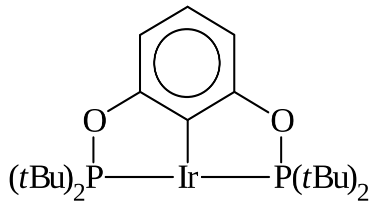
Written Qualifying Examination – Inorganic Chemistry I

July 18. 2011

Questions related to B. L. Dietrich, K I. Goldberg*, D. M. Heinekey*, T. Autrey, and J. C. Linehan, *Inorg. Chem.*, **2008**, *47*, 8583.

This paper discusses the dehydrogenation of substituted amine boranes catalyzed by an iridium pincer complex, referred to as Catalyst **1**, whose structure is shown below.



1

The general equation for the dehydrogenation reactions is given as

$$n\, RNH_2BH_3 \xrightarrow{\text{catalyst } \mathbf{1}} [RNHBH_2]_n + n\, H_2 \qquad R = H, Me$$

Questions Related to the Assigned Paper (10 points)

1. (2 points) In the introductory paragraph, the authors state that ammonia borane (NH_3BH_3, AB) and related amine boranes have emerged as attractive candidates for hydrogen storage materials. What is attractive about these compounds for this use? Relative to hydrogen storage, what performance characteristics are needed to make these a practical choice for this application?

2. (2 points) As described in this paper, the authors previously found that catalyst **1** facilitates the rapid dehydrogenation of AB, yielding one equivalent of H_2. What specific byproduct was formed in this reaction? How was this product characterized? What characteristic of this byproduct makes the dehydrogenation reaction of AB, as catalyzed by **1**, unsuitable for hydrogen storage applications, and why is this so?

3. (4 points) The primary focus of this paper is on the dehydrogenation reaction of $CH_3NH_2BH_3$ (MeAB) and MeAB/AB mixtures. Describe in detail how the kinetics and stoichiometry of the dehydrogenation of MeAB and MeAB/AB mixtures catalyzed by **1** compare to each other and to what was previous found for AB alone. How were the byproducts of the MeAB and MeAB/AB reactions characterized, and what conclusions are presented about their formulas and structures? What results are found when the AB:MeAB ratio exceeds 1:1, and what conclusions can be drawn from this about the structures of the byproducts formed?

4. (2 points) Using differential scanning calorimetry, the authors determined the enthalpy (ΔH) of the dehydration reactions of AB, MeAB, and 1:1 MeAB/AB in THF at 303 K with 2.5 mol % **1**. All had similar entahlpies, $\Delta H \approx -6.7$ kcal/mol = –28 kJ/mol. What do these results imply about the ability to use these dehydrogenation reactions in practical hydrogen storage applications?

Green Chemistry Question (2 points)

Consider the dehydrogenation equation (see above) for AB and MeAB, as described in this paper. In terms of Green Chemistry principles, what are positive aspects of these reactions and what are the less ideal aspects, particularly as they pertain to the intended use of hydrogen storage? What improvements need to be made to make these reactions a basis for practical hydrogen storage? Hypothetically, what would make an ideal "green" reaction to be the basis for a chemical hydrogen storage system?