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 ST060

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Overview

Timeline

- Project start date: Jan. 05
- Project end date: March 31, 2010
- Percent complete: 100%

Barriers

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

Budget

- Projected total project funding: $2,255,397
- DOE share: $1,649,495
- UA share: $605,901

- Funding for FY09: $389,495 (full funding DOE)
- Funding for FY10: 0(DOE)

Partners

- DOE Center of Excellence for Chemical Hydrogen Storage

- LANL, PNNL, UW, UC-Davis, Penn State, Penn, U. Missouri-Columbia, U. Oregon, Dow, and Rio Tinto.

Objectives/Relevance

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

  - Enable DOE to meet the technical objective: "*By 2010, develop and verify on-board hydrogen storage systems achieving 2 kWh/kg (6 wt%), 1.5 kWh/L, and $4/kWh.; by 2015, 3 kWh/kg (9 wt%), 2.7 kWh/L, and $2/kWh"* by using chemical hydrogen storage systems.

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

  - Focus on design of new materials and regeneration schemes.
  - Major source for thermodynamic data for entire Center
  - Develop new approaches for thermodynamic predictions

- Experimental focus on organic and main group chemistries with better release and regeneration properties due to improved energy balance. Longer term alternatives.

Approach

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

  Experiment: Arduengo, Masaaki Yoshifuji (visiting faculty), Luigi Iconaru (grad student), Jason Runyon (grad student), Andreea Cojocaru (grad student)

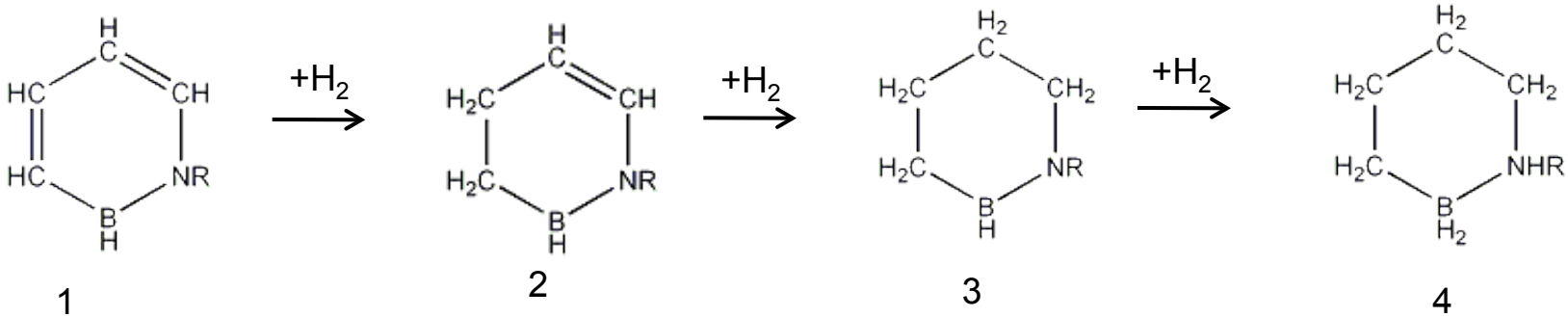
  Computation: Dixon, Daniel Grant (grad student), Ted Grant (grad student), Monica Vasilu (grad student), D.J. Outlaw (CBHP undergrad), Pierce Robinson (undergrad), Myrna H. Matus (visiting faculty, University of Veracruz-Xalapa), Minh T. Nguyen (visiting faculty, Leuven)

Key Accomplishments

- Developed approach to predict heats of vaporization (liquid heats of formation) with new atomic parameters derived from experiment (CoE, LANL, R&H). Tested against known values. Used for process simulations.
- Predicted reliable thermodynamics for large numbers of compounds for release and regeneration schemes to aid in chemical design and process design and simulation. Data provides guidance for experimental design and used in process simulations.
  - First reliable predictions of the properties of spent fuel BNH_x, x = 1 – 2.
  - Significant advances in reliable predictions of the thermodynamics of new H_2 chemical hydrogen storage systems to help groups focus experimental efforts. Example: Properties of new compounds: C_4BNH_{12}/C_4BNH_6 and $C_2B_2N_2H_{12}/C_2B_2N_2H_6$ (UO).
  - Predicted properties of borane-imidazole complexes with potential to improve release kinetics.
  - Extensive predictions of the thermodynamic and spectroscopic properties for hydrazine regeneration schemes.
  - Continued to predict thermodynamics for regeneration schemes for process simulations.
  - Developed new thermodynamic models for metal substituted $M/BH_2NH_3^-$ and $M/NH_2BH_3^-$ complexes. M = Sc, Ti, V, Cr (PNNL, LANL, U. Mo). Calculations of transition states for the elimination of H_2 from metal complexes
- Exploring different CBNH compounds based on BH_3-imidazole structure computationally and experimentally and new routes to AB.

C_4BN Ring Chemistry with S. Liu (Oregon)

- Dehydrogenation of C_4BN Cycles – Substituent Effects
- G3MP2 Reaction Energies as a Function of Substituent for the Sequential Addition of H_2 in kcal/mol at 298 K.

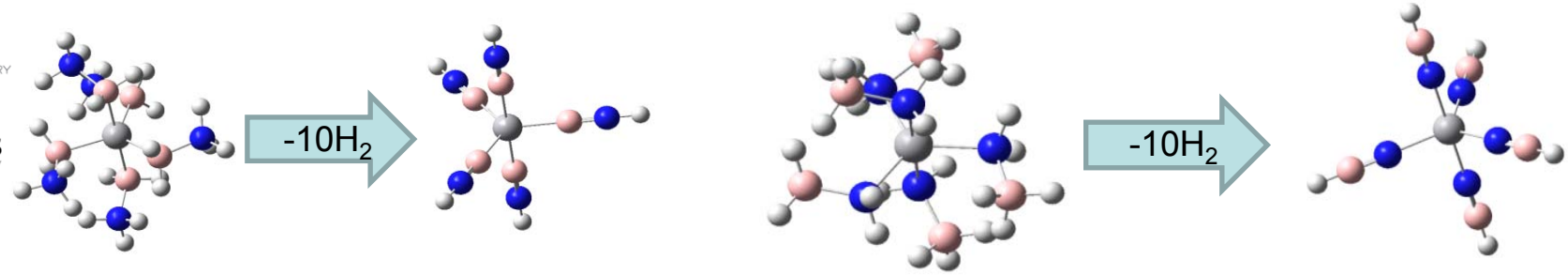


R	Energy	1 → 2	2 → 3	3 → 4	1 → 4
H	ΔH	-6.1	-24.4	7.0	-23.5 (-27.9)*
H	ΔG	2.0	-15.6	15.8	2.3
CH_3	ΔH	-5.8	-25.1	4.9	-26.0
CH_3	ΔG	2.5	-16.1	14.0	0.3
t-butyl	ΔH	-5.4	-24.7	4.9	-25.2
t-butyl	ΔG	3.0	-16.0	13.4	0.4

* CCSD(T)/CBS

- Provided detailed step-wise H_2 release energetics for new compounds and spectroscopic interpretations.
- Predicted optimal compounds to synthesize in terms of release energetics.
- Investigated role of substituent effects on thermodynamics.
- Close interaction with UO on choice of molecular systems.

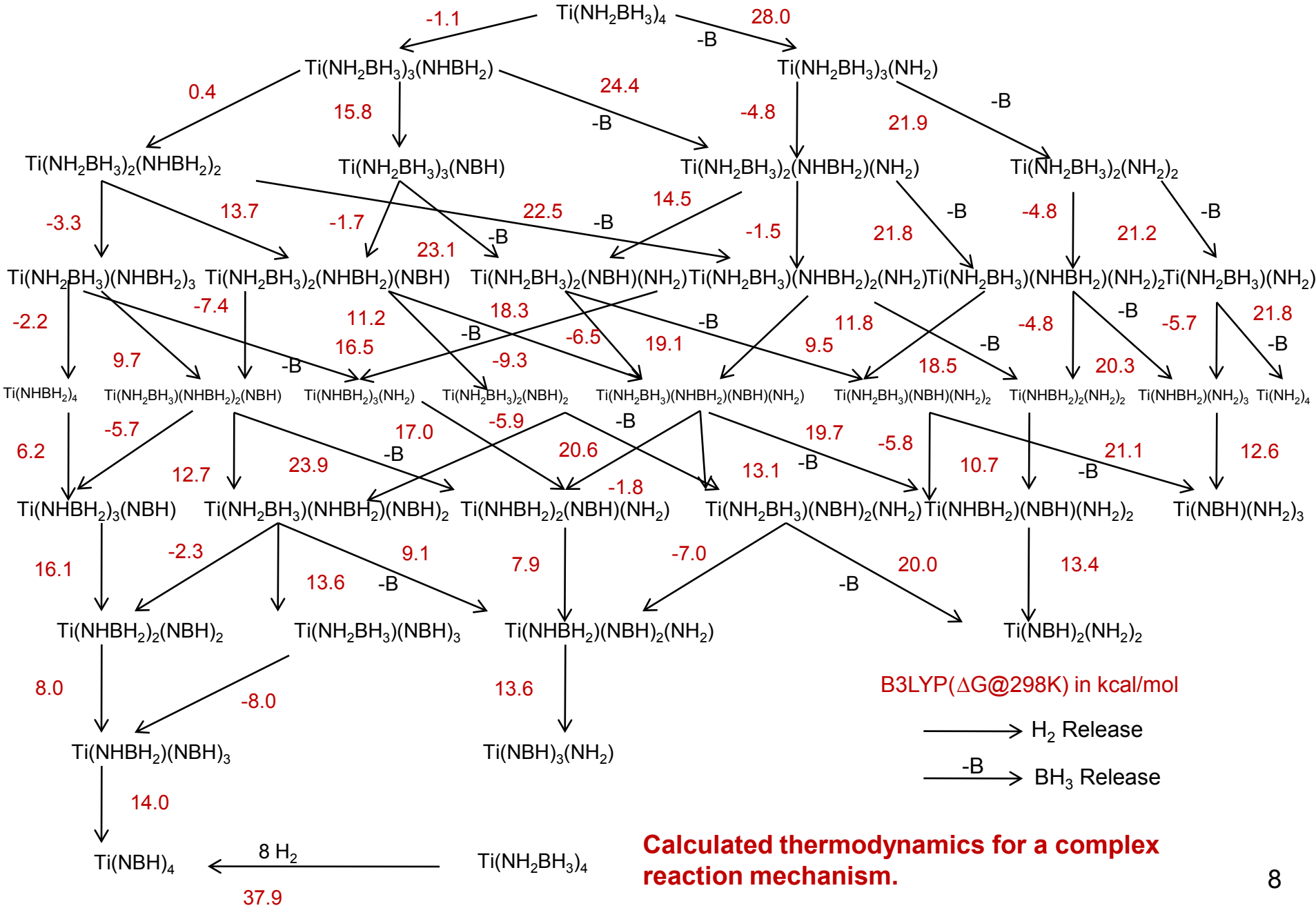
Dehydrogenation of Metal-Substituted Borane Amines



Reaction	Number of Species	Reaction Energy (298 K)	# H_2 released exothermically
$V(NH_2BH_3)_5 \rightarrow V(NBH)_5 + 10H_2$ (overall)	52 x 2 (C_{4v}/D_{3h})	149.0	7
$V(BH_2NH_3)_5 \rightarrow V(BNH)_5 + 10H_2$ (overall)	52 x 2 (C_{4v}/D_{3h})	142.4	9
$Ti(NH_2BH_3)_4 \rightarrow Ti(NBH)_4 + 8H_2$	35	112.2	5
$Ti(BH_2NH_3)_4 \rightarrow V(BNH)_4 + 8H_2$	35	75.8	7
$Si(NH_2BH_3)_4 \rightarrow Si(NBH)_4 + 8H_2$	35	62.8	5
$Si(BH_2NH_3)_4 \rightarrow Si(BNH)_4 + 8H_2$	35	90.3	6
$C(NH_2BH_3)_4 \rightarrow C(NBH)_4 + 8H_2$	35	111.2	5
$C(BH_2NH_3)_4 \rightarrow C(BNH)_4 + 8H_2$	35	94.8	6
$Al(NH_2BH_3)_3 \rightarrow Al(NBH)_3 + 6H_2$	20	74.3	4
$Al(BH_2NH_3)_3 \rightarrow Al(BNH)_3 + 6H_2$	20	48.2	5

- Predicted thermodynamics for $M^{+n}/(^{-}NH_2BH_3)_n$ & $M^{+n}/(^{-}BH_2NH_3)_n$ compounds.
- How many H_2 can be eliminated and energy for H_2 elimination vs. B-N bond breaking?
- Inverse binding species can store more H_2 in terms of the thermodynamics for release.

Dehydrogenation Pathways and B-N BDE for the Metal Borane Amines



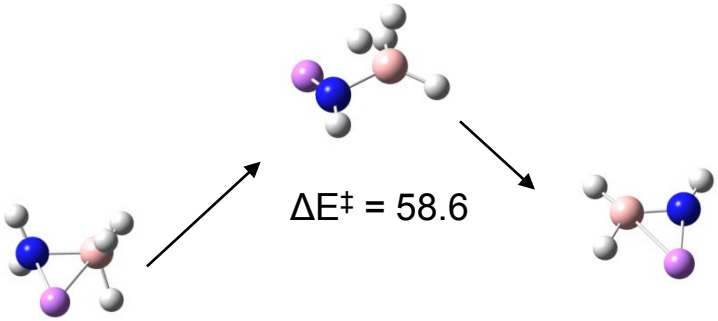
Calculated thermodynamics for a complex reaction mechanism.

Transition States for H_2 Removal from Li and Na-Substituted Ammonia Boranes

- Reaction energies (ΔH_{298K}) calculated at the B3LYP level with the DZVP2 (Li) and DZVP (Na) basis sets.

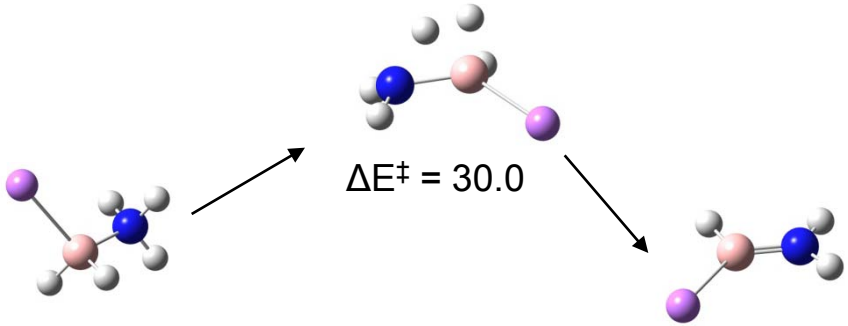
$Li(NH_2BH_3) \rightarrow [Li(NHBH_2)\cdots H_2]^{\ddagger} \rightarrow Li(NHBH_2) + H_2$

$\Delta H = 14.1$



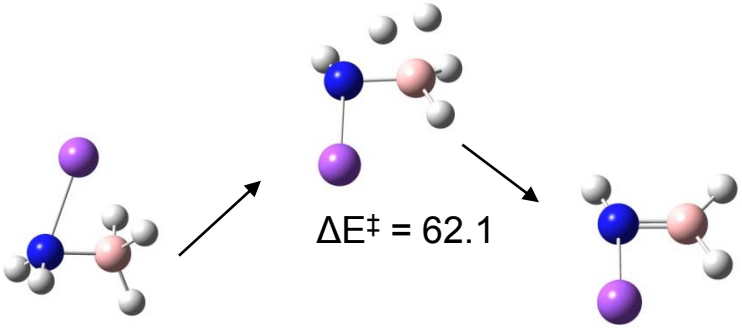
$Li(BH_2NH_3) \rightarrow [Li(BHNH_2)\cdots H_2]^{\ddagger} \rightarrow Li(BH_2NH_2) + H_2$

$\Delta H = -10.4$



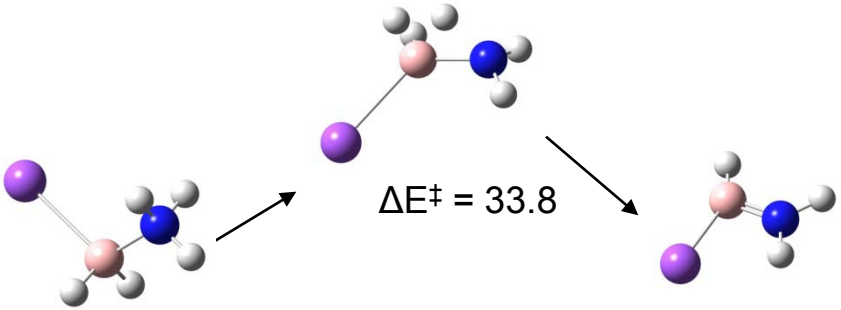
$Na(NH_2BH_3) \rightarrow [Na(NHBH_2)\cdots H_2]^{\ddagger} \rightarrow Na(NHBH_2) + H_2$

$\Delta H = 12.8$



$Na(BH_2NH_3) \rightarrow [Na(BHNH_2)\cdots H_2]^{\ddagger} \rightarrow Na(BH_2NH_2) + H_2$

$\Delta H = -11.1$



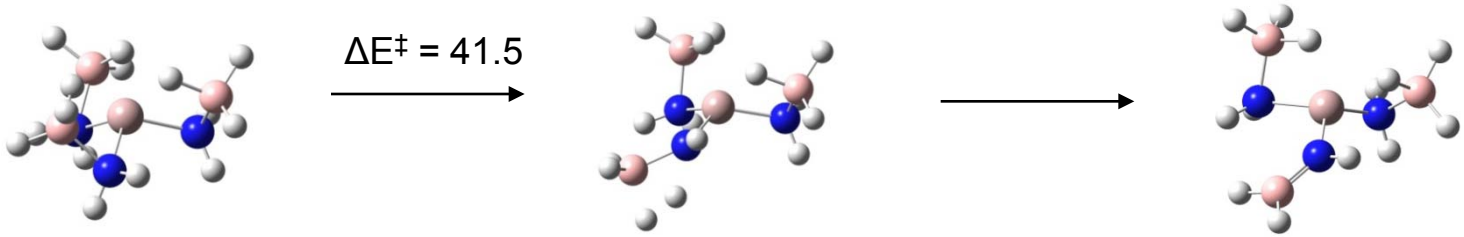
Reaction barriers higher than that in BH_3NH_3 of 34.6 kcal/mol (36.4 kcal/mol, CCSD(T)/CBS) showing that a catalyst is needed or possibly a dimer reaction as previously studied by us.

Transition States for H_2 Removal from Al-Substituted Ammonia Boranes

- Reaction energies (ΔH_{298K}) are calculated at the B3LYP/DZVP2 level.

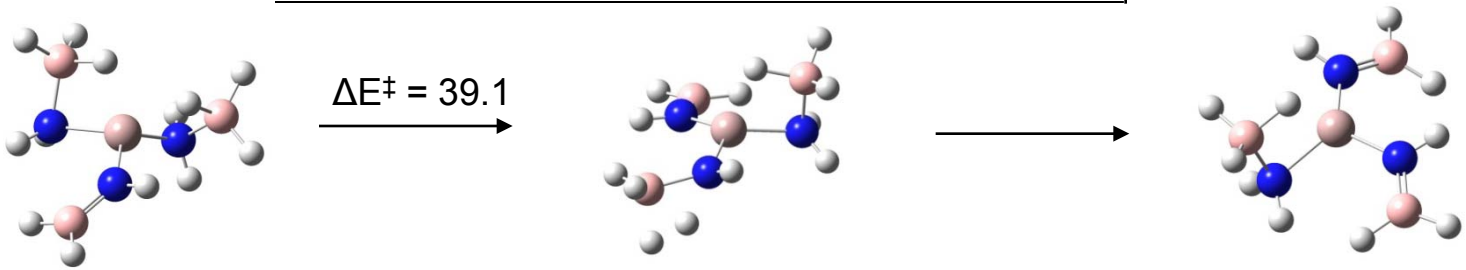
$$Al(NH_2BH_3)_3 \rightarrow [Al(NH_2BH_3)_2(NHBH_2)\cdots H_2]^{\ddagger} \rightarrow Al(NH_2BH_3)_2(NH_3BH_2) + H_2$$

$\Delta H = 1.1$



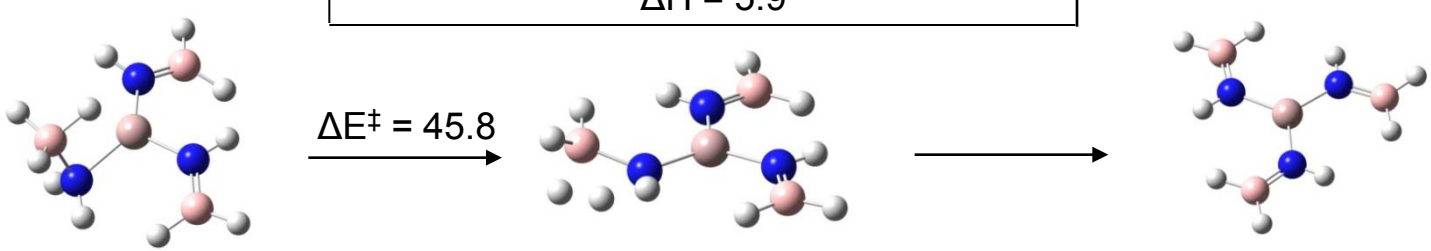
$$Al(NH_2BH_3)_2(NHBH_2) \rightarrow [Al(NH_2BH_3)(NHBH_2)_2\cdots H_2]^{\ddagger} \rightarrow Al(NH_2BH_3)(NHBH_2)_2 + H_2$$

$\Delta H = -1.3$



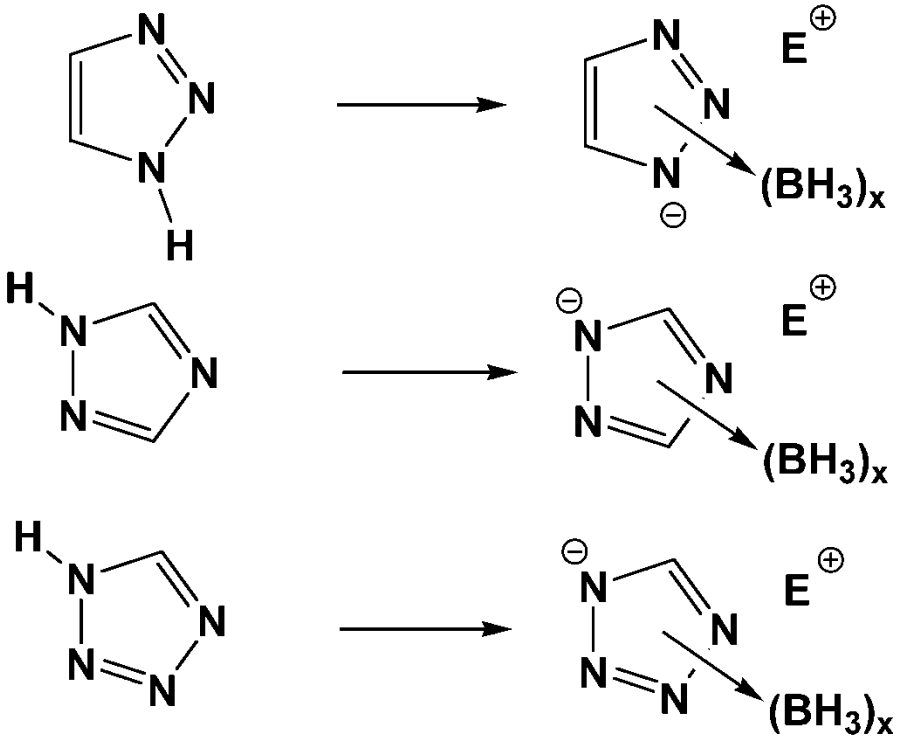
$$Al(NH_2BH_3)(NHBH_2)_2 \rightarrow [Al(NHBH_2)_3\cdots H_2]^{\ddagger} \rightarrow Al(NHBH_2)_3 + H_2$$

$\Delta H = 5.9$



Reaction barriers higher than that in BH_3NH_3 of 34.6 kcal/mol (36.4 kcal/mol, CCSD(T)/CBS) showing that a catalyst is needed or possibly a dimer reaction as previously studied by us.

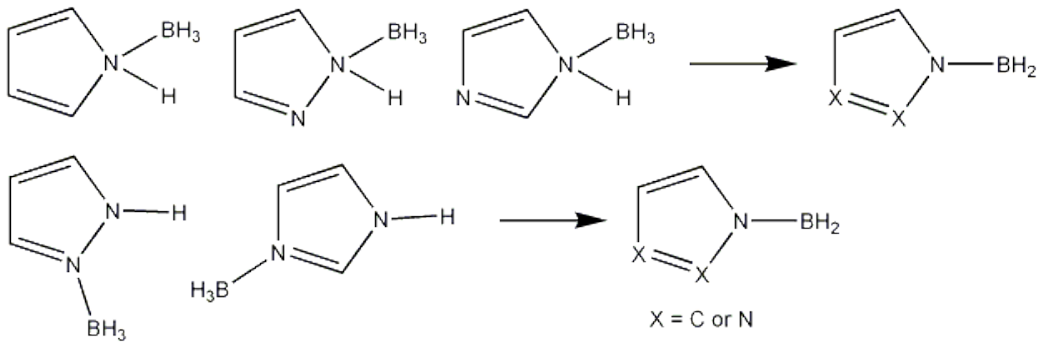
Amino(*Imidazolo*)-Boranes for Better H_2 activation



- Study hydrogen elimination from azolium borohydrides (polymeric amine borane analogs).
- Expand to include 1,2,4-triazoles and tetrazole.
- Reduced basicity of heterocyclic systems containing multiple nitrogens is such that amine-borane adduct formation from the neutral is difficult and the stability of the initially formed adducts is marginal.
- Hydrogen evolution was observed during the initial borane complexation step of these reactions.
- Azole-borane adducts by starting from the more basic azolides (azole-anions) showed only transient stability (loosing hydrogen, but reverse reaction not yet acheived in the laboratory).

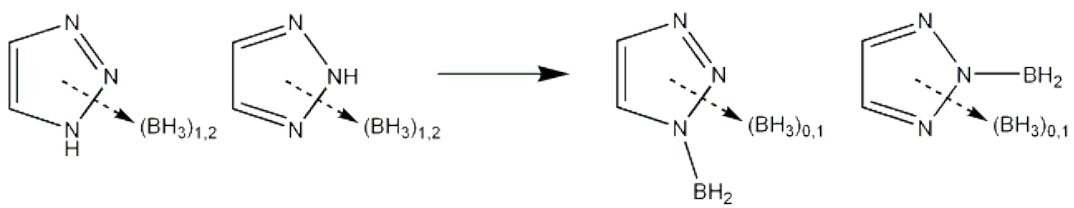
Amino(*Imidazolo*)-Boranes to improve H_2 activation

Dehydrogenation Reactions (298K) at the G3MP2 Level in kcal/mol

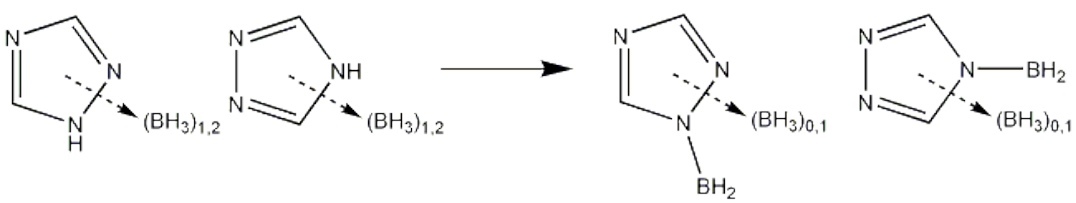


ΔH = -22 to -19

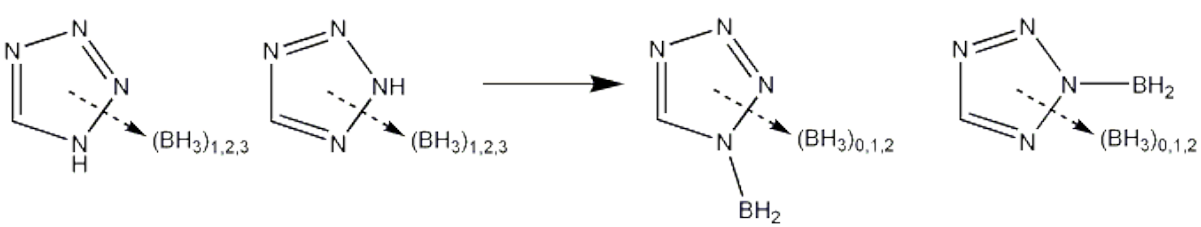
ΔH = 2 to 4



ΔH = -7 to 4
(6 reactions)



ΔH = -7 to 7
(6 reactions)

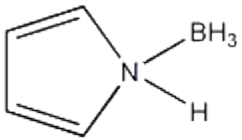


ΔH = -10 to 0
(22 reactions)

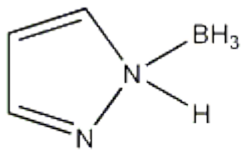
$BH_3NH_3 \rightarrow BH_2NH_2 + H_2$: ΔH = -5.1

- **Wide range of new candidates for H_2 elimination studied**
- **Most have favorable thermodynamics and are backup materials due to weight %**

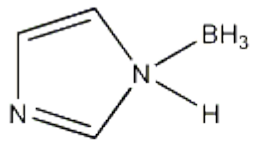
H_3B-N Bond Dissociation Energies (ΔE_{0K}) in kcal/mol for the Azole Boranes at the G3MP2 Level



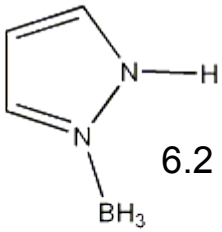
10.3



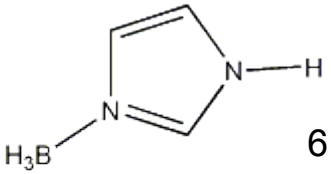
30.1



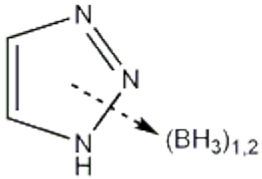
31.8

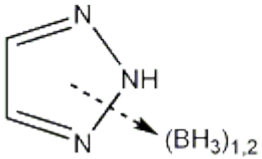


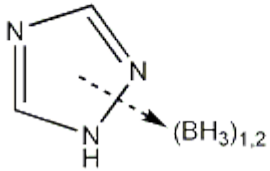
6.2

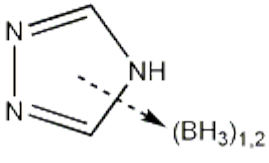


6.6

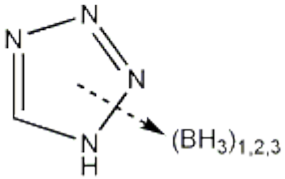


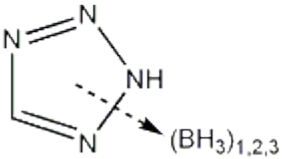




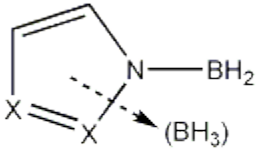


19 to 29



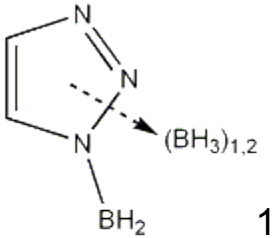


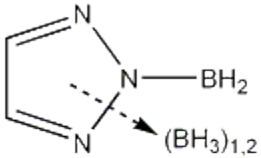
12 to 25



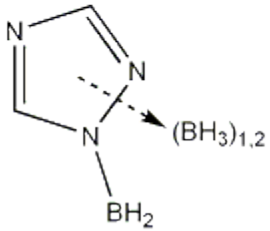
X = C or N

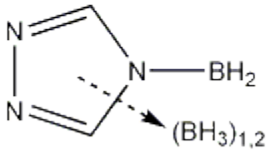
27 to 30

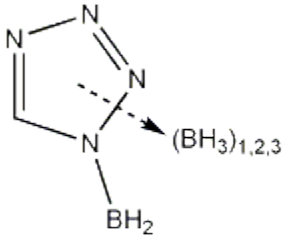


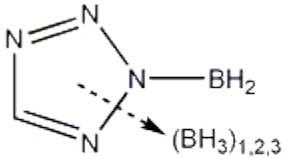


14 to 28







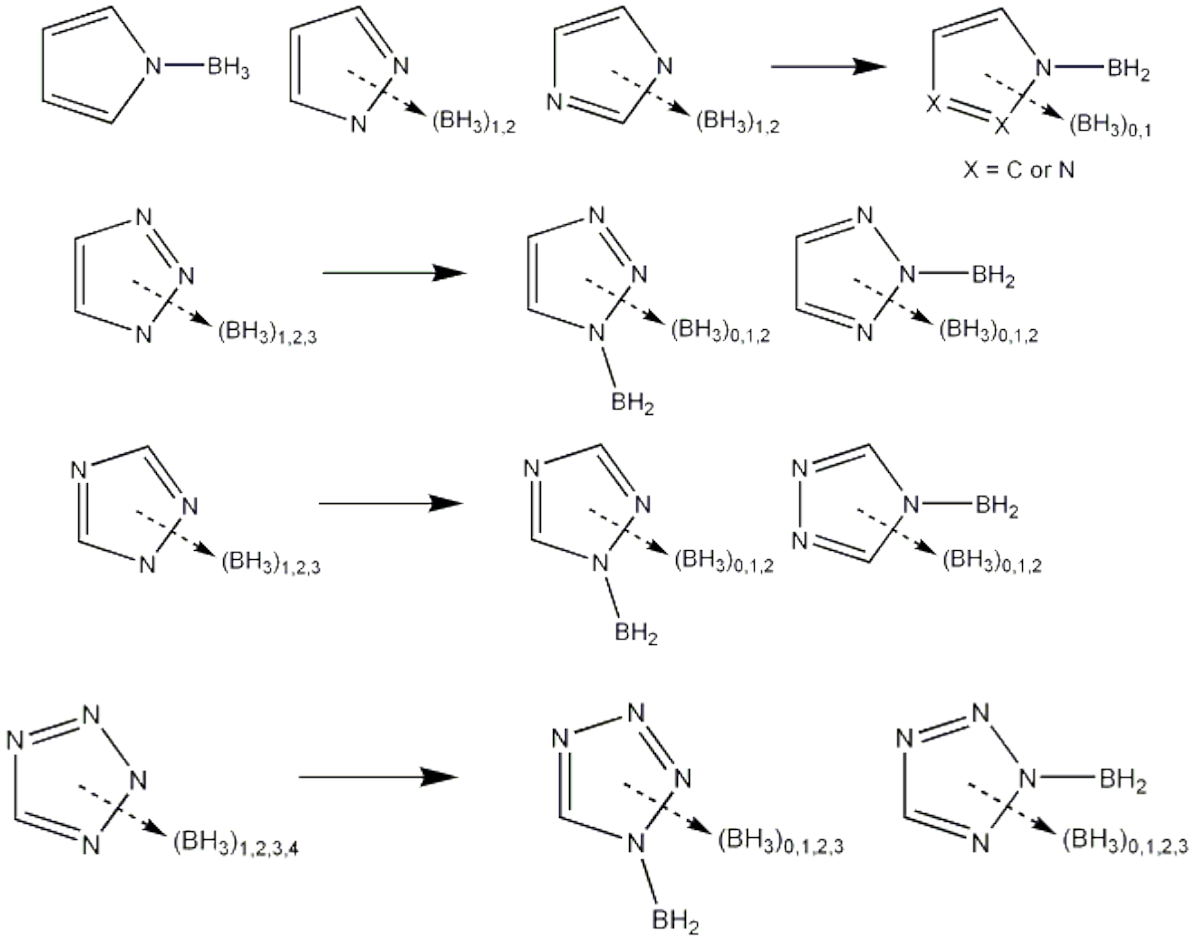


12 to 24

$BH_3NH_3 \rightarrow BH_3 + NH_3$: BDE = 26.1

- In some cases, B-N Lewis acid-base bond energies are low, especially to –N=X centers
- Can tuning the B-N bond energies improve the kinetics?

Calculated Hydride Affinities (HA, 298K) in kcal/mol for the Azole Boranes at the G3MP2 Level



HA = 77 to 103

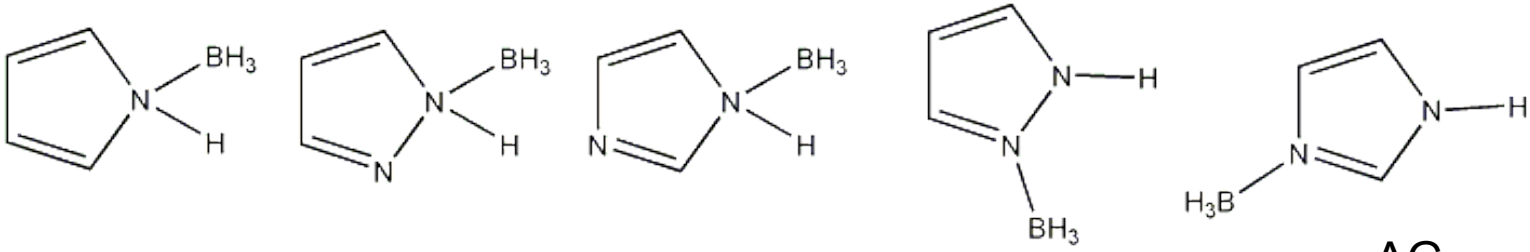
HA = 86 to 122

HA = 90 to 126

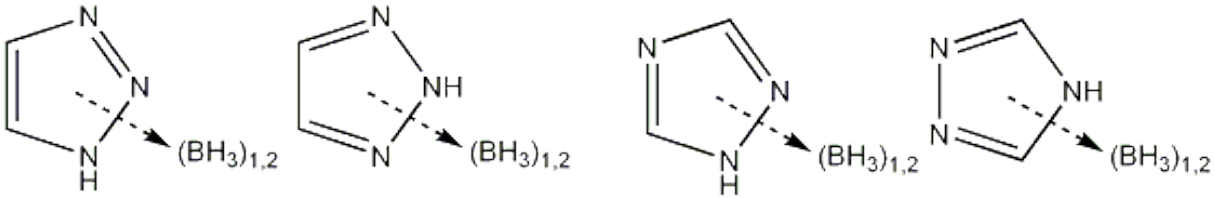
HA = 98 to 139

- These compounds are strong Lewis acids (large hydride affinities)
- New ways to control H_2 release?
- Serve as H^- transfer agents in regeneration processes?

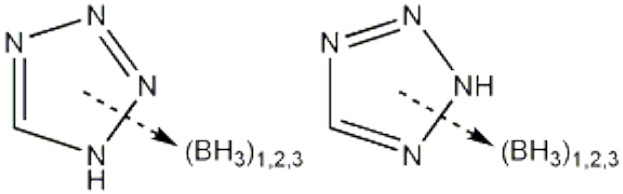
Acidities (298K) in kcal/mol and pKa's relative to nitric acid for the Azole Boranes at the G3MP2 Level



ΔG_{gas} = 294 to 323
pK_a = -4 to 14



ΔG_{gas} = 289 to 314
pK_a = -6 to 10



ΔG_{gas} = 264 to 300
pK_a = -18 to 3

- Compounds can be very strong acids
- Can this property be exploited to improve control of kinetics for H_2 release?

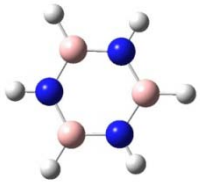
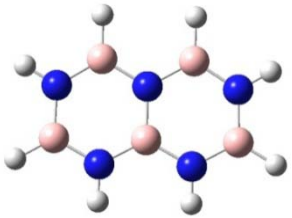
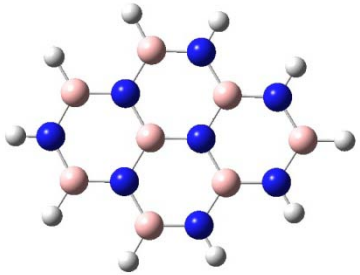
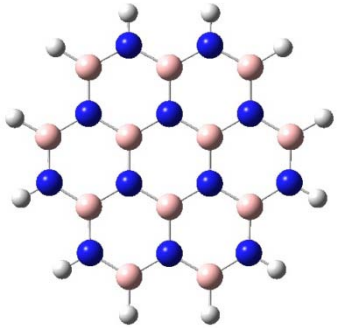
Thermodynamics for First Fill and Regeneration of Ammonia Borane

SPENT FUEL $\longrightarrow$ H_3NBH_3

- Lewis acid-base exchange reactions utilized as a strategy for the production of amine boranes.
- Routes involving digestion to LBX_3 compounds that are converted to LBH_3 by hydrogenolysis or metathesis with hydride donors followed by displacement of L with ammonia have been demonstrated.
- The B-N bond energies for AB and for methyl substituted AB on both B and C have been reliably predicted by us for the free molecules from high level ab initio electronic structure calculations. Ligand displacement reactions and liquid fuels.
- Explore new exchange mechanisms in the gas phase and in solution.
- New hydrazine process: develop mechanisms based on calculated thermodynamic and spectroscopic properties
- Develop first reliable models for the thermodynamic properties of different forms of spent fuel
- New approach to 1st fill chemistry.

Process Analysis & Simulation Requires Physical Properties Thermodynamics for Models of Spent Fuel

$B_3N_3H_6$ = "BNH_2" $B_5N_5H_8$ = "$BNH_{1.6}$" $B_8N_8H_{10}$ = "$BNH_{1.25}$" $B_{12}N_{12}H_{12}$ = "BNH"

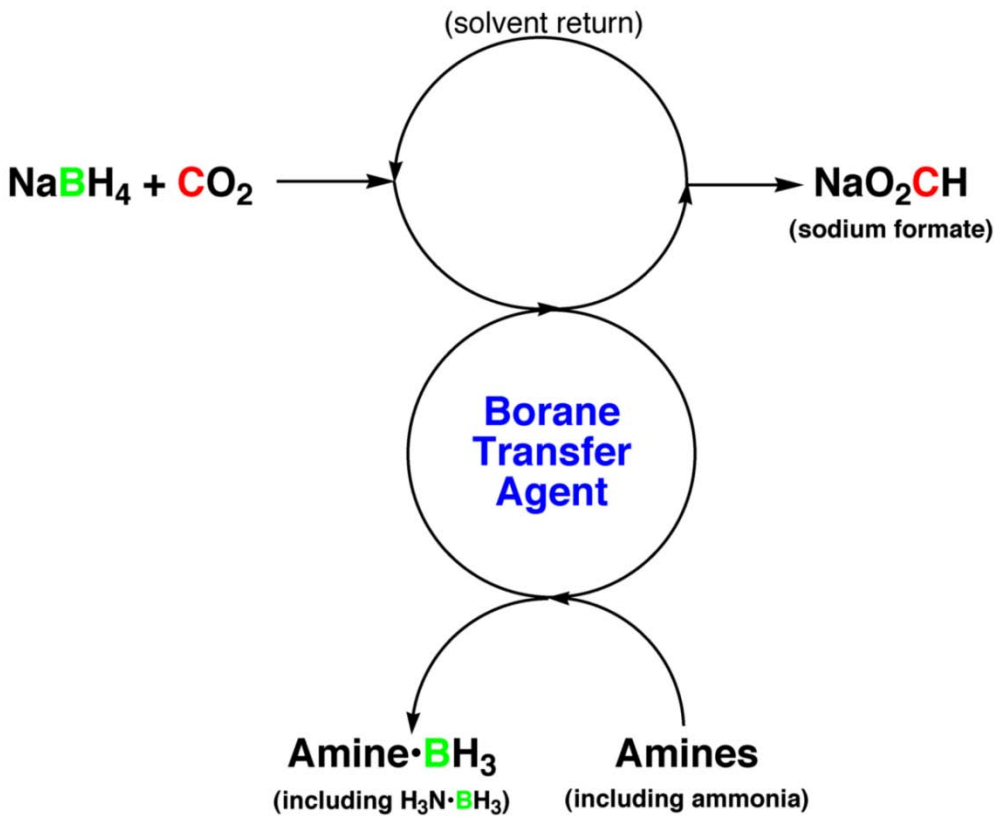





T = 298 K, Energies in kcal/mol

Compounds	ΔH_{gas}	ΔH_{liquid}	ΔH_{solid}(298K)	$BP_{calc/expt}$	ΔH_{vap}
"BNH_2"	-118.5	-126.0	-126.6	327/326	7.5
"$BNH_{1.6}$"	-215.5	-227.8	-232.5	492	12.3
"$BNH_{1.25}$"	-369.6	-386.5	-393.5	678	16.9
"BNH"	-569.0	-592.8	-606.0	951	23.8
BH_3NH_3	-14.6	-31 to -32	-36.6 ± 2.4	663	17

- Developed validated, new approach with new atomic parameters to predict T_{BP}, ΔH_{vap}, ΔH_{liquid} for reactor and separations design. Uses accurate calculated ΔH_{gas} values.
- Data used in process simulations at Dow for 1st fill and regeneration schemes.
- First reliable predictions of the thermodynamics of spent fuel models in different phases.
- Experimental feedback in terms of compounds to study T_{BP} fit to process simulation data.

Synthesis of AB: Borane Transfer Technology

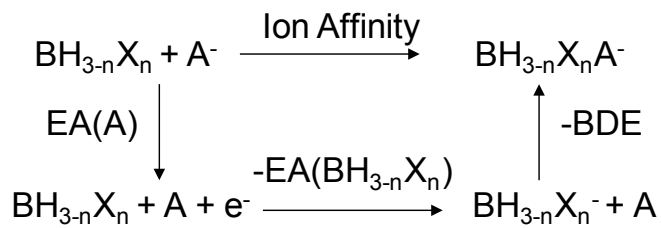


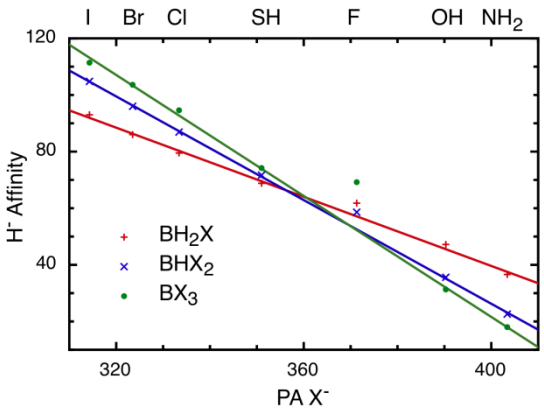
- A borane transfer process has been developed based on a DuPont Patent (No. 5,034,464; A.J. Arduengo, July 23, 1991))
- New process facilitates transfer of a BH_3 unit from sodium borohydride to a variety of amines (including ammonia) with the intermediacy of a proprietary borane transfer agent.
- Overall yield maxima is typically 80 – 95%.
- Ionic Liquids studies as Borane Transfer Agent/Reaction Medium

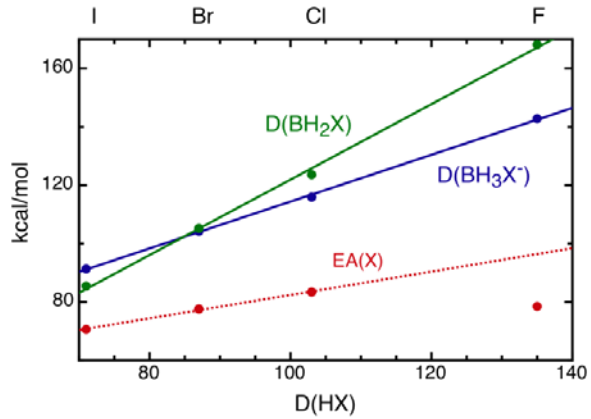
Lewis Acidities: The Ability to Bind H^-, F^-, and Other Bases

CCSD(T)/CBS values in kcal/mol

Molecule	HA	FA
H_3B	73.7	66.6
H_2BF	63.2	67.9
H_2BCl	80.9	79.4
H_2BBr	87.3	84.9
H_2BI	94.3	89.9
H_2BNH_2	37.8	39.7
H_2BOH	48.4	53.3
H_2BSH	69.8	67.0
HBF_2	60.0	72.1
$HBCl_2$	88.1	88.9
$HBBr_2$	97.3	95.8
HBI_2	106.0	99.9
$HB(NH_2)_2$	24.0	29.0
$HB(OH)_2$	36.6	47.3
$HB(SH)_2$	72.7	69.0
BF_3	70.5	82.1
BCl_3	95.8	96.0
BBr_3	104.9	102.4
BI_3	112.6	105.9
$B(NH_2)_3$	19.8	28.1
$B(OH)_3$	31.8	44.4
$B(SH)_3$	75.2	73.3







Lewis acid strength depends on the electron withdrawing and back donating ability of ligands on B. The OH, NH_2, and SH groups show low acidities. The H- and F- affinities of the $BH_{3-n}X_n$ compounds exhibit linear correlations with the proton affinity of X^- for most X ligands.

The dominant effect in determining the magnitude of the Lewis acidity is the strength of the BX_3^--F bond. The main contributor to the relative differences in the Lewis acidities of BX_3 for X a halogen is the electron affinity of BX_3. The electron affinity of BX_3 is strongly influenced by the charge density in the empty p_z LUMO on boron so the amount of π-back donation from the halogen to boron is crucial.

- First reliable predictions of the Lewis acidities and hydride affinities of these boron compounds
- Benchmarks for larger substituents for use in PNNL & LANL regeneration schemes

Gas phase binding energies (-Δ*H*°) of select Lewis bases (L) with BH_3 calculated at the DFT/B3LYP and G3MP2 levels of theory at 298 K

Ligand L	B3LYP/DZVP2	G3MP2
NH_3	25.2	27.7 (27.7)
NMe_3	30.4	38.0 (37.8) [39.2]
NEt_3	26.6	35.6
n-propylamine	30.1	33.7
s-butylamine	28.9	33.1
piperidine	32.5	38.0
NPh_3	5.6	17.6
Py	29.6	33.4
2,6-Lut	26.1	30.8
PH_3	18.4	22.1 (22.5)
PMe_3	32.6	38.3
PEt_3	32.5	39.1
PPh_3	29.2	35.2
$P(OMe)Me_2$	33.4	40.1
$P(OMe)_2Me$	32.2	39.8
$P(OMe)_3$	30.9	40.0
AsH_3	11.3	(17.8)
$AsEt_3$	22.3	30.1***
$AsPh_3$	19.9	24.2***
SMe_2	19.8	25.3 [25.8]
SEt_2	20.4	26.2
SPh_2	14.8	21.0
THF	16.7	21.4
Et_2O	12.1	17.7 [20.6]
Me_2O	14.9	19.8

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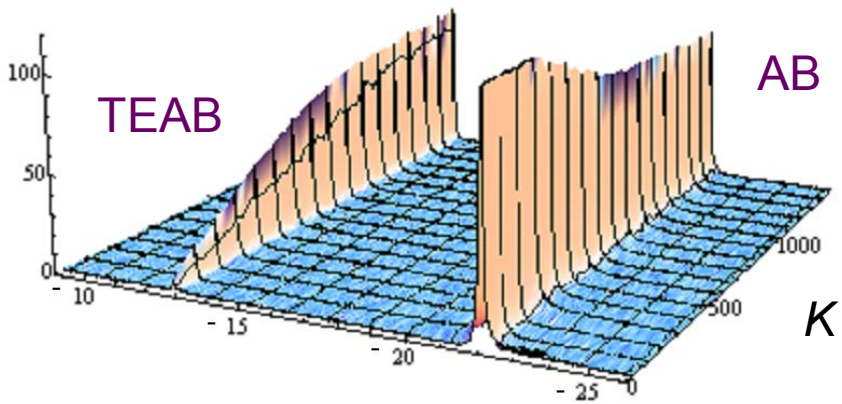
- First reliable set of A-B Lewis acid-base dative bond energies
- G3MP2 is in excellent agreement with experiment and accurate CCSD(T)/CBS calculations by us.
- DFT is not reliable enough for process simulations.
- Data needed for design of ligand displacement reactions for PNNL and LANL regeneration schemes.

Energies in kcal/mol
Values in () are CCSD(T)/CBS
Values in [] are experiment
*** MP2 isodesmic + CCSD(T) for AsH_3

Equilibrium and rate parameters determined for ammoniation of triethylamine:BH_3 (J. Potter & D. Camaioni, PNNL)

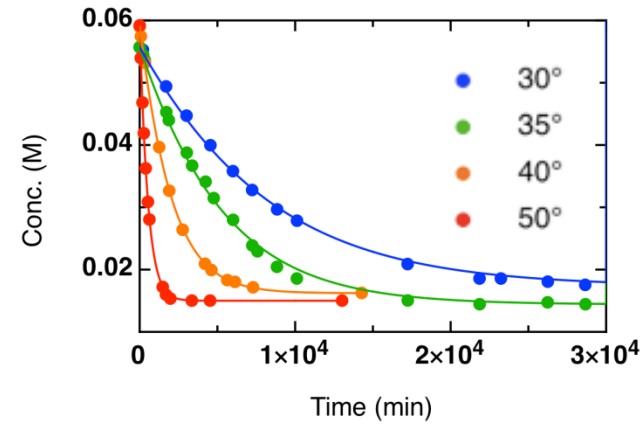
Time dependence of ^{11}B NMR spectrum for reverse reaction

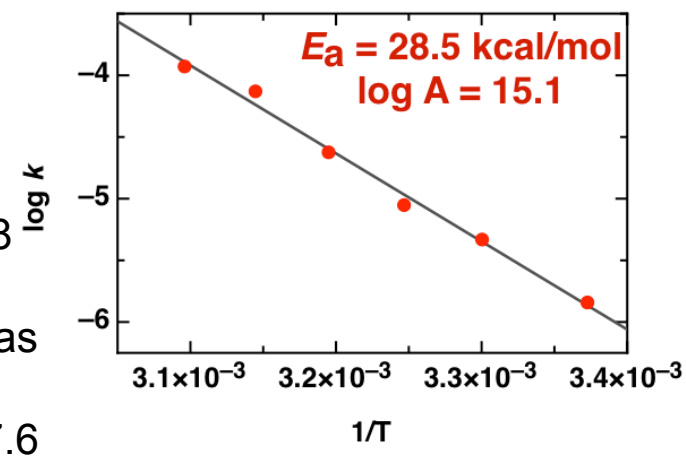
Initial conditions: .29 M TEA,.08 M AB in THF, 45 °C



K = 0.37

$$H_3NBH_3 + Et_3N \rightleftharpoons Et_3N{:}BH_3 + NH_3$$





- G3MP2B3 Gas Phase(298 K): ΔH = -7.9 kcal/mol, ΔG = -5.8 kcal/mol
- G3MP2B3 + COSMO: ΔG(solution, 298 K) = -2.6 kcal/mol (as compared to +0.6 kcal/mol from expt at 318 K)
- G3MP2B3 Gas Phase(298 K): $\Delta H^{\ddagger}$ = 8.5 kcal/mol, $\Delta G^{\ddagger}$ = 17.6 kcal/mol
- G3MP2B3 + COSMO: $\Delta G^{\ddagger}$ = 28.5 kcal/mol (electrostatic)

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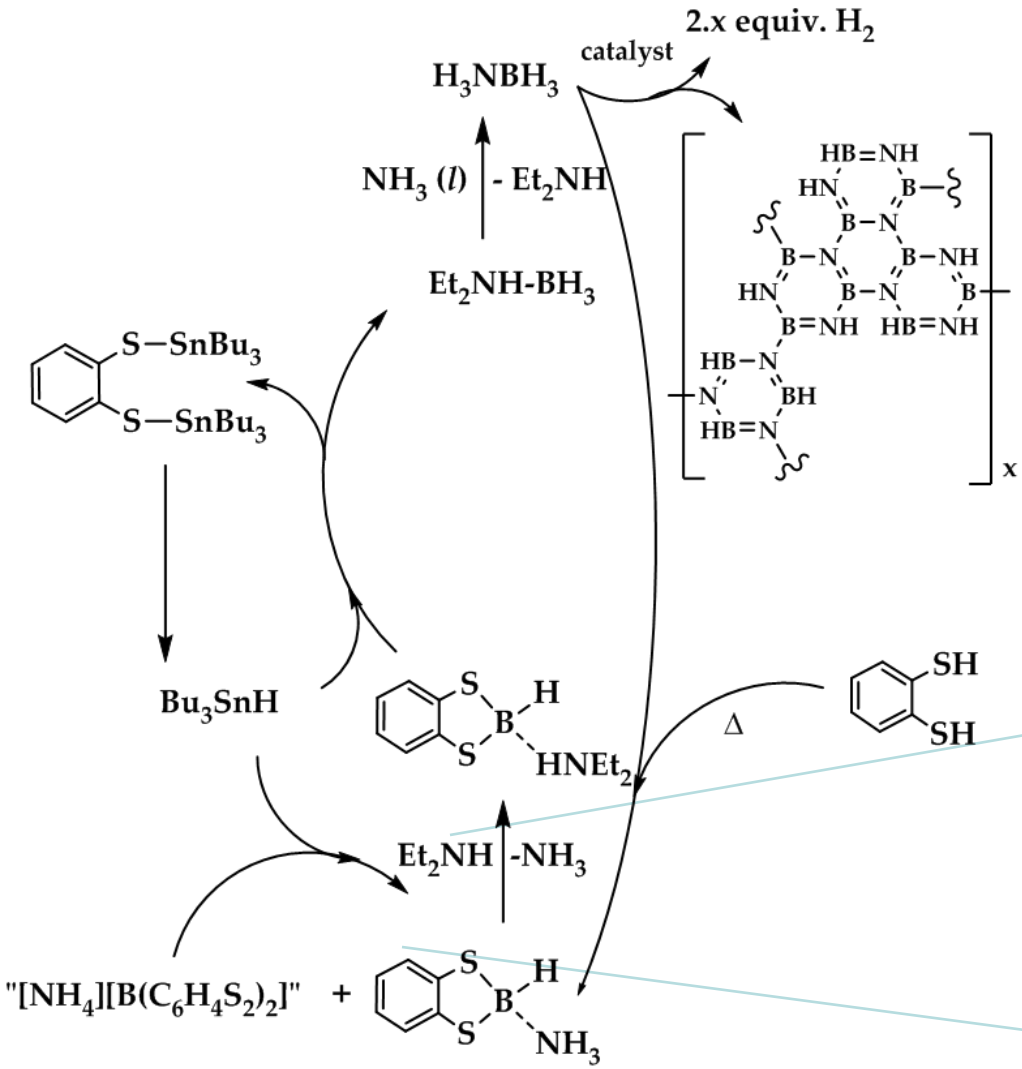
Favorable equilibrium, 2nd order kinetics, strong dependence of rate on T … AB can be recovered from product mixture.

LANL Novel Regeneration Process

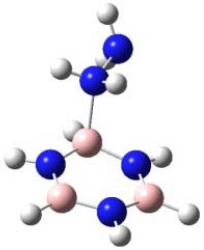


- New LANL regeneration process: Add hydrazine to spent fuel to make N_2 + BH_3NH_3
- Simpler one-pot process which needs only a single reactor to improve efficiency
- Complicated chemistry so need for mechanism interpretation & development.
- Need to regenerate N_2H_4 from N_2 + H_2

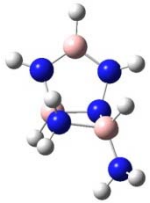
Original LANL multi-step regeneration scheme

Examples of 1st Addition of Hydrazine to BNH_x

$B_3N_3H_6(N_2H_4)$



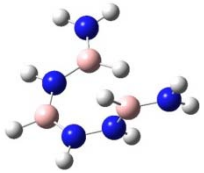
cis-$B_3N_3H_6(NH_2)_2$



ΔH_{298}= -44.6

+

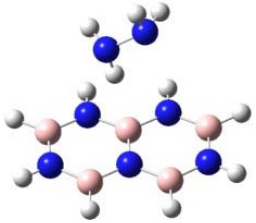
trans-$B_3N_3H_6(NH_2)_2$



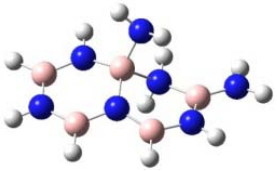
ΔH_{298}= -44.7

Reactions can be exothermic or endothermic depending on the specific addition point. Can lead to B-N bond breaking.

1, $B_5N_5H_8(N_2H_4)$



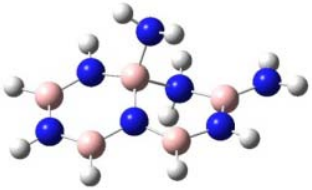
trans-1,2 $B_5N_5H_8(NH_2)_2$



ΔH_{298}= -26.2

or

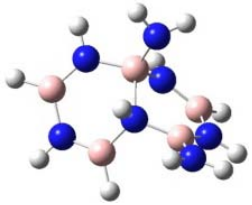
cis-1,2 $B_5N_5H_8(NH_2)_2$



ΔH_{298}= -26.2

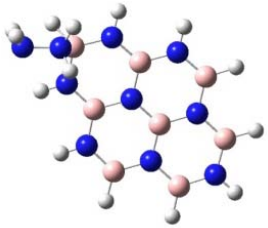
or

trans-1,3 $B_5N_5H_8(NH_2)_2$

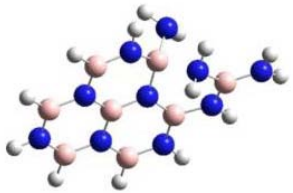


ΔH_{298}= -16.9

1, $B_8N_8H_{10}(N_2H_4)$



cis-1,2 $B_8N_8H_{10}(NH_2)_2$



ΔH_{298}= -37.8

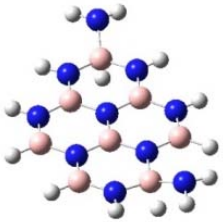
or

cis-1,3 $B_8N_8H_{10}(NH_2)_2$

ΔH_{298}= -8.9

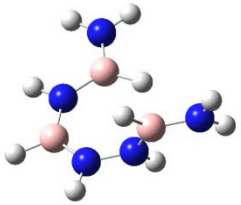
or

cis-1,4 $B_8N_8H_{10}(NH_2)_2$



ΔH_{298}= 62.1

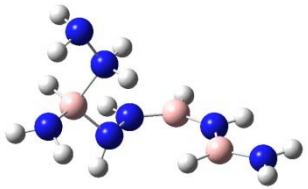
2nd addition of N_2H_4 to Trans-$B_3N_5H_{10}$: ΔH_{298} and ^{11}B NMR



+ N_2H_4

ΔH_{298}= -3.0

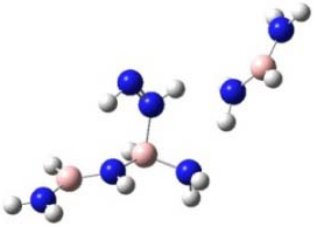
i1,$B_3N_5H_{10}N_2H_4$



	σ
B_1	24.2
B_2	25.5
B_3	-1.3

Cis-o1,2 trans-$B_3N_5H_{10}(NH_2)_2$

	σ
B_1	26.1
B_2	24.3
B_3	-0.9

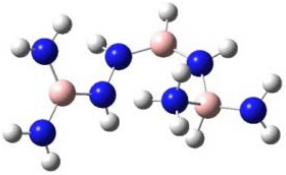


ΔH_{298}= -22.9

Reactions are approximately thermoneutral. Some lead fragmentation processes.

cis-o1,3 trans-$B_3N_5H_{10}(NH_2)_2$

	σ
B_1	22.2
B_2	22.9
B_3	-7.6

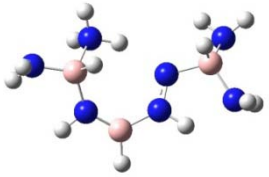


ΔH_{298}= -60.7

or

trans-o1,3 trans-$B_3N_5H_{10}(NH_2)_2$

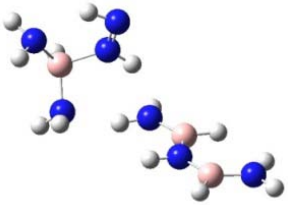
	σ
B_1	4.3
B_2	26.2
B_3	-9.6



ΔH_{298}= -0.8

trans-i1,2 trans-$B_3N_5H_{10}(NH_2)_2$

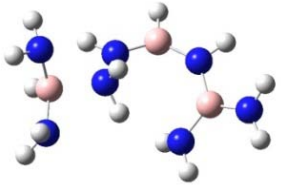
	σ
B_1	25.1
B_2	-2.5
B_3	25.5



ΔH_{298}= -22.6

trans-i1,3 trans-$B_3N_5H_{10}(NH_2)_2$

	σ
B_1	0.2
B_2	24.2
B_3	22.8



ΔH_{298}= -59.6

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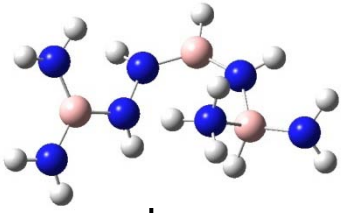
3rd addition of N_2H_4 to Cis-o1,3 trans-$B_3N_5H_{10}(NH_2)_2$: ΔH_{298} & ^{11}B NMR

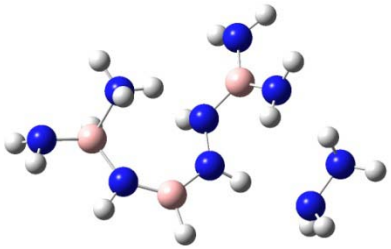
cis-o1,3 trans-$B_3N_5H_{10}(NH_2)_2$



+ N_2H_4

ΔH_{298}= -8.0

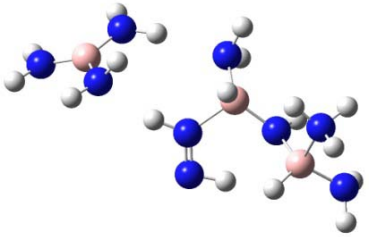
1a, cis-o1,3 trans-$B_3N_7H_{14}(N_2H_4)$



	σ
B_1	-7.3
B_2	22.6
B_3	23.7

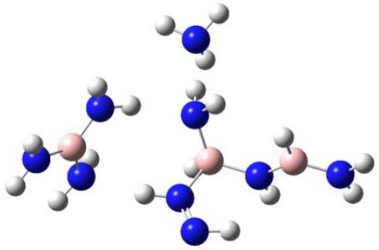
1a, 2a cis-o1,3, trans-$B_3N_7H_{14}(NH_2)_2$

	σ
B_1	22.9
B_2	-1.9
B_3	-0.3



ΔH_{298}= -12.0

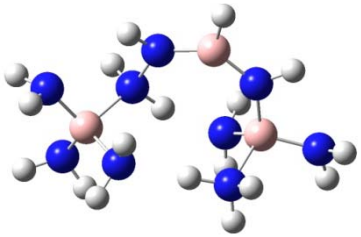
1a, 2b cis-o1,3, trans-$B_3N_7H_{14}(NH_2)_2$



	σ
B_1	22.9
B_2	-2.1
B_3	23.8

ΔH_{298}= -20.9

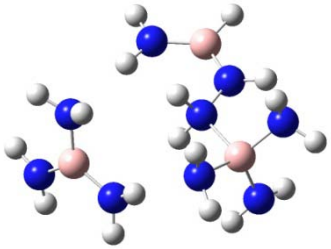
1a, 3a cis-o1,3 trans-$B_3N_7H_{14}(NH_2)_2$



	σ
B_1	-3.9
B_2	21.5
B_3	-2.9

ΔH_{298}= -50.9

1a,3b cis-o1,3 trans-$B_3N_7H_{14}(NH_2)_2$



	σ
B_1	1.5
B_2	23.2
B_3	22.3

ΔH_{298}= -57.5

3rd addition of hydrazine can lead to complex structures and continued fragmentation.

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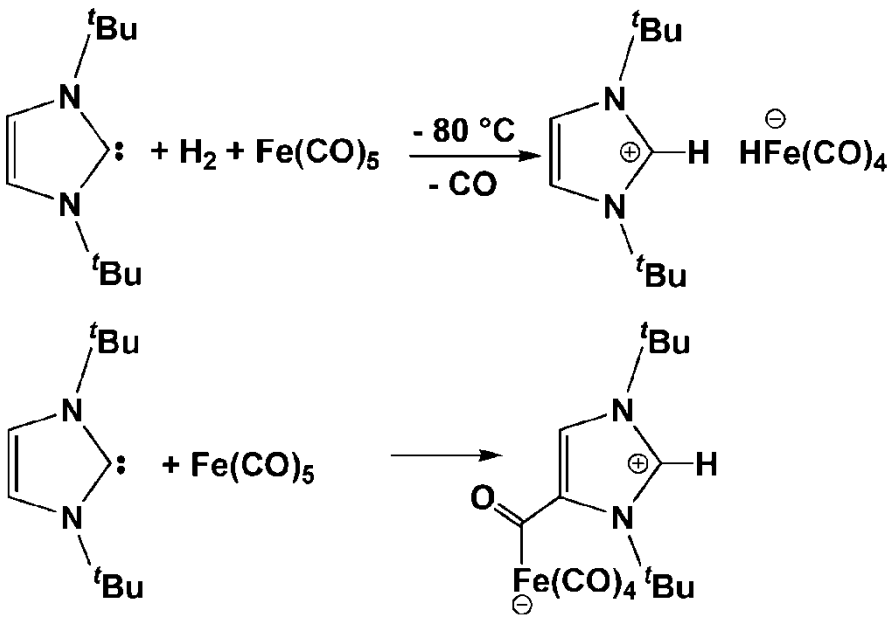
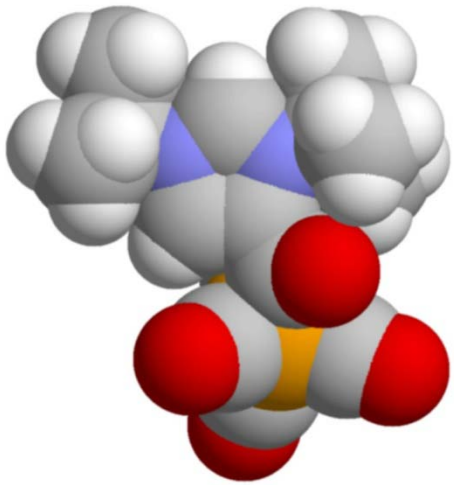
A Novel Hydrogen Activation Process

• Lewis acid-base pairs need not be "frustrated" in their reactivity towards activating H_2. Reaction can occur at temperatures as low as -80 ºC.





• Imidazolium acylferrate formed in the absence of H_2 (either at -78 ºC or RT).
• In the presence of H_2 at -78 ºC, obtained the imidazolium hydridoferrate salt formed (hydrogen fixation).
• Non-ferrous metals incorporated in process (Cr & Al)

• Established that the interaction of H_2 with the electrophile is a key step in the activation process.
• Electrophiles to replace the $Fe(CO)_5$ such as **BBr_3**, $B(OCH_3)_3$, 1-bora-adamantane, and **trityl cation** reacting with an imidazolylidene nucleophile have been investigated. **Crimson** compounds work.
• Provided another way to make H_2 into a proton and hydride (like BH_3NH_3) or like the PNNL work for regeneration cycles.

• The scope and utility of the reaction especially for regeneration investigated
• Experiments with a partner in Bonn, Germany allowed the study of the reaction in a low temperature atuoclave.

Collaborations

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

Examples:

External computational collaborations

- Energetics and spectroscopy for AB compounds: LANL, PNNL, Penn
- Release and regeneration mechanisms: LANL, PNNL, Penn, UC-Davis, UW
- Polymerization mechanisms: LANL, PNNL, Penn
- Catalyst design: CoE
- Spectroscopic predictions: CoE
- Nanoparticles & main group chemistry: UC-Davis
- $C_xB_yN_zH_{12}$ thermodynamics: UO & UW
- $(E(NH_2BH_3)_m$ "metal" thermodynamics & kinetics: U. Mo., PNNL, LANL

Experimental collaborations

- Organic/main group chemistry: LANL
- Institut für Anorganische Chemie: Bonn, Germany

Future Work: Beyond The End

- New funding had been obtained from the Deutscher Akademischer Austausch Dienst (DAAD) to fund further experimental studies into the promising carbene·H_2 Systems
- Frederic Luis Condin (Germany) selected as new co-worker for the experimental program.
- Funding applications pending for experimental work on phosphous-based chemical hydrogen storage systems (DAAD & NSF)
- Computational effort will continue to collaborate with Center partners for thermodynamic and kinetic predictions as support allows.

UA Summary

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

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

• Technical Accomplishments: Significant advances in predicting the thermodynamics of new H_2 chemical hydrogen storage systems and for a broad range of regeneration mechanisms. Developed new approaches for predicting thermodynamic properties for process simulations for 1st fill and regeneration. Synthesized imidazole borane adduct that readily releases hydrogen at room temperature. Developed new understanding of thermodynamic properties of spent fuel and hydrazine regeneration mechanisms.

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

• Future Research: Funding for project complete as of 3-31-2010 with extension (no additional funds) to complete final report. Support thermodynamic needs for completion of Center projects. Complete final report.

UA Summary Table

Storage Parameter: DOE 2010 System Targets	Carbene/Cyanocarbon	Imidazolo Borane
Material Gravimetric Capacity: 6 wt%	Current: 2% Ultimate for $C_2N_2H_6$ polymer: 10.3%	Current: 1% Ultimate: 7.1%
Material Volumetric Capacity: 0.045 kg/L	Current: 0.045 Ultimate: 0.098	Current: ~0.02 Ultimate: 0.098
Dehydrogenation Rate 0.02g/s-kW	In progress for polymer	Rate of H_2 release: $9.6 \pm 0.5\ M^{-1}s^{-1}$
Storage Efficiency Center Goal: 50% Near thermoneutral	Exothermic: -5 kcal/mol Ultimate: Thermoneutral	In progress