LA-UR- 09-01769

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Title: CHEMICAL HYDROGEN STORAGE AT LOS ALAMOS

Author(s): JOHN C. GORDON, BENJAMIN L. DAVIS, DAVID A. DIXON, MYRNA H. MATUS, FRANCES H. STEPHENS

Intended for: ACS TALK - AWARD SYMPOSIUM

Los Alamos
NATIONAL LABORATORY
EST. 1943

Chemical Hydrogen Storage at Los Alamos

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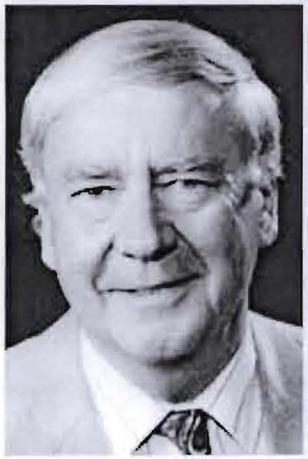
ABSTRACT

Los Alamos National Laboratory (LANL) researchers along with Pacific Northwest National Laboratory (PNNL) led the creation of a national center for researching chemical pathways to hydrogen storage. Working with industry, academia, and other government agencies, the Hydrogen Storage Center is the nation's leading facility for solving problems surrounding the transition to a hydrogen-fueled economy. The Center is one of three U.S. Department of Energy alternative energy storage research facilities. Along with the Carbon Storage Center at the National Renewable Energy Laboratory in Golden, Colorado, and the Metal Hydride Storage Center at Sandia National Laboratories in Livermore, California, these represent one of the nation's current best hopes for ending the reliance on foreign and unstable sources of energy. We will present some recent technical results from LANL in support of the development of a hydrogen based economy.

ACS Award Symposium in Honor of Professor Alan H. Cowley
Salt Lake City, UT March 24th 2009



Born; Manchester, England

Education - University of Manchester

B.Sc. – 1955…….
(March 5th, 1955 – Elvis Presley appears on TV for the first time)

M.Sc.; 1956…..
(March 12th - Dow Jones closes above 500 for first time (500.24))

Ph.D., 1958……
(March 27th, 1958 - Nikita Khrushchev becomes Soviet premier)

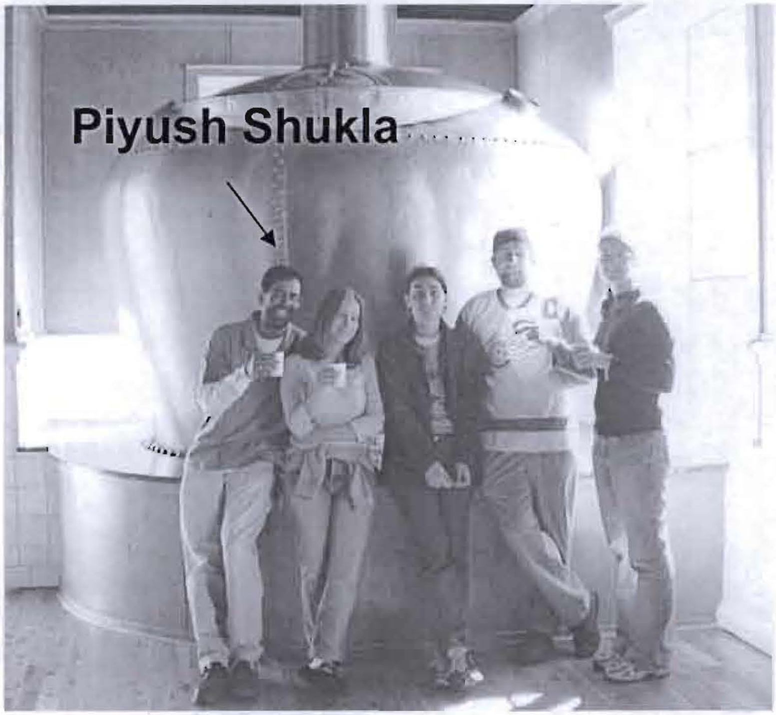
(*cf.* November 30th, 1963 - John Gordon, born in Kilmarnock, Scotland………)

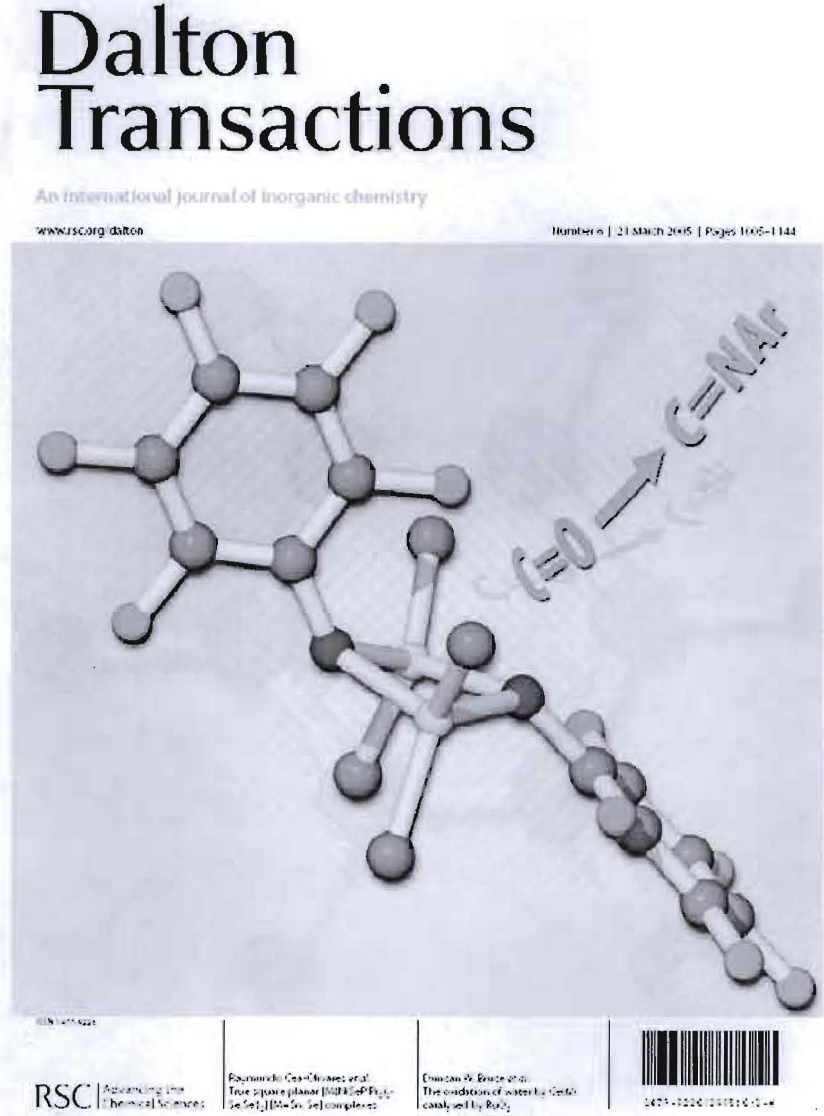
Many Awards; including;

Fellow of the Royal Society, 1999….

(May, Russian president Boris Yeltsin survives impeachment hearings..)

"Laboris Duris, Epulum Duris"





$$\tfrac{1}{n}\,[R_2Al\text{-}\mu\text{-}N(H)Ar]_n \;+\; {>}C{=}O \;\longrightarrow\; [R_2AlOH] \;+\; {>}C{=}NAr$$

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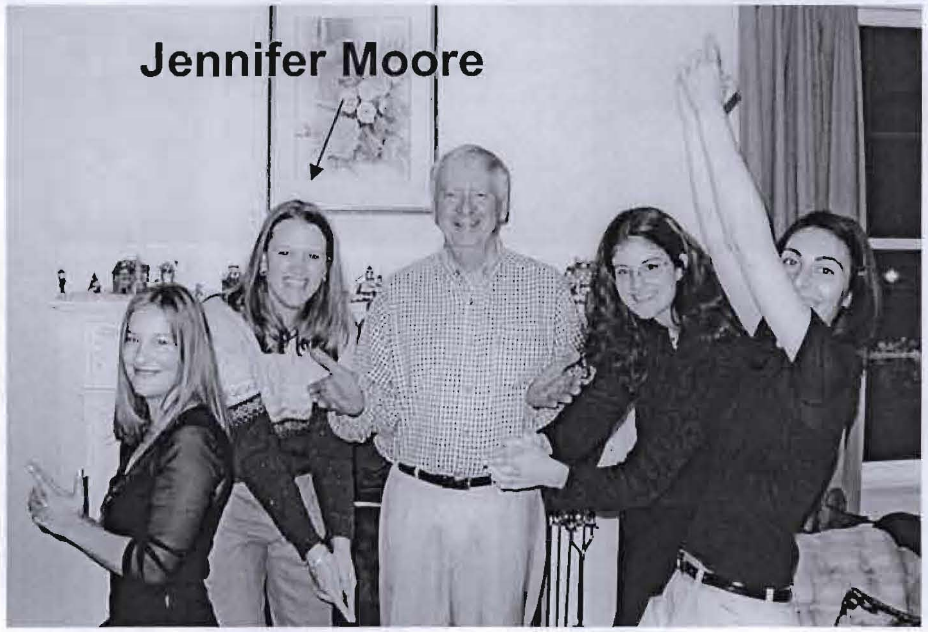
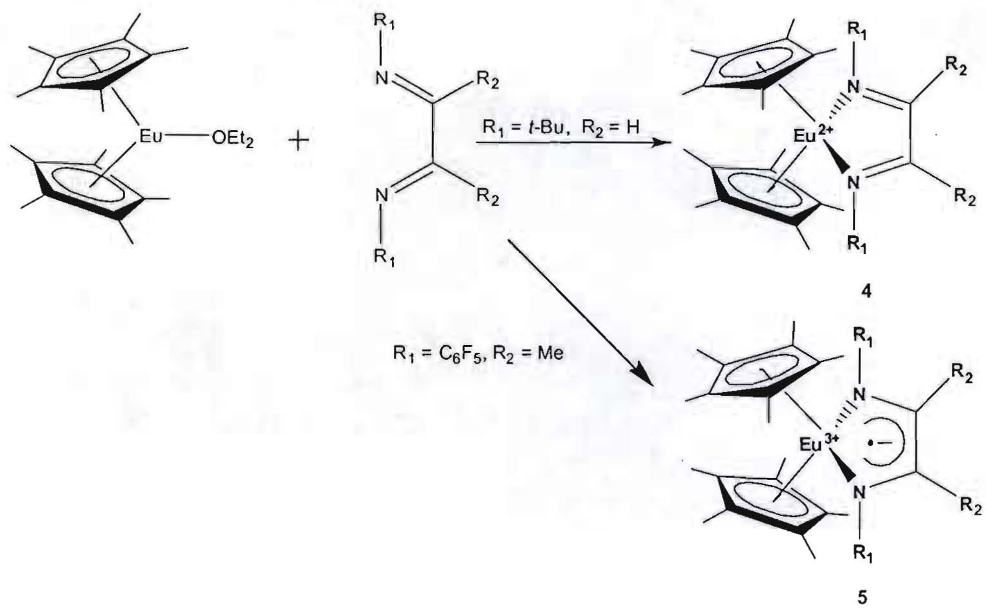
Cowley's Angels





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....

- *Develop materials, catalysts and new concepts to control thermochemistry and reaction pathways*
- *Assess concepts and systems using engineering analysis and studies*
- *Develop life cycle inventory and demonstrate a 1 kg storage system*

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Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy
The University of Alabama
Penn
The University of California Davis
University of Washington
PennState 1855
Rohm and Haas
Mizzou
University of Missouri-Columbia
TIAX
20 Mule Team Borax
Los Alamos National Laboratory

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?

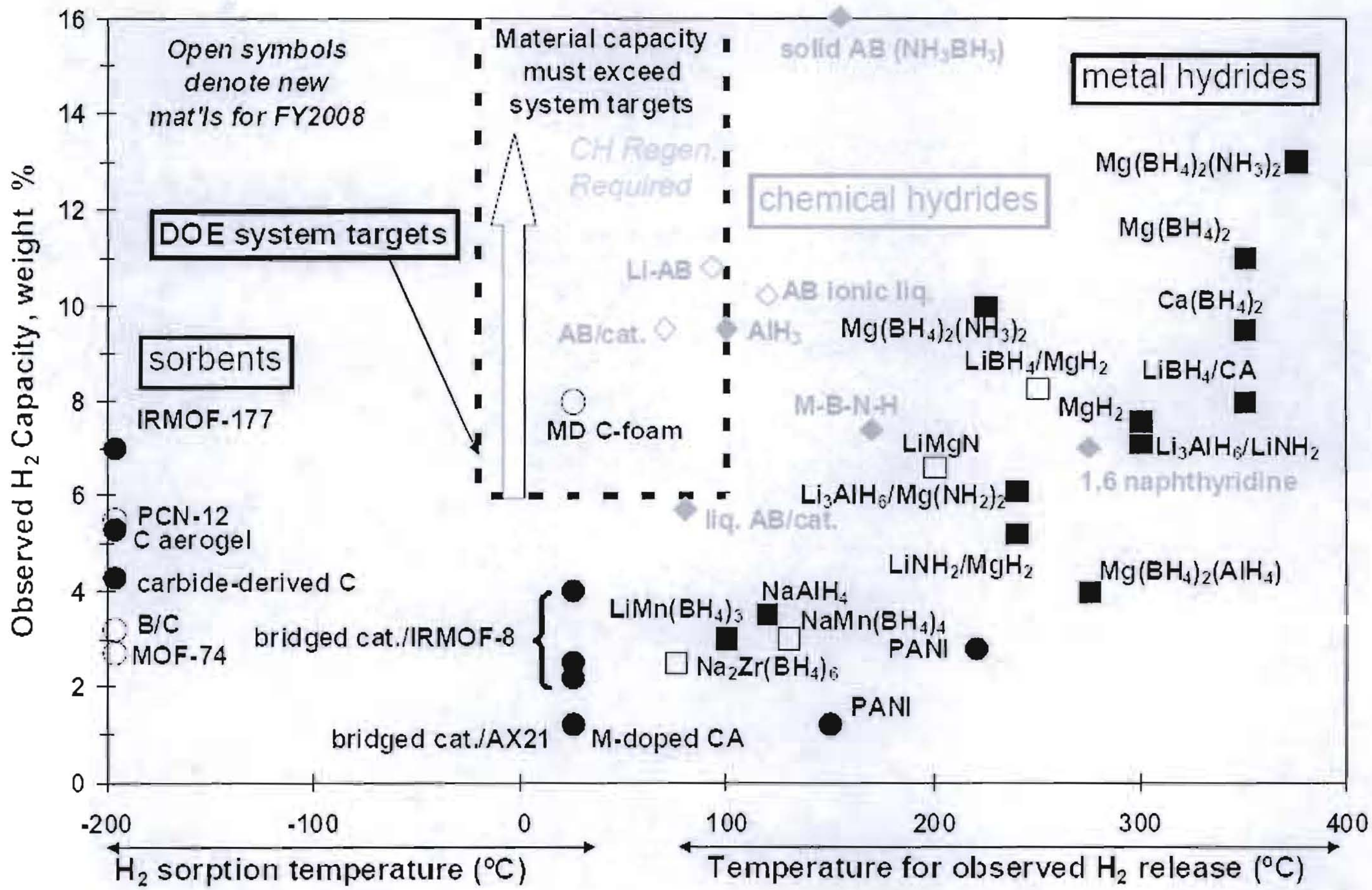
How to store it?

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

Chemical Hydrides versus other Materials

DOE Total System Targets for Hydrogen Storage Systems

Gravimetric Density (wt%)	**Volumetric Density ($Kg\text{-}H_2/L$)**
4.5 ***(2007)***, 6.0 ***(2010)***, 9.0 ***(2015)***	0.036 ***(2007)***, 0.045 ***(2010)***, 0.081 ***(2015)***

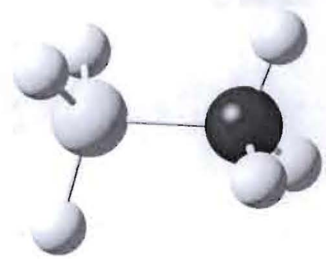


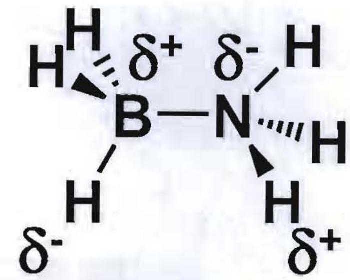
DOE: G. Thomas (2007), G. Sandrock (2008)

Ammonia-Borane (AB) = NH_3BH_3,

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

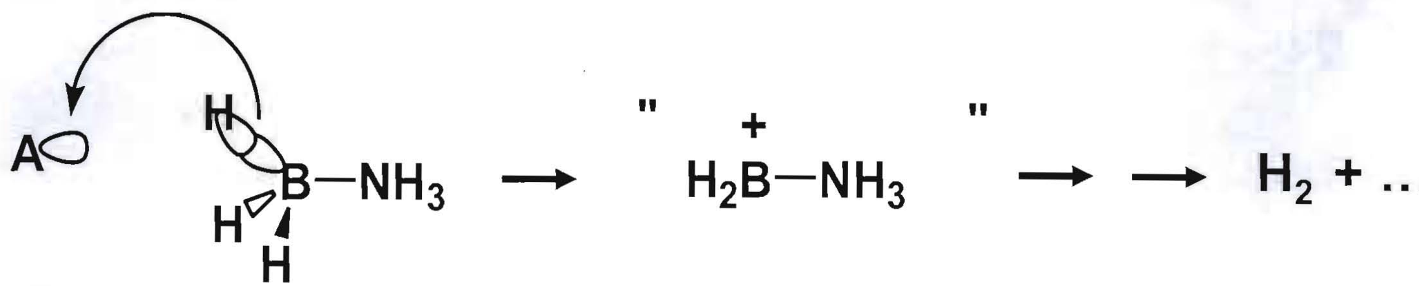
(up to 19.6 wt % H_2, 0.16 kg/L H_2)



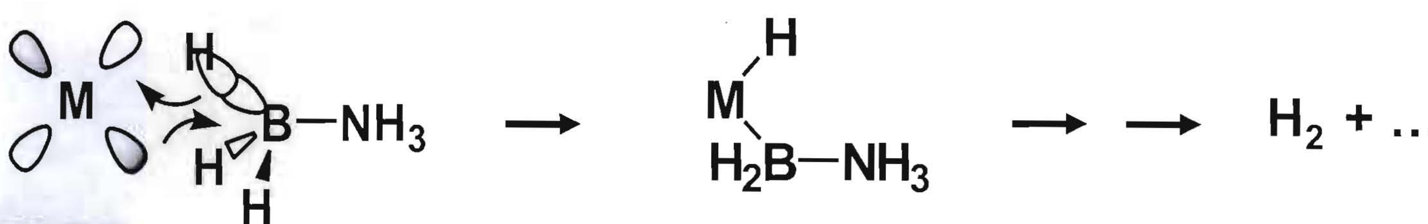


Thermal release of H_2 is too slow at T < 100°C - What catalyzes the process?

- **Acid Catalysis (Lewis Acid or Bronsted Acid)**



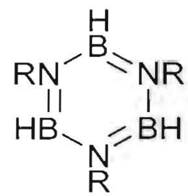
- **Metal Catalysis**



Metal Catalyzed Dehydrogenation – Rate/Extent/Selectivity

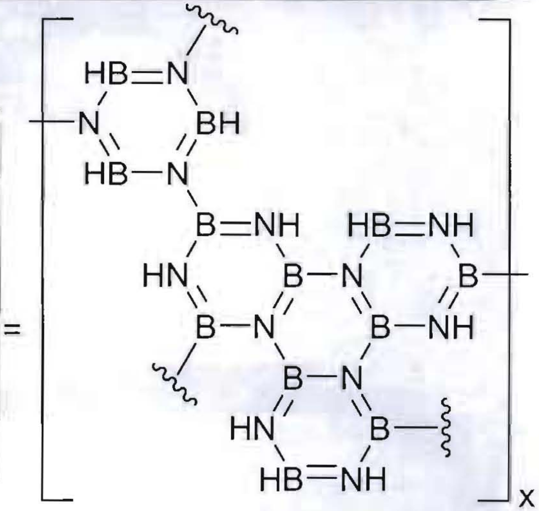
Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I.
JACS **2003**, *125*, 9424.

RH_2NBH_3 —[Rh(cod)Cl]$_2$, - > 2 H_2 →



borazine

+ P.B. = polyborazylene =

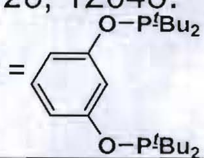


R = Ph, Me, H

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)

What About Regeneration of 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 BNH_x products

Dehydro-oligomerization

AB

Metal Based Catalysis

Thermolysis (solution or solid state)

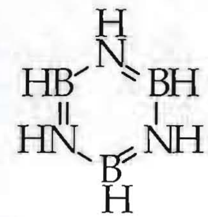
polyaminoboranes (1 eq. H_2 loss)
polyiminoboranes (2 eq. H_2 loss)
borazine (except nanomaterials)

Insoluble cyclic pentamer

$(H_2N-BH_2)_5$

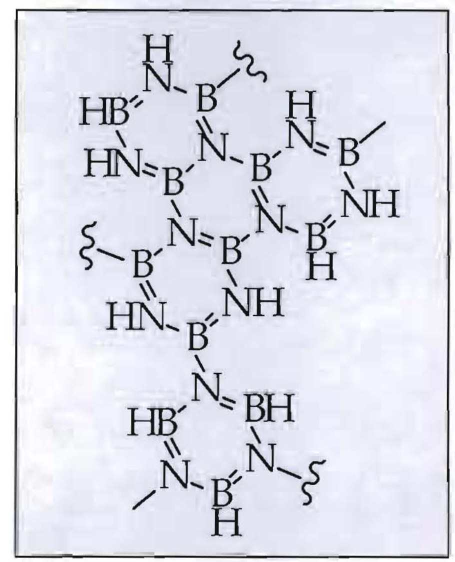
1 equiv. H_2 lost

borazine



2 equiv. H_2 lost

soluble polyborazylene



> 2 equiv H_2 lost

Off-Board Regeneration Required

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

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

(Miranda and Ceder 2007)

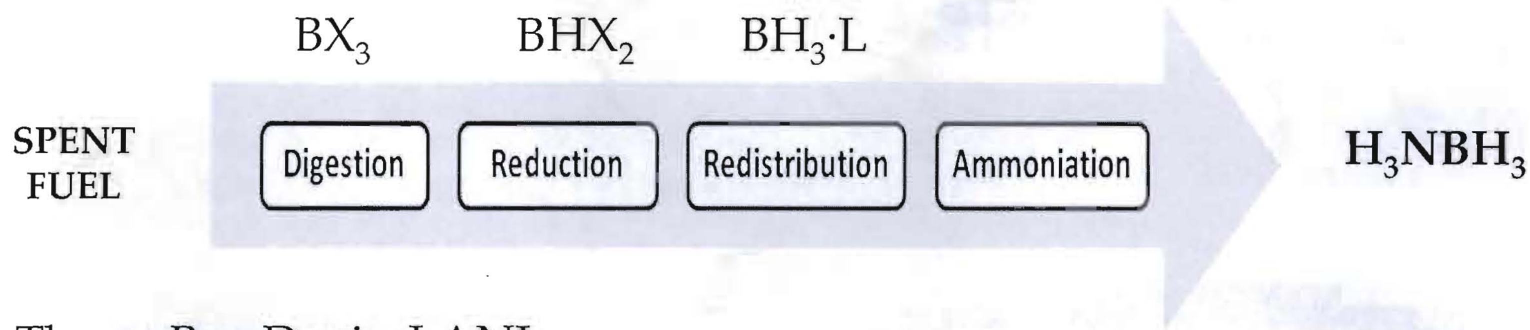
Hydrogen release -> **too exothermic** to merely re-pressurize with H_2

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

Approach



Dave Thorn, Ben Davis, LANL

Features of Chemistry:

Avoid formation of B-O bonds…..

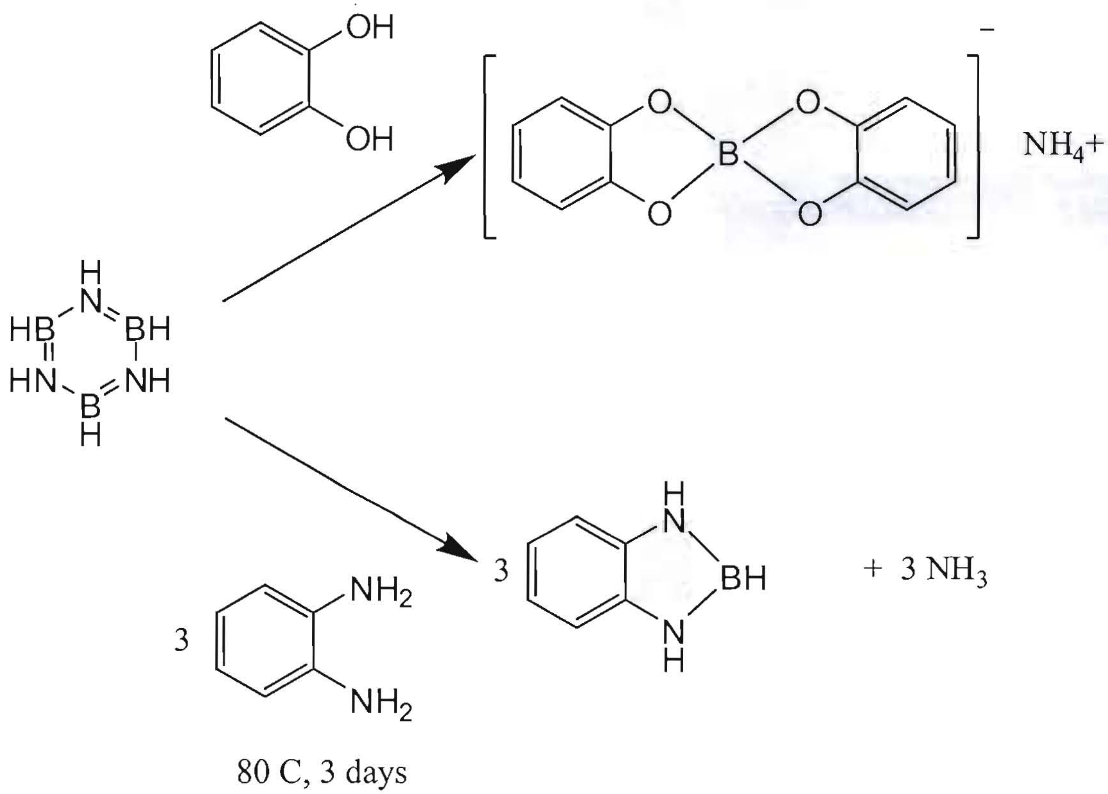
Steps have to be reasonably matched thermodynamically

Steps have to be high yielding

Recycle of reagents - *e.g.* reductant

Digestion of Spent Fuel

Preliminary Results with O- and N-chelates



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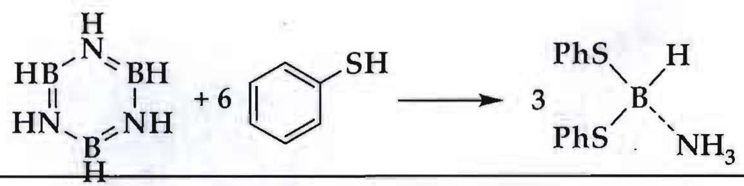
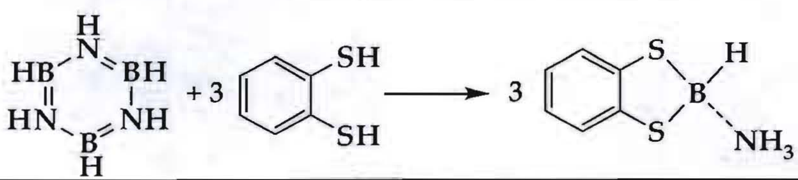
What about B-S bonds?

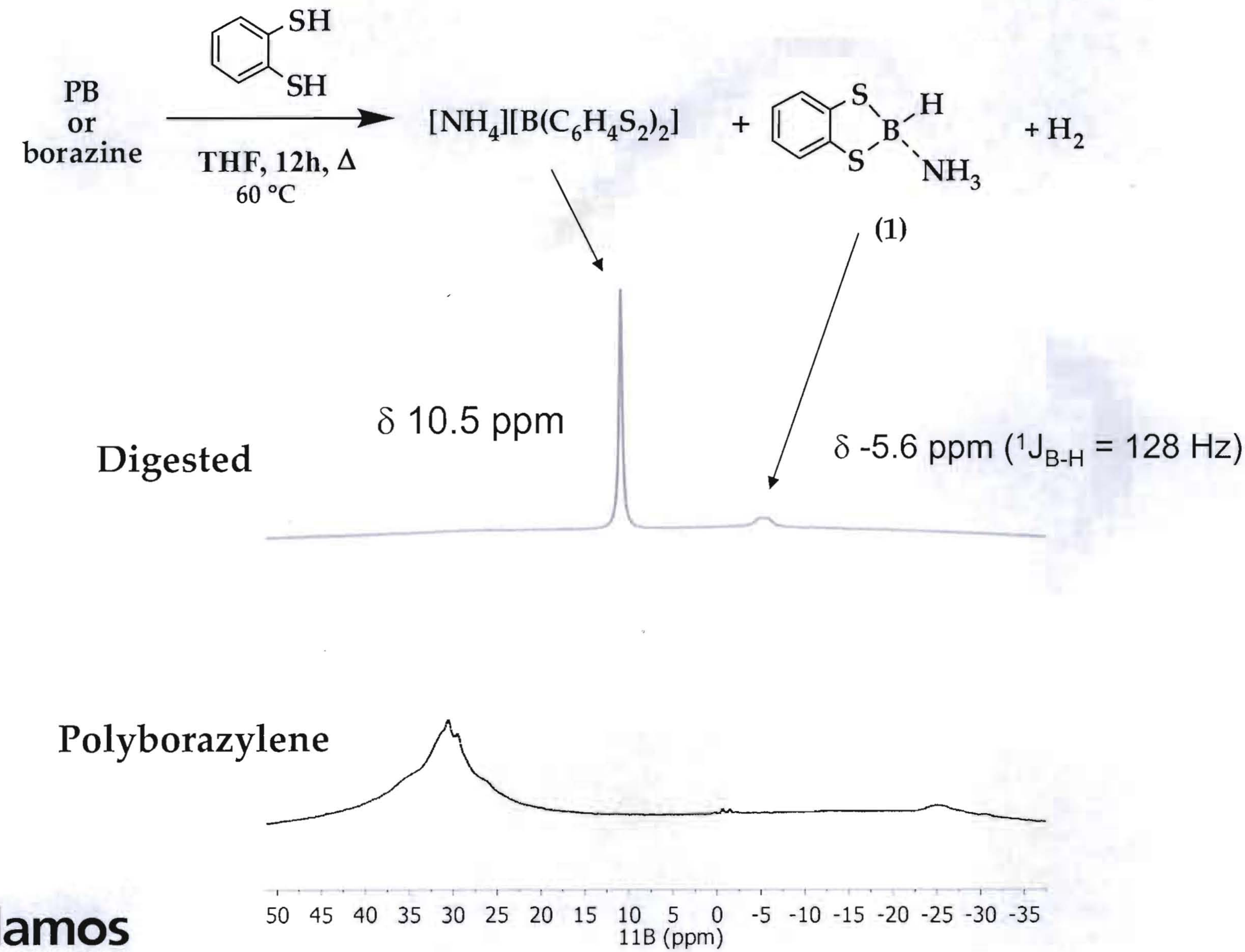
Weaker than B-O bonds (allows for subsequent chemistry)

Acidity of a thiol could still aid reaction…

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

Validation with Benzenedithiol



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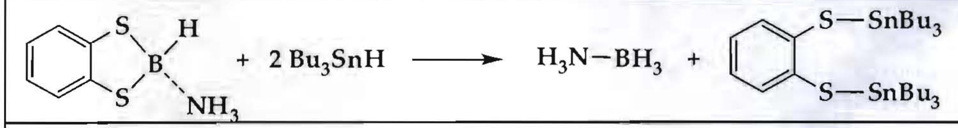
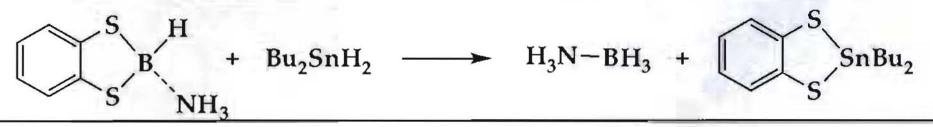
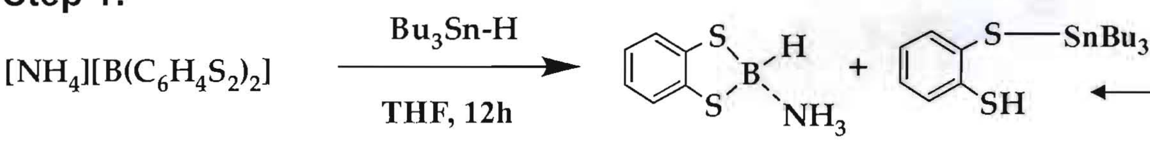
A Reductant is then Required

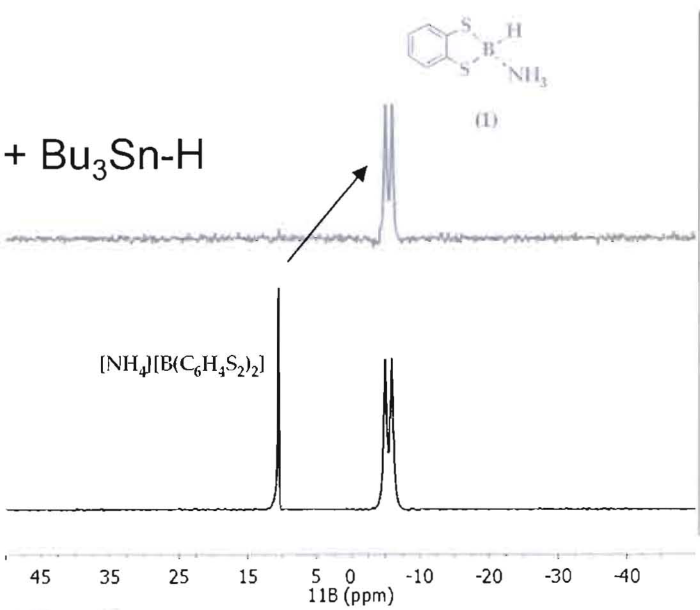
Estimates of Reaction Energies for Reduction	ΔH(298K)[a]
	-3.7/2.8
	-9.7/0.8

Step 1:



(1) (2)

← Verified by ^{119}Sn NMR

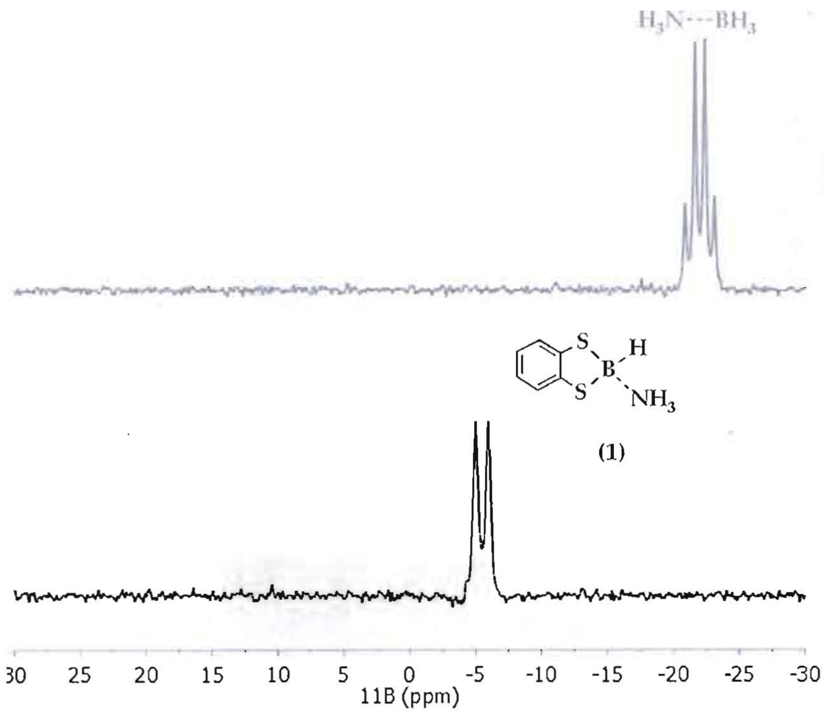


Fortuitously Bu_3Sn-H (commercially available) converts ammonium salt to (**1**)

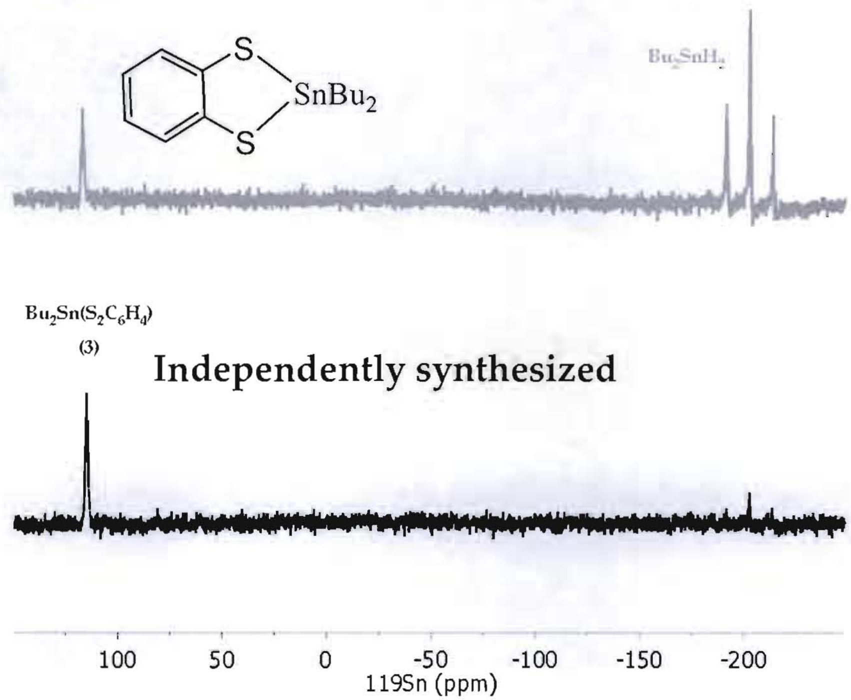
In 2 steps from PB we have a single Boron containing compound.

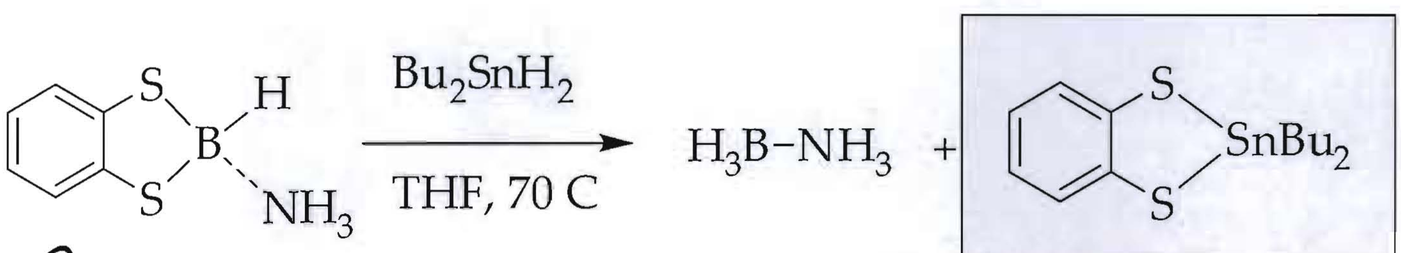
(In This Version) – Another Reduction Step is Required…

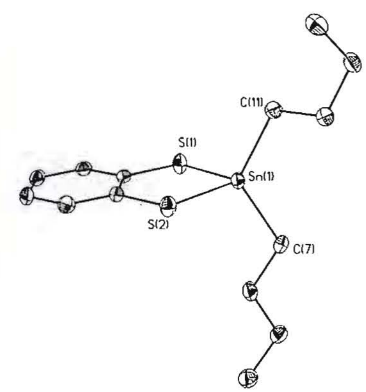
Subsequent Bu_2SnH_2 addition converts (1) to AB…..



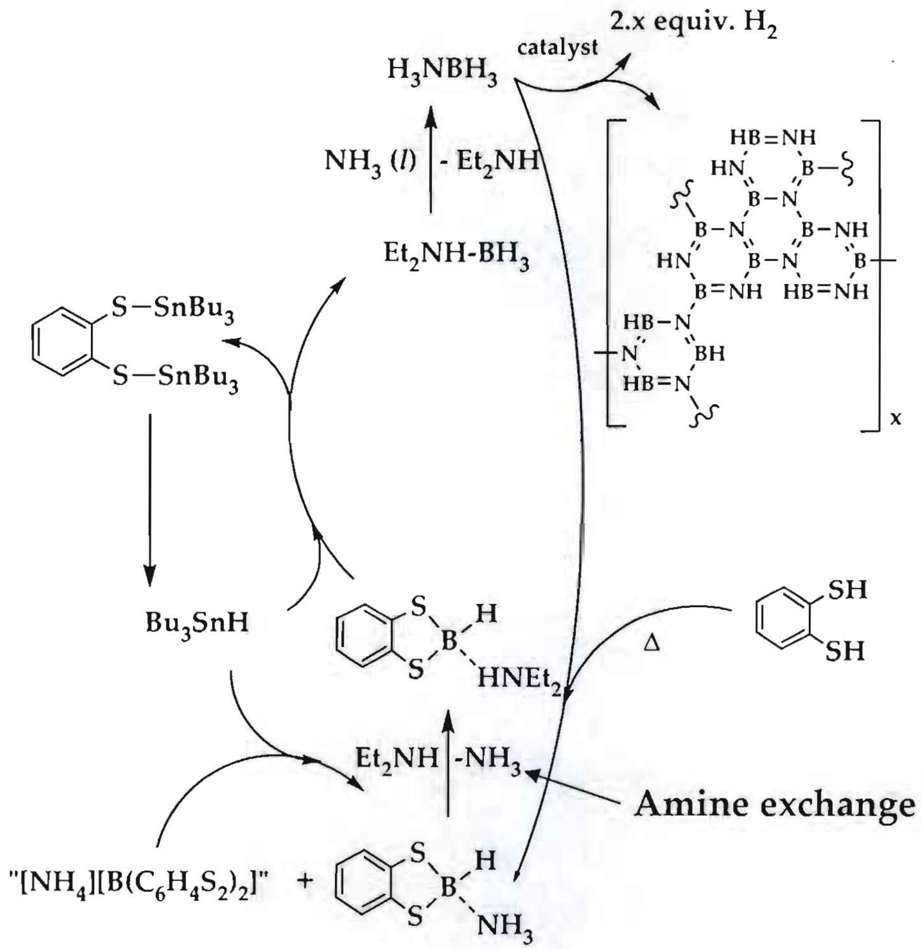
Tin by-product (^{119}Sn NMR)







Fall/Winter 2008/2009 Scheme



Amine exchange affords use of Bu_3SnH

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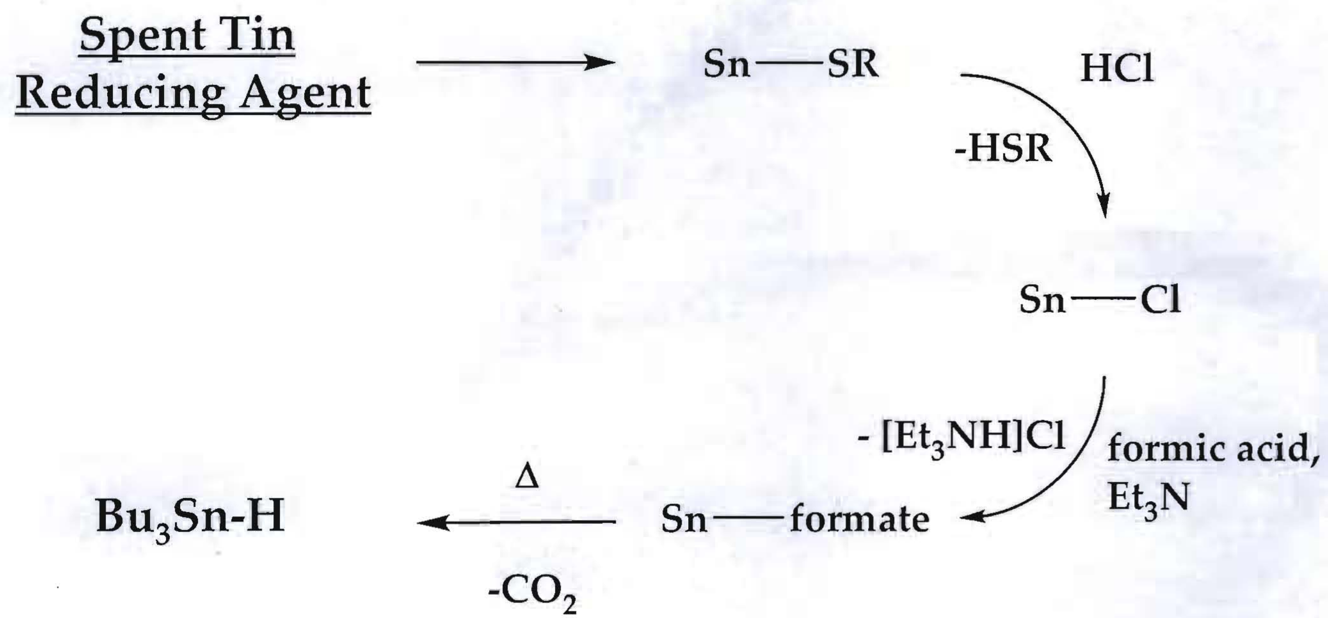
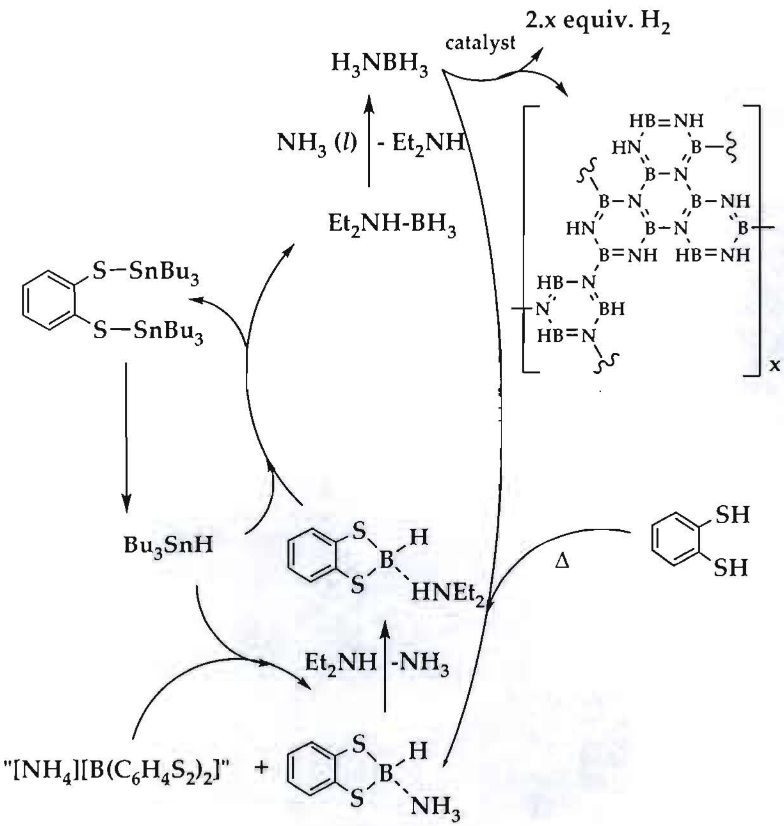
Completing the Recycle of Tin



CO_2 recompression energy costs may be avoided with integration with steam methane reforming

Evaluating direct regeneration by heterogeneous hydrogenation

Ultimate Goal



Less unit operations!

e.g. Less $C_6H_4(SH)_2$ in digestion = less Sn-H required = minimize recycle!

Evaluation of other reductants, etc.

Conclusions

Lots of work to be done......

Need to investigate liquid fuels (ongoing)

Multidisciplinary Center approach will get us there quicker than as a set of individuals


Come on lads; he'll no' notice it's missing until tomorrow....
Step away from the car, laddie....

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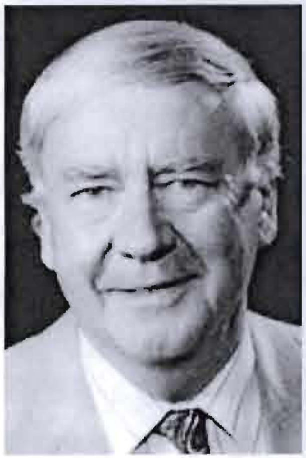

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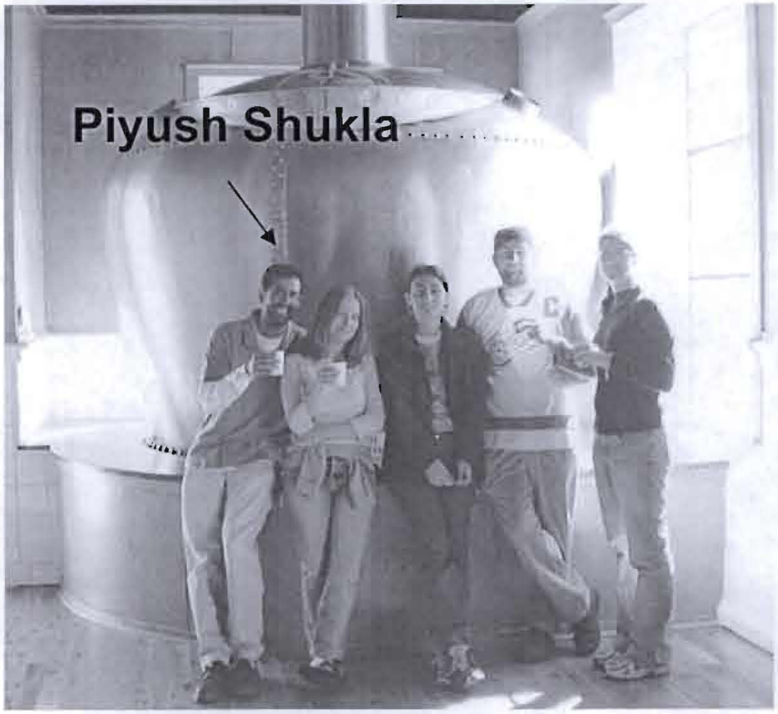

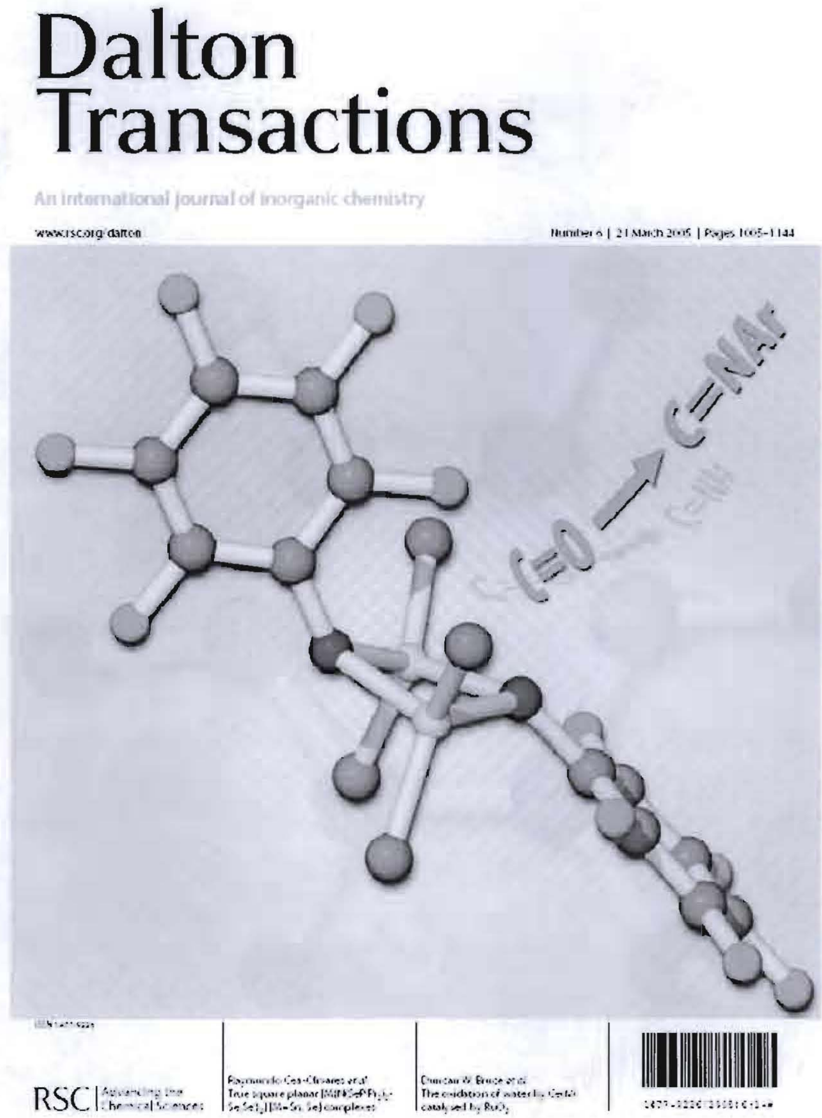

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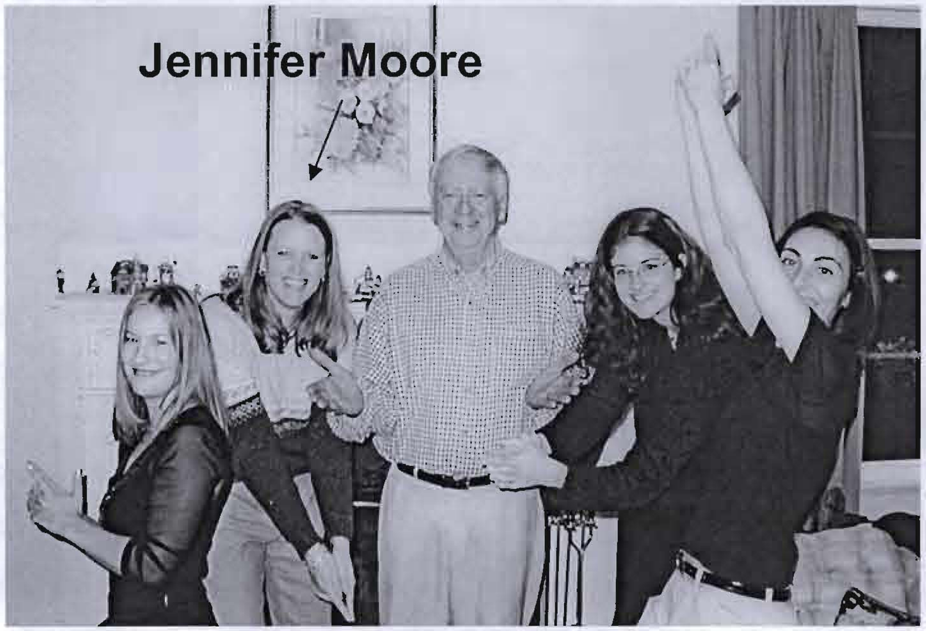

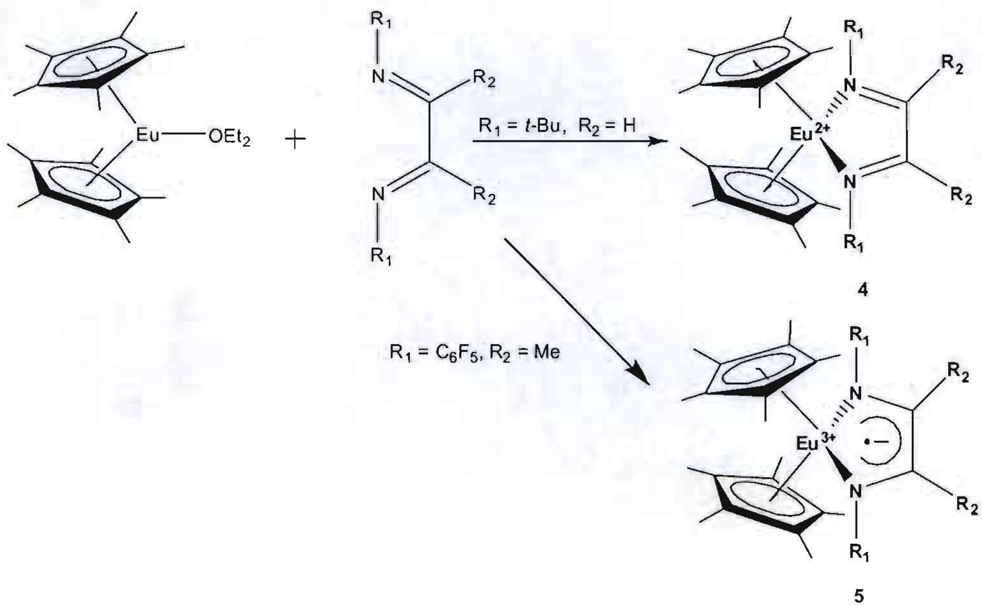

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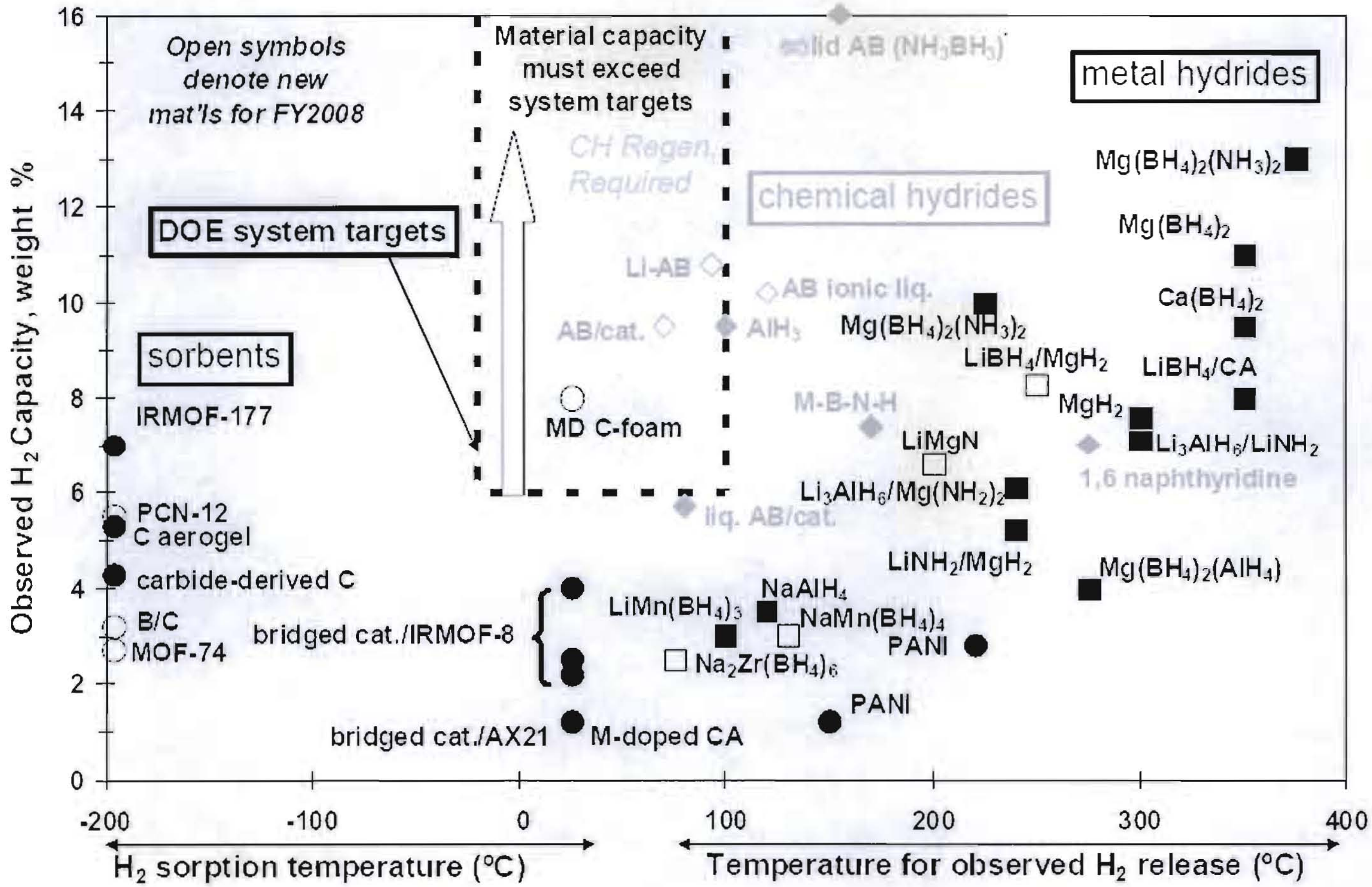

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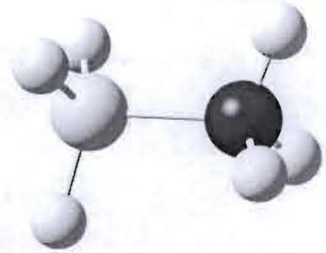

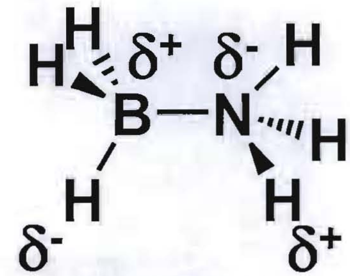

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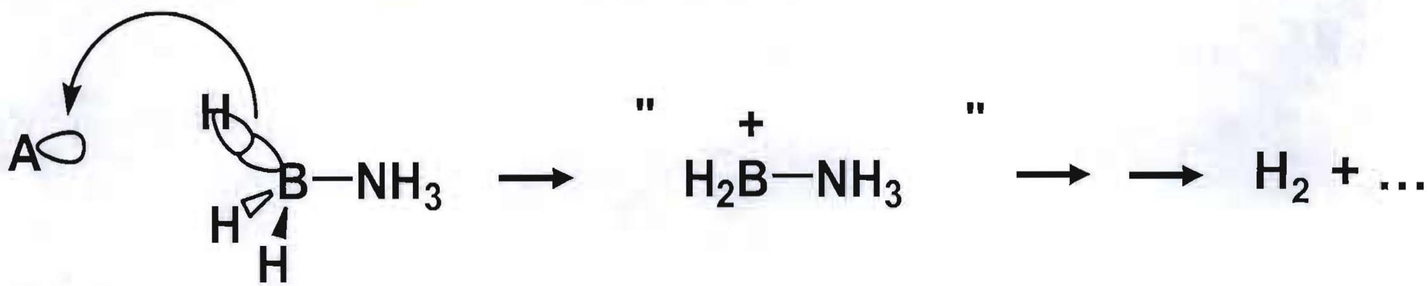
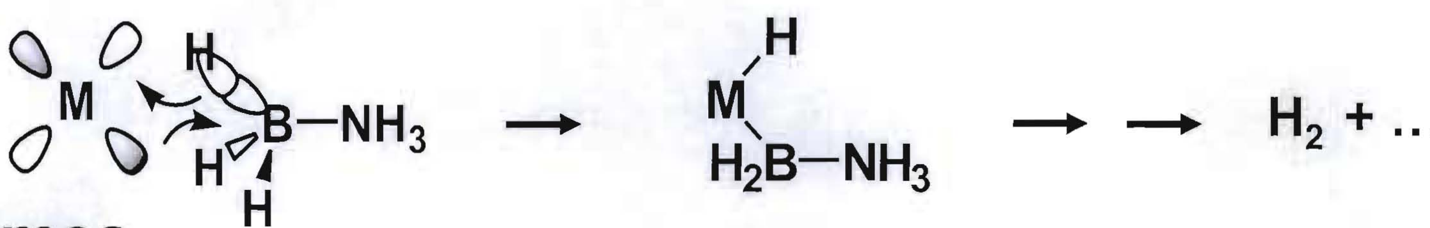


- **Metal Catalysis**



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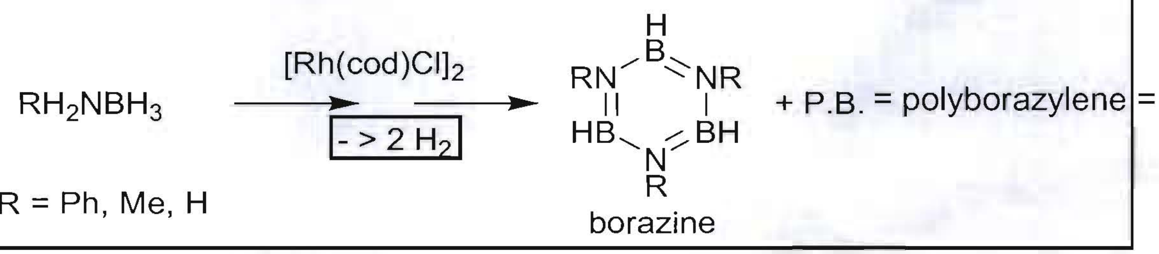
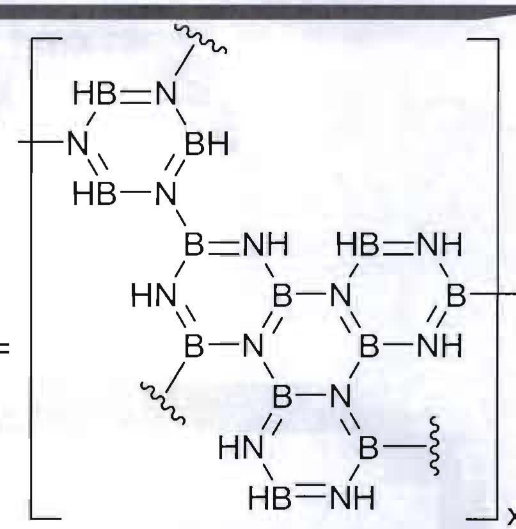
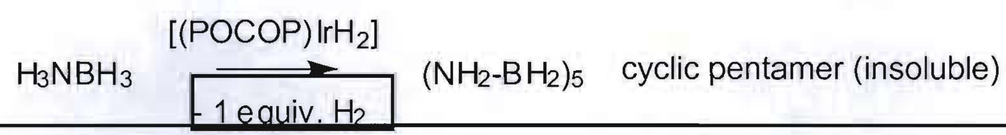
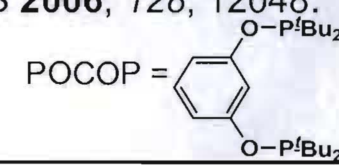


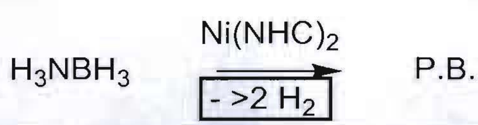


Denney, M. C.; Pons, V.; Hebden, T. J.; Heinekey, D. M.; Goldberg, K. I. *JACS* **2006**, *128*, 12048.





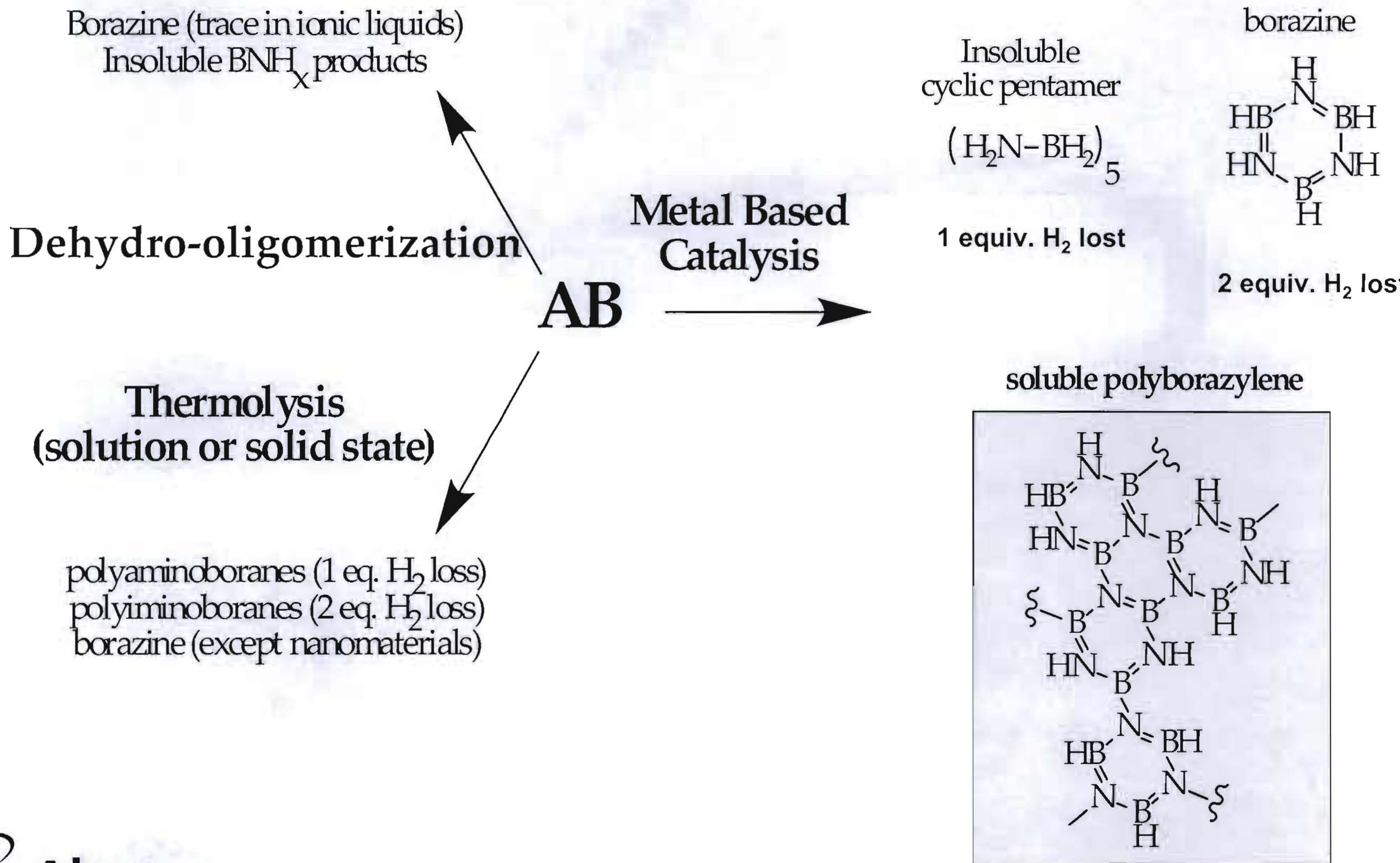
Keaton, R. J.; Blacquiere, J. M.; Baker, R. T. *JACS* **2007**, *129*, 1844.



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

What About Regeneration of Spent Fuel(s)?

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



> 2 equiv H_2 lost

Off-Board Regeneration Required

$$3 \text{ Ammonia Borane } (H_3N\text{-}BH_3) \rightarrow \text{Spent fuel } (B_3N_3H_4) + 7H_2\uparrow$$

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

(Miranda and Ceder 2007)

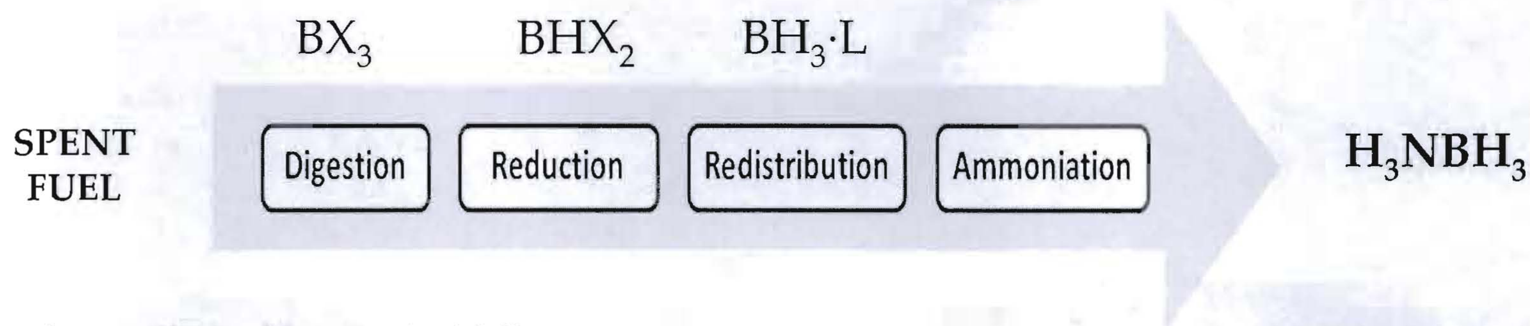
Hydrogen release -> **too exothermic** to merely re-pressurize with H_2

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

Approach



Dave Thorn, Ben Davis, LANL

Features of Chemistry:

Avoid formation of B-O bonds…..

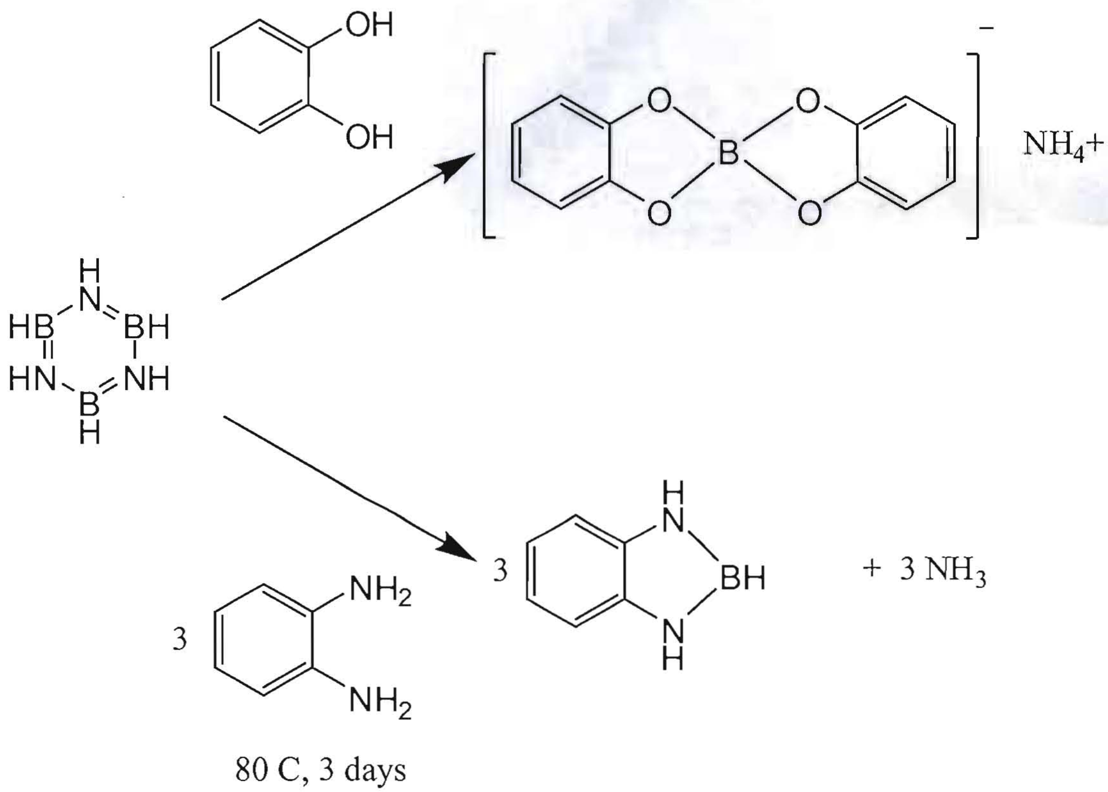
Steps have to be reasonably matched thermodynamically

Steps have to be high yielding

Recycle of reagents - *e.g.* reductant

Digestion of Spent Fuel

Preliminary Results with O- and N-chelates



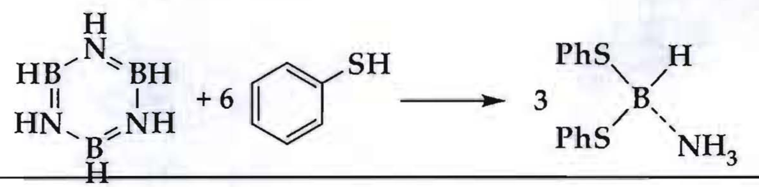
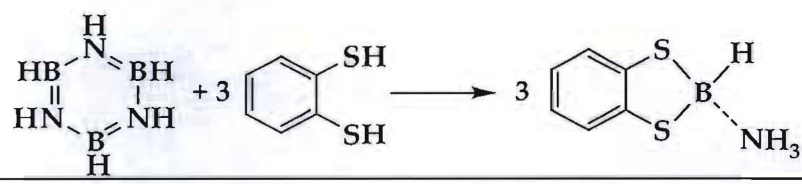
4

Dan Schwarz, David Thorn, LANL

What about B-S bonds?

Weaker than B-O bonds (allows for subsequent chemistry)

Acidity of a thiol could still aid reaction…

Estimates of Reaction Energies for Digestion	$\Delta H(298\ K)$[a]
	42.2/25.1
	-20.4/0.5

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

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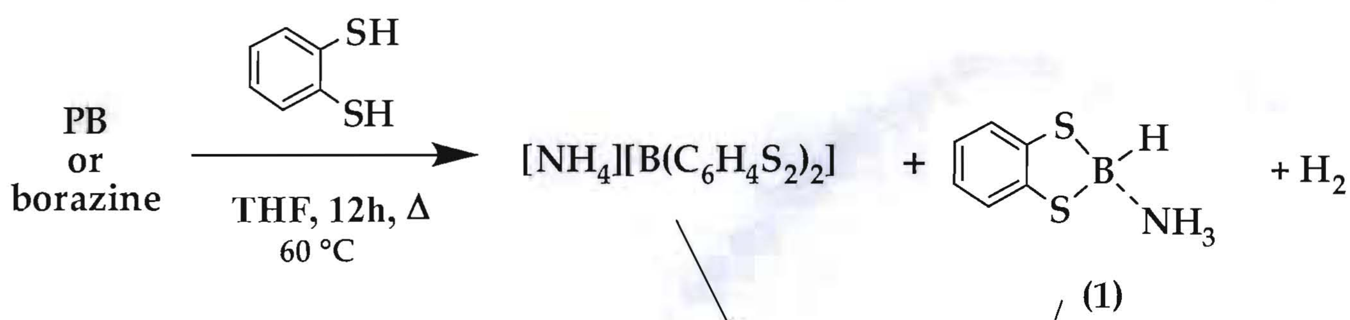
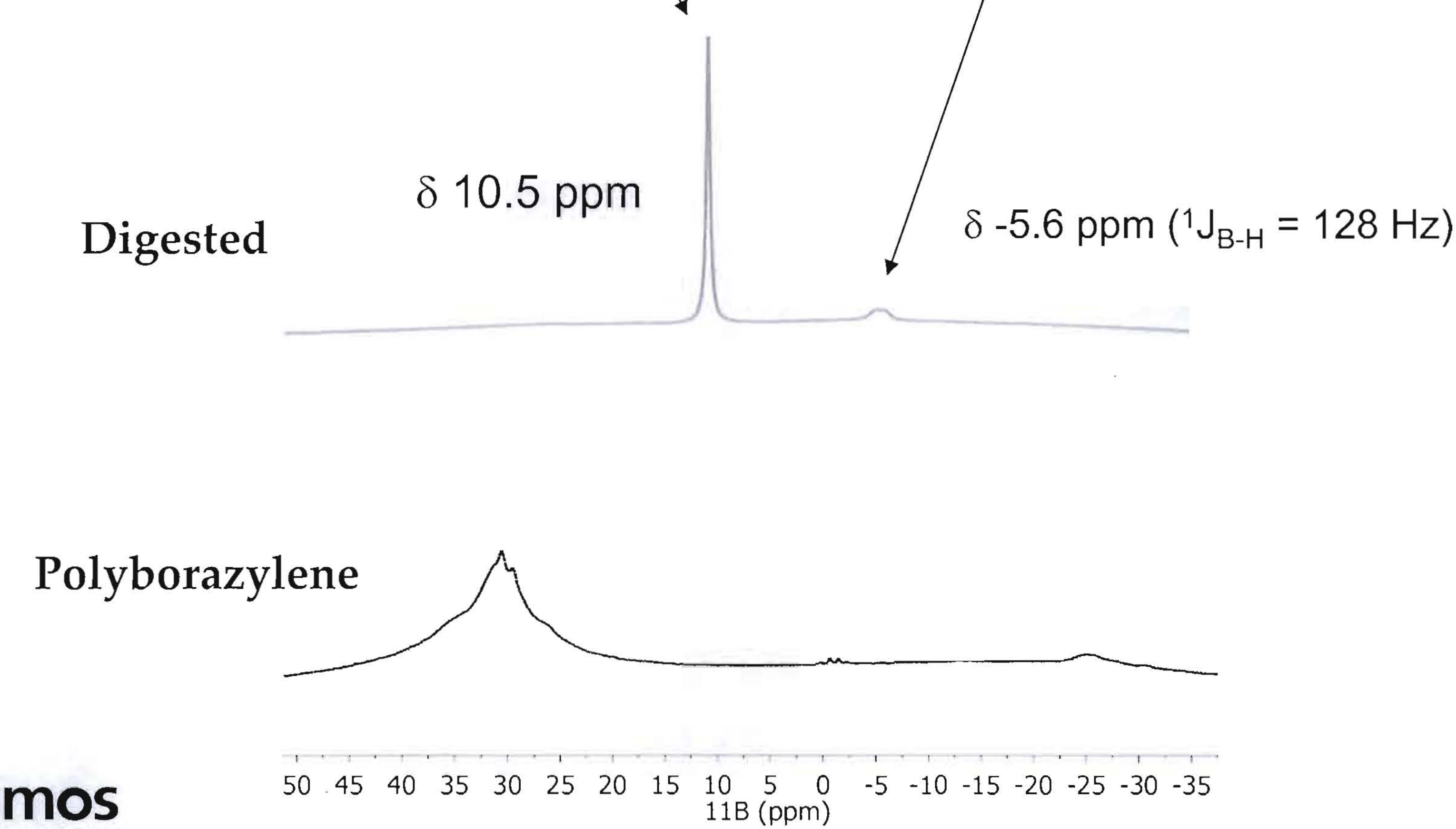
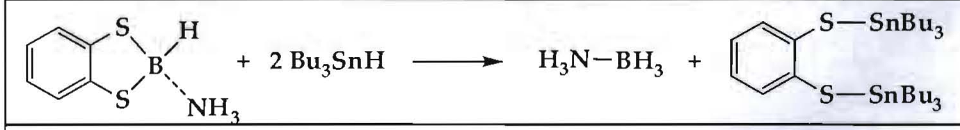
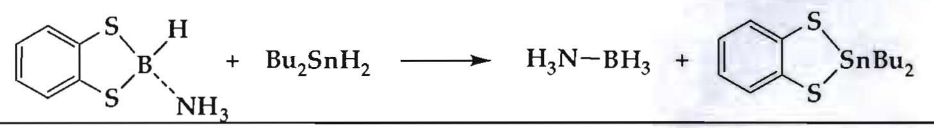
Validation with Benzenedithiol

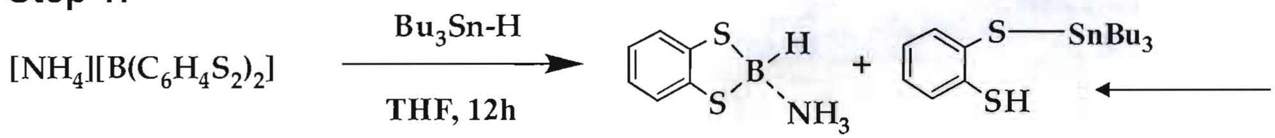




A Reductant is then Required

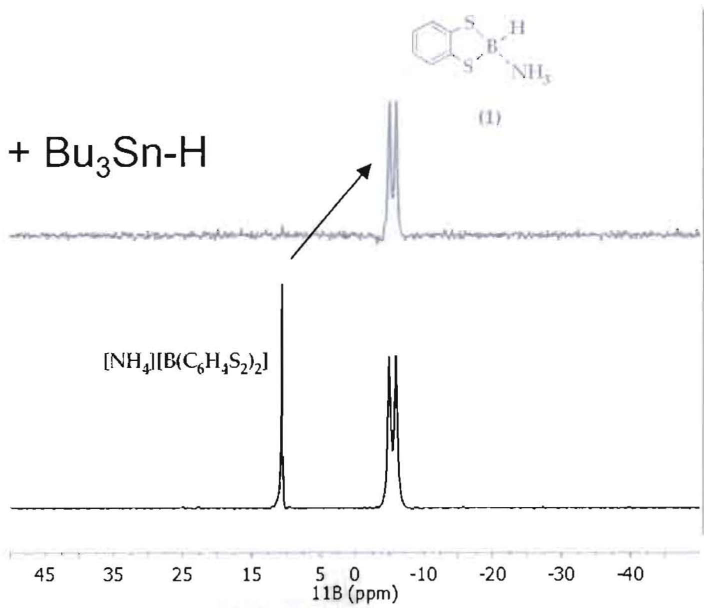
Estimates of Reaction Energies for Reduction	ΔH(298K)[a]
	-3.7/2.8
	-9.7/0.8

Step 1:



(1) (2)

Verified by ^{119}Sn NMR

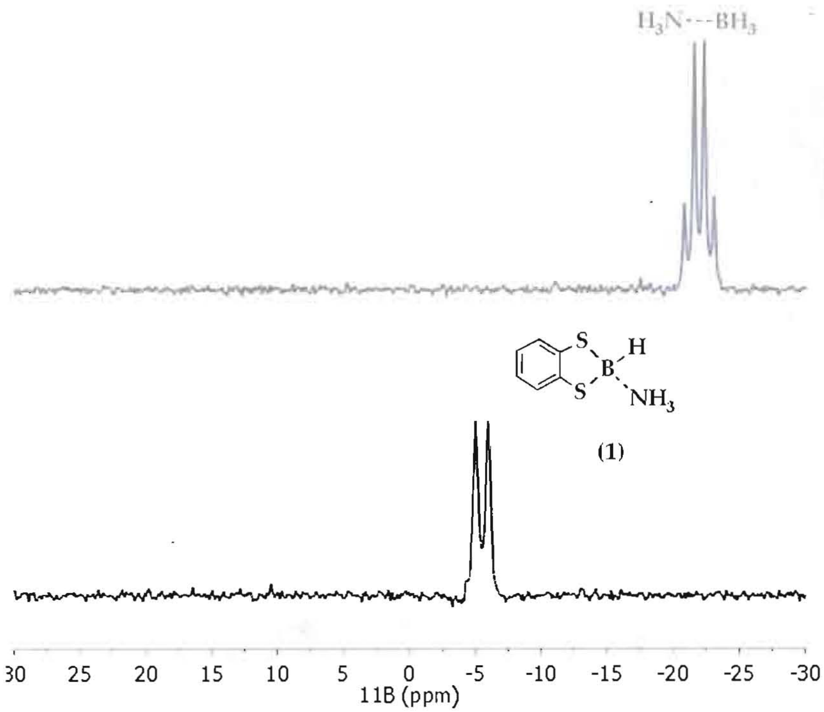


Fortuitously Bu_3Sn-H (commercially available) converts ammonium salt to (**1**)

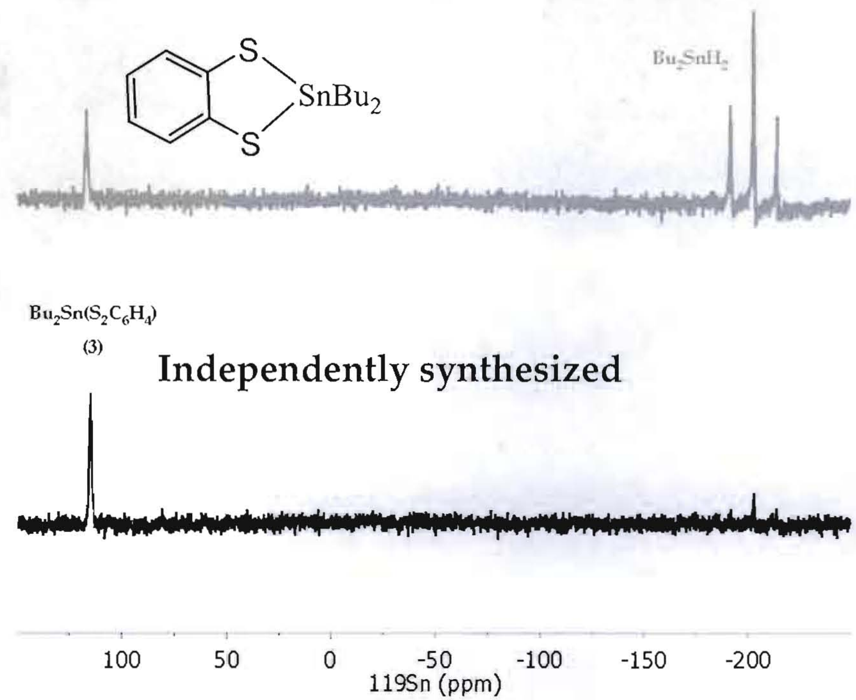
In 2 steps from PB we have a single Boron containing compound.

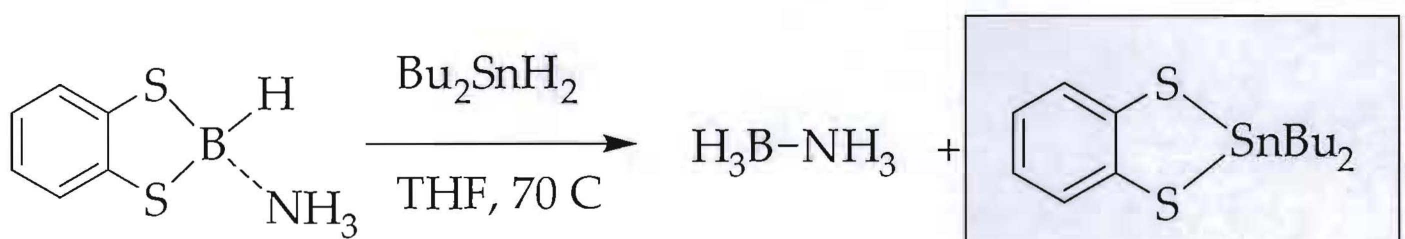
(In This Version) – Another Reduction Step is Required…

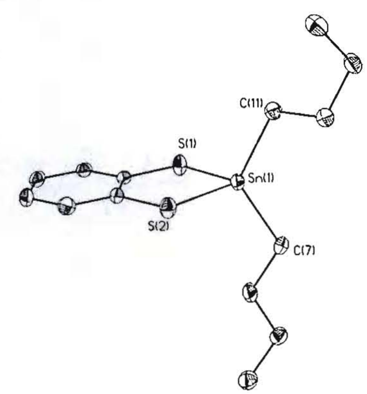
Subsequent Bu_2SnH_2 addition converts (1) to AB…..



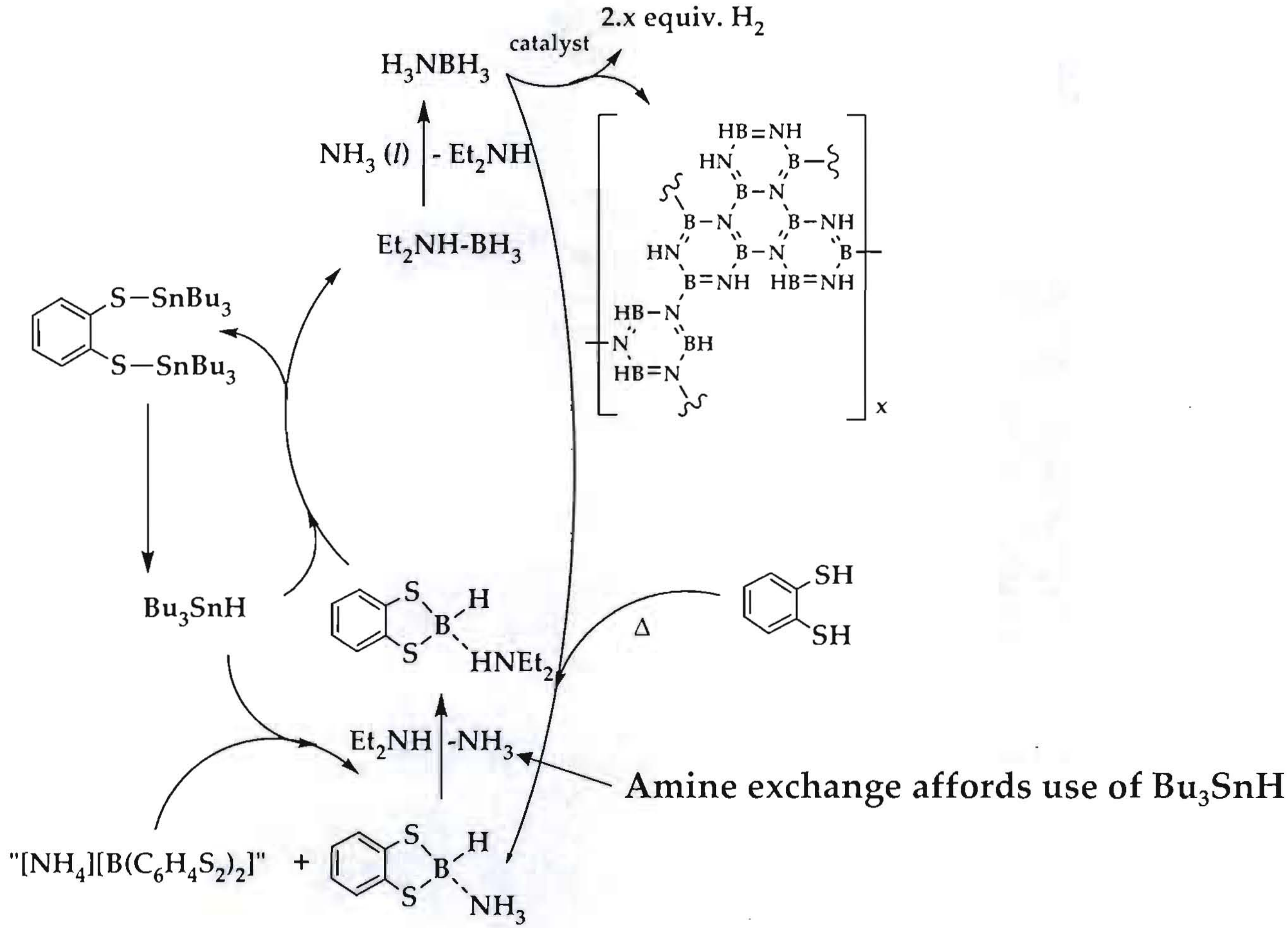
Tin by-product (^{119}Sn NMR)



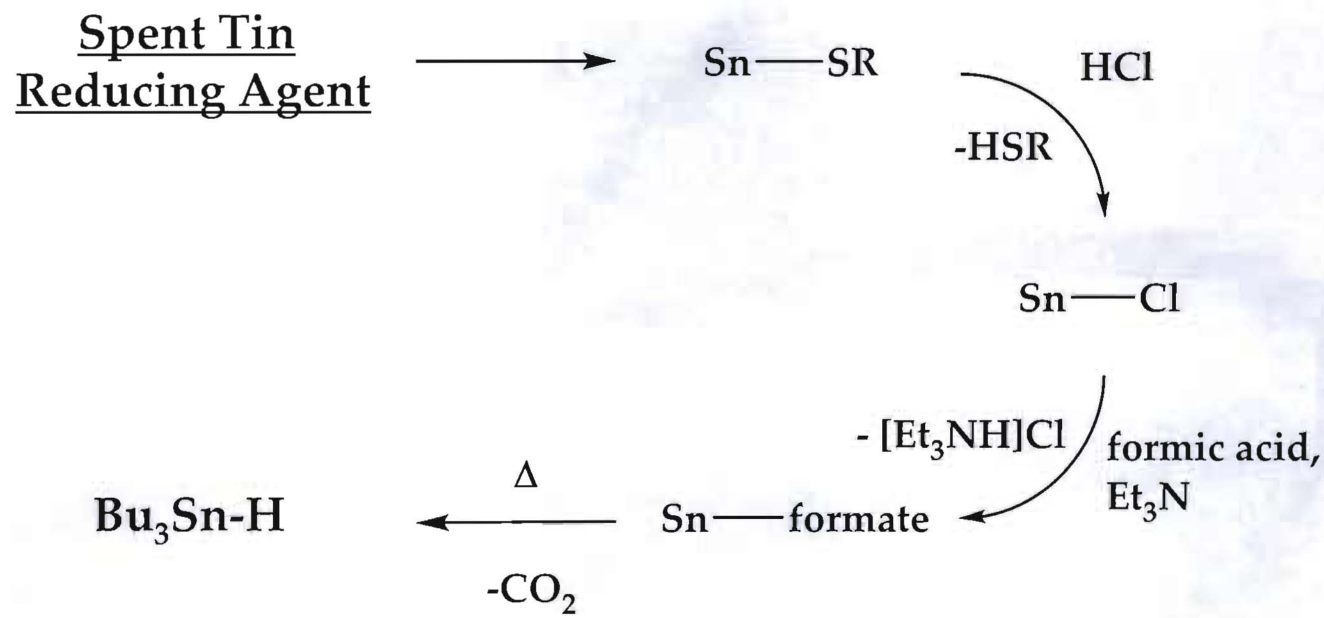




Fall/Winter 2008/2009 Scheme



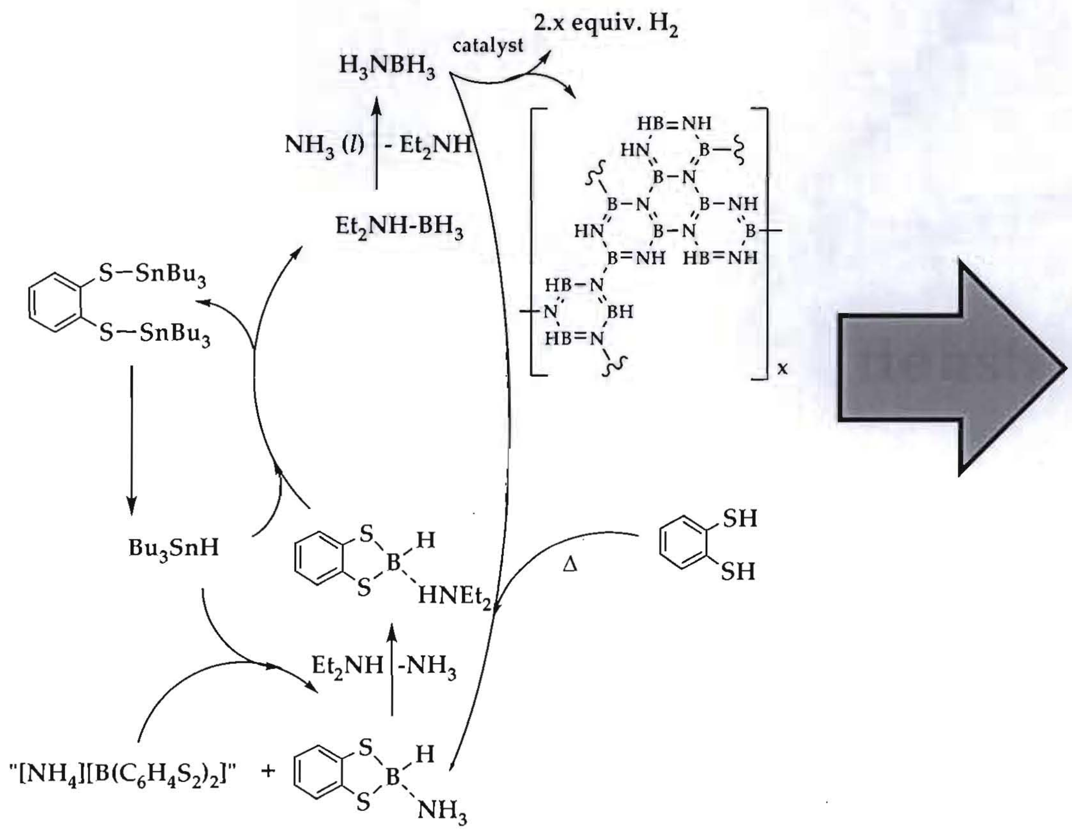
Completing the Recycle of Tin



CO_2 recompression energy costs may be avoided with integration with steam methane reforming

Evaluating direct regeneration by heterogeneous hydrogenation

Ultimate Goal



Less unit operations!

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

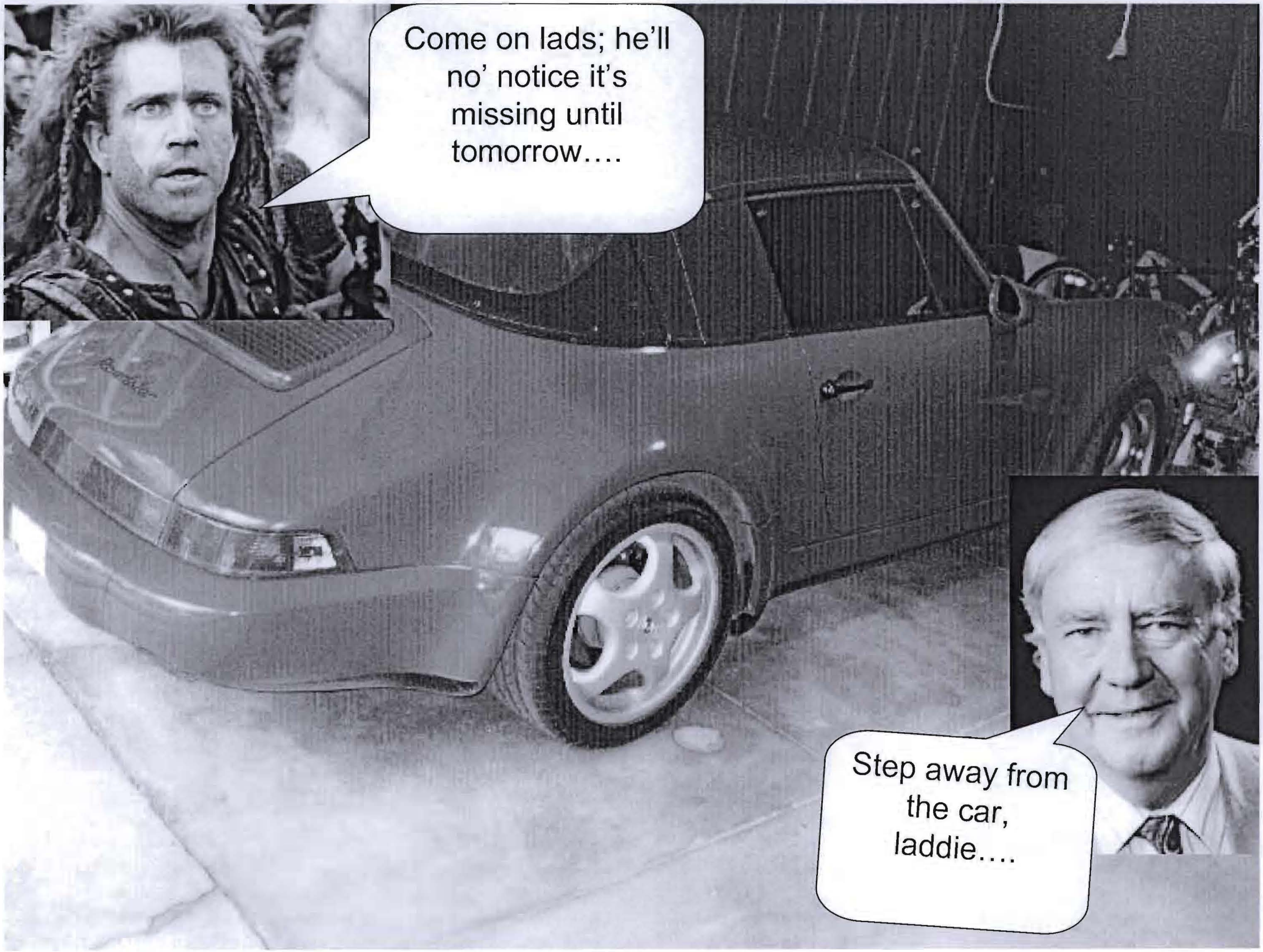
Evaluation of other reductants, etc.

Conclusions

Lots of work to be done……

Need to investigate liquid fuels (ongoing)

Multidisciplinary Center approach will get us there quicker than as a set of individuals


Come on lads; he'll no' notice it's missing until tomorrow....
Step away from the car, laddie....