

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 # **ST30**

Overview

Timeline

- Project start date: Jan. 05
- Project end date: FY10
- Percent complete: 50%

Budget

- Projected total project funding:
\$2,288,053
 - DOE share: \$1,540,567(requested)
 - UA share: \$747,486
- Funding for FY05: \$431K
\$225K (DOE), \$206K (UA)
- Funding for FY06: \$480K
\$350K (DOE), \$130K (UA)
- Funding for FY07: \$430K
\$300K (DOE), \$130K (UA)

Barriers

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

Partners

DOE Center of Excellence for Chemical Hydrogen Storage: with LANL, PNNL UW, UC-Davis, Penn State, UA, UPenn, Northern Arizona, UCLA, Millenium Cell, Rohm and Haas, and US Borax.

Objectives

- **Develop promising approaches to chemical H₂ storage for future DOE targets.**
- Develop new chemistries to 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.
- Focus on organic and main group compounds to enable new chemistries which may be able to perform better for release and regeneration by improving the energy balance. This will provide longer term alternatives.
- Develop and implement imidazolium (carbene) based H₂ activation chemistry.
- Develop and implement systems based on main group elements. Examples: nitrogen and phosphorus.
- Develop and implement cyanocarbon systems for H₂ storage.
- 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.

Approach

- Develop and identify new concepts to increase capacity and minimize weight (Example: Use storage medium for structural benefits.)
- Develop new concepts to improve energy balance. Especially relevant for ease of H₂ release/regeneration of H₂ storage system.
- Develop new approaches to release hydrogen from dihydroimidazoles, based on new chemistry and our world leadership in stable carbene chemistry.
- Demonstrate proof of concepts and key reactions.
- Key issue is to minimize weight by eliminating substituents or changing them into components that can store H₂ while maintaining kinetic and thermodynamic properties.
- Use highly accurate 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 catalysts to effect easy release and addition of H₂ (regeneration).
- Develop thermodynamic approach for chemical H₂ storage based on exploiting ΔH and ΔG coupled with Le Chatelier's principle to manage H₂ addition and release in chemical compounds.

- **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)

Accomplishments

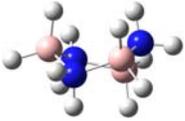
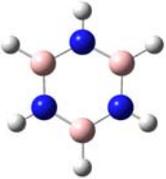
UA Experimental Studies

- Developed first tetracyanoethylene (TCNE) oligomerization procedure for making cyanocarbons for H₂ storage with potential of 11 weight %.
- Continued work on 4-member ring diradicals with P substituents shows H₂ addition and release. Serves as first model for H₂ release from C at room temperature.
- Initial studies demonstrate catalyst photoactivation for H₂ addition to cyanocarbons & carbenes. Potential for widespread applicability.
- Demonstrated weight reduction by oligomerization of carbenes. Demonstrated oxidized and reduced (H₂ on and off) carbenes. Develop mixed carbene/TCNE synthesis to make oligomers.

UA Computational Studies

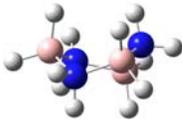
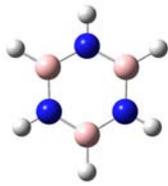
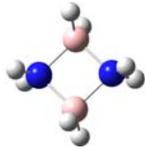
- 1st set of accurate thermodynamics for B_xN_xH_y compounds up to x = 3 and y = 14 for release and regeneration of AB (with PNNL).
- Accurate bond energies for AB (ammonia borane = BH₃NH₃) & derived systems for release and regeneration. (Center)
- H₂ release processes from AB (BH₃ as a Lewis acid catalyst). (LANL + Center)
- H₂ release processes studied via cationic chain polymerization mechanism (with LANL).
- First reliable thermodynamic properties of B₃H₇NH₃ and decomposition mechanism. (Penn)
- Study mechanism of H₂ release from AB dimer (BH₃NH₃)₂ and from zwitterionic isomer [NH₃BH₂NH₃⁺][BH₄⁻] – importance of seeding. (PNNL)
- Methyl substituent effects on energetics of borane amine compounds for release and regeneration (mixed solvents). (LANL, PNNL, UW, Penn, NAU)
- Extensive studies of energetics for H₂ AB regeneration mechanisms. (LANL, PNNL, Penn, UC-Davis, U. Washington).
- Energetics for novel chemical H₂ storage systems: carbenes, cyanocarbons, P-based diradicals.

Thermodynamic Properties of BN Compounds in Different Phases at 298 K (CCSD(T) + Expt)

Compound	Phase	ΔH_f° 298 K kcal/mol	S° 298 K cal/mol·K	Source
BH ₃ NH ₃	gas	-13.5 ± 1.0	57.1	Calc
	solid	-36.6 ± 2.4	23.0	Expt
B ₃ N ₃ H ₁₂	gas	-96.6 ± 1.0	79.3	Calc
	solid	-120.5 ± 4	21.0	ΔH_f° from calc ΔH_f° gas + expt ΔH_{sub} S° from expt Expt
B ₃ N ₃ H ₆	gas	-121.9 ± 3		
	liquid	-129.0 ± 3	47.7	Expt
	gas	-115.5 ± 1.0	68.7	Calc
	liquid	-122.6 ± 1.1		Calc + Expt
	solid	-123.6 ± 1.6		Calc + Expt

First complete set of high level values for use in regeneration and release studies for AB

Accurate Heats of Formation for B-N Compounds

Molecule	$\Delta H_f(0\text{ K})$	$\Delta H_f(298\text{ K})$				
BH ₃ NH ₃	-9.1	-13.5				
2a	-85.3	-96.6				
2b	-84.3	-95.5				
3	-109.3	-115.5				
4	-46.4	-53.6				
5	-79.8	-87.5				
6	-64.1	-71.8				
7	-75.9	-85.3				
8a	-27.4	-35.3				
8b	-39.2	-47.6				
9a	-48.5	-59.9				
9b	-72.1	-84.3				
10	-37.2	-43.9				
11	-52.6	-62.8				
12	-32.2	-41.3				
13	25.4	20.4				
14	-84.6	-91.2				
BH ₂ NH ₂	-15.9	-18.6				

2a

2b

3

4

5

6

7

8a

8b

9b

9a

10

11

12

13

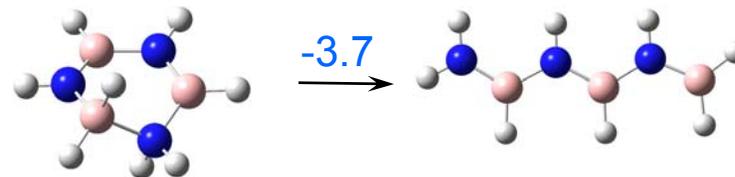
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Accurate Bond Energies for B-N Compounds (in kcal/mol at 298 K)

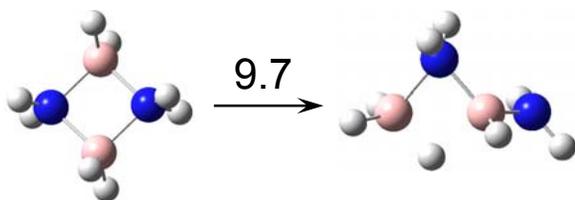
BN Dissociation for Cyclotriborazane



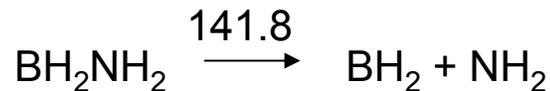
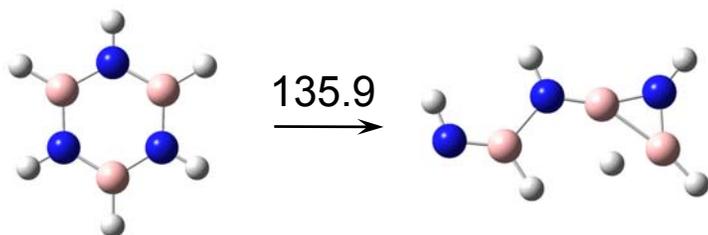
BN Dissociation for 1,2-dihydroborazine



BN Dissociation for Cyclodiborazane

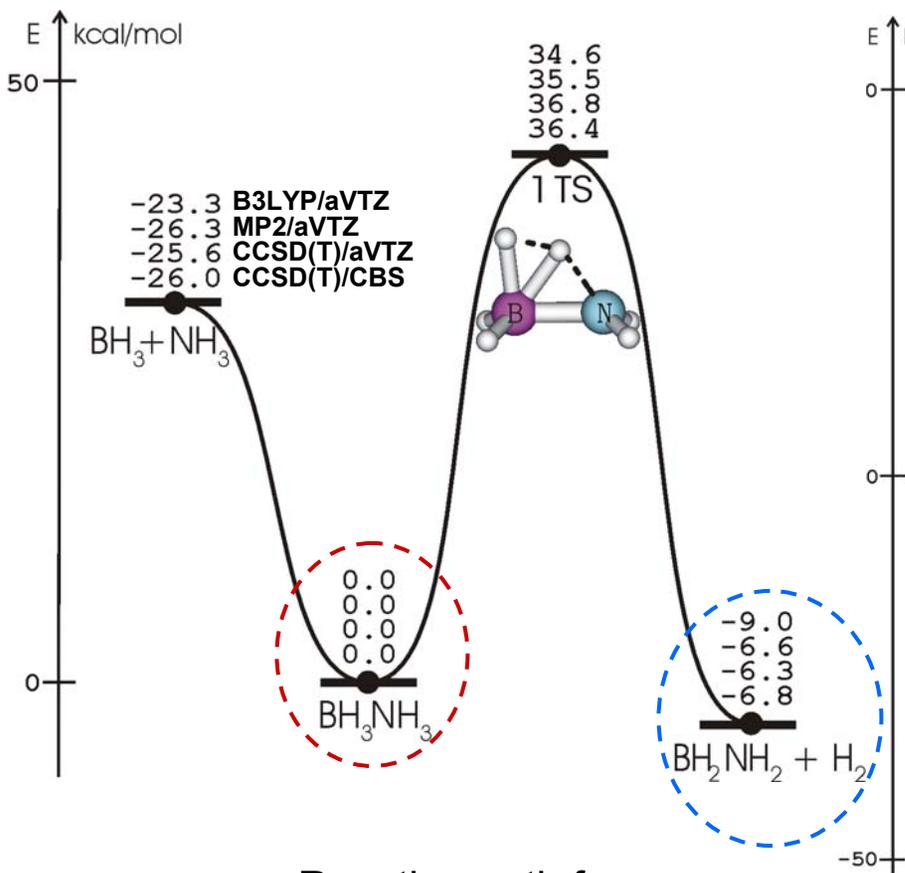


BN Dissociation for Borazine



Bond energies provide insights into mechanism design. Example: First release of H₂ from AB is driven by transition from dative B-N sigma bond to strong B-N sigma bond. Shows inherent instabilities of intermediates. Provides insights into ring formation vs. chain formation.

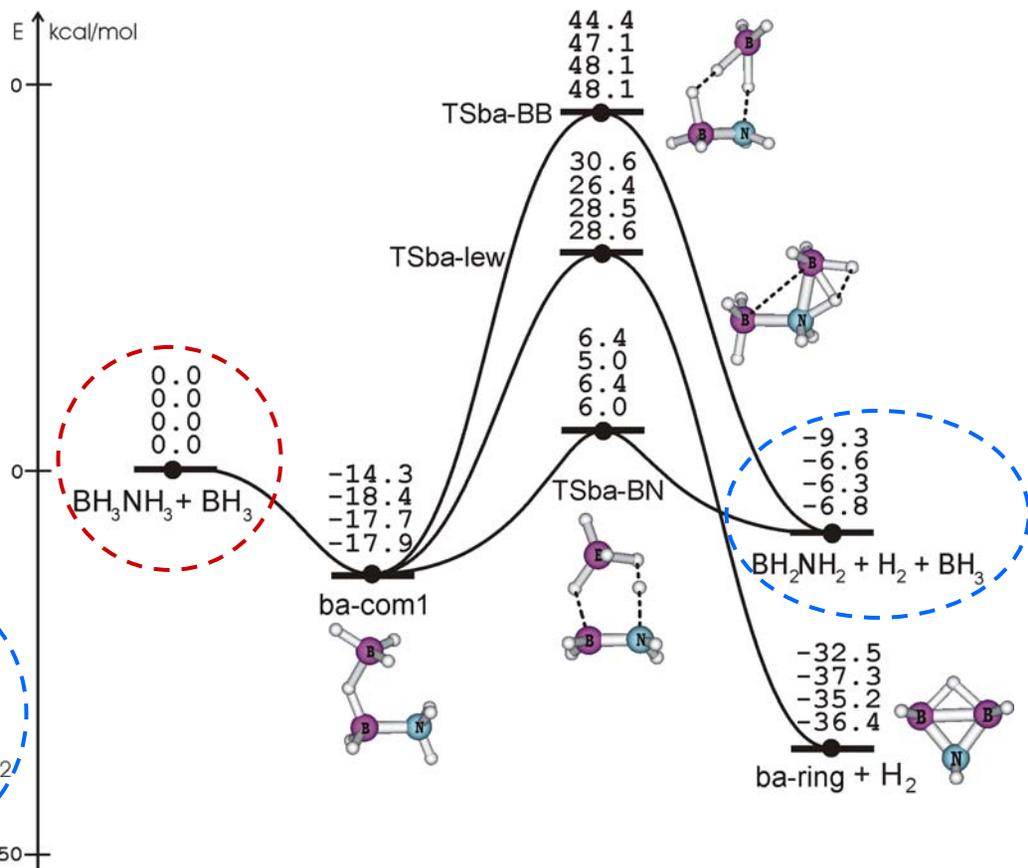
Reaction Pathway for H₂ Generation from BH₃NH₃



Reaction path for



B-N bond cleavage is energetically more favored over the unimolecular H₂ release from borane amine

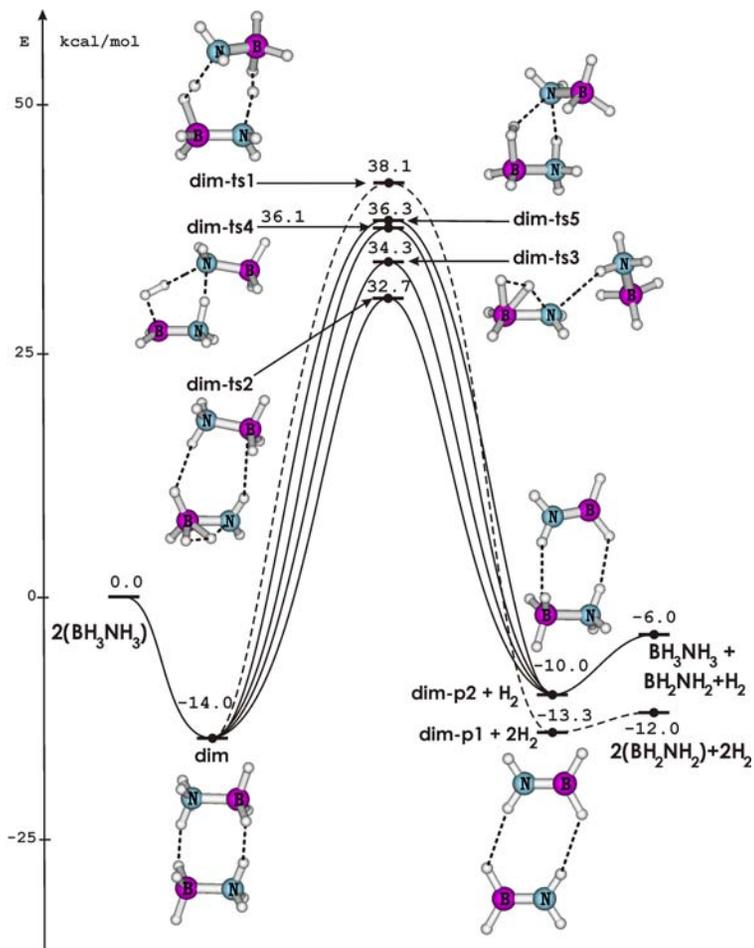


Different reaction paths for

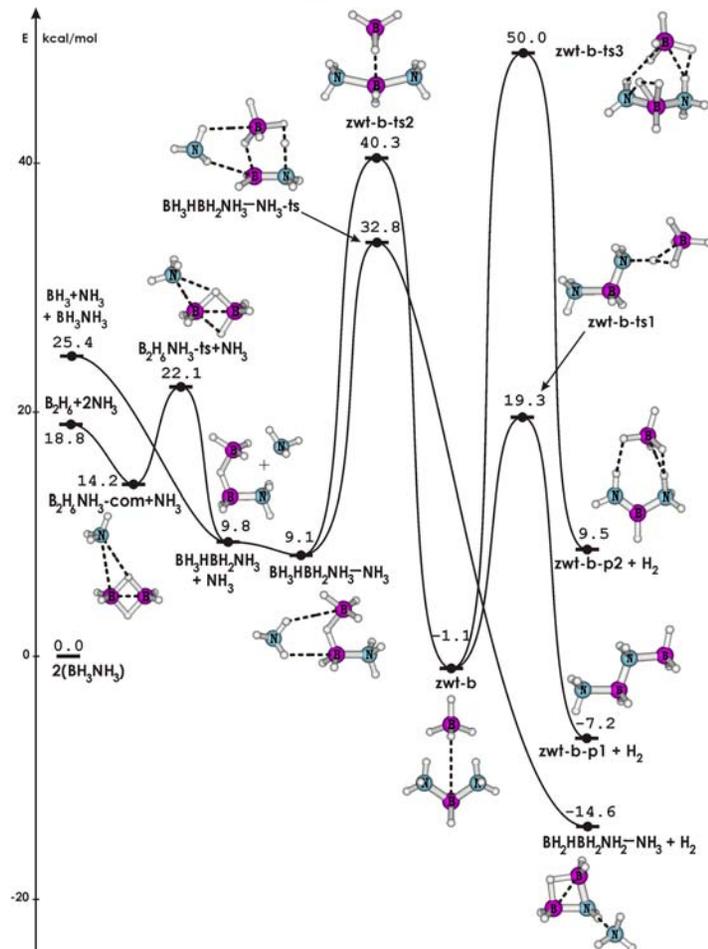


BH₃ can serve as a Lewis acid catalyst for H₂ elimination from BH₃NH₃

H₂ Elimination from (AB)₂



One or two H₂ molecules can be released through direct pathways with barrier heights ranging from 47 to 52 kcal/mol, relative to the dimer and 33 to 38 kcal/mol relative to 2 monomers. Energies are too high for this process to play a role.



[BH₄][NH₃BH₂NH₃]⁺ is ~ 13 kcal/mol less stable than (AB)₂. H₂-release is characterized by a much lower energy barrier of ~ 20 kcal/mol. **Consistent with seeding of AB with the zwitterion leading to improved rates.** No low-energy unimolecular rearrangements connecting AB dimer with zwitterion. 10

Thermodynamics (kcal/mol) of Disproportionation/ Conproportionation Equilibria at 298 K

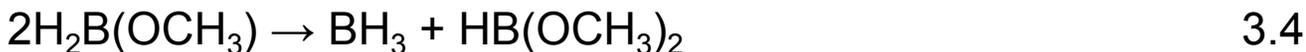
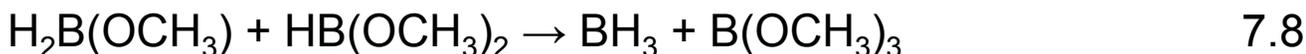
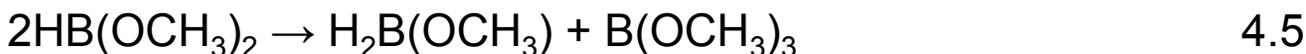
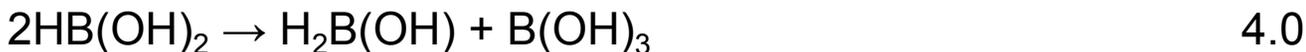
Digestion Reaction	ΔH	
$B_3N_3H_6 + 6HF \rightarrow 3NH_3 + 3HBF_2$	-53.7	
$B_3N_3H_6 + 6HCl \rightarrow 3NH_3 + 3HBCl_2$	38.7	
$B_3N_3H_6 + 6HBr \rightarrow 3NH_3 + 3HBBR_2$	60.5	
$B_3N_3H_6 + 6H_2O \rightarrow 3NH_3 + 3HB(OH)_2$	-30.9	
Disproportionation Reaction		G3MP2
$2HB(OH)_2 \rightarrow H_2B(OH) + B(OH)_3$	3.8	3.8
$H_2B(OH) + HB(OH)_2 \rightarrow BH_3 + B(OH)_3$	4.8	5.5
$2H_2B(OH) \rightarrow BH_3 + HB(OH)_2$	1.0	1.7
$2HB(OCH_3)_2 \rightarrow H_2B(OCH_3) + B(OCH_3)_3$		3.2
$H_2B(OCH_3) + HB(OCH_3)_2 \rightarrow BH_3 + B(OCH_3)_3$		6.9
$2H_2B(OCH_3) \rightarrow BH_3 + HB(OCH_3)_2$		3.7
$2HB(NH_2)_2 \rightarrow H_2B(NH_2) + B(NH_2)_3$	6.0	
$H_2B(NH_2) + HB(NH_2)_2 \rightarrow BH_3 + B(NH_2)_3$	19.2	
$2H_2B(NH_2) \rightarrow BH_3 + HB(NH_2)_2$	13.3	

Use as input for the experimental design of reaction steps. Reactions involving OR lead to exothermic or thermoneutral reactions. Need to form NH_4X for halogens.

Disproportionation Chemistry (kcal/mol)

B3LYP/DGDZVP2

ΔH (0K)



Optimize substituents on O for digestion reactions.

Optimize Regeneration Schemes 298 K (kcal/mol)

	ΔH
(1) $\frac{1}{3}(\text{B}_3\text{N}_3\text{H}_6) (\text{s}) + 4\text{HBr} (\text{g}) \rightarrow \text{NH}_4\text{Br} (\text{s}) + \text{BBr}_3 (\text{l}) + \text{H}_2 (\text{g})$	-45.8
(2) $\text{BBr}_3 (\text{l}) + 3 \text{HSn}(\text{Bu})_3 (\text{l}) + \text{NH}_3 (\text{g}) \rightarrow \text{BH}_3\text{NH}_3 (\text{s}) + 3\text{BrSn}(\text{Bu})_3 (\text{l})$	-82.8
(3) $\text{NH}_4\text{Br} (\text{s}) \rightarrow \text{HBr} (\text{g}) + \text{NH}_3 (\text{g})$	45.1
(4) $3\text{BrSn}(\text{nBu})_3 (\text{l}) + 3\text{H}_2 (\text{g}) \rightarrow 3\text{HBr} (\text{g}) + 3\text{HSn}(\text{nBu})_3 (\text{l})$	88.2
Overall reaction: $\frac{1}{3}(\text{B}_3\text{N}_3\text{H}_6) (\text{s}) + 2\text{H}_2 \rightarrow \text{BH}_3\text{NH}_3(\text{s})$	$\Delta H = 4.7$

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

$$(2 \times 58) / (3 \times 58 + 133 - (x\%)129) = 0.38 \text{ for } 0\% \text{ heat recovery}$$

↑	↑	↑	↑	↑
More H ₂ release	use less H ₂	Lower endo- thermics	Improve heat recovery	Raise efficiency

	ΔH
(1) $\frac{1}{3}(\text{B}_3\text{N}_3\text{H}_6) (\text{s}) + 4\text{HCl} (\text{g}) \rightarrow \text{NH}_4\text{Cl} (\text{s}) + \text{BCl}_3 (\text{l}) + \text{H}_2 (\text{g})$	-47.8
(2) $\text{BCl}_3 (\text{l}) + 3 \text{HSi}(\text{Et})_3 (\text{l}) + \text{NH}_3 (\text{g}) \rightarrow \text{BH}_3\text{NH}_3 (\text{s}) + 3\text{ClSi}(\text{Et})_3 (\text{l})$	-77*
(3) $\text{NH}_4\text{Cl} (\text{s}) \rightarrow \text{HCl} (\text{g}) + \text{NH}_3 (\text{g})$	42.1
(4) $3\text{ClSi}(\text{Et})_3 (\text{l}) + 3\text{H}_2 (\text{g}) \rightarrow 3\text{HCl} (\text{g}) + 3\text{HSi}(\text{Et})_3 (\text{l})$	88*

Optimize reaction energies and provide limitations to processes

B-H & Si-H Bond Energies (kcal/mol)

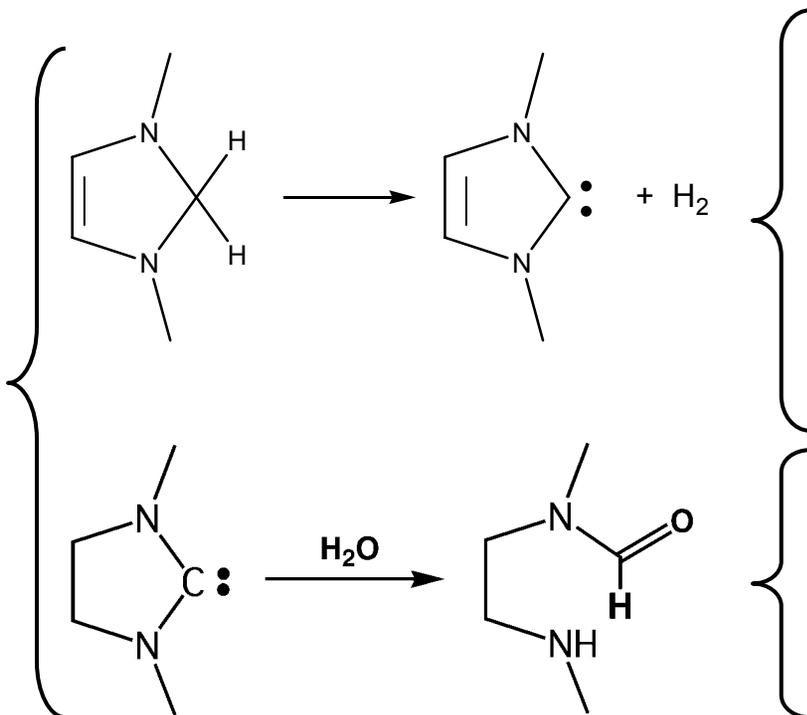
Molecule	ΔH_f	$D_e(\text{B-H})$ CCSD(T)/CBS	$D_e(\text{Si-H})$
BH ₂ SiH ₃	41.4	101.1	76.4
HBSiH ₃	90.8		
H ₂ BSiH ₂	66.2		
H ₃ BSiH ₃ ⁻	-14.9		
Isodesmic reactions			
BH(SiH ₃) ₂	55.4	96.4(95.5)	76.0(74.6)
B(SiH ₃) ₂	100.2		
HB(SiH ₃)(SiH ₂)	79.7		
B(SiH ₃) ₃	68.7		74.9(73.2)
B(SiH ₃) ₂ (SiH ₂)	91.9		
H ₂ Si(BH ₂) ₂	72.2	76.2(69.8)	71.9(71.9)
HSi(BH ₂) ₂	92.4		
H ₂ Si(BH ₂)(BH)	96.7		
HSi(BH ₂) ₃	100.4	101.0(100.2)	70.8(72.9)
Si(BH ₂) ₃	119.6		
HSi(BH ₂) ₂ (BH)	149.8		
Si(BH ₂) ₄	131.1	99.9(99.3)	
Si(BH ₂) ₃ (BH)	179.3		

- B-H bond energies are larger than Si-H bond energies for most molecules. B-H bond energies have more dependence on structure. Regeneration with Si nanoparticles.
- Si-H bond energies are not strongly dependent on substituent.
- Calculate activation energy to remove H₂ from Si_xH_y clusters and doped clusters. What is the role of strain?

The heats of formation for the molecules BH₂SiH₃, HBSiH₃, H₂BSiH₂, and H₃BSiH₃⁻ CCSD(T)/CBS level. Energies in () are at the G3MP2 level.

Heteroatom Organic Systems for Hydrogen Storage: The “Alabama Approach”

**1,1 -
elimination
to give
carbene
products**



- Hydrogen elimination is symmetric (non-polar (*))
- Metal catalyst required (currently substituents on N, C)
- Endothermic dehydrogenation, $P_{eq} < 1 \text{ atm}$

Ultimate: 7.2 %

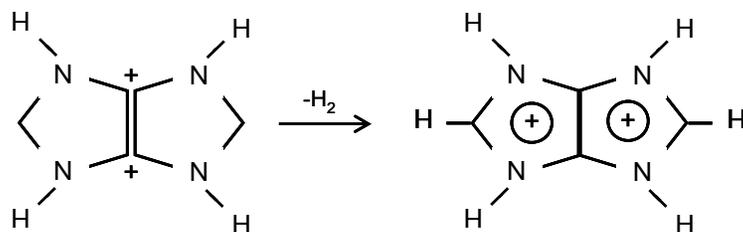
Currently: 2 % (1.8 % with catalyst)

Water reduction - extend range of hydrogen storage in 1,1- and 1,2-elimination systems

Ultimate: 8.0 %

Currently: 0.6 %

**1,5 -
elimination to
give fused
diimidazolium
rings**



- Hydrogen elimination is symmetric (non-polar (*))
- No metal catalyst required (substituents on N, C)
- Endothermic dehydrogenation, $P_{eq} < 1 \text{ atm}$

Ultimate: 7.2%

Currently: 2.5%

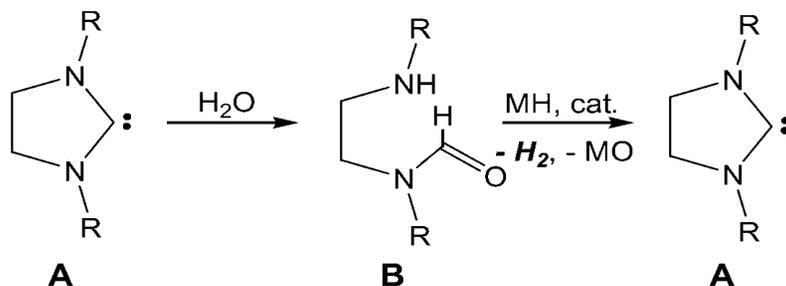
UA Summary Table

Storage Parameter: DOE 2010 System Targets	Carbene	Cyanocarbon	Phosphacarbon*
Material Gravimetric Capacity: 6 wt%	Current: 2% Ultimate: 7.2%	Current: <1% Ultimate**: 7.2%	Current: <1% Ultimate: 5% with P 7.2% by substituting N for P
Material Volumetric Capacity: 0.045 kg/L	Current: 0.045 Ultimate: 0.098	Current: 0.045 Ultimate: 0.092	Ultimate(P): 0.10 Ultimate(N): 0.092
Dehydrogenation Rate 0.02g/s-kW	In progress	Oxidation step diffusion limited	Model study
Storage Efficiency Center Goal: 50% Near thermoneutral	Exothermic: -5 kcal/mol Ultimate: Thermoneutral	Endothermic: 5 kcal/mol Ultimate: Thermoneutral	Model study

* Continue only as a model system to understand release and regeneration

** Ultimate for CN polymer is $C_2N_2H_6 = 10.3\%$

Alternative Approach to Increase H₂ Weight Percent: Incorporate H₂O into the Reduction Cycle



- MH = “metal” or organic hydride
- MO = “metal” oxide
- Works with NaH/LiH/KH at 25°C

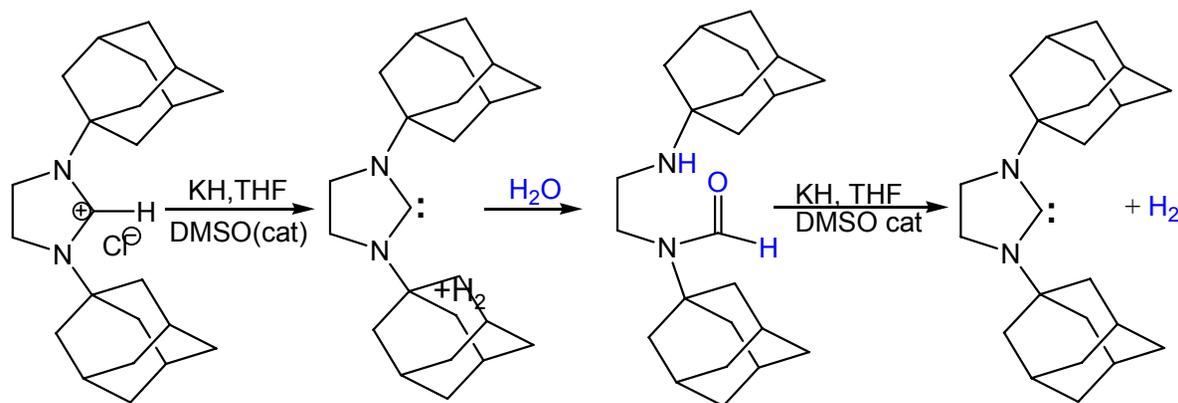
A + H₂O → B (DFT/B3LYP)

B *trans* linear ΔH(298K)= -33.1 ΔG(298K)= -24.4

B *cis* linear ΔH(298K)= -32.4 ΔG(298K)= -23.8

B *trans* twisted ΔH(298K)= -32.2 ΔG(298K)= -22.8

B *cis* twisted ΔH(298K)= -33.1 ΔG(298K)= -24.2



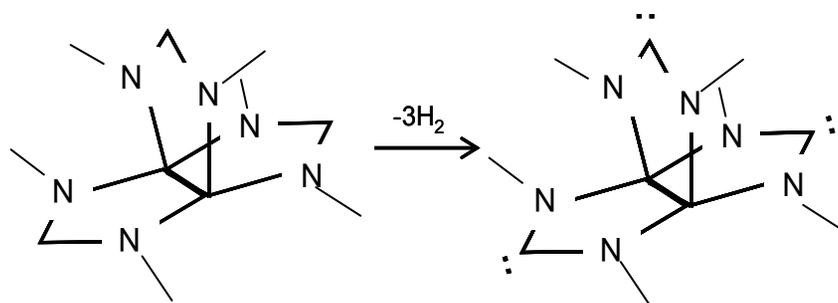
T = 25 °C
80 to 85% yield

Need to eliminate adamantyl substituents due to weight issues. Potentially go to polyethylene diamine.

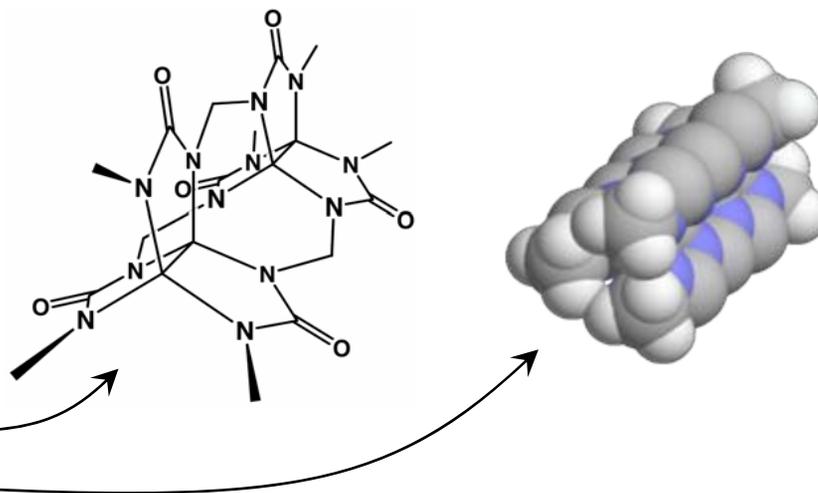
1,1-Elimination for Hydrogen Storage: Increasing Capacity

How to increase capacity by making more effective use of substituents? **2 to 3 ring storage units and oligomerization**

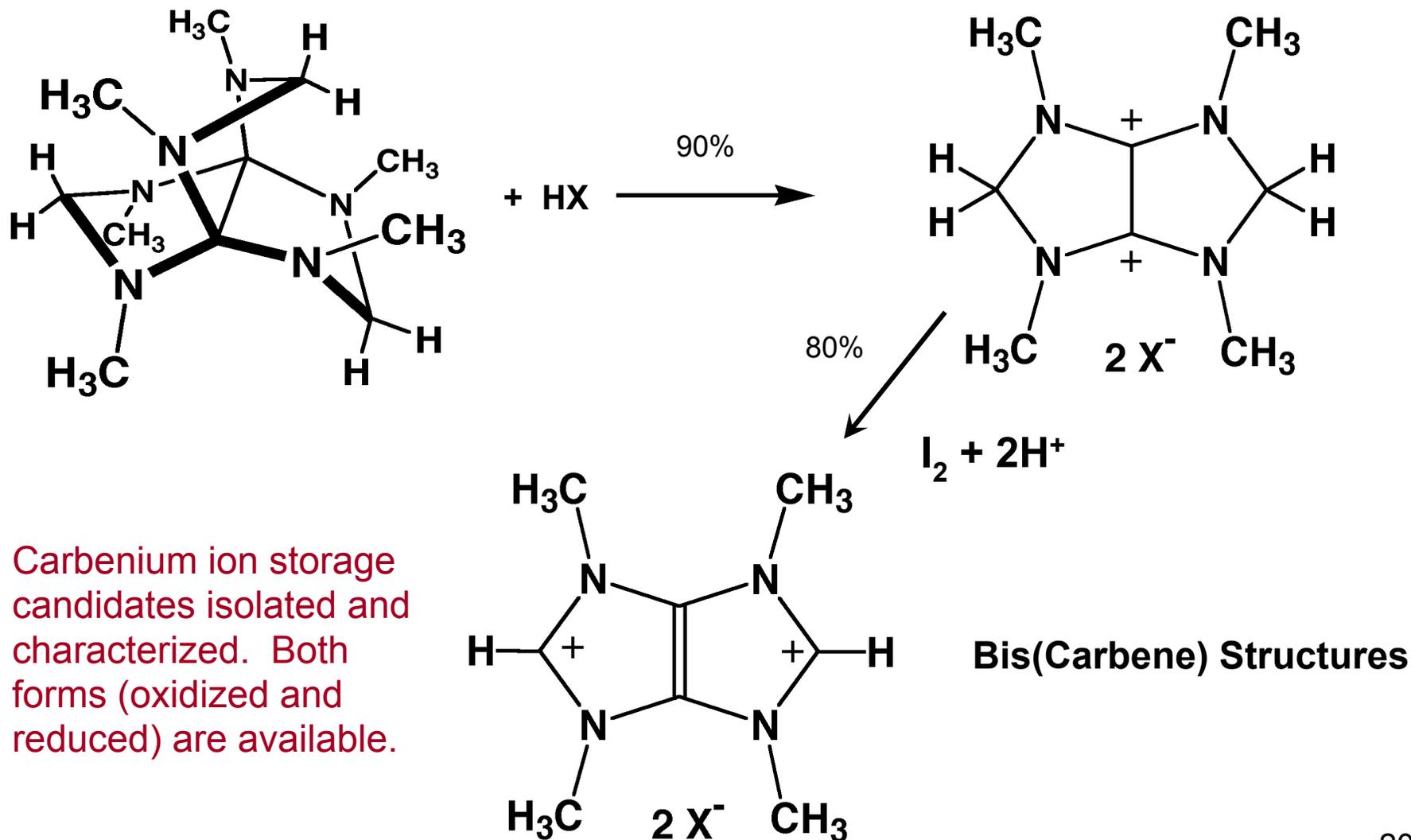
- Fuse 3 dihydroimidazole rings into “propellane” structure.
- Lightest possible material is $C_5H_{12}N_6$, forming $C_5H_6N_6 + 3 H_2$ (3.9 wt %)
- Reaction currently under study for N-substituted analogs



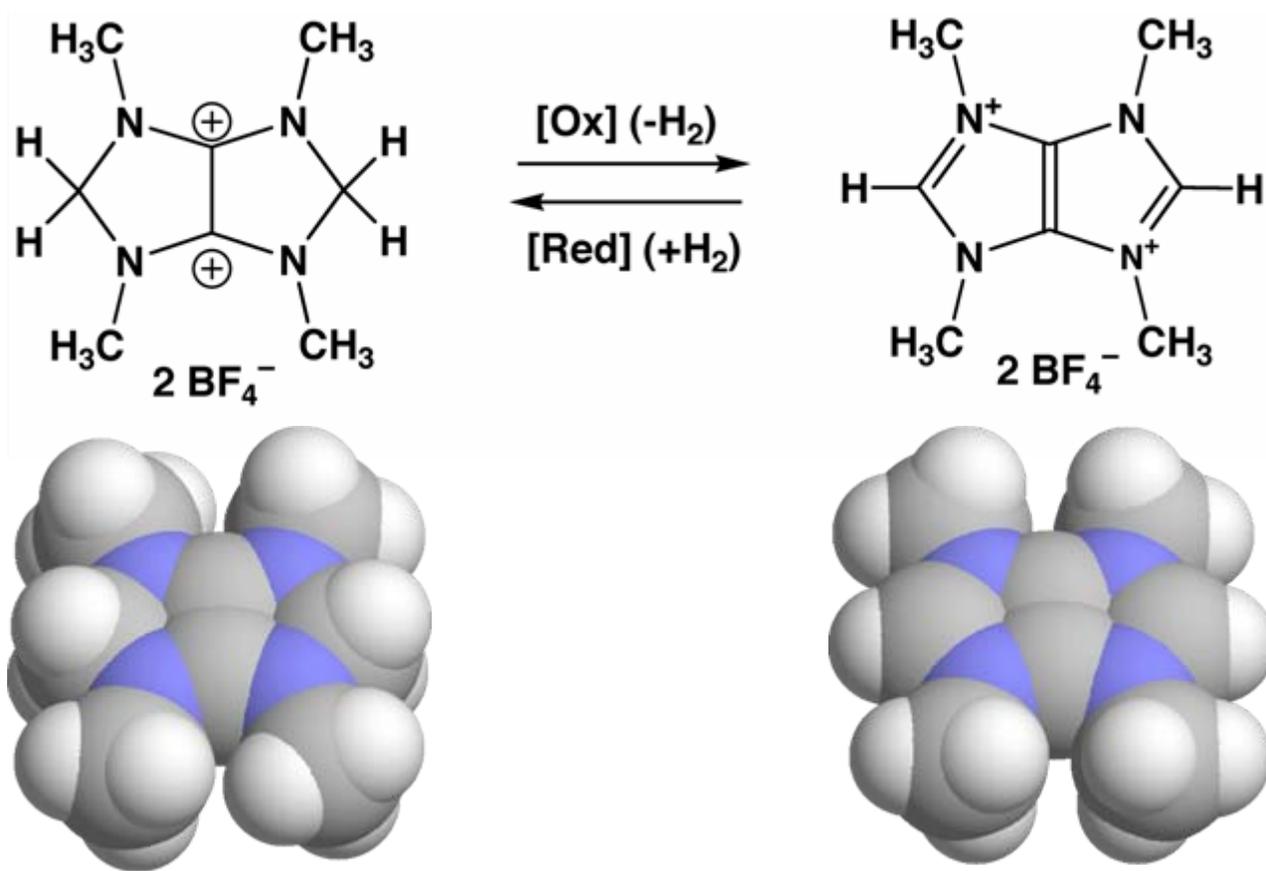
- Ultimate material with lateral condensation with $-CH_2-$ links gives $C_8H_{12}N_6$, forming $C_8N_6 + 6 H_2$ (6.3 wt %)
- Routes to such materials under study. Precursor is urea-based compound
- Poly-carbene product



Alternative Route to Fused Diimidazolium Rings for 1,5 Hydrogen Elimination Reactions

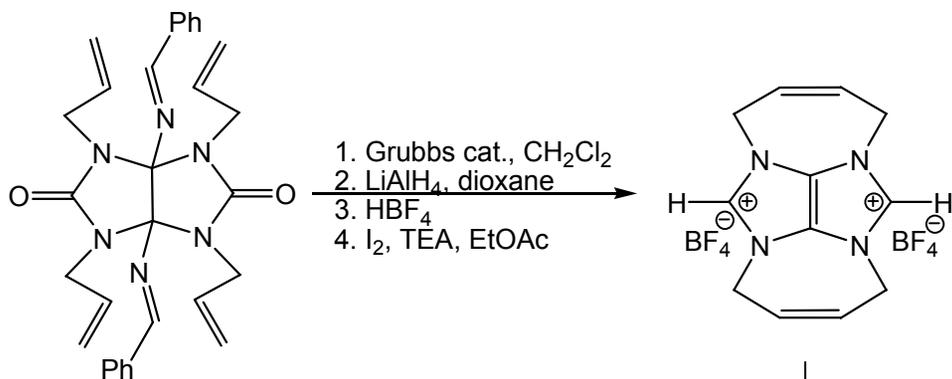


First Crystal Structures of Bis(imidazolium) Ions

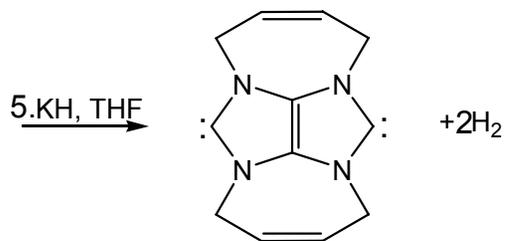


- Demonstrated oxidation to produce HI
- Need to demonstrate complete hydrogenation cycle
- Find appropriate catalyst

Poly-functional Cores for H₂ Storage: Future Focus

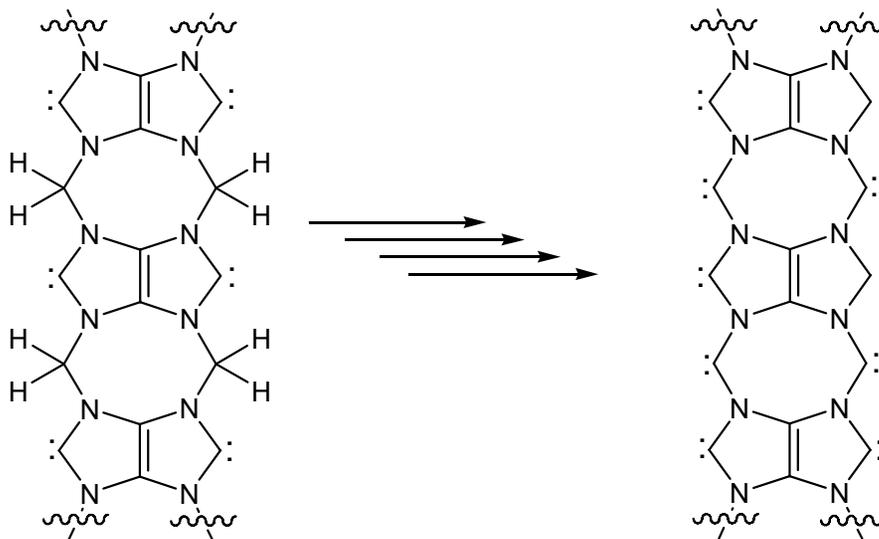


- Steps 1 to 3 demonstrated
- Step 4 done on tricyclic
- Step 5 to be demonstrated



Bis-carbene as
a model for an
extended
polymer

Extended carbene
polymer



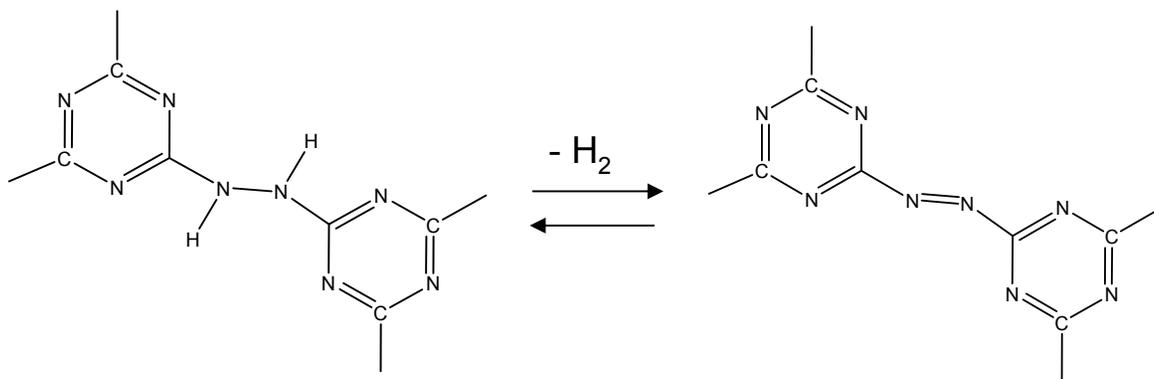
7.2 weight %, oligomer of TCNE (C₆N₄)

Cyanocarbons for Hydrogen Storage

Develop new concept to increase capacity and minimize weight by providing structural benefits

Can we use derivatives of cyanocarbons for chemical H₂ storage systems?

Need to understand chemistry of the azo linkage that appear in cyanocarbon oligomers



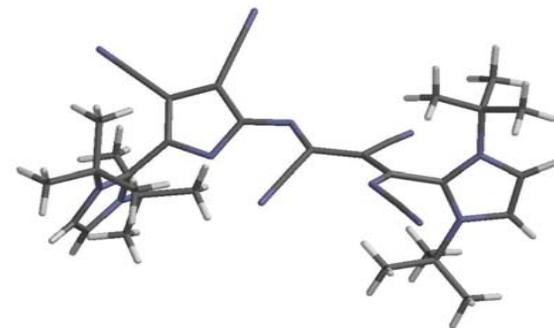
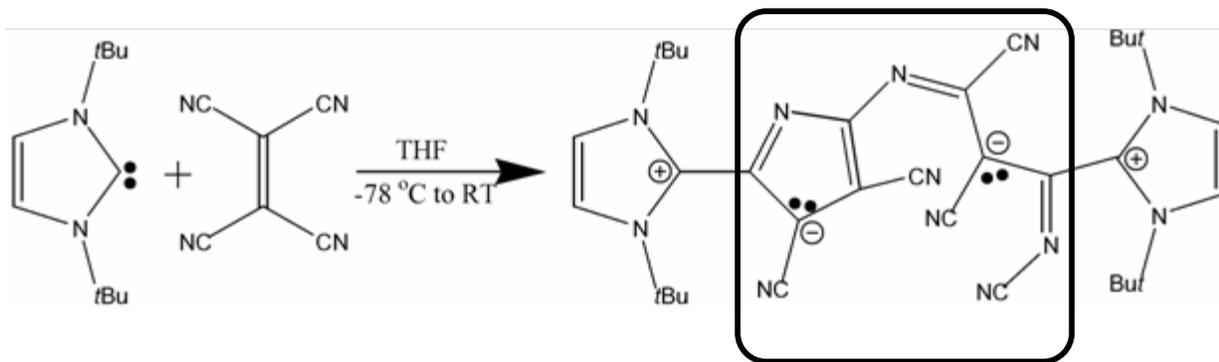
Materials prepared having both hydrazine and triazine moieties

Ultimate: 7.5%
Currently: 0.5%

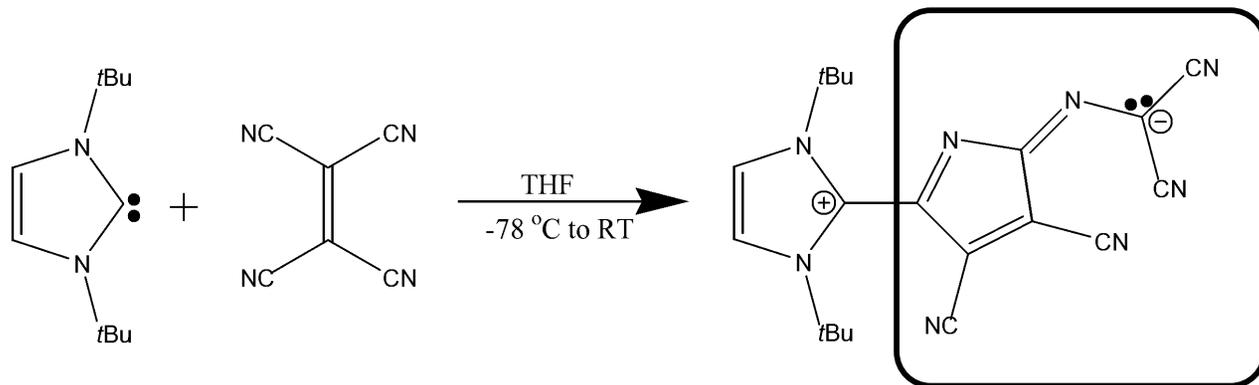
- Polymers based on these moieties, idealized composition: C₃H₉N₆ → C₃N₆ + 4.5 H₂ (7.0 wt % H₂)
- Combines both hexahydrotriazine → triazine, and hydrazo → diaza dehydrogenation concepts, expected to be more robust than unsubstituted hexahydrotriazine
- Expect will have similar needs for effective hydrogenation/dehydrogenation catalysts as hexahydrotriazine
- Substitution of an organic group for the H can dramatically change the energetics making favorable materials for H₂ release



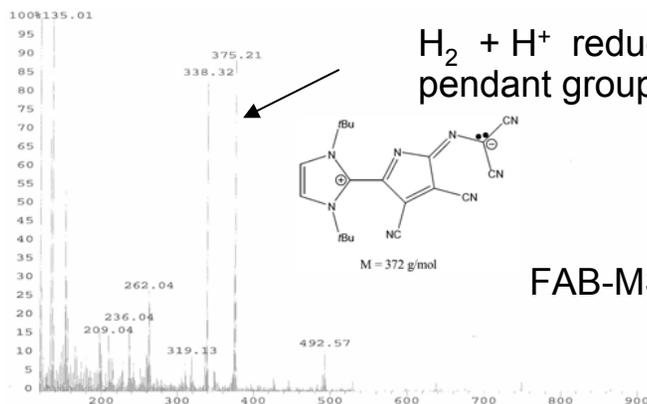
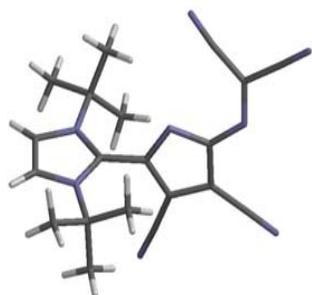
Reactions of Carbenes with TCNE



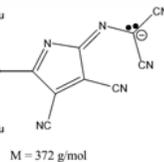
Central polycyanocarbon core designed for easy reduction (H_2 addition)



At longer reaction times dimer dissociates to generate pendant polycyanocarbon carbene • 1.5 TCNE

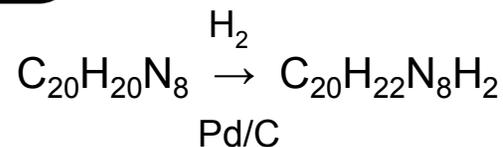


$H_2 + H^+$ reduced pendant group



M = 372 g/mol

FAB-MS



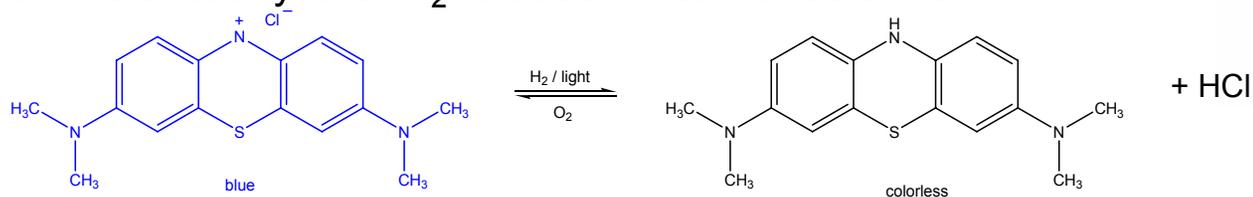
- Control chemistry & improve H_2 storage capacity
- New catalysts

UA: Future Experimental Work

- Synthesize extended carbene polymers (11.1 weight %, oligomer of TCNE (C_6N_4))

- Synthesis: Lower substituent weight % for carbenes

- Non-metal catalyst for H_2 release for carbenes & TCNE

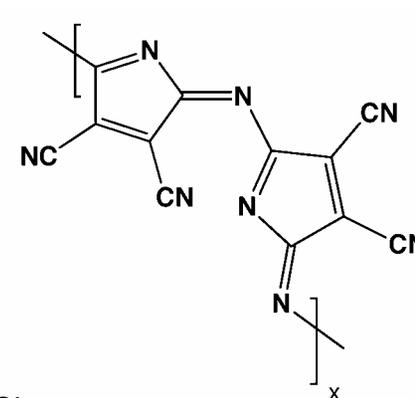


- Start with cyanocarbon radical anion (replaces Cl^- and takes H^+)

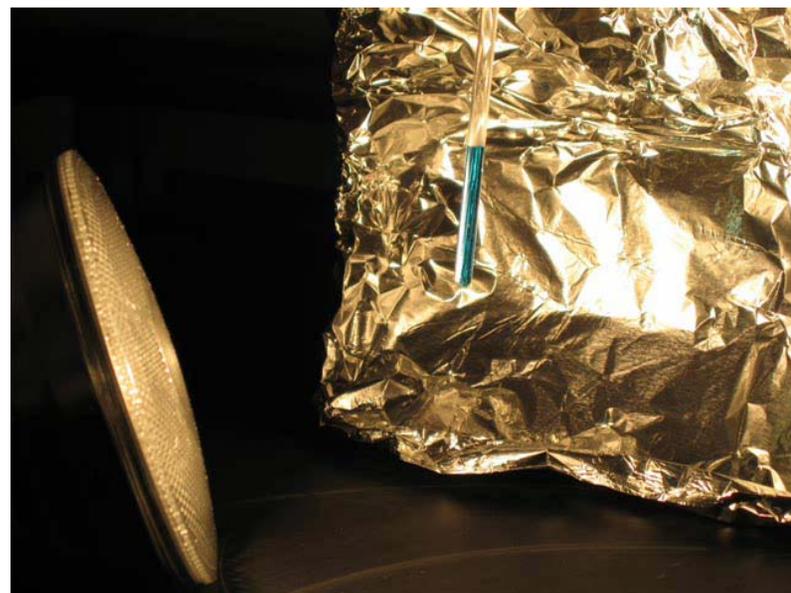
- Leuco-Methylene blue (colorless) delivers H^- to neutral cyanocarbon to form dihydrogenated anion and catalytic cycle restarts.

- Synthesize extended oligocarbene polymers from carbene chemistry

- Continue catalyst design for H_2 release for carbenes



+ HCl



Future Computational Work: Examples

- Continue to support overall center efforts in H₂ release, AB regeneration, new 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.
- Hydrogenation of TCNE. Which sites in what order? Hydrogenation of polycarbene- how?
- Release of H₂ from silanes for modeling nanocluster chemistry for regeneration.
- Computational design of new catalysts including acid/base catalysts (Lewis acidities, hydride affinities, proton affinities) and transition metals. Release and regeneration.
- B-H regeneration. Predict energetics and kinetics of key steps (examples: digestion, reduction, etc.) to optimize experimental approach.
- Predict spectroscopic properties (nmr, IR/Raman, UV-vis) for use in analyzing experimental data.
- Develop improved reaction mechanisms based on predictions of reaction kinetics to optimize processes.
- Ammonia borane/ammonia triborane reactions – AB polymers from anionic polymerization.