1) Background

Ammonia-Borane: a Promising Material for Hydrogen Storage

$$H_3NBH_3 \rightarrow H_2 + (H_2NBH_2)_n \rightarrow H_2 + (HNBH)_n \rightarrow H_2 + BN$$

6.5 wt% H 13.1 wt% 19.6 wt%

- 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

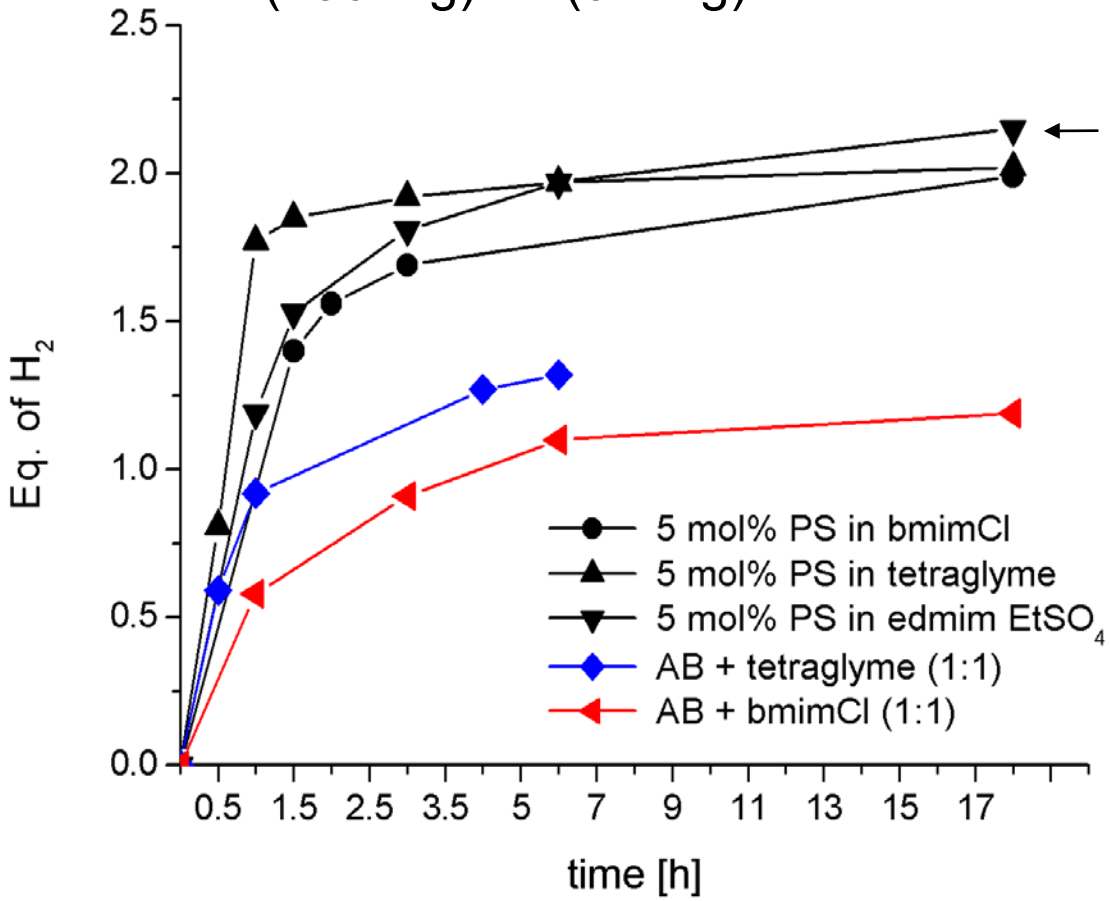
Cf. A. Staubitz *et al. Chem. Rev.* **2010**, *110*, 4079-4124.

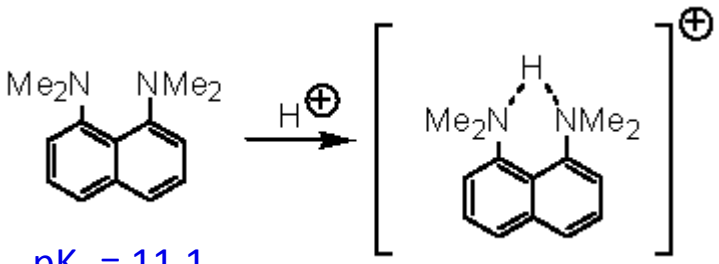
This presentation does not contain any proprietary or confidential information

2) Base-Promoted AB dehydrogenation

Enhanced AB H_2-Release with Proton Sponge in Ionic Liquids or Tetraglyme with Reduced Foaming

NH_3BH_3 + 5 mol % PS at 85 °C in Ionic Liquids or Tetraglyme
(250 mg) (91 mg) (250 mg)





pK_a = 11.1

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

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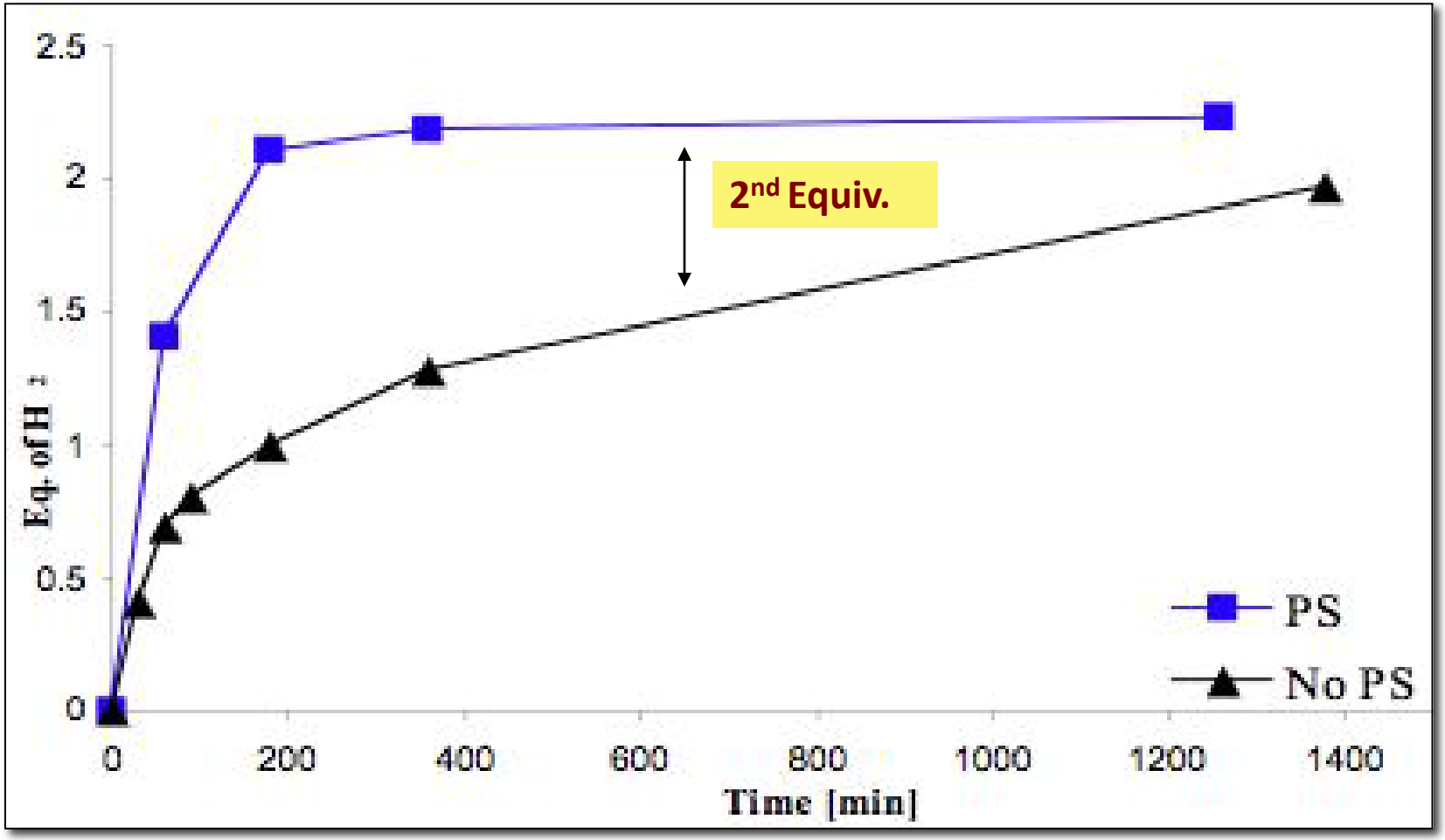
Proton Sponge Increases Release Rate of Second Equivalent of H_2 from AB



AB with 5 mol% PS in bmimCl at 85°C

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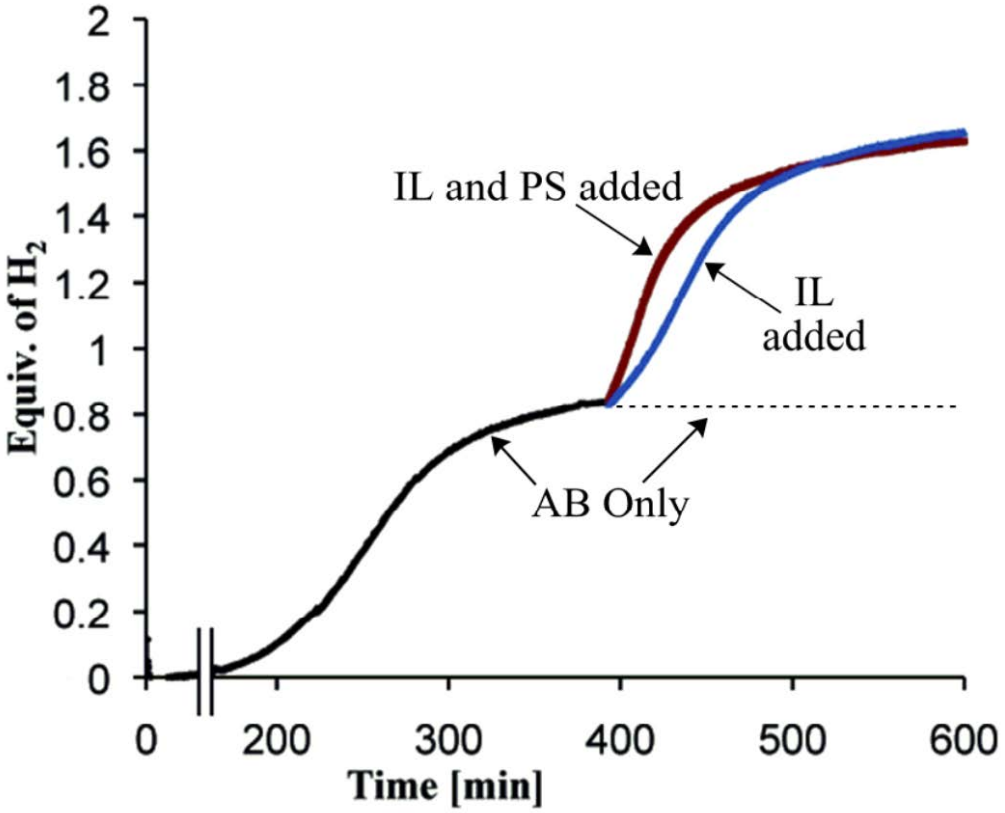
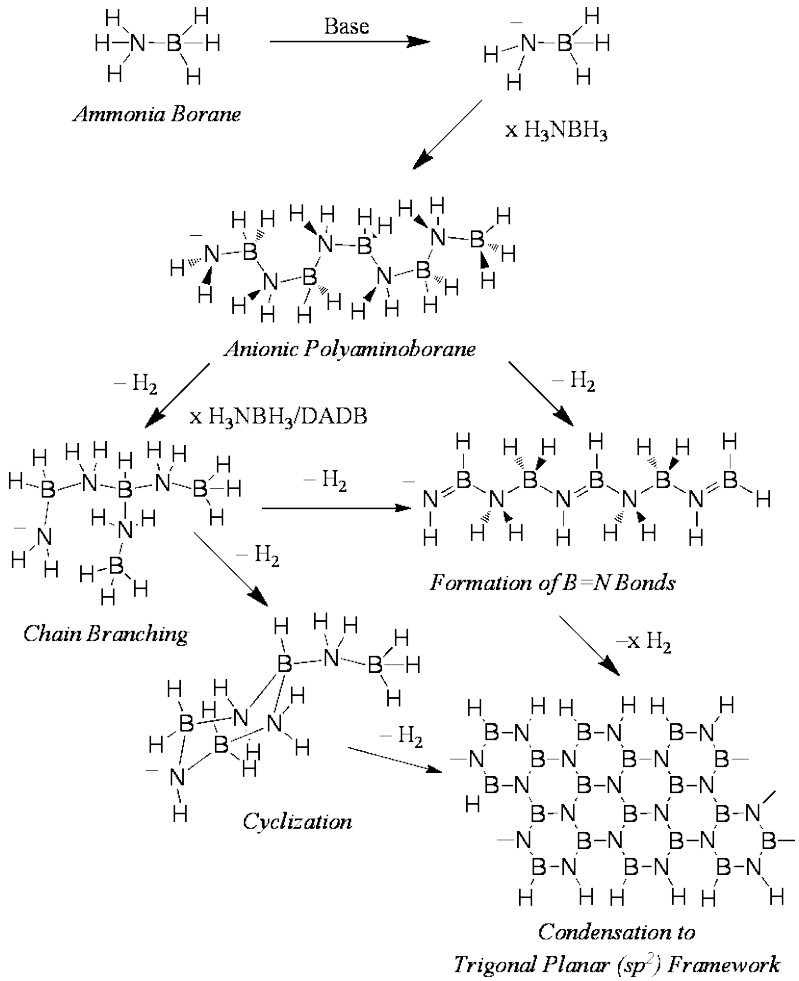
Proton Sponge Induces Loss of a Second H_2-Equivalent from Thermally Dehydrogenated AB





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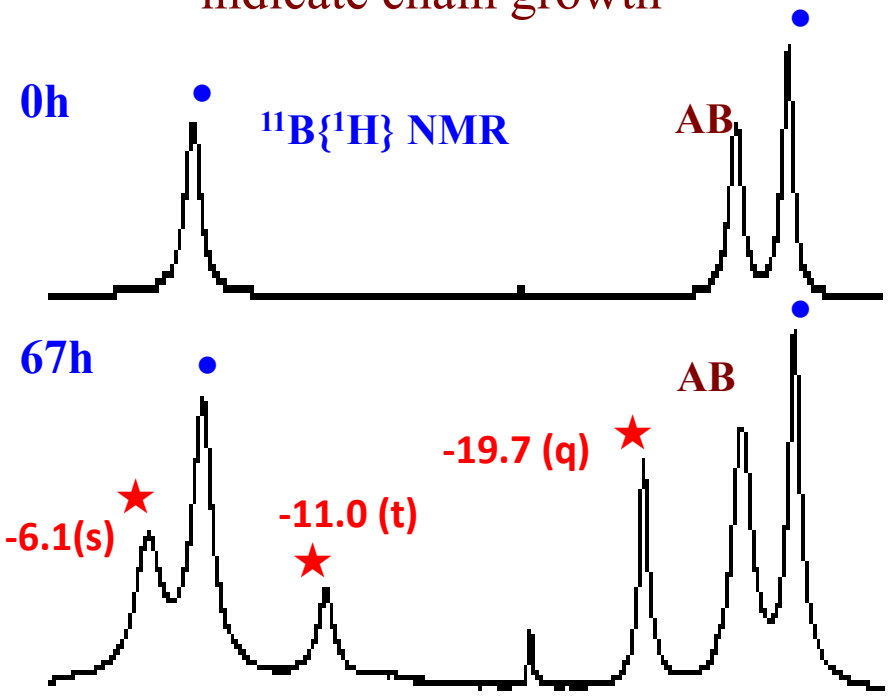
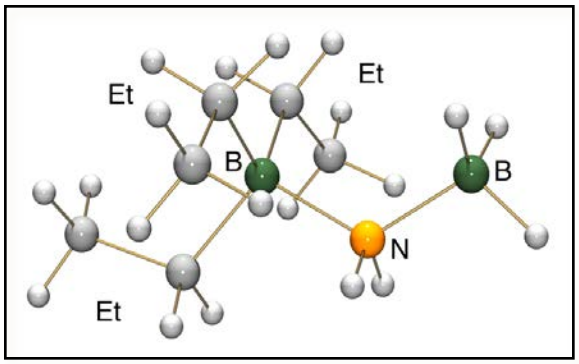
Model Studies: AB/$[Et_3BNH_2BH_3]^-$ Reactions Show Chain Growth

$NH_3BH_3 + Li^+BEt_3H^- \xrightarrow{-H_2} Et_3BNH_2BH_3^-$

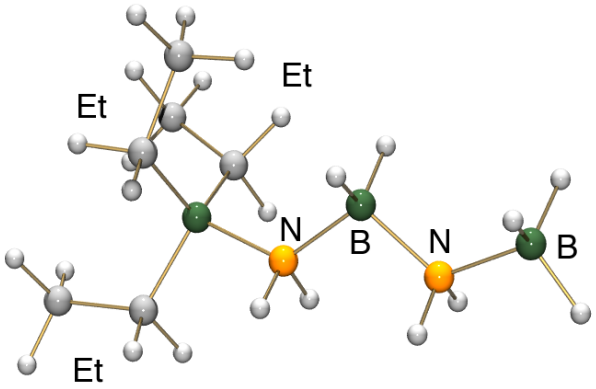
$[Et_3BNH_2BH_2NH_2BH_3]^- \xleftarrow{-H_2} NH_3BH_3$

Mass spec and GIAO/NMR studies indicate chain growth





X-ray structure $Et_3BNH_2BH_3^-$



DFT optimized structure of $[Et_3BNH_2BH_2NH_2BH_3]^-$

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

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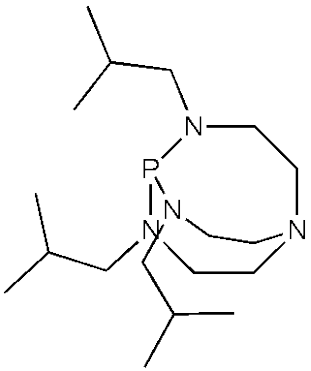
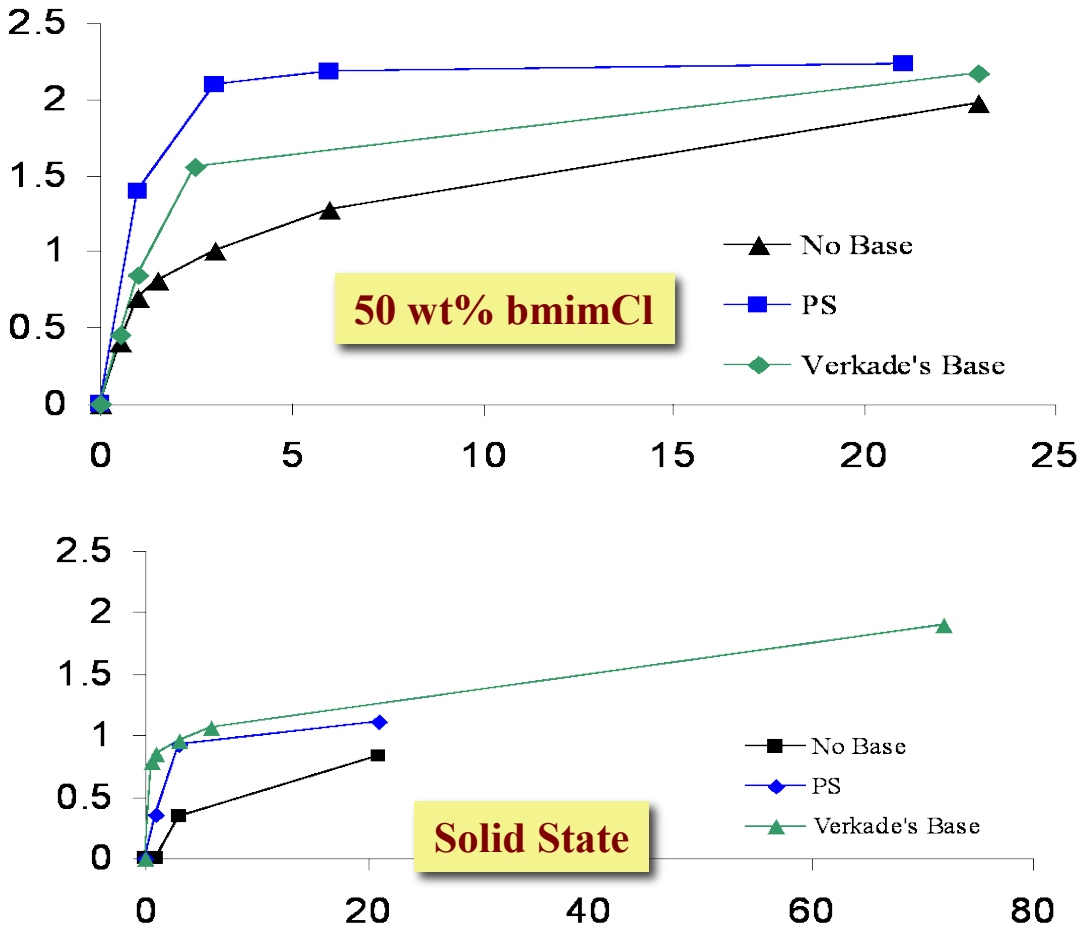
Verkade's Base Also Activates AB H_2-Release



Verkade's Base

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



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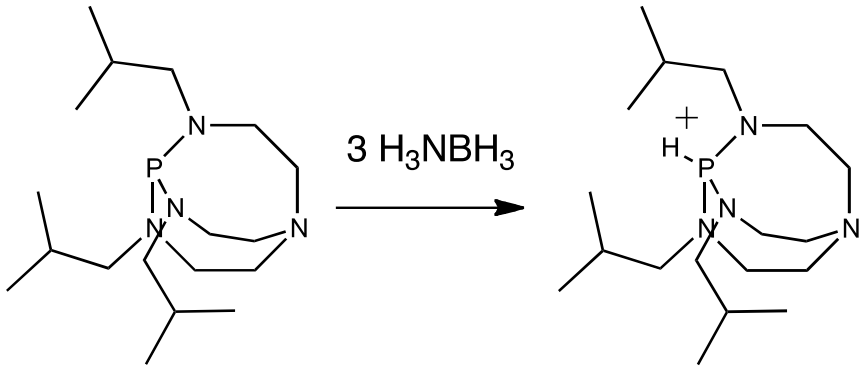
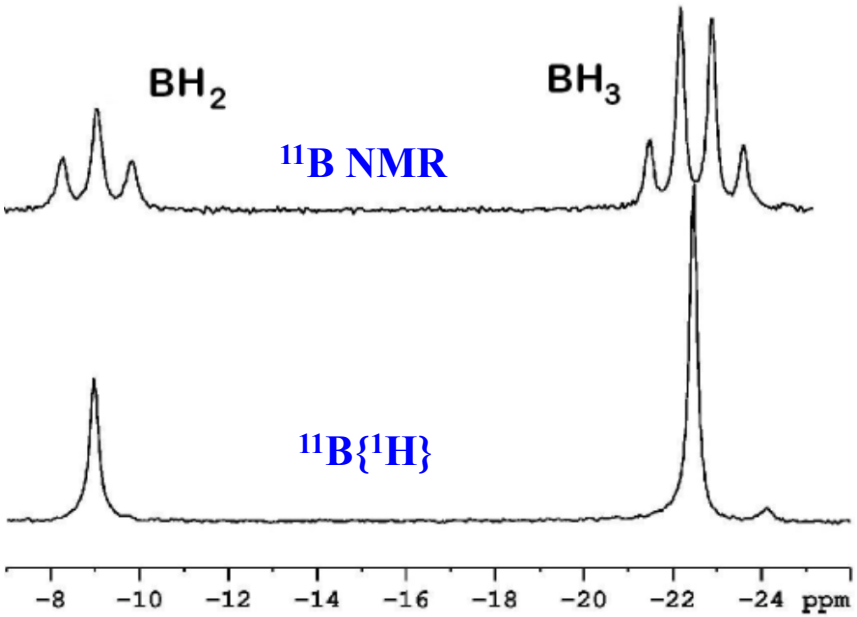
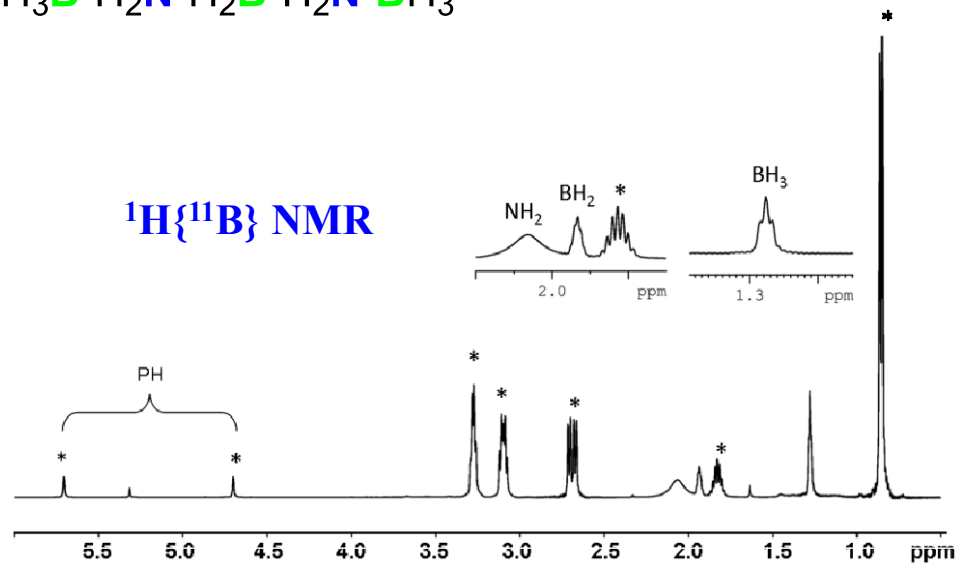
Verkade's Base / AB Reactions Allow Isolation of Chain Growth Products!



H_3B-H_2N-H_2B-H_2N-BH_3^-





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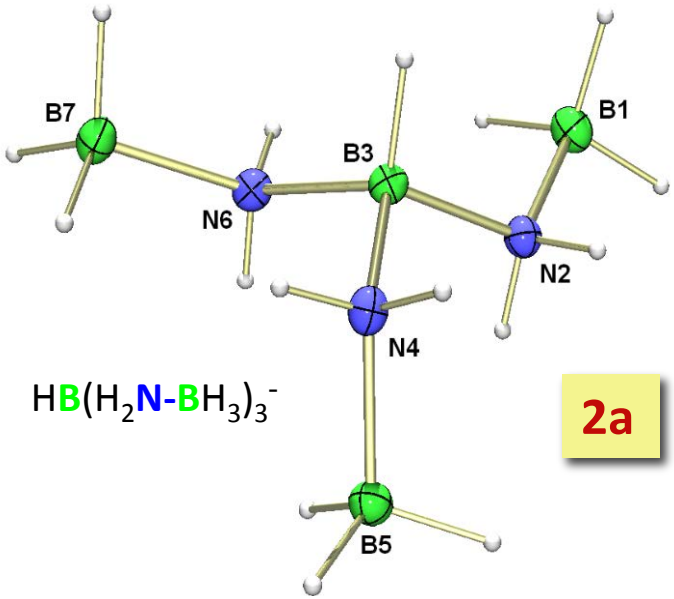
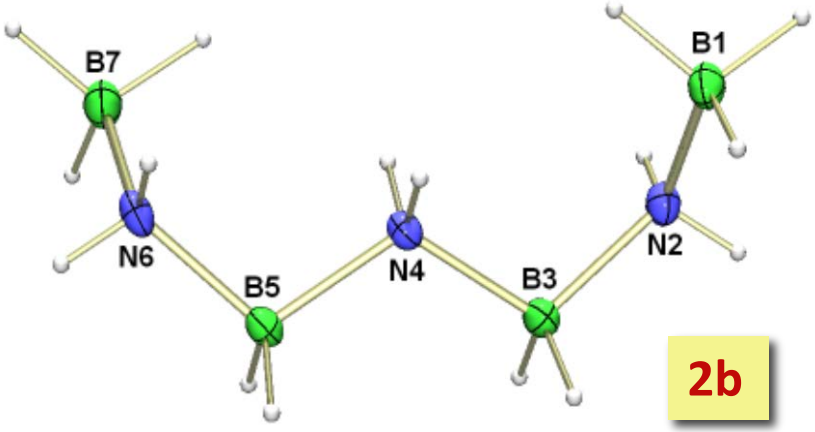
Crystallographic Studies Confirm Formation of Isomeric Chain Growth Products



$HB(H_2N\text{-}BH_3)_3^-$

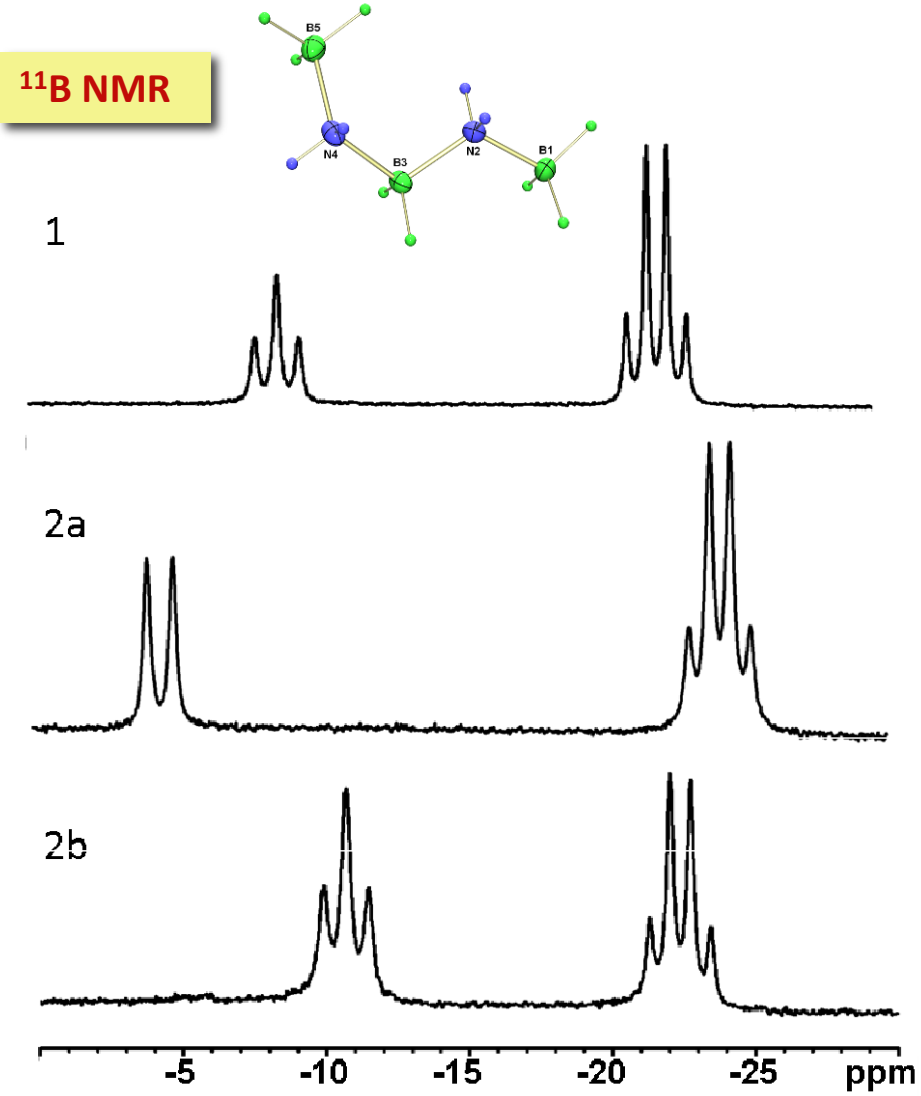
2a



$H_3B\text{-}H_2N\text{-}H_2B\text{-}H_2N\text{-}BH_2\text{-}H_2N\text{-}BH_3^-$

2b

^{11}B NMR



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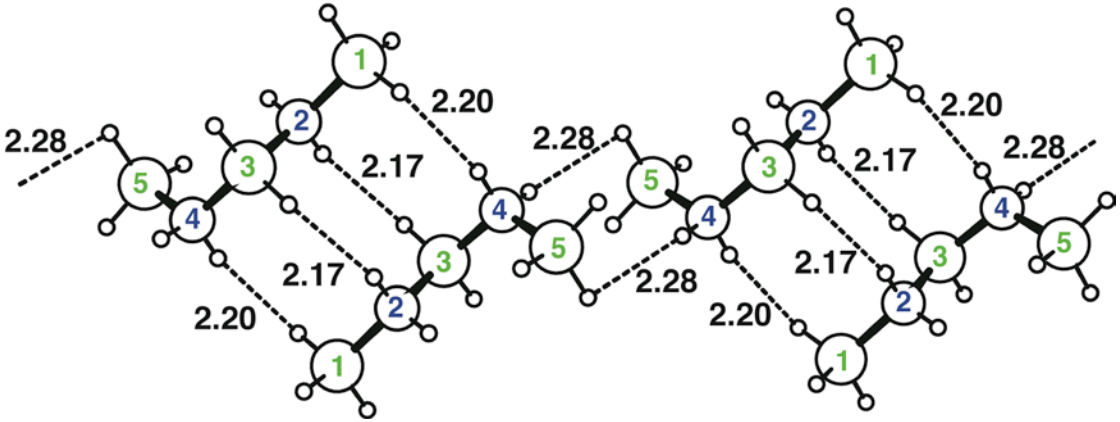
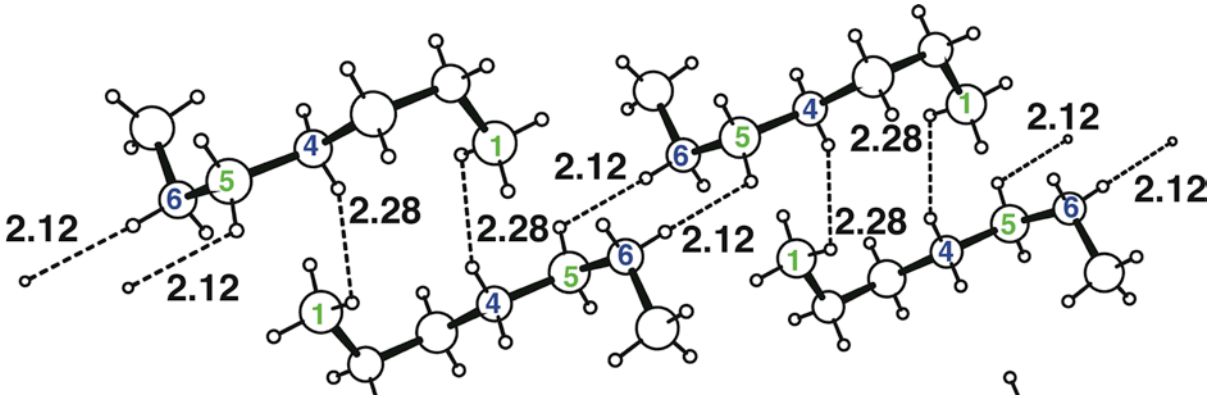
Anions Show Extensive N-H--H-B Hydrogen-Bonding in the Solid State



H_3B-H_2N-H_2B-H_2N-BH_3^-



H_3B-H_2N-H_2B-H_2N-BH_2-H_2N-BH_3^-

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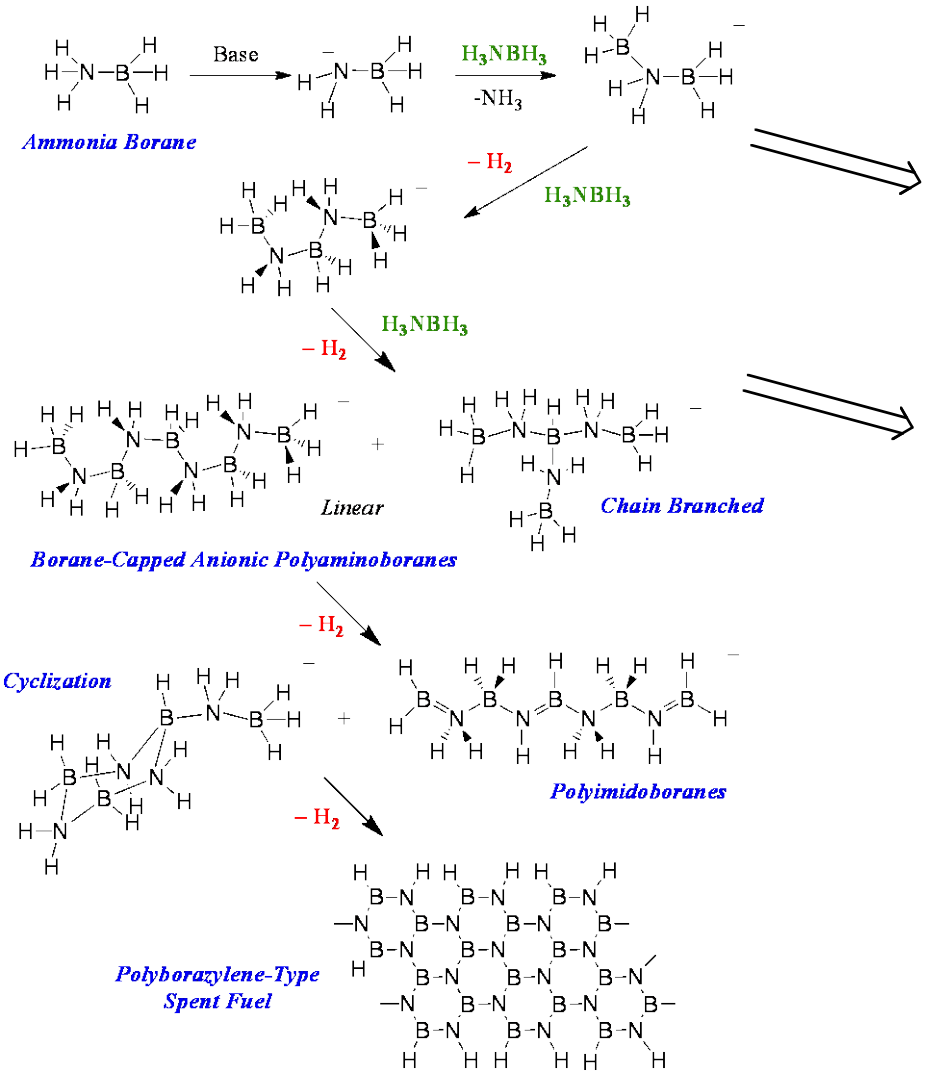
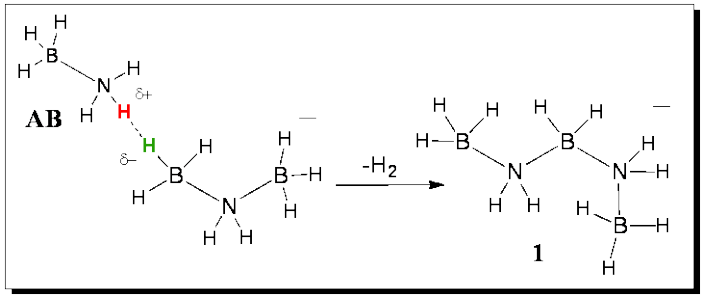
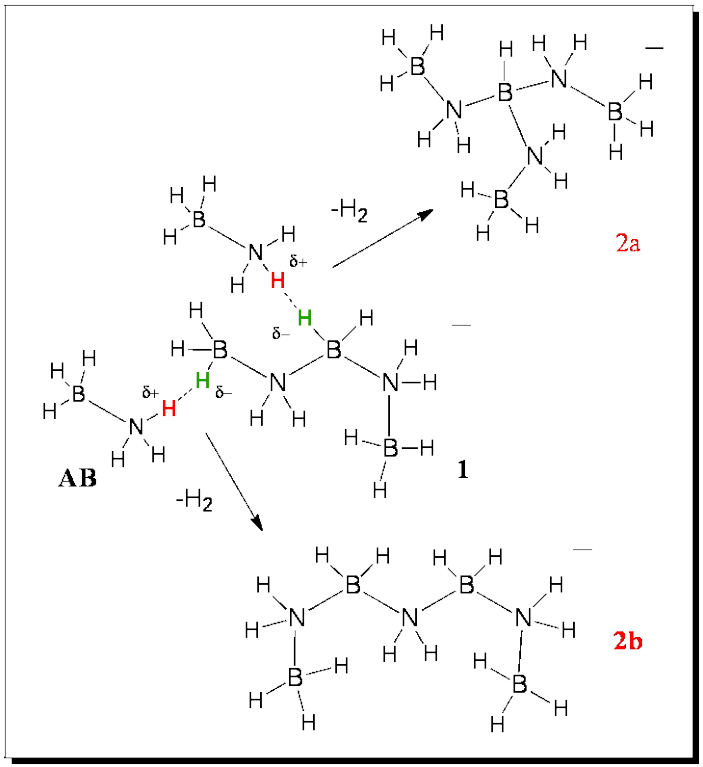
Anionic H_2-Release/Chain-Growth Reactions Facilitated by N-H--H-B Bonding







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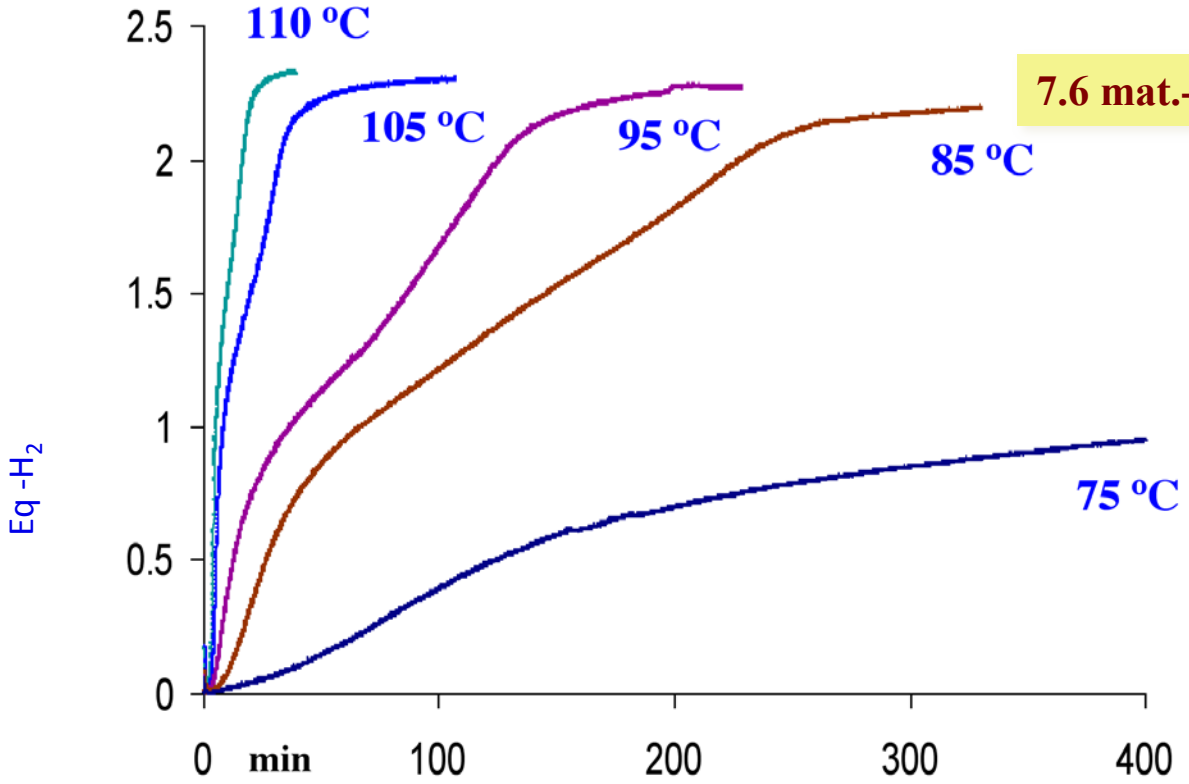
3) Activated AB Dehydrogenation in Ionic Liquids

Significantly Faster Rates for AB H_2-Release In Ionic Liquids with Only Small Temperature Increases

AB H_2-Release versus Temperature for 50 wt. % bmimCl/AB



bmim =

Conclusion: Fast H_2-Release at higher temperatures, but need to increase mat.-wt. % by decreasing % ionic liquid

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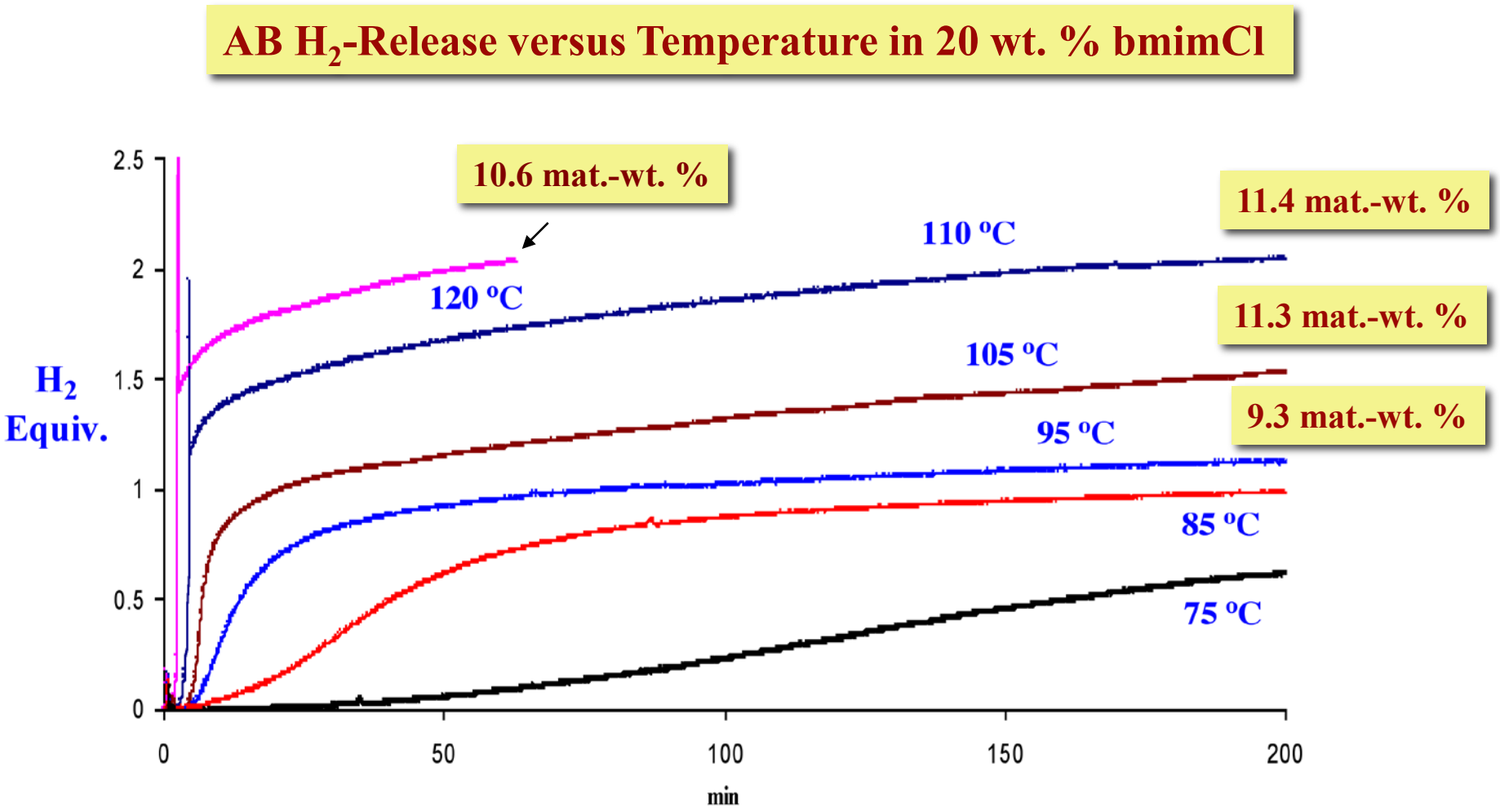
Fast Rate and 11.4 mat.-wt. % H_2-Release Demonstrated for 20 wt. % IL/AB at 110 °C



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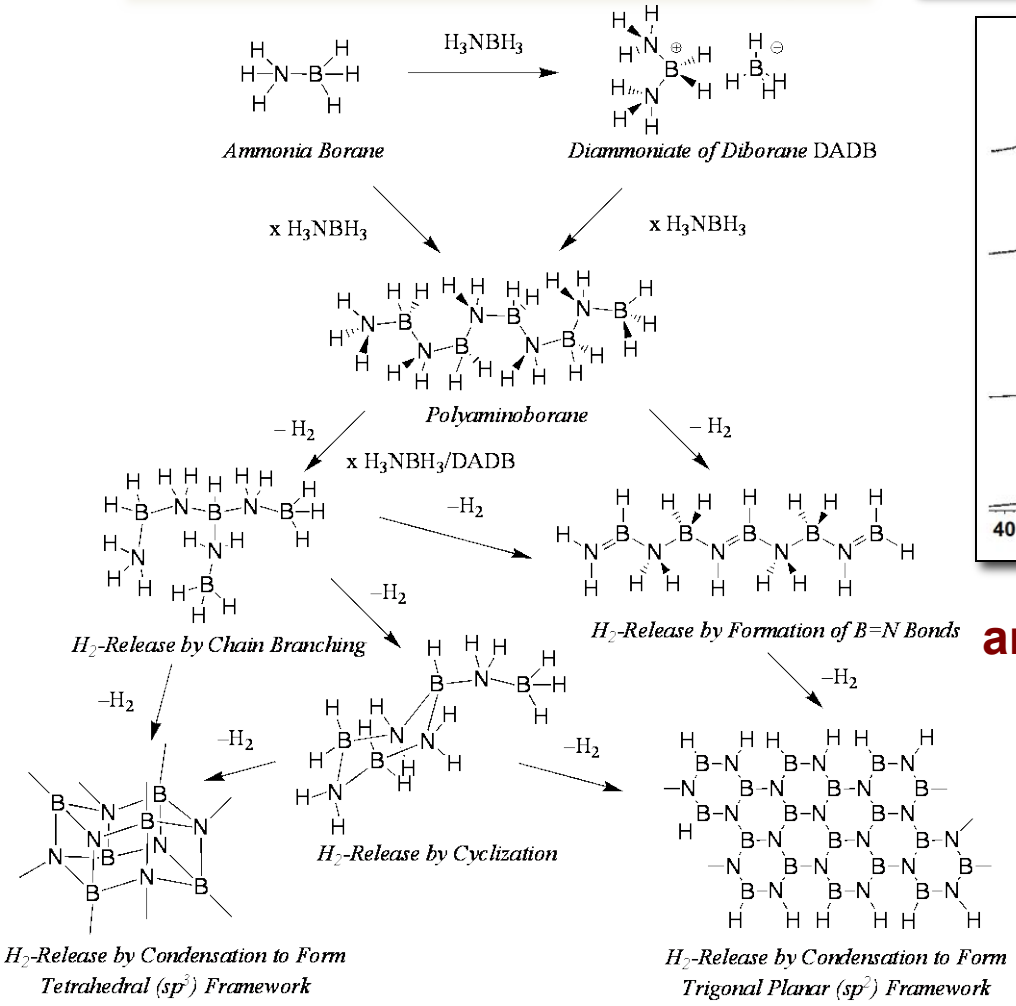
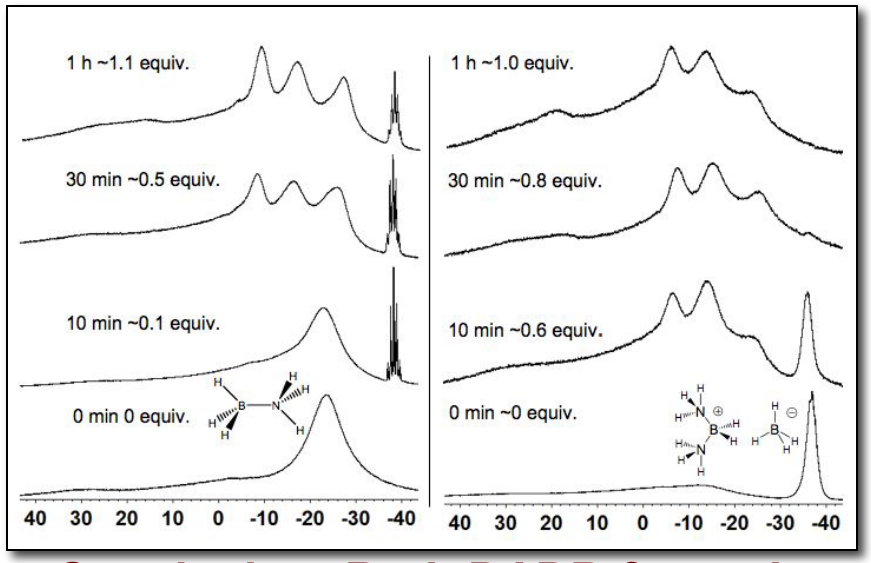
NMR Studies Identify Initial and Final Release Products

Possible Mechanistic Steps



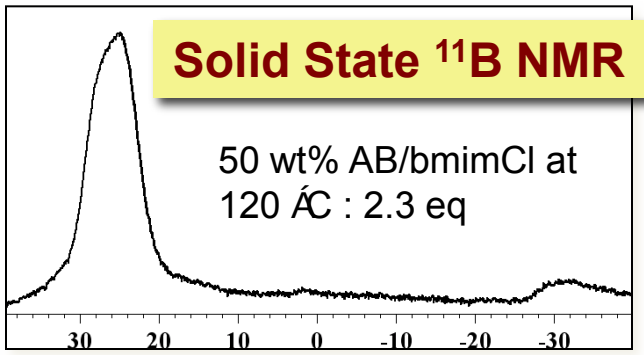
Solution ^{11}B NMR

10 wt% AB and DADB in bmimOTf at 85 ÁC



Conclusion: Both DADB formation and decomposition is enhanced in ILs

Solid State ^{11}B NMR



Conclusion: Final spent fuel product has sp^2-type framework

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

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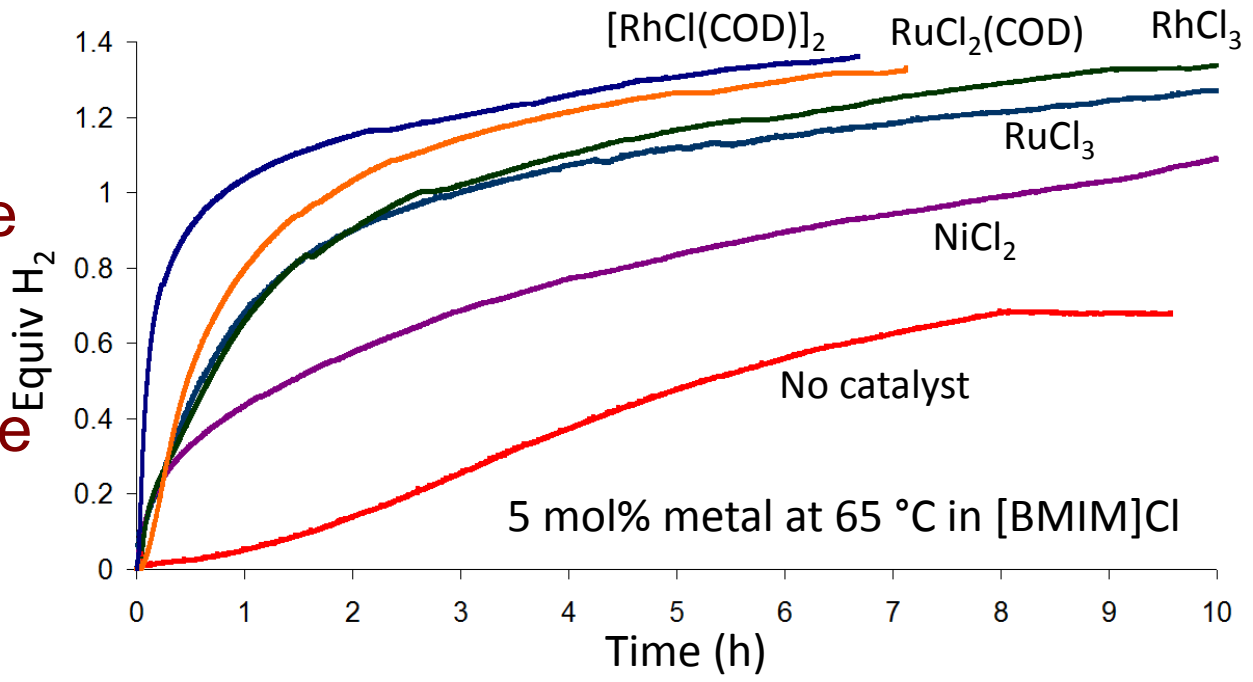
Why Use Metal Catalysts for AB Dehydrogenation in Ionic Liquids?

Catalysts in Conjunction with Ionic Liquids Could Provide:

- Faster H_2-Release
- Better Control of H_2-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.

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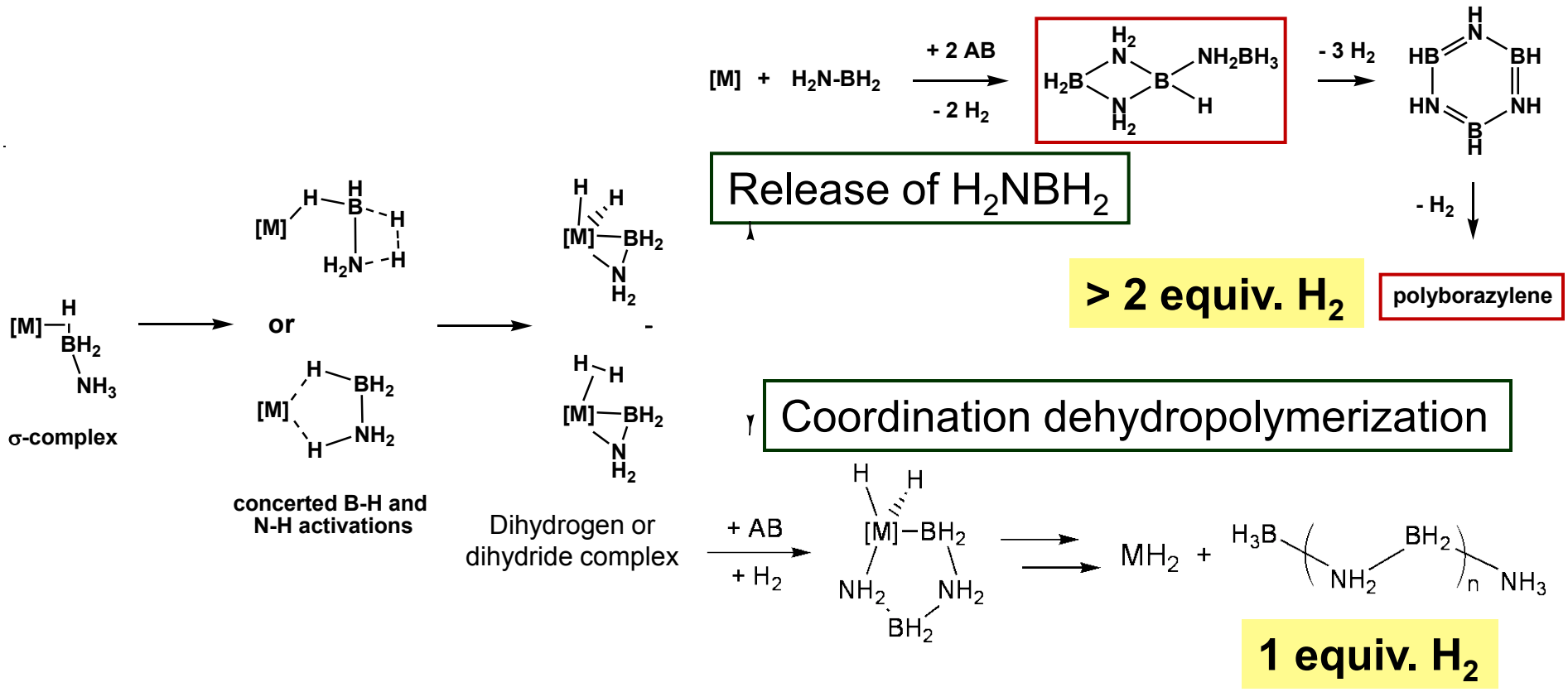
Selectivity of Metal-Catalyzed AB Dehydrogenation Dictates Extent of H_2 Release



- Release of H_2NBH_2 and formation of BN-ethylcyclobutane intermediate are key to greater hydrogen release
- Details of borazine and polymer formation not yet fully understood

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Ru Complex Catalyst is More Active in IL Solvent

$$RuCl_2(PMe_3)_4 \xrightarrow[-\ H_3B{\cdot}PMe_3]{\text{xs } NH_3BH_3} RuH(BH_4)(PMe_3)_3 \xrightarrow[-\ H_2]{NH_3BH_3} H_3N(BH_2NH_2)_nBH_3$$

insoluble colorless solid

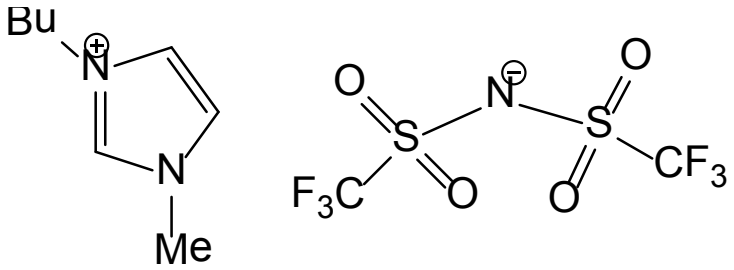
R.T. Baker *et al.*, unpublished results

1 TO /min diglyme at 60°C

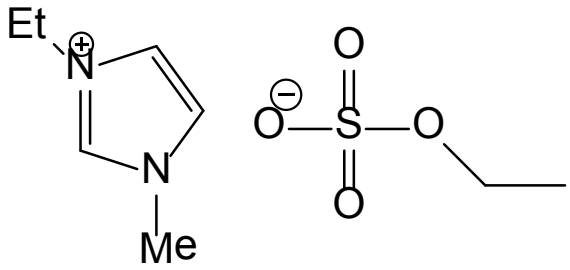
Catalyst is more active in Ionic Liquids

Solvent	Equivalents H_2 (60 mins)
THF	0.28
[EMIM][O_3SOEt]	0.85
[BMIM][NTf_2]	0.93

60 °C, 40 wt% NH_3BH_3, 2 mol% Ru cat.



[BMIM][NTf_2]



[EMIM][O_3SOEt]

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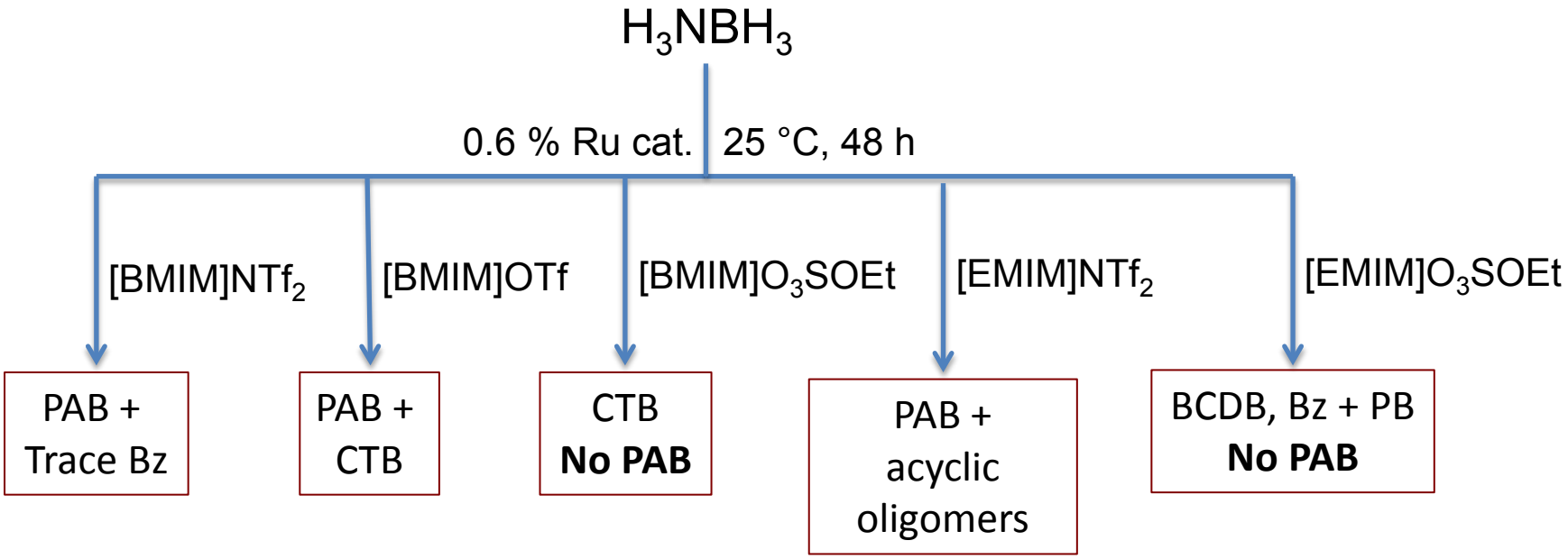
Ru-catalyzed AB Dehydrogenation Selectivity best with more Strongly Coordinating IL Anions



- Ionic Liquids with weakly coordinating anions afford similar products as those from diglyme reactions using $RuCl_2(PMe_3)_4$ 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)

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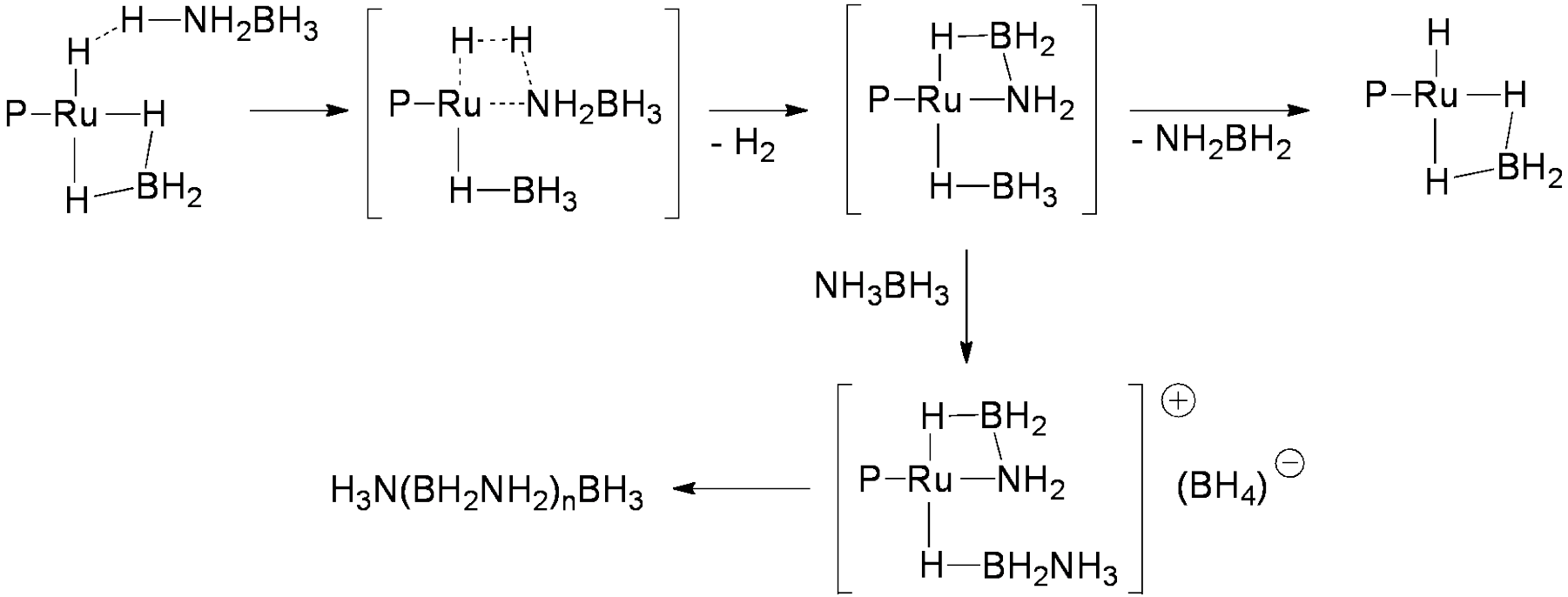
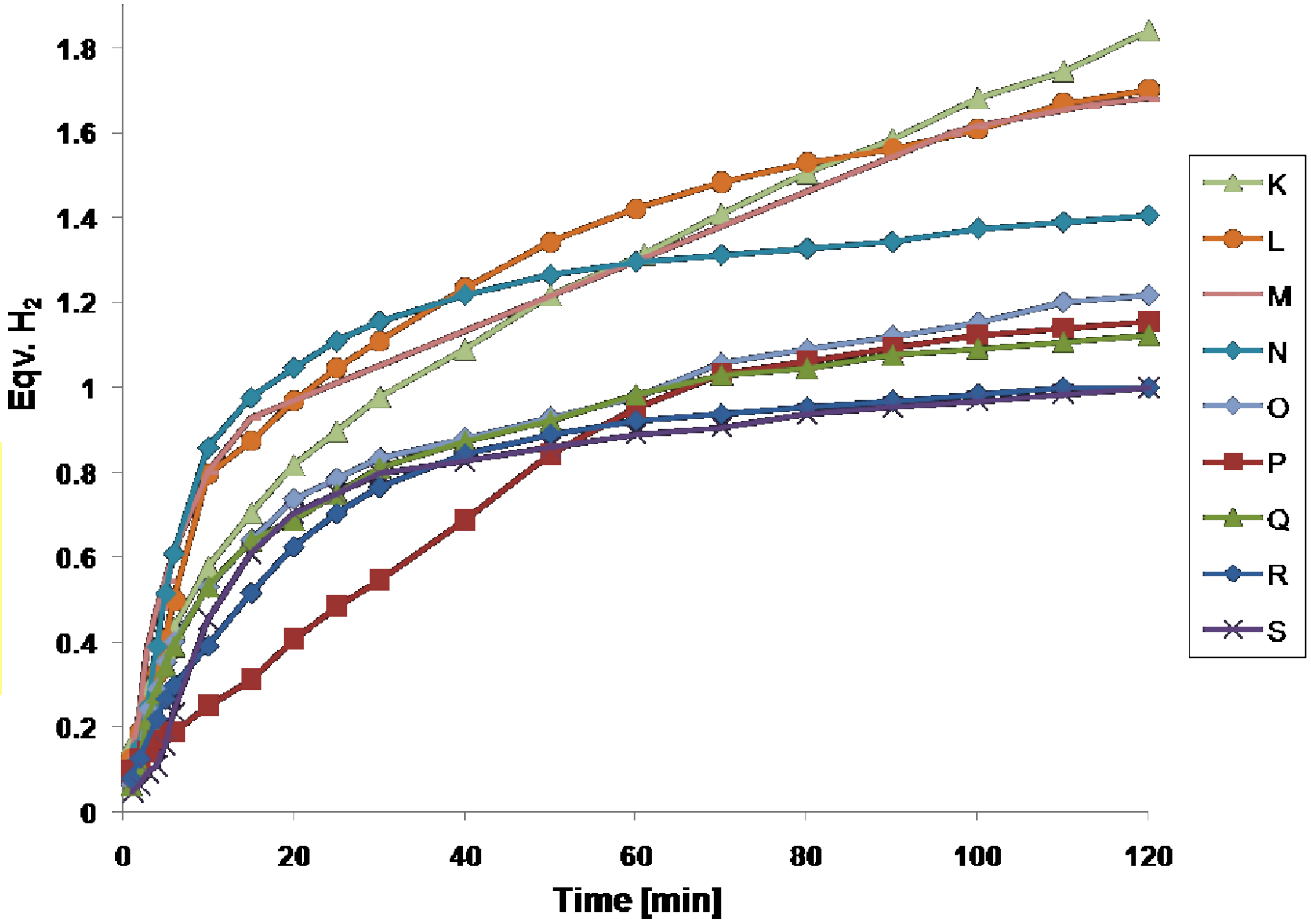
Possible Origin of Observed Selectivity

- 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% $[RuCl_2(PMe_3)_4]$ (**1**). K = $[P(n\text{-}Bu)_4][Cl]$, L = $[P(n\text{-}Bu)_4][O_3SOEt]$, M = $[P(n\text{-}Bu)_4][OAc]$, N = $[P(n\text{-}Bu)_4][OTf]$, O = $[P(n\text{-}Bu)_4][Br]$, P = $[P(C_{14})_3C_6][OTf]$, Q = $[P(C_{14})_3C_6][O_3SOEt]$, R = $[P(C_{14})_3C_6][NTf]$, S = $[P(n\text{-}Bu)_4][NTf_2]$.

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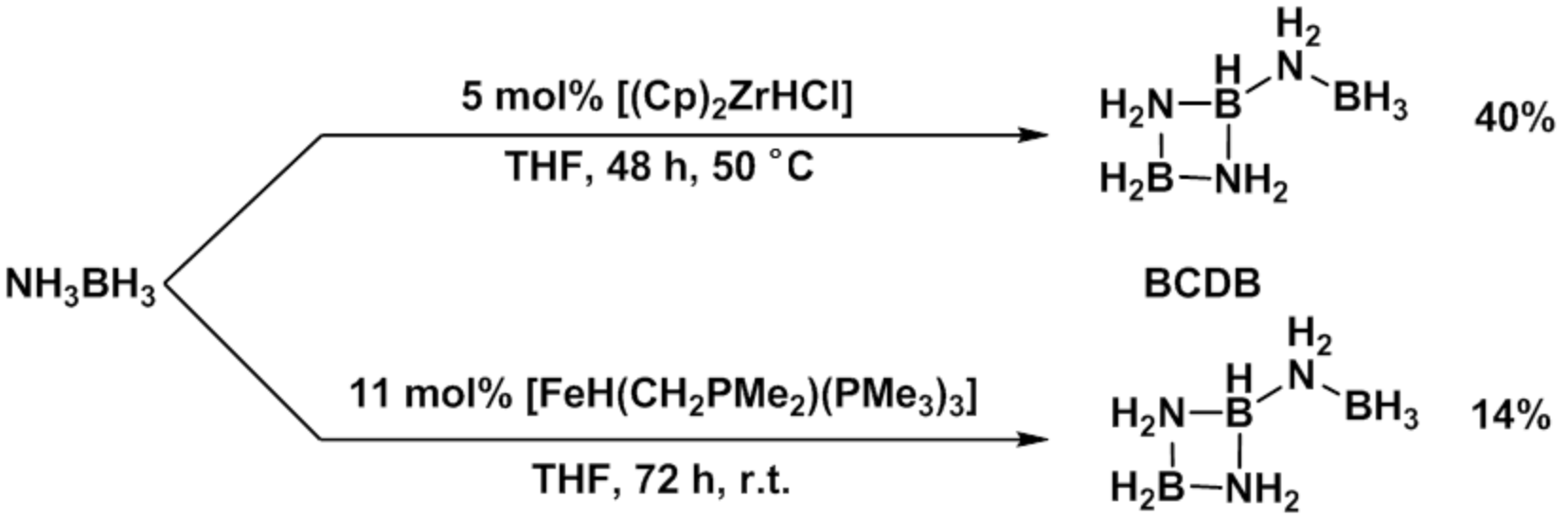
4) Investigating the 2nd Equivalent of H_2 from AB

Synthesis of BN Ethylcyclobutane

- In previous work we showed that Ni-*N*-heterocyclic carbene and Fe-PMe_3 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!



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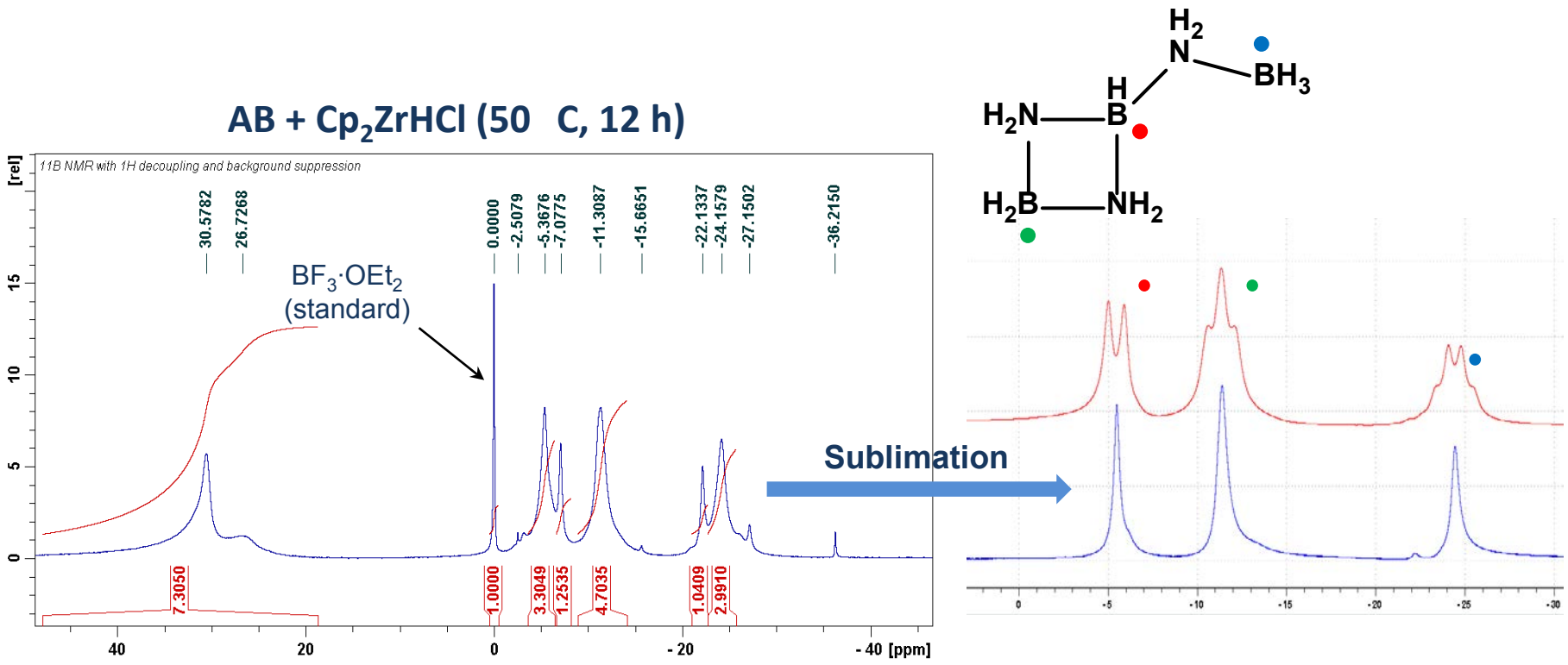
Characterization of BCDB



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

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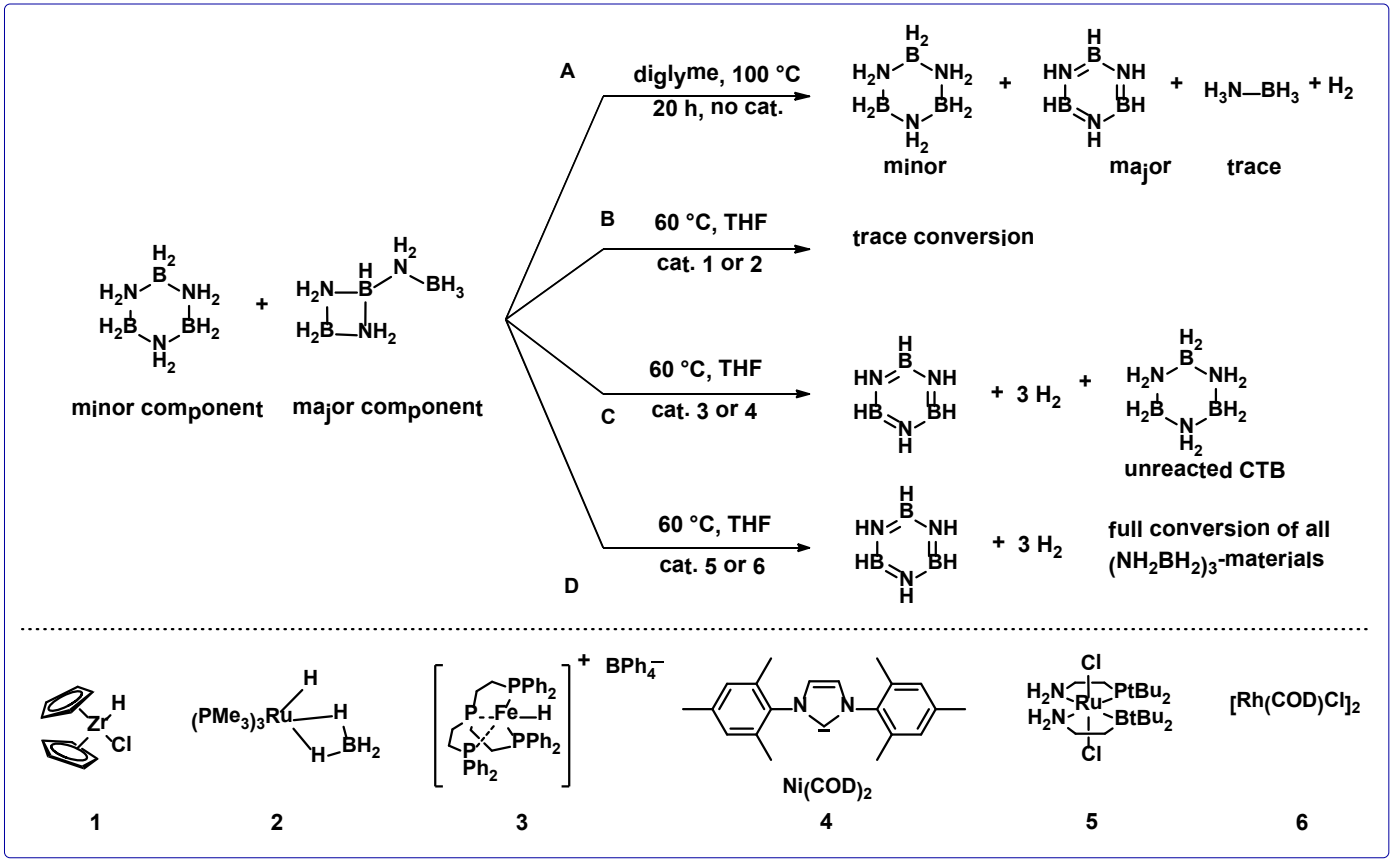
Thermal and Catalytic Dehydrogenation of BCDB



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

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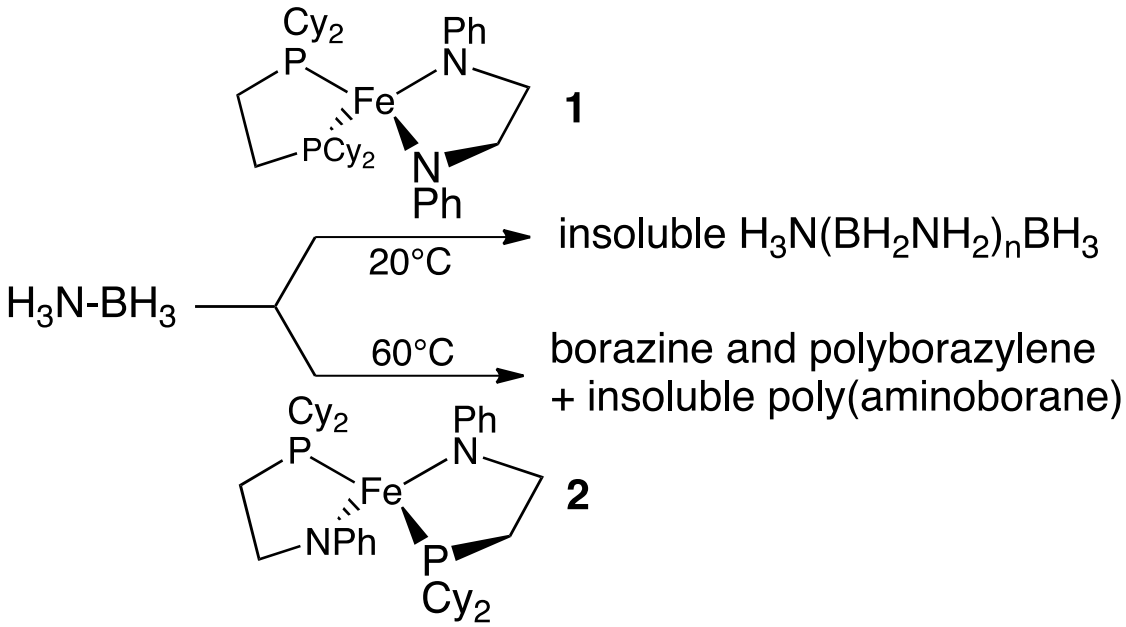
5) Iron Catalysts for AB dehydrogenation

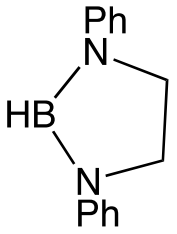
Iron Amido Phosphine Complexes

- 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 Fe(0) and cyclic diazaborane:



• Complex **2** is unselective catalyst and decomposes to Fe(0) and phosphine-borane

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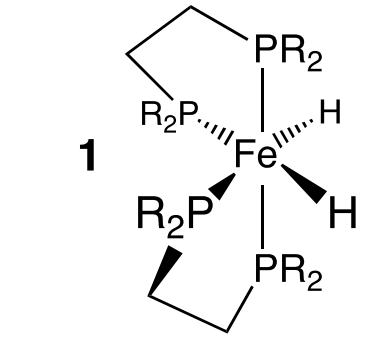
Robust Iron Complex Catalysts for Selective Synthesis of Poly(aminoborane)s

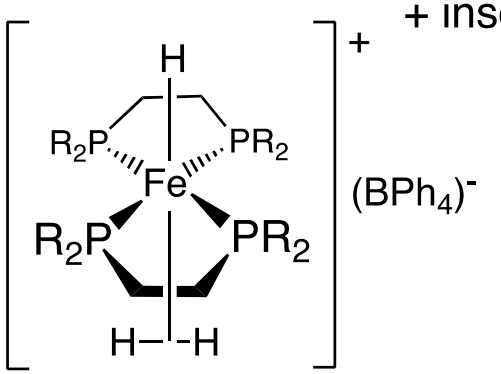


1

R = Me, Et

H_3N-BH_3 → 20°C → insoluble $H_3N(BH_2NH_2)_nBH_3$

H_3N-BH_3 → 60°C → borazine and polyborazylene + insoluble poly(aminoborane)



2

- Complex **1** is selective for poly(amino-borane) and only observable catalyst resting state under reaction conditions
- Complex **2** is unselective and decomposes to Fe(0) and phosphine-borane even at 20 °C

Using 5 mol% 1 primary amine-boranes H_2RNBH_3, are converted cleanly to poly(amino-borane)s (R = Me, *n*-Bu); will chiral bis(phosphines) allow for tacticity control?

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isotactic

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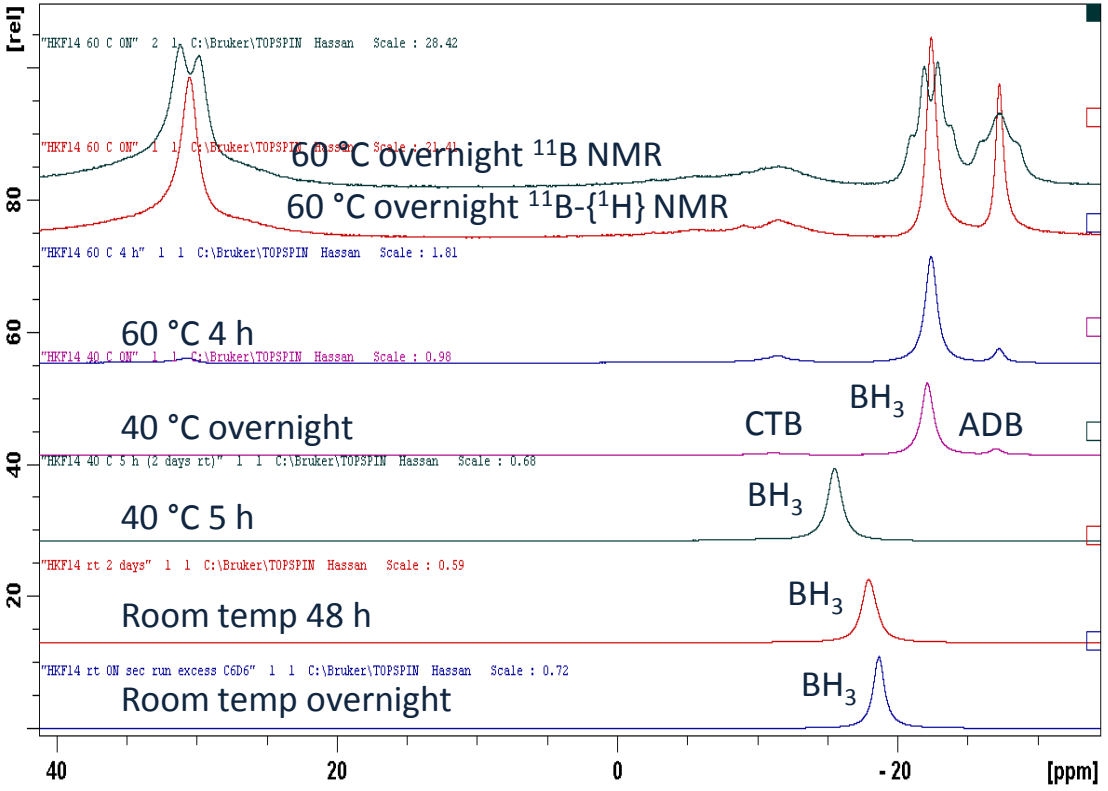
Iron Chloride Generates Effective Heterogeneous Catalyst for AB Dehydrogenation

- Mixtures of AB and $FeCl_2$ in diglyme release hydrogen as solution turns black and deposits a mirror on vial wall

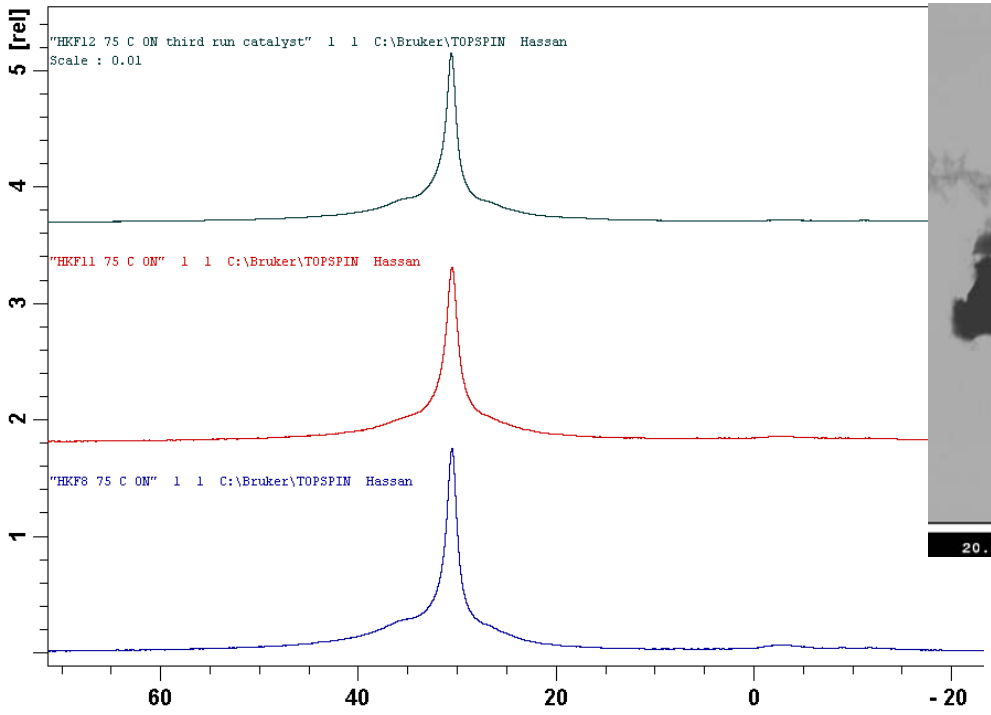
- 5 mol% $FeCl_2$ precatalyst was used in all the above experiments; however 1 mol% catalyst loading gave similar results.

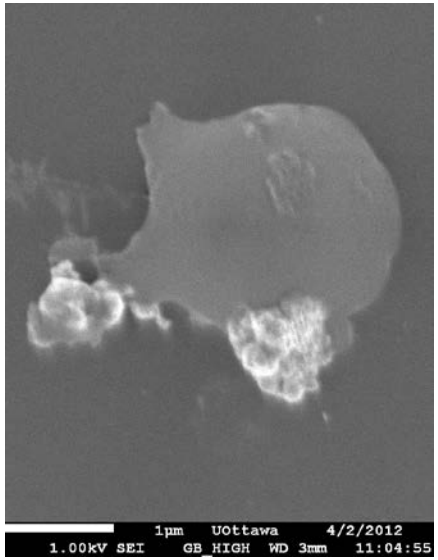


This system exhibits unprecedented selectivity to borazine and polyborazylene (minimal insoluble poly(aminoborane) by-product) for a heterogeneous catalyst. Now preparing high surface area samples on BN support for higher reaction rates.

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

$^{11}B\{^{1}H\}$ 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.

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Conclusions

- Detailed studies of base-promoted AB dehydrogenation confirmed chain growth mechanism to give linear and branched aminoborane oligomers that undergo further H_2 release to sp^2 BN products - analogous to solid-state AB thermolysis pathway
- Use of metal complex catalysts in ionic liquid solvents led to synergistic pathways for H_2 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 $FeCl_2$ 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

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Mechanistic Studies of Activated Hydrogen Release from Ammonia-Borane

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