

# 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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# Overview

## Timeline

- Project start date: Jan. 05
- Project end date: FY10
- Percent complete: 40%

## Budget

- Projected total project funding:  
\$1,780,690
  - DOE share: \$1,273,711(requested)
  - UA share: \$506,979
- Funding for FY05: \$431K  
\$225K (DOE), \$206K (UA)
- Funding for FY06: \$430K  
\$300K (DOE), \$130K (UA)

## Barriers

DOE Barriers addressed

- Cost
- Weight and Volume
- Efficiency
- Regeneration

## Partners

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

# Objectives

- 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
- Develop and implement imidazolium-based H<sub>2</sub> activation chemistry
- Develop and implement systems based on polyhydrides of main group elements: phosphorus, boron, nitrogen
- Develop and implement cyanocarbon systems for H<sub>2</sub> 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 new materials and develop materials that meet the 2010 and 2015 DOE objectives.

# Approach

- Use novel chemistry approaches to synthesize compounds for easily reversible addition/elimination of  $H_2$  based on our novel, stable carbene chemistry for use in  $H_2$  storage systems.
- Develop new synthetic approaches to use organo-nitrogen compounds for hydrogen storage. Potential weight savings by using storage media as structural material
- Use 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  $H_2$ .
- Develop thermodynamic approach for chemical  $H_2$  storage based on exploiting  $\Delta H$  and  $\Delta G$  coupled with Le Chatelier's principle to manage  $H_2$  addition and release in chemical compounds. Potential solution for cold-start issues and regeneration. Develop kinetic models for hydrogen storage, release, and material regeneration.

# Partnerships/Collaborations

- Los Alamos National Laboratory (LANL)
  - Coordinate on the design, synthesis and characterization of new organic compounds with higher H<sub>2</sub> storage capability
  - Computational chemistry predictions for borane-amine chemistry
  - Computational chemistry predictions of regeneration reaction pathways

## Pacific Northwest National Laboratory (PNNL)

- Computational chemistry predictions for borane-amine chemistry

## Penn State University and the University of Pennsylvania

- Computational chemistry predictions for borane-amine chemistry and prediction of nmr chemical shifts

## University of California – Los Angeles

- Computational chemistry predictions of borane chemistry – heats of formation

## University of California – Davis

- Computational chemistry predictions of boron/silicon bond energies

# UA Experimental Technical Accomplishments

- Carbenes

Structural characterization of an imidazolium borohydride.

Formation of carbene·H<sub>2</sub> adducts.

Carbenium ions isolated in both reduced (hydrogen storage) and oxidized (hydrogen released forms).

Polycarbene architecture synthesized.

- Cyanocarbons

Model compound available for cyanocarbon·H<sub>2</sub> adducts.

New pyridazine hydrogen storage candidate isolated.

- Phosphocarbons

Room temperature (uncatalyzed) hydrogen uptake achieved.

# UA Computational Technical Accomplishments

## Borane-amine mechanisms

- First reliable predictions of the energetics of borane amine molecules
- Developed model of the chemical bonds and bond energies in borane amines
- First predictions of borane amine reaction dehydrogenation kinetics
- Identified bridging intermediate in borane-amine polymerization mechanism based on calculated nmr chemical shifts
- Studied isoelectronic compounds
- Full configuration interaction calculations on states of diatomics
- Predicted heats of formation of borane amine salts including  $B_{12}H_{12}^{2-}(NH_4^+)_2$

## Borane-amine regeneration chemistry

- First predictions of energetics for regeneration reactions

## Carbene and cyanocarbon chemistry

- First reliable predictions of the energetics of carbenes. Discovered new scale for defining carbene reactivity
- First reliable predictions of the energetics of model nitrogen based compounds. Discovered important effect of organic substituents in making  $H_2$  release energetics more favorable.

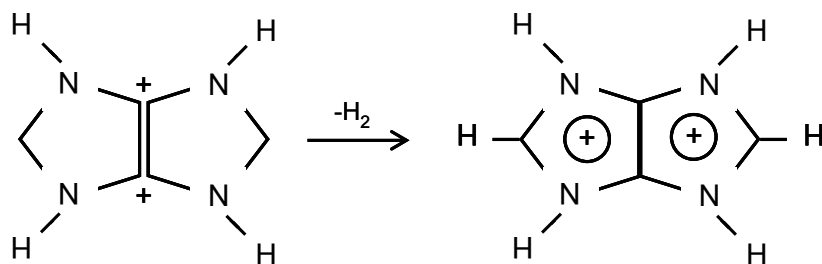
## BH/SiH bond energies

- First reliable predictions of the bond energies in B/Si compounds

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

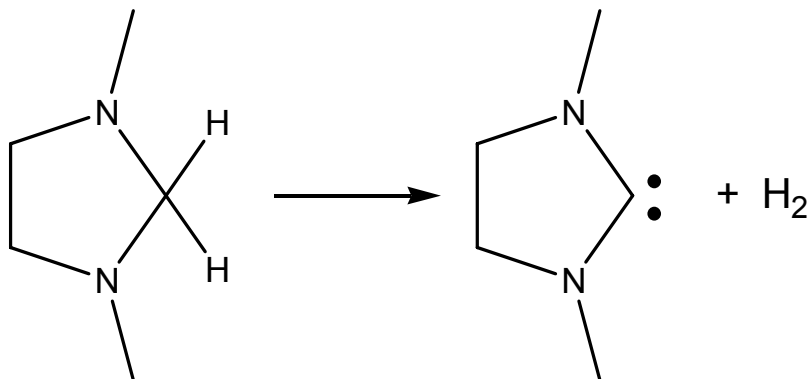
**Developed new approaches to release hydrogen from dihydroimidazoles, based on new chemistry and our world leadership in stable carbene chemistry**

1,5 elimination to give fused diimidazolium rings:



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

1,1 elimination to give carbene products:



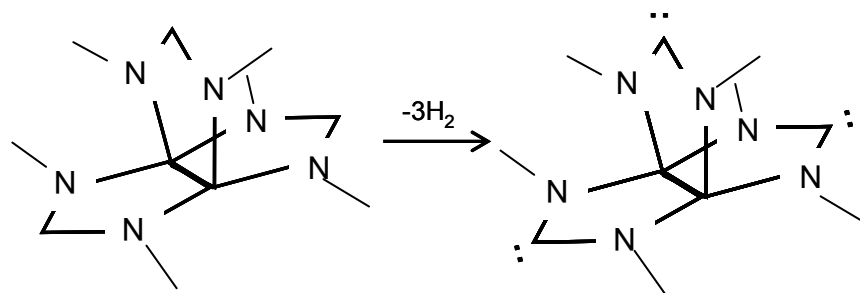
- Hydrogen elimination is symmetric (non-polar (\*))
- Metal catalyst required (substituents on N, C)
- Endothermic dehydrogenation,  $P_{eq} < 1 \text{ atm}$



# 1,1-Elimination for Hydrogen Storage: Increasing Capacity

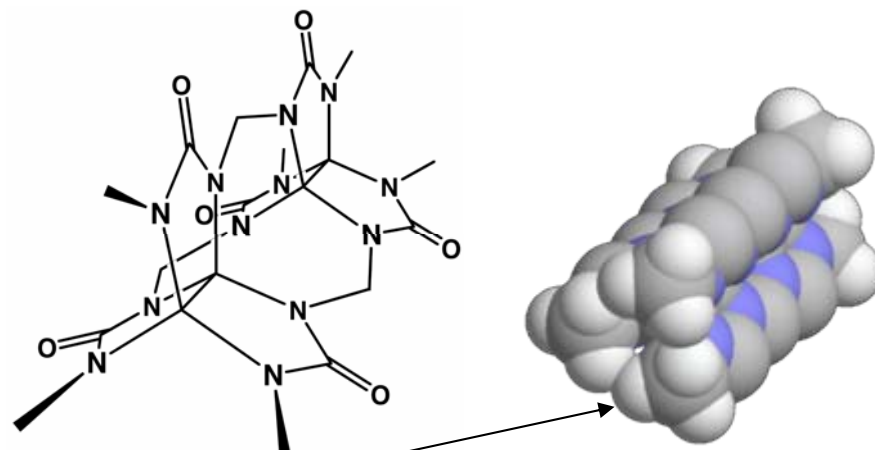
## Developed new chemistry concept to increase capacity

- Fusing 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



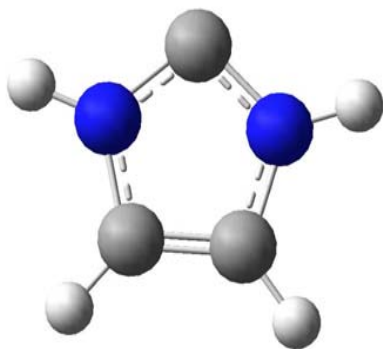
Ultimate goal:

- Lateral condensation with  $-CH_2-$  links -gives material  $C_8H_{12}N_6$ , forming  $C_8N_6 + 6 H_2$  (6.3 wt %)
- Routes to such materials under study;  
- one possible precursor is the urea compound
- Designed poly-carbene product

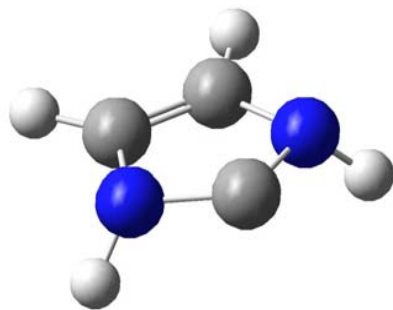


# Carbenes for H<sub>2</sub> Storage Systems

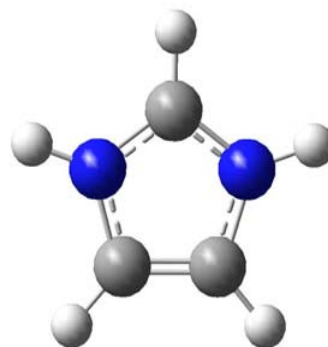
Showed that carbon-based systems exist that have more accessible CH bonds than traditional hydrocarbons:  $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$   $\Delta\text{H}(298) = 32.6 \text{ kcal/mol}$



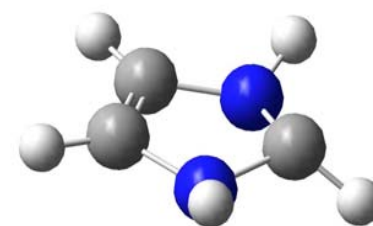
carbene



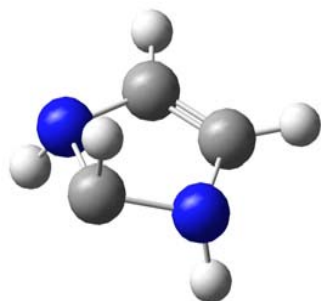
<sup>3</sup>carbene



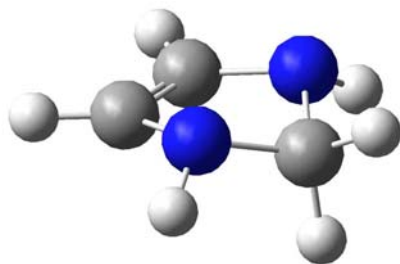
carbeneH<sup>+</sup>



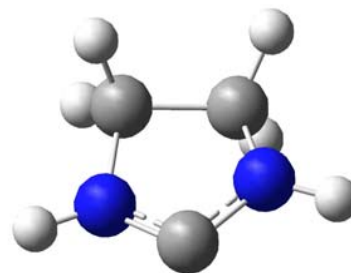
carbeneH



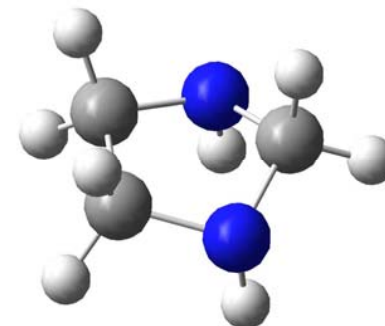
carbeneH<sup>-</sup>



carbeneH<sub>2</sub>



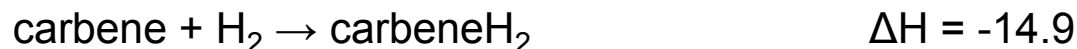
carbeneH<sub>6</sub>



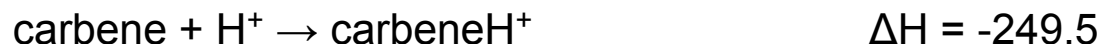
carbeneH<sub>8</sub>

Based on Arduengo's stable carbene

# Carbene Reaction Energetics for H<sub>2</sub> storage at 298K in kcal/mol to $\pm 1$ kcal/mol



Adding H<sub>2</sub> to the carbene is exothermic by 14.9 kcal/mol -- very nice in managing release because we can use  $\Delta G$  to pull it off using Le Chatelier's Principle.  $T\Delta S(298\text{K}) = +8.2$  kcal/mol



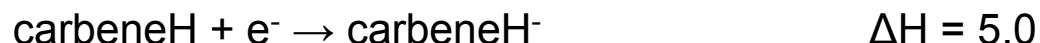
The PA of the simplest carbene is 249.1 kcal/mol. Very basic!



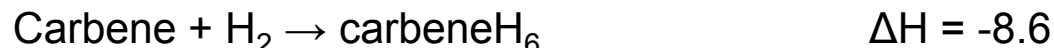
The singlet triplet splitting of the carbene is very large!



The C-H bond energy for adding an H to the carbene shows a weak C-H bond.



Addition of H<sup>-</sup> to the simplest carbene leads to autodetachment of the e<sup>-</sup>.

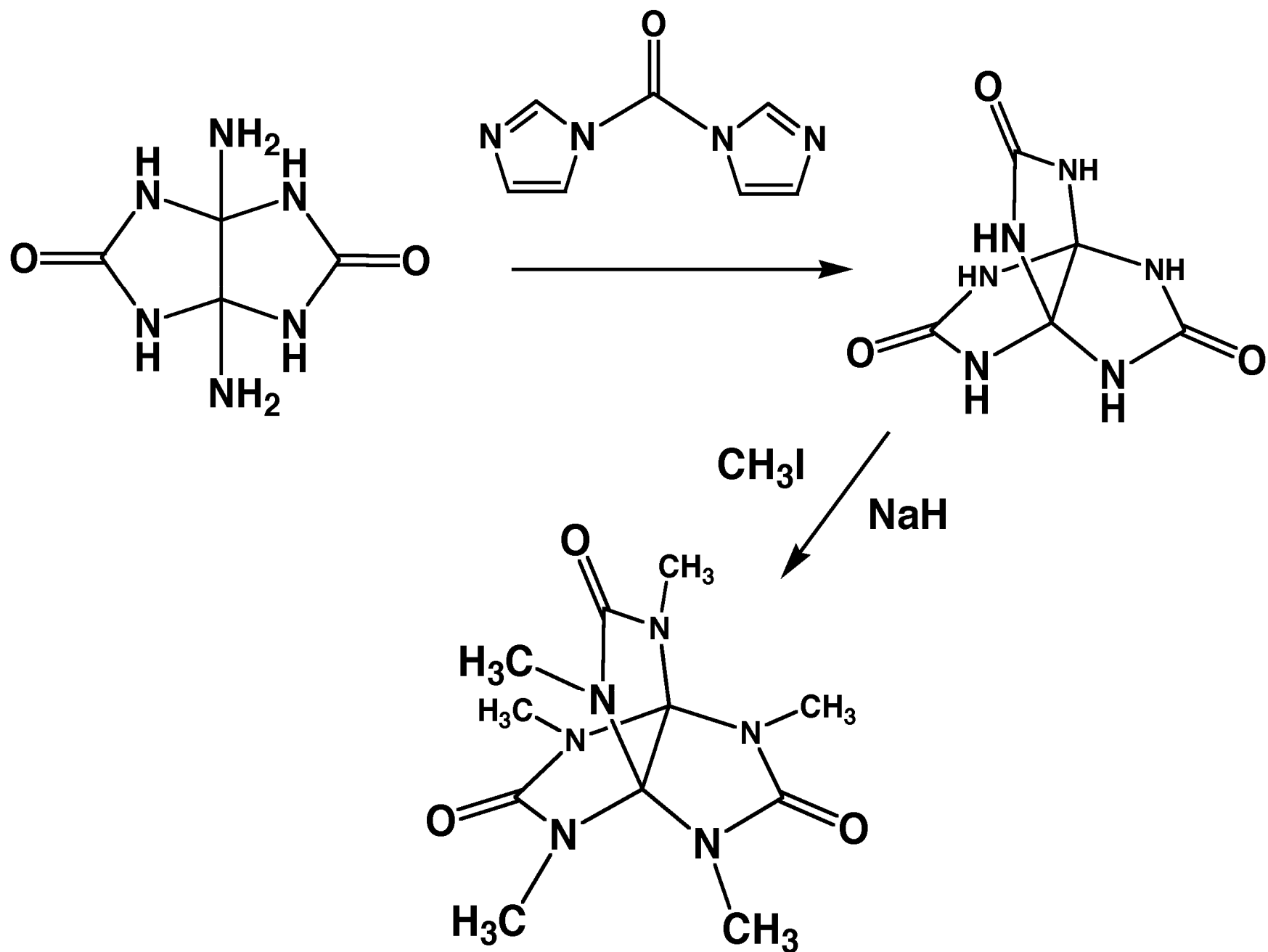


Adding H<sub>2</sub> to hydrogenate the double bond is exothermic by only 9 kcal/mol as compared to -31 kcal/mol for hydrogenation of C<sub>2</sub>H<sub>4</sub>.

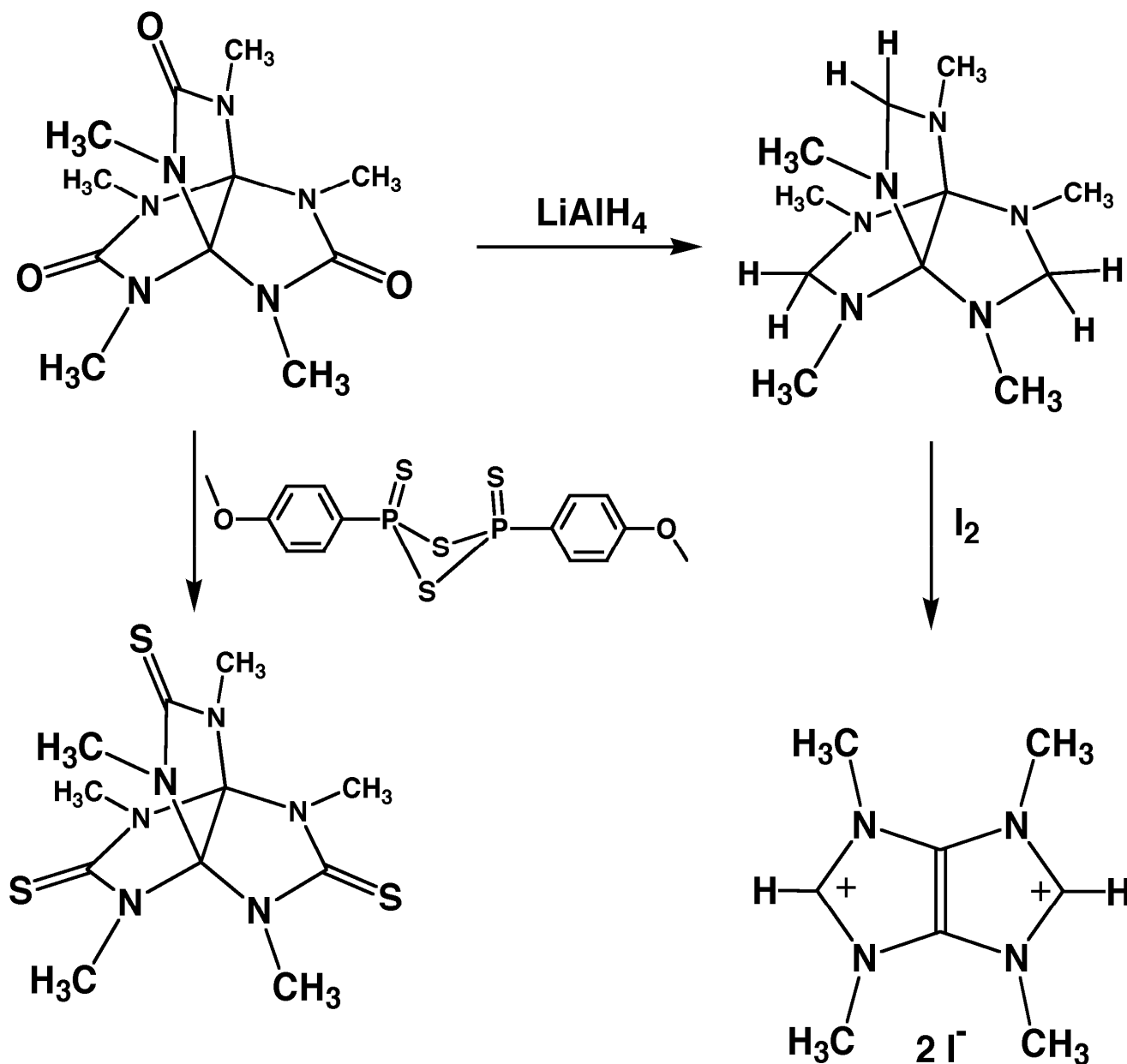


Adding H<sub>2</sub> to the hydrogenated carbene is quite exothermic – develop carbene reactivity scale.

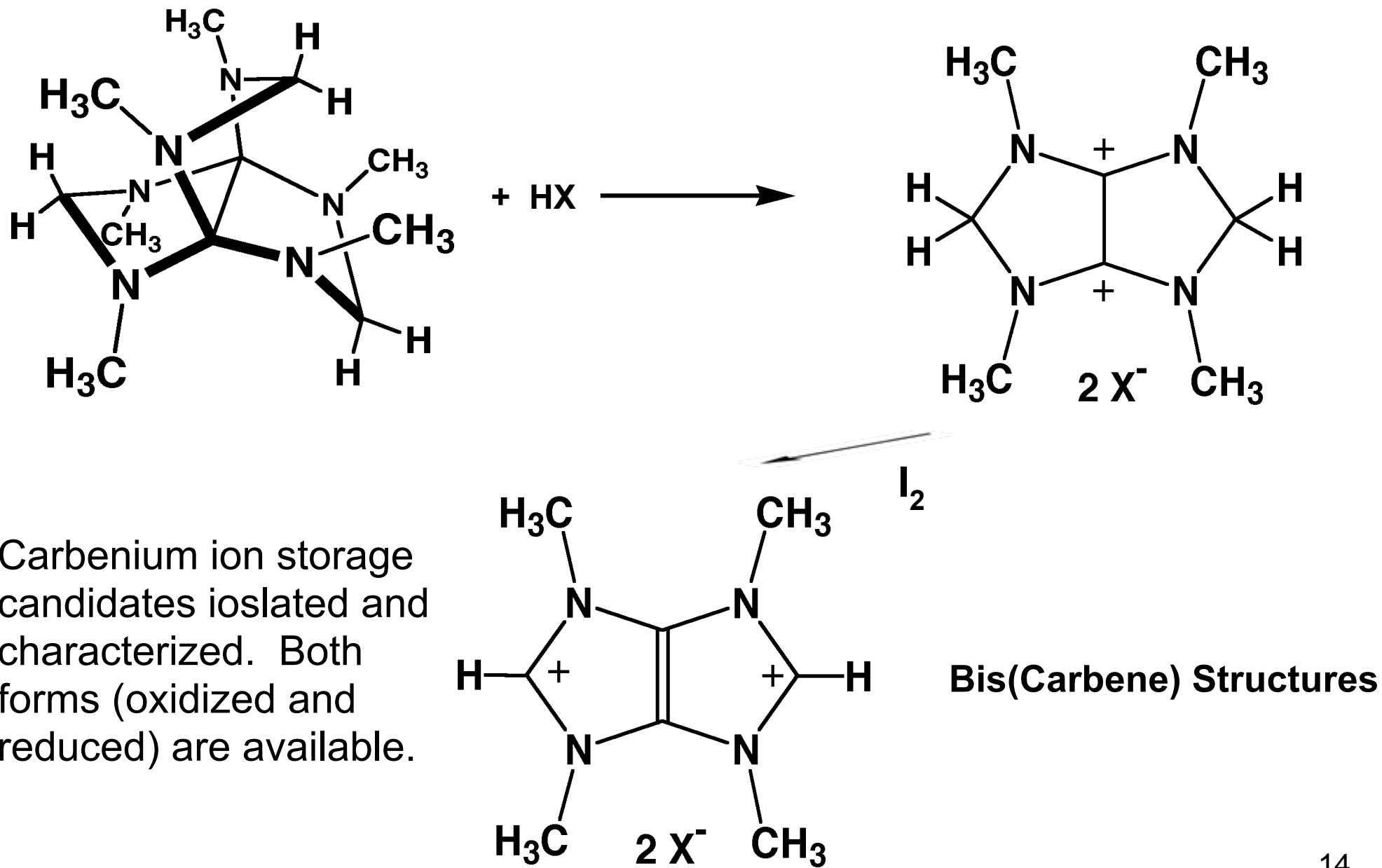
# First Synthesis of Tris(carbene)



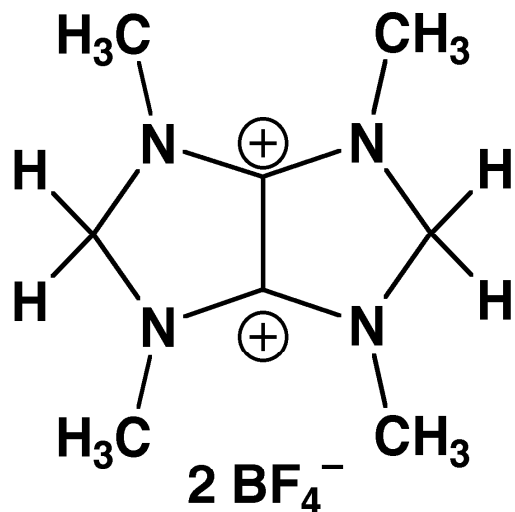
# Interconversion of Tricyclics and First Synthesis of Fused Diimidazolium rings for 1,5 Hydrogen Elimination Reactions



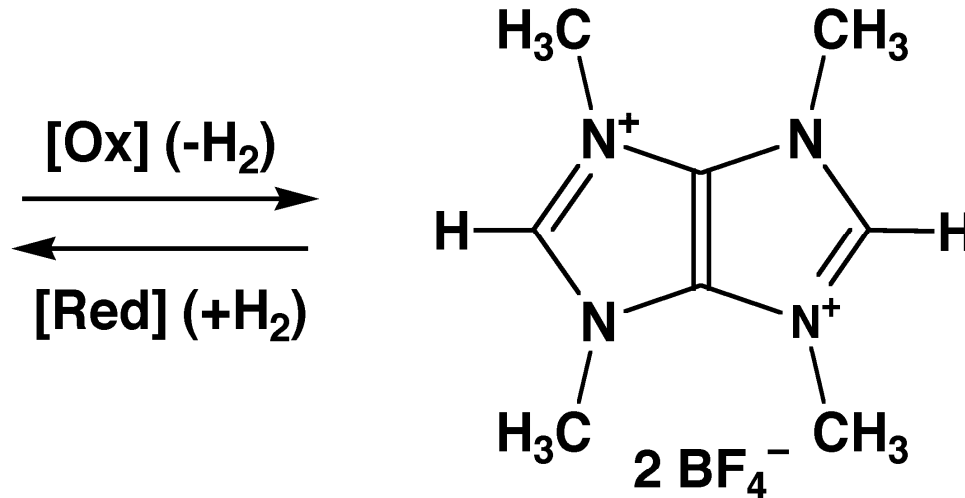
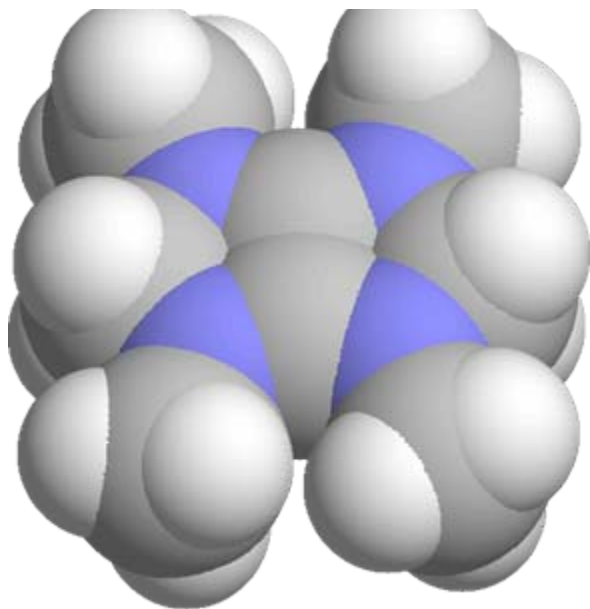
# Another Approach to Fused Diimidazolium rings for 1,5 Hydrogen Elimination Reactions



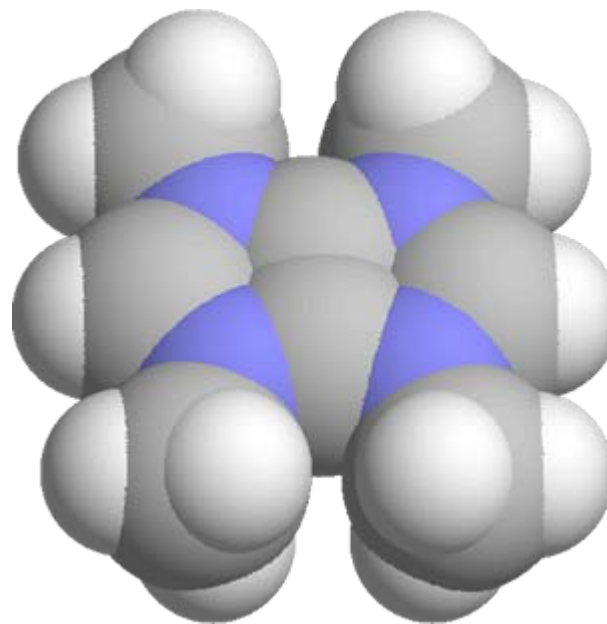
# First Crystal Structures of Bis(imidazolium) Ions



9



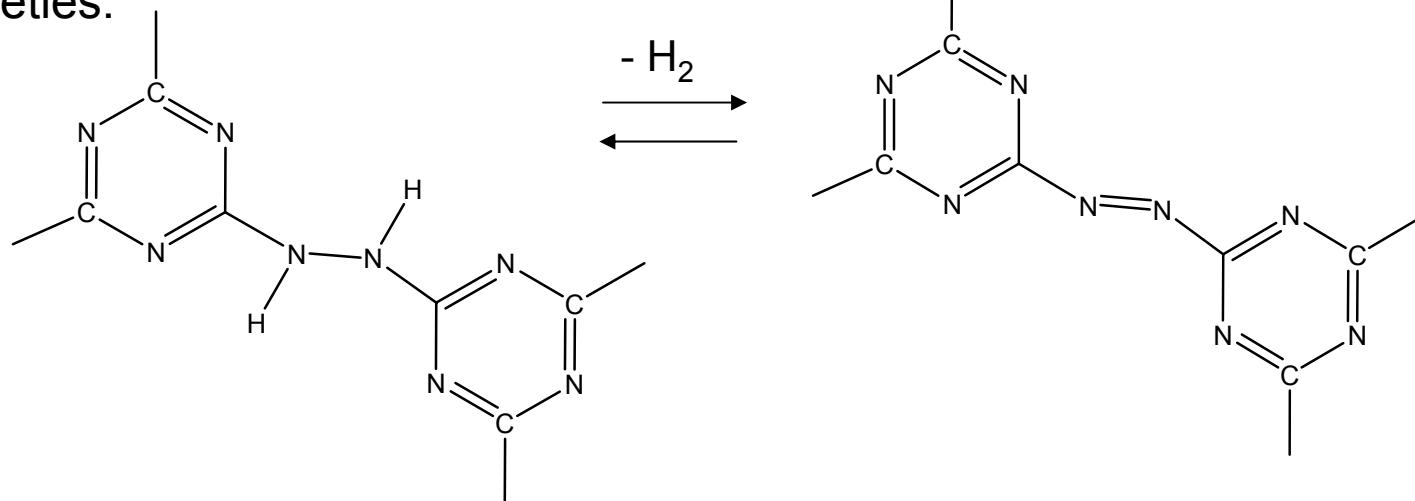
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# Cyanocarbons for Hydrogen Storage

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

Materials prepared having both hydrazine and triazine moieties:



Ultimate goal:

- Polymers based on these moieties, idealized composition  $C_3H_9N_6 \longrightarrow C_3N_6 + 4.5 H_2$  (7.0 wt %  $H_2$ )
- Combines both hexahydrotriazine  $\rightarrow$  triazine, and hydrazo  $\rightarrow$  diaza dehydrogenation concepts, expected to be more robust than unsubstituted hexahydrotriazine
- Expect will have similar needs for effective hydrogenation/dehydrogenation catalysts as hexahydrotriazine

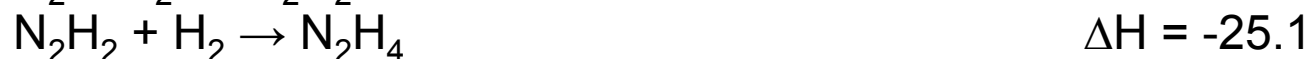


# Cyanocarbon chemistry

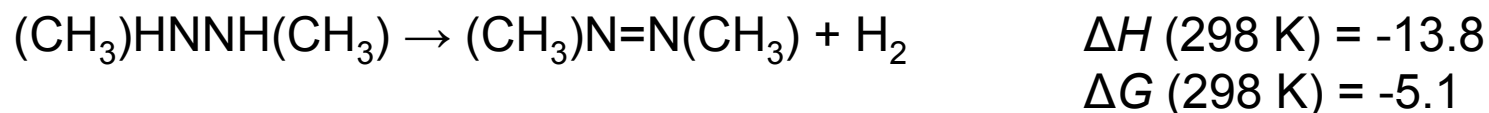
- Can we use derivatives of cyanocarbons for chemical H<sub>2</sub> storage systems?  
*Similar to melamine chemistry so we can generate stable structural components.*

- Predicted reaction energies (kcal/mol) due to limited available data.

- Simplest model is conversion of N=N bonds to N-N bonds

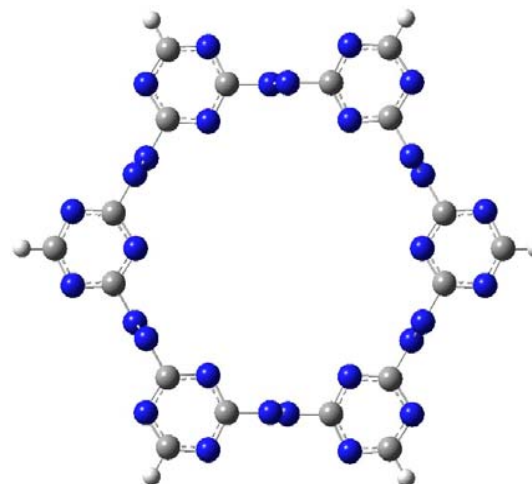


- Substitution of an organic group for the H can dramatically change the energetics making favorable materials for H<sub>2</sub> release

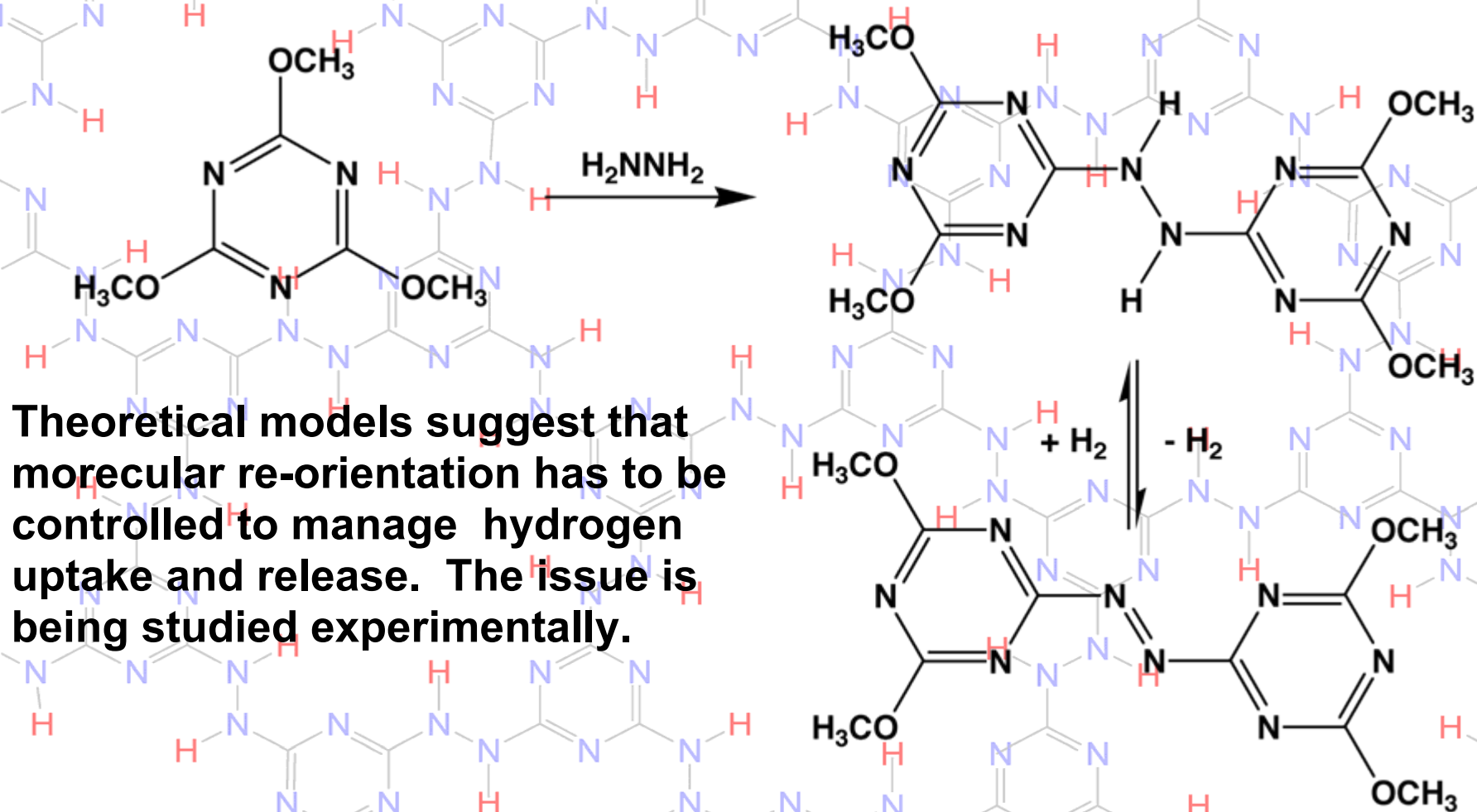


## Work to be done

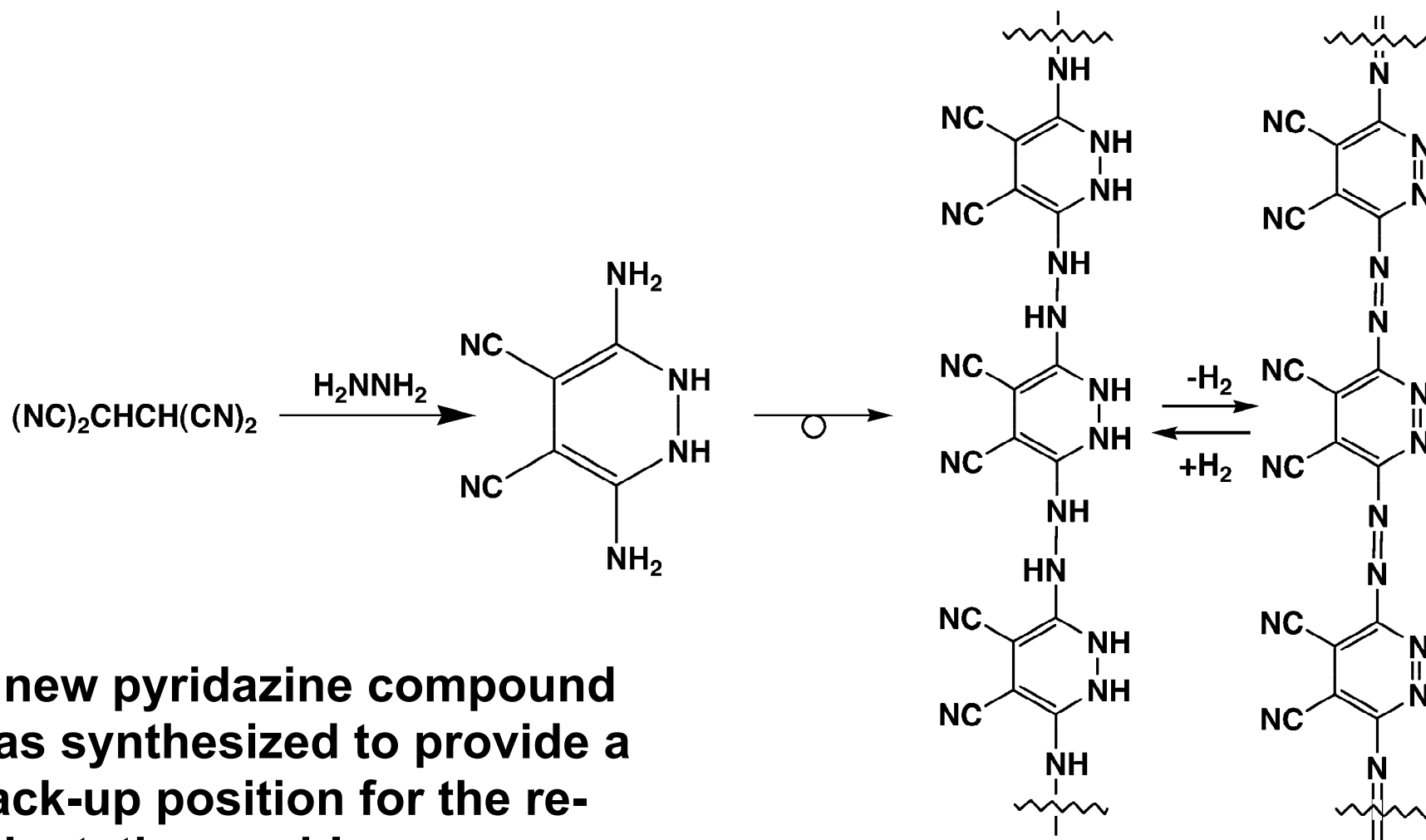
- Predict reaction energies for more complex systems
- Design appropriate catalysts
- Structural properties - geometric effects (polymer vs model compounds)
- Effects of conjugation,
- Ease of reduction/ oxidation
- Polymer synthesis



# Cyanocarbon-H<sub>2</sub> Adduct Synthesis

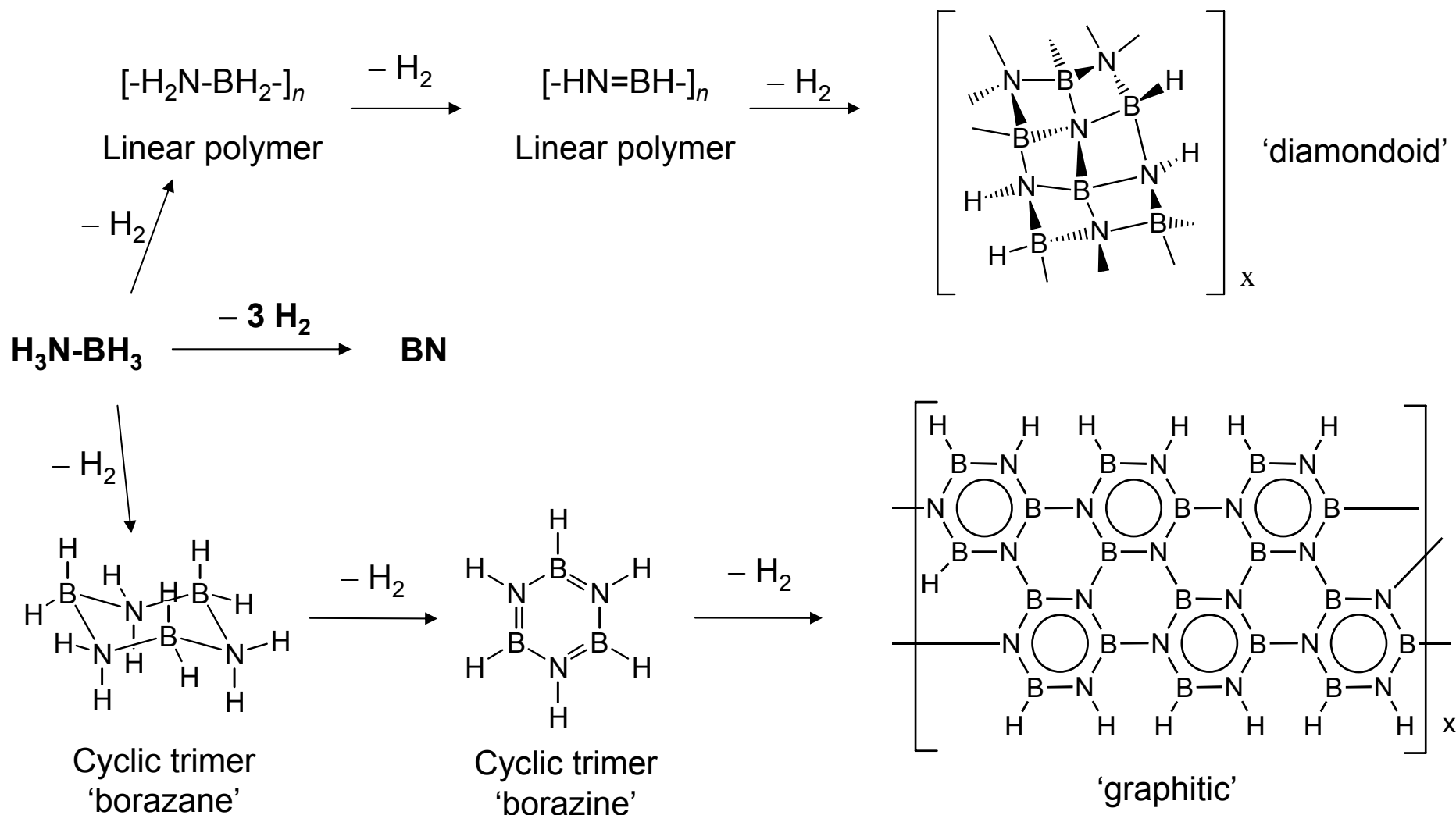


# Pyridazine Solution to Conjugation: An approach to deal with the re-orientation issue



A new pyridazine compound was synthesized to provide a back-up position for the re-orientation problem.

# Hydrogen Production Using Ammonia-Borane



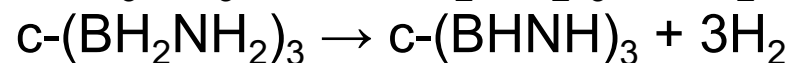
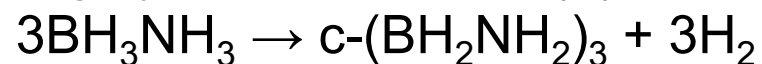
# Energetics (kcal/mol) for the Release of H<sub>2</sub> (Gas Phase Model)

| <u>Reaction</u>   | <u>ΔH (298K)</u> | <u>TS Energy</u> | <u>Bond Energy</u> |
|---|------------------|------------------|--------------------|
| BH <sub>3</sub> NH <sub>3</sub> → BH <sub>2</sub> NH <sub>2</sub> + H <sub>2</sub>  | -8.3             | 34.5             | 25.9               |
| BH <sub>2</sub> NH <sub>2</sub> → HBNH + H <sub>2</sub>   | 31.4             |                  |                    |
| HBNH → BN + H <sub>2</sub>  | 134.3            |                  |                    |
| AlH <sub>3</sub> NH <sub>3</sub> → AlH <sub>2</sub> NH <sub>2</sub> + H <sub>2</sub>                                      | 5.0              | 27.6             | 26.1               |
| AlH <sub>2</sub> NH <sub>2</sub> → HAlNH + H <sub>2</sub>   | 61.9             |                  |                    |
| AlHNH → AlN + H <sub>2</sub>  | 74.9             |                  |                    |
| BH <sub>3</sub> PH <sub>3</sub> → BH <sub>2</sub> PH <sub>2</sub> + H <sub>2</sub>  | 17.4             | 30.4             | 21.1               |
| BH <sub>2</sub> PH <sub>2</sub> → HBPH + H <sub>2</sub>   | 31.4             |                  |                    |
| BPHH → BP + H <sub>2</sub>  | 82.5             |                  |                    |
| AlH <sub>3</sub> PH <sub>3</sub> → AlH <sub>2</sub> PH <sub>2</sub> + H <sub>2</sub>                                      | 5.6              | 34.4             | 14.0               |
| AlH <sub>2</sub> PH <sub>2</sub> → HAlPH + H <sub>2</sub>   | 34.6             |                  |                    |
| AlHPH → AlP + H <sub>2</sub>  | 45.4             |                  |                    |
| [BH <sub>4</sub> <sup>-</sup> ][NH <sub>4</sub> <sup>+</sup> ] (s) → BH <sub>3</sub> NH <sub>3</sub> (g) + H <sub>2</sub> | 0.2              |                  |                    |
| [BH <sub>4</sub> <sup>-</sup> ][PH <sub>4</sub> <sup>+</sup> ] (s) → BH <sub>3</sub> PH <sub>3</sub> + H <sub>2</sub>     | -13.2            |                  |                    |
| [AlH <sub>4</sub> <sup>-</sup> ][NH <sub>4</sub> <sup>+</sup> ] (s) → AlH <sub>3</sub> NH <sub>3</sub> + H <sub>2</sub>   | -3.3             |                  |                    |
| [AlH <sub>4</sub> <sup>-</sup> ][PH <sub>4</sub> <sup>+</sup> ] (s) → AlH <sub>3</sub> PH <sub>3</sub> + H <sub>2</sub>   | -9.3             |                  |                    |

- Isoelectronic species – no obvious advantage energetically and less capacity due to mass.
- Direct H<sub>2</sub> elimination above dative bond energy (consistent with experiment) – need catalysts.

# Predicted cyclization reaction energetics in the gas phase in kcal/mol

Highly accurate CCSD(T)/CBS

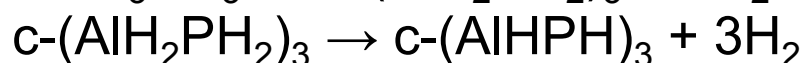
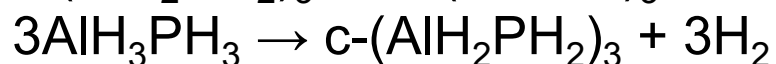
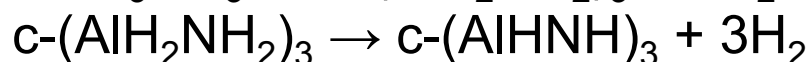
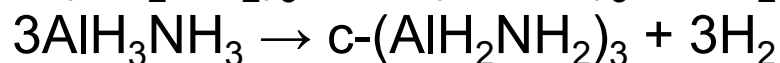
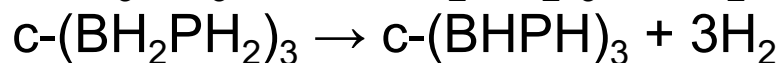
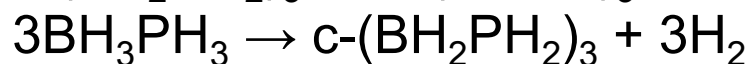
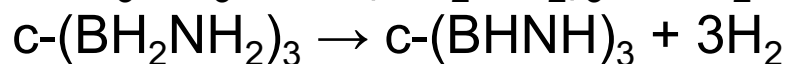
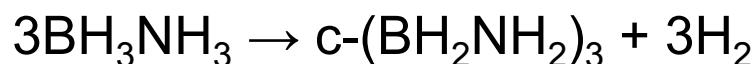


$\Delta\text{H}$  (298K)

-54.5

-20.4

G3MP2



$\Delta\text{H}$  (298K)

-60.8

-23.4

-49.1

57.0

-83.6

25.1

-64.7

17.2

- Very exothermic processes in the gas phase. Need to investigate condensed phase energetics.
- Key issues are the heat of fusion and vaporization of  $\text{BH}_3\text{NH}_3$  and the associated intermolecular interactions.

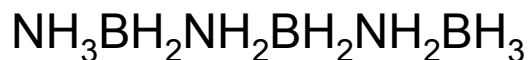
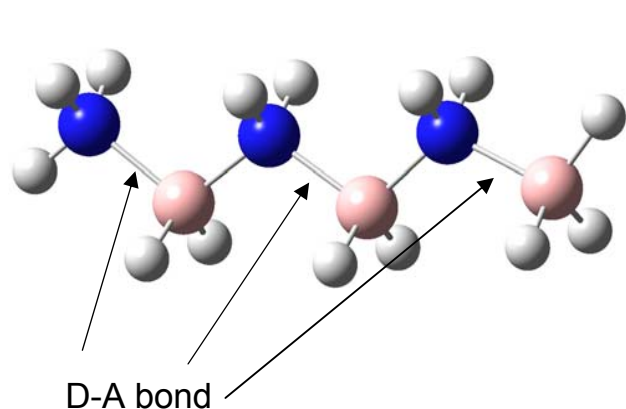
# BN Cyclization reaction energetics in kcal/mol

Formation of boron-nitrogen cycles,  $(\text{BH}_2\text{NH}_2)_n$ , for  $n = 2$  to  $7$ ,  $9$  and  $13$ ,  
(B3LYP/DGDZVP2 at 0K)

| Reaction   | $\Delta E$ | $\Delta E/n$ |
|--|------------|--------------|
| $2\text{BH}_3\text{NH}_3 \rightarrow \text{c}-(\text{BH}_2\text{NH}_2)_2 + 2\text{H}_2$      | -26.9      | -13.4        |
| $3\text{BH}_3\text{NH}_3 \rightarrow \text{c}-(\text{BH}_2\text{NH}_2)_3 + 3\text{H}_2$      | -52.3      | -14.5        |
| $4\text{BH}_3\text{NH}_3 \rightarrow \text{c}-(\text{BH}_2\text{NH}_2)_4 + 4\text{H}_2$      | -64.6      | -16.2        |
| $5\text{BH}_3\text{NH}_3 \rightarrow \text{c}-(\text{BH}_2\text{NH}_2)_5 + 5\text{H}_2$      | -78.2      | -15.6        |
| $6\text{BH}_3\text{NH}_3 \rightarrow \text{c}-(\text{BH}_2\text{NH}_2)_6 + 6\text{H}_2$      | -94.1      | -15.7        |
| $7\text{BH}_3\text{NH}_3 \rightarrow \text{c}-(\text{BH}_2\text{NH}_2)_7 + 7\text{H}_2$      | -113.9     | -16.3        |
| $9\text{BH}_3\text{NH}_3 \rightarrow \text{c}-(\text{BH}_2\text{NH}_2)_9 + 9\text{H}_2$      | -144.0     | -16.0        |
| $13\text{BH}_3\text{NH}_3 \rightarrow \text{c}-(\text{BH}_2\text{NH}_2)_{13} + 13\text{H}_2$ | -217.7     | -16.8        |

- Dative bond to B-N  $\sigma$  bond transition is always energetically favorable.

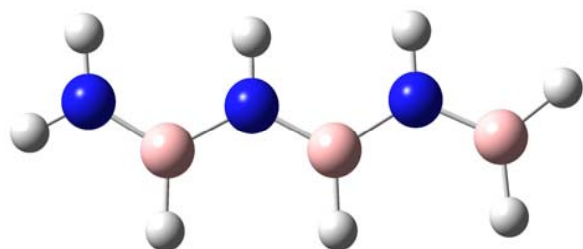
# Energetics (kcal/mol) for H<sub>2</sub> release in polymeric chains



Donor-Acceptor N-B bond  $\approx 1.66$  Å

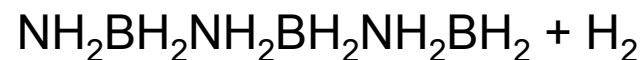
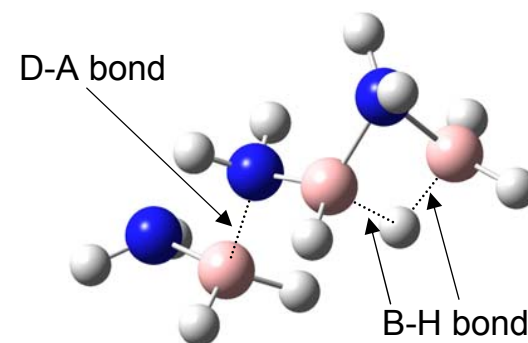
Normal N-B bond  $\approx 1.56$  Å

$\Delta H(\text{B3LYP}) = -42.9$   
 $\Delta H(\text{G3MP2, 298 K}) = -40.8$



N-B bond = 1.42 Å and 1.45 Å

$\Delta H(\text{B3LYP}) = -4.4$   
 $\Delta H(\text{G3MP2, 298 K}) = -4.1$



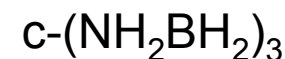
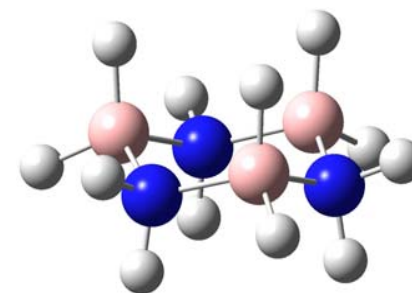
**Bridge structure**

Donor-Acceptor N-B bond = 1.73 Å

Normal N-B bond  $\approx 1.54$  Å

B-H bond  $\approx 1.34$  Å

$\Delta H(\text{B3LYP}) = -32.8$   
 $\Delta H(\text{G3MP2, 298 K}) = -34.6$

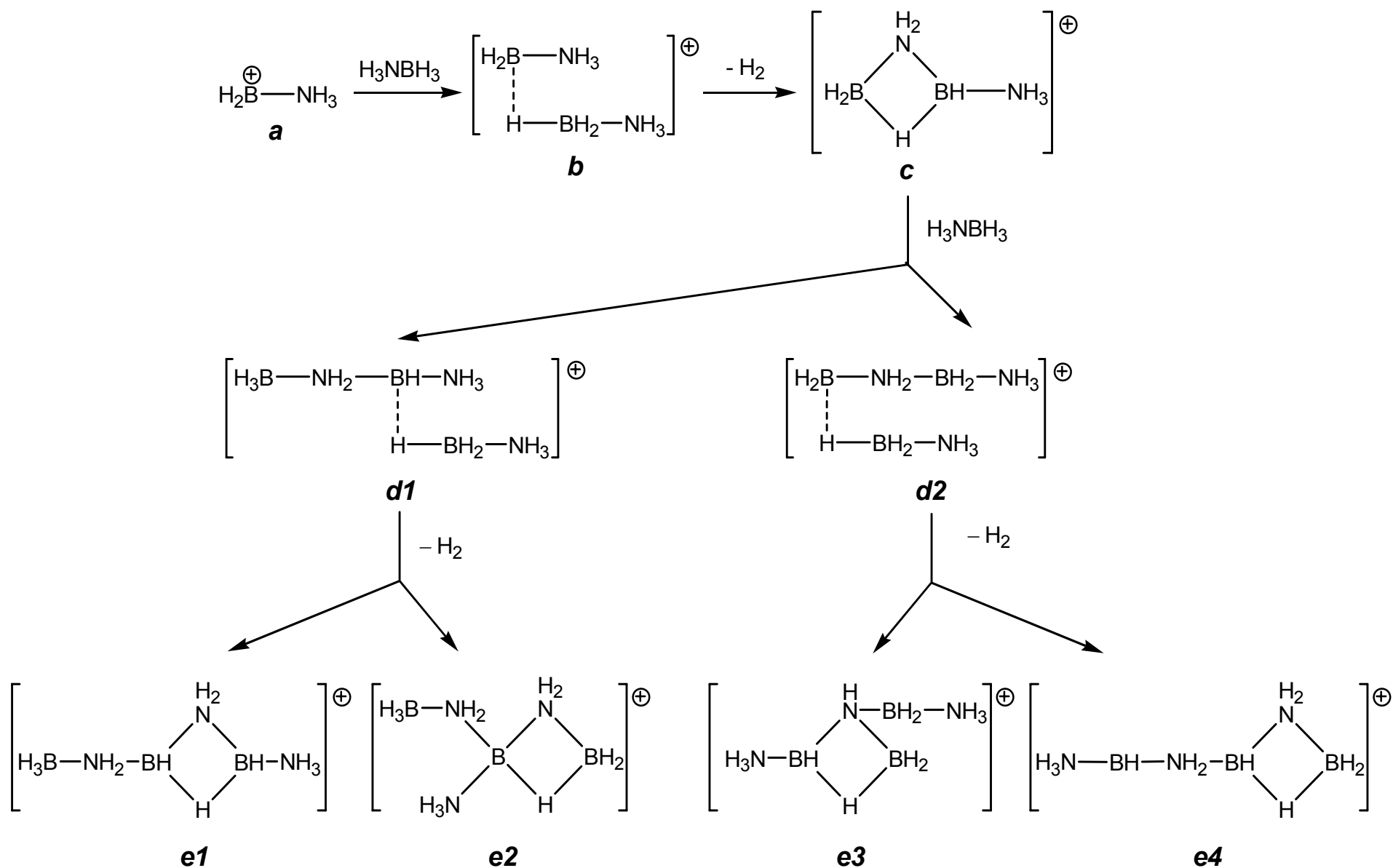


N-B bond = 1.59 Å

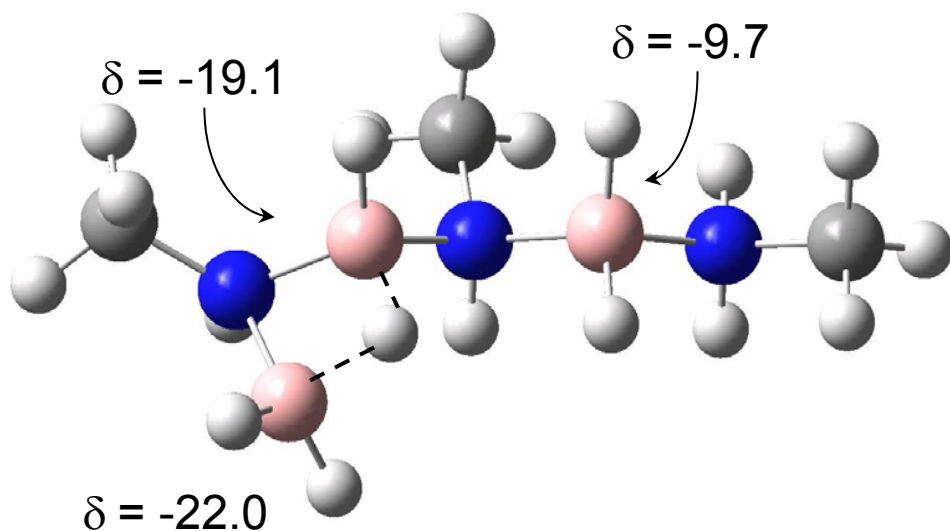
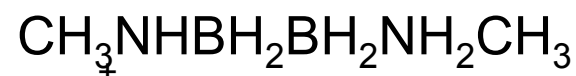
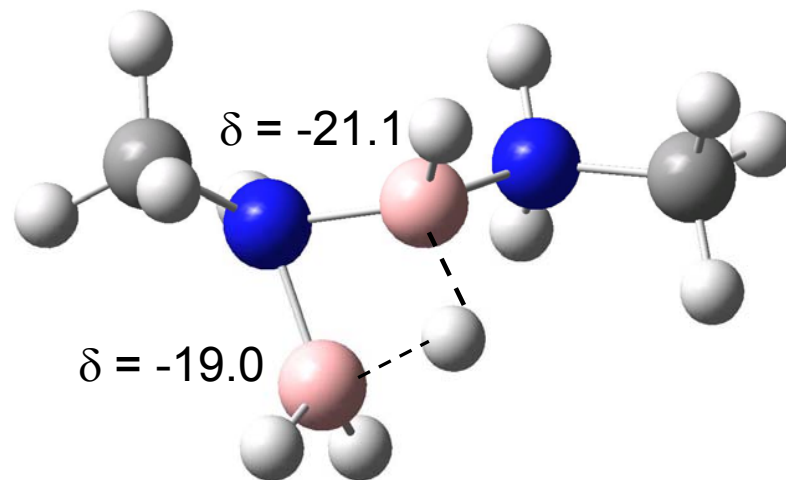
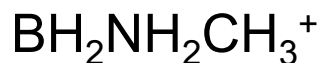
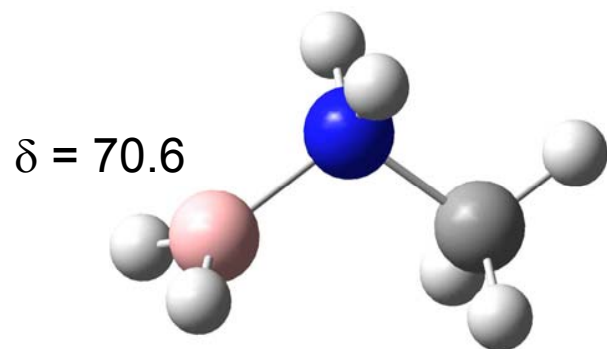
• Evidence that polymer to polymer is not as exothermic as forming the ring – need condensed phase interactions.



# Proposed cationic mechanism for chain growth

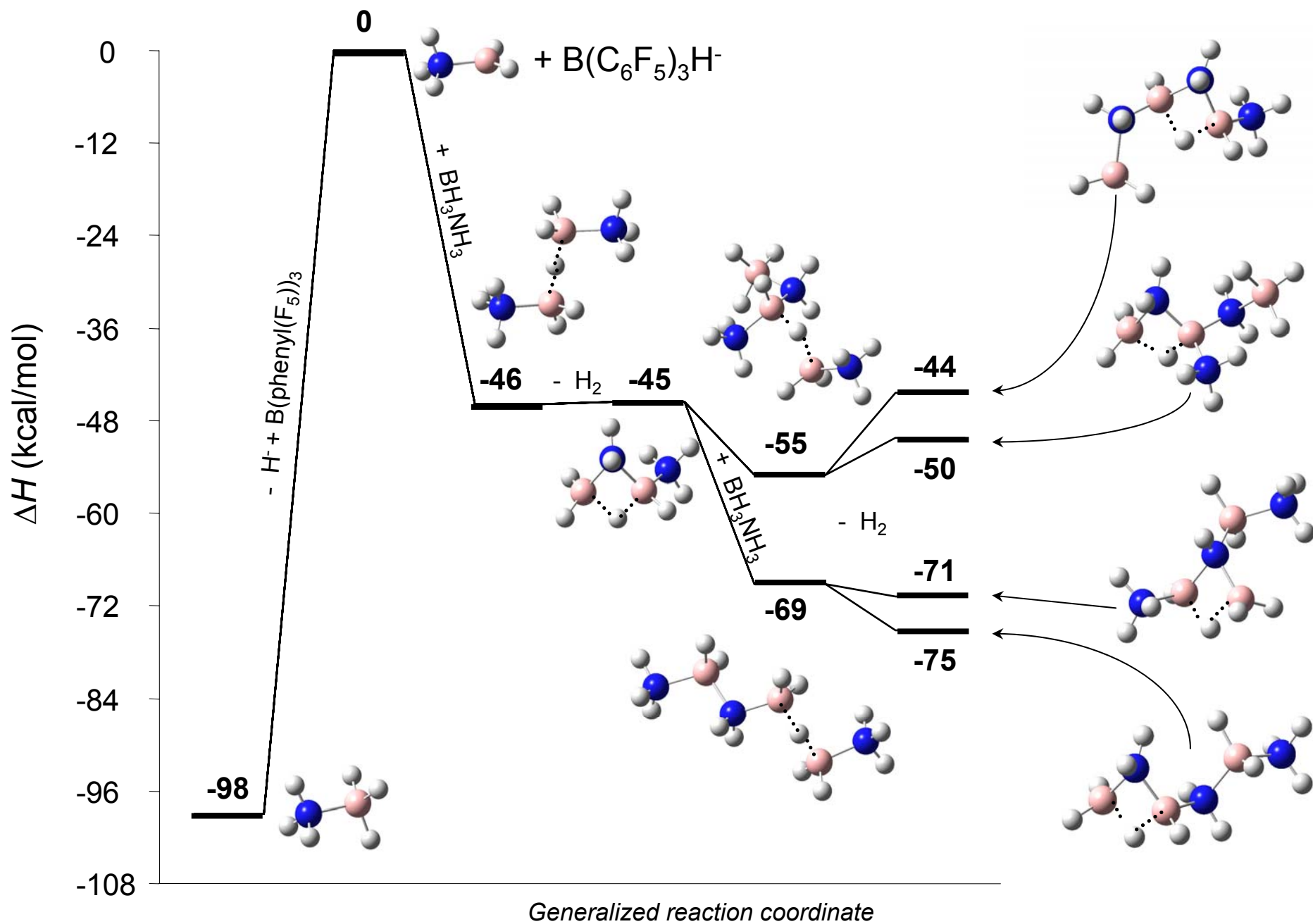


# NMR Chemical Shifts: Cations



- $^{11}\text{B}$  chemical shifts can be reliably predicted at the DFT level and used to aid in the interpretation of experiment. Potential for bridging H and  $\text{NH}_2^+$  groups exists in cationic polymer chains.

# Proposed cationic mechanism for chain growth



Energy level diagram in kcal/mol

# Reaction energies (kcal/mol) for Lewis Acid abstraction of H<sup>-</sup>

## Gas Phase Reaction

ΔH

|   |     |
|---|-----|
| $\text{BH}_3\text{NH}_3 + \text{BH}_3 \rightarrow \text{BH}_2\text{NH}_3^+ + \text{BH}_4^-$   | 139 |
| $\text{BH}_3\text{NH}_3 + \text{B}(\text{C}_6\text{H}_5)_3 \rightarrow \text{BH}_2\text{NH}_3^+ + \text{B}(\text{C}_6\text{H}_5)_3\text{H}^-$ | 139 |
| $\text{BH}_3\text{NH}_3 + \text{B}(\text{C}_6\text{F}_5)_3 \rightarrow \text{BH}_2\text{NH}_3^+ + \text{B}(\text{C}_6\text{F}_5)_3\text{H}^-$ | 98  |
| $\text{BH}_3\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{BH}_2\text{NH}_3^+ + \text{HSO}_4^- + \text{H}_2$                           | 124 |
| $\text{BH}_3\text{NH}_3 + \text{CF}_3\text{SO}_3\text{H} \rightarrow \text{BH}_2\text{NH}_3^+ + \text{CF}_3\text{SO}_3^- + \text{H}_2$        | 115 |

## Salt reactions (± 5 kcal/mol)

|   |      |
|---|------|
| $\text{BH}_3\text{NH}_3 + \text{BH}_3 \rightarrow \text{BH}_2\text{NH}_3^+ / \text{BH}_4^-$   | 0.5  |
| $\text{BH}_3\text{NH}_3 + \text{B}(\text{C}_6\text{H}_5)_3 \rightarrow \text{BH}_2\text{NH}_3^+ / \text{B}(\text{C}_6\text{H}_5)_3\text{H}^-$ | 38.1 |
| $\text{BH}_3\text{NH}_3 + \text{B}(\text{C}_6\text{F}_5)_3 \rightarrow \text{BH}_2\text{NH}_3^+ / \text{B}(\text{C}_6\text{F}_5)_3\text{H}^-$ | 1.6  |
| $\text{BH}_3\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{BH}_2\text{NH}_3^+ / \text{HSO}_4^- + \text{H}_2$                           | -7.0 |
| $\text{BH}_3\text{NH}_3 + \text{CF}_3\text{SO}_3\text{H} \rightarrow \text{BH}_2\text{NH}_3^+ / \text{CF}_3\text{SO}_3^- + \text{H}_2$        | -9.6 |

## Lattice Energies

U<sub>L</sub>

|  |      |
|--|------|
| $\text{BH}_2\text{NH}_3^+ / \text{B}(\text{C}_6\text{F}_5)_3\text{H}^-$  | 96.9 |
| $\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_3^+(\text{bridge}) / \text{B}(\text{C}_6\text{F}_5)_3\text{H}^-$                       | 94.8 |
| $\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_3^+(\text{bridge}) / \text{B}(\text{C}_6\text{F}_5)_3\text{H}^-$ | 92.6 |

- Need strong Lewis acids or very strong acids for this chemistry to work.
- Have the most extensive Lewis acidity scale available and strong Brönsted acid scale

# Regeneration of Ammonia Borane: Thermodynamics for Reprocessing Schemes – The 5 Step approach and what we can predict

Digestion: Mechanisms, bond energies

Activation: Mechanisms, bond energies

Reduction: Mechanisms, bond energies

Disproportionation: Mechanisms, reaction energies ( $2\text{BHR}_2 \rightarrow \text{BH}_2\text{R} + \text{BR}_3$ )

Ammoniation: Cone angles, steric effects,  $\text{BH}_3$ -L binding energies

# Thermodynamics (kcal/mol) of Disproportionation/ Conproportionation Equilibria

| <u>Reaction</u>  | <u><math>\Delta E</math></u> |
|--|------------------------------|
| $2\text{HB}(\text{OCH}_3)_3^- \rightarrow \text{H}_2\text{B}(\text{OCH}_3)_2^- + \text{B}(\text{OCH}_3)_4^-$   | -1.4                         |
| $\text{HB}(\text{OCH}_3)_3^- + \text{H}_2\text{B}(\text{OCH}_3)_2^- \rightarrow \text{H}_3\text{B}(\text{OCH}_3)^- + \text{B}(\text{OCH}_3)_4^-$     | -4.2                         |
| $\text{HB}(\text{OCH}_3)_3^- + \text{H}_3\text{B}(\text{OCH}_3)^- \rightarrow \text{B}(\text{OCH}_3)_4^- + \text{BH}_4^-$                            | -                            |
| 11.4   |                              |
| $2\text{HAl}(\text{OCH}_3)_3^- \rightarrow \text{H}_2\text{Al}(\text{OCH}_3)_2^- + \text{Al}(\text{OCH}_3)_4^-$                                      | 0.3                          |
| $\text{HAl}(\text{OCH}_3)_3^- + \text{H}_2\text{Al}(\text{OCH}_3)_2^- \rightarrow \text{H}_3\text{Al}(\text{OCH}_3)^- + \text{Al}(\text{OCH}_3)_4^-$ | -0.4                         |
| $\text{HAl}(\text{OCH}_3)_3^- + \text{H}_3\text{Al}(\text{OCH}_3)^- \rightarrow \text{Al}(\text{OCH}_3)_4^- + \text{AlH}_4^-$                        | -3.3                         |
| $2\text{HGa}(\text{OCH}_3)_3^- \rightarrow \text{H}_2\text{Ga}(\text{OCH}_3)_2^- + \text{Ga}(\text{OCH}_3)_4^-$                                      | 2.7                          |
| $\text{HGa}(\text{OCH}_3)_3^- + \text{H}_2\text{Ga}(\text{OCH}_3)_2^- \rightarrow \text{H}_3\text{Ga}(\text{OCH}_3)^- + \text{Ga}(\text{OCH}_3)_4^-$ | 2.6                          |
| $\text{HGa}(\text{OCH}_3)_3^- + \text{H}_3\text{Ga}(\text{OCH}_3)^- \rightarrow \text{Ga}(\text{OCH}_3)_4^- + \text{GaH}_4^-$                        | 1.6                          |

- Can predict H transfer reaction energies and see periodic trends

# Thermodynamics (kcal/mol) of Disproportionation/ Conproportionation Equilibria: Hydride Transfer

| <u>Reactions</u>  | <u><math>\Delta E</math></u> |
|---|------------------------------|
| $\text{HAl}(\text{OCH}_3)_2 + \text{B}(\text{OCH}_3)_4^- \rightarrow \text{Al}(\text{OCH}_3)_3 + \text{HB}(\text{OCH}_3)_3^-$                               | 16.5                         |
| $\text{HAl}(\text{CH}_3)_2 + \text{B}(\text{OCH}_3)_4^- \rightarrow (\text{CH}_3)_2\text{Al}(\text{OCH}_3) + \text{HB}(\text{OCH}_3)_3^-$                   | 12.8                         |
| $\text{HSi}(\text{CH}_3)_3 + \text{B}(\text{OCH}_3)_4^- \rightarrow (\text{CH}_3)_3\text{Si}(\text{OCH}_3) + \text{HB}(\text{OCH}_3)_3^-$                   | 6.2                          |
| $\text{HSi}(\text{OCH}_3)_3 + \text{B}(\text{OCH}_3)_4^- \rightarrow \text{Si}(\text{OCH}_3)_4 + \text{HB}(\text{OCH}_3)_3^-$                               | 2.1                          |
| $\text{HSn}(\text{CH}_3)_3 + \text{B}(\text{OCH}_3)_4^- \rightarrow (\text{CH}_3)_3\text{Sn}(\text{OCH}_3) + \text{HB}(\text{OCH}_3)_3^-$                   | 21.7                         |
| $\text{HSn}(\text{OCH}_3)_3 + \text{B}(\text{OCH}_3)_4^- \rightarrow \text{Sn}(\text{OCH}_3)_4 + \text{HB}(\text{OCH}_3)_3^-$                               | 25.5                         |
| <br>  |                              |
| $\text{HSi}(\text{CH}_3)_3 + \text{BCl}_3 \rightarrow \text{ClSi}(\text{CH}_3)_3 + \text{HBCl}_2$   | -7.8                         |
| $\text{HSi}(\text{CH}_3)_3 + \text{B}(\text{OCH}_3)_3 \rightarrow (\text{OCH}_3)\text{Si}(\text{CH}_3)_3 + \text{HB}(\text{OCH}_3)_2$                       | 8.2                          |
| $\text{HSi}(\text{CH}_2\text{CH}_3)_3 + \text{BCl}_3 \rightarrow \text{ClSi}(\text{CH}_2\text{CH}_3)_3 + \text{HBCl}_2$                                     | -8.3                         |
| $\text{HSi}(\text{CH}_2\text{CH}_3)_3 + \text{B}(\text{OCH}_3)_3 \rightarrow (\text{OCH}_3)\text{Si}(\text{CH}_2\text{CH}_3)_3 + \text{HB}(\text{OCH}_3)_2$ | 9.4                          |
| $\text{HSi}(\text{OCH}_3)_3 + \text{BCl}_3 \rightarrow \text{ClSi}(\text{OCH}_3)_3 + \text{HBCl}_2$   | -5.9                         |
| $\text{HSi}(\text{OCH}_3)_3 + \text{B}(\text{OCH}_3)_3 \rightarrow \text{Si}(\text{OCH}_3)_4 + \text{HB}(\text{OCH}_3)_2$                                   | 3.7                          |
| $\text{HSi}(\text{Ph})_3 + \text{BCl}_3 \rightarrow \text{ClSi}(\text{Ph})_3 + \text{HBCl}_2$   | -6.6                         |
| $\text{HSi}(\text{Ph})_3 + \text{B}(\text{OCH}_3)_3 \rightarrow (\text{OCH}_3)\text{Si}(\text{Ph})_3 + \text{HB}(\text{OCH}_3)_2$                           | 7.5                          |

- Can transfer H from trialkyl silanes to  $\text{BCl}_3$  but not to  $\text{B}(\text{OCH}_3)_3$ . Consistent with experimental observations.

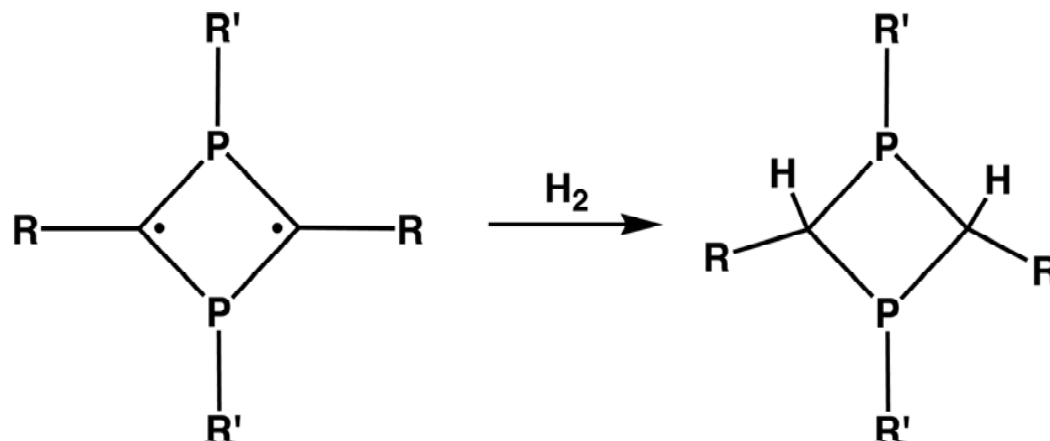
# Planned Experimental Activities

- Continue synthesis and characterization of cyanocarbons for H<sub>2</sub> storage – Develop molecules with improved weight percent and as structural components.
  - Extend newly discovered pyridazine chemistry to improve performance and weight percent hydrogen
- Continue synthesis and characterization of carbenes to improve performance and weight percent hydrogen.
  - Continue studies on imidazol(in)ium borohydrides and carbene-borane adducts
- Develop improved synthesis of and continue characterization of newly discovered phosphocarbons for improved hydrogen release characteristics.

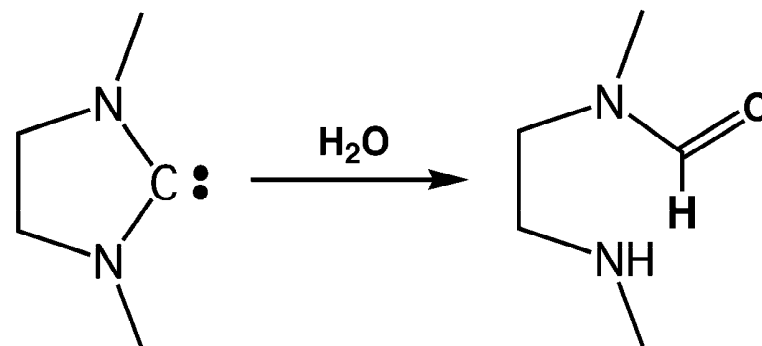


# New Experimental Opportunities: More Main Group Chemistry and a way to improve the weight percent

A new, non-metallic,  
uncatalyzed hydrogen  
storage system:  
 $\text{H}_2$  release at ambient  
temperature & pressure.



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



# Planned Computational Activities

- Predict Thermodynamics for reactions:
  - Borane-amine chemistry to optimize and control the H<sub>2</sub> release process
  - Reprocessing: B-O to B-H regeneration. Predict the energetics and kinetics of key steps in 5-step process to optimize experimental approach.
  - Continue to predict the energetics for larger boron hydrides and salts following our efforts on  $(B_{12}H_{12})^{2-}(NH_4^+)_2$
  - Complete studies on borane-amine ionic pathway energetics
  - Develop approaches to predict intermolecular interactions and heats of vaporization/fusion and complete studies of borane amine thermodynamics
  - Continue to incorporate solvent effects
  - Continue prediction of thermodynamics and kinetics for carbenes and cyanocarbons including pyridazines
  - Predict thermodynamic and kinetics of phosphocarbons
- Develop improved reaction mechanisms based on predictions of reaction kinetics to optimize processes
- Use computational approaches to design new catalysts including acid/base catalysts (Lewis acidities, hydride affinities, proton affinities) and transition metals
- Predict spectroscopic properties (nmr, IR/Raman, UV-vis) for use in analyzing experimental data
- Manage Center website and develop data archival capability

# Summary

- Developed new conceptual models for improving weight percent beyond 1:1 stoichiometry to enable us to meet DOE 2015 goals. Developed thermodynamic approach to meet desorption temperature and plateau pressures.
- Developed carbene and carbenium ion chemistry to meet DOE 2010 goals.
- Developed new cyanocarbon chemistry to meet DOE 2010 goals.
  - Discovered new pyradizine compound to manage conformational issues
- Electronic structure methods were used to successfully predict reliable values of the thermodynamic, kinetic, and spectroscopic properties of compounds for chemical hydrogen storage for the design of new molecular based systems.
  - Carbenes and cyanocarbons
  - Borane-amines and isoelectronic molecules
  - Borane-amine reaction mechanism
  - Borane-amine regeneration mechanisms

# UA - 2006

## On-Board Hydrogen Storage System Targets

| Storage Parameter                 | DOE 2010 System Targets   | carbene  | cyanocarbon  |
|-----------------------------------|---------------------------|--|--|
| Weight % H <sub>2</sub>           | 6%                        | 2%<br>Ultimate: 6.3%                                     | 1%<br>Ultimate: 7.0%                                     |
| Dehydrogenation Rate              | 0.02g/s-kW                | In progress  | Oxidation step<br>diffusion limited                      |
| Storage Efficiency<br>Center Goal | Near thermoneutral<br>70% | Exothermic:<br>-5 kcal/mol<br>Ultimate:<br>Thermoneutral | Endothermic:<br>5 kcal/mol<br>Ultimate:<br>Thermoneutral |

*Data is based on material only, not system value*

# Publications and Presentations

“Heats of Formation of the Arduengo Carbene and Various Adducts Including H<sub>2</sub> from Ab Initio Molecular Orbital Theory,” D. A. Dixon and A. J. Arduengo, III, *J. Phys. Chem., A*, **2006**, *110*, 1968

“Thermodynamic Properties of Molecular Borane Phosphines, Alane Amines, and Phosphine Alanes and the [BH<sub>4</sub>]<sup>-</sup>[PH<sub>4</sub>]<sup>+</sup>, [AlH<sub>4</sub>]<sup>-</sup>[NH<sub>4</sub>]<sup>+</sup>, and [AlH<sub>4</sub>]<sup>-</sup>[PH<sub>4</sub>]<sup>+</sup> Salts for Chemical Hydrogen Storage Systems from Ab Initio Electronic Structure Theory,” D. J. Grant and D. A. Dixon *J. Phys. Chem., A*, **2005**, *109*, 10138

“Thermodynamic Properties of the C<sub>5</sub>, C<sub>6</sub>, and C<sub>8</sub> n-Alkanes from Ab Initio Electronic Structure Theory,” L. Pollack, T. L. Windus, and W. A. de Jong, and D.A. Dixon, *J. Phys. Chem. A*, **2005**, *109*, 6934

“Thermodynamic Properties of Molecular Borane Amines and the [BH<sub>4</sub>]<sup>-</sup>[NH<sub>4</sub>]<sup>+</sup> Salt for Chemical Hydrogen Storage Systems from Ab Initio Electronic Structure Theory,” D. A. Dixon and M. Gutowski, *J. Phys. Chem. A*, **2005**, *109*, 5129

Invited Lecture, “High level computational approaches to the prediction of the thermodynamics of chemical hydrogen storage systems, hydrocarbon fuels, and main group chemistry,” Structure and Function in Chemistry and Biology, Symposium Celebrating the 85th Birthday of Prof. William N. Lipscomb, Shanghai, China, August, 2005

Invited Lecture, “Applications of electronic structure theory at the teraflop level and beyond,” Computational Chemistry at the Teraflop and Beyond Symposium, ACS National Meeting, Washington, DC, Aug. 2005

Invited Lecture, Computational studies of metal oxide clusters and catalytic reactions,” XVI Undergraduate Research Symposium, Nanotechnology, Computational Chemistry, and Computational Biology Workshop, San Juan, Puerto Rico, Sept., 2005.

Invited Lecture, Pacific Chem 2005, “Computational inorganic fluorine chemistry,” Inorganic Fluorine Chemistry: From Basic Research to Applications, Honolulu, HI, Dec. 2005.

Invited Lecture, “Computational Thermochemistry,” Quantitative Quantum Chemistry, Symposium in honor Thom Dunning, Santa Fe, March, 2006.

Invited Lecture, “Computational Approaches to the prediction of reaction kinetics for catalysis and chemical hydrogen storage,” Solvay Three Day Symposium on Chemical Reactivity, Brussels, April 2006.

Tutorial on Hydrogen Storage, “Computational Chemistry for H<sub>2</sub> Storage: Theoretical Background and Applications,” Materials Research Society Annual Spring Meeting, April, 2006.

Invited Lecture, “High level computational approaches to the prediction of the thermodynamics of chemical hydrogen storage systems,” Symposium on Advances in Hydrogen Storage, Materials Research Society Annual Spring Meeting, April, 2006.