Chemical Hydrogen Storage using Ultra-High Surface Area Main Group Elements

(part of the DOE Chemical Hydrogen Storage Center of Excellence)

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Project ID #

STP 26

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Overview--Innovation Beyond Boron

Timeline

Project Start Date: FY05
Project End Date: FY09
20 % complete

Barriers

- Cost
- Weight and volume
- Hydrogen capacity

Targets

- Gravimetric capacity: >8%

Budget

- Total project funding
  - DOE share
  - Contractor share $0.5 M
- Funding for FY05
  $100K (DOE) $ $20K (cost share)
- Funding for FY06
  - $193K (DOE) $40K (cost share)

Direct Collaborators

- Participant in the DOE Chemical Hydrogen Storage Center of Excellence
- LANL, PNNL, Penn, Alabama

Objectives – Innovation Beyond Boron

Overall

- To identify hydrogen storage material enabling DOE targets and increase the understanding of synthetic approaches and physical properties of main group element clusters, such as Si, B, Al, and alloys thereof, BP and BN compounds.

2005-2006

- To design simple routes to such compounds using mild conditions to provide commercially viable materials.

- To investigate the viability of the synthesized materials for commercial application by studying weight and volume as well as the reversibility of hydrogen uptake.

2007-2009

- To analyze measurements to identify compounds that offer relatively lightweight, easily handled solid materials capable of hydrogen storage that are synthesized, activated and regenerated in a simple manner.

Approach

Methods	Synthesis	Materials
Utilize standard laboratory equipment to produce materials. Synthesis will ideally not require specialist equipment	Design mild routes to Si, B, Al alloys, BP and BN compounds otherwise produced under harsh conditions	Characterize the materials using common spectroscopic methods and investigate the production of hydrogen

Results

1) Room temperature synthesis of amide-capped silicon nanoparticles (Task 1)

2) Solution and solid-state synthesis of nanocrystalline silicon with hydrogen (Task 1)

3) First synthesis of organo-capped boron nanoparticles (Task 1)

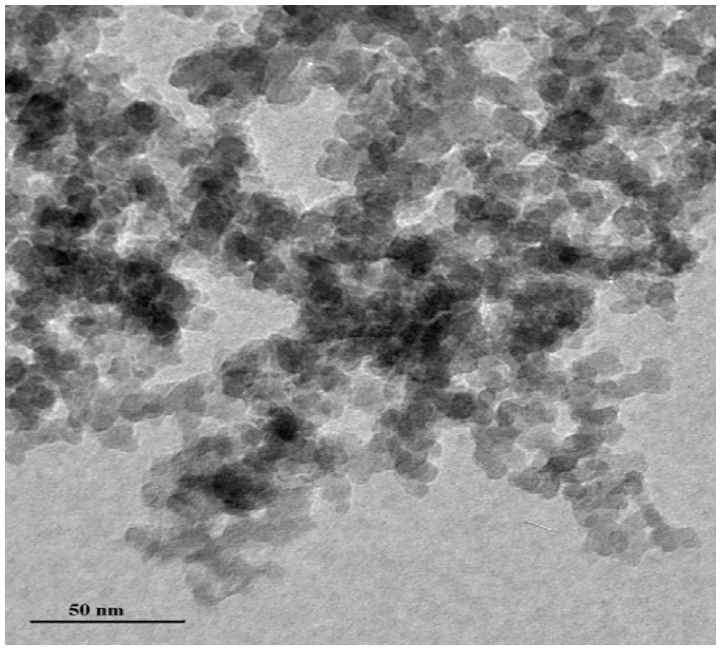
4) Synthesis of molecular compounds by addition of hydrogen across a multiply-bonded system (Task 2)

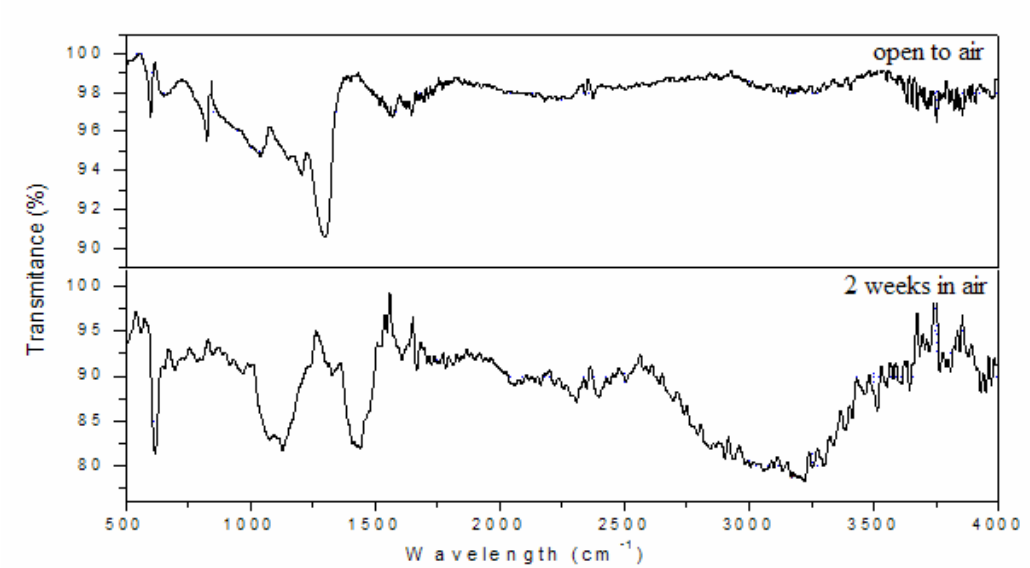
Results-1

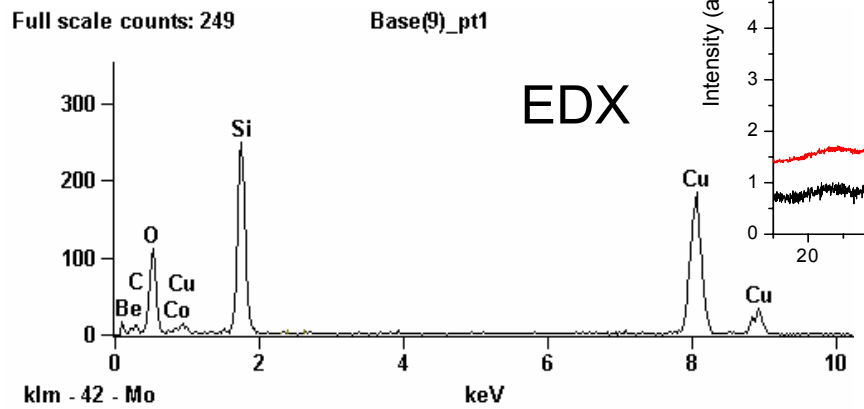
$Si_x(NH_2)_n \rightarrow Si_xN_n + nH_2$

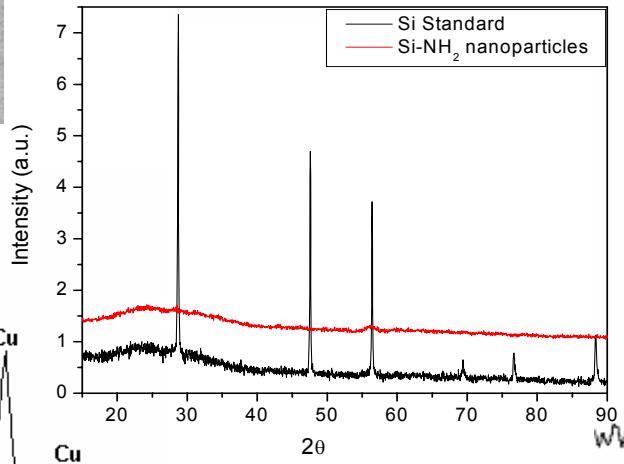
$SiCl_4$ + Na.naphthalenide $\xrightarrow{\text{glyme}}$ $(Cl)_n$ + NaCl

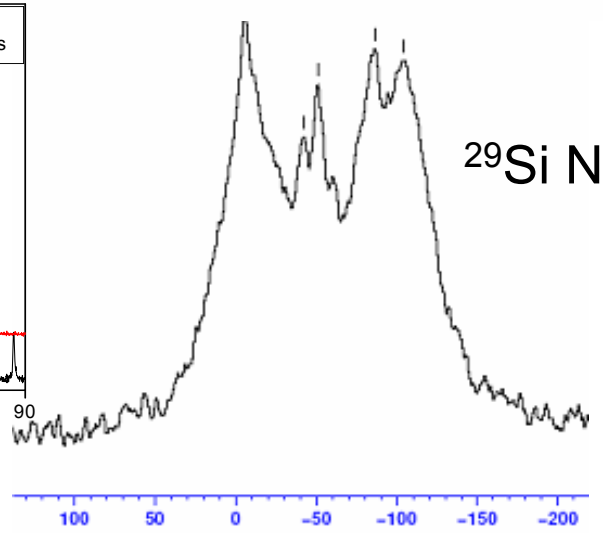
$(Cl)_n \xrightarrow{NH_3\ (g)} (NH_2)_n$ + NH_4Cl







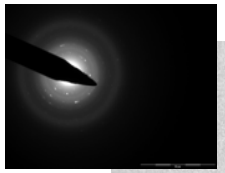


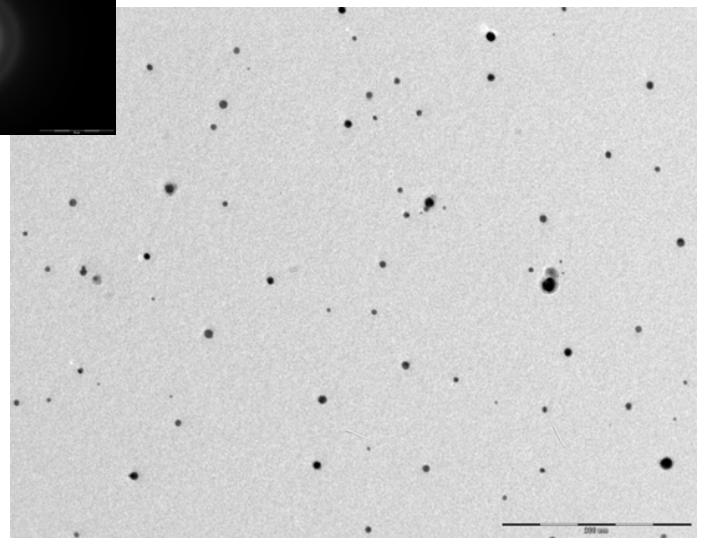


Results - 2

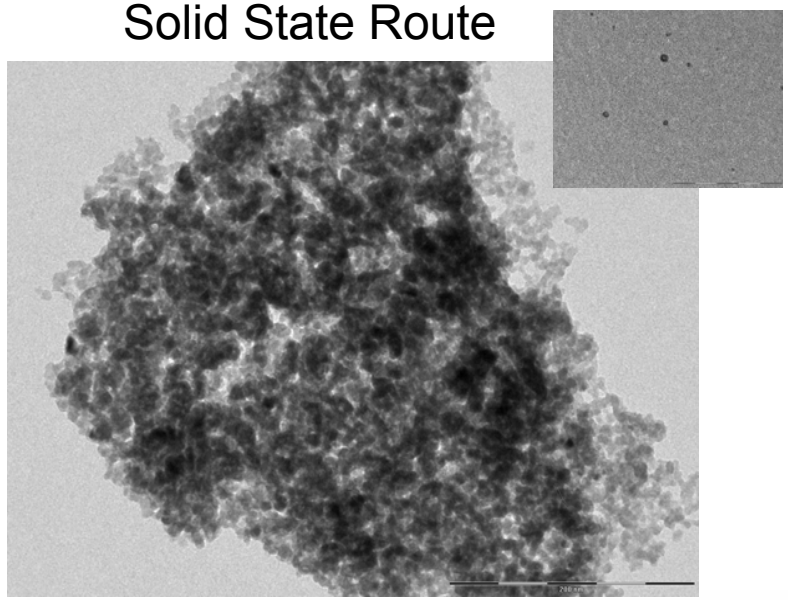
SiH_n --> Si + n/2 H_2

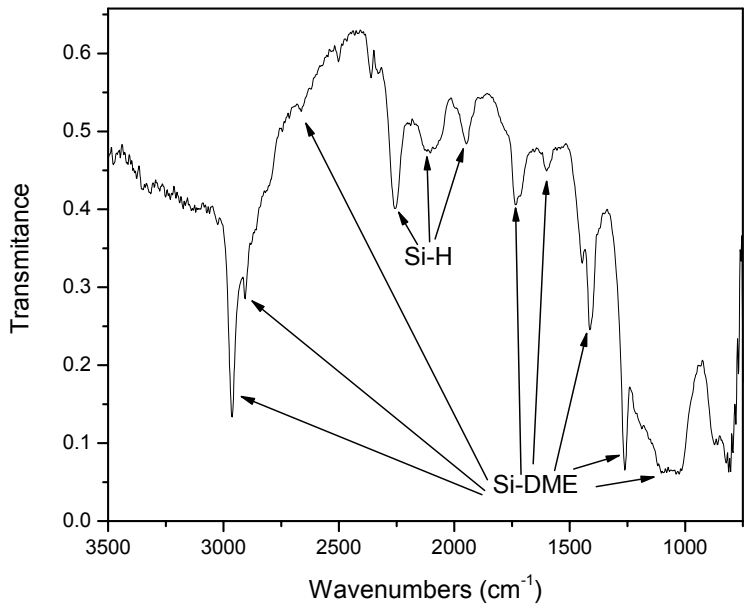
Solution Route

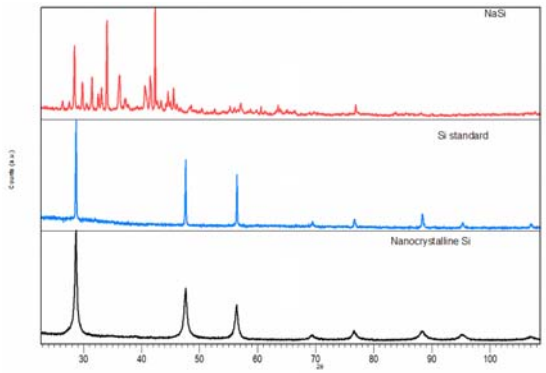




Solid State Route

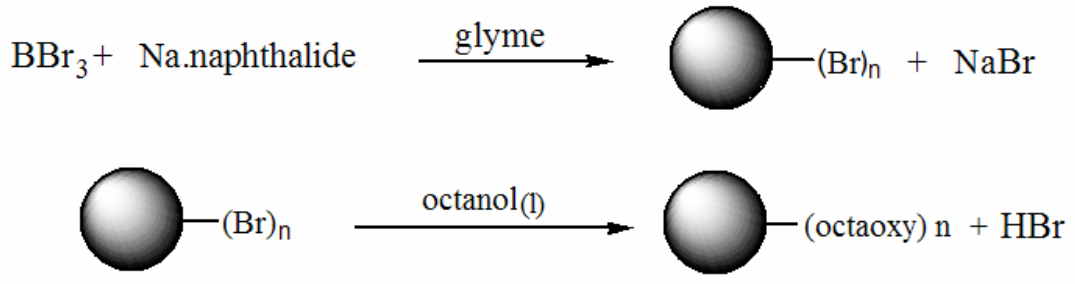


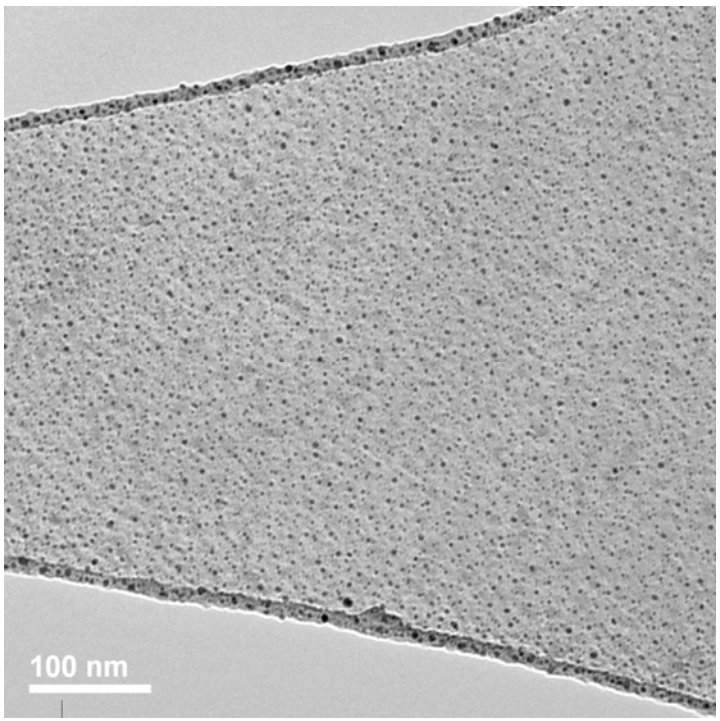


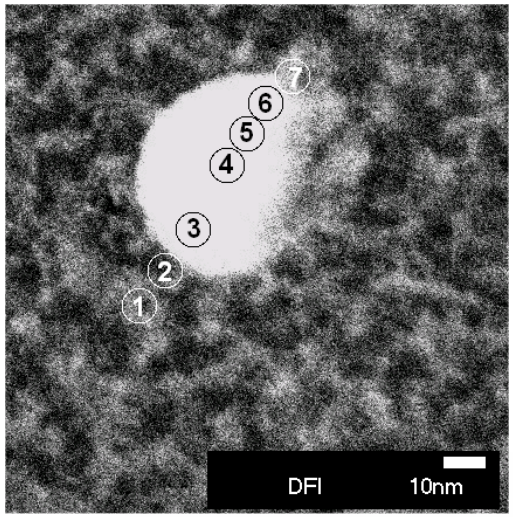


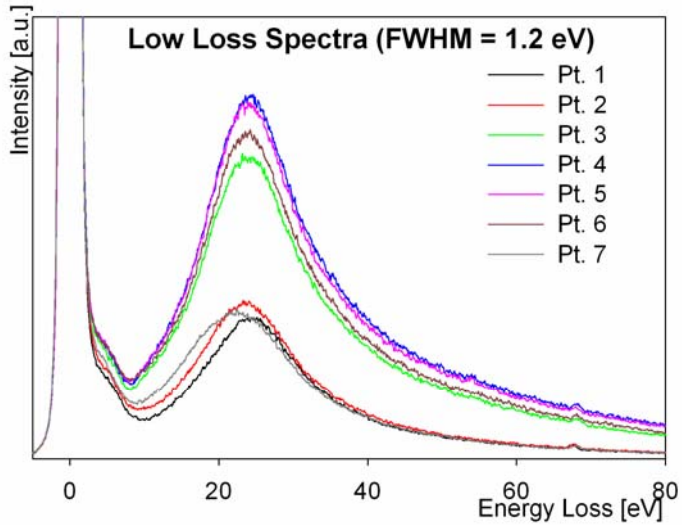
Results - 3

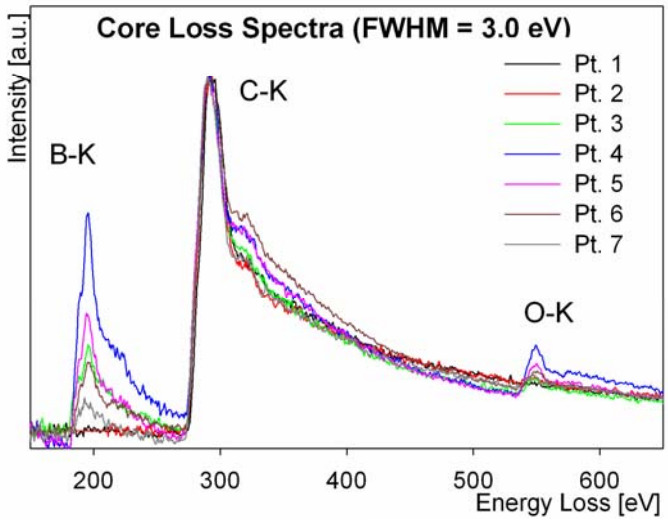
Boron Nanoparticles



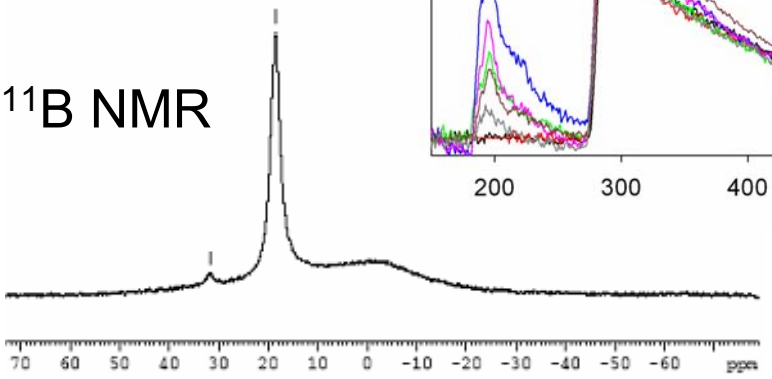








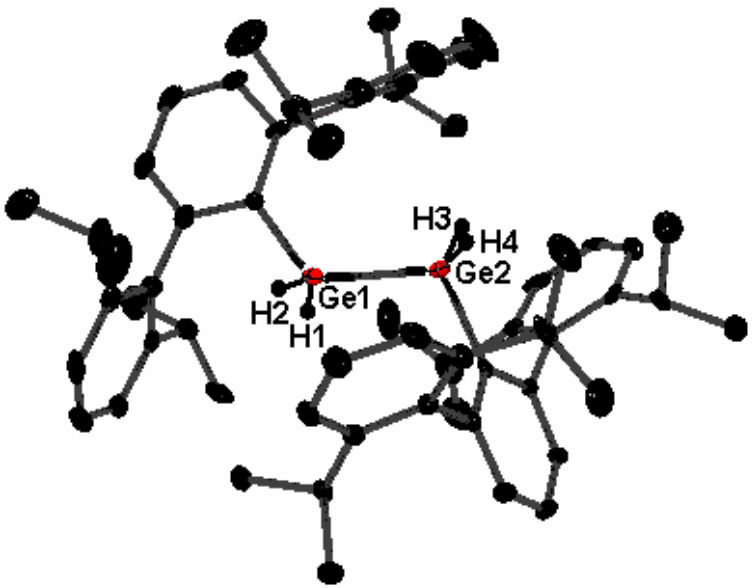
^{11}B NMR



A.L. Pickering, C. Mitterbauer, N.D. Browning, S.M. Kauzlarich, P.P. Power, **Nature Materials**, *submitted*

Molecular Compounds

Results - 4

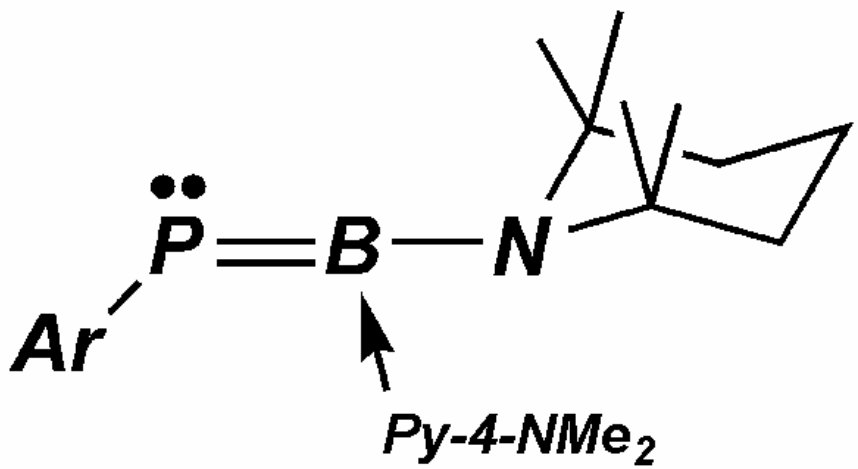


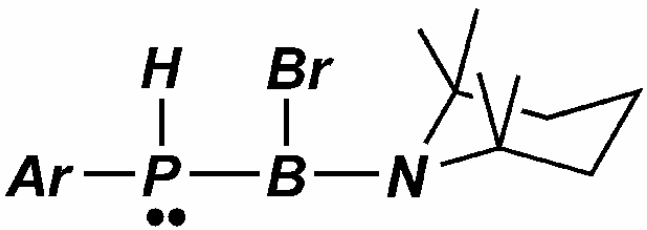
Facile Activation of Dihydrogen by an Unsaturated Heavier Main Group Compound G.H. Spikes, J.C. Fettinger, P.P. Power JACS, 2005

$Ar'GeGeAr'$ (**1**) + $1H_2$ → 60% $Ar'GeGeAr'$ (**1**) (1)
+ 21% $Ar'HGeGeHAr'$ (**2**)
+ 10% $Ar'H_2GeGeH_2Ar'$ (**3**)
+ 9% $Ar'GeH_3$ (**4**)

$Ar'GeGeAr'$ (**1**) + $2H_2$ → 2% $Ar'HGeGeHAr'$ (**2**) (2)
+ 85% $Ar'H_2GeGeH_2Ar'$ (**3**)
+ 13% $Ar'GeH_3$ (**4**)

$Ar'GeGeAr'$ (**1**) + $3H_2$ → 65% $Ar'H_2GeGeH_2Ar'$ (**3**) (3)





Crystal structure determined

Future Work

- FY05-06
  - Prepare hydrogen and amine terminated Si nanoparticles and characterize. Investigate alloy nanoparticle synthesis and characterize.
  - Prepare main group compounds and characterize.
- FY07
  - Determine the most promising composition with highest hydrogen gravimetric amount. Explore reaction mechanism and prepare materials in high yield.
- FY08
  - Provide materials to partners for testing.
- FY09
  - Optimize synthesis for further testing.

Timeline

Task	Year 1	Year 2	Year 3	Year 4	Year 5
Task 1: Nanoparticle Synthesis					
Synthesis of SiH and $Si(NH_2)$					
Characterization of SiH and $Si(NH_2)$					
Synthesis of $Si_{1-x}M_xH$ and $Si_{1-x}MNH_2$					
Characterization of $Si_{1-x}M_xH$ and $Si_{1-x}MNH_2$ composition and reactivity					
Optimization of reaction to provide material to partners					
Task 2: Main group Compound Synthesis					
Synthesis of (H2BXH2)n					
Characterization of composition and reactivity					
explore main group analogs					
Task 3: Characterization and Testing					
Test reactivity and thermolysis of various alloys and main group compounds					

Summary

- Amide capped and hydrogen capped Si nanoparticles have been synthesized by two different low temperature routes.
- These nanoparticles have been shown to evolve substantial amounts of gas when heated.
- Boron nanoparticles capped with -OR groups have been synthesized by a low temperature route.
- H_2 has been shown to react with a “digermyne”,RGeGeR at room temperature and pressure.

Publication List

1. *Facile Activation of Dihydrogen by an Unsaturated Heavier Main Group Compound*
   G. H. Spikes, J. C. Fettinger, P. P. Power, **JACS** 2005, *127*, 12232.
2. *Nanocrystalline Silicon for Hydrogen Storage*
   D. Neiner, C. N. Chervin, H. W. Chiu, M. J. Blessent, S. M. Kauzlarich, 2006 MRS Spring Meeting, San Francisco, CA, April 17 - 21, 2006, EE3.19.

2. *Room Temperature Synthesis of Surface-Fuctionalised Boron Nanoparticles*
   A. L. Pickering, C. J. Mitterbauer, N. D. Browning, S. M. Kauzlarich, P. P. Power, **Nature Materials** 2006, *submitted.*