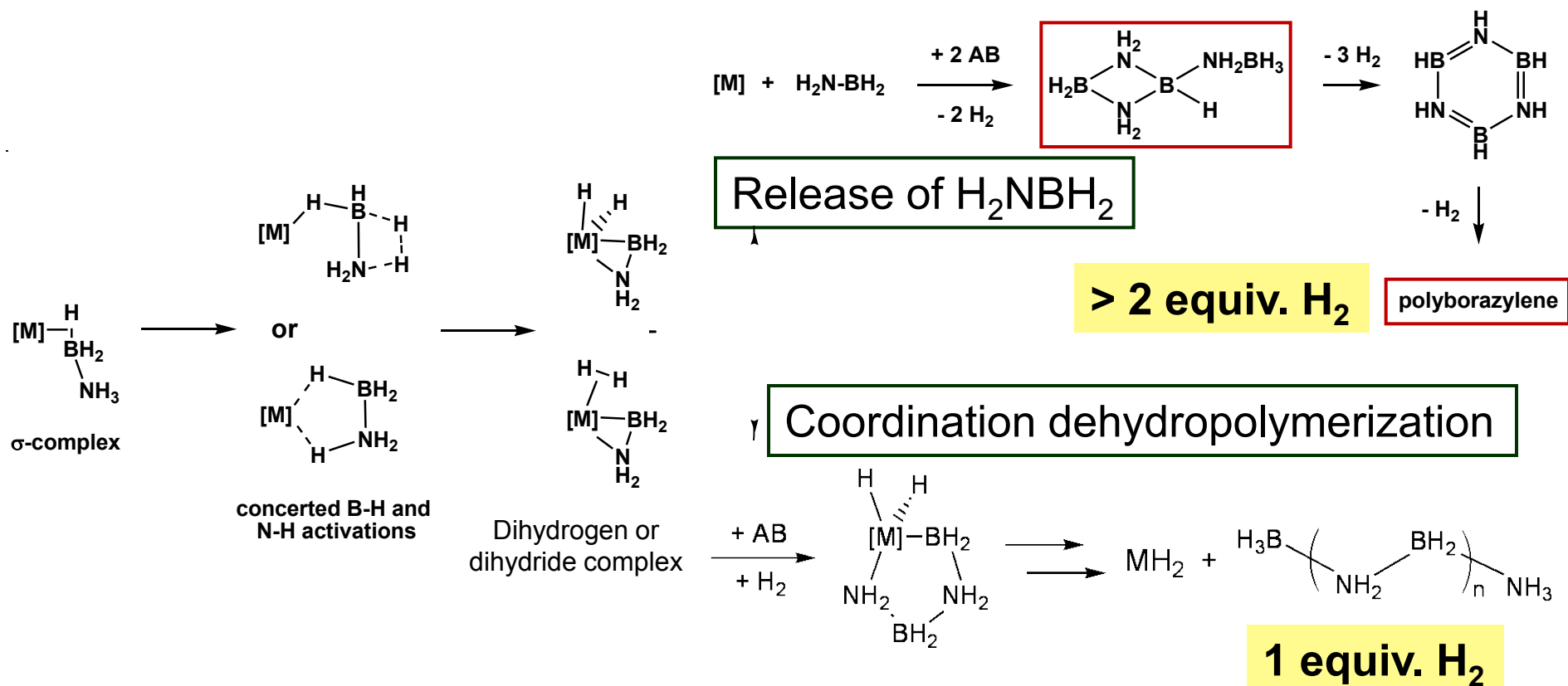
Catalysts in Conjunction with Ionic Liquids Could Provide:

- Faster H₂-Release
- Better Control of H₂-Release Rates
- Lower Temperature Reactions
- Synergistic Release Mechanisms



Wright, W. R. H.; Berkeley, E. R.; Alden, L. R.; Baker, R. T.; Sneddon, L.G. *Chem. Commun.* **2011**, 47, 3177.

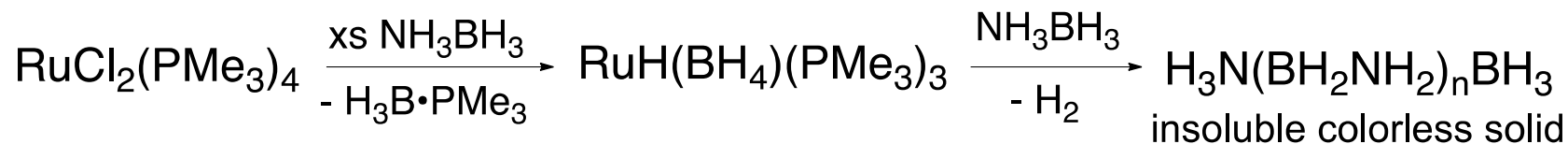
Selectivity of Metal-Catalyzed AB Dehydrogenation Dictates Extent of H₂ Release



- Release of H₂NBH₂ and formation of BN-ethylcyclobutane intermediate are key to greater hydrogen release
- Details of borazine and polymer formation not yet fully understood



Ru Complex Catalyst is More Active in IL Solvent



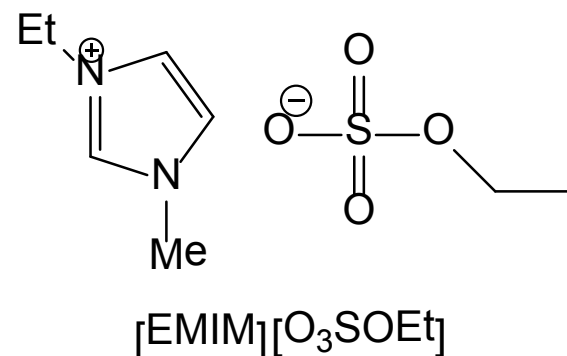
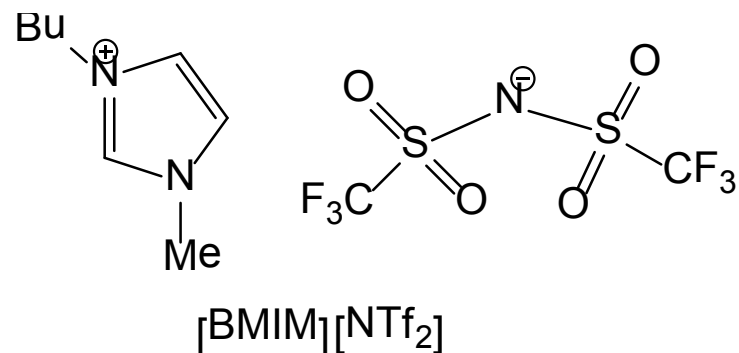
R.T. Baker *et al.*, unpublished results

1 TO /min diglyme at 60°C

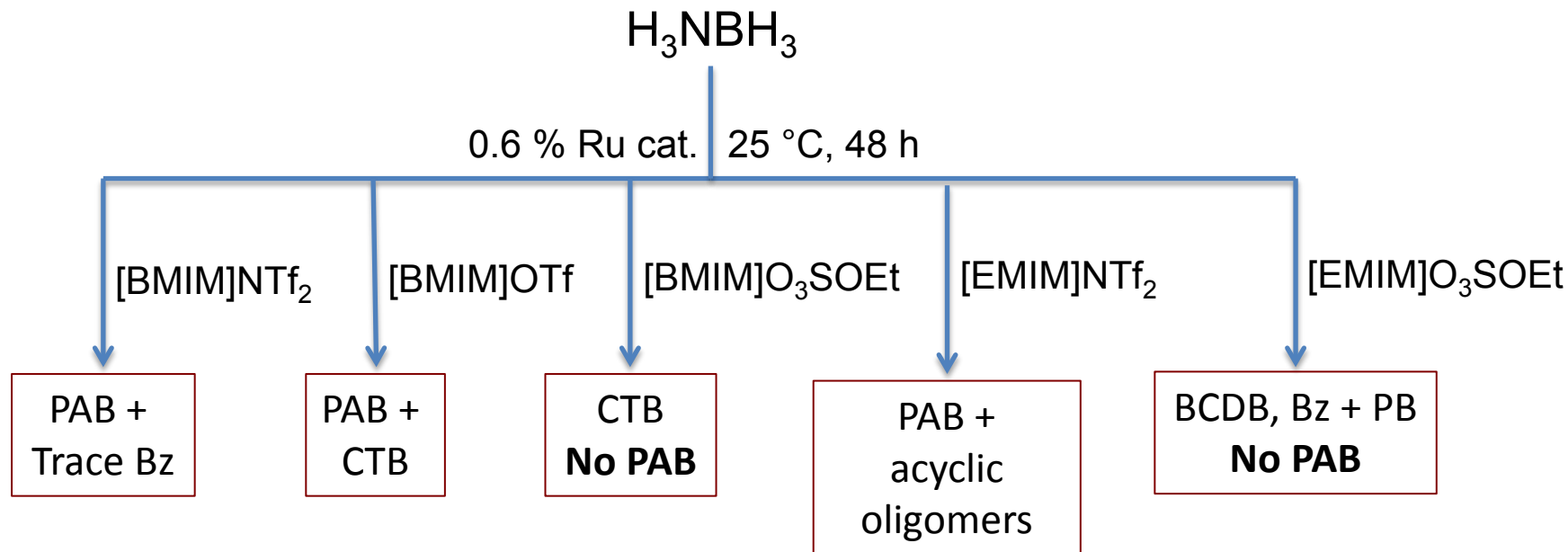
Catalyst is more active in Ionic Liquids

Solvent	Equivalents H ₂ (60 mins)
THF	0.28
[EMIM][O ₃ SOEt]	0.85
[BMIM][NTf ₂]	0.93

60 °C, 40 wt% NH₃BH₃, 2 mol% Ru cat.



Ru-catalyzed AB Dehydrogenation Selectivity best with more Strongly Coordinating IL Anions

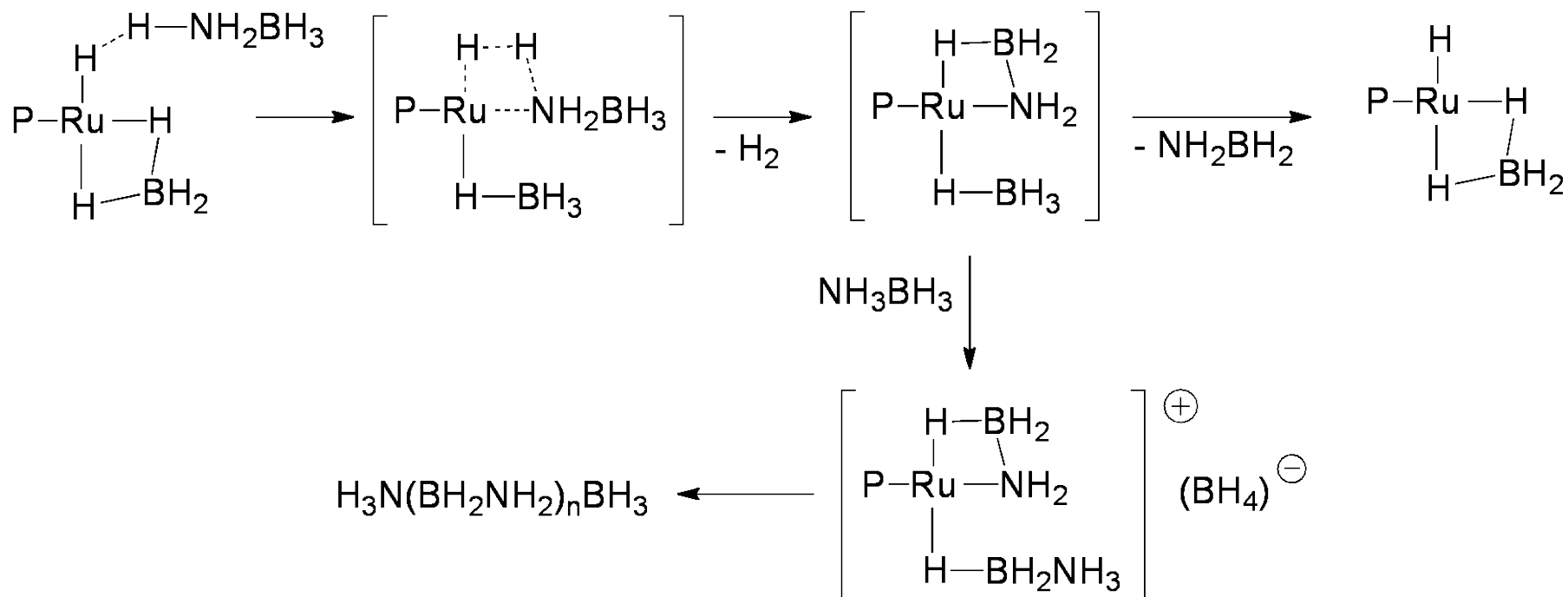


- Ionic Liquids with weakly coordinating anions afford similar products as those from diglyme reactions using $\text{RuCl}_2(\text{PMe}_3)_4$ catalyst precursor: PAB = insoluble poly(aminoborane); CTB = BN cyclohexane analog; Bz = BN benzene analog
- With more strongly coordinating anions, no PAB is formed and more hydrogen is thus released with formation of BCDB (BN-ethylcyclobutane analog), Bz and polyborazylene (BN polyaromatic hydrocarbon analog)

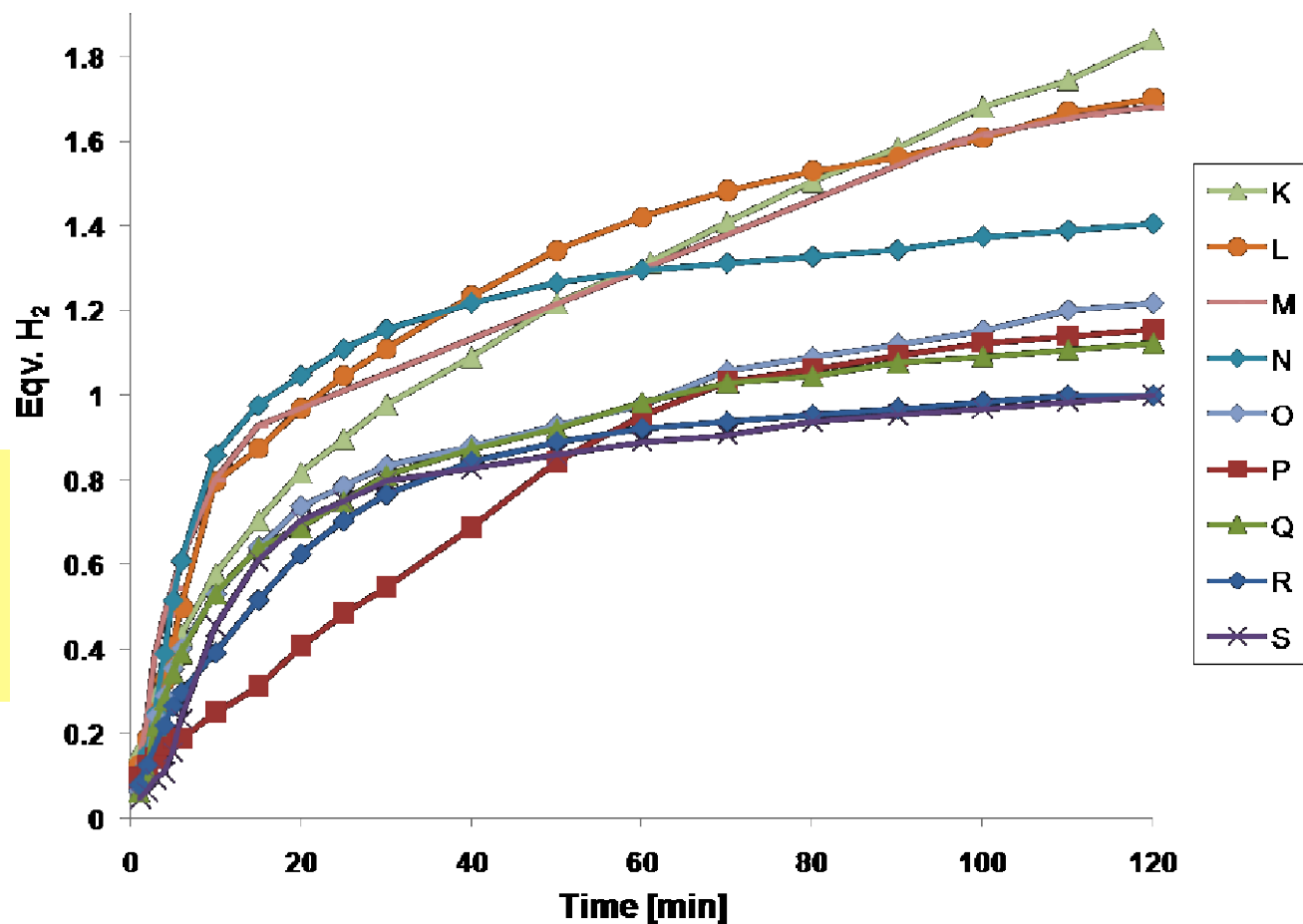


Possible Origin of Observed Selectivity

- AB dehydrogenation needs a single coordination site
- Ionization of the catalyst to borohydride salt creates second vacant coordination site needed for metal-catalyzed dehydro-oligomerization



IL 'Cation Effect'



Rate differences correlate roughly with IL viscosity

General conditions: AB (80 mg), IL (200 mg) and 0.8 mol% $[\text{RuCl}_2(\text{PMe}_3)_4]$ (**1**). K = $[\text{P}(n\text{-Bu})_4][\text{Cl}]$, L = $[\text{P}(n\text{-Bu})_4][\text{O}_3\text{SOEt}]$, M = $[\text{P}(n\text{-Bu})_4][\text{OAc}]$, N = $[\text{P}(n\text{-Bu})_4][\text{OTf}]$, O = $[\text{P}(n\text{-Bu})_4][\text{Br}]$, P = $[\text{P}(\text{C}_{14})_3\text{C}_6][\text{OTf}]$, Q = $[\text{P}(\text{C}_{14})_3\text{C}_6][\text{O}_3\text{SOEt}]$, R = $[\text{P}(\text{C}_{14})_3\text{C}_6][\text{NTf}]$, S = $[\text{P}(n\text{-Bu})_4][\text{NTf}_2]$.



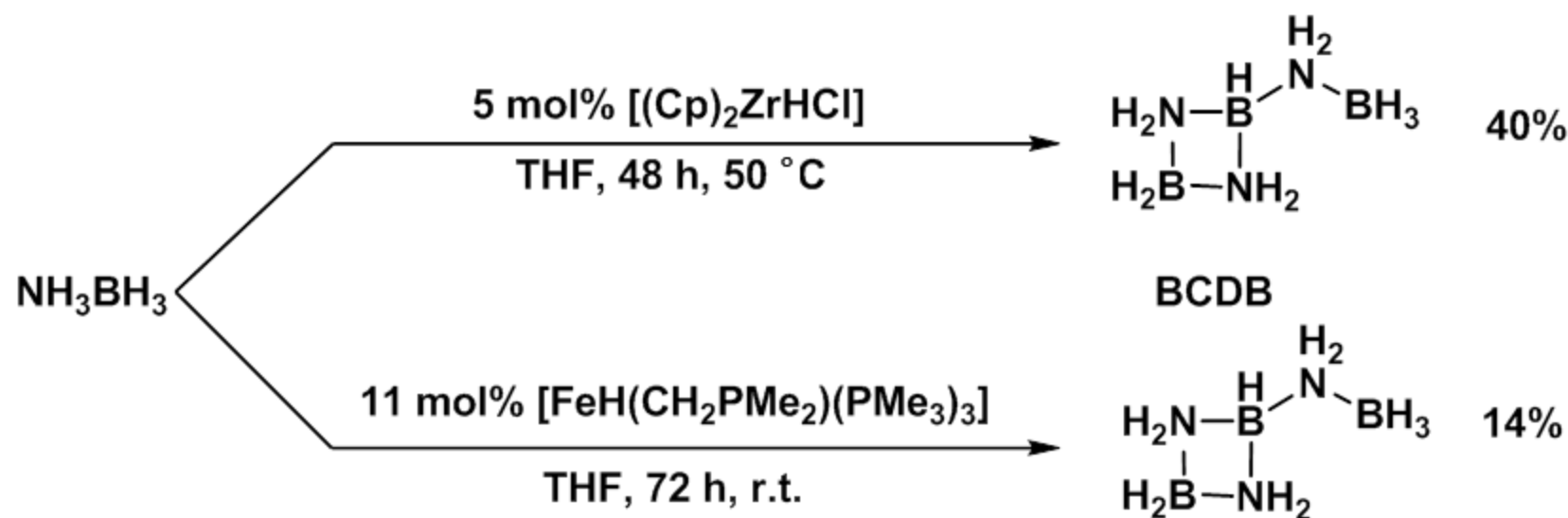
4) Investigating the 2nd Equivalent of H₂ from AB

Synthesis of BN Ethylcyclobutane

- In previous work we showed that Ni-*N*-heterocyclic carbene and Fe-PMe₃ complexes and AB allowed for significant build-up of BCDB intermediate.

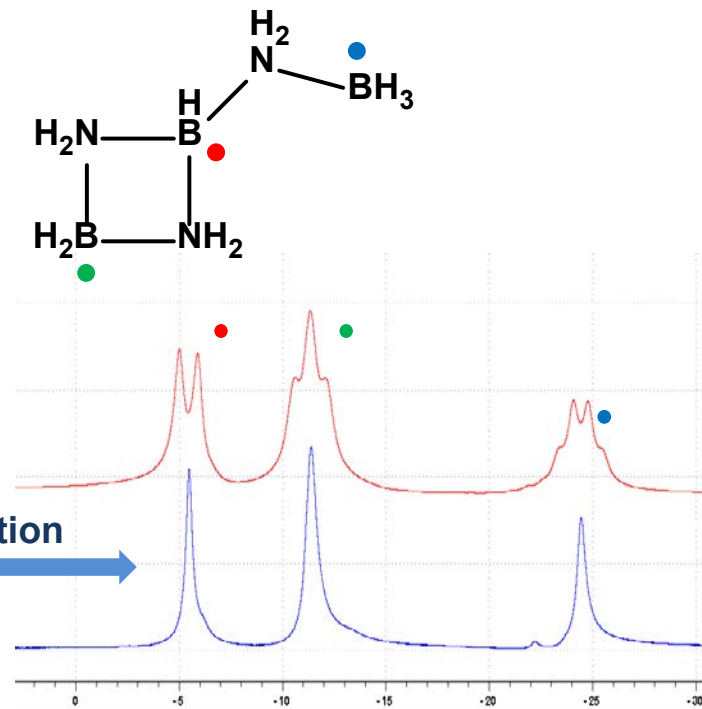
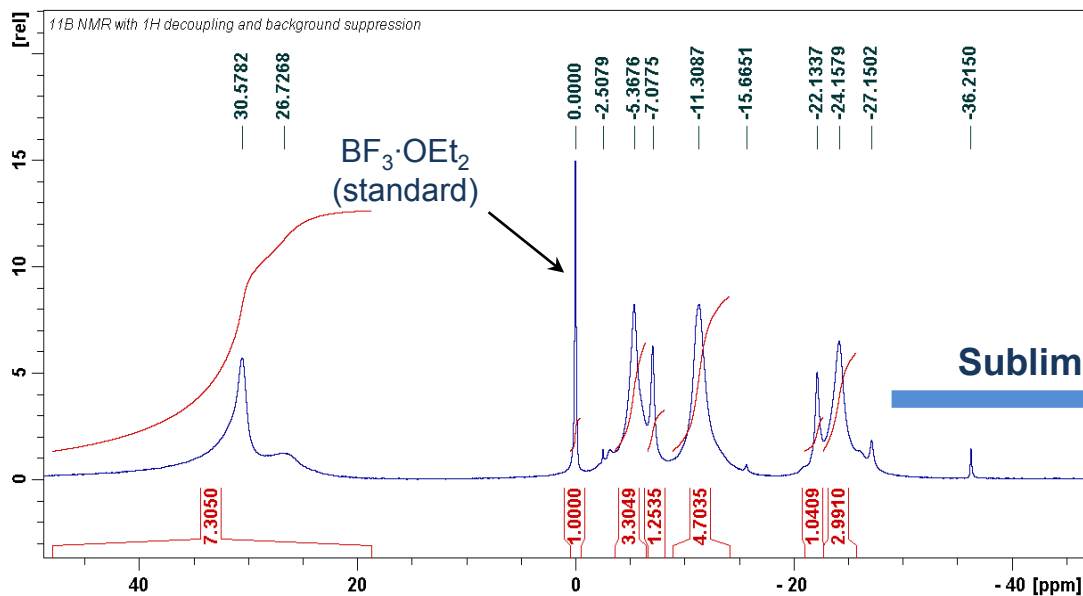
R.T. Baker *et al.* *J. Am. Chem. Soc.*, 2007, **129**, 1844-1845.

- Early work showed that Zr complexes are poor catalysts for AB dehydrogenation but we find that Schwartz's reagent affords workable yields of BCDB!



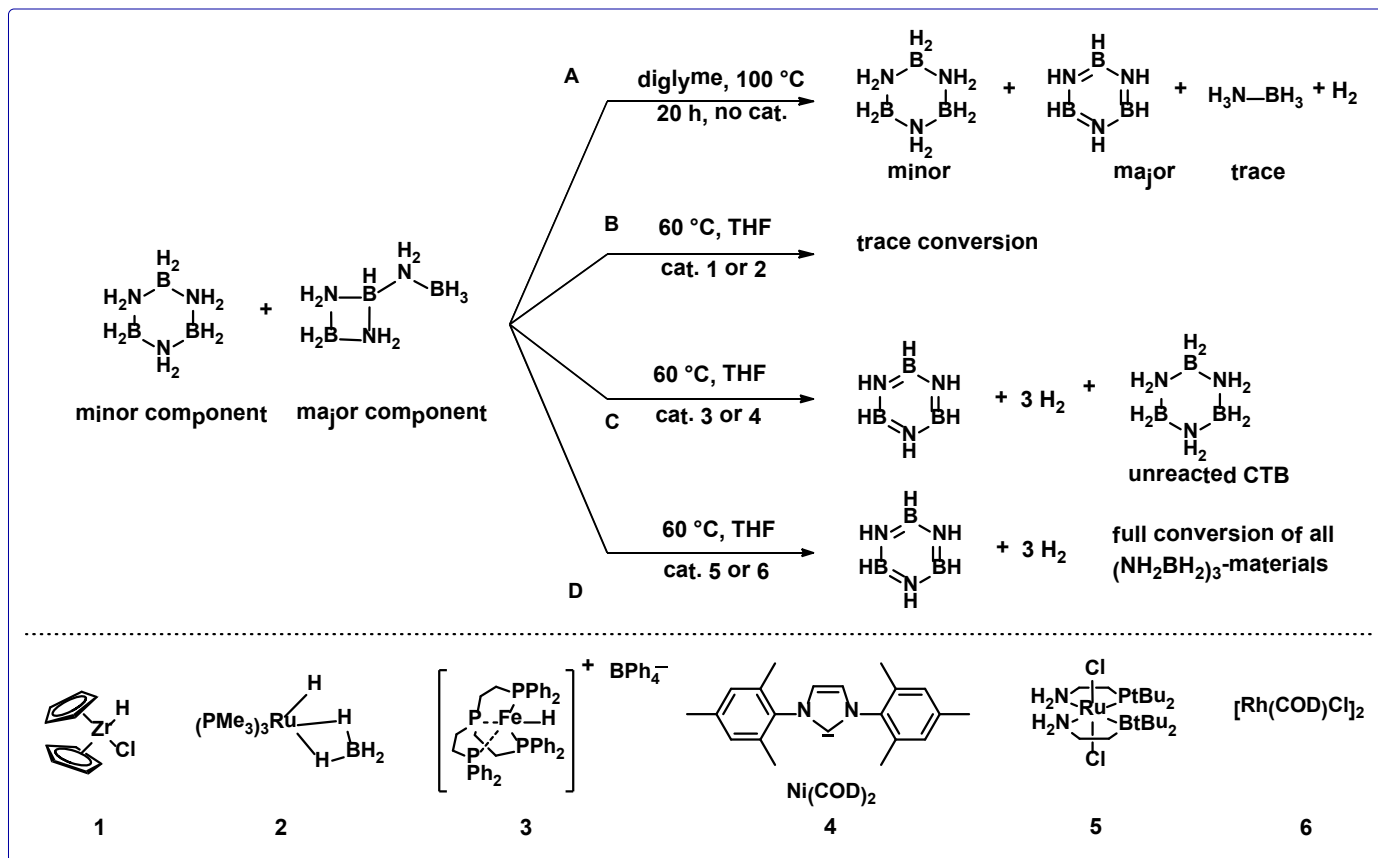
Characterization of BCDB

AB + Cp₂ZrHCl (50 °C, 12 h)



¹¹B NMR (blue) and ¹¹B {¹H} NMR (red) of crude reaction mixture and purified BCDB. Sublimed (80 ° C @ < 1 torr) sample contains ca. 10% CTB.

Thermal and Catalytic Dehydrogenation of BCDB



Reaction conditions for B-D: 15 mol % catalyst, THF, 60 °C, 16 h.

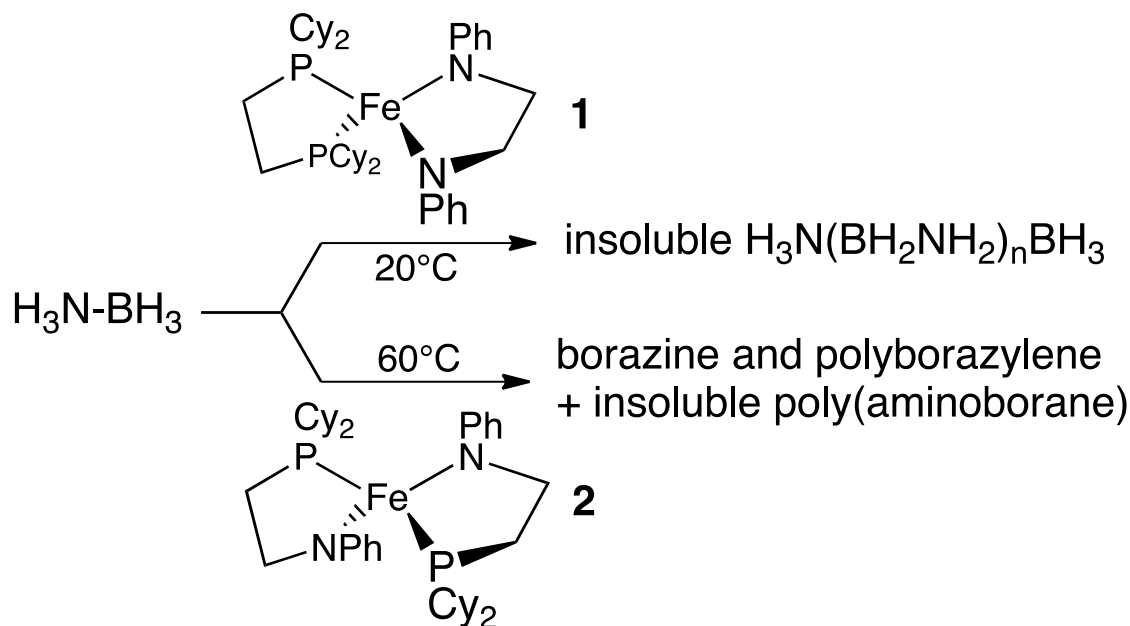
- Thermolysis of BCDB effects isomerization to CTB and undergoes a minor hydrogen redistribution reaction to give borazine and AB
- While catalysts **3** or **4** convert BCDB (but not CTB) to borazine and polyborazylene, **5** and **6** convert both isomers

5) Iron Catalysts for AB dehydrogenation

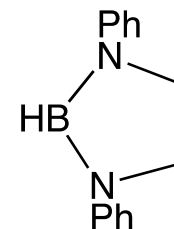
Iron Amido Phosphine Complexes

- Earth abundant, inexpensive, non-toxic iron catalysts would be best for transportation applications
- Previous work on bifunctional iron amido complexes showed selectivity control but unwanted reactivity of N-ligands

R. T. Baker *et al.* *J. Am. Chem. Soc.* **2012**, *134*, 5598.



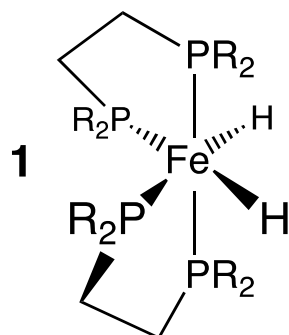
- Complex 1 is selective for poly(aminoborane) but basic N-ligand leads to $\text{Fe}(0)$ and cyclic diazaborane:



- Complex 2 is unselective catalyst and decomposes to $\text{Fe}(0)$ and phosphine-borane



Robust Iron Complex Catalysts for Selective Synthesis of Poly(aminoborane)s



R = Me, Et

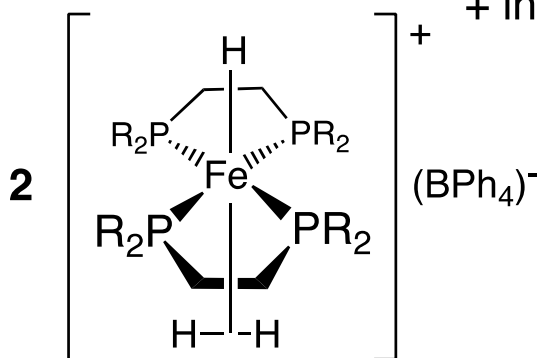
H₃N-BH₃

20 °C

insoluble H₃N(BH₂NH₂)_nBH₃

60 °C

borazine and polyborazylene
+ insoluble poly(aminoborane)



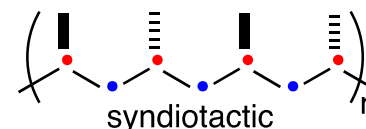
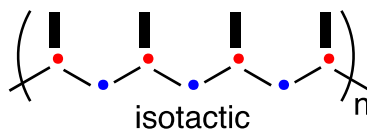
- Complex **1** is selective for poly(aminoborane) and only observable catalyst resting state under reaction conditions

- Complex **2** is unselective and decomposes to Fe(0) and phosphineborane even at 20 °C

Using 5 mol% **1** primary amine-boranes H₂RNBH₃, are converted cleanly to poly(aminoborane)s (R = Me, *n*-Bu); will chiral bis(phosphines) allow for tacticity control?

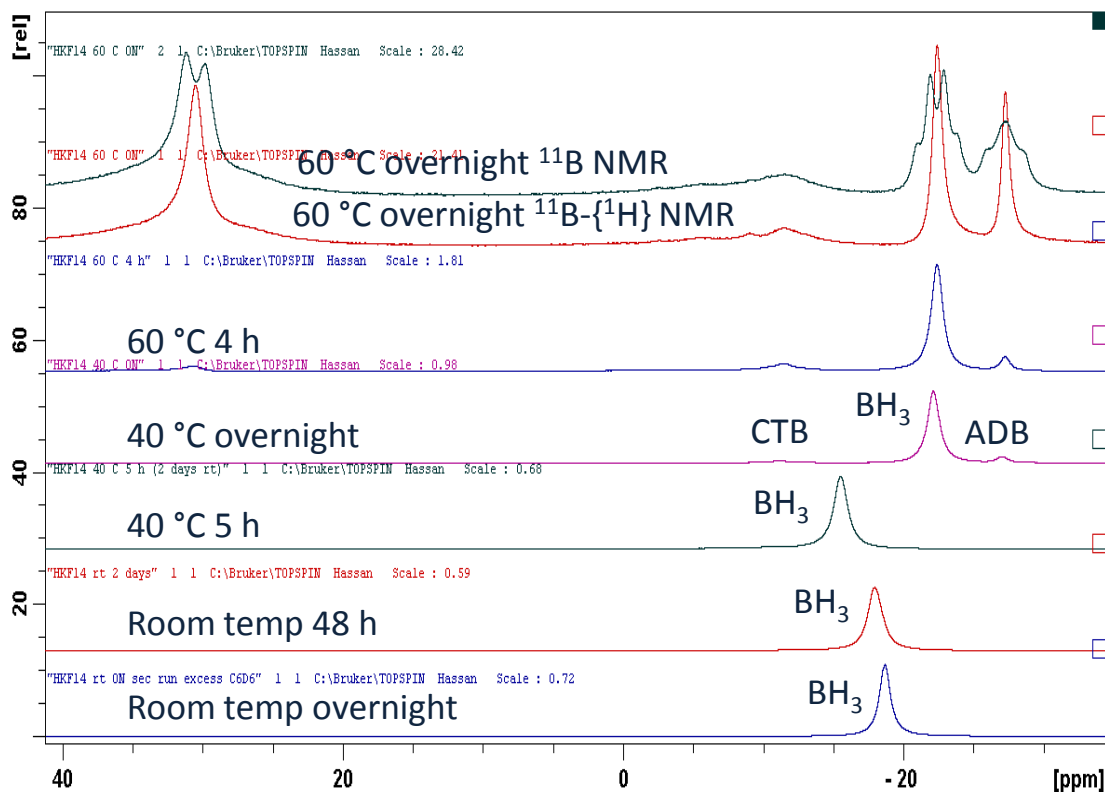


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Iron Chloride Generates Effective Heterogeneous Catalyst for AB Dehydrogenation

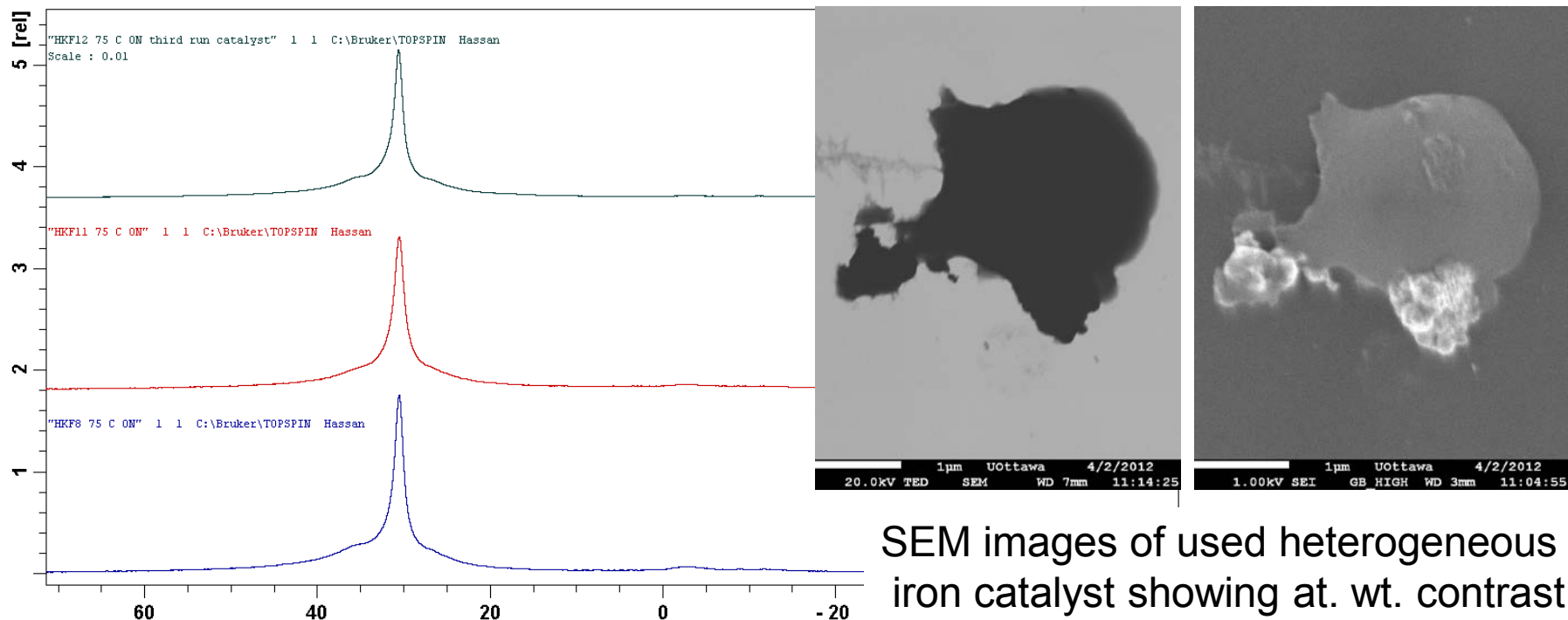
- Mixtures of AB and FeCl_2 in diglyme release hydrogen as solution turns black and deposits a mirror on vial wall
- 5 mol% FeCl_2 precatalyst was used in all the above experiments; however 1 mol% catalyst loading gave similar results.



This system exhibits unprecedented selectivity to borazine and polyborazylene (minimal insoluble poly(aminoborane) by-product) for a heterogeneous catalyst. Now preparing high surface area samples on BN support for higher reaction rates.

Iron-on-iron-boride Catalyst is Reusable

Catalyst recycling experiment for AB dehydrogenation at 75 °C.



SEM images of used heterogeneous iron catalyst showing at. wt. contrast

$^{11}\text{B}\{^1\text{H}\}$ NMR spectra of the first (blue), second (red) and the third (green) runs. The iron mirror on the reaction vial was used for the second and third runs.

Conclusions

- Detailed studies of base-promoted AB dehydrogenation confirmed chain growth mechanism to give linear and branched aminoborane oligomers that undergo further H₂ release to sp² BN products - analogous to solid-state AB thermolysis pathway
- Use of metal complex catalysts in ionic liquid solvents led to synergistic pathways for H₂ release from AB wherein nature of IL anion can dictate catalyst selectivity
- New preparation method for BN ethylcyclobutane intermediate allowed for determination of its thermolytic- and metal complex-catalyzed dehydrogenation properties
- Iron bis(phosphine) dihydride complexes are first selective base metal catalysts for poly(aminoborane) formation
- Iron-on-iron-boride catalysts derived from FeCl₂ and AB are first reusable, selective heterogeneous catalysts – operation of BN-supported catalysts in ionic liquid solvents will be pursued with Hydrogen Storage Engineering Center of Excellence



Acknowledgements

- This project was generously supported by DOE BES grant DE-FG02-05ER15719-AO.
- Thank you also to the DOE-EERE Chemical Hydride and Engineering Hydrogen Storage Centers of Excellence for useful discussions and leveraged instrumentation.
- Prof. Baker thanks the University of Ottawa, Canada Research Chairs program, Canada Foundation for Innovation and the Ontario Ministry of Economic Development and Innovation for equipment and lab support, and H2CAN participants for useful discussions.



Matt Rankin

Felix Gaertner

Hassan Kalviri

Will Wright



Emily Berkeley

Dan Himmelberger

Chang Yoon

Martin Bluhm

Bill Ewing

Mechanistic Studies of Activated Hydrogen Release from Ammonia-Borane

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R. Tom Baker,* Richard Burchell, Felix Gaertner, Hassan Kalviri, Morgane Le Fur, Larena Menant, Giovanni Rachiero Matthew Rankin, Johannes Thomas, and William Wright, University of Ottawa, Department of Chemistry and Centre for Catalysis Research and Innovation, 30 Marie Curie, Ottawa, ON K1N 6N5 Canada



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