

## IV.B.5k Main Group Element and Organic Chemistry for Hydrogen Storage and Activation

Anthony J. Arduengo, III and  
David A. Dixon (Primary Contact)  
Chemistry Department  
The University of Alabama  
Box 870336  
Shelby Hall  
Tuscaloosa, AL 35487-0336  
Phone: (205) 348-3556; Fax: (205) 348-4704  
E-mail: ajarduengo@worldnet.att.net  
Phone: (205) 348-8441; Fax: (205) 348-4704  
E-mail: dadixon@bama.ua.edu

DOE Technology Development Manager:  
Grace Ordaz  
Phone: (202) 586-8350; Fax: (202) 586-9811  
E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: Jim Alkire  
Phone: (303) 275-4795; Fax: (303) 275-4753  
E-mail: James.Alkire@goe.doe.gov

Contract Number: DE-FC36-05GO15059

Start Date: January 1, 2005  
Projected End Date: December 31, 2009

### Objectives

- Develop new chemistries to 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.
- Focus on organic and main group compounds to enable new chemistries which may be able to perform better for release and regeneration by improving the energy balance and to provide longer term alternatives.
- Develop and implement imidazolium (carbene)-based H<sub>2</sub> activation chemistry.
- Develop and implement systems based on main group elements (examples: nitrogen and phosphorus).
- Develop and implement cyanocarbon systems for H<sub>2</sub> storage.
- Provide computational chemistry support (prediction of thermodynamics, kinetics, spectroscopic properties, mechanisms, etc.) to the experimental efforts of the DOE Chemical Hydrogen Storage Center of Excellence (CHSCoE)

to reduce the time to design new materials and develop materials that meet the 2010 and 2015 DOE objectives. Focus on new materials, hydrogen release mechanisms and regeneration processes.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (R) Regeneration Processes

### Technical Targets

| Storage Parameter: DOE 2010 System Targets                      | Carbene  | Cyanocarbon  | Phosphacarbons*   |
|---|--|--|---|
| Material Gravimetric Capacity: 6 wt%                            | Current: 2%<br>Ultimate: 7.2%                            | Current: <1%<br>Ultimate**:<br>7.2%                      | Current: <1%<br>Ultimate: 5%<br>with P<br>7.2% by<br>substituting N for P |
| Material Volumetric Capacity: 0.045 kg/L                        | Current: 0.045<br>Ultimate:<br>0.098                     | Current: 0.045<br>Ultimate: 0.092                        | Ultimate(P): 0.10<br>Ultimate(N): 0.092                                   |
| Dehydrogenation Rate: 0.02g/s-kW                                | In progress  | Oxidation step<br>diffusion<br>limited                   | Model Study   |
| Storage Efficiency<br>CHSCoE Goal:<br>50% Near<br>Thermoneutral | Exothermic:<br>-5 kcal/mol<br>Ultimate:<br>Thermoneutral | Endothermic:<br>5 kcal/mol<br>Ultimate:<br>Thermoneutral | Model Study   |

\* Continue only as a model system to understand release and regeneration

\*\* Ultimate for CN polymer is C<sub>2</sub>N<sub>2</sub>H<sub>6</sub> = 10.3%

## Accomplishments

- Developed first tetracyanoethylene (TCNE) oligomerization procedure for making cyanocarbons for H<sub>2</sub> storage with potential of 10 wt%.
- Continued work on 4-member ring diradicals with P substituents shows H<sub>2</sub> addition and release. Serves as first model for H<sub>2</sub> release from C at room temperature.
- Initial studies demonstrate catalyst photoactivation for H<sub>2</sub> addition to cyanocarbons and carbenes. Potential for widespread applicability.
- Demonstrated weight reduction by oligomerization of carbenes. Demonstrated oxidized and reduced (H<sub>2</sub> on and off) carbenes. Develop mixed carbene/TCNE synthesis to make oligomers.
- First demonstration of **non-metal catalysis using organic compounds** which are photoactivated for release of H<sub>2</sub>.
- First set of accurate thermodynamics for B<sub>x</sub>N<sub>x</sub>H<sub>y</sub> compounds up to x = 3 and y = 14 for release and regeneration of ammonia borane (AB) (with Pacific Northwest National Laboratory [PNNL]).
- Accurate bond energies for AB (ammonia borane = BH<sub>3</sub>NH<sub>3</sub>) and derived systems for release and regeneration (CHSCoE).
- H<sub>2</sub> release processes from AB (BH<sub>3</sub> as a Lewis acid catalyst) (Los Alamos National Laboratory [LANL] and CHSCoE).
- H<sub>2</sub> release processes studied via cationic chain polymerization mechanism (with LANL).
- First reliable thermodynamic properties of B<sub>3</sub>H<sub>7</sub>NH<sub>3</sub> and decomposition mechanism (University of Pennsylvania [Penn]).
- Study mechanism of H<sub>2</sub> release from AB dimer (BH<sub>3</sub>NH<sub>3</sub>)<sub>2</sub> and from zwitterionic isomer [NH<sub>3</sub>BH<sub>2</sub>NH<sub>3</sub><sup>+</sup>][BH<sub>4</sub><sup>-</sup>] – importance of seeding. (PNNL).
- Methyl substituent effects on energetics of borane amine compounds for release and regeneration (mixed solvents) (LANL, PNNL, University of Washington [UW], Penn, Northern Arizona University).
- Extensive studies of energetics for H<sub>2</sub> AB regeneration mechanisms (LANL, PNNL, Penn, University of California, Davis [UC-Davis], UW).
- Energetics for novel chemical H<sub>2</sub> storage systems: carbenes, cyanocarbons, P-based diradicals.



## Introduction

The focus of the work is the development of new chemistries to 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 (0.045 kg H<sub>2</sub>/L), and \$4/kWh.; by 2015, 3 kWh/kg (9 wt%), 2.7 kWh/L (0.081 kg H<sub>2</sub>/L), and \$2/kWh” by using chemical hydrogen storage systems. We are developing and implementing imidazolium-based H<sub>2</sub> activation chemistry; developing and implementing chemical systems based on polyhydrides of main group elements, e.g., phosphorous; developing and implementing cyanocarbon systems for H<sub>2</sub> storage; developing new non-metal catalysts that can be photoactivated for the release of H<sub>2</sub>; and providing computational chemistry support (thermodynamics, kinetics, properties prediction) to the experimental efforts of the DOE CHSCoE to reduce the time to design new materials and develop materials that meet the 2010 and 2015 DOE objectives.

## Approach

To achieve the goals described in the Introduction, we are **developing and identifying new concepts** to increase capacity and minimize weight (example: use storage medium for structural benefits); developing new concepts to improve energy balance which is especially relevant for ease of H<sub>2</sub> release and regeneration of the chemical H<sub>2</sub> storage system; developing new approaches to release hydrogen from dihydroimidazoles, based on new chemistry and our world leadership in stable carbene chemistry; and demonstrating proof-of-concepts and key reactions. A key issue is to minimize weight by eliminating substituents or changing them into components that can store H<sub>2</sub> while maintaining kinetic and thermodynamic properties; **developing** new non-metal catalysts that can be photoactivated for the release of H<sub>2</sub>; using highly accurate 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 catalysts to effect easy release and addition of H<sub>2</sub> (regeneration); and developing computational thermodynamic and kinetic approaches for chemical H<sub>2</sub> storage based on exploiting  $\Delta H$  and  $\Delta G$  coupled with Le Chatelier’s principle to manage H<sub>2</sub> addition and release in chemical compounds. For the experimental effort, there are close interactions with the partners (LANL and UC-Davis). The computational effort supports the entire CHSCoE with special interactions with LANL, PNNL, UW, Penn, UC-Davis, and the University of California, Los Angeles.

## Results

Substantial progress has been made this year in terms of the experimental and computational efforts. Experimental advances include: (1) **development of the first TCNE oligomerization procedure** for making

cyanocarbons for H<sub>2</sub> storage with potential of 10 weight %. This is the first time that this has been accomplished even though many man years of research at DuPont were spent on this. This chemistry is directly linked to the carbene/imidazolium chemistry that we have been pursuing and we have been able to demonstrate that the two chemistries will lead to the same storage compositions. The synthesis route for carbene oligomerization is shown in Figure 1 and the

cyanocarbon/carbene condensation approach in Figure 2 together with its x-ray structure; and (2) development of new non-metal catalysts that can be photoactivated for the fixation of H<sub>2</sub> as shown in Figure 3. This is based on our discovery that a stable phosphorus-based bi-radical would chemically add (fix) hydrogen without the need for a transition metal catalyst. We have been able to reduce dyes like methylene blue with dihydrogen in the presence of light. This added hydrogen can be

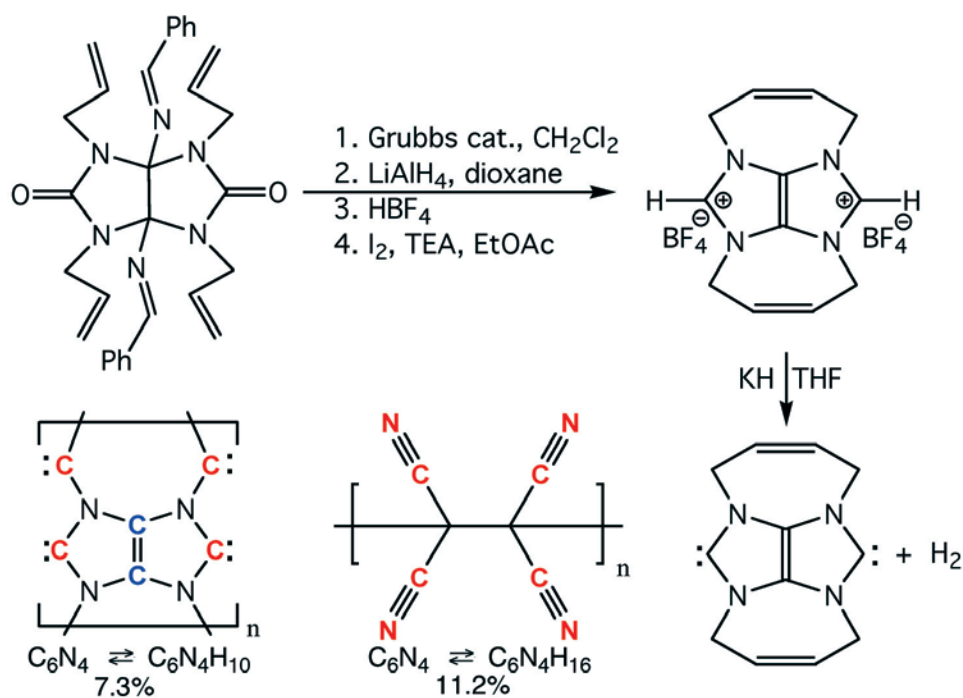


FIGURE 1. Synthetic Approach for the Polymerization of Carbenes to Generate Chemical Hydrogen Storage Materials with Minimal Substituent Weight

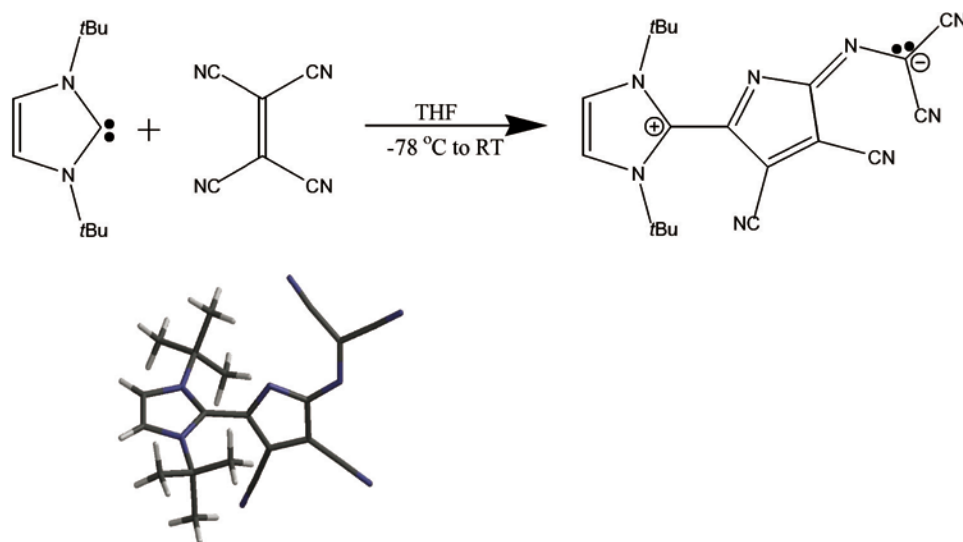
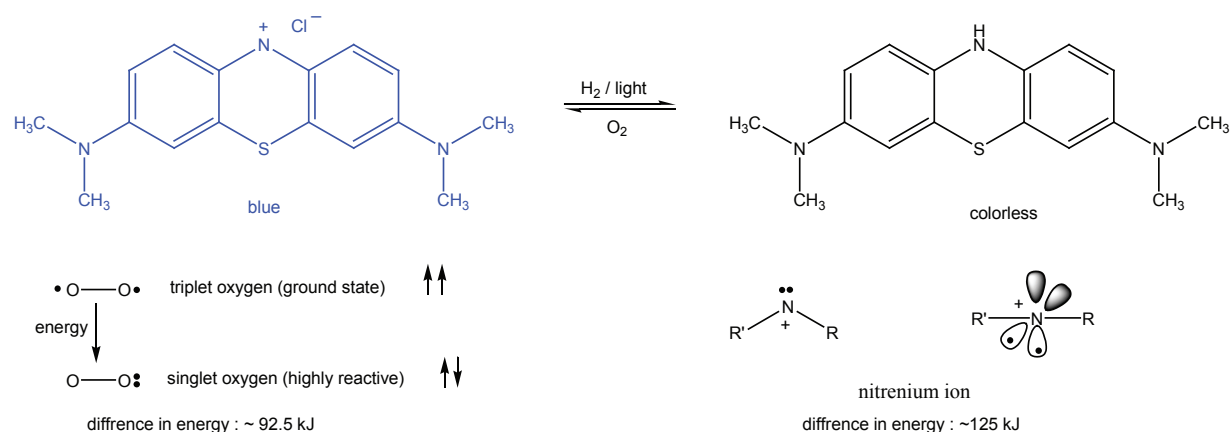


FIGURE 2. Carbene/TCNE Condensation Process and Crystal Structure of the Product



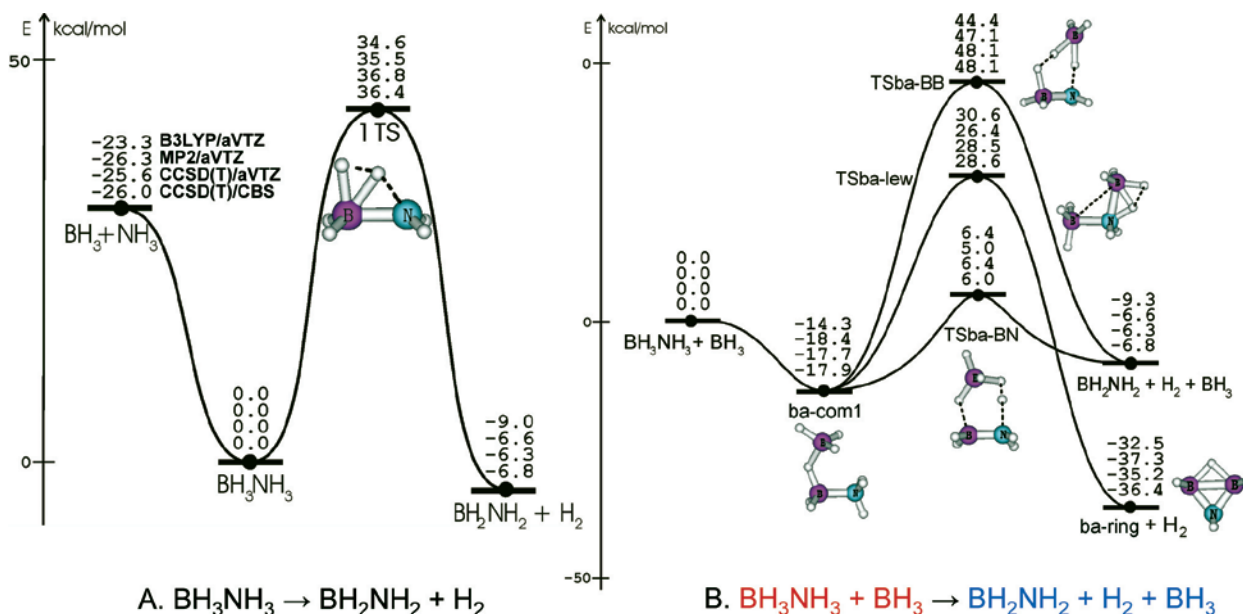
**FIGURE 3.** Non-Metal Catalyst for  $\text{H}_2$  Fixation and Release that is Photoactivated

transferred from the reduced dye to a hydrogen storage substrate to release heat (corresponding to the original light energy absorbed by the dye) and liberate the original dye molecule in its ground state to re-enter the catalytic cycle.

Computational advances include: (1) first set of accurate thermodynamics for  $\text{B}_x\text{N}_x\text{H}_y$  compounds up to  $x = 3$  and  $y = 14$  for release and regeneration of AB in the gas and condensed phases (Table 1). This work includes rings and chains which are critical intermediates in the release of hydrogen; (2) accurate bond energies for AB and related isoelectronic systems which show the strength of the B-N  $\sigma$ -bond in  $\text{BH}_2\text{NH}_2$  and its importance in driving the overall energetics; (3) studies of the mechanism for  $\text{H}_2$  release from AB which identify the potential role of  $\text{BH}_3$  as a Lewis acid catalyst (Figure 4) as well as the role of strong Brønsted and Lewis acids in a cationic chain polymerization mechanism for release of  $\text{H}_2$ ; (4) predicted the first reliable thermodynamic properties of  $\text{B}_3\text{H}_7\text{NH}_3$  and its decomposition mechanism as well as studies of the mechanism of  $\text{H}_2$  release from AB dimer  $(\text{BH}_3\text{NH}_3)_2$  and from its zwitterionic isomer  $[\text{NH}_3\text{BH}_2\text{NH}_3^+][\text{BH}_4^-]$  which show the importance of seeding; (5) continue our reliable, extensive predictions of the energetics for a wide range of regeneration reactions; and (6) continue our extensive studies of carbene, cyanocarbon, and heteroatom diradical chemistry including prediction of the energetics of phosphorus substituted diradicals.

**TABLE 1.** Thermodynamic Properties of BN Compounds in Different Phases at 298 K from CCSD(T)/CBS (complete basis set) Calculations and Experiment

| Compound                            | Phase  | $\Delta H_f^\circ$ 298 K<br>kcal/mol | $S^\circ$ 298 K<br>cal/mol-K | Source  |
|-------------------------------------|--------|--------------------------------------|------------------------------|---|
| $\text{BH}_3\text{NH}_3$            | gas    | $-13.5 \pm 1.0$                      | 57.1                         | Calc  |
|                                     | solid  | $-36.6 \pm 2.4$                      | 23.0                         | Expt  |
| $\text{B}_3\text{N}_3\text{H}_{12}$ | gas    | $-96.6 \pm 1.0$                      | 79.3                         | Calc  |
|                                     | solid  | $-120.5 \pm 4$                       | 21.0                         | $\Delta H_f^\circ$ from calc<br>$\Delta H_f^\circ$ gas +<br>expt $\Delta H_{\text{sub}}$<br>$S^\circ$ from expt |
| $\text{B}_3\text{N}_3\text{H}_6$    | gas    | $-121.9 \pm 3$                       |                              | Expt  |
|                                     | liquid | $-129.0 \pm 3$                       | 47.7                         | Expt  |
| $\text{B}_3\text{N}_3\text{H}_6$    | gas    | $-115.5 \pm 1.0$                     | 68.7                         | Calc  |
|                                     | liquid | $-122.6 \pm 1.1$                     |                              | Calc + Expt   |
|                                     | solid  | $-123.6 \pm 1.6$                     |                              | Calc + Expt   |



**FIGURE 4.** Calculated reaction pathways for  $\text{H}_2$  release from  $\text{BH}_3\text{NH}_3$ . Energies in kcal/mol. (A) Reaction path for  $\text{BH}_3\text{NH}_3 \rightarrow \text{BH}_2\text{NH}_2 + \text{H}_2$ . B-N bond cleavage is energetically more favored over the unimolecular  $\text{H}_2$  release from AB. (B) Different reaction paths for  $\text{BH}_3\text{NH}_3 + \text{BH}_3 \rightarrow \text{BH}_2\text{NH}_2 + \text{H}_2 + \text{BH}_3$ .  $\text{BH}_3$  generated by breaking the B-N bond in AB can serve as a Lewis acid catalyst for  $\text{H}_2$  elimination from  $\text{BH}_3\text{NH}_3$ .

## Conclusions and Future Directions

We have made substantial progress in the development of new chemistries and computational approaches to meet DOE needs for chemical hydrogen storage. We have developed new models for improving weight percent beyond 1:1 stoichiometry to enable us to meet DOE 2015 goals; shown convergence in the carbene and cyanocarbon approaches; designed a new photoactivated catalyst for  $\text{H}_2$  fixation; developed computational thermodynamic and kinetic approaches to meet temperature and pressure requirements as well as stability requirements; used these computational approaches to design new storage systems and design new regeneration mechanisms; and discovered new mechanism for  $\text{H}_2$  release and the potential role of Lewis acid catalysts.

Our experimental chemistry goals include:

- Synthesize extended carbene polymers (10.3 wt%, oligomer of TCNE [ $\text{C}_2\text{N}_2\text{H}_6$ ]).
- Synthesis: lower substituent wt% for carbenes.
- Non-metal catalyst for  $\text{H}_2$  release for carbenes and TCNE. We are presently scouting other dyes like methyl violet and methyl blue to see what classes of dyes will exhibit this chemistry and which ones can function as hydrogen transfer agents to some ultimate hydrogen storage medium.
- Synthesize extended oligocarbene polymers from carbene chemistry.
- Continue catalyst design and development for  $\text{H}_2$  release for carbenes.

Our computational chemistry goals include:

- Continue to support overall CHSCoE efforts in  $\text{H}_2$  release, AB regeneration, and new concepts including alternative inorganic and organic compounds and mechanisms. We will use density functional theory benchmarked by accurate molecular orbital theory methods to calculate thermodynamics and kinetics and to develop reaction mechanisms.
- Study the hydrogenation of TCNE. Which sites are hydrogenated in what order? How does hydrogenation of the polycarbene occur?
- Model release of  $\text{H}_2$  from silanes for modeling nanocluster chemistry for regeneration.
- Computational design of new catalysts including acid/base catalysts (Lewis acidities, hydride affinities, proton affinities) and transition metals for release and regeneration.
- For B-H regeneration, predict energetics and kinetics of key steps (examples: digestion, reduction, etc.) to optimize experimental approach.
- Predict spectroscopic properties for use in analyzing experimental data.
- Develop improved reaction mechanisms based on predictions of reaction kinetics to optimize processes.
- Study ammonia borane/ammonia trisborane reactions – AB polymers from anionic polymerization.

## Special Recognitions & Awards/Patents Issued

1. D.A. Dixon presented the 20<sup>th</sup> Annual Charles A. Coulson Lecture at the University of Georgia, April, 27, 2007.

## FY 2007 Publications/Presentations

1. “The lowest energy states of the Group IIIA – Group VA heteronuclear diatomics: BN, BP, AlN, and AlP from Full Configuration Interaction Calculations,” Z. Gan, D. J. Grant, R. J. Harrison, and D. A. Dixon, *J. Chem. Phys.* 2006, **125**, 124311 (6 pages).
2. “The Heats of Formation of Diazene, Hydrazine,  $N_2H_3^+$ ,  $N_2H_5^+$ ,  $N_2H$ , and  $N_2H_3$  and the Methyl Derivatives,  $CH_3NNH$ ,  $CH_3NNCH_3$ , and  $CH_3HNNHCH_3$ ,” M. H. Matus, A. J. Arduengo, III, and D. A. Dixon, *J. Phys. Chem. A*, **2006**, *110*, 10116.
3. “Oxidation of 2,4-Diphosphacyclobutane-1,4-diyl with Ammoniumyl Antimonate and EPR Study of the Corresponding Cation Radical,” M. Kikuchi, M. Yoshifuji, A.J. Arduengo, III, T. A. Konovalova, L. Kispert, and S. Ito, *Chem. Lett.* **2006**, *35(10)*, 1136.
4. “Acid Initiation of Ammonia-Borane Dehydrogenation for Hydrogen Storage” F. H. Stephens, R. T. Baker, M. H. Matus, D. J. Grant, and D. A. Dixon, *Angew Chem. Int. Ed.*, **2007**, *46*, 746 (Cover and VIP article).
5. “ $\sigma$ - and  $\pi$ -Bond strengths in Main Group 3-5 Compounds,” D. Grant and D. A. Dixon, *J. Phys. Chem. A*, **2006**, *110*, 12955.
6. “Theoretical Prediction of the Heats of Formation of  $C_2H_5O$  Radicals Derived from Ethanol and of the Kinetics of  $\beta$ -C–C Scission in the Ethoxy Radical,” M. H. Matus, M. T. Nguyen, and D. A. Dixon, *J. Phys. Chem. A*, **2007**, *111*, 113.
7. “The Molecular Mechanism for  $H_2$  Release from Amine Borane,  $BH_3NH_3$ , Including the Catalytic Role of the Lewis Acid  $BH_3$ ,” M. T. Nguyen, V. S. Nguyen, M. H. Matus, G. Gopakumar, D. A. Dixon, *J. Phys. Chem. A*, **2007**, *111*, 679.
8. “Heats of Formation of Diphosphine, Phosphinophosphinidene, Diphosphine and their Methyl Derivatives, and Mechanism of the Borane-Assisted Hydrogen Release,” Myrna H. Matus, Minh Tho Nguyen, and David A. Dixon, *J. Phys. Chem. A*, **2007**, *111*, 1726.
9. “Reliable Predictions of the Thermochemistry of Boron-Nitrogen Hydrogen Storage Compounds:  $B_xN_xH_y$ ,  $x = 2, 3$ ,” M. H. Matus, K. D. Anderson, D. M. Camaioni, S. T. Autrey, and D. A. Dixon, *J. Phys. Chem. A*, **2007**, *111*, 4411.
10. “Ammonia Triborane: Theoretical Study of the Mechanism of Hydrogen Release,” V. S. Nguyen, M. H. Matus, M. T. Nguyen, and D. A. Dixon, *J. Phys. Chem. A*, WEB ASAP, June, 2007.
11. “Computational Study of the Release of  $H_2$  from Ammonia Borane Dimer  $(BH_3NH_3)_2$  and Its Ion Pair Isomers,” V. S. Nguyen, M. H. Matus, D. J. Grant, M. T. Nguyen, and D. A. Dixon, *J. Phys. Chem. A*, accepted for publication, June 2007.
12. D.A. Dixon, Invited Lecture, *High level computational approaches to the prediction of the thermodynamics of chemical hydrogen storage systems*, Theory Focus Session on Hydrogen Storage Materials, U.S. DOE H2 Review Meeting, Crystal City, VA, May 2006.
13. A. J. Arduengo, *Novel Architectures Involving Imidazol-2-ylidenes: Structure and Chemistry*, Chemistry Department, University of Zurich, Switzerland, November 2007.
14. A. J. Arduengo, *Novel Architectures Involving Imidazol-2-ylidenes: Structure and Chemistry*, Chemistry Department, University of Bonn, Germany, November 2007.
15. A. J. Arduengo, *Novel Architectures Involving Imidazol-2-ylidenes: Structure and Chemistry*, Chemistry Department, Technical University of Braunschweig, Germany, December 2007.
16. D.A. Dixon, Invited Lecture, *Recent Advances in Computational Inorganic Chemistry*, Loker Hydrocarbon Research Institute and Department of Chemistry Symposium Honoring Professor Karl O. Christe on the Occasion of his 70<sup>th</sup> Birthday, University of Southern California, Los Angeles, CA, January 2007.
17. D.A. Dixon, Invited Lecture, *Recent Advances in Computational Inorganic Chemistry*, Chemical Engineering Department, Mississippi State, Starksville, MS, January 2007.
18. D.A. Dixon, Invited Lecture: *Recent Advances in Computational Inorganic Chemistry*, Physical Chemistry Division, Chemistry Department, University of Maryland, College Park, MD, February 2007.
19. D.A. Dixon, Invited Lecture: *Recent Advances in Computational Inorganic Chemistry*, Inorganic Division, Chemistry Department, Florida State University, Tallahassee, FL, March 2007.
20. D.A. Dixon, *Recent Advances in Computational Inorganic Chemistry*, 20<sup>th</sup> Annual Charles A. Coulson Lecture at the University of Georgia, April, 27, 2007, Athens, GA.
21. Myrna H. Matus, Kevin D. Anderson, and David A. Dixon, Donald M. Camaioni and S. Thomas Autrey, Poster, *Computational Studies on Boron-Nitrogen Compounds and Methylated Derivatives For Chemical Hydrogen Storage*, 36<sup>th</sup> Annual Conference of the Southeast Theoretical Chemists’ Association, May 18 and 19, 2007, Virginia Tech, Blacksburg, VA.
22. Minh Tho Nguyen Myrna H. Matus, Vinh Son Nguyen, and David A. Dixon, Talk, *Molecular Mechanism of Hydrogen Release Reactions from Boron-Nitrogen Compounds*, 36<sup>th</sup> Annual Conference of the Southeast Theoretical Chemists’ Association, May 18 and 19, 2007, Virginia Tech, Blacksburg, VA.