Main Group Element and Organic Chemistry for Hydrogen Storage and Activation

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The University of Alabama

DOE Center of Excellence for Chemical Hydrogen Storage

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Project ID ST-9

Overview

Timeline

- Project start date: Jan. 05
- Project end date: FY10
- Percent complete: 75%

Barriers

DOE Barriers addressed
- System Cost
- System Weight and Volume
- Spent Fuel Regeneration

Budget

Projected total project funding:$2,255,397
DOE share: $1,649,496(requested)
UA share: $605,901

Funding for FY07: $375K (DOE)

Funding for FY08: $310K (DOE)

Partners

DOE Center of Excellence for Chemical Hydrogen Storage

LANL, PNNL, UW, UC-Davis, Penn State, UA, Penn, U. Missouri-Columbia, Millenium Cell, Rohm and Haas, Intematix, and Rio Tinto.

Objectives

- **Develop promising approaches to chemical H_2 storage for current and future DOE targets using computational chemistry and synthetic organic/inorganic chemistry.**
  - Enable DOE to meet the technical objective: "*By 2010, develop and verify on-board hydrogen storage systems achieving 2 kWh/kg (6 wt%), 1.5 kWh/L, and $4/kWh.; by 2015, 3 kWh/kg (9 wt%), 2.7 kWh/L, and $2/kWh*" by using chemical hydrogen storage systems.

- Provide computational chemistry support (thermodynamics, kinetics, properties prediction) to the experimental efforts of the DOE Center of Excellence for Chemical Hydrogen Storage to reduce the time to design and develop new materials that meet the DOE targets.
  - Focus on design of new materials and regeneration schemes

- Experimental focus is on organic and main group chemistries which may be able to perform better for release and regeneration by improving the energy balance. This will provide longer term alternatives.
  - Convergence of imidazolium (carbene) and cyanocarbon based H_2 storage and activation chemistry.

Approach

- Use highly accurate and validated first principles computational chemistry approaches on advanced computer architectures to predict the electronic structure of molecules to obtain thermodynamic and kinetic information in support of the design of hydrogen storage materials and of regeneration systems – release and addition of H_2.
  - Use combination of molecular orbital theory and density functional theory
  - Key issues: Accuracy/reliability of models
- Develop new concepts to improve energy balance. Especially relevant for ease of H_2 release/regeneration of H_2 storage system.
- Develop new approaches to release hydrogen from organic and main group compounds, based on new chemistry and our world leadership in stable carbene chemistry.
  - Demonstrate proof of concepts and key reactions.
- Key experimental issues:
  - Minimize weight by eliminating substituents or changing them into components that can store H_2 while maintaining kinetic and thermodynamic properties.
  - Demonstrating H_2 release reactions under expected operating conditions.
- Our team

Expt. Arduengo, Masaaki Yoshifuji (visiting faculty), Luigi Iconaru (grad student), Monica Vasiliu (grad student), Christian Schiel (postdoc),

Comp. Dixon, Myrna H. Matus (postdoc), Daniel Grant (grad student), Jackson R. Switzer (undergrad), Jacob R. Batson (undergrad), Minh T. Nguyen (visiting faculty)

Key Accomplishments

UA Computational Studies

- Predicted reliable thermodynamics for > 500 reactions for regeneration schemes.
  - Enabled reliable efficiency estimates and improvements in efficiencies to near 90% to help guide experimental studies within CoE
- Made significant advances in reliable predictions of the thermodynamics of new H_2 chemical hydrogen storage systems. Examples:
  - $C_xB_yN_zH_{12}$ (x+y+z = 6) chemistries
  - Methyl substituted amine-boranes for improved fuel properties (liquids) and improved thermochemistry
- Developed models of new catalytic and H_2 release processes.
  - Predicted orders of magnitude improvement in kinetics
- Developed new understanding of alane chemistries for metal hydride regeneration schemes based on amine complexation.
  - Identified multiple transition states and new complexes
- Developed improved models for carbene/TCNE thermochemistry
  - Enabled the choice of new chemistries

UA Experimental Studies

- Demonstrated cyclization to pure cyclopentamers and cyclohexamers for TCNE/carbene polymers.
- New reduction methodology ($BHCl_2$) under development for TCNE/carbene polymers.
- Imidazole borane chemistry has yielded an imidazole borane adduct that readily releases hydrogen at room temperature. Proof of concept validated.

Lewis Acid/Bases Catalyze H₂ Release from BH₃NH₃

Monomer

+ NH₃

+ BH₃

+ AlH₃

Proposed synthesis of
AlH₄⁻/BH₂NR₃⁺ in Center
(U. Mo.)

k_{AlH3} = 2.6 x 10⁻² s⁻¹ at 298K
8.4 x 10¹ s⁻¹ at 400K
Fast!

- Alane is a good Lewis acid catalyst. Why?
  - Al-H--H-N framework with a polar $N^{\delta-} H^{\delta+} {}^{\delta-}H Al^{\delta+}$
  - A double Al-H-B bridge
- Link to Metal Hydride Center
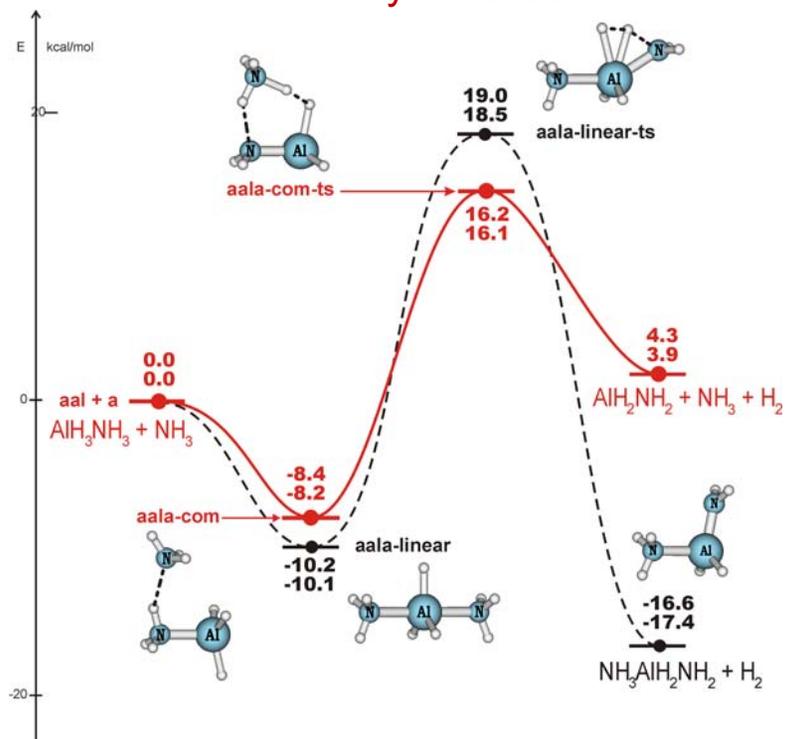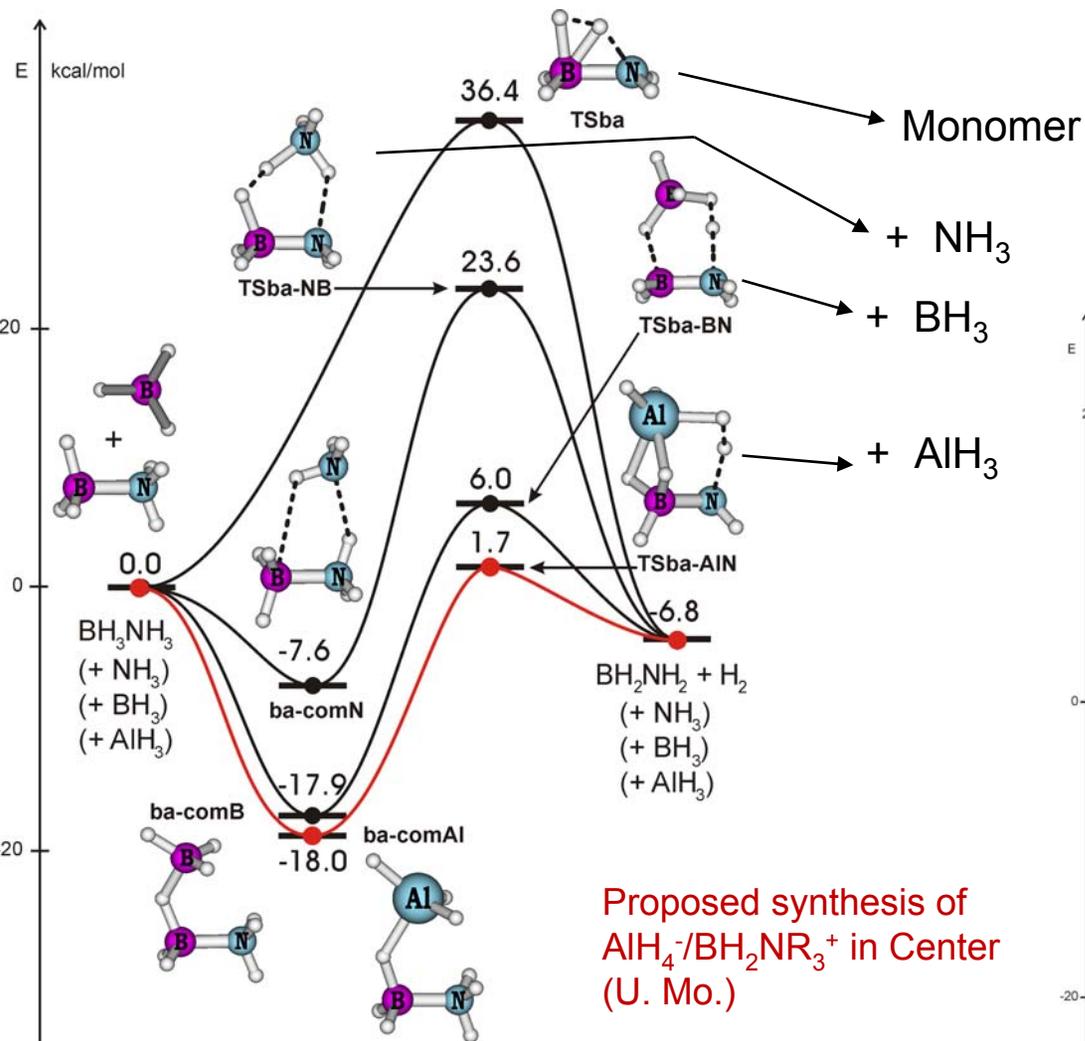
- NH₃ acts a Lewis-base catalyst on Al clusters.
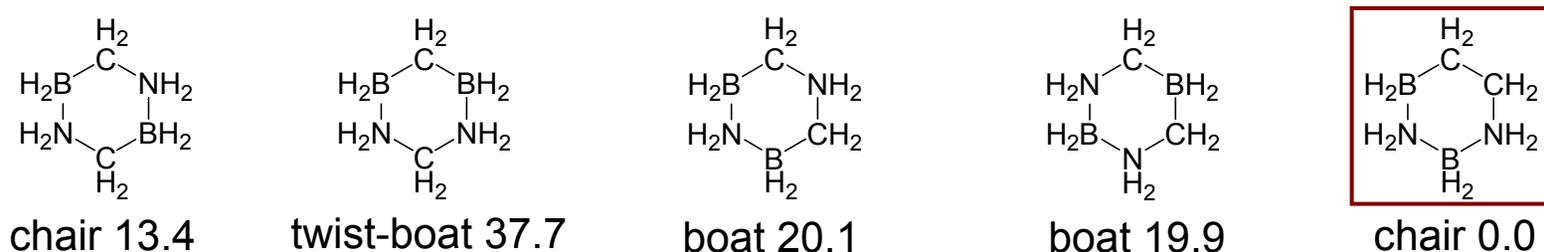- Linear trimer NH₃AlH₃NH₃ is stable.
- Zwitterion dimer readily releases H₂.

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How can we combine our exothermic B-N chemistry with endothermic C-C chemistry – $B_2N_2C_2H_{12}$?

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Relative G3MP2 Energies of at 298 K

C atoms in para

42.4   34.6   131.4

C atoms in meta

37.6   78.1   39.6   86.9

C atoms in ortho

0.0   51.2   43.8   93.4
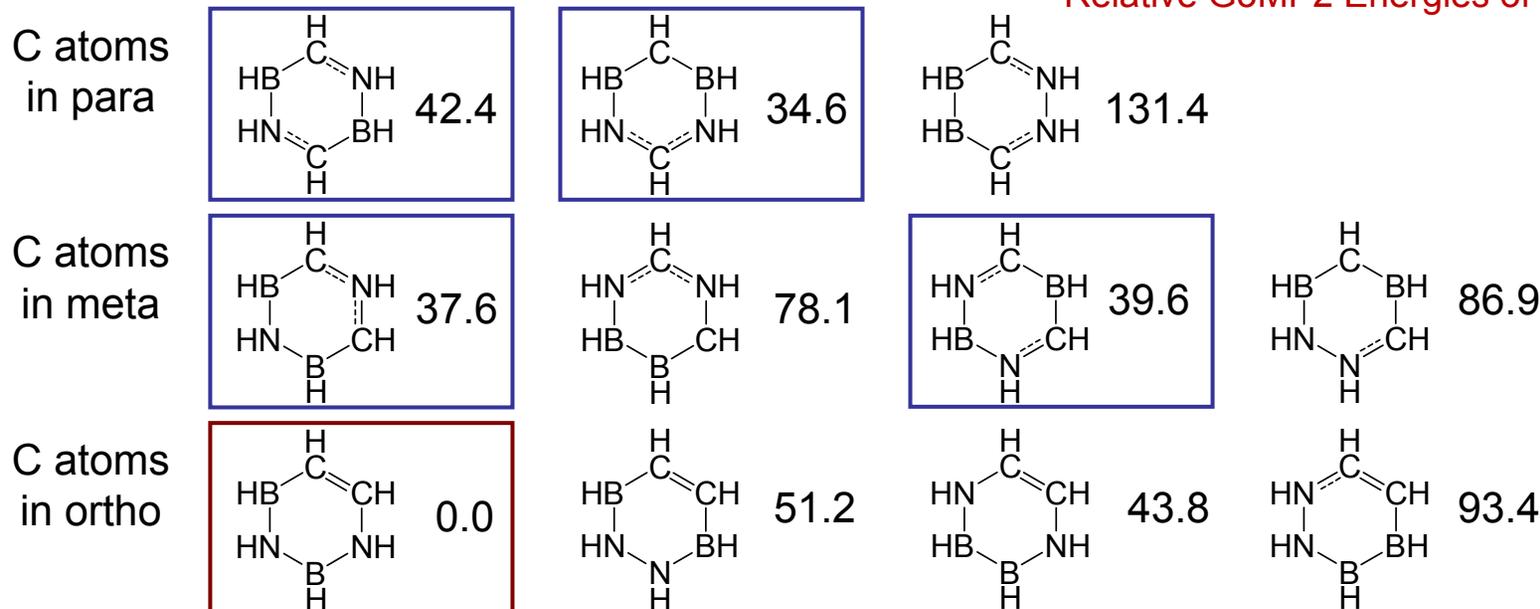
$B_2N_2C_2H_{12}$ conformations: b = boat; tw-b = twist-boat; c = chair

chair 13.4   twist-boat 37.7   boat 20.1   boat 19.9   chair 0.0

- Cycles with the **C-C-B-N-B-N** sequence are the lowest energy isomers either with 6H or 12H.
- What are the thermodynamics of the different pathways for the loss of 3 H_2?
- UW using thermodynamic data for experimental design.

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Stepwise dehydrogenation G3MP2 energies of the most stable $B_2N_2C_2H_{12}$ isomer is possible for selected paths. Always lose from B-N first!!
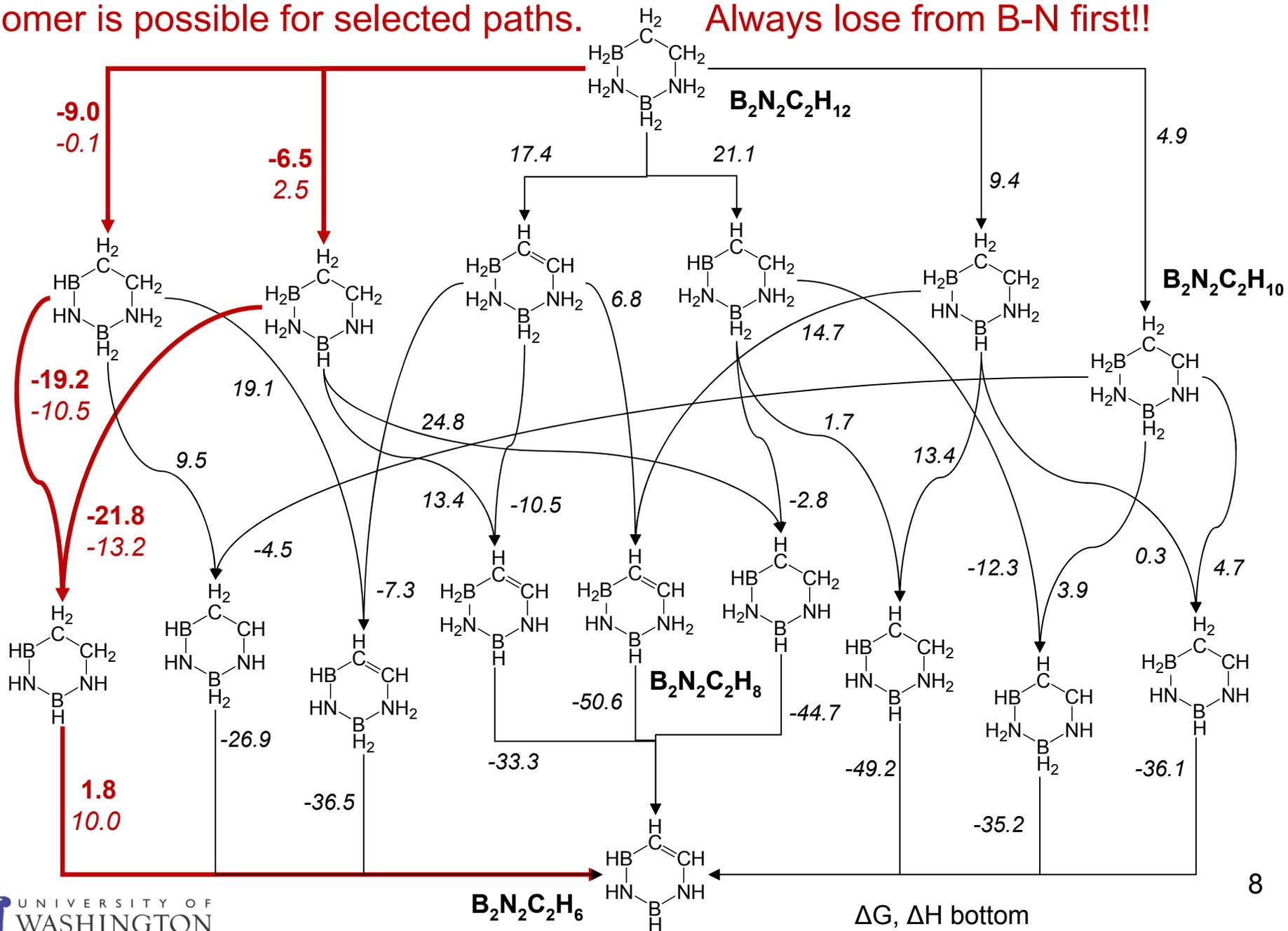
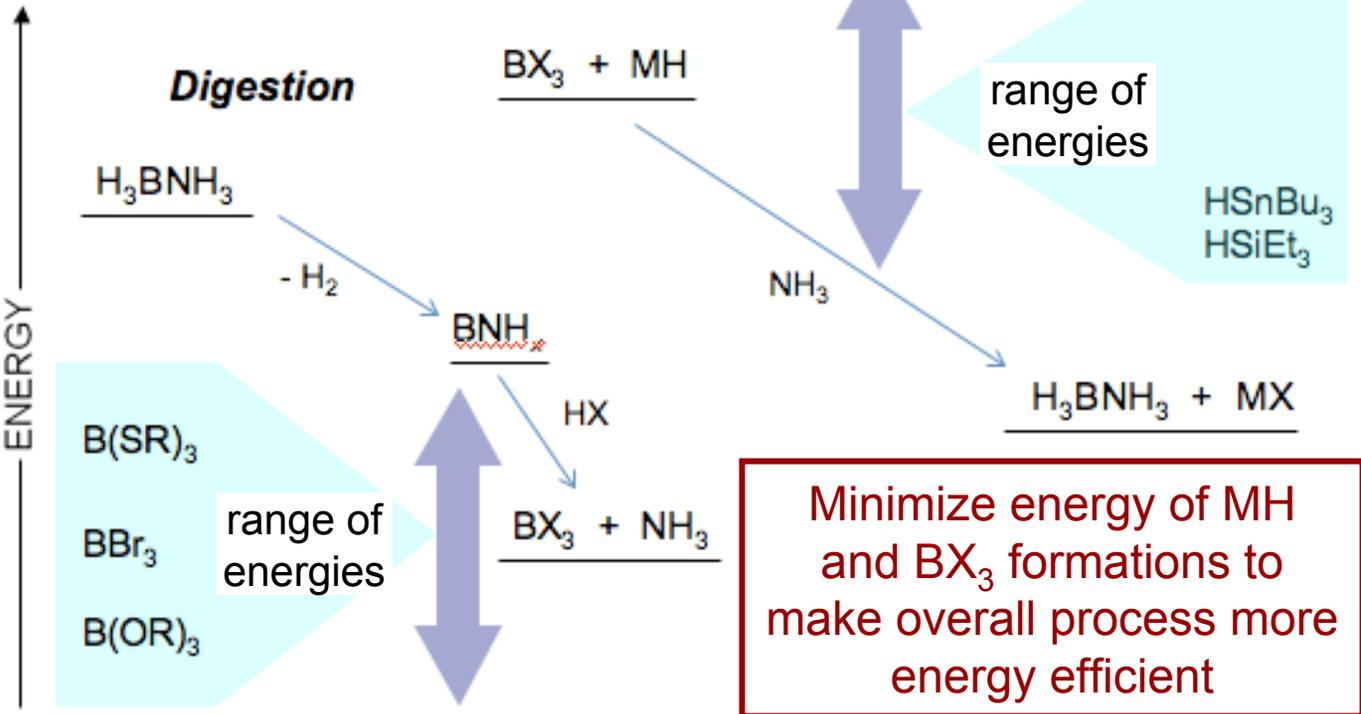# How can we combine our exothermic B-N chemistry with endothermic C-C chemistry - BNC_4H_{12}?

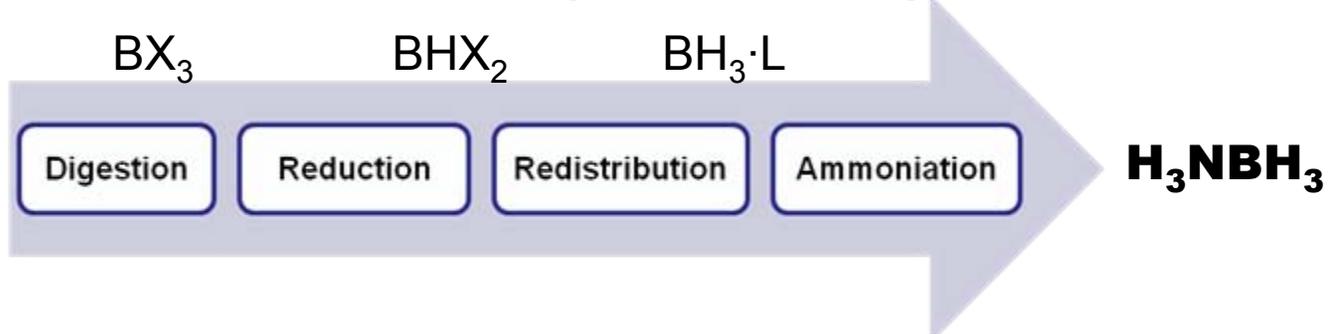Stepwise G3MP2 dehydrogenation energies for the most stable BNC_4H_{12} isomer at 298 K in kcal/mol
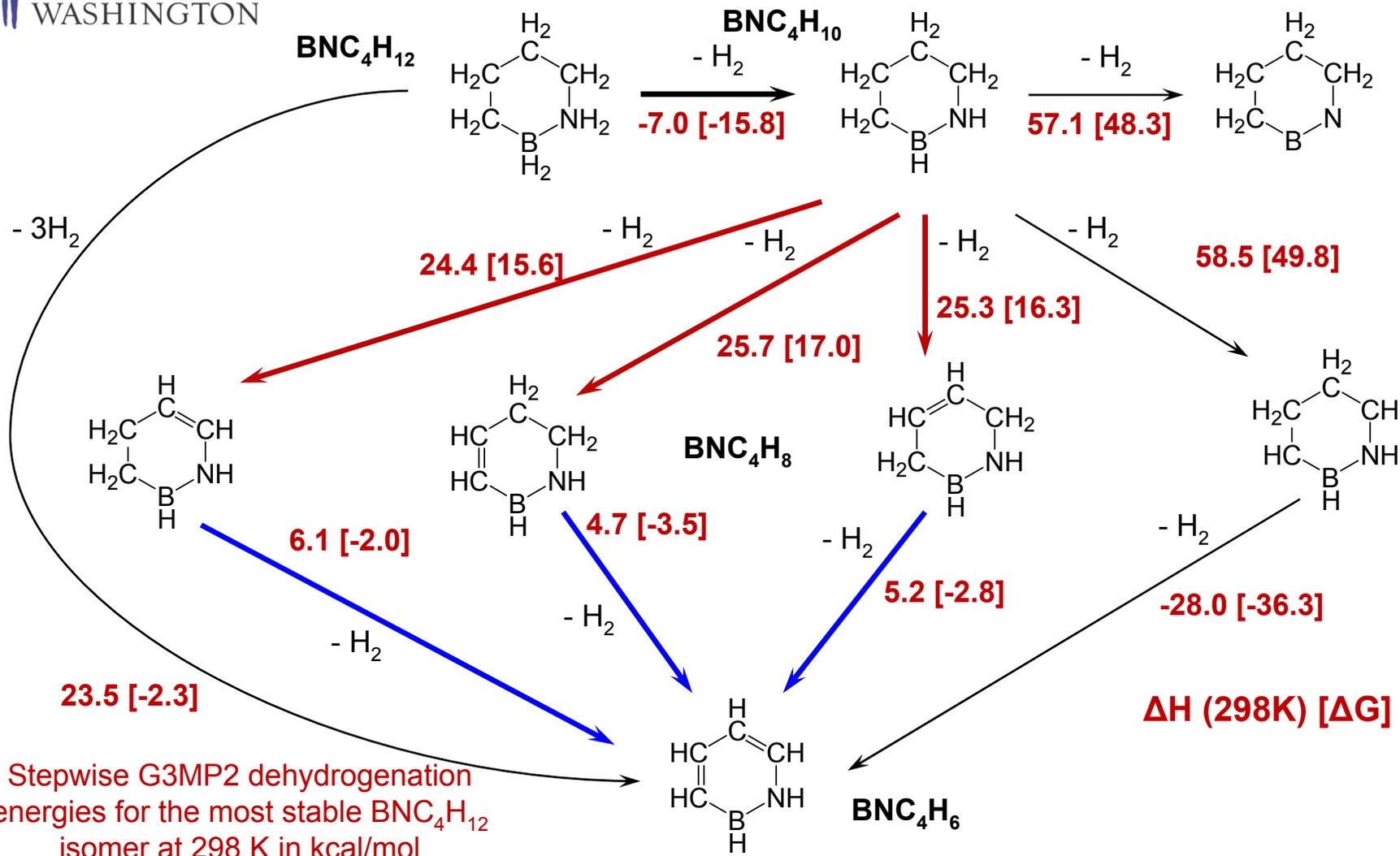
- 1st step is loss of H_2 from B-N bond (exo)
- 2nd step is loss of H_2 from C-C (endo)

- 3rd step is loss of H_2 from C-C bond and leads to aromaticity, near thermoneutral

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Thermodynamics for Regeneration of Ammonia Borane (LANL/UA)

SPENT FUEL → [Digestion] BX_3 → [Reduction] BHX_2 → [Redistribution] $BH_3 \cdot L$ → [Ammoniation] → H_3NBH_3

Reduction

NaH

range of energies

HSnBu$_3$
HSiEt$_3$

Digestion

$BX_3 + MH$

H_3BNH_3

$-H_2$

BNH_x

NH_3

HX

$H_3BNH_3 + MX$

ENERGY

$B(SR)_3$

range of energies

BBr_3

$BX_3 + NH_3$

$B(OR)_3$

Minimize energy of MH and BX_3 formations to make overall process more energy efficient

Recycle of reducing agents

– LANL, UC Davis, & Alabama working on M-X to M-H recycle and energetics

– This is crucial to overall efficiency

– Penn and PNNL also working on recycle

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Reduction: Thermodynamics of hydride transfer at 298 K in kcal/mol

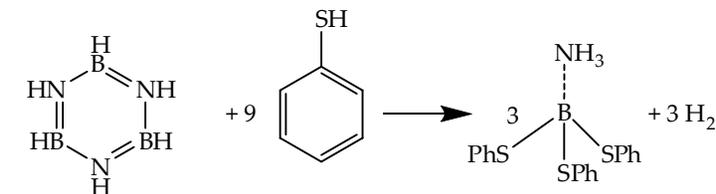| Reaction	ΔH (298K)	ΔG
$HSi(CH_3)_3 + BF_3 \rightarrow FSi(CH_3)_3 + HBF_2$	-2.0	-2.8
$HSi(CH_3)_3 + BCl_3 \rightarrow ClSi(CH_3)_3 + HBCl_2$	-7.6	-8.4
$HSi(CH_3)_3 + BBr_3 \rightarrow BrSi(CH_3)_3 + HBBr_2$	-10.4	-11.2
$HSi(CH_3)_3 + B(OH)_3 \rightarrow (OH)Si(CH_3)_3 + HB(OH)_2$	8.3	6.6
$HSi(CH_3)_3 + B(OCH_3)_3 \rightarrow (OCH_3)Si(CH_3)_3 + HB(OCH_3)_2$	7.9	7.5
$HSi(CH_3)_3 + B(SPh)_3 \rightarrow (SPh)Si(CH_3)_3 + HB(SPh)_2$	-2.0	-3.4
$HSn(CH_3)_3 + BF_3 \rightarrow FSn(CH_3)_3 + HBF_2$	12.9	11.6
$HSn(CH_3)_3 + BCl_3 \rightarrow ClSn(CH_3)_3 + HBCl_2$	-8.8	-9.5
$HSn(CH_3)_3 + BBr_3 \rightarrow BrSn(CH_3)_3 + HBBr_2$	-15.5	-16.4
$HSn(CH_3)_3 + B(OH)_3 \rightarrow (HO)Sn(CH_3)_3 + HB(OH)_2$	23.4	22.7
$HSn(CH_3)_3 + B(OCH_3)_3 \rightarrow (CH_3O)Sn(CH_3)_3 + HB(OCH_3)_2$	23.4	22.9

- Only possible digestion steps with strong acids are for HF or H_2O or NH_3.
- Redistribution reactions of strong acids have reasonable energetics except for NH_2 chemistry.
- Reduction of BX_3 can be accomplished by Si or Sn compounds.
- Theory directs experiment by determining candidate reagents and reactions. Used for mechanistic development by LANL.

Alternatives to Digestion: S and Sn Compounds (298K)

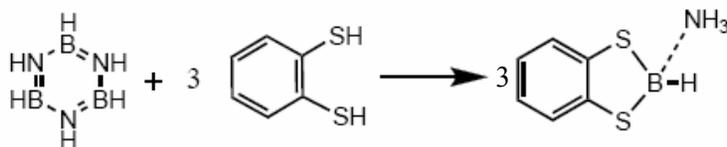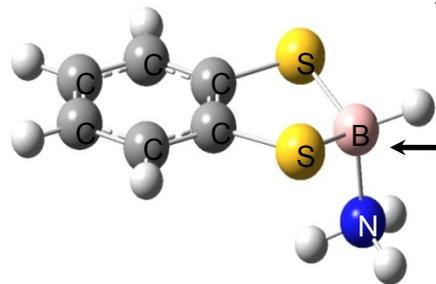**Reaction: B3LYP/DZVP2 and cc-pVDZ-PP(ECP) for Sn** ΔH ΔG
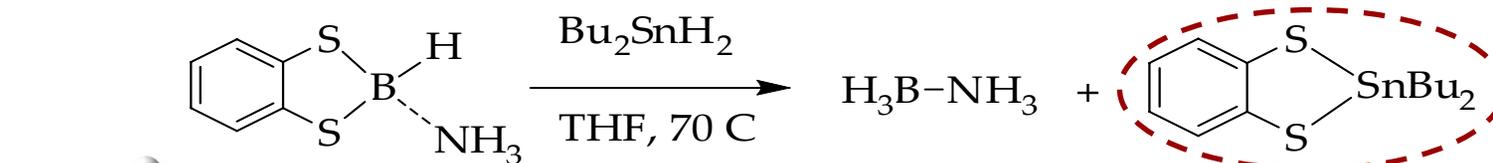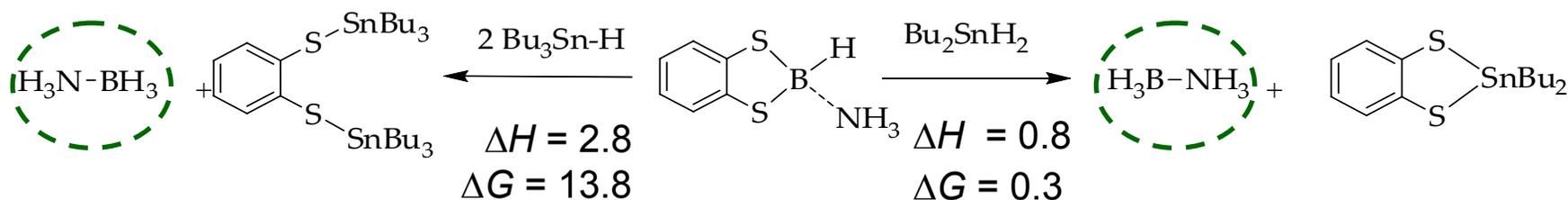

13.1   71.0

• Di-thiol for digestion is better than thiol.

0.5   15.5

Reduction

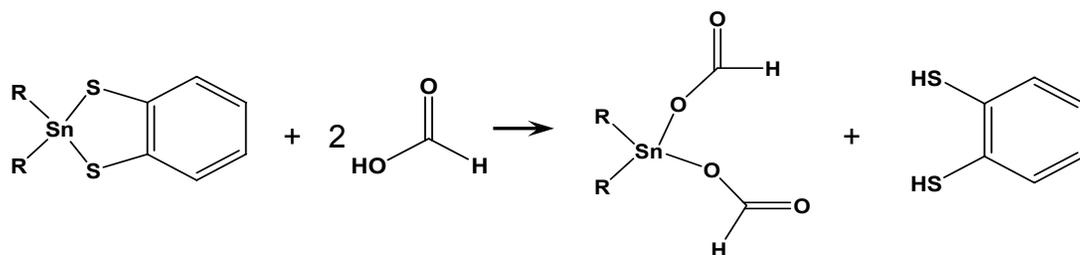$\Delta H = 2.8$
$\Delta G = 13.8$

$\Delta H = 0.8$
$\Delta G = 0.3$

$$H_3B-NH_3 \quad + $$

$\delta_{calc} = -1.8$ ppm
$\delta_{expt} = -5.6 \pm 0.2$ ppm

• Sn dihydride is a better reductant than monohydride but mono-hydride will work & is commercially available.
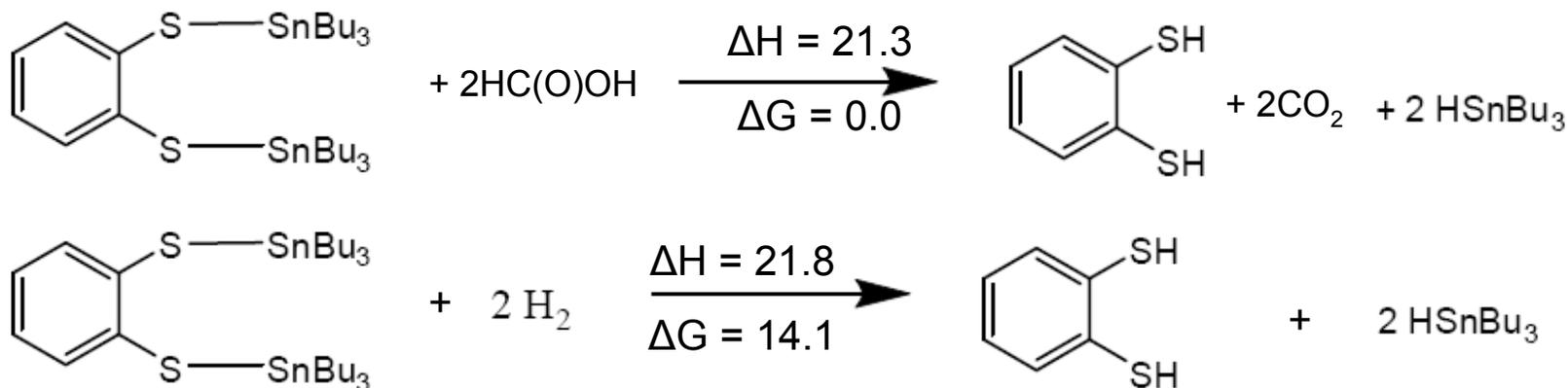• Used for LANL process design.

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Dihydride Recycle:
Thermodynamics of metathesis reactions

Use computations to predict energy balances

R	ΔH	ΔG
H	2.1	12.4
nBu	-1.4	7.7
tBu	0.1	12.0
Ph	1.8	12.2

Theory confirmed for metathesis: Excess formic acid results in no reaction of dihydride

$\Delta H = 21.3$

$\Delta G = 0.0$

+ 2HC(O)OH → + 2CO$_2$ + 2 HSnBu$_3$

$\Delta H = 21.8$

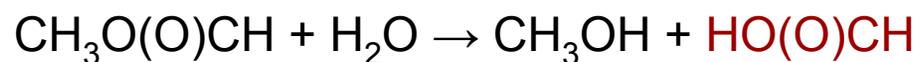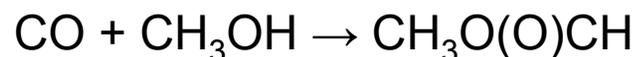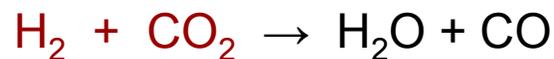$\Delta G = 14.1$

+ 2 H$_2$ → + 2 HSnBu$_3$

- Monohydride is more reactive than dihydride and reaction free energy is OK.
- LANL has validated tin hydride formation step with H$_2$ as a reagent.
- Goal is to eliminate formic acid cycle step. Scout other possible reaction schemes with improved thermodynamics for mechanism design.

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NATIONAL LABORATORY

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Dihydride Recycle CO₂ extrusion from tin diformates at 298 K in kcal/mol
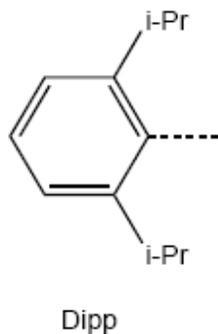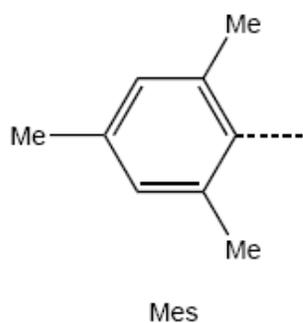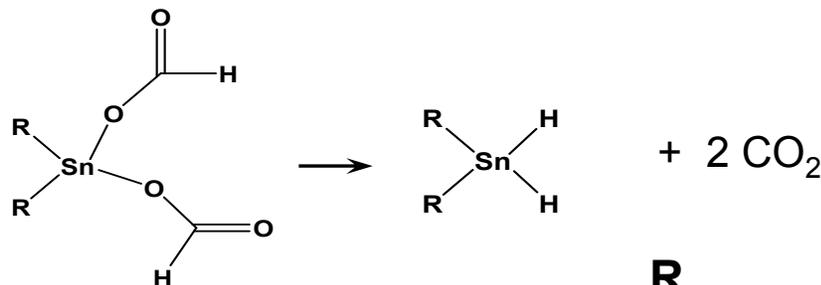
R	ΔH	ΔG
H	14.6	-4.5
nBu	24.7	5.8
tBu	24.5	3.1
Ph	20.4	-0.6
Mes	18.2	-2.4
Dipp	17.2	-5.7

HOOCH commercial synthesis

$$H_2 + CO_2 \rightarrow H_2O + CO \qquad \Delta H = -0.7$$
$$CO + CH_3OH \rightarrow CH_3O(O)CH \qquad \Delta H = -32.2$$
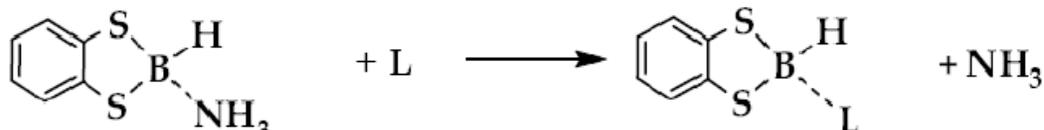$$CH_3O(O)CH + H_2O \rightarrow CH_3OH + HO(O)CH \qquad \Delta H = 25.3$$

$\Delta H = -7.6$
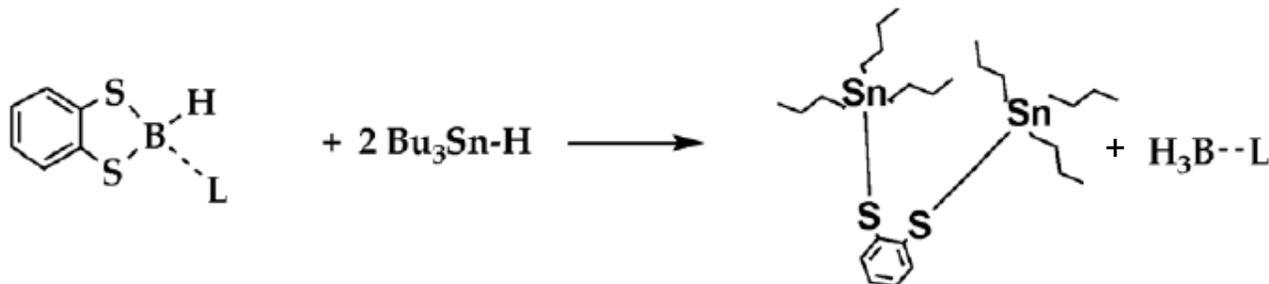
- CO₂ extrusion chemistry favored for free energy due to loss of CO₂.
- Issue is inefficiency of formic acid recycle. Work with LANL to improve the process.

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Alternatives to Reduction: Nitrogen ligands

Reaction A

Reaction B

Reaction C
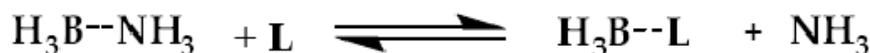
L =	(piperidine)	(DMAP)	(propylamine)	(diethylamine)	(triethylamine)
Reaction A ΔH	-5.5	-5.4	-4.5	**-1.0**	**6.2**
ΔG	-3.7	-4.5	-3.3	**1.0**	**9.2**
Reaction B ΔH	1.5	2.1	2.7	0.1	**-4.7**
ΔG	11.6	11.5	13.0	10.0	**5.6**
Reaction C ΔH	-6.8	-6.0	-4.6	-3.7	-1.3
ΔG	-5.9	-6.7	-4.1	-2.8	1.0

- $(CH_2CH_3)_2NH$ is the most useful facilitator of all 3 reactions.
- $(CH_2CH_3)_3N$ best for reduction reaction B.

Blue results verified experimentally at LANL. Energies at 298 K in kcal/mol

Characteristics of a Desirable Regeneration System

Overall regeneration efficiencies calculated

- Obtain high yield in all steps
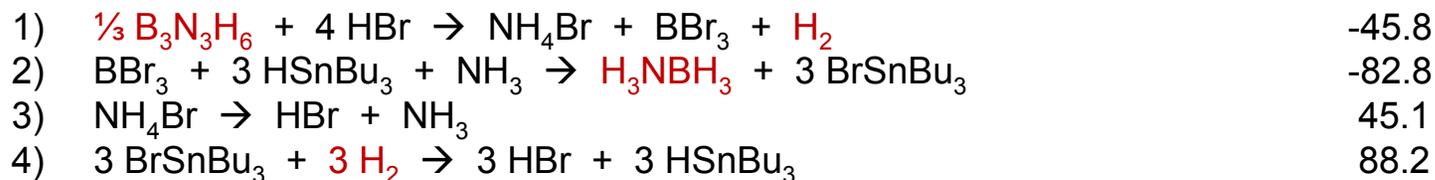- Avoid the formation of thermodynamically stable bonds
- Avoid the formation of diborane (B_2H_6) or NH_3 = increase atom efficiency
- Recover and recycle all products
- Minimize the number of operations
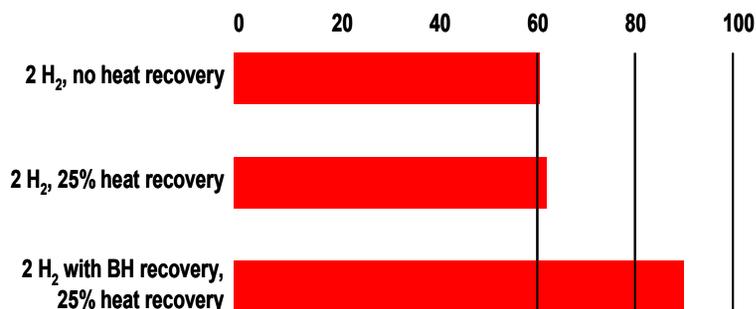
DOE goal: 60% well to tank

$$\frac{(\text{Equiv. H}_2 \text{ stored})(57.8)}{(\text{Equiv. H}_2 \text{ used})(57.8) + \sum (\Delta H_{endo}) - (\% \text{ heat recovery}) \sum (-\Delta H_{exo})} = efficiency$$

1)	$\frac{1}{3}$ $B_3N_3H_6$ + 4 HBr → NH_4Br + BBr_3 + H_2	-45.8
2)	BBr_3 + 3 $HSnBu_3$ + NH_3 → H_3NBH_3 + 3 $BrSnBu_3$	-82.8
3)	NH_4Br → HBr + NH_3	45.1
4)	3 $BrSnBu_3$ + 3 H_2 → 3 HBr + 3 $HSnBu_3$	88.2

(2 x 57.8) / (3 x 57.8 + 133.3 − (x%)128.6) = 0.41 for 20% heat recovery (& H_2 reuse)

↑ More H_2 storage

↑ Use less H_2

↑ Lower endo-thermics

↑ Improve heat recovery

↑ Raise efficiency

Dehydrogenation design

Digestion design

Use comp chem for opt design

Engineering design

DOE Chemical H_2 Storage COE

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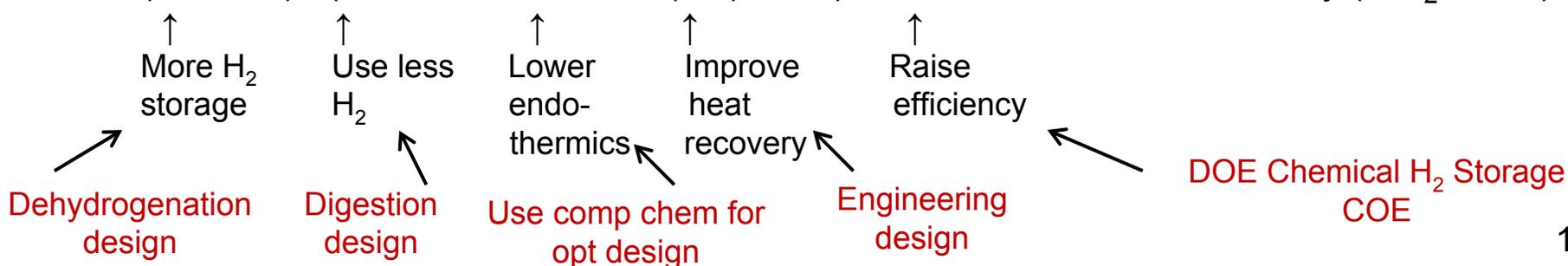
Predicted Regeneration Efficiencies

Diethylamine with CO_2 production

1) $\frac{1}{3}$ $B_3N_3H_6$ (s) + $C_6H_4(SH)_2$ (l) → $HB(C_6H_4S_2)\cdot NH_3$ (l)   -4.5

2) $HB(C_6H_4S_2)\cdot NH_3$ (l) + Et_2NH (l) → $HB(C_6H_4S_2)\cdot NHEt_2$ (l) + NH_3 (g)   7.9

3) $HB(C_6H_4S_2)\cdot NHEt_2$ (l) + 2 Bu_3SnH (l) → Et_2NHBH_3 (l) + $C_6H_4(SSnBu_3)_2$ (l)   13.9

4) Et_2NHBH_3 (l) + NH_3 (g) → H_3NBH_3 (s) + Et_2NH (l)   -16.9

5) $C_6H_4(SSnBu_3)_2$ (l) + 2 HCOOH (l) → $C_6H_4(SH)_2$ (l) + 2 CO_2 (g) + 2 Bu_3SnH (l)   19.3

6) 2 CO_2 (g) + 2 H_2 (g) → 2 CO (g) + 2 H_2O (l)   -1.4

7) 2 CO (g) + 2 MeOH (l) → 2 MeCOOH (l)   -64.3

8) 2 MeCOOH (l) + 2 H_2O (l) → 2 HCOOH (l) + 2 MeOH (l)   50.6

Estimated efficiency w/ 20% heat recovery: 61%

Commercial synthesis

Diethylamine

1) $\frac{1}{3}$ $B_3N_3H_6$ (s) + $C_6H_4(SH)_2$ (l) → $HB(C_6H_4S_2)\cdot NH_3$ (l)   -4.5

2) $HB(C_6H_4S_2)\cdot NH_3$ (l) + Et_2NH (l) → $HB(C_6H_4S_2)\cdot NHEt_2$ (l) + NH_3 (g)   7.9

3) $HB(C_6H_4S_2)\cdot NHEt_2$ (l) + 2 Bu_3SnH (l) → Et_2NHBH_3 (l) + $C_6H_4(SSnBu_3)_2$ (l)   13.9

4) Et_2NHBH_3 (l) + NH_3 (g) → H_3NBH_3 (s) + Et_2NH (l)   -16.9

6) $C_6H_4(SSnBu_3)_2$ (l) + 2 H_2 (g) → $C_6H_4(SH)_2$ (l) + 2 Bu_3SnH (l)   4.2

Estimated efficiency w/ 20% heat recovery: 84%

Can get high regeneration efficiency if avoid formic acid cycle

Summary of Potential Regeneration Scheme with Et₂NH with Formic and CO₂

Summary of Potential Regeneration Scheme with Et$_2$NH with Formic and CO$_2$

2.x equiv. H$_2$

catalyst

H$_3$NBH$_3$

NH$_3$

$\Delta H = -16.9$ - Et$_2$NH

Et$_2$NH-BH$_3$

S—SnBu$_3$
S—SnBu$_3$

H$_2$

$\Delta H = 4.2$

Bu$_3$SnH

$\Delta H = 13.9$

SH
SH

Et$_2$NH

$\Delta H = 7.9$ -NH$_3$

$\Delta H = -10.8$ { H$_2$ + "[NH$_4$][B(C$_6$H$_4$S$_2$)$_2$]" + }

$\Delta H = -4.5$
(borazine surrogate to only this product)

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Carbene/TCNE Systems for Hydrogen Storage: The "Alabama Approach"

Synthetic Strategy to "Endless" Polymer Developed
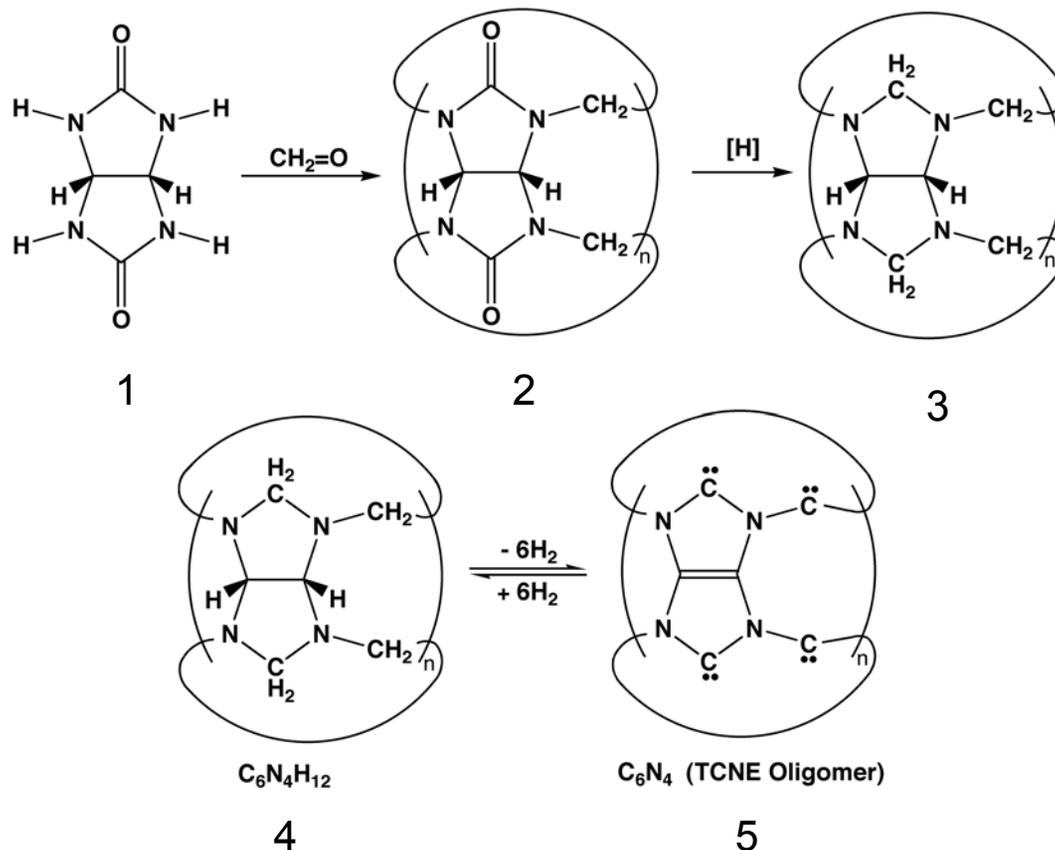
- Cyclization to pure cyclopentamers and cyclohexamers accomplished
- Reduction of Ureas (2) to Aminals(3) Problematic – Different from Unimolecular Models
- New Reduction Methodology under Development to Provide Samples for Testing by Center Partners

Amino(*Imidazolo*)-Boranes

• Imidazole borane chemistry has yielded an imidazole borane adduct that readily releases hydrogen at room temperature.

• Hydrogen release is catalyzed by electrophiles (BH_3) in accord with theoretical models.
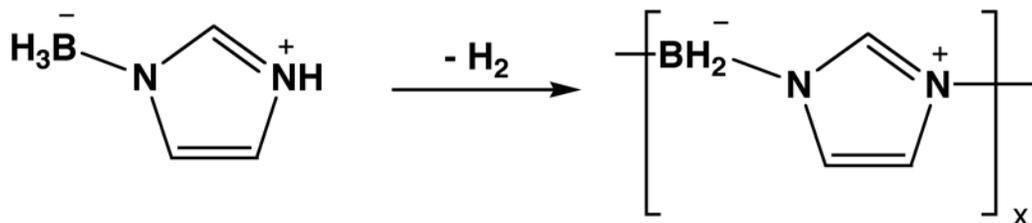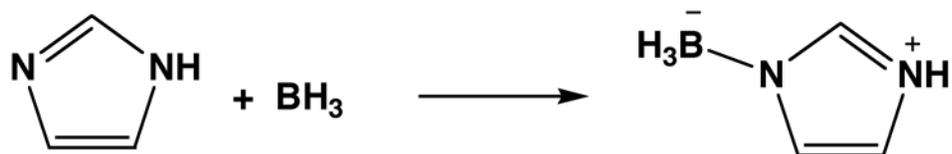
New – Higher Capacity Models Under Development
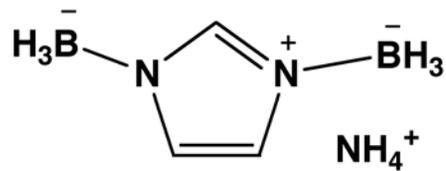
Potential for co-additive to produce liquid fuels – like methyl substituted amine boranes.

Future Work

- Continue to support overall center efforts in H_2 release, AB regeneration, new storage concepts including alternative inorganic and organic compounds and mechanisms.
  - Use density functional theory (DFT) benchmarked by accurate methods.
  - Calculate thermodynamics and kinetics.
  - Predict reaction mechanisms and efficiencies.
- Computational design of new catalysts including acid/base catalysts (Lewis acidities, hydride affinities, proton affinities) and transition metal catalysts. Release and regeneration.
- Regeneration mechanisms. Predict energetics and kinetics of key steps (examples: digestion, reduction, etc.) to optimize experimental approach.
- Ammonia borane chemistry – new metal/main group BNH compounds ($E(NH_2BH_3)_m$ for activation & AB polymers from anionic polymerization.
- Further studies of $CBNH_x$ mechanisms.
- Predict spectroscopic properties (nmr, IR/Raman, UV-vis) for use in analyzing experimental data.
- Improve % H_2 by mass stored in carbene/TCNE systems and in Amino(*Imidazolo*)-Boranes by reducing substituent mass.
- Improve kinetics for release and regeneration of H_2 for carbene/TCNE systems and in Amino(*Imidazolo*)-Boranes.

Collaborations

The UA team is involved in extensive collaborations with Center partners as outlined in the presentation especially in the use of computational chemistry to support Center goals. The UA computational effort is fully integrated with the Center partners.

Examples:

External computational collaborations
- Energetics for AB compounds: LANL, PNNL, Penn
- Release and regeneration mechanisms: LANL, PNNL, Penn, UC-Davis, UW
- Polymerization mechanisms: LANL, PNNL, Penn
- Catalyst design: Center
- Spectroscopic predictions: Center
- Boron hydride anions: U. Missouri
- Nanoparticles & main group chemistry: UC-Davis
- $C_xB_yN_zH_{12}$ thermodynamics: UW & new Center collaborators
- $(E(NH_2BH_3)_m$ thermodynamics & kinetics: U. Mo. & new Center collaborators

Experimental collaborations
- Organic/main group chemistry: LANL

UA Summary

• **Relevance:** Develop new materials for chemical H_2 storage to meet DOE needs. Address issues of System Cost, System Weight and Volume, and Spent Fuel Regeneration.

• **Approach:** Develop promising approaches to chemical H_2 storage for current and future DOE targets using computational chemistry and synthetic organic/inorganic chemistry

• **Technical Accomplishments:** Significant advances in predicting the thermodynamics of new H_2 chemical hydrogen storage systems and for a broad range of regeneration mechanisms. New alane chemistries. Synthesized imidazole borane adduct that readily releases hydrogen at room temperature. Continue TCNE/carbene polymer chemistry integration

• **Collaborations:** Provide computational chemistry support for the DOE Center of Excellence in Chemical Hydrogen Storage. Interact with all partners. Interact closely with LANL on organic chemistry synthetic strategies.

• **Future Research:** Use computational chemistry to support overall Center efforts in H_2 release, spent fuel regeneration, new concepts including alternative inorganic and organic compounds, and mechanisms for H_2 release and regeneration. Improve % H_2 by mass stored and kinetics for H_2 release for main group substituted organic compounds.

UA Summary Table

Storage Parameter: DOE 2010 System Targets	Carbene/Cyanocarbon	Imidazolo Borane
Material Gravimetric Capacity: 6 wt%	Current: 2% Ultimate for $C_2N_2H_6$ polymer: 10.3%	Current: 1% Ultimate: 8.1%
Material Volumetric Capacity: 0.045 kg/L	Current: 0.045 Ultimate: 0.098	Current: ~0.02 Ultimate: 0.098
Dehydrogenation Rate 0.02g/s-kW	In progress for polymer	Rate of H_2 release: 9.6 ± 0.5 M-1s-1
Storage Efficiency Center Goal: 50% Near thermoneutral	Exothermic: -5 kcal/mol Ultimate: Thermoneutral	In progress