

High Level Computational Chemistry Approaches to the Prediction of the Energetic Properties of Chemical Hydrogen Storage Systems

David A. Dixon Chemistry, University of Alabama, Tuscaloosa, AL

Cast: Myrna Hernandez-Matus, Daniel Grant, Jackson Switzer, Jacob Batson, Ronita Folkes, Minh Nguyen

Anthony J. Arduengo & co-workers

Maciej Gutowski (PNNL)

Chemical H₂ Storage Center of Excellence

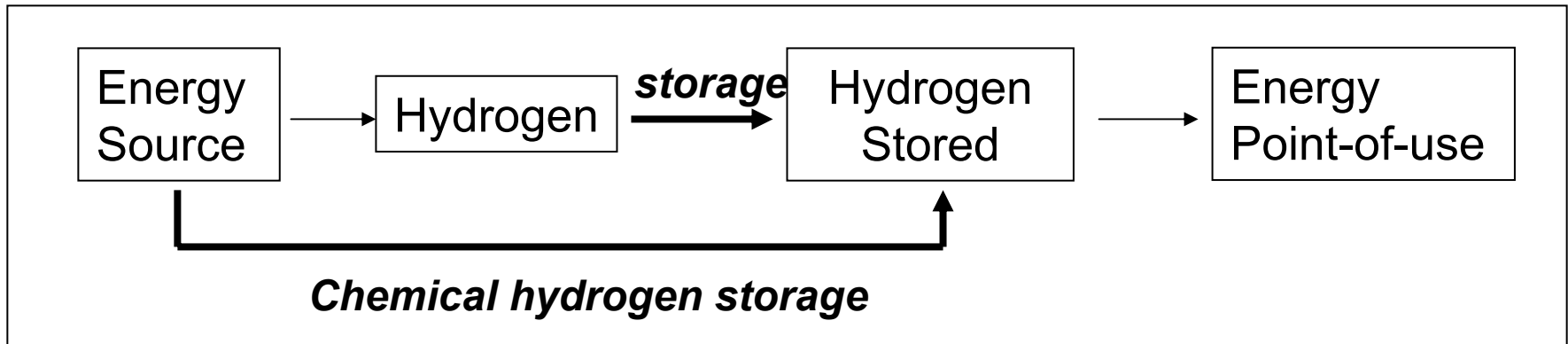
Funding provided in part by the
Department of Energy, Office of
Energy Efficiency and Renewable
Energy under the Hydrogen
Storage Grand Challenge,
Solicitation No. DE-PS36-
03GO93013

Robert Ramsay Chair Fund



Shelby Hall

The Promise of Chemical Hydrogen Storage



- Chemical reaction releases H_2 at suitable pressures and temperatures
 - Reaction *thermodynamics* dictate max. H_2 pressure as function of T – need to manage both ΔH and ΔG
 - Reaction *kinetics* dictate rate of release of H_2 – need to develop catalysts to control kinetics and release
 - Enables significant storage capacity at “zero” pressure – improve safety issues
- Infrastructure based on a solid or liquid fuel
 - Spent fuel regenerated “off-board” using industrial chemical engineering process technology to reduce cost
 - Bypass direct consumer contact with gaseous hydrogen
 - Hydrogen need only appear when required at the fuel cell anode

What's needed for chemical accuracy?

Example: reaction energetics, catalyst design, or separations systems for hydrogen storage

Catalyst *design* will require quantitative information about *transition states* for critical reaction processes in catalysis. These are *only* accessible by computational methods, which hold the key to the fundamental understanding of catalytic processes thus enabling reliable catalyst design

Predict equilibrium chemistry: *Selectivity*

Change in K_{eq} @ 298 K

$K_{eq} = 1$	50:50	$\Delta G = 0$ kcal/mol
$K_{eq} = 10$	90:10	$\Delta G = 1.4$ kcal/mol
$K_{eq} = 100$	99:1	$\Delta G = 2.8$ kcal/mol

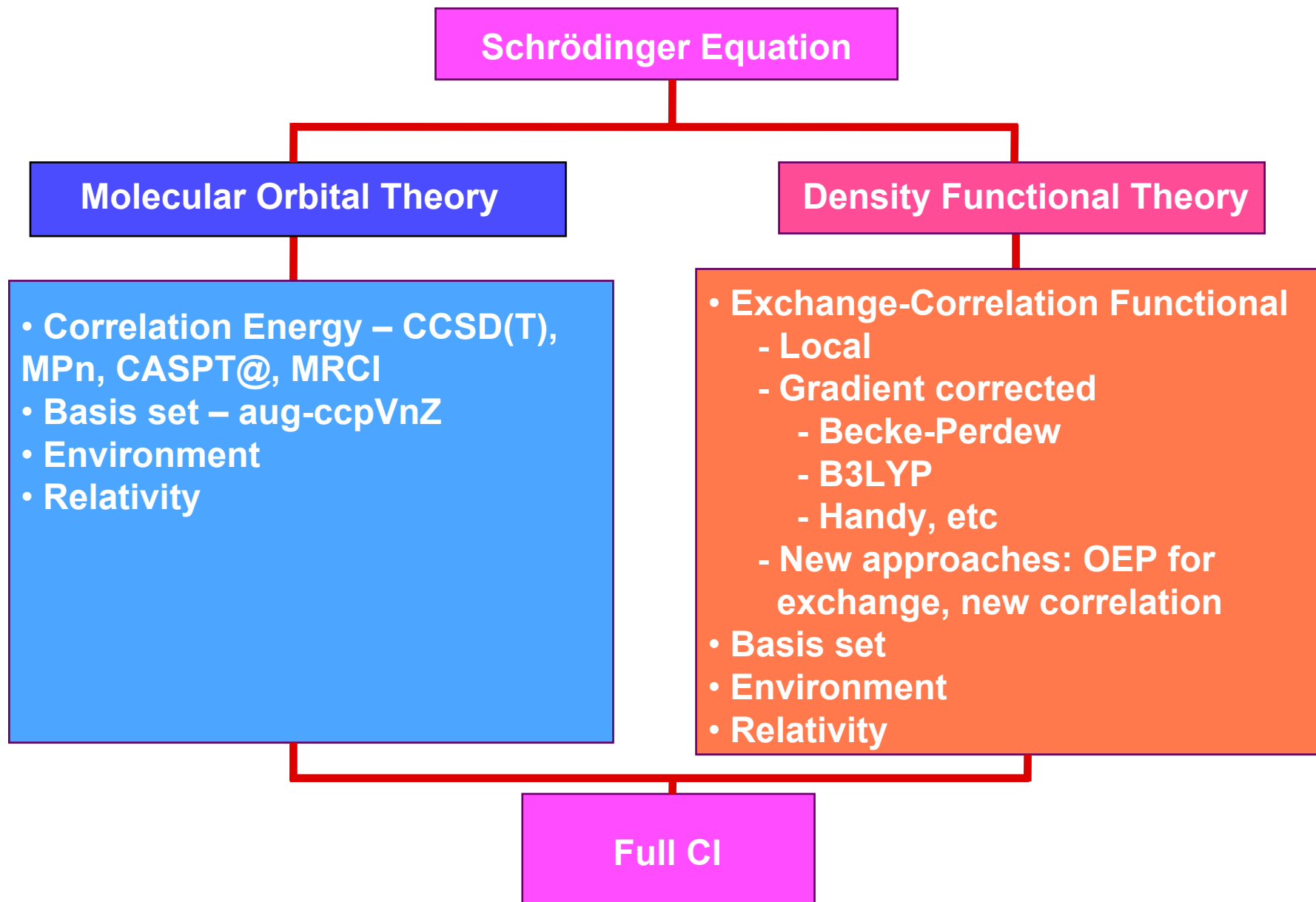
Predict accurate rates: *Reactivity*

Absolute Rates @ 298 K

Factor of 10 in rate @ 25°C is a change in E_a of 1.4 kcal/mol

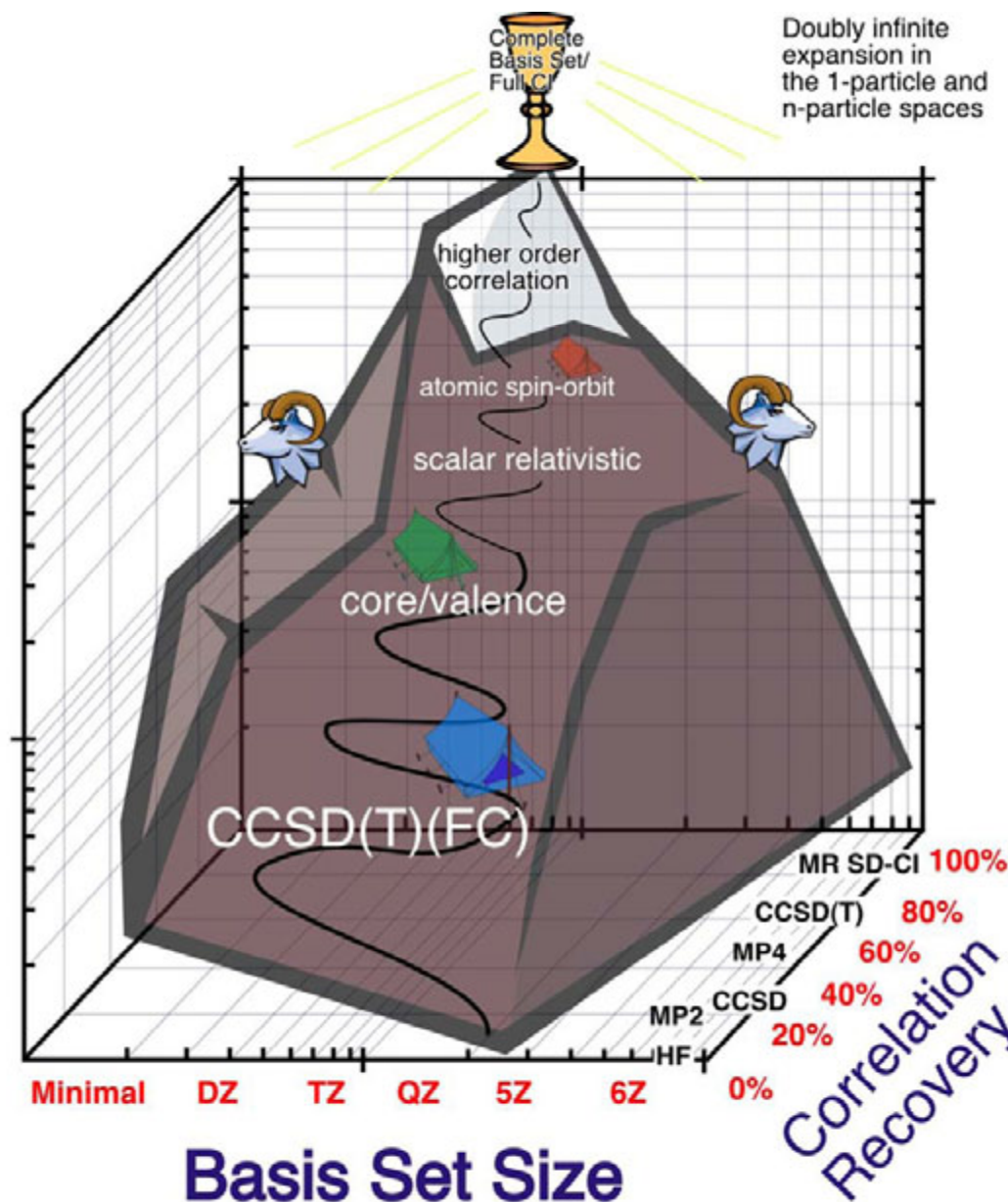
Molecular design will require being able to do accurate calculations and/or being very clever!

Solving the Schrödinger Equation



High level electronic structure theory

Computational Cost



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)

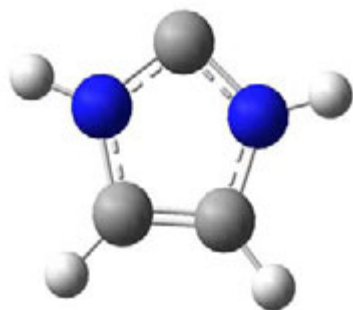
Use atomic heats of formation to get molecular heats of formation

Use CCSD(T) or MP2 geometries

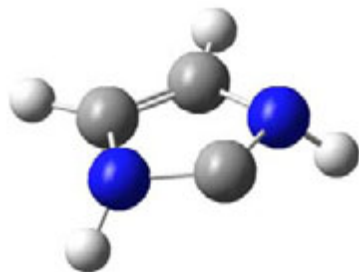
IP's and EA's

Carbenes for H₂ Storage Systems

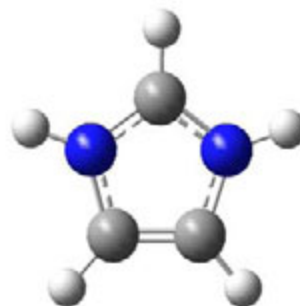
Do carbon-based systems exist that have more accessible CH bonds than traditional hydrocarbons? $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$ $\Delta\text{H}(298) = 32.6 \text{ kcal/mol}$



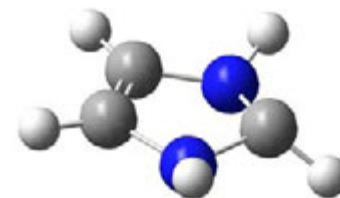
carbene



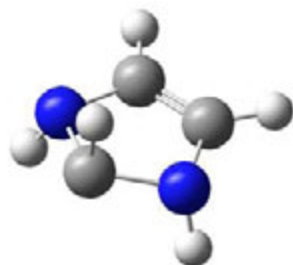
³carbene



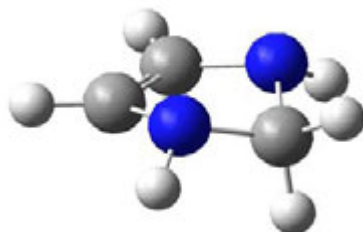
carbeneH⁺



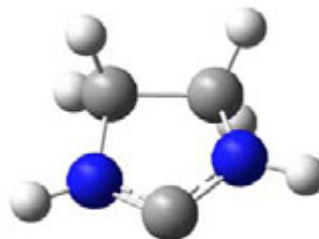
carbeneH



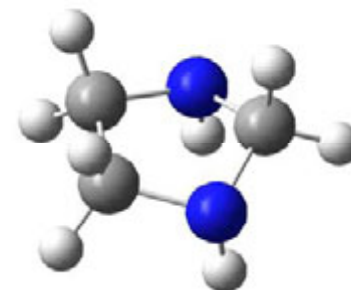
carbeneH⁻



carbeneH₂



carbeneH₆



carbeneH₈

Based on Arduengo's stable carbene

Calculated atomization energies for carbenes

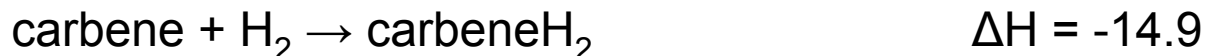
Molecule	CCSD(T)/CBS	ΔE_{ZPE}	ΔE_{CV}	ΔE_{SR}	ΔE_{SO}	ΣD_0 (0K)
carbene	922.38	43.78	3.93	-1.15	-0.24	881.14
³ carbene	834.15	45.10	3.78	-1.23	-0.24	791.36
carbH ₂	1052.90	57.85	3.99	-1.15	-0.24	997.65
carbH ⁺	865.93	52.11	4.27	-1.21	-0.24	816.64
carbH ⁻	952.83	47.58	3.55	-1.18	-0.24	1125.84
carbH	962.78	53.23	4.11	-1.24	-0.24	912.18
CarbH ₆	1047.49	57.93	3.85	-1.20	-0.24	907.38
carbH ₈	1196.52	73.07	3.87	-1.24	-0.24	1,125.84

Carbene CCSD(T) Heats of Formation (kcal/mol)

Molecule	CCSD(T) (0K)	CCSD(T) (298K)
carbene	60.4	55.4
³ carbene	150.2	145.9
carbeneH ₂	47.1	41.5
carbeneH ⁺	176.5	171.6
carbeneH ⁻	85.8	80.7
carbeneH	81.0	75.7
CarbeneH ₆	52.8	46.8
CarbeneH ₈	22.2	14.3

“Heats of Formation of the Arduengo Carbene and Various Adducts Including H₂ from Ab Initio Molecular Orbital Theory,” D. A. Dixon and A. J. Arduengo, III, *J. Phys. Chem., A* **2006**, *110*, 1968

Carbene Reaction Energetics for H₂ storage at 298K in kcal/mol to ± 1 kcal/mol



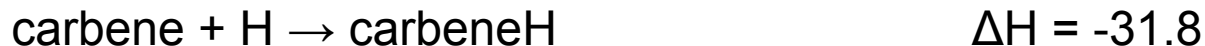
Adding H₂ to the carbene is exothermic by 14.9 kcal/mol -- very nice in managing release because we can use ΔG to pull it off using Le Chatelier's Principle. $T\Delta S(298\text{K}) = +8.2$ kcal/mol



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



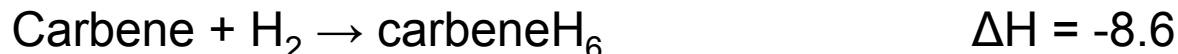
The singlet triplet splitting of the carbene is very large!



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



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



Adding H₂ to hydrogenate the double bond is exothermic by only 9 kcal/mol as compared to -31 kcal/mol for hydrogenation of C₂H₄.



Adding H₂ to the hydrogenated carbene is quite exothermic – develop carbene reactivity scale.

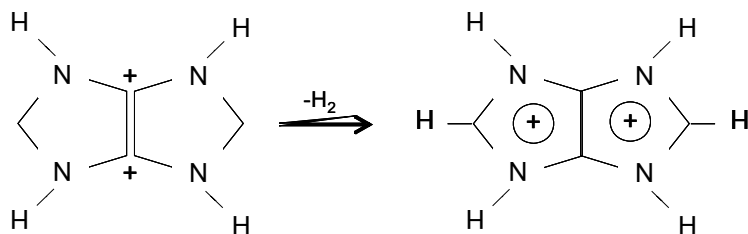
Hydrogenation energies (kcal/mol) of carbenes

Reaction	$-\Delta H_{\text{rxn}}(298\text{K})$
carbene + $\text{H}_2 \rightarrow \text{carbeneH}_2$	14.9
carbeneH ₆ + $\text{H}_2 \rightarrow \text{carbeneH}_8$	32.6
$^1\text{CF}_2 + \text{H}_2 \rightarrow \text{CF}_2\text{H}_2$	62.2
$^3\text{carbene} + \text{H}_2 \rightarrow \text{carbeneH}_2$	101.3
$^3\text{CF}_2 + \text{H}_2 \rightarrow \text{CF}_2\text{H}_2$	108.2
$^3\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4$	110.9

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

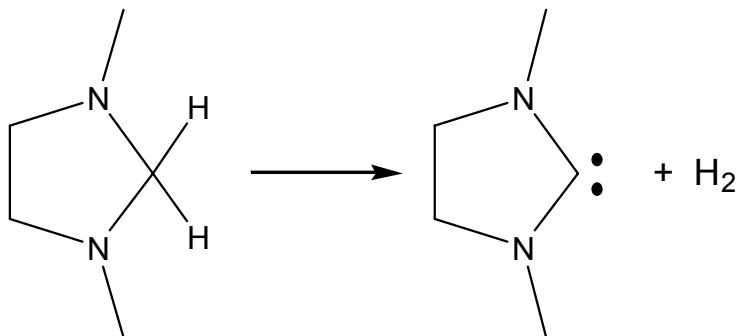
Other ways to release hydrogen from dihydroimidazoles, not previously known

1,5 elimination to give fused diimidazolium rings:



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

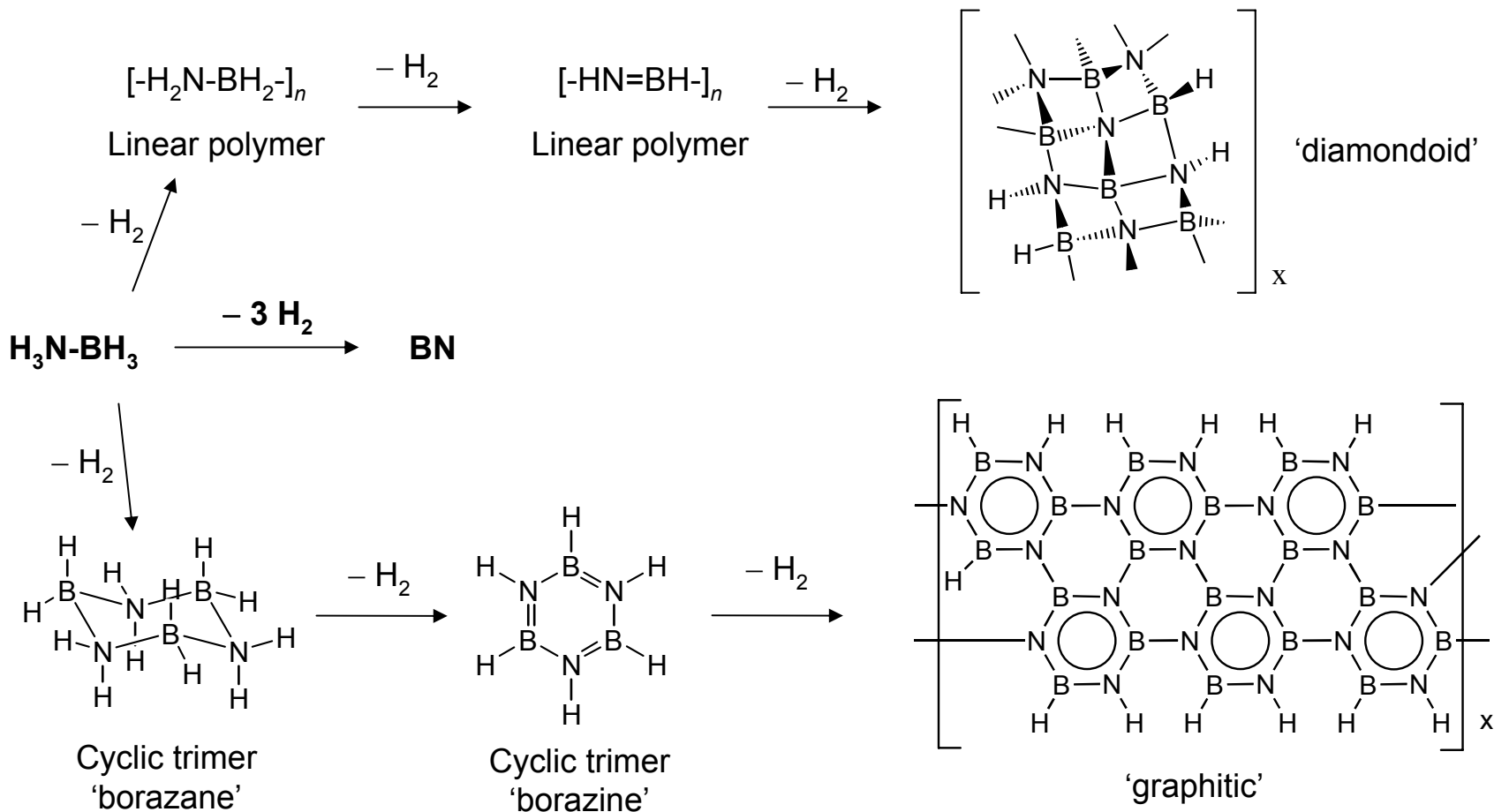
1,1 elimination to give carbene products:



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

Bo Arduengo

Hydrogen Production Using Ammonia-Borane



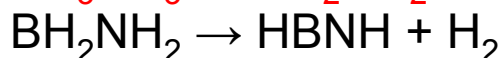
Collaborators: Fran Stephens & Tom Baker (LANL)

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

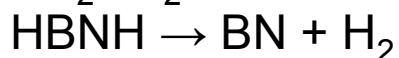
- Reaction energies for the sequential release of H₂ from borane amines (gas phase) based on the most accurate heats of formation now available – our calculated values.



$$\Delta H = -5.1$$



$$\Delta H = 31.4$$



$$\Delta H = 134.3$$

- BH₃NH₃ will be a good source of H₂ as the release of H₂ from this species is not far from thermoneutral due to the donor-acceptor bond. Cannot make T too high as entropy also favors release of H₂.
- The reaction energies for forming BN/C₂ and BHNH/CHCH are ~ equal. Similarity of the isoelectronic C₂H_{2m} and BNH_{2m} systems except for m = 3. Due to differences in σ bond energies.
- Can the salt [BH₄⁻][NH₄⁺] serve as an H₂ storage system? Estimate the lattice energy, U_L, of the salt from the empirical expression dependent on the volume.



$$\Delta H(0\text{K}) = 0.2 \text{ kcal/mol}$$



$$\Delta H(0\text{K}) = -16.8 \text{ kcal/mol}$$

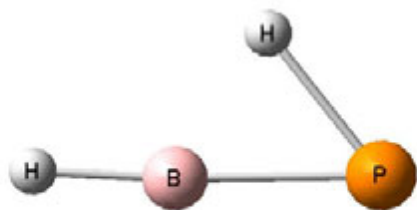
- We need to predict condensed phase interactions. Strong dipolar interactions.

“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**, 109, 5129

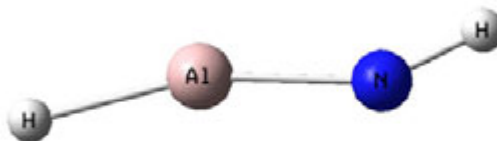
Bond Energies in kcal/mol for chemical hydride storage

Reaction	B.E. ($\Delta H(0K)$)	Bond
$BH_3-NH_3 \rightarrow BH_3 + NH_3$	25.9	dative
$CH_3-CH_3 \rightarrow 2 CH_3$	87.9	C-C σ
$BH_2=NH_2 \rightarrow BH_2 + NH_2$	139.6	B-N π + B-N σ
$CH_2=CH_2 \rightarrow 2 CH_2 (^3B_1)$	171.9	C-C π + C-C σ
$BH_2NH \rightarrow BH + NH$	178.5	
$HCCH \rightarrow 2 CH$	228.1	

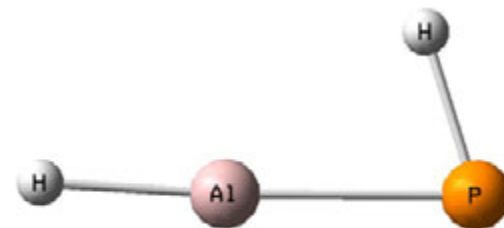
- For C_2H_4 , the C-C π bond is ~ 65 kcal/mol giving a C-C σ bond energy of 107 kcal/mol. Due to sp^2-sp^2 bonding, not sp^3-sp^3 bonding.
- Estimate the B=N π bond energy by calculating the rotation barrier in BH_2NH_2
 - Electronic contribution = 31.99 kcal/mol
 - Zero point contribution = 2.02 kcal/mol
 - Barrier at 0K = 30.0 kcal/mol
- Gives a very strong B-N single bond of 109.6 kcal/mol, comparable to the C-C σ bond. The high B-N $\sigma + \pi$ bond energy in BH_2NH_2 is consistent with the fact that it does not release H_2 readily.



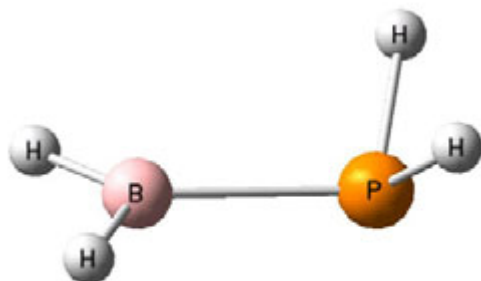
HBPH



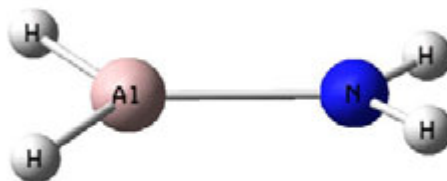
HAINH



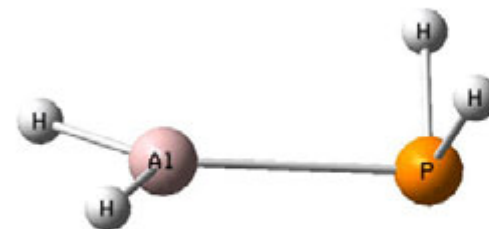
HAIPH



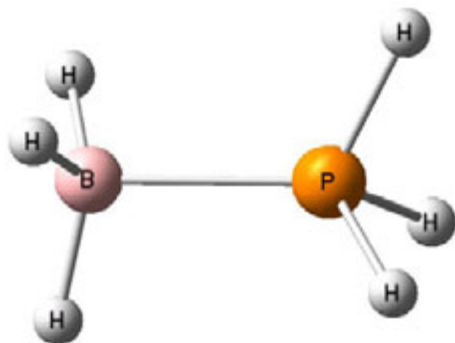
H₂BPH₂



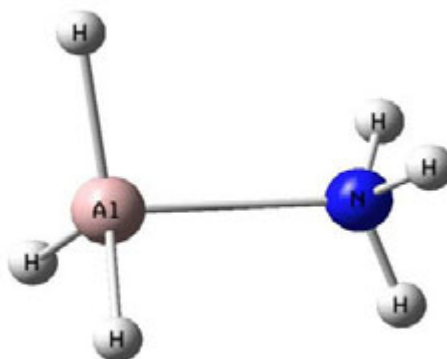
H₂AlNH₂



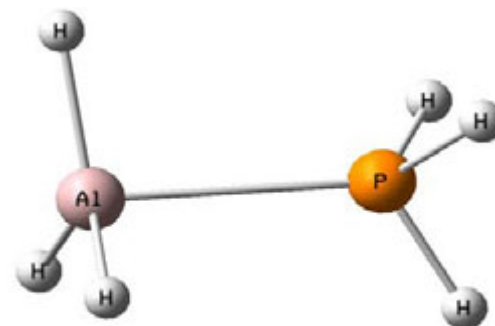
H₂AlPH₂



H₃BPH₃



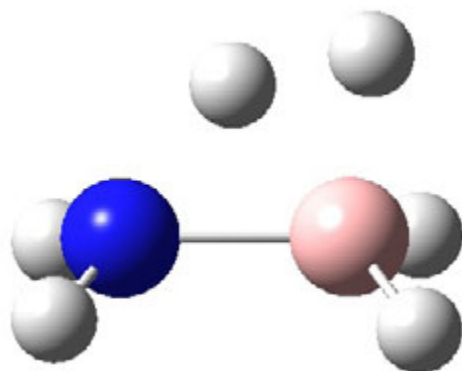
H₃AlNH₃



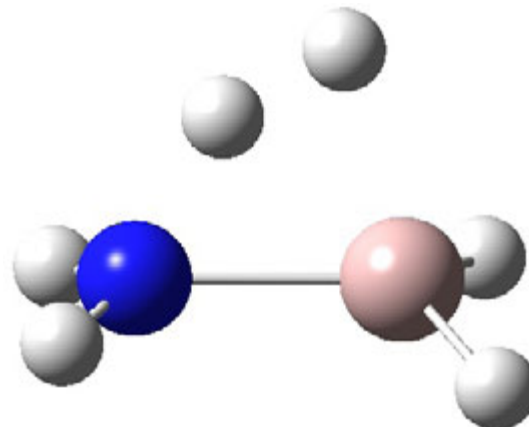
H₃AlPH₃

“Thermodynamic Properties of Molecular Borane Phosphines, Alane Amines, and and Phosphine Alanes and the [BH₄][PH₄⁺], [AlH₄][NH₄⁺], and [AlH₄][PH₄⁺] 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

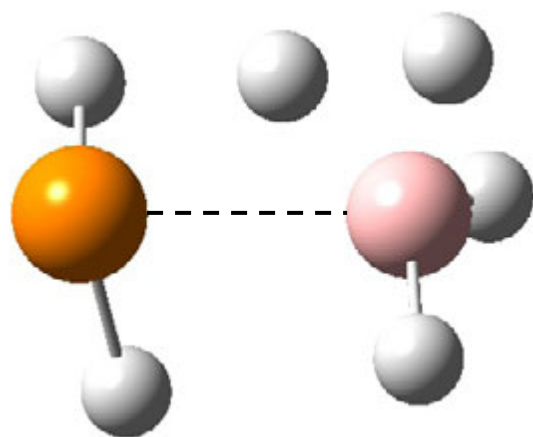
$\text{BH}_2\text{NH}_2\cdots\text{H}_2$ (TS)



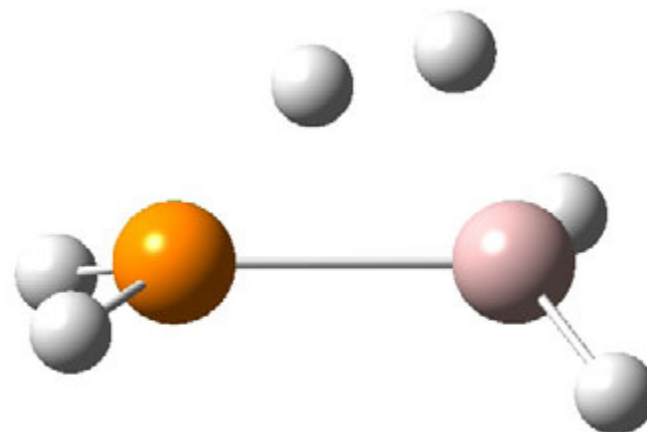
$\text{AlH}_2\text{NH}_2\cdots\text{H}_2$ (TS)



$\text{BH}_2\text{PH}_2\cdots\text{H}_2$ (TS)



$\text{AlH}_2\text{PH}_2\cdots\text{H}_2$ (TS)

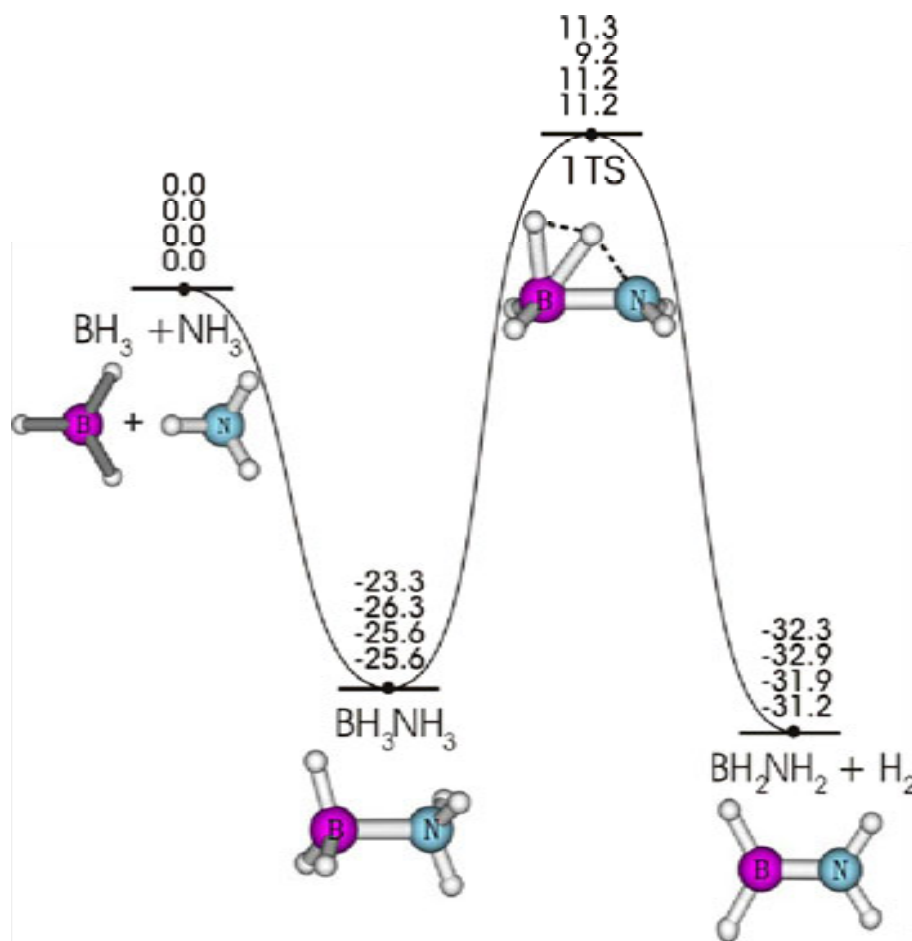


Energetics (kcal/mol) for the Release of H₂ (gas phase products)

Reaction	ΔH (298K)	TS Energy	Bond Energy
$\text{AlH}_3\text{NH}_3 \rightarrow \text{AlH}_2\text{NH}_2 + \text{H}_2$	5.0	27.6	26.1
$\text{AlH}_2\text{NH}_2 \rightarrow \text{HAlNH} + \text{H}_2$	61.9		
$\text{AlHNNH} \rightarrow \text{AlN} + \text{H}_2$	74.9		
$\text{BH}_3\text{PH}_3 \rightarrow \text{BH}_2\text{PH}_2 + \text{H}_2$	17.4	30.4	21.1
$\text{BH}_2\text{PH}_2 \rightarrow \text{HBPH} + \text{H}_2$	31.4		
$\text{BHPH} \rightarrow \text{BP} + \text{H}_2$	82.5		
$\text{AlH}_3\text{PH}_3 \rightarrow \text{AlH}_2\text{PH}_2 + \text{H}_2$	5.6	34.4	14.0
$\text{AlH}_2\text{PH}_2 \rightarrow \text{HAlPH} + \text{H}_2$	34.6		
$\text{AlHPH} \rightarrow \text{AlP} + \text{H}_2$	45.4		
$\text{BH}_3\text{NH}_3 \rightarrow \text{BH}_2\text{NH}_2 + \text{H}_2$	-8.3	34.5	25.9
$[\text{BH}_4^-][\text{PH}_4^+] (\text{s}) \rightarrow \text{BH}_3\text{PH}_3 + \text{H}_2$	-13.2		
$[\text{AlH}_4^-][\text{NH}_4^+] (\text{s}) \rightarrow \text{AlH}_3\text{NH}_3 + \text{H}_2$	-3.3		
$[\text{AlH}_4^-][\text{PH}_4^+] (\text{s}) \rightarrow \text{AlH}_3\text{PH}_3 + \text{H}_2$	-9.3		

- Isoelectronic species – no obvious advantage energetically and less capacity due to mass.
- Direct H₂ elimination above dative bond energy – need catalysts.

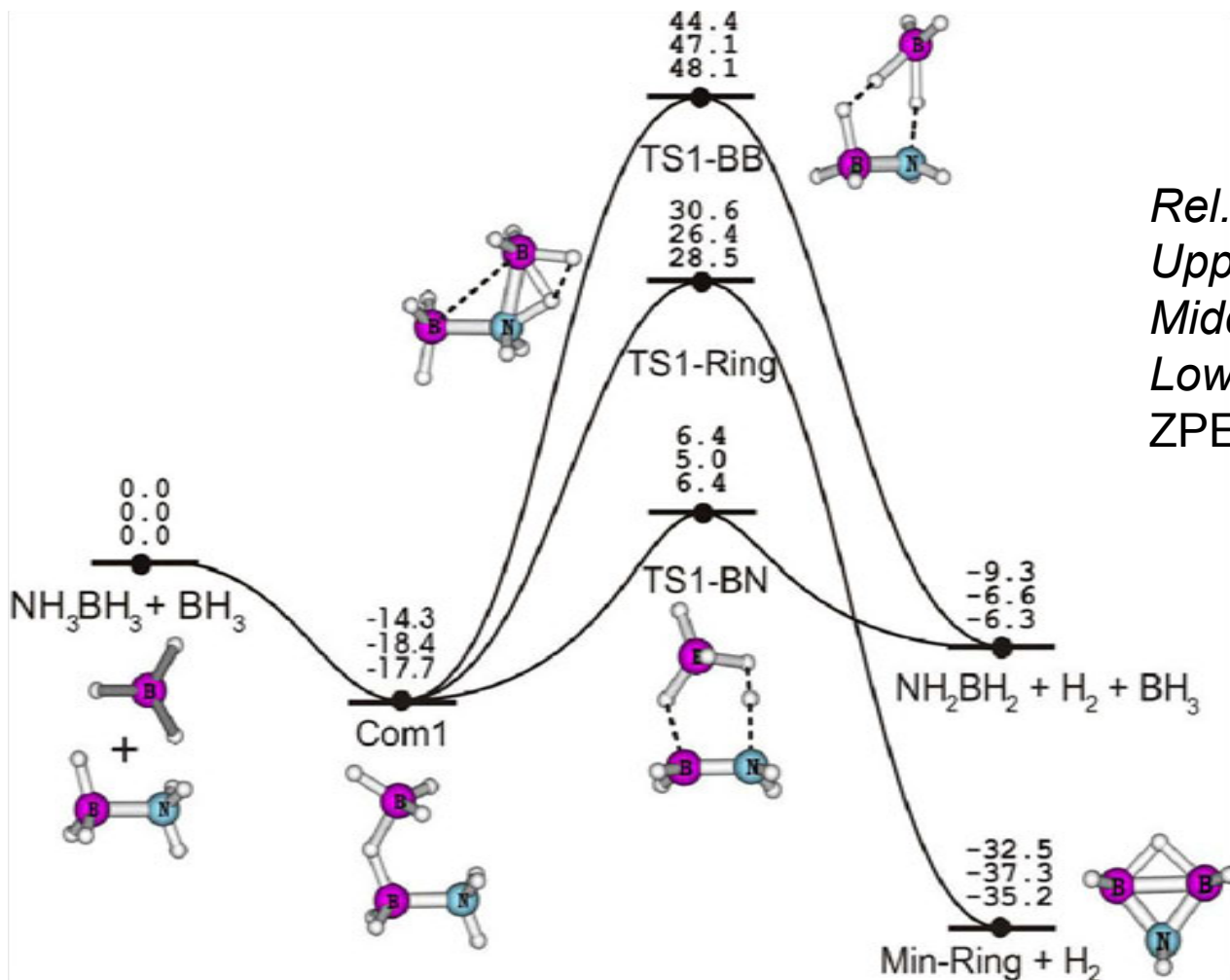
Reaction Pathway for H₂-Generation from BH₃NH₃



Relative energies in kcal/mol: Upper:
B3LYP
Middle: MP2 and CCSD(T)//MP2
Lower: CCSD(T)//CCSD(T)
using aug-cc-pVTZ basis set.
ZPE: MP2/aug-cc-pVTZ

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

Pathways for H₂-Generation from BH₃NH₃ + BH₃

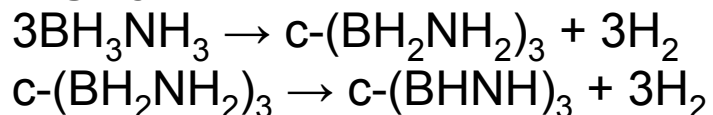


Rel. energies in kcal/mol:
 Upper: B3LYP
 Middle: MP2
 Lower: CCSD(T)//MP2
 ZPE: MP2/aVTZ

BH₃ can serve as a catalyst for H₂ elimination from BH₃NH₃.

Cyclization reaction energetics in the gas phase in kcal/mol

Highly accurate CCSD(T)/CBS

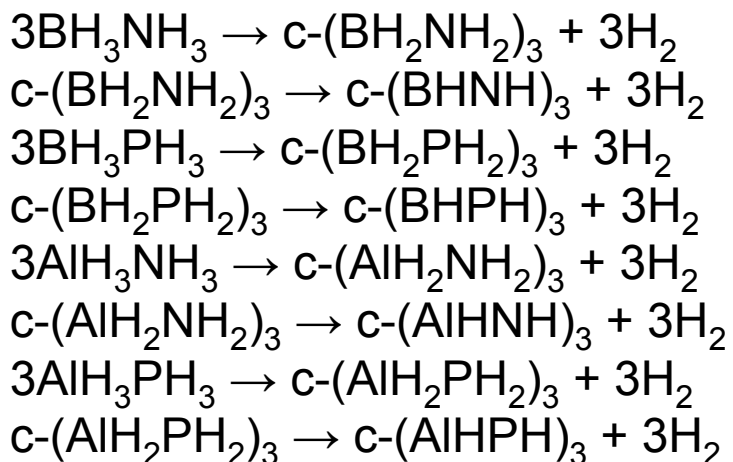


ΔH (298K)

-54.5

-20.4

G3MP2



ΔH (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 BH_3NH_3 and the associated intermolecular interactions.

Conclusions

- Electronic structure methods can be used to get highly accurate values of the thermodynamic properties of compounds related to fuels for combustion and hydrogen storage.
- Chemical hydrogen storage offers a significant opportunity for enabling the hydrogen economy as well as for SCRAMJet applications.
- We already have some potential materials – borane amines and carbenes as well as others (substituted NN compounds).
- We are designing affordable chemical materials and reactions that permit:
 - adequate hydrogen storage in terms of weight percent
 - acceptable stability until exposed to catalyst or activator
 - controlled evolution of hydrogen at usable pressure when catalyzed or activated
 - efficient (reasonable cost), safe regeneration