

New Strategies Towards Photochemical Nitrogen Fixation

Afrah Faraz, Tamara Jurado, Alexander Miller

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC USA



THE UNIVERSITY
of NORTH CAROLINA
at CHAPEL HILL

Abstract

Nitrogen Fixation is the chemical process in which molecular dinitrogen (N_2) is reduced to ammonia (NH_3). Over the past century, the catalytic synthesis of ammonia has been implemented in industry through the Haber-Bosch process. The Haber-Bosch process relies on fossil fuels and contributes significantly to global carbon dioxide emissions. The Miller lab at UNC Chapel Hill has widely explored more sustainable alternatives to the Haber-Bosch process with transition metal-dinitrogen complexes as catalysts for the reaction. This project aims to produce ammonia from a photochemical approach, using light to drive nitrogen fixation. The synthesis of N_2 reducing catalysts and photocatalysts will be presented along with N_2 reduction reactivity studies. The research offers opportunities to gain insight into photochemical pathways for ammonia synthesis.

Background

The conversion of N_2 to NH_3 is a significant biological process yet it is difficult to accomplish in industry. This is due to the inert nature of N_2 from its stable, non-polar triple bond and the large energy gap between its molecular orbitals. Nitrogen fixation has been industrialized through the Haber-Bosch process.

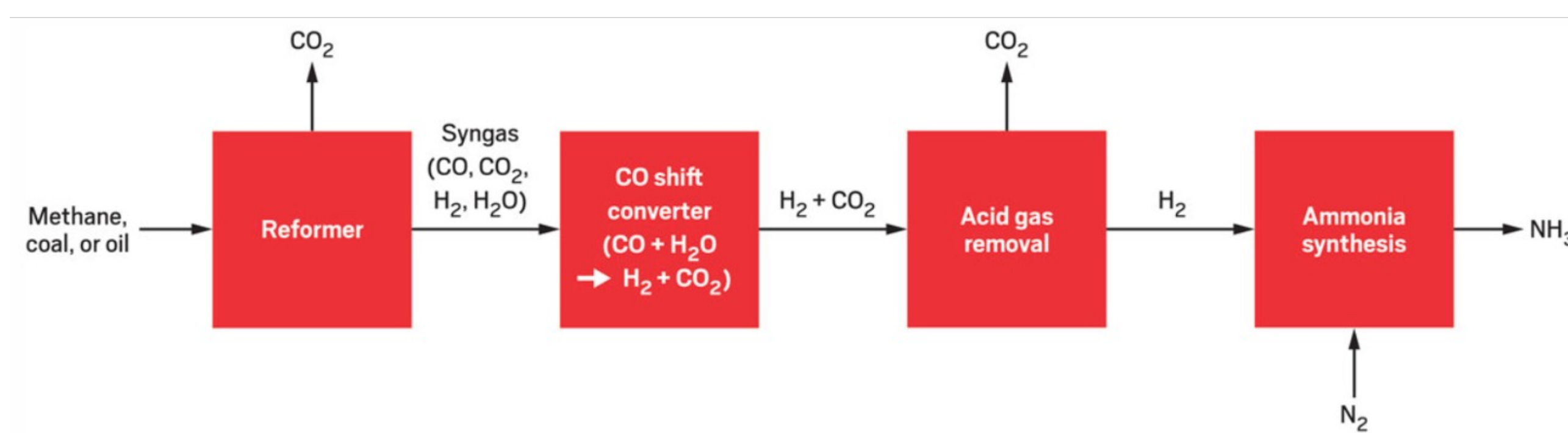


Figure 1: Industrial scheme for ammonia synthesis via the Haber-Bosch process.¹

The Haber-Bosch process requires high temperatures and pressures, fossil fuels, and results in 1.5% of global CO_2 emissions. This process is not sustainable and motivates research towards more sustainable pathways.

One alternative pathway involves the catalytic conversion of N_2 to NH_3 with transition metal-dinitrogen complexes. The first successful catalyst (Schrock catalyst) was designed by Yandulov and Schrock.²

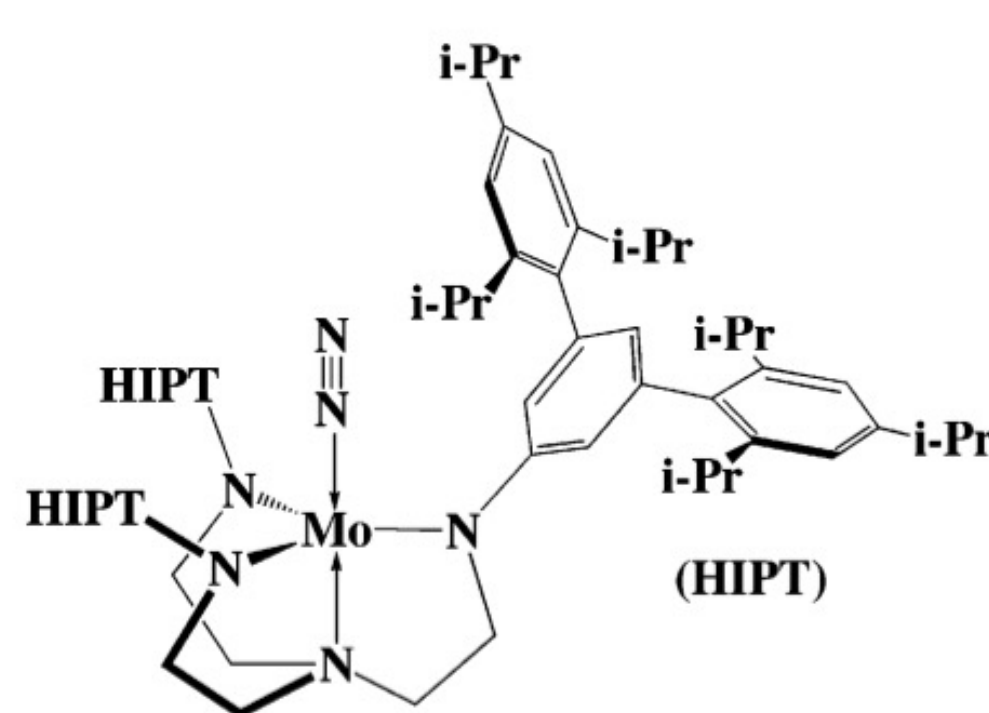


Figure 2: Schrock catalyst for ammonia production.

Methodology

The pathway of interest of ammonia production from a metal-dinitrogen complex involves the stepwise reduction of dinitrogen and removal of ammonia as product. This mechanism is referred to as a distal pathway and can be accomplished with a variety of Hydrogen and electron sources as shown:

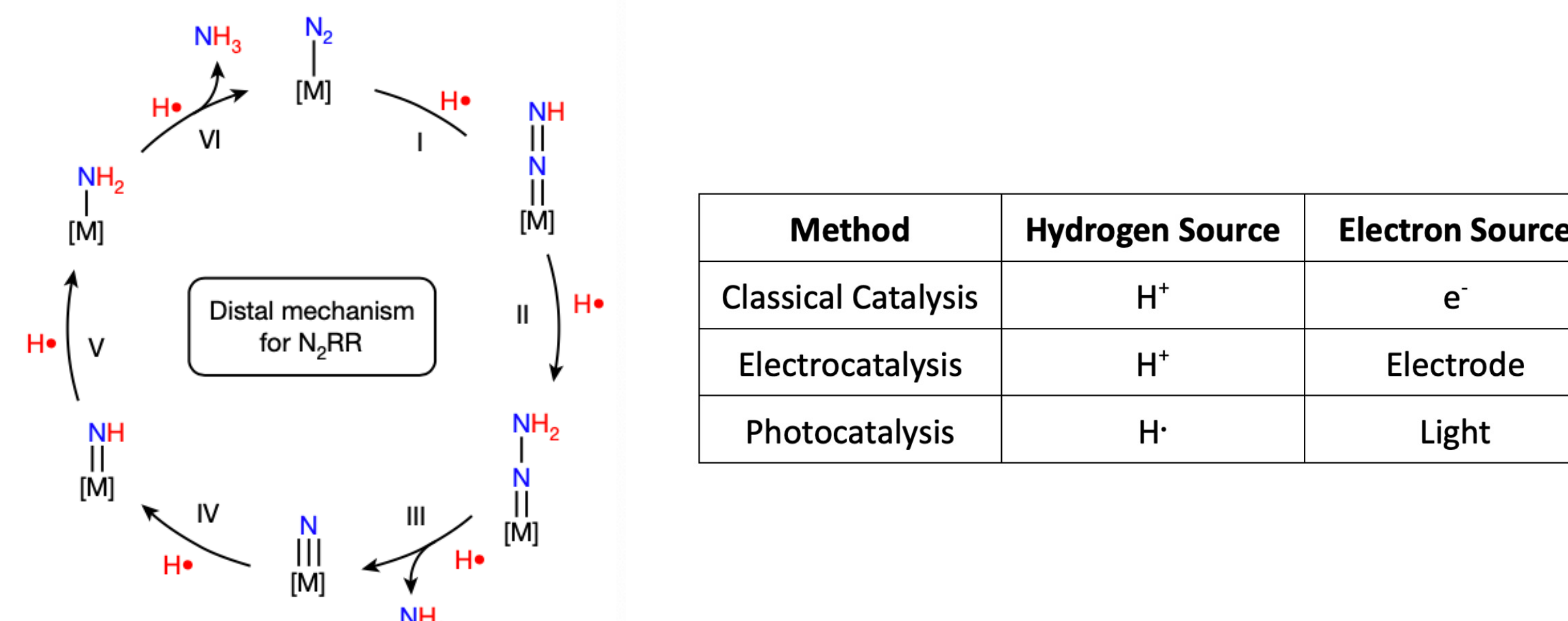


Figure 3: catalytic cycle of mechanism for N_2RR production and potential types of catalysis for pathway.³

This project aims to follow a photocatalytic approach. In order to perform the catalytic process, transition metal complexes are required. The complexes of interest for this project are shown below:

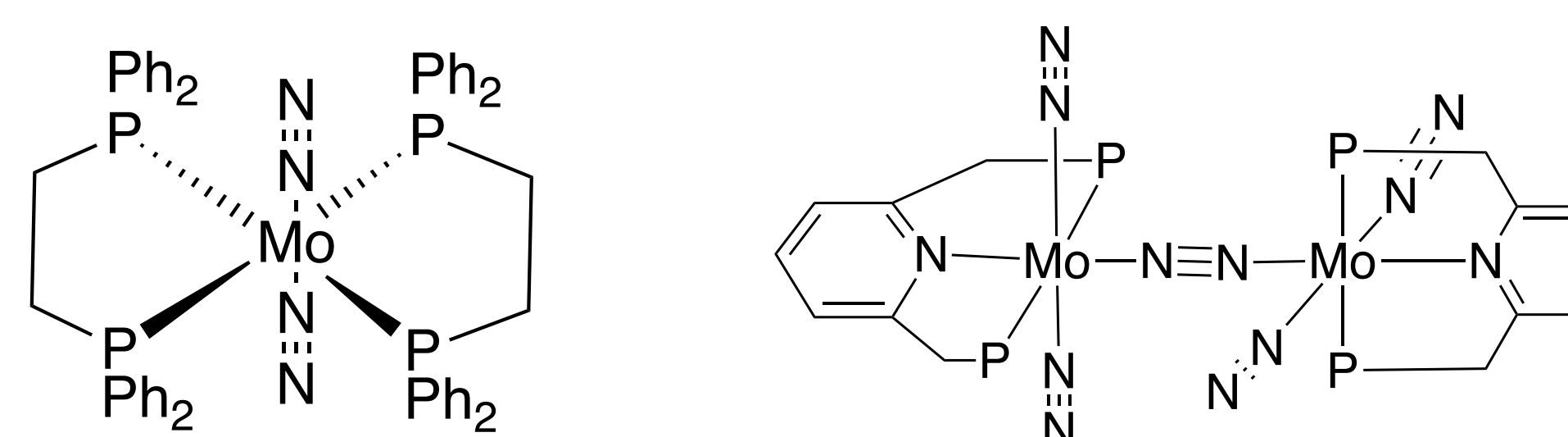


Figure 4: Molybdenum-dinitrogen complexes of interest. On the left is a complex with 1,2-Bis(diphenylphosphino)ethane (dppe) ligands. The complex on the right is a dimolybdenum bridged complex bearing PNP pincer type ligands.

These are known complexes with prior success in ammonia production in the presence of acid. The syntheses of the complexes are as follows^{3,4}:

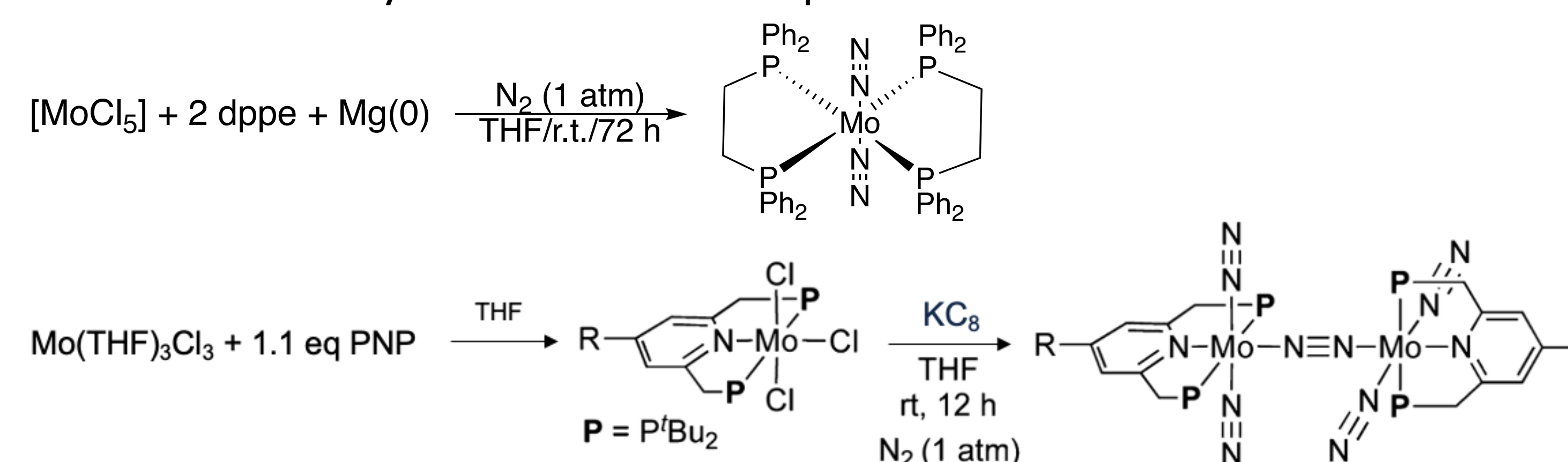


Figure 5: Reported syntheses of complexes of interest

Experimental

The reported syntheses of the complexes of interest use either activated $Mg(0)$ or KC_8 as the reducing agents. Most of the project to date has focused on an optimal synthesis of the complexes using a variety of reducing agents including Mg activated by different methods, $Na(s)$, and KC_8 . Among all the synthetic attempts, $Mg(0)$ activated through HCl and rinsed with alcohol has had the most promising results as shown through ^{31}P -NMR spectroscopy.

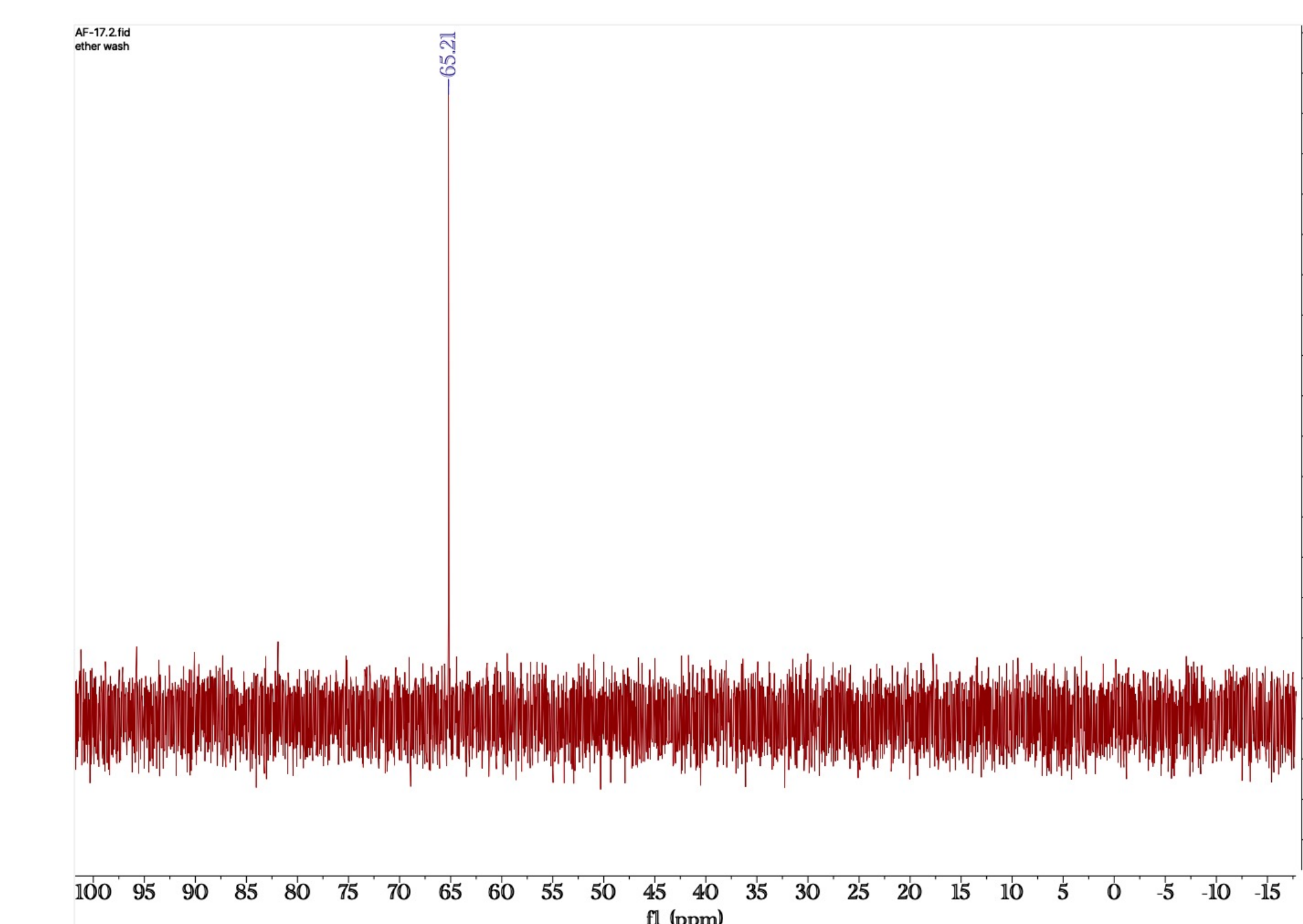


Figure 6: ^{31}P -NMR spectrum of $trans-[Mo(N_2)_2(dppe)_2]$ with $Mg(0)$ as the reductant. Complex peak at 65 ppm.

Future Directions

Currently, synthesis of the complexes of interest is in progress. Once the complexes are synthesized in a large scale and characterized, photochemical N_2 reduction will be explored.

References and Acknowledgements

1. C&EN, **2019**, 97, 24
2. Science, **2003**, 301, 76-78
3. Nature, **2022**, 609, 71-76
4. Nature, **2011**, 3, 120-125
5. Chemical Reviews, **78**, 6, **1978**, 593
6. J. Am. Chem. Soc. **2021**, 143, 21388-21401

I would like to thank the Miller lab for helping me throughout the year and allowing for this project to be possible. Additionally, the continuation of this project through the summer will be supported by the SURF grant through the office of undergraduate research.