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Title:	Some Recent Efforts in Chemical Hydrogen Storage at Los Alamos
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Form 836 (7/06)

Some Recent Efforts in Chemical Hydrogen Storage at Los Alamos

Abstract

Within the transportation sector, a necessity towards realizing the use of hydrogen (H_2) as an alternative fuel, is its storage for controlled delivery.[1] The U.S. DOE's Centers of Excellence (CoE) in H_2 storage have pursued different methodologies (metal hydrides, chemical hydrides, and sorbents), for the express purpose of supplanting gasoline's current > 300 mile driving range. Chemical H_2 storage has been dominated by one material, ammonia borane (H_3B–NH_3, AB), due to its high gravimetric capacity of H_2 (19.6 wt %) and low molecular weight (30.7 g mol^{-1}). As such, a number of publications have described H_2 release from amine boranes, yielding various rates depending on the method applied.[2-5] The viability of any storage system is also dependent on efficient recyclability. Within our CoE we have thus endeavored to find efficient base-metal catalyzed AB dehydrogenation pathways and regeneration schemes[6] for the spent fuel from H_2 depleted AB. We will present some recent results in these areas in this vein.

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(1) Stephens, F. H.; Pons, V.; Baker, R. T. J. Chem. Soc. *Dalton Trans.* **2007**, 2613-262.

(2) Bluhm, M. E.; Bradley, M. G.; Butterick, R., III; Kusari, U.; Sneddon, L. G. *J. Am.Chem. Soc.* **2006**, *128*, 24, 7748-7749.

(3) Denney, M. C.; Pons, V.; Hebden, T. J.; Heinekey, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2006**, *128*, 37, 12048-12049.

(4) Keaton, R. J.; Blacquiere, J. M.; Baker, R. T. *J. Am. Chem. Soc.* **2007**, *129*, 7, 1844-1845.

(5) Stephens, F. H.; Baker, R. T.; Matus, M. H.; Grant, D. J.; Dixon, D. A. *Angew. Chem. Int. Ed.* **2007**; Vol. 46, p 746-749, S746/1-S746/4.

(6) (a) Davis, B. L.; Dixon, D. A.; Garner, E. B.; Gordon, J. C.; Matus, M. H.; B. L. Scott, B. L.; Stephens, F. H.: "Efficient Regeneration of Partially Spent Ammonia Borane Fuel", *Angew. Chem. Int. Ed.* **2009**, *37*, 6812. (b) Sutton, A. D.; Burrell, A. K.; Gordon, J. C.; Ott, K. C., unpublished results.

Some Recent Efforts in Chemical Hydrogen Storage at Los Alamos

Experimental

R. Thomas Baker (U. Ottawa), Benjamin L. Davis, Anthony K. Burrell,

John C. Gordon, Charles W. Hamilton (QD Vision, Inc.), Tessui Nakagawa,

Kevin C. Ott, Nathan C. Smythe, Andrew D. Sutton

Theory

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Neil J. Henson

$$$s

DOE Office of Energy Efficiency and Renewable Energy

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CHS CoE

DOE's Chemical Hydrogen Storage Center of Excellence

One of 3 DOE Centers – others focused on Sorbents and Metal Hydrides
($$$'s: DOE, Office of Energy Efficiency and Renewable Energy)

CHS CoE - A coordinated approach to identify, research, develop and validate advanced on-board *chemical* hydrogen storage systems to overcome technical barriers and meet 2010 DOE system goals with the potential to meet 2015 goals….

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Hydrogen as Energy Carrier for Transportation

- Combination of hydrogen and air in a fuel cell produces water and electricity, with no NO_x, SO_x , CO_2 or particulates

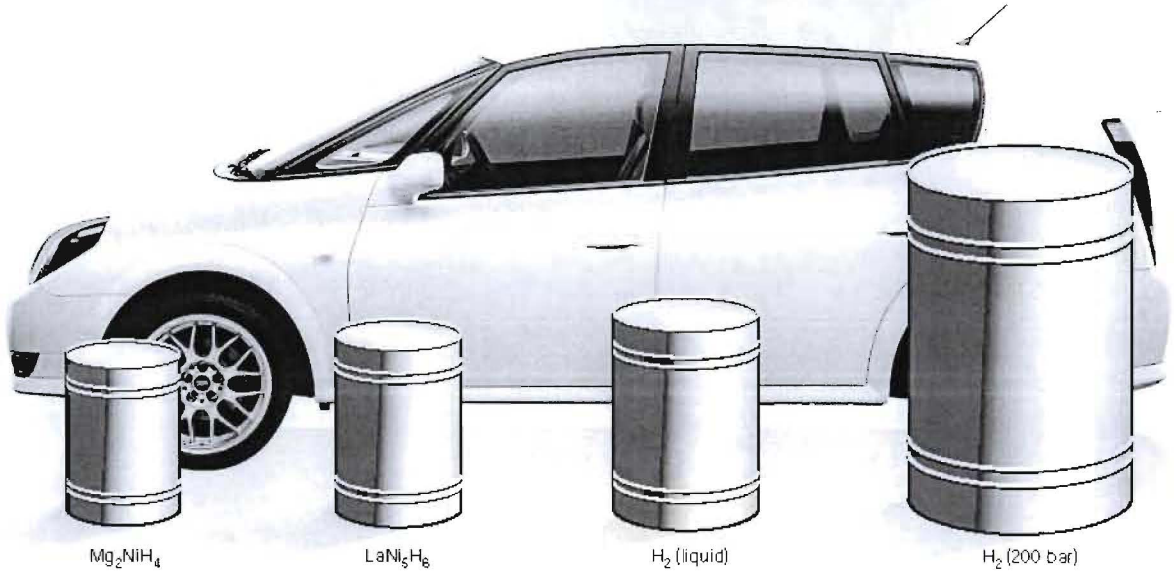
- Apart from current expense and precious metal burden of fuel cells, problems facing hydrogen economy include:

How to produce it?

How to store it?

High Pressure Tanks **Low volumetric storage capacity and safety issues**	***Metal Hydrides*** **Low gravimetric capacity and heterogeneous**
Sorbents **Limited H_2 binding energy requires low T**	***Chemical Hydrides*** **Energy input needed for fuel regeneration**

DOE Volumetric and Gravimetric Targets[1]



Relative volumes of 4 kg of H_2[2]

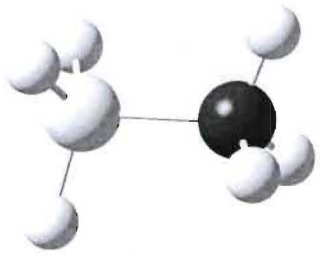
	2010	2015	Ultimate
Gravimetric (wt. %)	4.5	5.5	7.5
Volumetric (MJ/L)	3.2	4.7	8.3

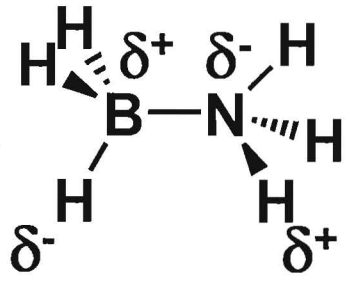
[1]http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf
[2]Schlapbach, L.; Zuettel, A. *Nature* ***2001, 414,*** 353-358.

Ammonia-Borane (AB) = NH_3BH_3

Contains both Protic N-H and Hydridic B-H Hydrogen Atoms

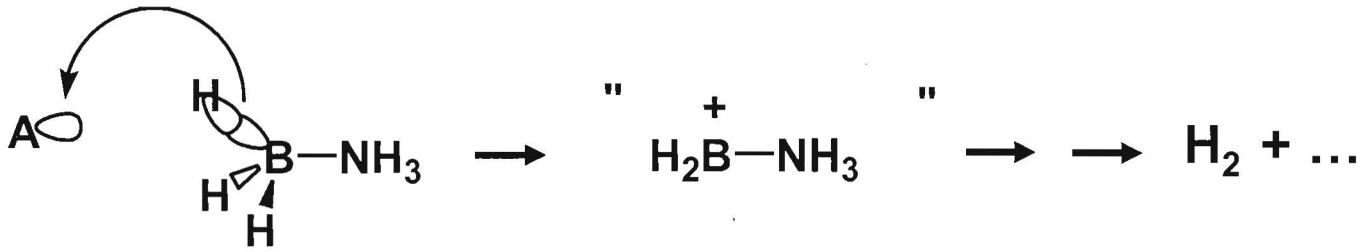
(up to 19.6 wt % H_2, 0.16 kg/L H_2)



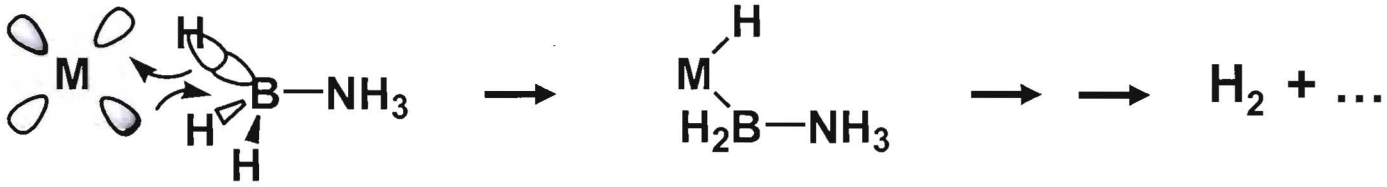


Thermal release of H_2 is too slow at T < 100°C - What catalyzes the process?

- Acid Catalysis (Lewis Acid or Bronsted Acid)



- Metal Catalysis



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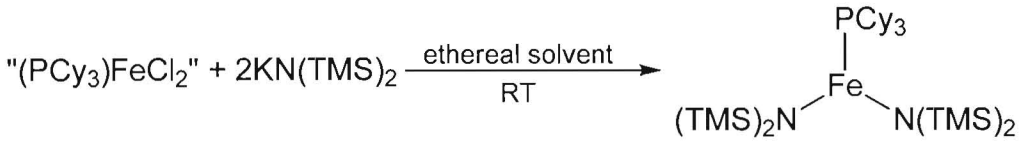
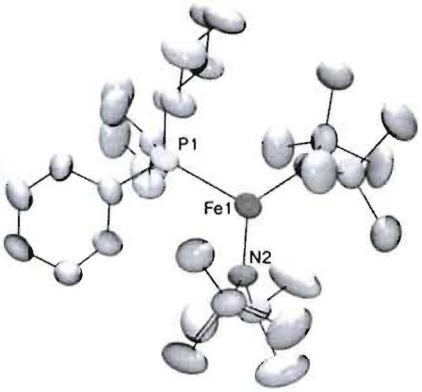
Some Base-Metal Catalysts

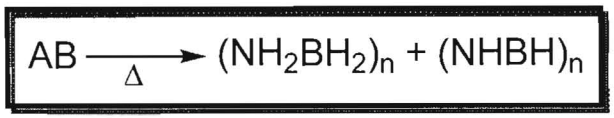


Colorless solid, *ca.* 18 % purified yield
Cy = Cyclohexyl, TMS = Trimethylsilyl

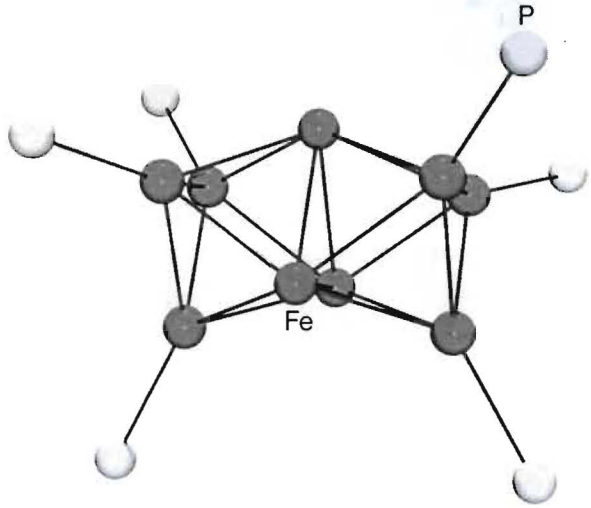


Thermal ellipsoids at 50% probability with hydrogen atoms omitted.

$P2_1/n$	
R_1	7.4 %
	(Å)
Fe(1)-P(1)	2.619(4)
Fe(1)-N(1)	1.927(10)
Fe(1)-N(2)	1.932(8)
	(°)
P(1)-Fe(1)-N(1)	116.3(3)
N(1)-Fe(1)-N(2)	127.9(4)
N(2)-Fe(1)-P(1)	115.8(3)
N(1)-N(2)-P(1)-Fe(1)	~1



- Mixture of products
  - Depends on rxn. conditions
- 2.5 – 3 h reaction time
- *ca.* 3.5 mol. % catalyst loading
- 1.5 – 1.7 eq. H_2 per AB
- Very sensitive to oxidation/decomp.
- Trigonal planar coordination geom.



$PCy_3Fe[N(TMS)_2]_2$ + AB in THF at RT. $P6_3$, R1 = 11.5 %, 50 % thermal ellipsoids, cyclohexyl P substituents omitted.

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Baker, Gordon, Hamilton, Henson, Smythe

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What About Regeneration of AB Spent Fuel(s)?

Ideally would like chemistry to be general enough to regenerate a variety of spent fuel types..

Borazine (trace in ionic liquids)
Insoluble BHN_x products

Dehydro-oligomerization

AB

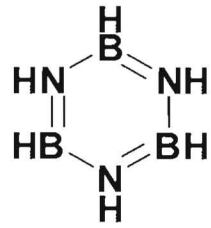
Metal Based Catalysis

insoluble cyclic "pentamer"

$(H_2N\text{-}BH_2)_5$

1 equiv. H_2 lost

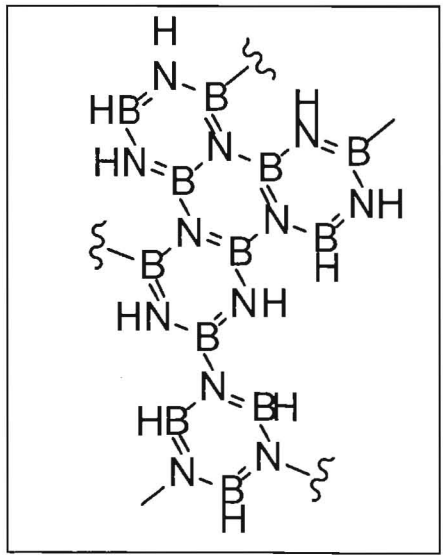
borazine



2 equiv. H_2 lost

Thermolysis solution or solid state

soluble polyborazylene



> 2 equiv H_2 lost

Polyaminoboranes (1 eq. H_2 loss)
Polyaminoboranes (1 eq. H_2 loss)
Borazine (except nanomaterials)

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Off-Board Regeneration Required

3 Ammonia Borane (H_3N-BH_3) → Spent fuel ($B_3N_3H_4$) + $7H_2\uparrow$

$\Delta H \approx$ -7 kcal/mol

(Miranda and Ceder 2007)

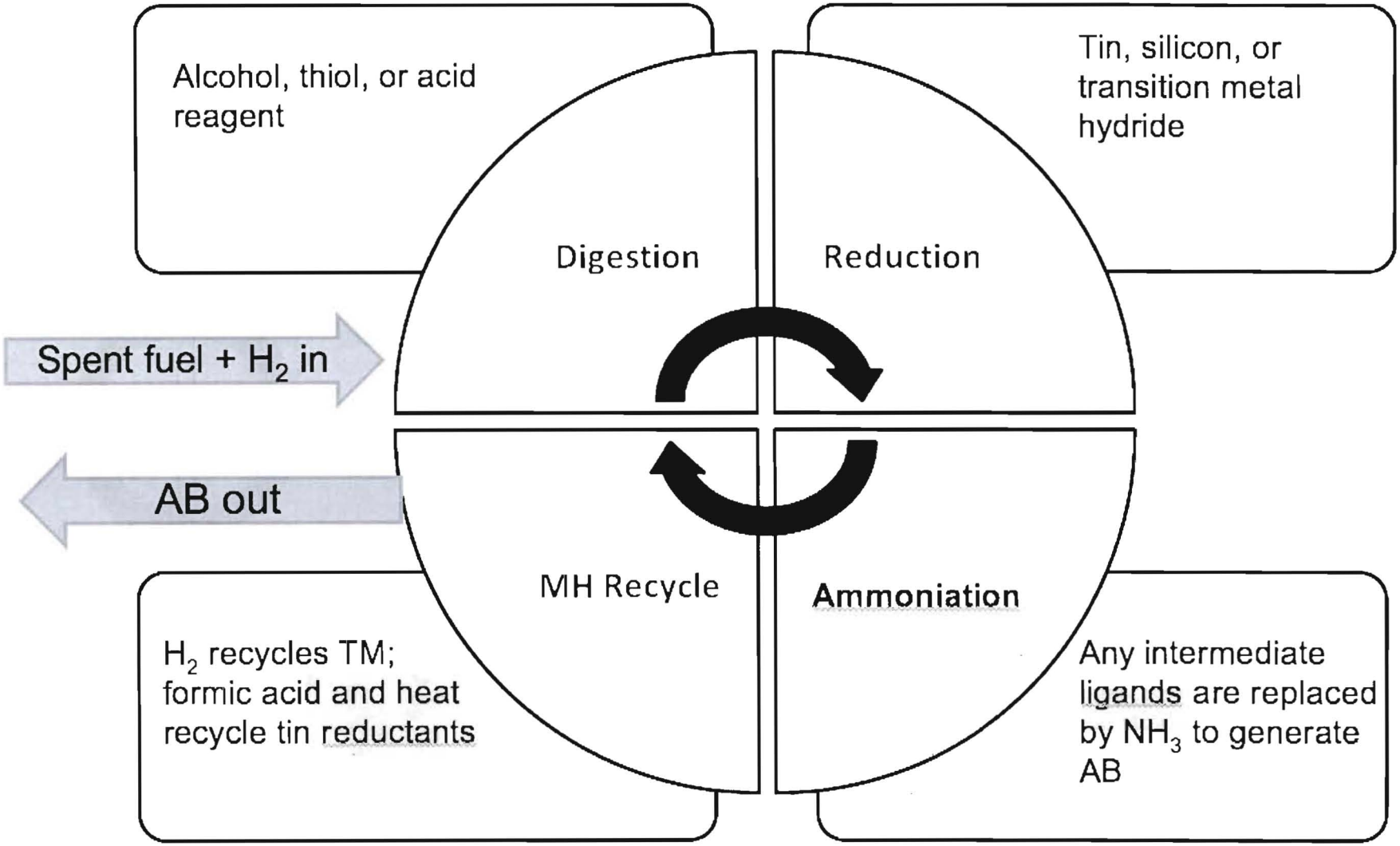
Hydrogen release -> **too exothermic** to merely re-pressurize with H_2

Off-board chemistry required to regenerate ammonia borane (AB)

N.B. Within the Center we are working on systems that are potentially directly regenerable (on-board??):

e.g. $Ca(NH_2BH_3)_2$ (Burrell et. al. *Angew. Chem. Int. Ed.* **2007**, *46*, 8995).

Regeneration Strategy



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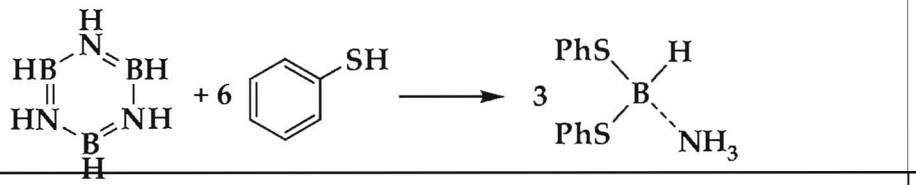
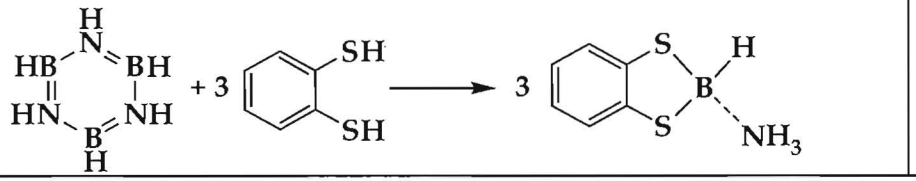
Key Concepts for Regeneration

Avoid formation of B-O bonds….
Theory using borazine as a model suggests
boron-sulfur chemistry feasible – see below…..

- Steps have to be reasonably matched thermodynamically
- Steps have to be high yielding
- Recycle of reagents - *e.g.* reductant

Estimates of Reaction Energies for Digestion ΔH(298 K)[a]

	42.2/25.1
	-20.4/0.5

[a] Condensed phase/Gas phase values in kcal/mol

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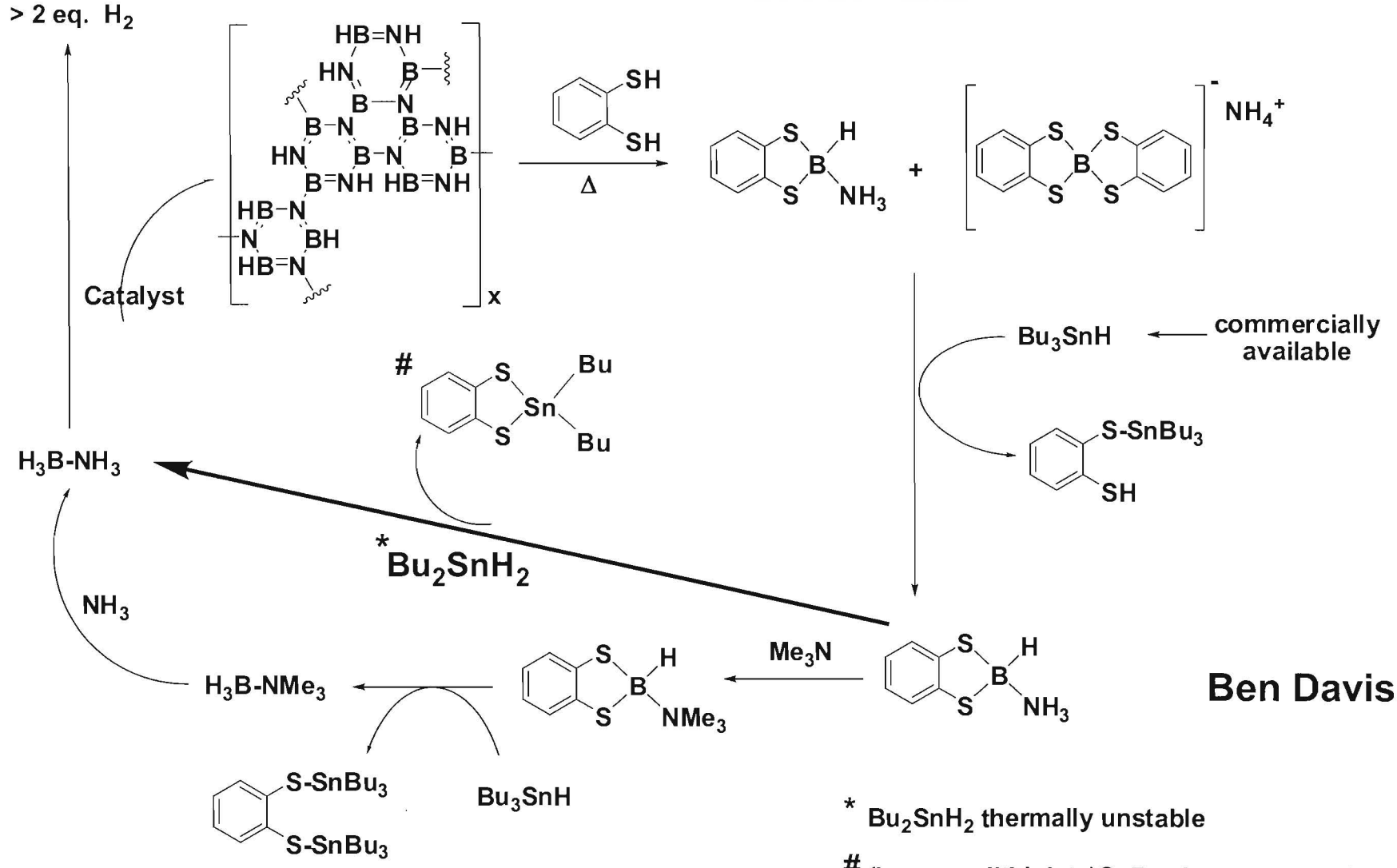
Benzenedithiol Chemistry Works with Borazine and PB…



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Davis, Dixon, Garner, Gordon, Matus, Scott, Stephens, *Angew. Chem. Int. Ed.*, **2009**, *48*, 6812.

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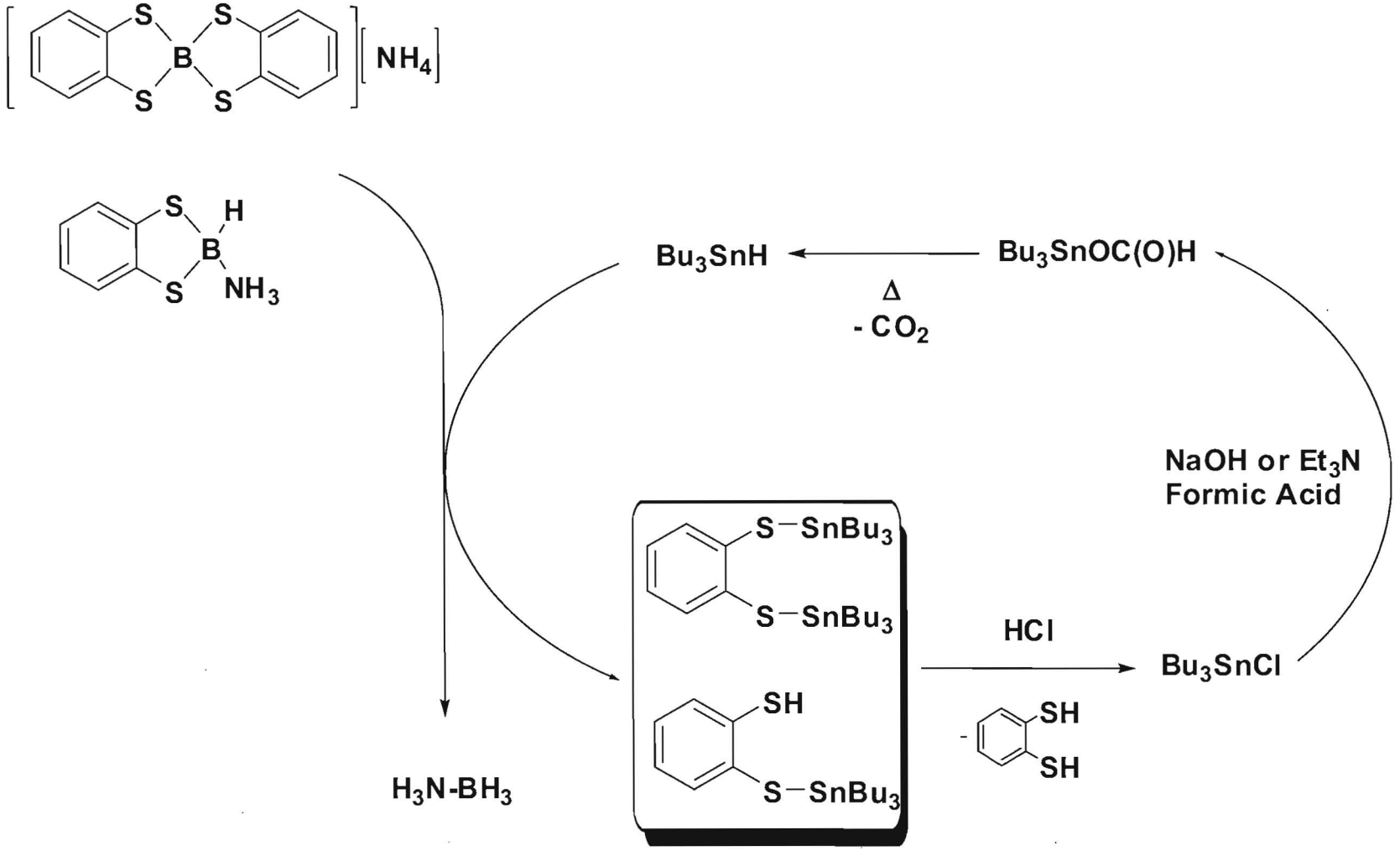
Sn-H Recycle from Sn-S is Also Required



Sutton, Davis, Bhattacharyya, Ellis, Power, Gordon, *Chem. Commun.*, **2010**, *46*, 148.

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To This Point....

Regeneration of AB using benzenedithiol demonstrated

Regeneration of tin reductants demonstrated

However, cost of regeneration processes largely impacted by mass of tin and its effect on plant scale manipulations of such a heavy reagent.

Economic analysis showed that if the mass of reductant can be minimized, overall cost of regeneration can be reduced.

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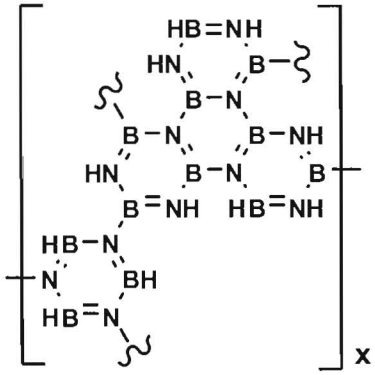
Can We Get Away Completely From Tin Use?

Direct Hydrazine Reduction of PB!

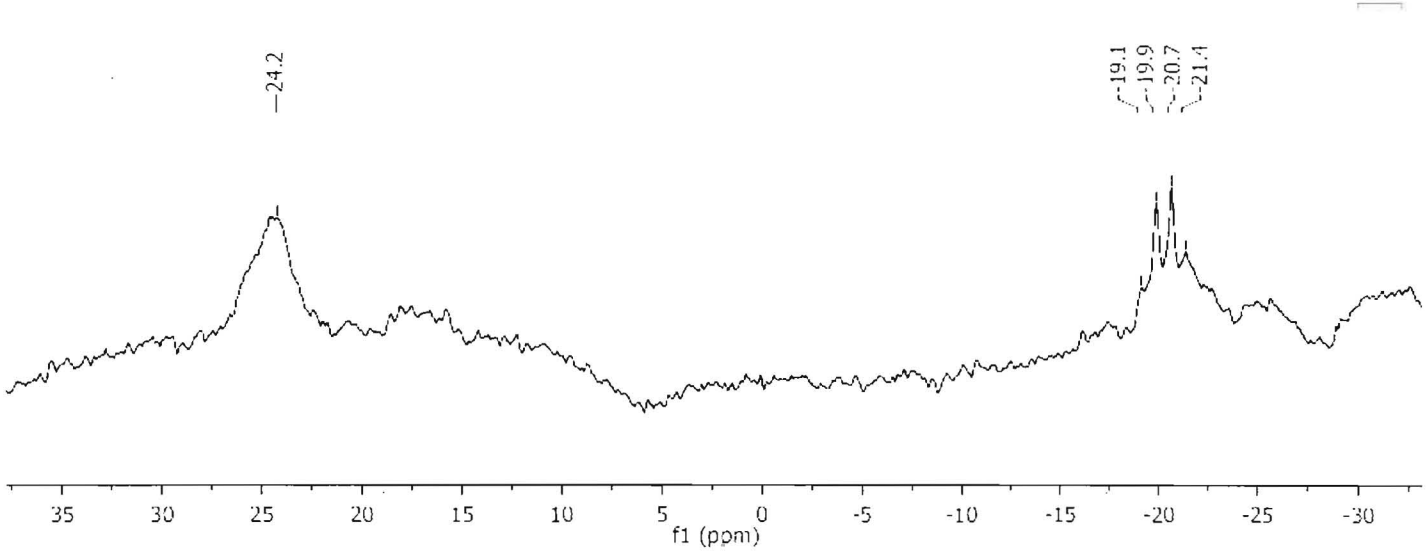


N_2H_4

Heat

$H_3N\text{-}BH_3$ + $(H_4N_2)\text{-}BH_3$ + "$B(N_2H_3)_3$"

Major Product



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How to Displace Hydrazine and Replace with Ammonia?

Hydrazine-BH_3 + R → R-BH_3 + Hydrazine Calculations

Reactant	B3LYP ΔΔH(rel BDE)		G3MP2 ΔΔH(Rel BDE		B3LYP BDE absolute rel to CCSD(T) NH2NH2		G3MP2 BDE absolute rel to CCSD(T) NH2NH2	
	0K	298K	0K	298K	0K	298K	0K	298K
Ph-NH_2	8.0	8.2	7.0	7.3	39.0	40.4	38.0	39.5
$(C_8H_{18})_3N$	3.0	2.9			34.0	35.1		
Et_3N	3.3	3.0	-1.9	-2.0	34.3	35.2	29.1	30.2
Et_2NH	0.8	0.9	-1.5	-1.5	31.8	33.1	29.5	30.7
EtMeNH	-0.7	-0.6	-2.6	-2.5	30.4	31.6	28.4	29.7
Me_3N	-0.9	-0.8	-4.4	-4.4	30.1	31.4	26.6	27.8
Me_2NH	-1.6	-1.5	-3.3	-3.3	29.5	30.7	27.7	28.9
NH_3	4.7	4.4	6.2	5.9	35.7	36.6	37.2	38.1
Me_2S	9.4	9.8	7.8	8.3	40.4	42.0	38.8	40.5
Et_2S	8.8	9.2	6.9	7.4	39.8	41.4	37.9	39.6
Ph_2S	14.4	14.8	12.1	12.7	45.7	47.0	43.1	44.9
Me_2O	14.5	14.7	13.4	13.8	45.5	46.9	44.4	46.0

Dave Dixon, Monica Vasiliu, University of Alabama.

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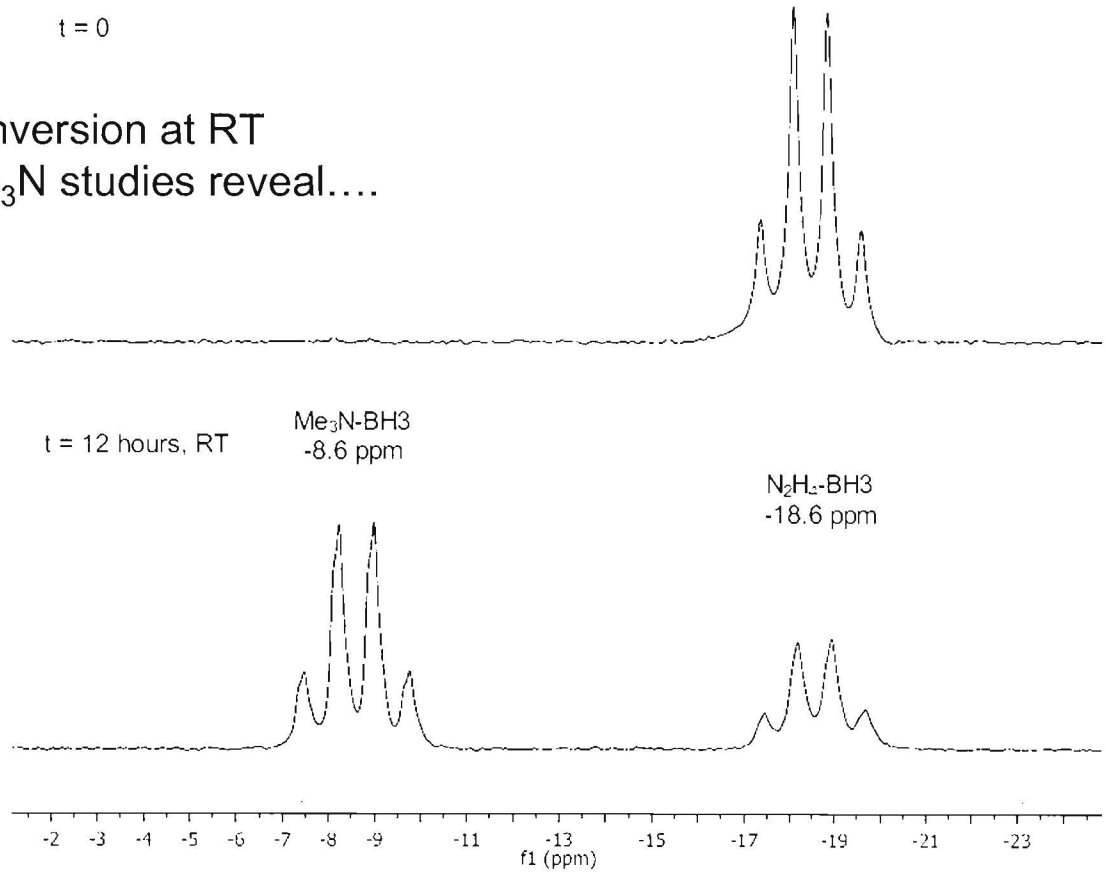
Hydrazine-BH_3 + NMe_3

$$(H_4N_2)\text{-}BH_3 + Me_3N \xrightarrow{THF,\ RT} Me_3N\text{–}BH_3 + N_2H_4$$

Proceeds to ~ 60 % conversion at RT
Heating and excess Me_3N studies reveal….



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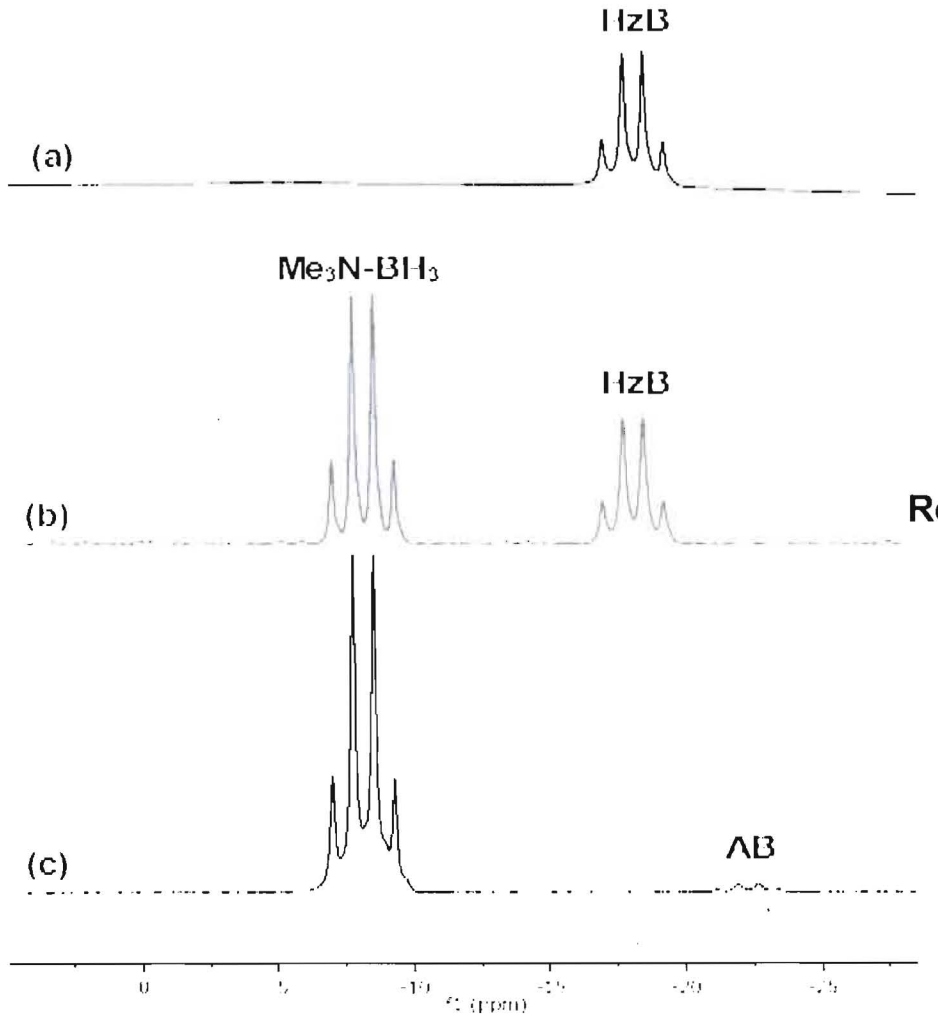
Hydrazine-BH_3 + NMe_3



Pure HzB

Reaction of HzB and Me_3N in THF overnight:
~ 60% conversion to Me_3NBH_3

Independently synthesized Me_3NBH_3 with excess NH_3 in THF heated at 50°C for 5 days: < 5 % conversion to AB

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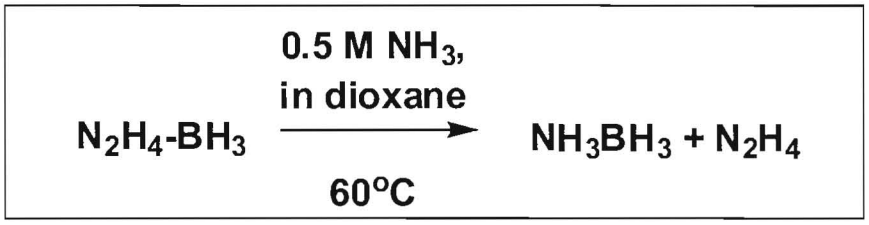
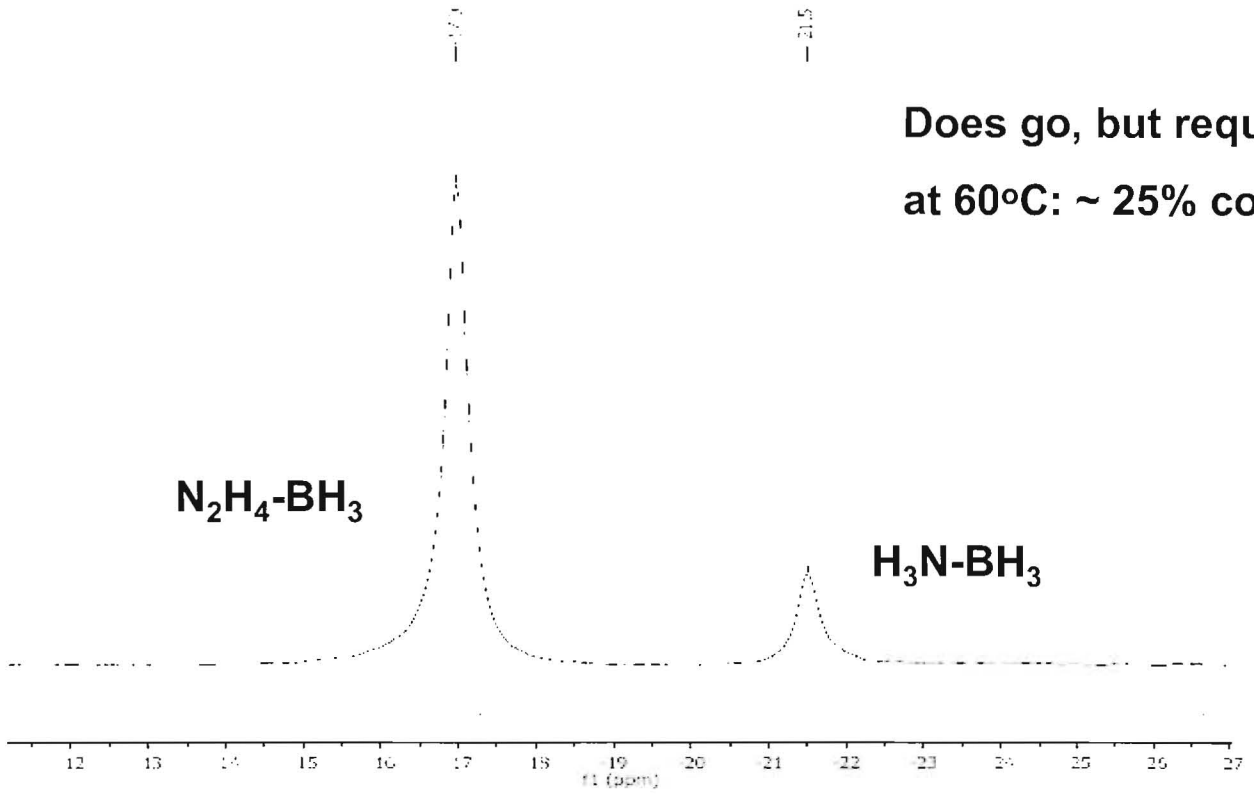
What About N_2H_4-BH_3 + NH_3 Directly?





Does go, but requires heat:

at 60°C: ~ 25% conversion....

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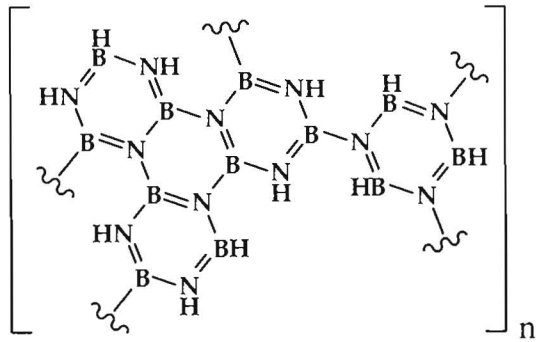
What About Spent Fuel + Liq. NH_3 in Sealed (One –Pot) System to Drive Reaction?

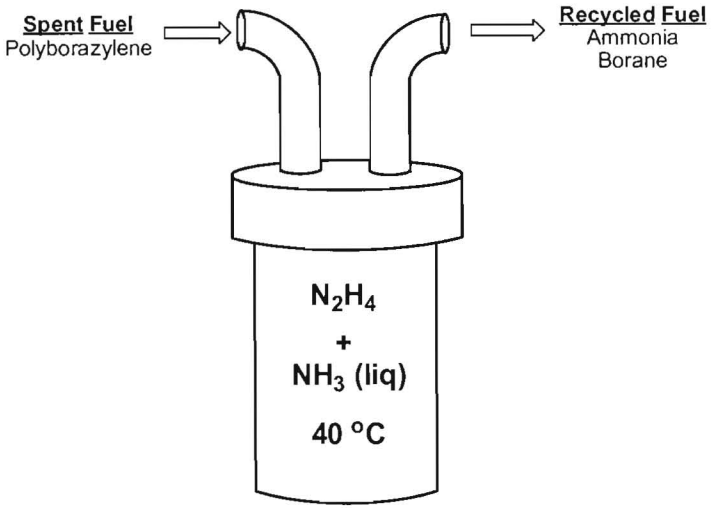


N_2H_4

liq. NH_3, 40°C, 24hr

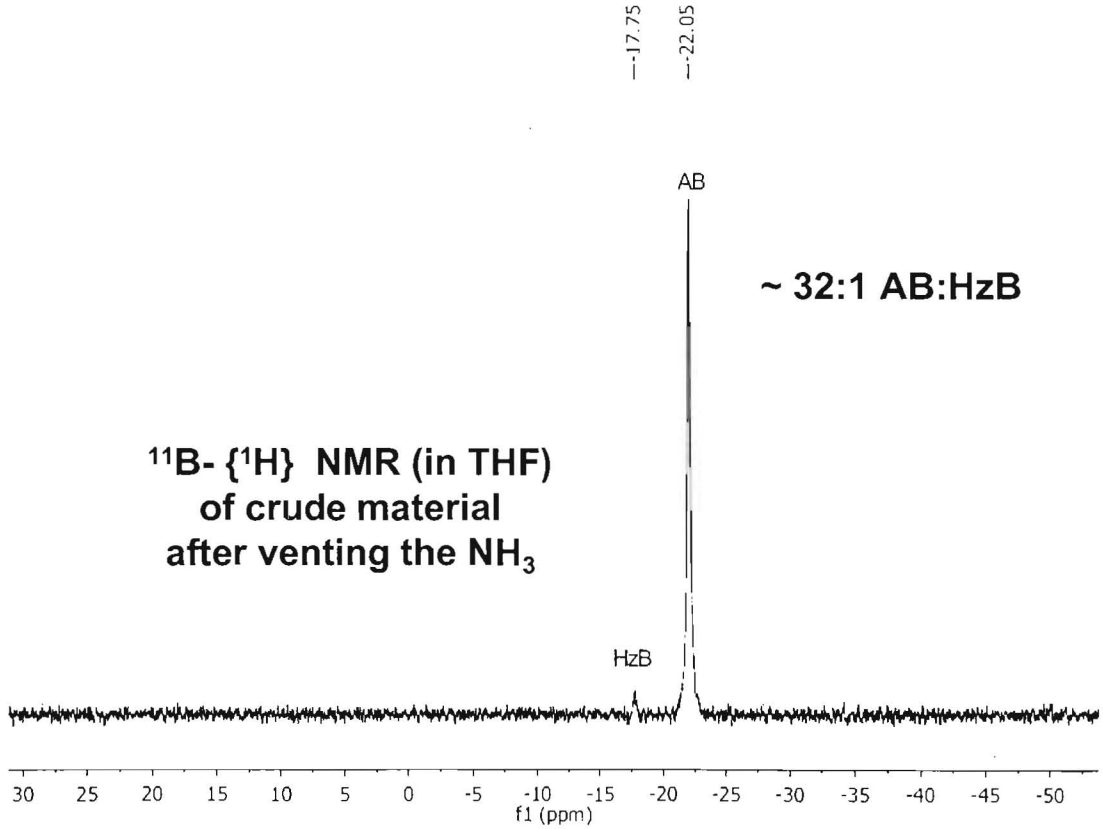
????

Can isolate pure samples of AB in > 90% yield using "one–pot" approach.....



i.e. pressure + moderate heat drives the desired rxn

^{11}B- {^1H} NMR (in THF) of crude material after venting the NH_3



~ 32:1 AB:HzB

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Sutton, Burrell

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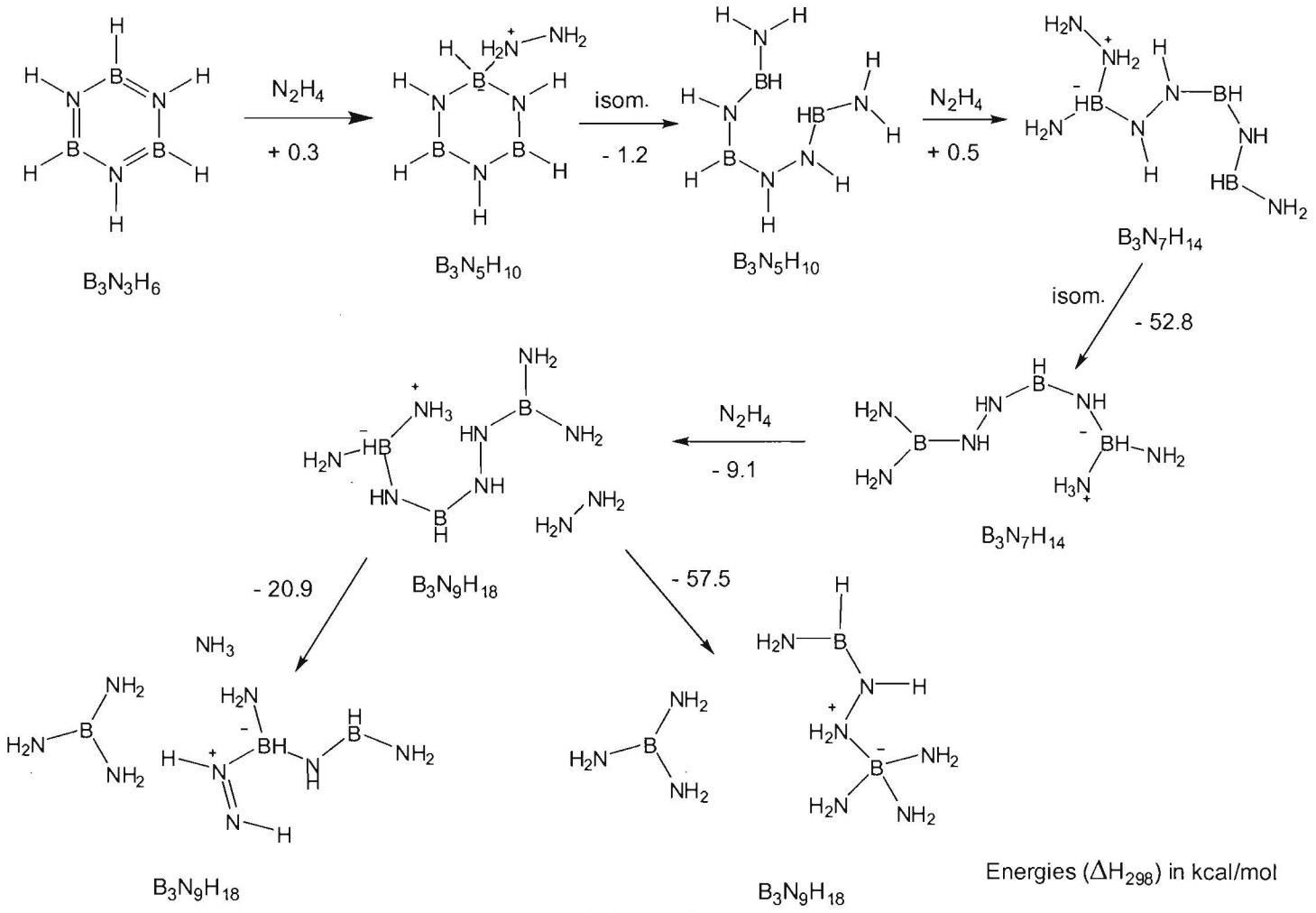
How Does This Work? Some Insight From Theory..

***cyclo*-$B_3N_3H_6$ (i.e."BNH_2") used as a model fragment i.e. loss of 2 eq. H_2 from AB**
***Complicated* - many intermediates (only some shown..) on addition(s) of N_2H_4**



Energies (ΔH_{298}) in kcal/mol

DFT/G3MP2B3

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Some General Observations From Calculations

These computational results indicate that the initial reactions are near thermoneutral - subsequent reactions are exothermic.

Of even greater importance, is that the addition of N_2H_4 can lead to cleavage of the B-N bonds within "BNH_2"units in the first step.

In addition, later steps lead to the generation of $BH(NH_2)$ fragments as a potential intermediate provides a possible pathway for hydrogen transfer to reform BH_3 units?

Conclusions and Some Thoughts

At the inception of CHS CoE (~5 yrs ago), many "naysayers" thought that regeneration of AB spent fuel was impossible….

Clearly this is not the case…..

Remarkable discoveries have been enabled through Center model of collaboration and sharing of information among interdisciplinary experts

Extra Slides

Chemical Hydrides Versus Other Materials

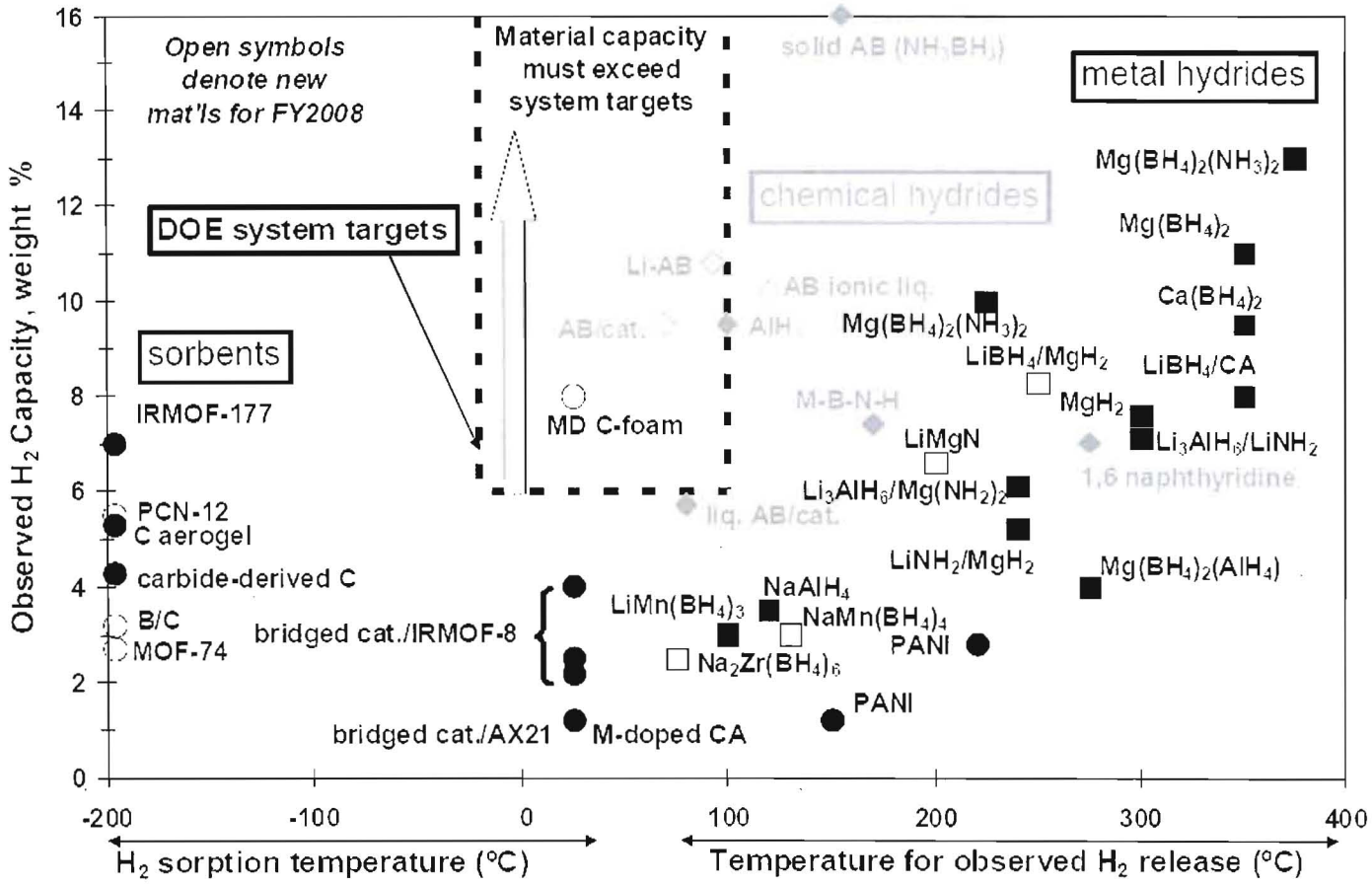
Original DOE Total System Targets for Hydrogen Storage Systems (> 300 miles)

Gravimetric Density (wt%)

4.5 ***(2007)***, 6.0 ***(2010)***, 9.0 ***(2015)***

Volumetric Density (Kg-H_2/L)

0.036 ***(2007)***, 0.045 ***(2010)***, 0.081 ***(2015)***



DOE: G. Thomas (2007), G. Sandrock (2008)

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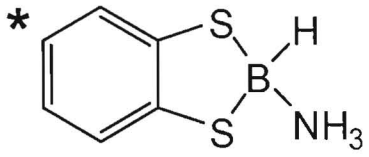
Incorporate Lighter Reductant – What About Hydrazine?



N_2H_4 →

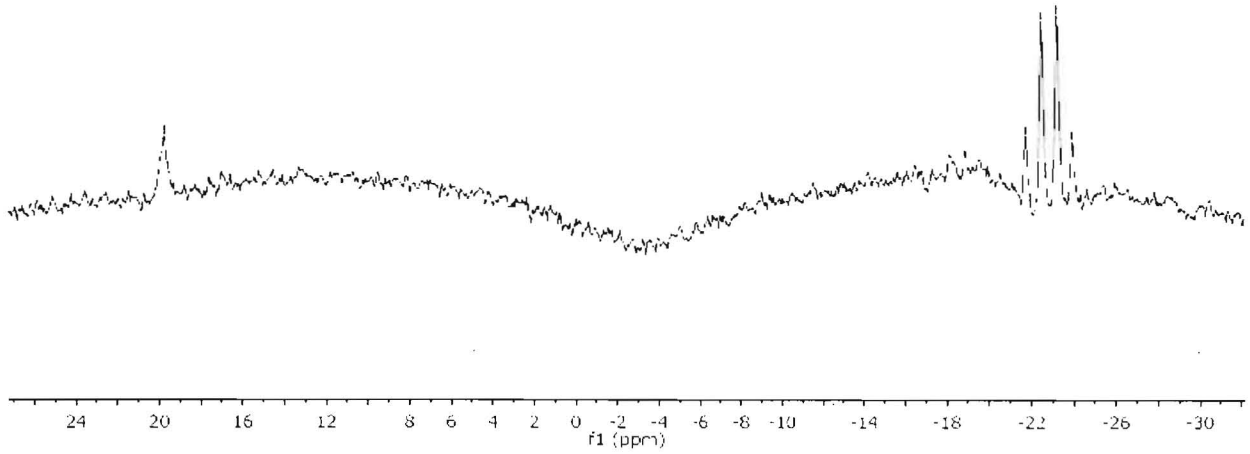
$H_3N\text{-}BH_3$ + $(H_4N_2)\text{-}BH_3$ + "$B(N_2H_3)_3$"

upto ~ 80 %

* **Still requires use of tin reductant in dithiol approach…**

Can be isolated in good yield by running digestion step "lean" in dithiol….

^{11}B NMR of $(C_6H_5S_2)BH.NH_3$ + N_2H_4 in thf.
Room temperature, 5 hours.



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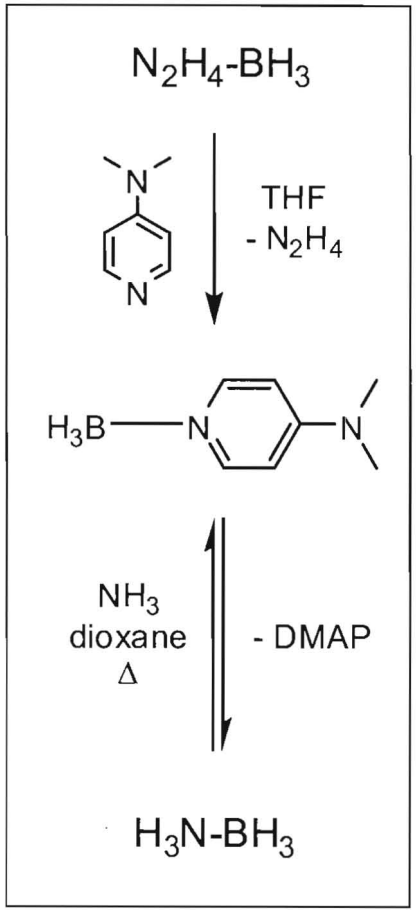
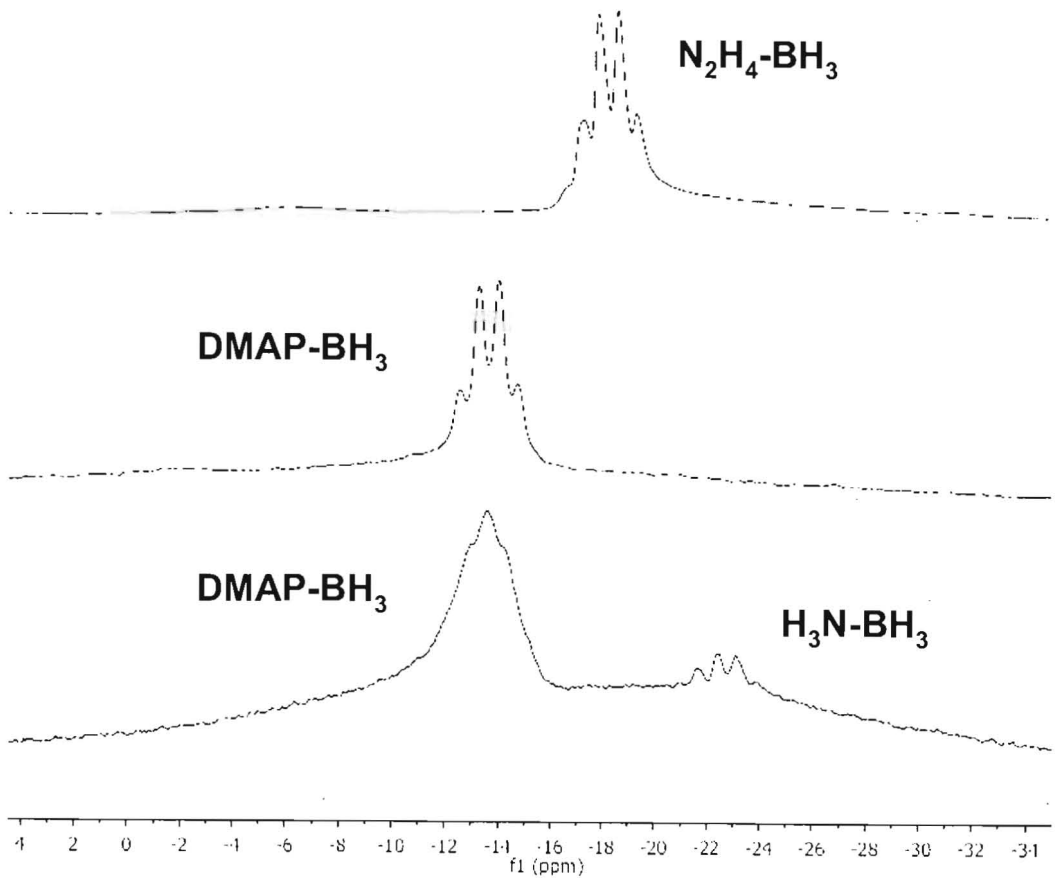
AB accessible via $DMAP\text{-}BH_3$





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$B(NH_2)_3$ to $BH_3NH_3 + N_2$ will likley not go based on thermo.
Quite endothermic (~60 kcal/mol) as the gas.

$B(NH_2)_3$ as a gas and BH_3NH_3 it is less endothermic but still not favorable

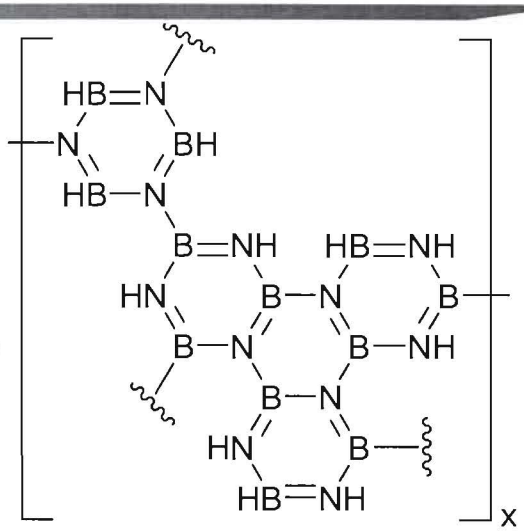
$$B_3N_3H_6(g) + 3N_2H_4(g) \rightarrow 3BH_3NH_3(g) + 3N_2(g) \quad \Delta H(298K) = 5.9 \text{ kcal/mol}$$

$$B_3N_3H_6(s) + 3N_2H_4(g) \rightarrow 3BH_3NH_3(s) + 3N_2(g) \quad \Delta H(298K) = -52.5 \text{ kcal/mol}$$

Metal Catalyzed Dehydrogenation – Rate/Extent/Selectivity

Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I.
JACS **2003**, *125*, 9424.

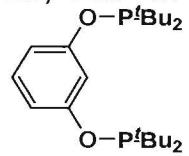
RH_2NBH_3 —[Rh(cod)Cl]$_2$, - > 2 H_2→ borazine + P.B. = polyborazylene =



R = Ph, Me, H

Denney, M. C.; Pons, V.; Hebden, T. J.; Heinekey, D. M.; Goldberg, K. I. *JACS* **2006**, *128*, 12048.

H_3NBH_3 —[(POCOP)IrH_2], - 1 equiv. H_2→ $(NH_2\text{-}BH_2)_5$ cyclic pentamer (insoluble)

POCOP = 

Keaton, R. J.; Blacquiere, J. M.; Baker, R. T. *JACS* **2007**, *129*, 1844.

H_3NBH_3 —$Ni(NHC)_2$, - >2 H_2→ P.B.

How to improve catalyst performance?
(both rate and extent of dehydrogenation)

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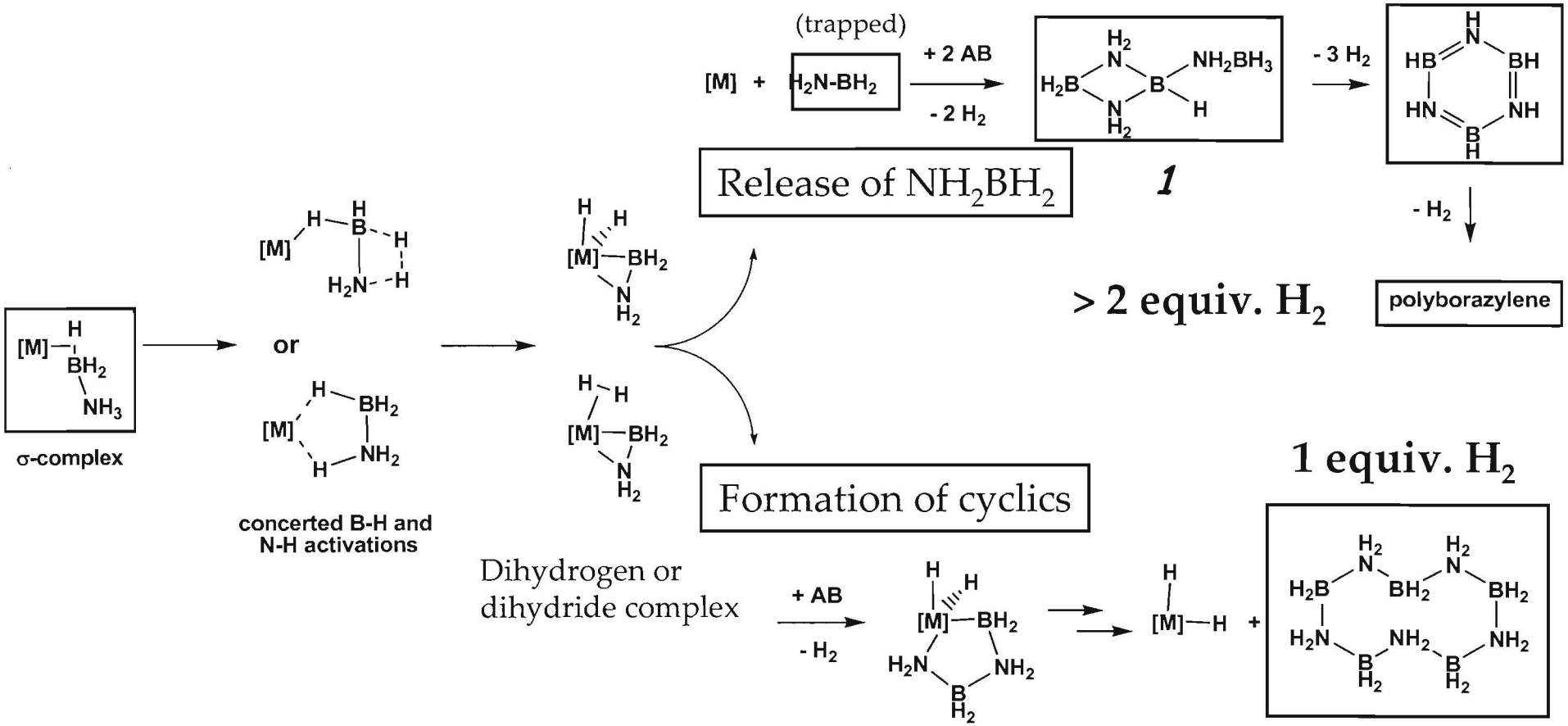
Proposed Metal Catalyzed AB Dehydrogenation Mechanisms



*Release of NH_2BH_2 and formation of BN-Ethylcyclobutane (**1**) are key to greater hydrogen release.....*
Heating liberates NH_2BH_2 from metal coordination sphere.
Formation of borazine and cyclics not yet fully understood.....

Evidence for the Formation and Release of NH_2BH_2 From Metal Center?

- Alkylaminoboranes RNH-BH_2 or R_2N-BH_2 observed by ^{11}B NMR (signal at 35-45 ppm) during the metal catalyzed dehydrogenation of alkylamine borane adducts

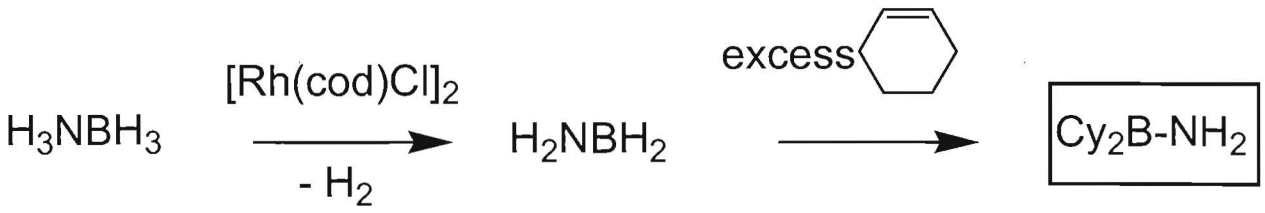
Linehan/Manners/Baker

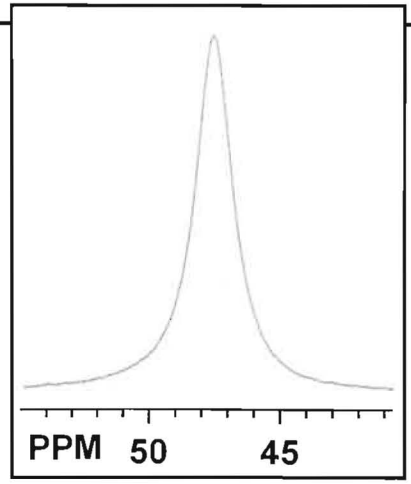
- NH_2BH_2 prepared at low temperature (-120 °C), rapidly oligomerizes upon warming

McGee/Shore

- No direct evidence for its generation in the presence of a transition metal catalyst

Trapping of NH_2BH_2: hydroboration of cyclohexene

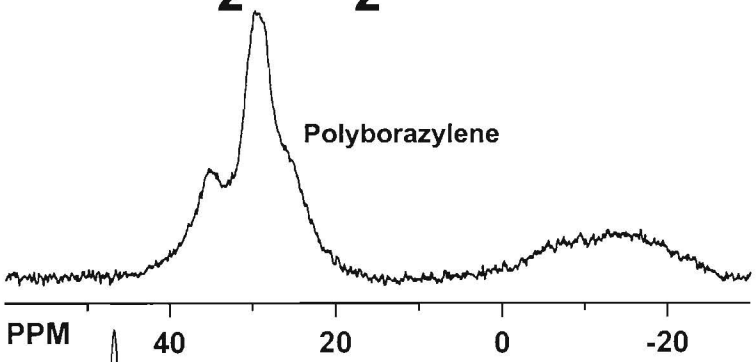




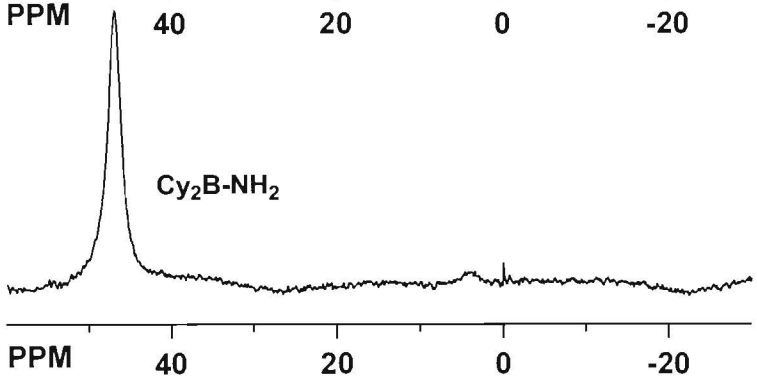
^{11}B NMR (128 MHz, C_6D_6, 298K)

NH_2BH_2 Release-Temperature Dependence

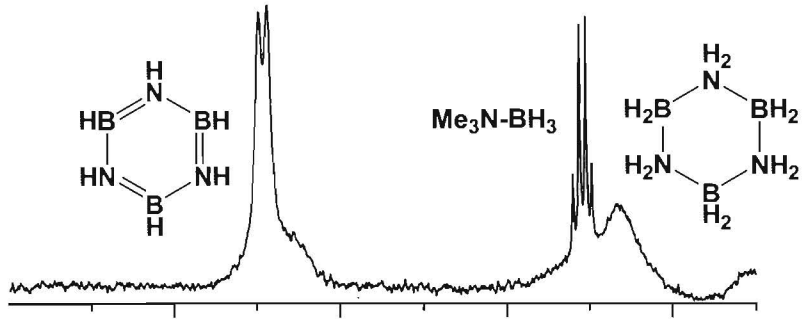
^{11}B NMR, 160 MHz, 25 °C
10 mol % [cat] / AB



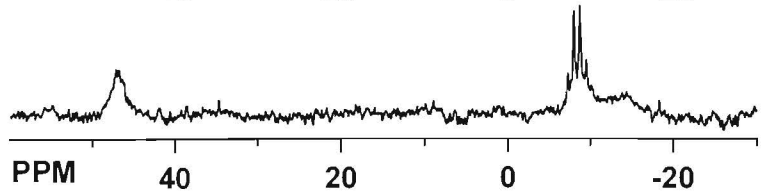
$[Rh(cod)Cl]_2$ diglyme, 60 °C



$[Rh(cod)Cl]_2$ diglyme/cyclohexene, 60 °C



$[Cr(CO)_5NMe_3]$ Diglyme, 60 °C

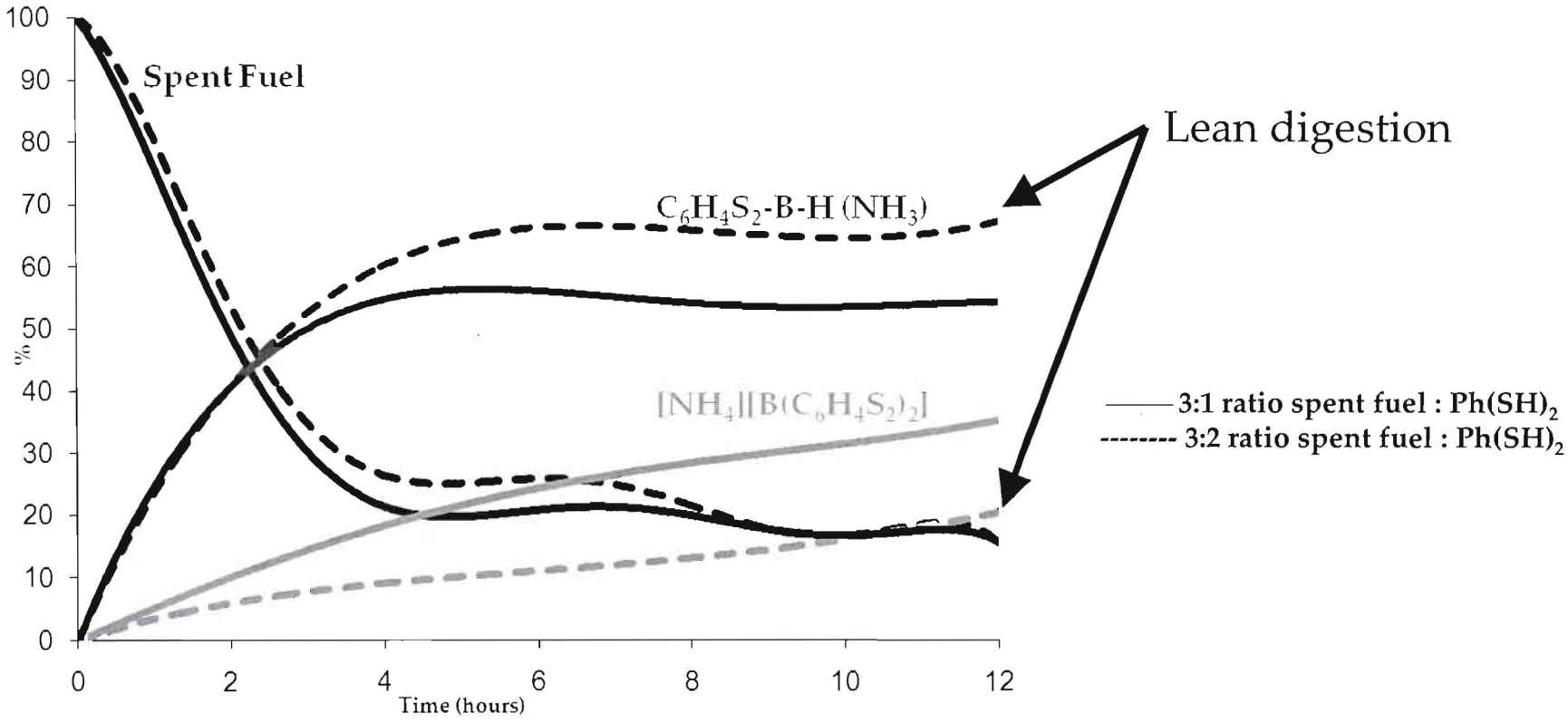


$[Cr(CO)_5NMe_3]$ Diglyme/cyclohexene, 60 °C

$(NH_2BH_2)_n$ Cyclics vs. Polyborazylene

Catalyst (10 mol%)		Diglyme	Diglyme/ cyclohexene
[Ni] $Ni(NHC)_2$	25 °C	Borazine/PB/intermediate	PB/intermediate
	60 °C	PB	PB/Cy_2BNH_2
[Rh] $[Rh(cod)Cl]_2$	25 °C	Borazine/PB/BN cleavage	Cy_2BNH_2
	60 °C	PB	Cy_2BNH_2
[Ir] $Ir(POCOP)H_2$	25 °C	$(BH_2NH_2)_5$	$(BH_2NH_2)_5$
	60 °C	Borazine/PB/intermediate $(BH_2NH_2)_5$	Cy_2BNH_2
[Ru] $(PMe_3)_4RuCl_2$	25 °C	Borazine/PB/$(BH_2NH_2)_5$	Cy_2BNH_2
	60 °C	Borazine/PB/$(BH_2NH_2)_5$	Cy_2BNH_2
[Cr] $(CO)_5Cr(NMe_3)$	25 °C	CTB/Borazine/PB	CTB/Borazine/PB
	60 °C	CTB/Borazine/PB	Cy_2BNH_2

Maximization of (BDT)BH.NH_3 yield



Less $C_6H_4(SH)_2$ in digestion = less Sn-H required = <u>minimize recycle!</u>

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Drive to Reduce Mass

Rohm & Haas Report Detail

	Digestion	Metal Reduction / Amine Exchange	Ammoniation	Metal Recovery
H_2		431		1,145
NH_3		15,645	3,303	
$(Et)_2NH$		14,930	67,187	
THF	86,989	86,989		
Toluene			88,773	
BNH	5,272			
$C_6H_4(SH)_2$	22,505	2,250		222,795
Bu_3SnH		162,797		908,777
$(Et)_2NHBH_3$		79,896	8,877	
$HB(C_6H_4S_2)NH_3$	69,895	17,258		17,258
$(NH_4)B(C_6H_4S_2)_2$	156,278	17,364		17,364
$HB(C_6H_4S_2)NH(Et)_2$		22,985		22,985
$(C_6H_4)(SH)(SSnBu_3)$		276,252		27,625
$C_6H_4(SSnBu_3)_2$		792,217		79,222
NH_3BH_3			28,354	
Total, kg/hr	340,938	1,489,015	196,494	1,295,171

Reduce mass of reducing agent – reduce cost of recycle

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