

Main Group Element Chemistry for Hydrogen Storage and Activation

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DOE Center of Excellence for Chemical
Hydrogen Storage
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This presentation does not contain any proprietary or confidential information

Project ID #
STP5

Overview

Timeline

- Project start date: FY05
- Project end date: FY09
- Percent complete: New Start

Budget

- Total project funding:
\$1,780,690
 - DOE share:
\$1,273,711(requested)
 - UA share: \$506,979
- \$0K in FY04
- Funding for FY05: \$432,077K
\$226,510(DOE), \$205,567 (UA)

Barriers

- 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

- New Project: Start CY2005
- Focus is the development of 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 H₂ activation chemistry
- Develop and implement systems based on polyhydrides of main group elements, e.g., phosphorous
- 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 new materials and develop materials that meet the 2010 and 2015 DOE objectives.

Approach

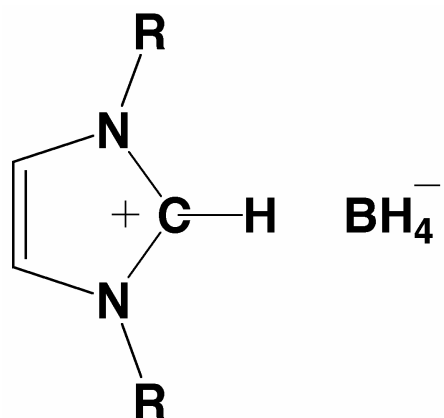
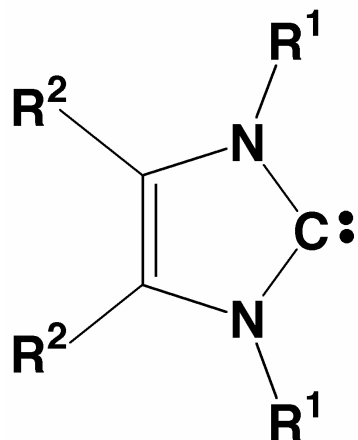
- Use novel chemistry approaches to synthesize compounds for easily reversible addition/elimination of H₂ based on our novel, stable carbene chemistry for use in H₂ storage systems.
- Use first principles computational chemistry approaches on advanced computer architectures to predict the electronic 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 H₂.
- Develop a 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. Potential approach for cold-start issues.
- Experimental close interactions with partners: LANL, UC-Davis
- Computational interactions with LANL, PNNL, UW, UPenn, UC-Davis, UCLA

Technical Accomplishments/ Progress/Results

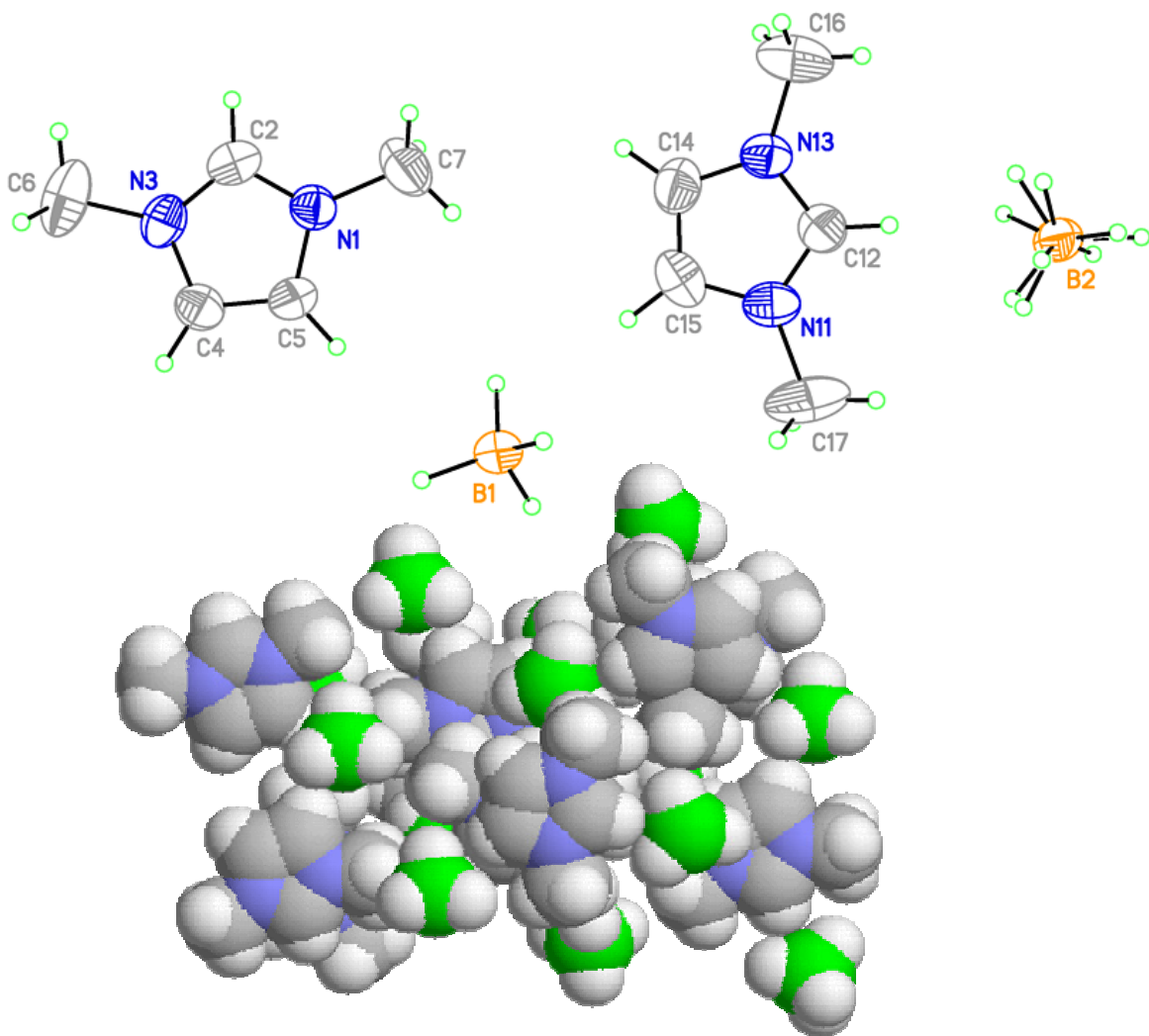
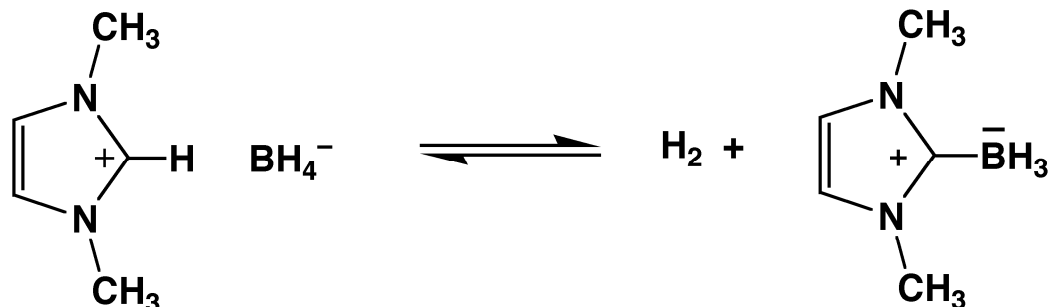
- Structural characterization of an imidazolium borohydride.
- Formation of carbene·H₂ adducts.
- Model compound available for cyanocarbon·H₂ adducts.
- Reliable computational chemical prediction of H₂ release energetics from borane amines and carbenes –demonstration of methodology and further development of $\Delta G/\Delta H$ concepts.

Examples of % by weight of H₂ of compounds under study

<u>Reaction or compound</u>	<u>% H₂</u>
NH ₄ BH ₄ (s) → NH ₃ BH ₃ + H ₂	6.1%
NH ₃ BH ₃ → NH ₂ BH ₂ + H ₂	6.5%
[PH ₄][BH ₄] (release all H ₂)	16%
PH ₃ BH ₃ (release all H ₂)	13%
[BH ₄][NH ₄] (release all H ₂)	24%
carbene-derived compounds	7-14%



Imidazolium Borohydride Solid State Structure Determined

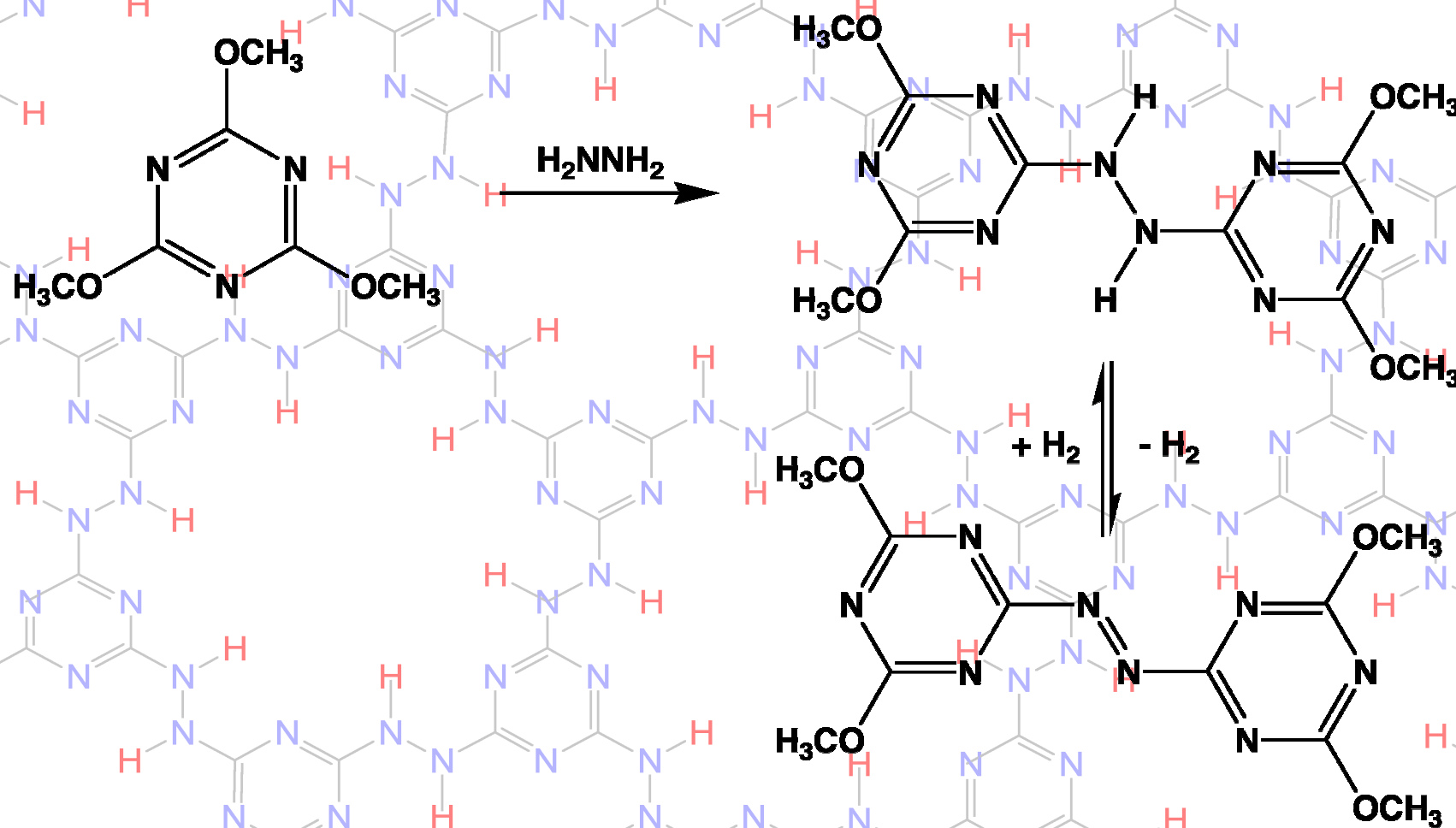


The first X-ray structure of an imidazolium borohydride was determined.

Structure shows interactions between hydrogen at C-2, C-4 and the borohydride and evidence for an H-H "hydrogen bond"

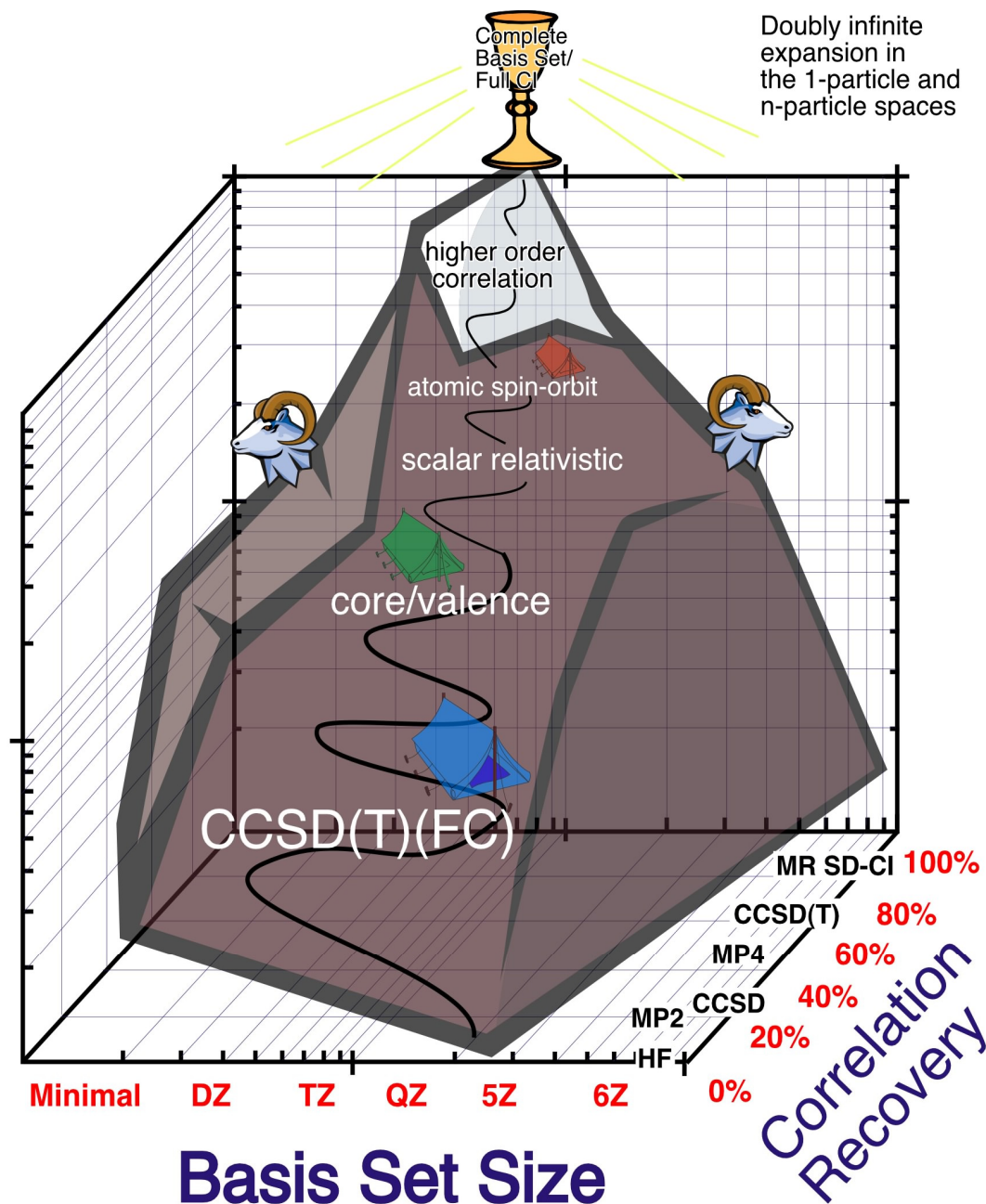
Cyanocarbon-H₂ Adducts Synthesis

Work initiated on a 2-dimensional cyanocarbon polymer (illustrated in the background) as a candidate for hydrogen uptake and release. The first unimolecular models have been synthesized. Characterization of these materials is in progress.



High Level Computational Chemistry for H₂ Storage

Computational Cost



Calculate accurate molecular heats of formation (± 1 kcal/mol) by ab initio molecular orbital theory:

Total atomization energy at the CCSD(T) level extrapolated to the complete basis set limit using the augmented-correlation consistent basis sets

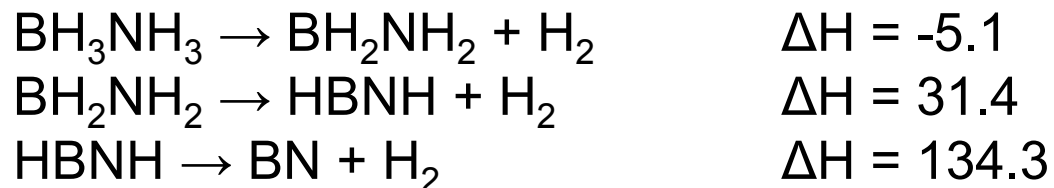
- + core-valence corrections
- + scalar relativistic
- + spin orbit
- + zero point energy
- + thermal corrections (0 \rightarrow 298K)

Use atomic heats of formation to get molecular heats of formation

Use MP2 or CCSD(T) geometries and frequencies

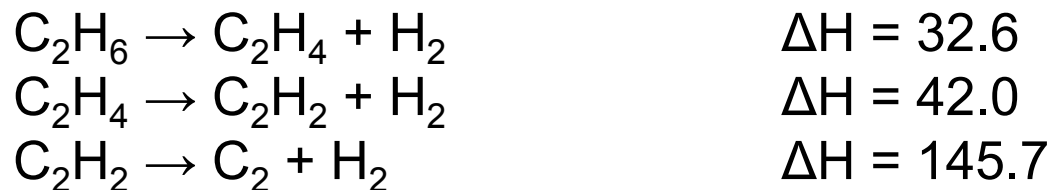
Reaction Energies in borane amines in kcal/mol @ 298K for chemical hydride storage

Reaction energies for the sequential release of H₂ from borane amines (gas phase) based on the most accurate heats of formation now available (calculated by us).



BH₃NH₃ will be a good source of H₂ as the release of H₂ from this species is not far from thermoneutral. Cannot make T too high as entropy also favors release of H₂.

Reaction energies for the sequential release of H₂ from hydrocarbons (gas phase)



C2 gaseous hydrocarbons cannot release H₂ (except at high T due to TΔS).

The reaction energies for forming BN/C2 and BHNH/CHCH are ~ equal. Manifestation of similarity of the isoelectronic C₂H_{2m} and BNH_{2m} systems except for m = 3.

Bond Energies in borane amines in kcal/mol @ 0K in kcal/mol for chemical hydride storage

Reaction	B.E.	Bond type
$\text{BH}_3\text{-NH}_3 \rightarrow \text{BH}_3 + \text{NH}_3$	25.9	dative
$\text{CH}_3\text{-CH}_3 \rightarrow 2 \text{CH}_3$	87.9	C-C σ
$\text{BH}_2\text{=NH}_2 \rightarrow \text{BH}_2 + \text{NH}_2$	139.6	B-N π + B-N σ
$\text{CH}_2\text{=CH}_2 \rightarrow 2 \text{CH}_2$ ($^3\text{B}_1$)	171.9	C-C π + C-C σ
$\text{BHNH} \rightarrow \text{BH} + \text{NH}$	178.5	
$\text{HCCH} \rightarrow 2 \text{CH}$	228.1	

For C_2H_4 , the C-C π bond is ~65 kcal/mol giving a C-C σ bond energy of 107 kcal/mol. Due to $\text{sp}^2\text{-sp}^2$ bonding, not $\text{sp}^3\text{-sp}^3$ bonding.

Estimate the B=N π bond energy by calculating the rotation barrier in BH_2NH_2
 Rotation Barrier at 0K = 30.0 kcal/mol = π bond energy

Low π bond energy yields a very strong B-N single bond of 109.6 kcal/mol, comparable to the C-C σ bond in C_2H_4 . The high B-N σ + π bond energy in BH_2NH_2 is consistent with the fact that it does not release H_2 readily.

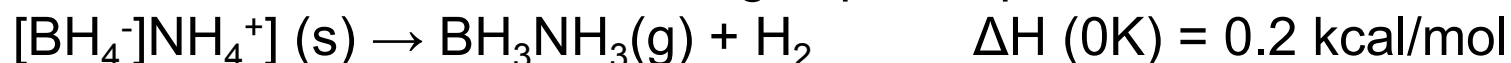
Can the salt $[\text{BH}_4^-][\text{NH}_4^+]$ serve as an H_2 storage system?

Estimate the lattice energy U_L of the salt from the empirical expression:

$U_L = 2 / [\alpha V_m^{-1/3} + \beta]$ where l is the ionic strength ($l = 1$), V_m is the molecular (formula unit) volume α and β are empirical parameters. Equation good to ± 5 kcal/mol

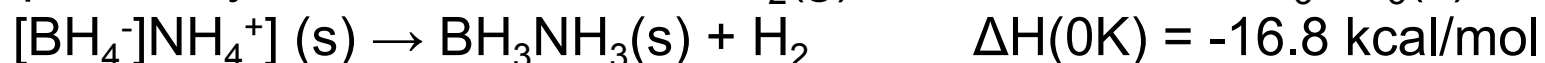
Use experimental volumes for BH_4^- and NH_4^+ to obtain a lattice energy of 151.3 kcal/mol and $\Delta H(0\text{K})$ for the salt of -9.3 kcal/mol.

The reaction from the ionic solid to the gas phase products



is essentially thermoneutral and the salt would be a good source of H_2 .

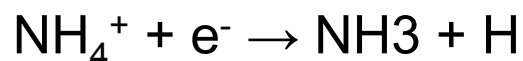
Another possibility for the formation of $\text{H}_2(\text{g})$ is formation of $\text{NH}_3\text{BH}_3(\text{s})$



The calculated cohesive energy for BH_3NH_3 is 17 kcal/mol and the enthalpy change for the hydrogen release reaction is substantially more exothermic than if $\text{BH}_3\text{NH}_3(\text{g})$ is produced.

Stability of a salt requires that electron transfer cannot occur between the cation and anion

-Electron affinity (EA) of NH_4^+ is very low as NH_4 is a Rydberg molecule with only a weak binding of H to NH_3 if at all. Estimate $\text{EA}(\text{NH}_4^+)$ as the energy of the following reaction giving -4.84 eV



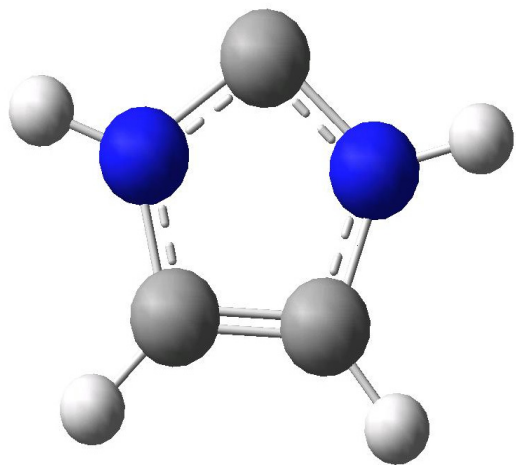
-Ionization potential (IP) of BH_4^- is given by the reaction



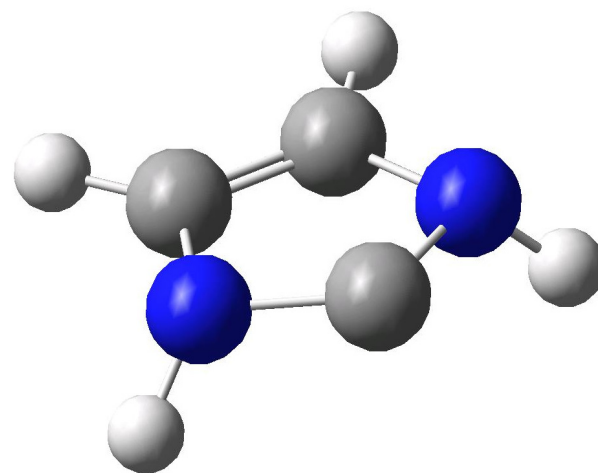
as BH_4 is also a very weakly bonded system and $\text{EA}(\text{BH}_3)$ is very small (0.038 ± 0.015 eV, *J. Chem. Phys.*, **1989**, 90, 795). The ionization potential of BH_4^- is low, 3.89 eV.

The fact that $\text{EA}(\text{NH}_4^+)$ and $\text{IP}(\text{BH}_4^-)$ are comparable within 1 eV of each other is consistent with the fact that this salt can be synthesized.

Carbene Structures for H₂ Storage Systems

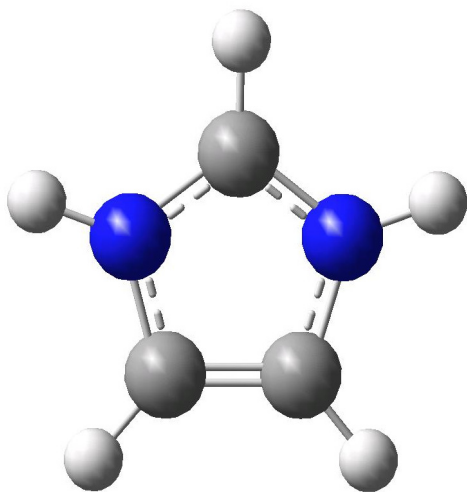


carbeneH₄

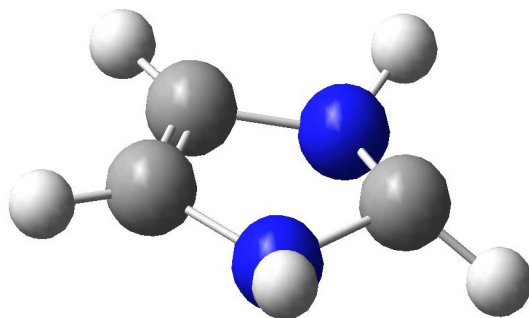


³carbeneH₄

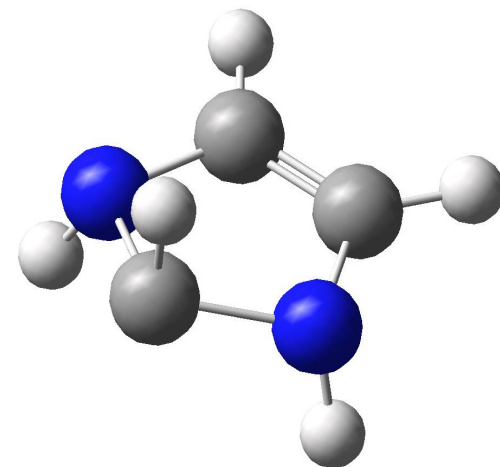
Based on Arduengo's stable carbene



carbeneH₅⁺

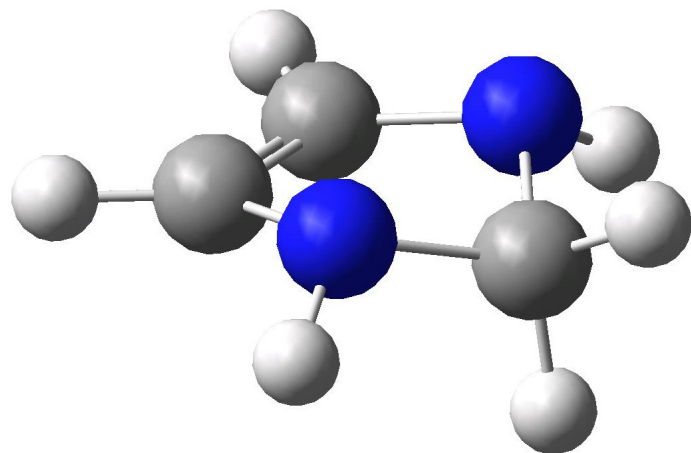


carbeneH₅

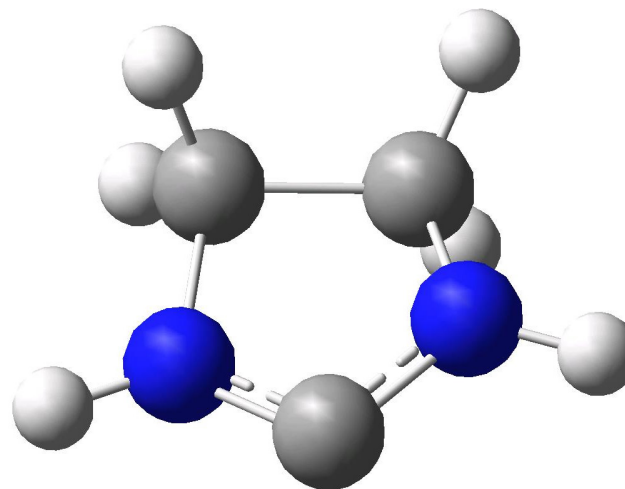


carbeneH₅⁻

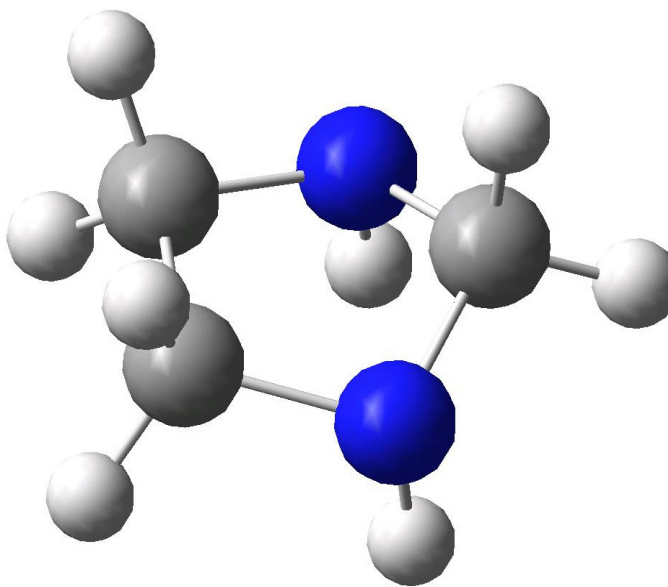
Carbene structures for H₂ Storage Systems



carbeneH₄H₂

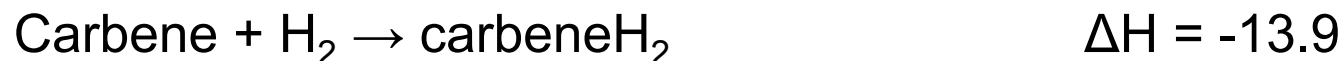


carbeneH₆

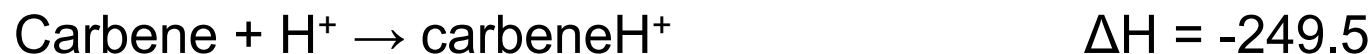


carbeneH₈

Carbene Reaction Energetics (kcal/mol) for H₂ storage at 298K



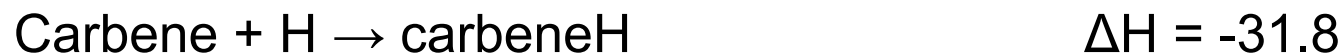
Adding H₂ to the carbene is exothermic by 13.3 kcal/mol -- very nice in managing release because we can use ΔG to pull it off using Le Chatlier's Principle. $T\Delta S(298\text{K}) = +8.2$ kcal/mol



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



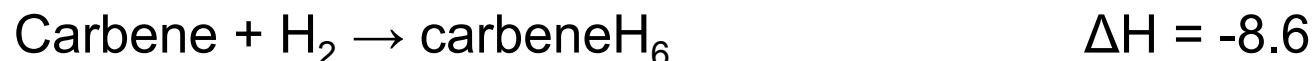
The singlet triplet splitting of the carbene is very large, 89.8 kcal/mol!



The C-H bond energy for adding an H to the carbene is only 32 kcal/mol.



Addition of H⁻ to the simplest carbene leads to autodetachment of the e⁻.



Adding H₂ to hydrogenate the double bond is exothermic by only 8.6 kcal/mol as compared to -31 kcal/mol for hydrogenation of C₂H₄.

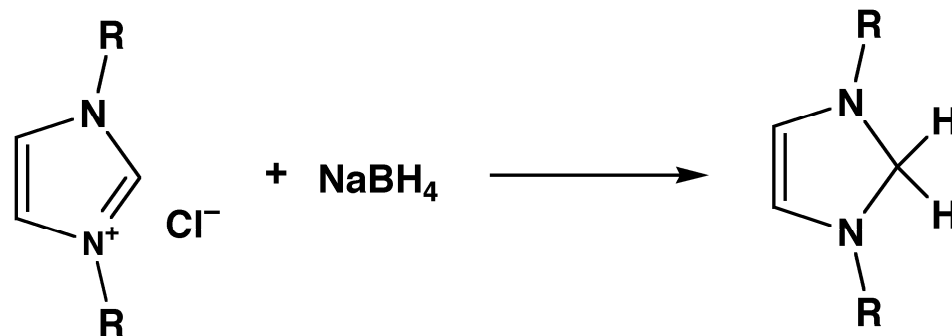


Adding H₂ to the hydrogenated carbene is exothermic by 32.5 kcal/mol.

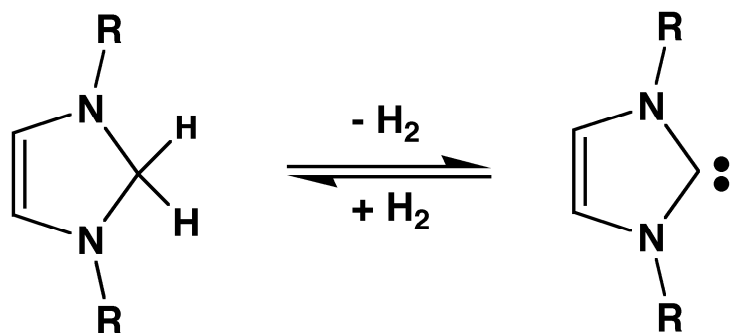
Future Work

- Experimental and computational characterization of cyanocarbons for H₂ storage
- Experimental and computational studies on Carbene-H₂ adducts.
- Experimental and computational studies on imidazol(in)ium borohydrides and carbene-borane adducts
- Continue computational chemistry studies in overall support of DOE Center of Excellence for Chemical Hydrogen Storage

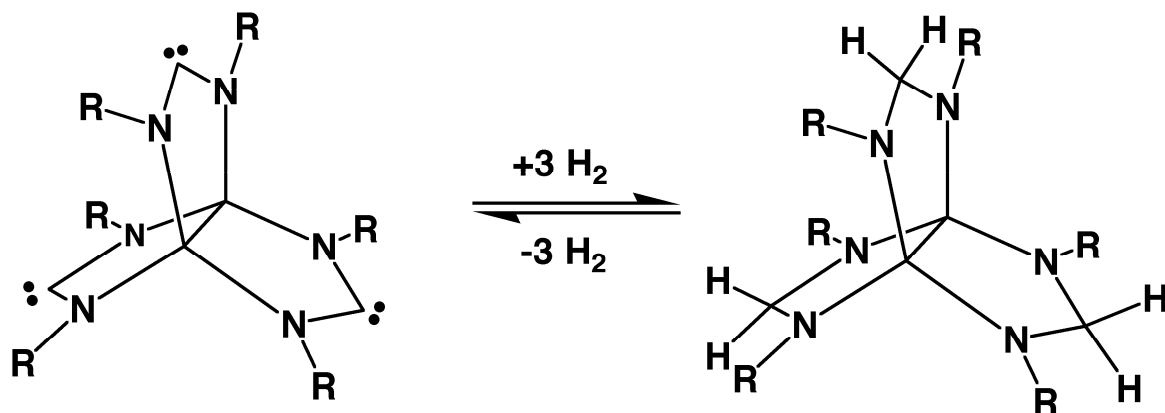
Carbene·H₂ Adducts: Proposed Experimental Work



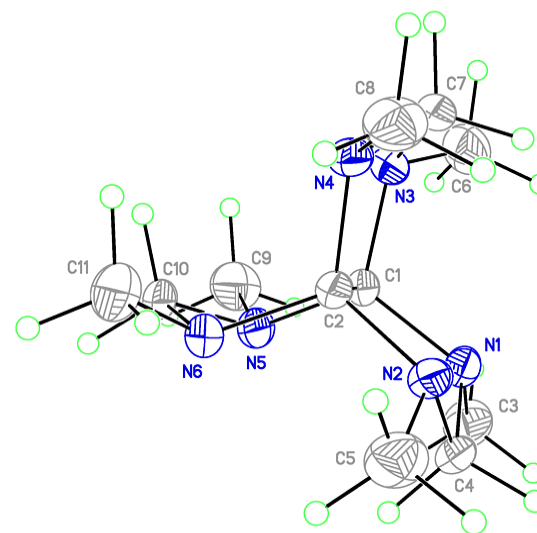
Concept reaction



Extended Reaction



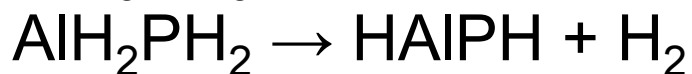
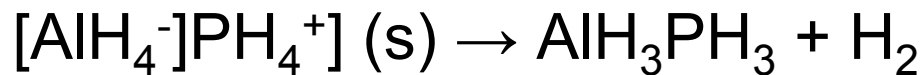
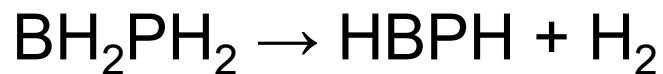
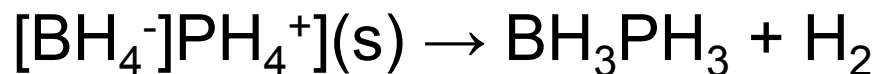
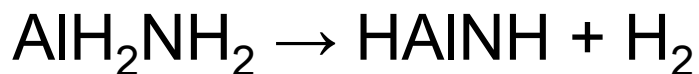
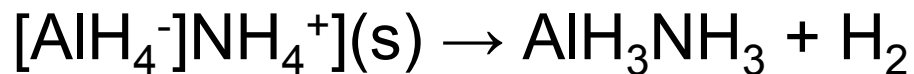
X-ray structure of product



Computational studies of other potential molecular systems for H₂ chemical hydrogen storage

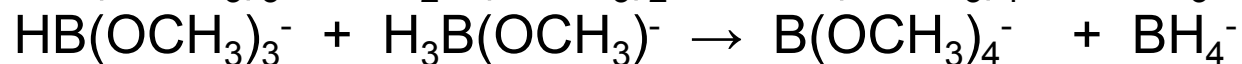
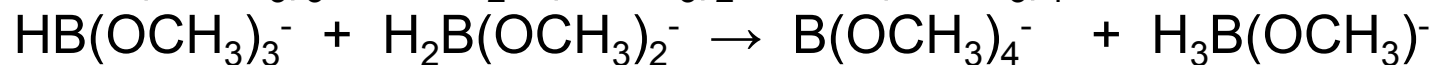
Look at isoelectronic molecules in the Periodic Table.

Use our advanced electronic structure methods on parallel computers to predict reaction energies for the following

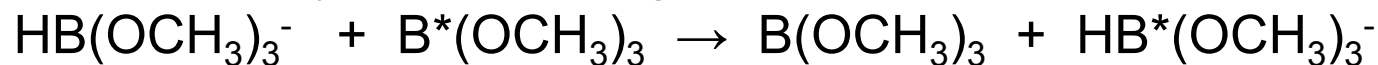


Predict the thermodynamics and rate constants for reactions of alkoxyboron compounds with metal hydrides

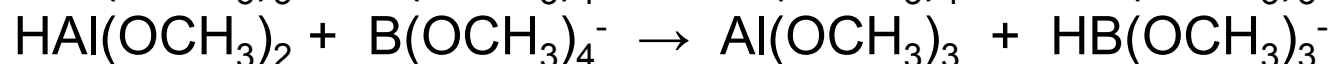
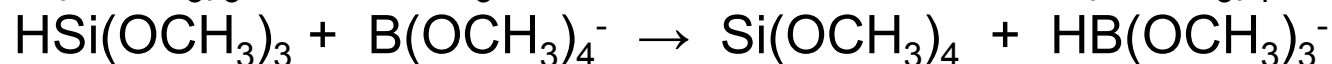
Examples of disproportionation/conproportionation equilibria:



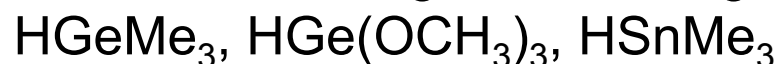
Reaction profile for hydride exchange:



Thermodynamics of hydride exchange with other hydrides



Similar reactions involving other main group elements including:



Other Reaction modeling and Cyber-Infrastructure support

- Borane amine reactions: Predictions of reaction mechanisms including dehydro-oligomerization reactions, Lewis acid base addition reactions, hydride extraction, proton loss
- Predict nmr chemical shifts, infrared spectra, and UV-vis spectra for use in analyzing experimental data
- Boron hydride cluster modeling
- Electronic infrastructure support
 - Develop website for Center partners to share data, publications, presentations
 - Implement electronic communication approaches to enable Center partners to communicate better
 - Data management: Develop and construct database for thermodynamic, kinetic, and spectroscopic data for the Center

University of Alabama: Experimental Effort Timeline:
Go/No Go Decision point is end of year 3

Task	Year 1	Year 2	Year 3	Year 4	Year 5
Synthesis of pendant functionalized imidazoles and imidazolines as candidates for H ₂ activation	██████████				
Find conditions for H ₂ activation by imidazole based systems	██████████	██████████			
H ₂ elimination from imidazolium and/or imidazolinium borohydrides	██████████	██████████	██████████		
H ₂ uptake by imidazolylidene boranes and/or imidazolinylidene boranes	██████████	██████████	██████████		
Synthesize and characterize LiH-carbene complexes	██████████	██████████			
Synthesize hindered imidazole-2-thione for red/ox studies		██████████	██████████		
Oxidize imidazole-2-thione with chemical reagents		██████████			
“Hydride” reduction of Imidazolethione oxid state +2		██████████	██████████		
Synthesis of oxidation state +4 sulfur derivatives		██████████	██████████		
Reduction of high oxidation sulfur species		██████████	██████████		
Synthesize carbene-SiH ₄ complexes		██████████	██████████		
MW/struct. control of 2D cyanocarbon polymer	██████████	██████████			
Reduction of Cyanocarbon polymer	██████████	██████████			
Reversible Cyanocarbon H ₂ uptake	██████████	██████████			
Optimize carbene MW				██████████	██████████
Optimize cyanocarbon MW				██████████	██████████
Develop catalysts for H ₂ release from carbene-based compounds		██████████	██████████	██████████	██████████
Develop catalysts for H ₂ release from cyanocarbons			██████████	██████████	██████████
Develop production chemistry				██████████	██████████

University of Alabama: Computational Effort Timeline:

Go/No Go Decision Points in collaboration with Center Experimental Efforts

Task	Year 1	Year 2	Year 2	Year 4	Year 5
Benchmark of density functional theory (DFT) method against accurate molecular orbital methods and experiment					
Accurate predictions of heats of formation of main group compounds for H ₂ storage/release					
Computational results for B-O → B-H conversions – birate complexation/reduction					
Imidazolium borohydrides and carbene-borane adducts					
Cyanocarbon chemistry					
Carbene-main group compound adducts					
Polyhedral borane chemistry					
Initial database constructed for thermodynamic and kinetic data					
Continuous evaluation of go-no go decisions for different compounds and approaches by combining computational and experimental results in combination with partners					
Web site construction and maintenance					
Computational chemistry calculations on proposed Tier 3 compounds to predict thermochemistry and kinetics for novel H ₂ storage compounds and materials based on C, N, and main group elements					
Computational chemistry calculations on proposed catalysts for Center including main group, organic, and boron-based compounds					

Publications and Presentations

Publication:

“Thermodynamic Properties of Molecular Borane Amines and the [BH₄-][NH₄+]⁻ Salt for Chemical Hydrogen Storage Systems from Ab Initio Electronic Structure Theory,” D. A. Dixon and M. Gutowski, *J. Phys. Chem. A*, 2005, accepted, April

Presentations:

Invited Presentation at the 229th National American Chemical Society Meeting, San Diego CA, March, 2005, Division of Fuel Chemistry, Computational Methods and Modeling in Fuel Chemistry Symposium (+ 2 page extended abstract):

“High Level Computational Approaches to the Prediction of the Thermodynamics of Chemical Hydrogen Storage Systems and Hydrocarbon Fuels” David A. Dixon, Maciej Gutowski, Lisa Pollack, Theresa L. Windus, Wibe de Jong, University of Alabama, and Pacific Northwest National Laboratory

2nd Undergraduate Research Symposium, Arts and Sciences, University of Alabama, April 8, 2005

(1) “High level computational approaches to the prediction of the thermodynamics of chemical hydrogen storage systems,” Jacob Batson and David A. Dixon, 2nd place in sciences

(2) “Cyanocarbons and Their Role in Chemical Hydrogen Storage,” Michael Phillips and Anthony J. Arduengo

Hydrogen Safety

The most significant hazards associated with this project are:

Compound Flammability and Toxicity

- § At present no unique hazards have arisen as a result of these studies. Our approach avoids the use of free H₂ which minimizes safety issues
- § All new reduced compounds are handled under inert atmospheres (N₂) until combustion hazards are determined.
- § All cyanocarbon compounds are treated as toxic and worker exposure is strictly controlled.

Laboratory Safety

Our approach to deal with this hazard is:

- § All new reduced compounds are handled under inert atmospheres (N₂) until combustion hazards are determined.
- § All cyanocarbon compounds are treated as toxic and worker exposure is strictly controlled
- § All procedures are reviewed by other laboratory personnel before execution.
- § Working alone in a chemical laboratory is not permitted.
- § A strict “Take-Two” policy is followed by all experimentalists.