Chemical Hydrogen Storage in Ionic Liquid Media

Larry G. Sneddon and R. Thomas Baker

University of Pennsylvania
Los Alamos National Laboratory

BES Hydrogen Review

May 2006

PENN

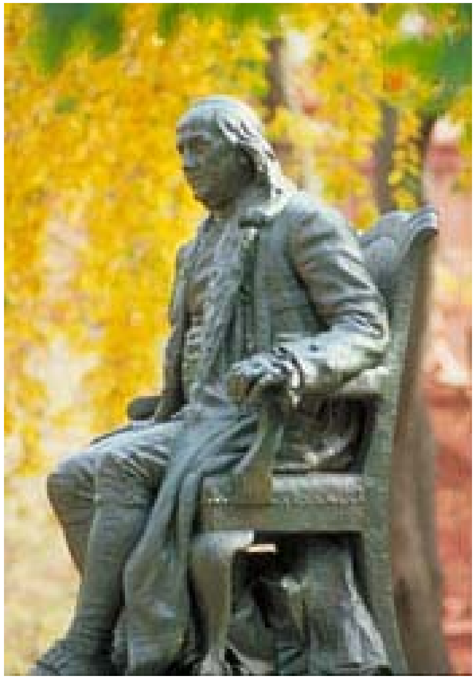
UNIVERSITY of PENNSYLVANIA

Initial Objectives and Achievements

1943 - 2003 Los Alamos NATIONAL LABORATORY *Ideas That Change the World*

Initial Objectives:

- Quantify the hydrogen release and characterize the products of ammonia borane dehydrogenation
- Carry out comparison studies of ammonia borane dehydrogenations in the solid state versus in ionic liquid solvents
- Develop metal catalysts for ammonia borane dehydrogenations in ionic liquids



Summary of Initial Discoveries/Achievements:

- Toepler measurements, NMR studies and DFT/GIAO computations were used to identify the major species produced in ammonia borane dehydrogenations.
- Ionic liquids were found to improve the extent and rate of hydrogen release from ammonia borane.
- Ionic-liquid stabilized metal-catalysts show promise for further increasing the extent and rate of dehydrogenation of both ammonia borane and ammonia triborohydride.

Research Team:
PIs, Larry Sneddon (Penn), R. Tom Baker (Los Alamos)
Postdoctorals, Vincent Pons, Martin Bluhm

Why Amineboranes for Hydrogen Storage?

Because of their protonic N-H and hydridic B-H hydrogens, amineboranes are unique in their ability to store and release hydrogen

$NH_4BH_4 \longrightarrow BN + 4\ H_2$		(24.5 wt%, 0.20 H_2-kg/L)
→	$NH_3BH_3 \longrightarrow BN + 3\ H_2$	(19.6 wt%, 0.16 kg-H_2/L)
$B_3N_3H_{12} \longrightarrow 3\ BN + 6\ H_2$		(14 wt%, 0.11 kg-H_2/L)
$B_3N_3H_6 \longrightarrow 3\ BN + 3\ H_2$		(7.5 wt%, 0.06 kg-H_2/L)
$NH_3B_3H_7 \longrightarrow B_3N + 5\ H_2$		(17.8 wt%, 0.14 kg-H_2/L)

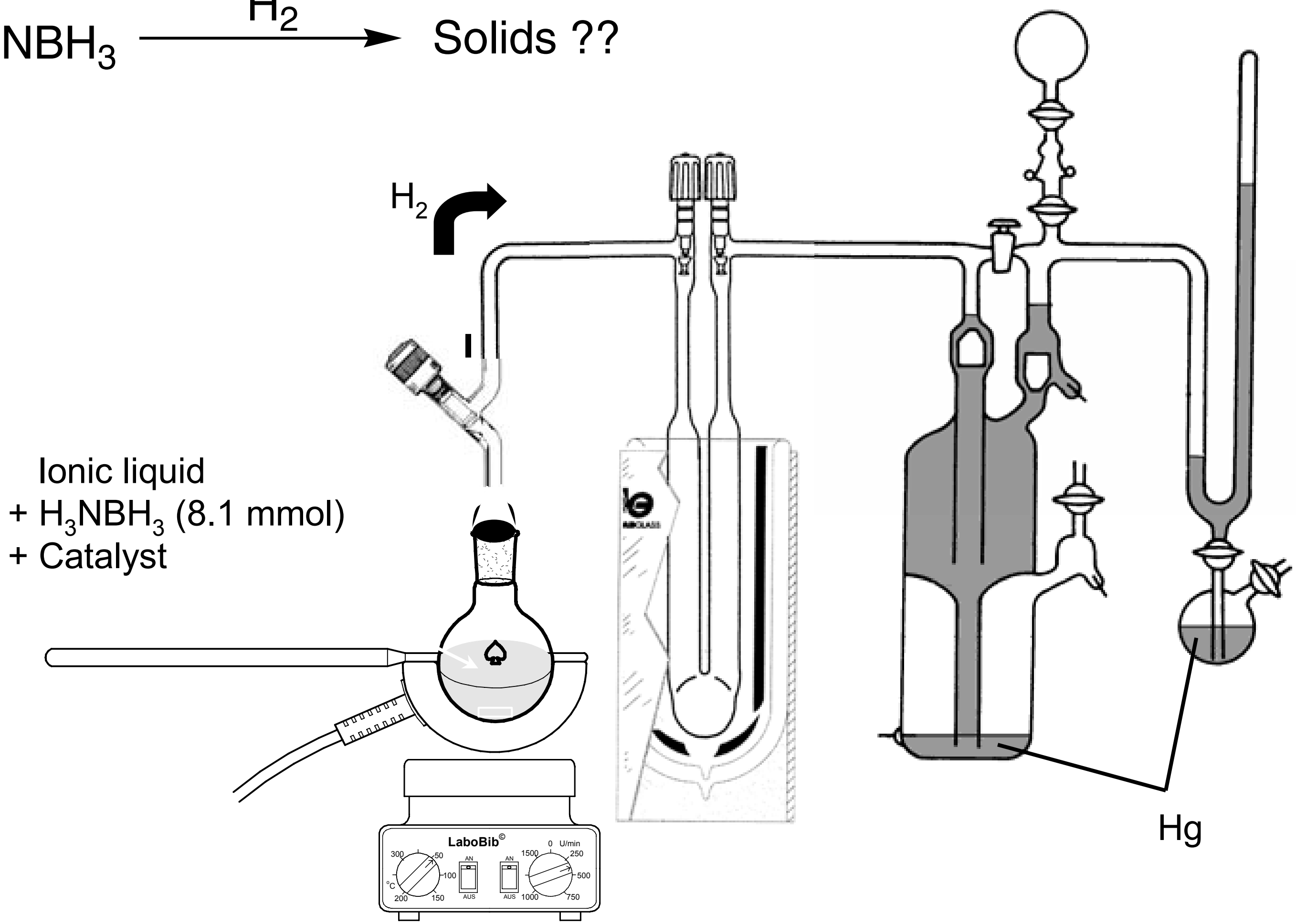
DOE Targets

2007: 4.5 wt%, 0.036 kg-H_2/L; **2010:** 6.0 wt%, 0.045 kg-H_2/L;

2015: 9.0 wt%, 0.081 kg-H_2/L

Hydrogen Measurements with Toepler Pump

$$H_3NBH_3 \xrightarrow{H_2} \text{Solids ??}$$



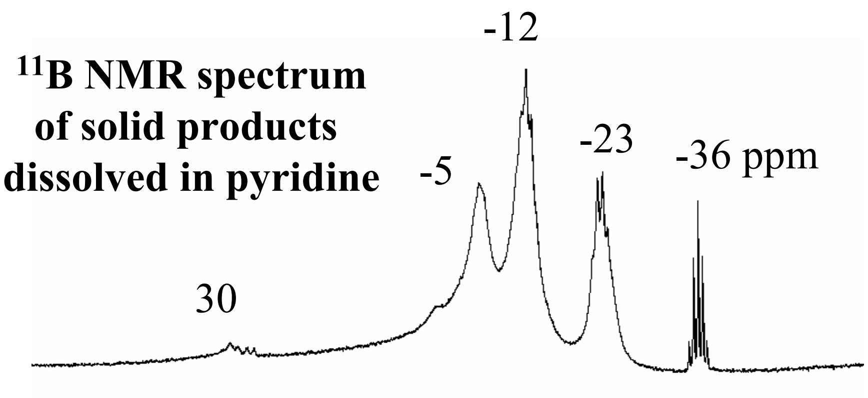
System connected to high vacuum

DFT/GIAO/NMR Polymer Characterization

$H_3NBH_3 \xrightarrow{H_2}$ Solids ??

-22.4 ppm

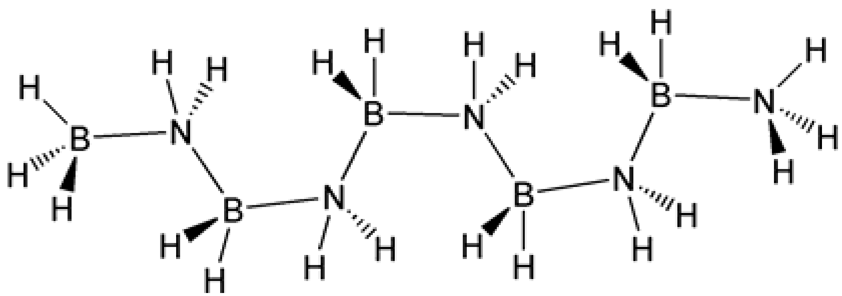
^{11}B NMR spectrum of solid products dissolved in pyridine

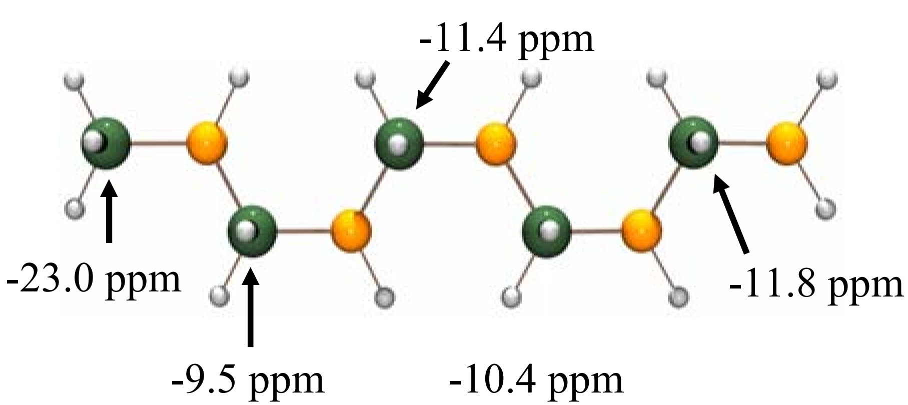


DFT/GIAO Calculated Chemical Shifts

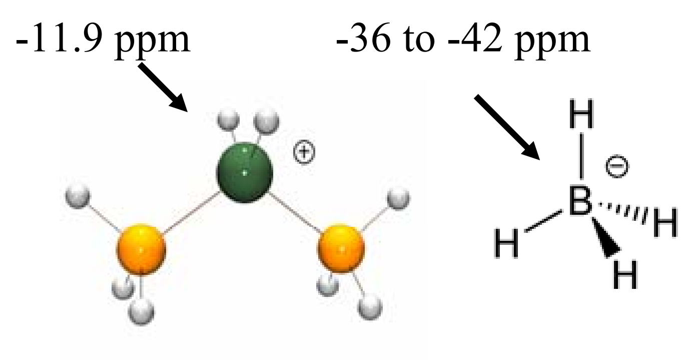
B3LYP 6-311G*

Polyaminoborane



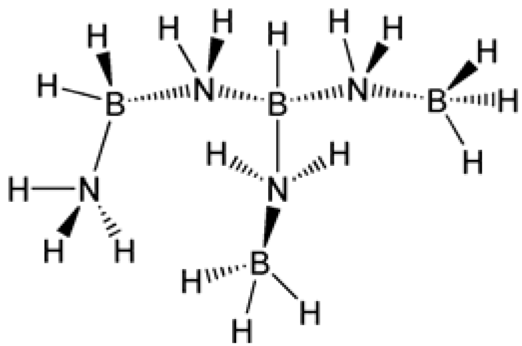


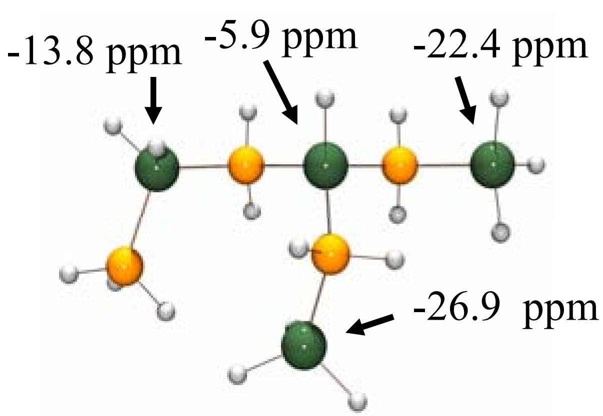
Diammoniate of diborane: $[(NH_3)_2BH_2]BH_4$



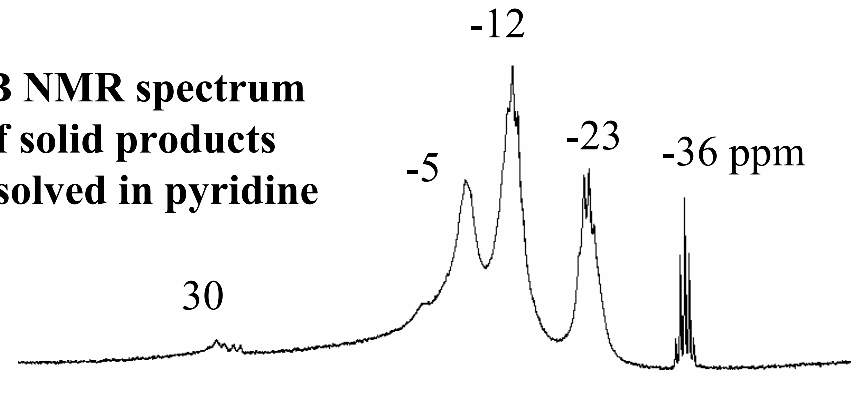
DFT/GIAO/NMR Polymer Characterization

Branched chain polyaminoborane

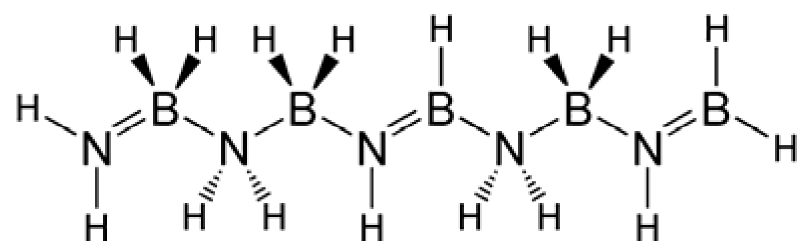


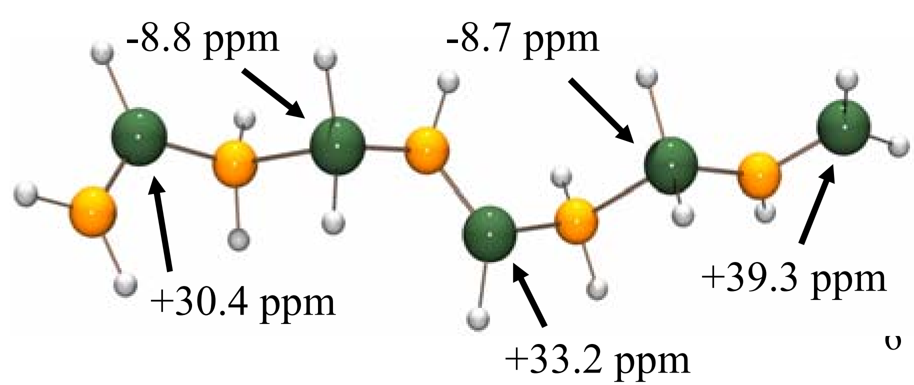


^{11}B NMR spectrum of solid products dissolved in pyridine



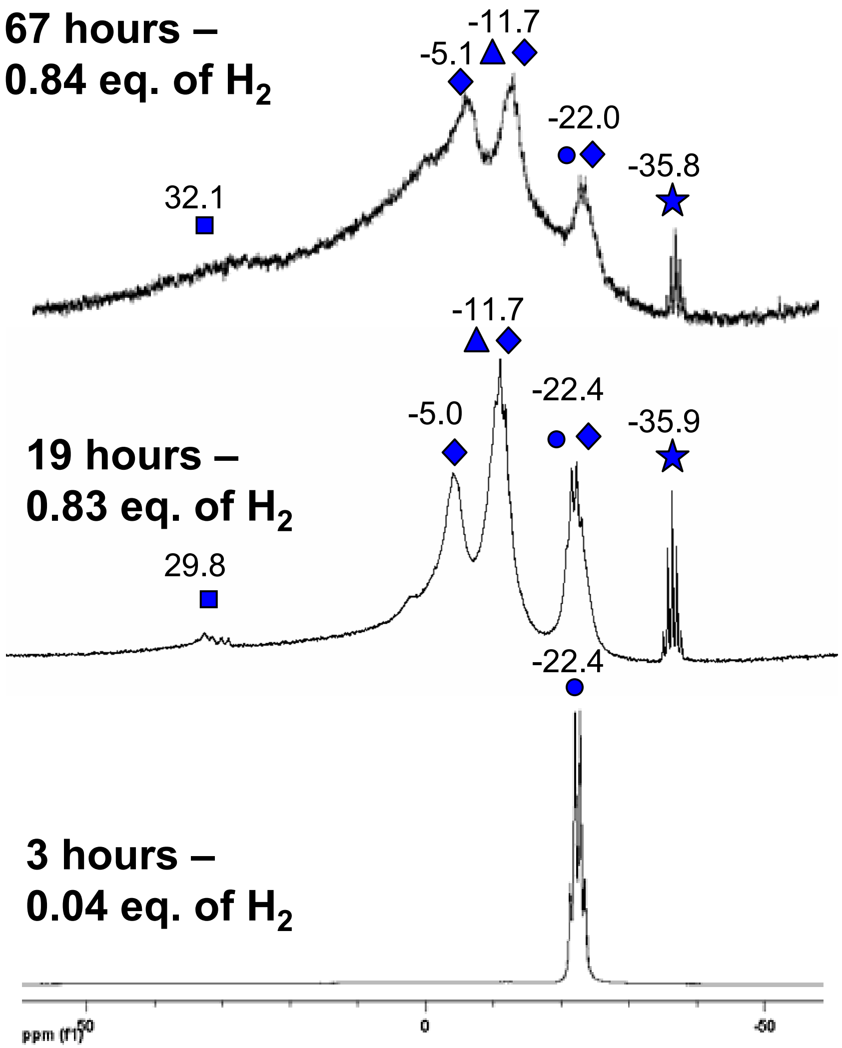
Unsaturated polyaminoborane



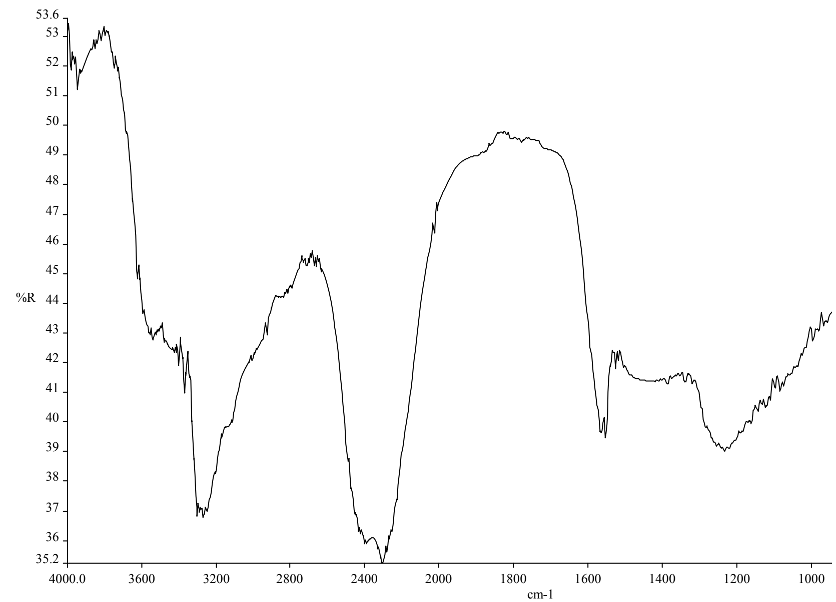


NH_3BH_3 Decomposition at 85°C

^{11}B NMR spectra of the residue in pyridine



DRIFT-IR spectrum of residue after 67 hours
Polyaminoborane $(-NH_2-BH_2-)_n$

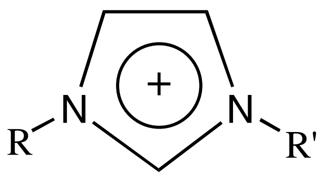


- ● Ammonia Borane NH_3BH_3
- ★ BH_4^- (from diammoniate diborane, $[(NH_3)_2BH_2]BH_4$)
- ▲ BH_2^+ (from diammoniate diborane, $[(NH_3)_2BH_2]BH_4$)
- ◆ Polyaminoborane
- ■ Unsaturated B=N

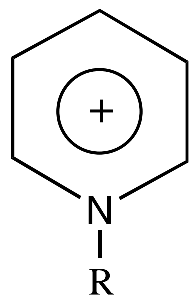
Why Ionic Liquid Solvents for Amineborane Dehydrogenations?

Ionic Liquid Solvents

Cations:



N,N'-imidazolium



N-pyridinium

Anions:

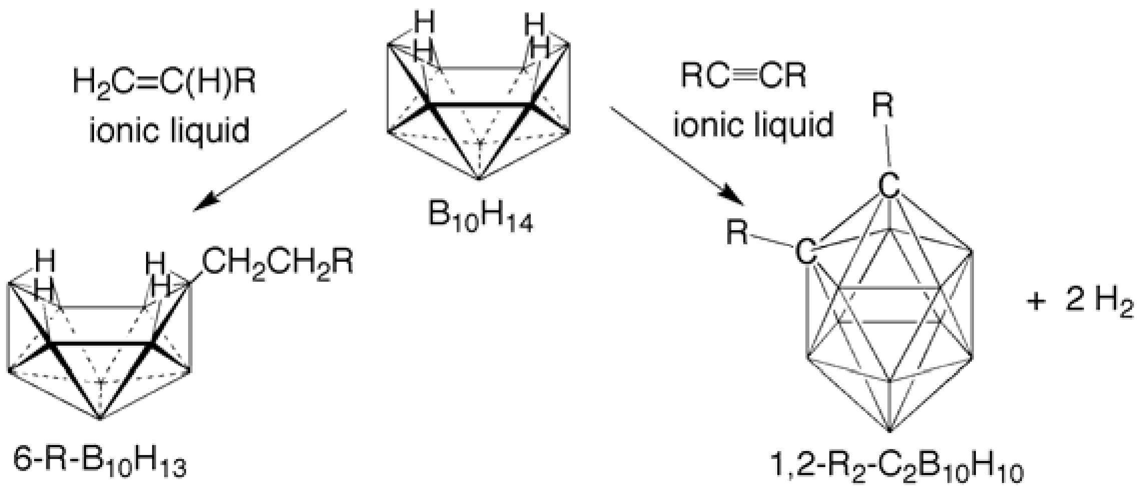
Reactive: $AlCl_4^-$, $Al_2Cl_7^-$

Inert: PF_6^-, BF_4^-, Cl^-

Advantages

- Dissolve both neutral and ionic species, promote polar transition states
- Negligible vapor pressures
- Non-coordinating anions and cations provide polar, inert reaction medium for catalytic reactions.

Ionic Liquids Promote Polyborane Reactions



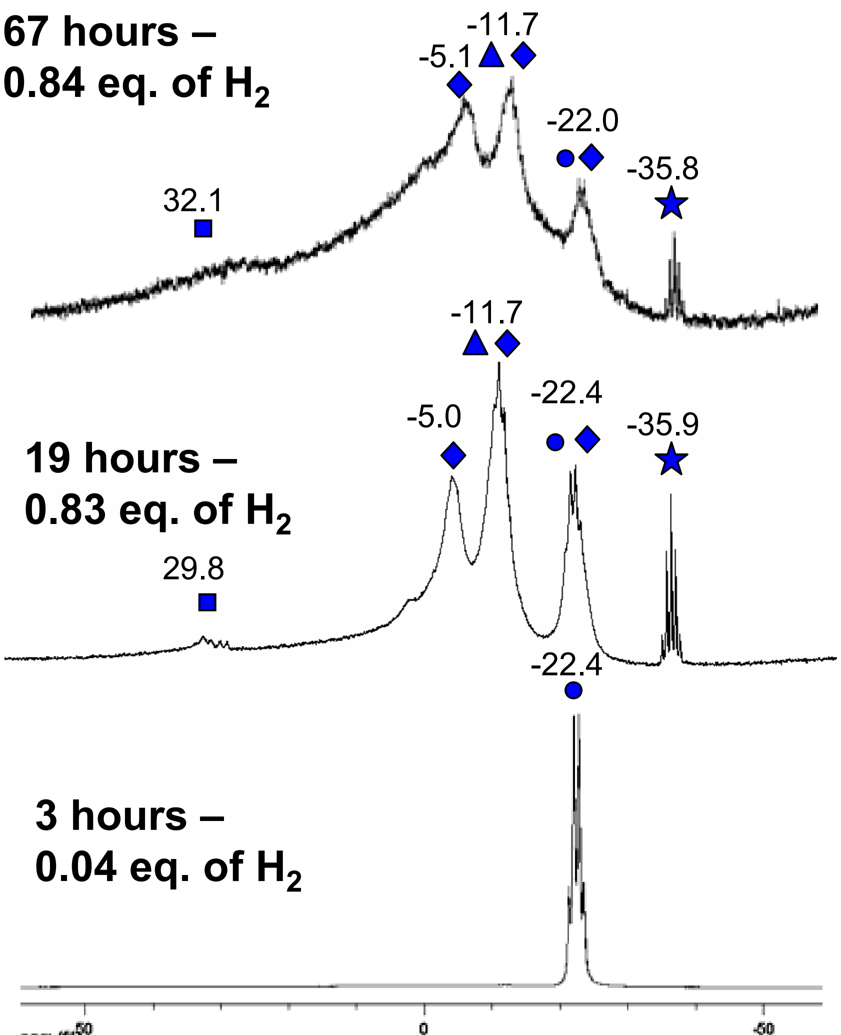
Kusari. U.; Li, Yuqi; Bradley, M. G; Sneddon, L. G. *J. Am. Chem. Soc.* **2004**, *126*, 8662-3

Do ILs have similar advantages for H_3NBH_3 Dehydrogenations?

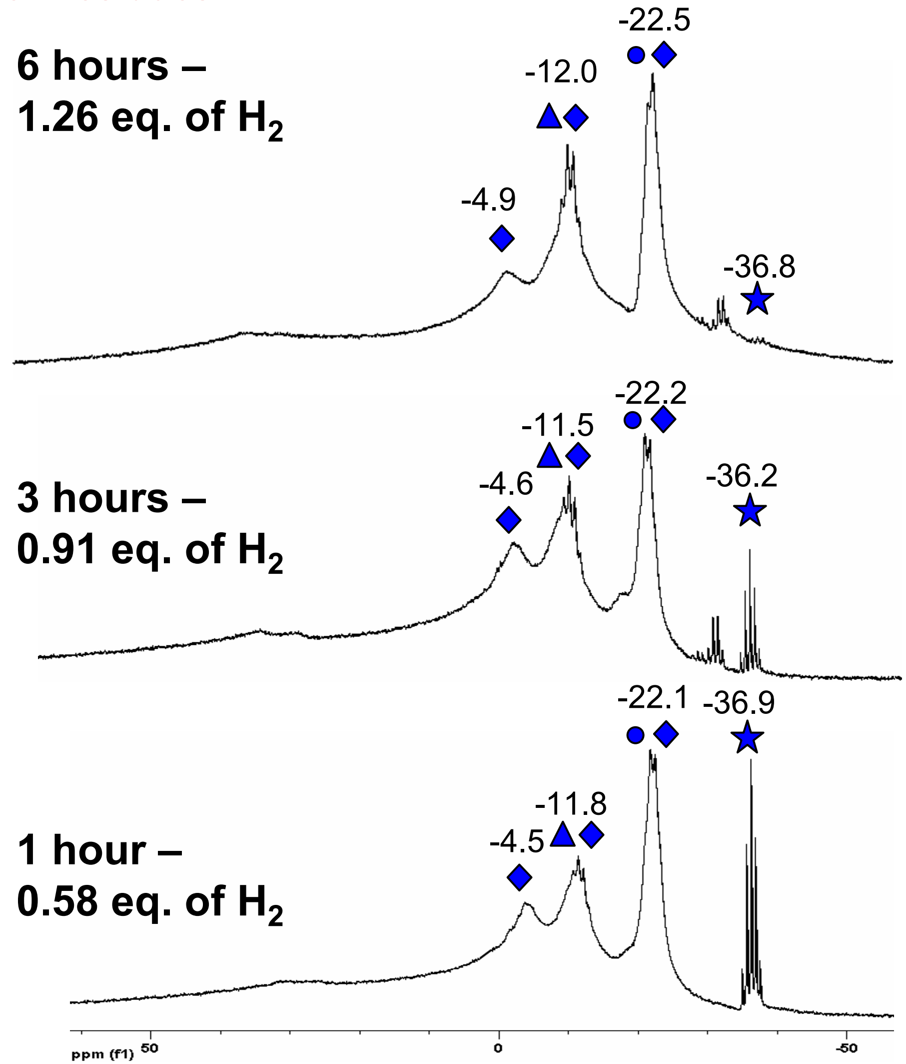
Ionic Liquids Increase H_2 Release at 85°C

^{11}B NMR Spectra of Residues

Neat NH_3BH_3



NH_3BH_3 + Ionic Liquid‡



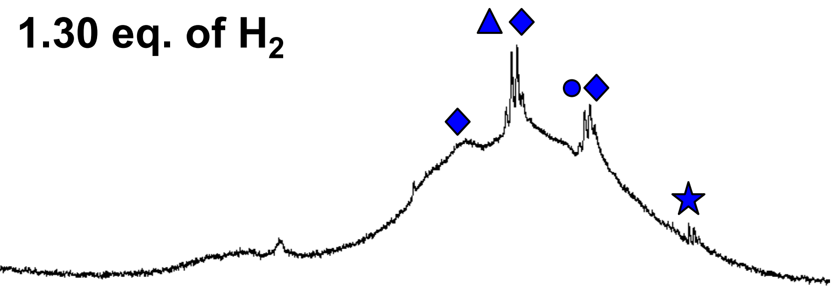
● ammonia borane, ★ BH_4^-, ▲ BH_2^+, ◆ polyaminoborane, ‡1-Butyl-3-methylimidazolium chloride

NH_3BH_3 / Ionic Liquid at 90°C

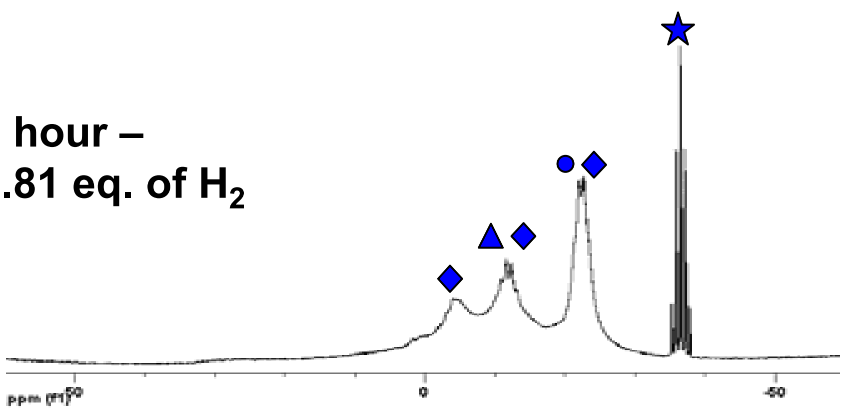
NH_3BH_3 + Ionic Liquid‡ | **Neat NH_3BH_3**

^{11}B NMR spectra

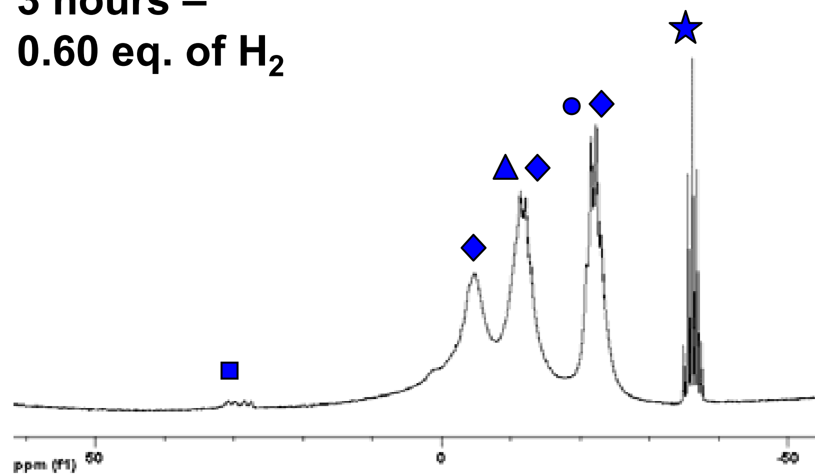
6 hours – 1.30 eq. of H_2



1 hour – 0.81 eq. of H_2



3 hours – 0.60 eq. of H_2



- ● Ammonia Borane NH_3BH_3
- ★ BH_4^- (from diammoniate diborane, $[(NH_3)_2BH_2]BH_4$)
- ▲ BH_2^+ (from diammoniate diborane, $[(NH_3)_2BH_2]BH_4$)
- ◆ Polyaminoborane
- ■ Unsaturated B=N

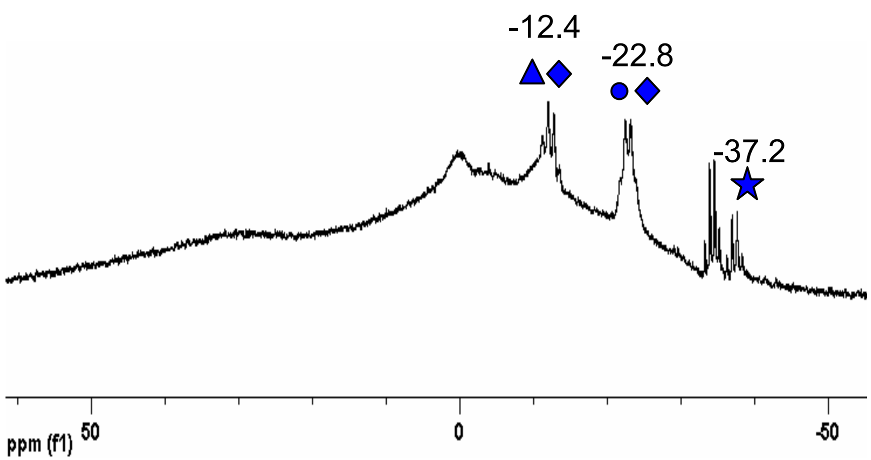
‡ 1-Butyl-3-methylimidazolium chloride

NH_3BH_3 / Ionic Liquid at 110°C

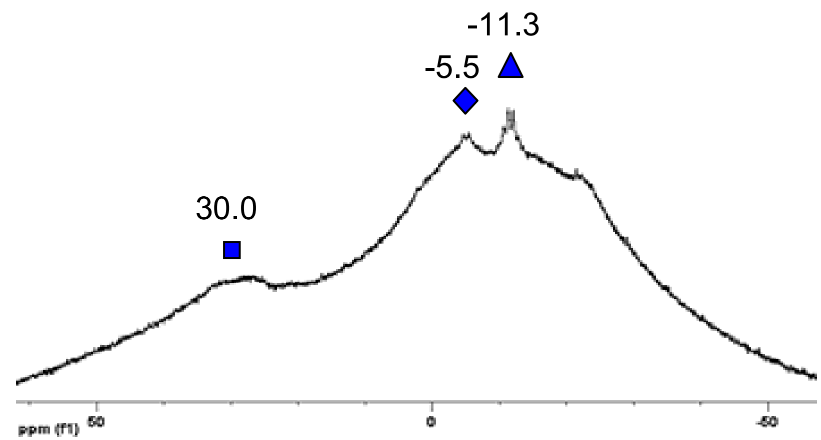
NH_3BH_3 + Ionic Liquid‡ — **Neat NH_3BH_3**

^{11}B NMR spectra

1 hour – 1.45 eq. of H_2



16 hours – 1.30 eq. of H_2

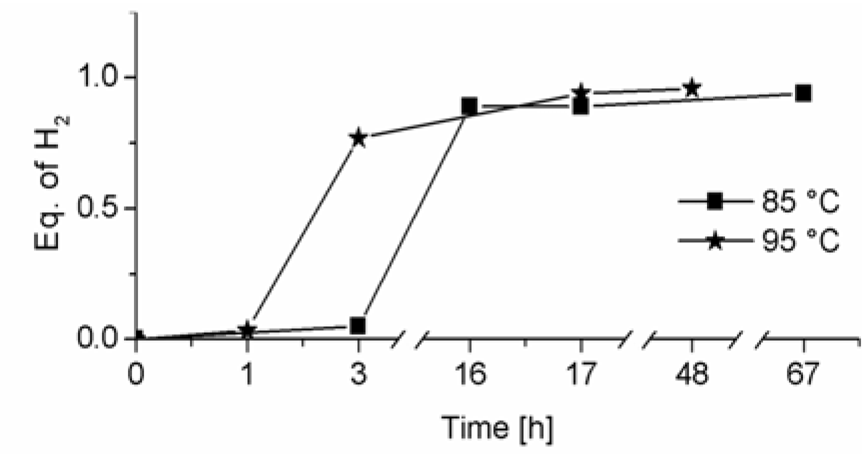


- ● Ammonia Borane NH_3BH_3
- ★ BH_4^- (from diammoniate diborane, $[(NH_3)_2BH_2]BH_4$)
- ▲ BH_2^+ (from diammoniate diborane, $[(NH_3)_2BH_2]BH_4$)
- ◆ Polyaminoborane
- ■ Unsaturated B=N

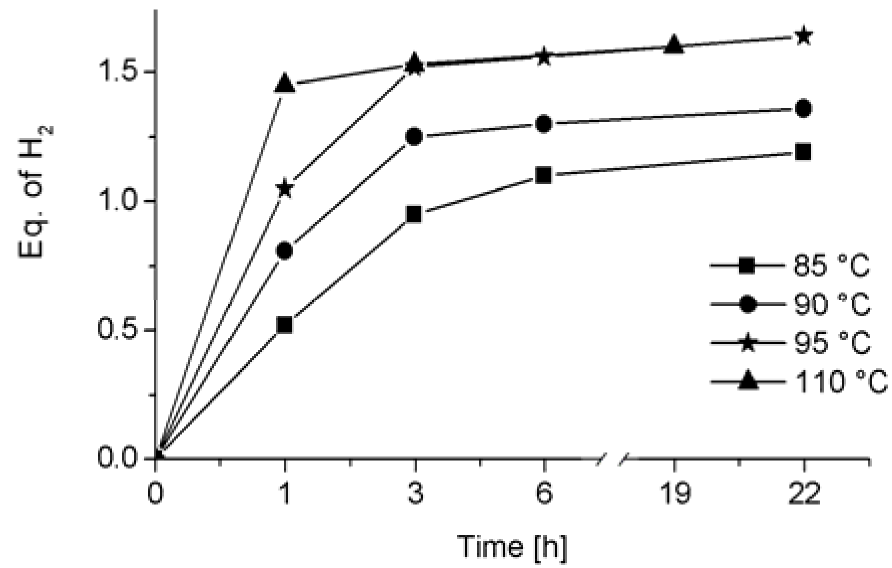
‡ 1-Butyl-3-methylimidazolium chloride

Summary of Ionic Liquid Studies

Neat NH_3BH_3



NH_3BH_3 + Ionic Liquid‡



‡ 1-Butyl-3-methylimidazolium chloride

Ionic liquids accelerate the hydrogen release from NH_3BH_3!

Metal Catalyzed H_2 Release at 85°C

$$NH_3BH_3 \xrightarrow{\text{catalyst}} BNH_x + 3\text{-}x\ H_2$$

No.	Solvent, wt [mg][a]	H_3NBH_3	Catalyst [mg]	Total System wt [mg]	T [°C][b]	time [h]	H_2 released[c] mmol	wt%	Complete H_2 after 15h, wt%
1	BMI-Cl, 150	8.1 mmol, 250 mg	–	400	85	6	7.2	3.6	
2	BMI-Cl, 200	8.1 mmol, 250 mg	–	450	85	6	8.1	3.6	
3	BMI-Cl, 250	8.1 mmol, 250 mg	–	500	85	6	9.5	3.8	
4	BMI-Cl, 250	8.1 mmol, 250 mg	–	500	85	8	10.4	4.2	
5	BMI-PF_6 250	8.1 mmol, 250 mg	–	500	85	6	7.5	3.0	
6	BMI-Cl, 250	8.1 mmol, 250 mg	Nanoscale Ni, 0.7 mol%, 3.5	503.5	85	6	11.5	4.6	5.3 (1.62 eq)
7	BMI-Cl, 250	8.1 mmol, 250 mg	$Ni(cod)_2$, 0.9 mol%, 20	520	85	6	11.5	4.5	5.1 (1.63 eq)
8	BMI-Cl, 250	8.1 mmol, 250 mg	Nanoscale Pd, 0.8 mol%, 7	507	85	6	11.6	4.6	5.1 (1.57 eq)
9	BMI-Cl, 250	8.1 mmol, 250 mg	Pd, 0.5 mol%, 4.3	504.3	85	6	12.0	4.8	
10	BMI-Cl, 250	8.1 mmol, 250 mg	Pd, 2.5 mol%, 21.5	521.5	85	6	11.7	4.5	
11	BMI-Cl 250	16.2 mmol, 500 mg	Pd, 2.5 mol%, 21.5	771.5	85	6	16.7	4.4	
12	BMI-Cl 500	16.2 mmol, 500 mg	Pd, 2.5 mol%, 21.5	1021.5	85	6	21.4	4.2	5.2 (1.62 eq)

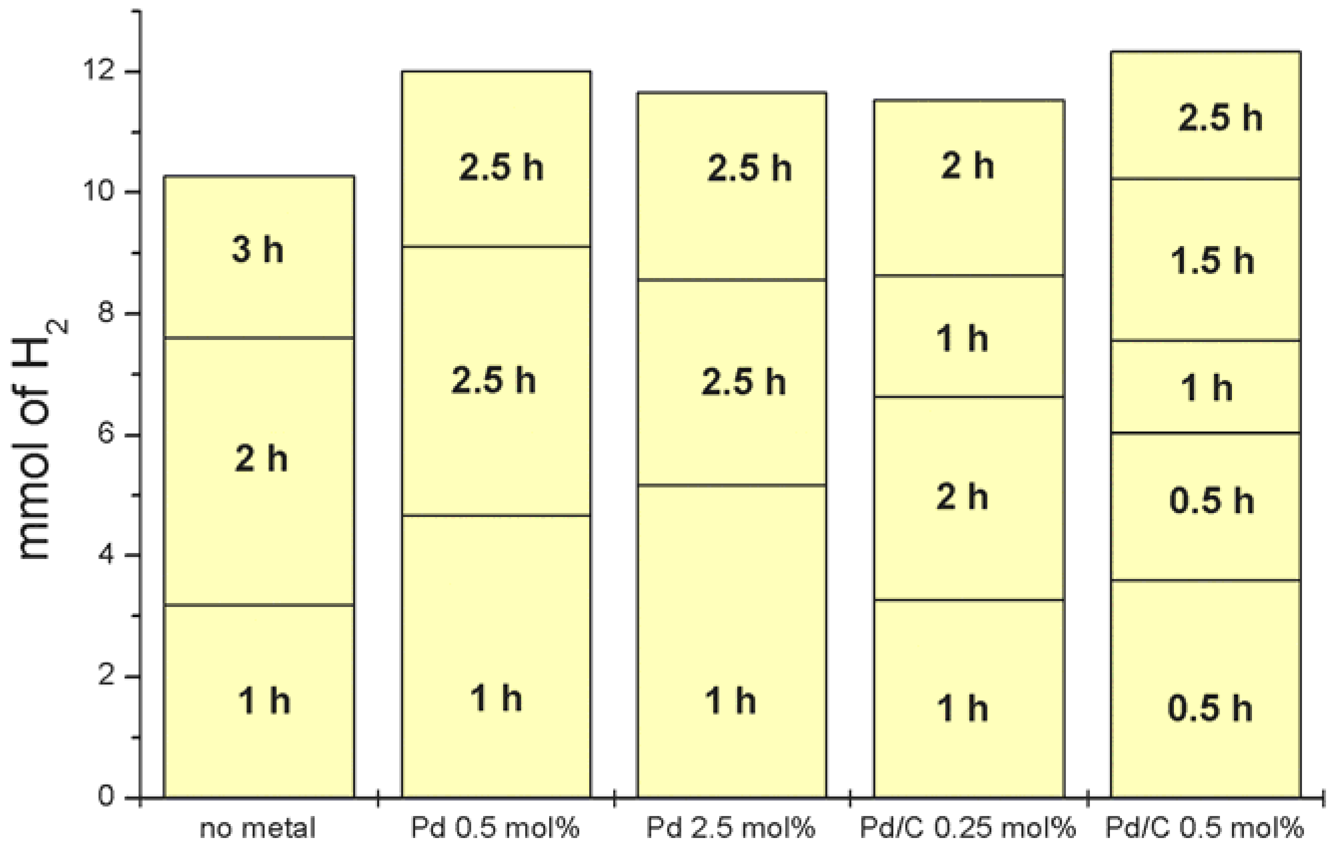
Metal Catalyzed H_2 Release at 85°C

No.	Solvent, wt [mg][a]	H_3NBH_3	Catalyst [mg]	Total System wt [mg]	T [°C][b]	time [h]	H_2 released[c] mmol	wt%	Complete H_2 after 15h, wt%
13	BMI-Cl, 250	8.1 mmol, 250 mg	Pd, 10% on C, 0.25 mol%, 20	520	85	6	11.5	4.5	
14	BMI-Cl, 250	8.1 mmol, 250 mg	Pd, 10% on C, 0.5 mol%, 43	543	85	6	12.3	4.6	
15	BMI-Cl, 250	8.1 mmol, 250 mg	Nanoscale Pt, 0.8 mol%, 12	512	85	6	10.9	4.3	5.1 (1.56 eq)
16	BMI-Cl, 250	8.1 mmol, 250 mg	$(Ph_3P)_3RhCl$, 0.5 mol%, 37.5	537.5	85	6	12.3	4.6	
17	BMI-Cl, 250	8.1 mmol, 250 mg	Rh, 5% on Al, 0.5 mol%, 82.3	582.3	85	6	11.1	3.9	
18	BMI-Cl, 350	8.1 mmol, 250 mg	$[Rh(cod)(\mu\text{-}Cl)]_2$, 0.5 mol%, 20	620	85	6	12.3	4.0	
19	BMI-Cl, 250	8.1 mmol, 250 mg	$[Rh(cod)(\mu\text{-}Cl)]_2$, 0.5 mol%, 20	520	45	6	2.3	0.9	
20	BMI-Cl, 250	8.1 mmol, 250 mg	$RuH_2(CO)(PPh_3)_3$ 0.4 mol%, 31	531	85	6	12.2	4.6	5.1 (1.66 eq)
21	BMI-Cl, 250	8.1 mmol, 250 mg	Ru, 0.5 mol%, 4	504	85	6	12.0	4.8	5.2 (1.61 eq)
22	BMI-Cl, 250	8.1 mmol, 250 mg	Ir(I) catalyst[d], 0.5 mol%, 32	532	85	6	11.7	4.4	4.8 (1.57 eq)
23	Mineral oil, 250	8.1 mmol, 250 mg	–	500	85	6	3.4	1.4	

[a] BMI-Cl: dry 1-Butyl-3-methylimidazolium chloride. [b] Oil bath temperature. [c] Hydrogen gas is collected in calibrated volumes using a Toepler pump. To avoid the collection of other gases and volatiles formed in these reactions, a nitrogen cooled trap is connected between the reaction flask and the pump system. [d] (Tricyclohexylphosphine)(1,5-cyclooctadiene)(pyridine)irridium(I) hexafluorophosphane.

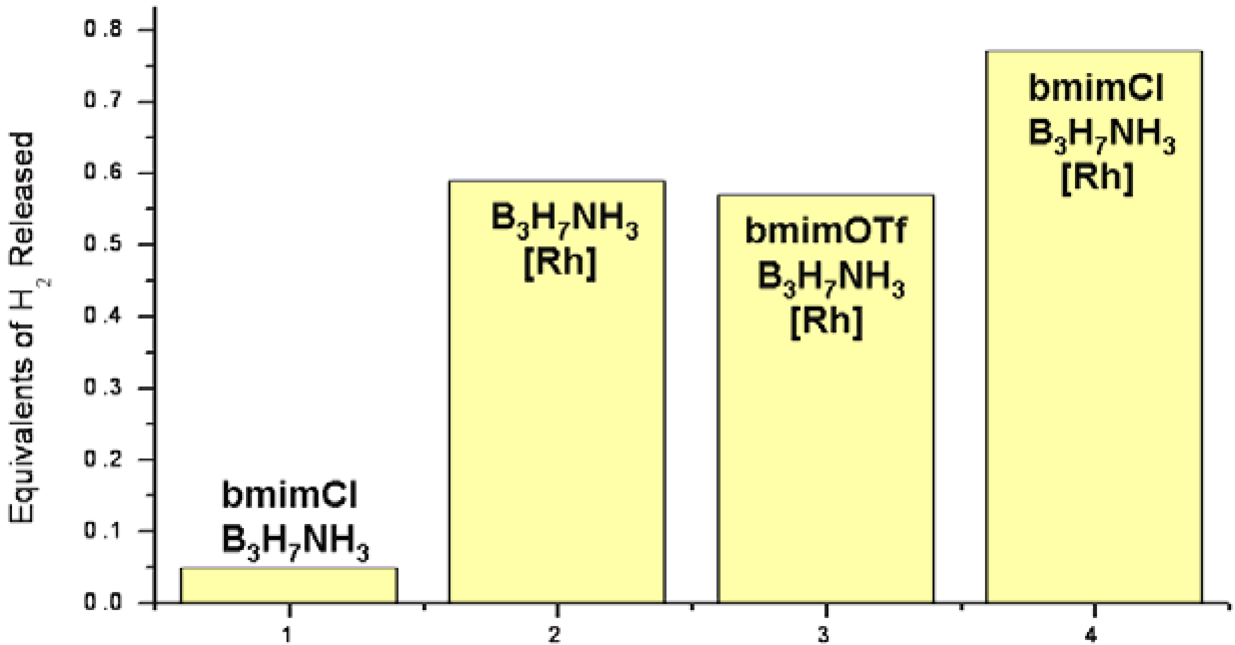
Increased H_2 Release with Pd at 85°C

mmol of H_2:	10.18	12.01	11.66	11.53	12.34
System wt%	4.1	4.8	4.5	4.5	4.6



"System" = wt of H_3NBH_3 + Catalyst + bmimCl

Metals Catalyze Dehydrogenation of Ammonia Triborohydride at 50^{o}C



[Rh] = $[Rh(COD)Cl]_2$ (COD=1,5-cyclooctadiene)
bmim**Cl** = 1-butyl-3-methylimidazolium chloride
bmim**OTf** = 1-butyl-3-methylimidazolium trifluoromethanesulfonate

Summary and Future Studies

Achievements

- The major species produced in the thermal decomposition of ammonia borane have been identified.
- Ionic liquids have been shown to increase both the extent and rate of hydrogen release from ammonia borane.
- Metal catalyzed reactions in ionic liquids have been shown to promote ammonia borane dehydrogenation.

Ongoing and Future Studies

- Investigate a wider range of ionic liquids for ammonia borane and ammonia triborohydride dehydrogenations.
- Elucidate the mechanisms of dehydrogenations in ionic liquids and determine the effects of chemical initiators.
- Use the ability of ionic liquids to stabilize nanoparticle metals to develop new metal-catalyzed dehydrogenation systems with improved rates of hydrogen release.