UNH Chemistry 775: Synthesis of a Nickel Electrocatalyst for H_2 Production

Eric Guinto, Christian Tooley, and Dr. Roy Planalp
eav66@unh.edu, Parsons Hall, 23 Academic Way, Durham NH 03824

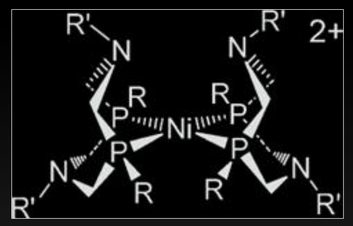
INTRODUCTION

Hydrogen production is a sector of industrial methods for generating dihydrogen which can be used for:

- Fuel cells,
- Clean energy
- Producing ammonia

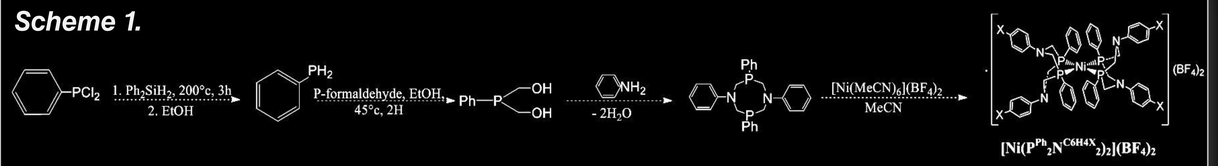
Currently, hydrogen production is dominated by steam reforming hydrocarbons. Hydrogen production is estimated to be a 100 billion dollar industry;[1] however its cost effectiveness decreases dramatically since it is produced by consumption of fossil fuels. The nickel catalyst in figure 1 is a metal catalyst that utilizes pendant bases (N-R') in the second coordination sphere to act as a proton relay to the metal center.

Figure 1.



By addition of water to an acidic solution containing the nickel catalyst, dihydrogen can be evolved and potentially captured. Because of the nature of a catalyst, it can be reused as long as it does not become oxidized. Scheme 1 illustrates the procedure and progress towards synthesis of this nickel catalyst.

Scheme 1.



RESULTS AND DISCUSSION

Reduction of compound (1) was initially approached with a procedure utilizing lithium aluminum hydride which formed a bulk salt in the reaction flask. This method required an extensive workup to attempt to retrieve phenyl phosphine (2). By adding .1M sodium hydroxide, the salt was dissolved however (2) was isolated in an insignificant yield.

The procedure in **scheme 1** was implemented and features a facile substitution reaction. This reaction required no workup and the phenyl phosphine was sparged with N_2 from solution and trapped in a nitrogen cooled flask using the apparatus from **figure 2**. Qualitative determination of this product was made by visual inspection of a clear solution.

Subsequent reaction with para-formaldehyde in ethanol yielded a red solid compound (3). This compound is also extremely sensitive to oxidation and was found to be characteristic of the product described by Kilgore and coworkers.

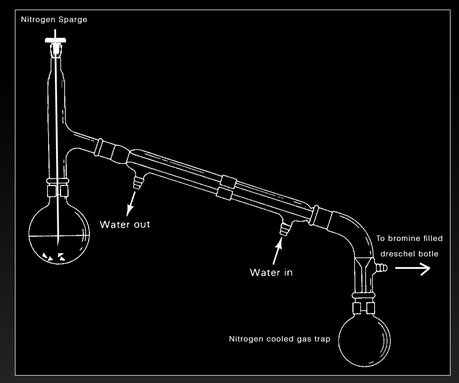
EXPERIMENTAL

*Synthesis of **1** and **2** located in **scheme 1** were carried out using standard schlenk techniques.*

Synthetic Methods:

- Dreschel tube filled with bromine water to neutralize toxic phosphine gas.
- Liquid nitrogen gas trap to condense phenyl phosphine 2.
- Sparging w/ nitrogen to evolve phenyl phosphine from solution.

Figure 2.



Standard Dreschel bottle

FUTURE WORK

- To synthesize $[Ni(MeCN)_6](BF_4)_2$ for reaction with **4.**
- Characterize complex **5** via Xray diffraction.
- Detect dihydrogen after addition of water via gas chromatography.

CONCLUSIONS

Phosphorous chemistry is extremely sensitive to oxidation and requires the use of rigorous schlenk techniques preferably carried out within a glovebox. Phenylphosphine 2 and compound 3 were suspected to be synthesized by visual examinations; however due to the air sensitivity, further characterizations were not completed.

ACKOWLEDGEMENTS

I would like to thank Christian Tooley and Dr. Roy Planalp for their guidance as well as the Department of Chemistry, and UNH for funding this project.

REFERENCES

1) Barlow, Zeke. Breakthrough in hydrogen fuel production could revolutionize alternative energy market. *Virginia Tech News*. Virginia Tech.
2) Kilgore, U. J., et al. (2011). "[Ni(PPh2NC6H4X2)2]2+ Complexes as Electrocatalysts for H2 Production: Effect of Substituents, Acids, and Water on Catalytic Rates." Journal of the American Chemical Society **133**(15): 5861-5872.
3) Silver, S. C., et al. (2013). "Protein Delivery of a Ni Catalyst to Photosystem I for Light-Driven Hydrogen Production." Journal of the American Chemical Society **135**(36): 13246-13249.
4) Hathaway, B. J.; Holah, D. G.; Postlethwaite, J. D., 630. The preparation and properties of some tetrakis(methylcyanide)copper(I) complexes. Journal of the Chemical Society (Resumed) 1961, (0), 3215-3218.