Kinetic and Mechanistic Studies of B-N Hydrogenation/Dehydrogenation

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University of Washington

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Project ID #
STP9

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Overview

Timeline

Project start date: FY05

Project end date: FY09

New Start

Budget

Total project funding (requested):

$ 1.1 M DOE share

$ 0.28 M Cost Share

Funding from FY05:

$171 K (DOE + Cost Share)

Barriers Addressed

Weight and Volume

Efficiency

Regeneration Processes

Amineboranes offer high hydrogen storage capacity in principle, but thermal hydrogen release from amineboranes is erratic and inefficient. Effective catalysts for dehydrogenation/ hydrogenation of BN are needed.

Partners

DOE Center of Excellence for Chemical Hydrogen Storage

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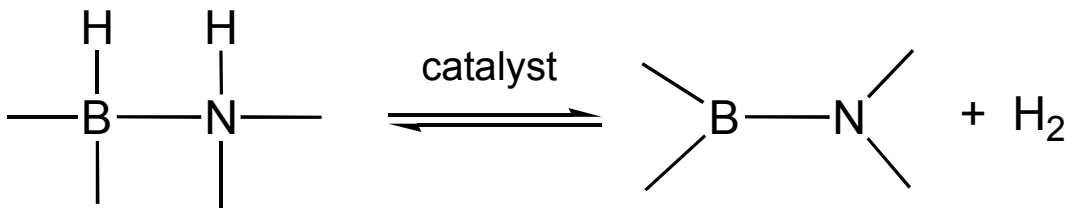
Kinetic and Mechanistic Studies of B-N Hydrogenation/Dehydrogenation

Objectives: To understand the mechanism(s) of amineborane dehydrogenation and B-N hydrogenation and to use this insight to develop catalysts exhibiting satisfactory rates to allow for efficient hydrogen storage.



Why are Mechanistic Studies Needed?

Metal complexes catalyze dehydrogenation/hydrogenation of BN materials.

$$BH_3NH_3 \overset{ML_n}{\rightleftharpoons} BH_2NH_2 + H_2 \overset{ML_n}{\rightleftharpoons} BHNH + H_2$$

HOW?

Detailed mechanistic studies using well-characterized models of likely intermediates will lead to improved catalysts. This work will be synergistic with the amineborane work being carried out by COE partners at LANL, PNNL and Penn.

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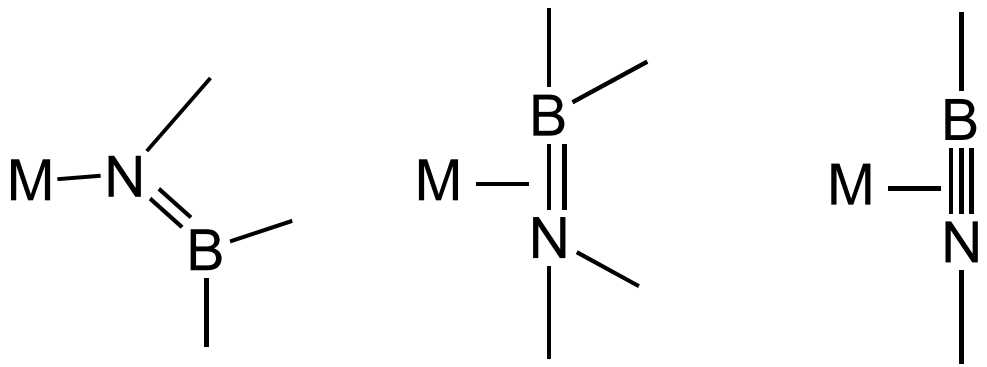
Task 1 - Prepare Metal Complexes with B-N Ligands



Select substituents to stabilize analogs of metal imine, alkene and alkyne complexes.

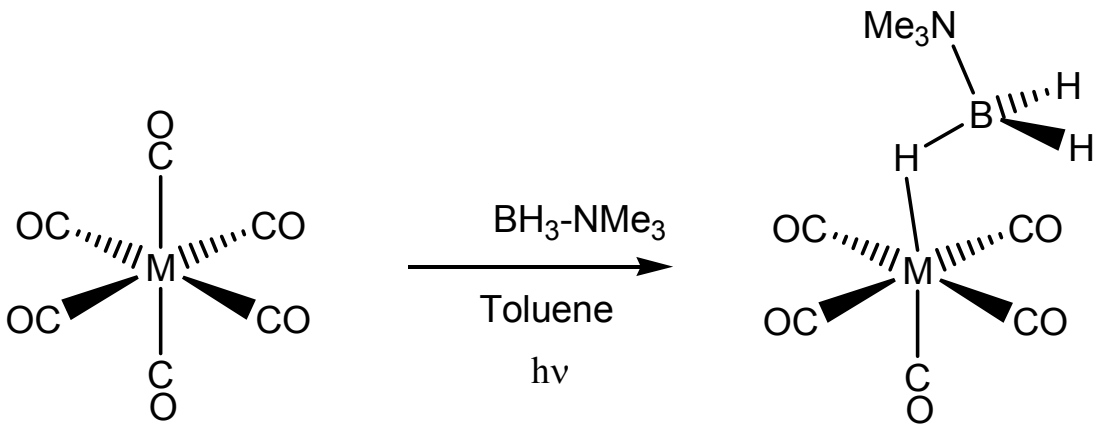
Characterize and investigate the reactivity of these novel species.

Our Plan: Generate Ligand Deficient L_nM Species to Observe Coordination of B-H Bonds

- Generation of unsaturated L_nM species by photolysis and chemical means in the presence of Me_2NHBH_3, $PhNH_2BH_3$ and NH_3BH_3.
- Reactions will be monitored by ^{1}H and ^{11}B NMR at low temperature.
- Low temperatures are needed to prevent dehydrogenation.
- Problems anticipated: poor solubility of NH_3BH_3 in non-coordinating solvents, possible dehydrogenation of the amineborane which would lead to the formation of the corresponding dihydrogen or dihydride complex.

Example of a Transition Metal Complex of an Amineborane

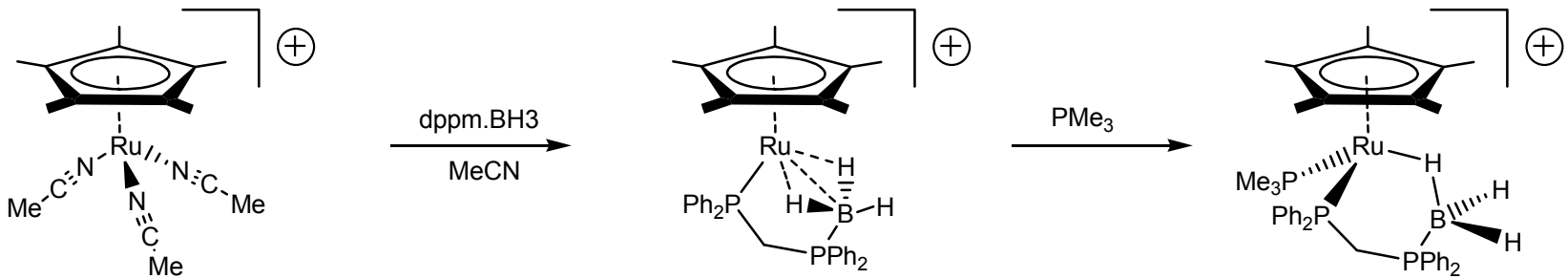
Shimoi *et al.* have isolated a series of borane adduct complexes of chromium and tungsten $[(OC)_5M(H_3B\text{-}NMe_3)]$ (M = Cr, W).



Shimoi, M.; Nagai, S.I.; Ichikawa, M.; Kawano, Y.; Katoh, K.; Uruichi, M.; Ogino, H. *J. Am. Chem. Soc.* **1999**, *121*, 11704 -11712.

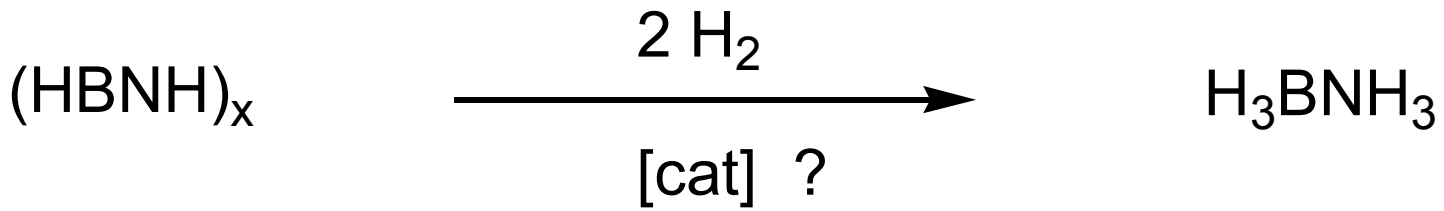
Example of a Ruthenium Borane Complex

Weller and coworkers reported the synthesis of a complex with a chelating phosphine borane ligand.



Merle, N.; Koicok-Köhn, G.; Mahon, M.F.; Frost, C.G.; Ruggerio, G.D.; Weller, A.S.; Willis, M.C. *J. Chem. Soc., Dalton Trans.* **2004**, 3883-3892.

Task 2 - Investigate Reactivity of Hydrogen Deficient B-N Species with H_2



Reactivity studies with different metal complexes will help identify different mechanisms and best catalysts.

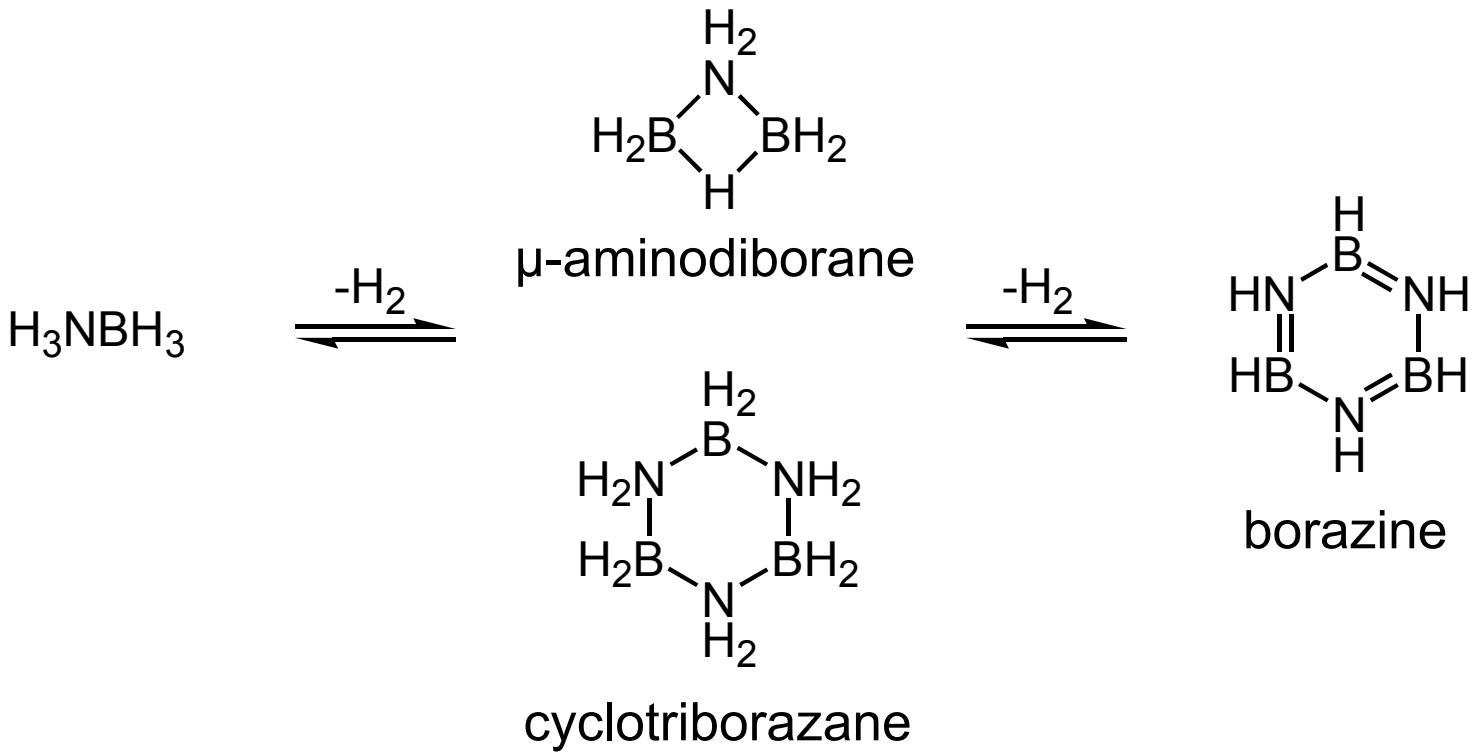
Task 3 - Screen Homogeneous Catalysts for Hydrogenation/Dehydrogenation of B-N Model Compounds

Use Task 1 & 2 results to identify and test both platinum group metal and non-PGM catalysts.

$$x\ H_3NBH_3 \xrightleftharpoons{[ML_n]} (HNBH)_x + 2x\ H_2$$

Thermal Dehydrocoupling of H_3N-BH_3

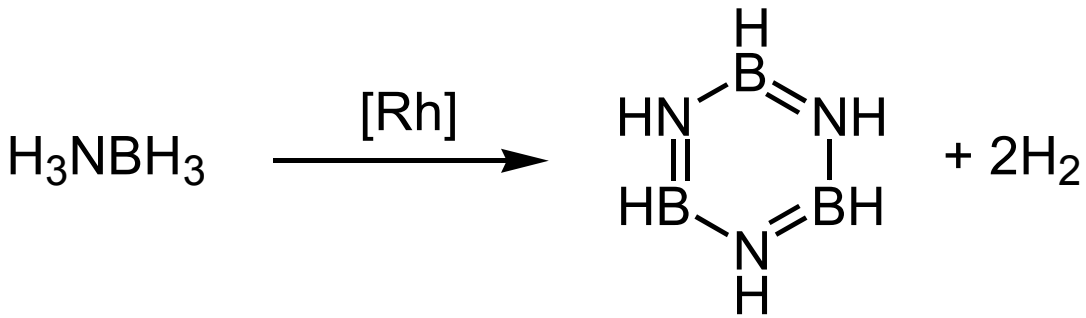
Ammonia-borane undergoes thermal decomposition at high temperatures to borazine, accompanied by hydrogen evolution. Intermediates include cyclotriborazane and μ-aminodiborane (oligomers of H_2NBH_2).

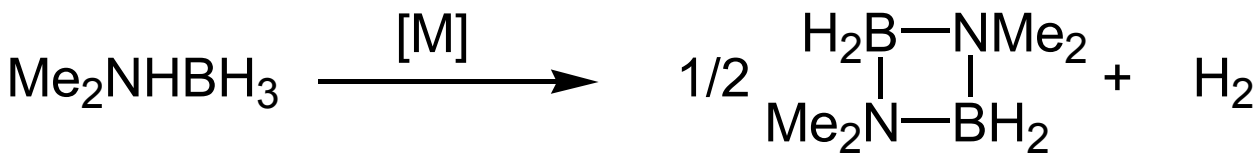


Wang, J. S.; Geanangel, R. A. *Inorg. Chim. Acta* **1988**, *148*, 185.

Catalytic Dehydrocoupling of Aminoboranes

Dehydrocoupling of H_3NBH_3 and Me_2NBH_3 occur under mild conditions in the presence of various transition metal catalysts.





Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 9776 (and references therein).

Chen, Y.; Fulton, J.; Linehan, J.; Autrey, T. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **2004**, *49*, 972.

Chen, Y.; Fulton, J.; Linehan, J.; Autrey, T. *J. Am. Chem. Soc.* **2005**, *127*, 3254.

Task 4 - Screen Non-PGM Catalysts for Activity with Amineborane Derivatives

Coordinate with other Center partners to apply new non-PGM catalysts to complex boranes and other amineborane derivatives.

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Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- The rapid buildup of high pressures of hydrogen in dehydrogenation reactions with successful catalysts.

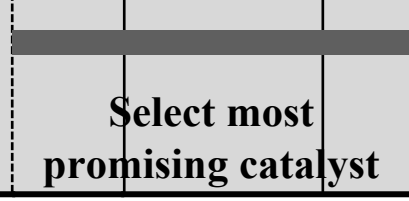
Hydrogen Safety

Our approach to deal with this hazard is:

- Reactions will be carried out on small scale.
- The maximum amount of hydrogen pressure will be calculated and the safety of the reaction assessed prior to commencing experiments.

Timeline of Project Tasks

	Year 1	Year 2	Year 3	Year 4	Year 5
Task 1: Prepare and characterize metal complexes with B-N ligands.					
Task 2: Explore homogeneous hydrogenation of B=N model complexes and study mechanisms.					
Task 3: Screen and identify PGM and non-PGM catalysts for BN hydrogenation/ dehydrogenation reactions in model complexes.					
Task 4: Screen and identify PGM and non-PGM catalysts for BN hydrogenation/ dehydrogenation reactions of BH_3NH_3 and polymeric $(BH_2NH_{2)n}$.					



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