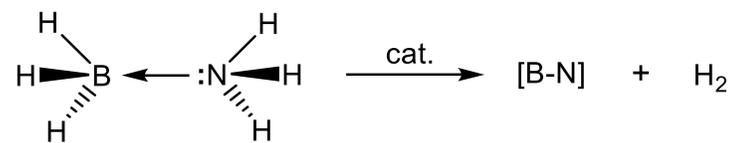


H₂ Release from Amino-Boranes by Diiron Hydrogenase Active Site Model Compounds

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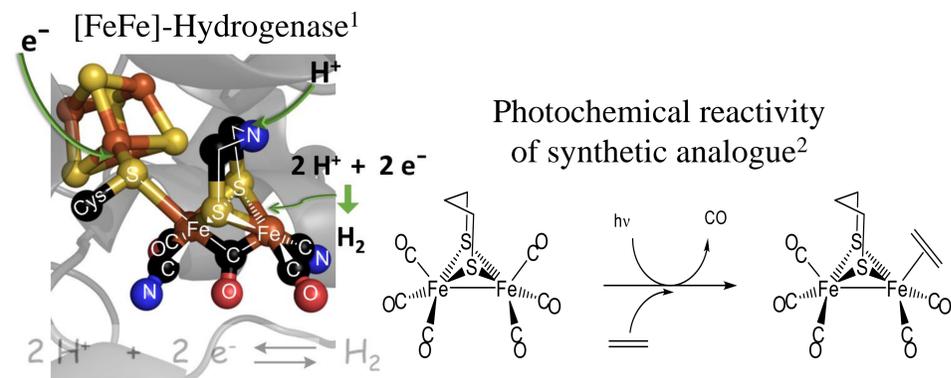
Introduction



Catalysts: Rh, noble metals

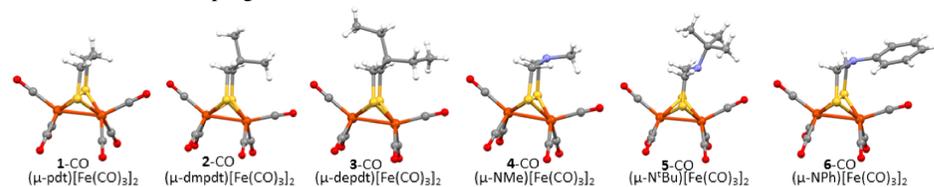
- **Goal:** Base metal, molecular catalysts

- **Inspiration:** An enzyme active site that performs H₂ chemistry and synthetic analogues known to coordinate weakly binding substrates



Gaining interest for their H₂-storage capabilities as well as chemical utility as hydroboration reagents, the controlled release of H₂ from amino boranes requires catalysts, many of which are based on precious metals³. Due to its similarity to a natural diiron catalyst for reversible H₂ production/hydrogen oxidation reactions performed by hydrogenases the synthetic analogue has been extensively characterized and studied. Photolysis-induced CO loss and solvent capture followed by substrate binding has established the propensity of this diiron unit to scavenge and bind substrates such as olefins and alkynes. The (μ-SRS)[Fe(CO)₃]₂ organometallic unit is well formulated for the binding of substrates including hydrides and H₂ which are both involved in the dehydrogenation mechanism of previously characterized catalysts which focused on the dehydrogenation of amine boranes.

Such complexes were shown to be photocatalysts for H₂ release from the secondary amino-borane H₃B←NMe₂H. A mechanistic study focuses on the reactivity of the initial species formed upon photolysis of the diiron complexes below in the presence of the tertiary amino-borane H₃B←NEt₃, an adduct that does not release H₂, is also presented. A prominent feature of the selection of diiron complexes is the potential for a pendant base effect on the progress of the reaction.



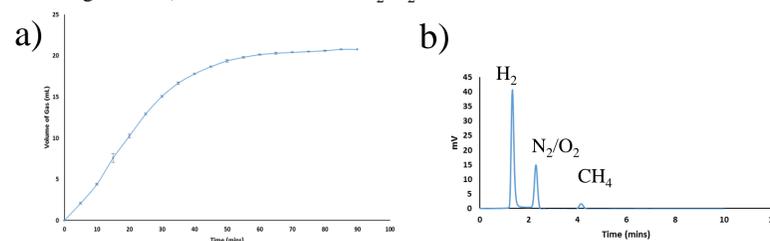
Experimental Conditions for H₂ Production

- Conditions:
- UV (Hg-arc) lamp
 - H₃B←NMe₂H in THF
 - 10 mol % catalyst
 - H₂ gas collected and identified by GC

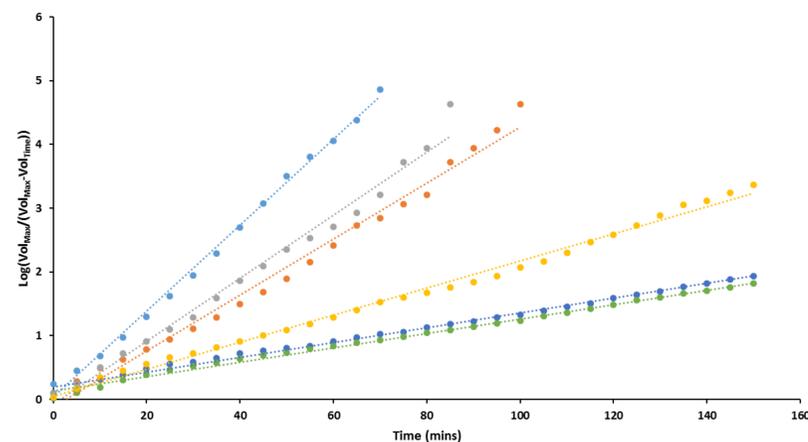
Controls: No H₂ release for a) no catalyst; b) the H₃B←NEt₃ c) dark; d) no H₃B←NMe₂H

Results for H₂ Production

a) Reaction profile of gas evolved from photolysis of 1-CO in the presence of H₃B←NHMe₂ dissolved in THF; gas measurements taken every 5 minutes. b) chromatogram from a catalytic run with 1-CO catalyst. Note: CO gas (from degradation) buried underneath N₂/O₂.



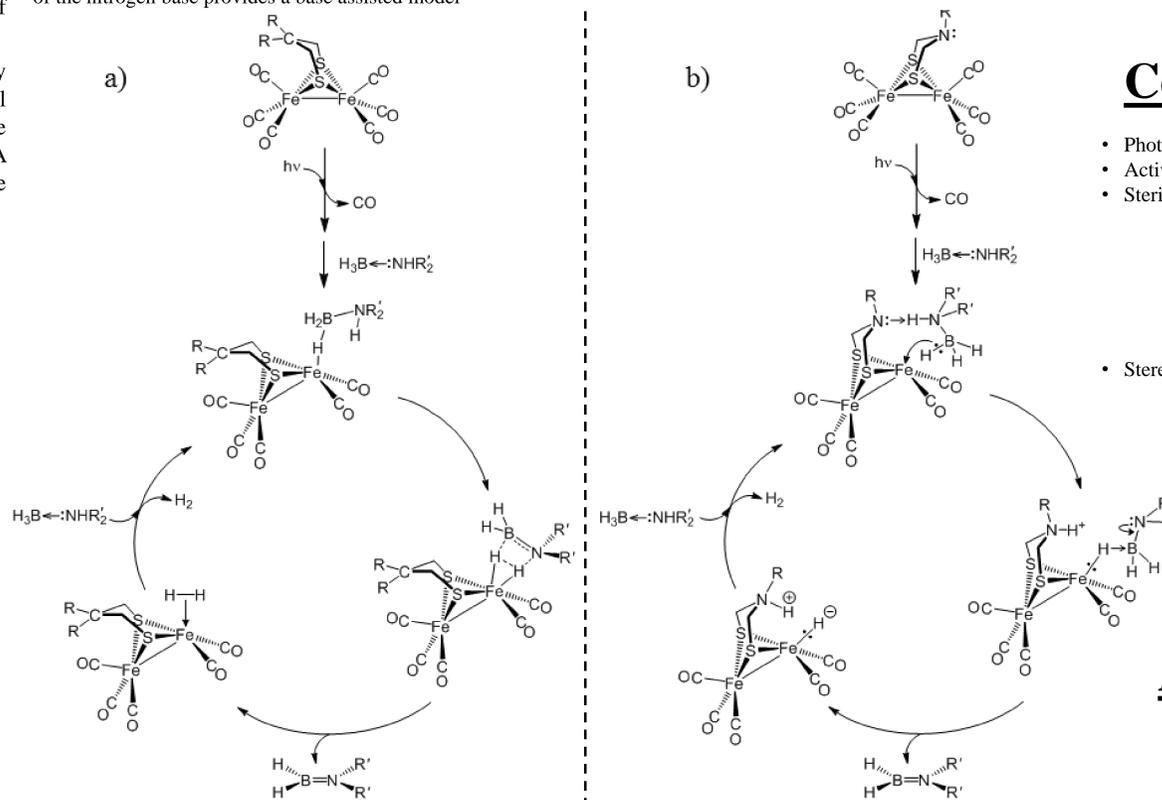
Plotting $\ln \frac{V_{Max}}{V_{Max}-V_{Time}}$ vs. time reveals the reaction is first order and allows a direct comparison of H₂ production rates of the six complexes via the slope of the fitted line.



Relative Ranking of Catalytic Efficiency

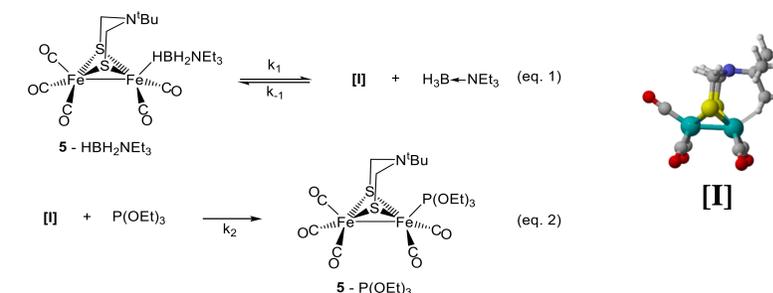
1-CO > 6-CO > 4-CO > 5-CO > 2-CO ≈ 3-CO

Minimal Mechanisms for Dehydrogenation of Aminoborane by a) C-Bridgehead and b) N-Bridgehead Diiron Complexes. Presence of the nitrogen base provides a base assisted model

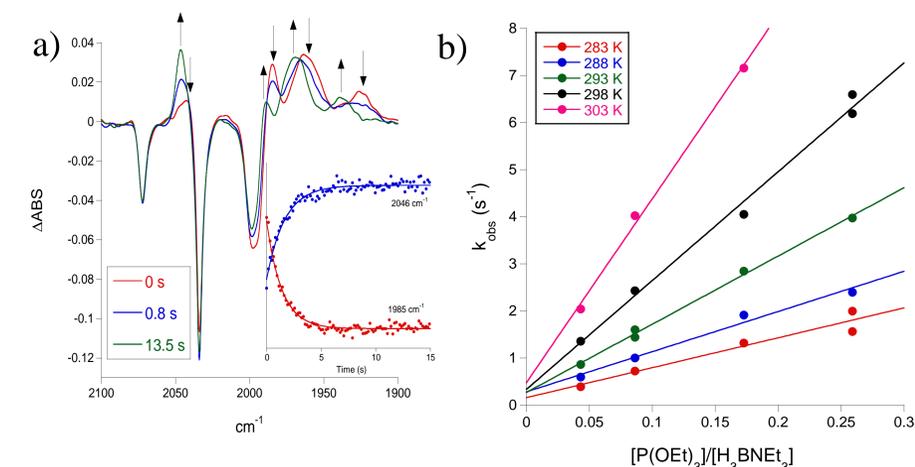


Adduct Binding Ability: Kinetic Study

A comparative kinetic study investigated the binding strength of H₃B←NEt₃, BA, unit through the B-H bond σ-interaction with the hv-generated open site on the #CO catalyst to the diiron catalysts. The intermediate [I] undergoes BA/P(OEt)₃ displacement via a dissociative mechanism, the E_{act} of which represents the strength of the Fe-σ(H-B) interaction.



a) Spectral changes observed upon photolysis of 1-CO in the presence of H₃B-NEt₃ and P(OEt)₃ at 283 K. Peaks due to 1-HBH₂NEt₃ and 1-P(OEt)₃ decay and grow, respectively, at the same rate as shown in the scatter plot inset. Bb) A plot of the k_{obs} versus [P(OEt)₃]/[H₃B-NEt₃] at several temperatures



Conclusions

- Photochemical induction of CO loss produces catalysts for H₂ release from amine-borane.
- Activation parameters confirm dissociative mechanism for kinetic study
- Steric constraint in bridgehead serves to
 - a) Stabilize intermediate I, the (μ-SRS)Fe₂(CO)₅ species, via an agostic interaction between bridgehead and open site which increases rate of BA adduct displacement and P(OEt)₃ addition.
 - b) Discourages formation of H-B σ interaction resulting in lower rates of H₂ release.
- Steric importance of substrate binding/residence time for activation.

References

- 1) Lubitz, W. *Chem. Rev.* **2014**, *114*, 4081–4148
- 2) Muhammad, S.; et al. *Inorg. Chem.* **2012**, *51*, 7362–7369.
- 3) Douglas, T. M. et al. *J. Am. Chem. Soc.* **2009**, *131*, 15440–15456.

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