

# A Review of Schrock's Abiological Nitrogen Fixation Cycle

Steven Labalme

Department of Chemistry, University of Chicago

CHEM 20200: Inorganic Chemistry II

Dr. John Anderson

26 May 2021

Nitrogen must be fixed in order to be biologically useful, and nature does not fix enough nitrogen on its own to sustain the current human population. Thus, in order to fertilize humanity's food, the Haber-Bosch process is employed to artificially fix nitrogen. However, since it is only one (albeit extremely effective) process, there is great interest in understanding other potential methods of nitrogen fixation. The first big step came when researchers synthesized some of the first abiotic transition metal dinitrogen complexes, loosely modeling them after nitrogenase enzymes<sup>[1][2]</sup>. From there, potential catalytic intermediates were characterized, but a complete catalytic reaction remained elusive. However, Yandulov and Schrock outline in *Catalytic Reduction of Dinitrogen to Ammonia at a Single Molybdenum Center* their discovery<sup>[3]</sup> of the first catalytic system with observable intermediates analogous to those proposed by Chatt<sup>[4]</sup>.

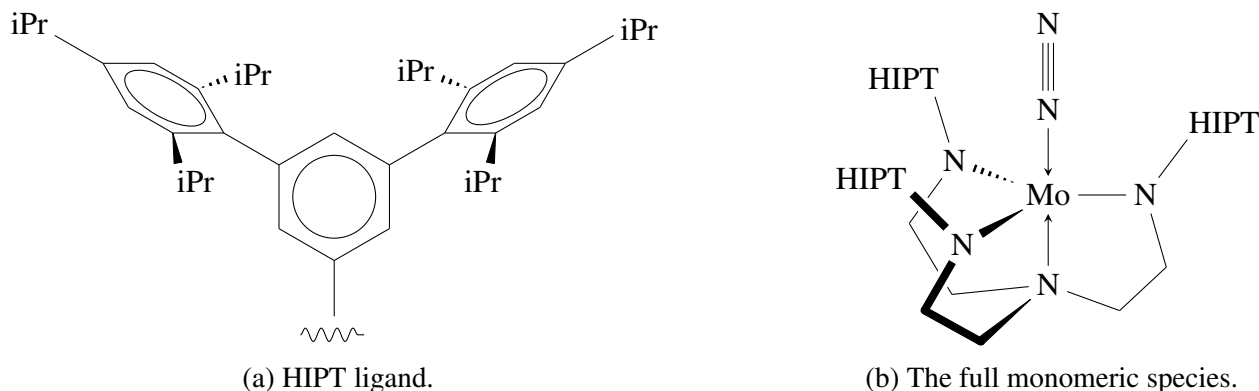


Figure 1: The catalyst.

Having studied nitrogen fixation for 20 years, Yandulov and Schrock suspected that the key to a well-defined molecular nitrogen fixation catalyst lay in high oxidation state molybdenum and tungsten species. In order to isolate and study some of these high oxidation state intermediates, the previously semi-successful triamidoamine ligand  $[(\text{ArNCH}_2\text{CH}_2)_3\text{N}]^{3-}$  (see Figure 1b) was modified to incorporate the extremely bulky ligand motif HIPT (hexa-iso-propyl-terphenyl or 3,5-(2,4,6- $\text{iPr}_3\text{C}_6\text{H}_2$ ) $_2\text{C}_6\text{H}_3$ ; see Figure 1a). These ligands, they hoped, would sterically inhibit formation of previously observed, unreactive bimetallic  $\text{N}_2$ -bridging species. Indeed, they were able to synthesize from  $\text{MoCl}$  (where  $\text{Mo} = [\text{HIPTN}_3\text{N}]\text{Mo}$ ) the six boxed intermediates in Figure 2, as characterized by NMR and x-ray studies<sup>[5][6]</sup>. To support these “intermediates” relevance to the predicted Chatt-type mechanism, they were additionally able to show that some of them are interconvertible (i.e., could be prepared from others).

With this result, Yandulov and Schrock introduced the first well-defined abiological nitrogen-fixation system with relatively high yields and observable, interconvertible intermediates. Additionally, to eliminate the possibility that their nitrogen-containing tetradentate  $[\text{HIPTN}_3\text{N}]^{3-}$  ligand or acid was furnishing the nitrogen that was moving around the intermediates, they conducted a study with radiolabeled dinitrogen. Having established that all intermediates and products contained only  $^{15}\text{N}$  at the proposed active site pocket, they concluded that no isotopically labeled nitrogen was exchanged between the HIPT ligand and acid, and the substrate, as would be expected in a true catalytic mechanism. Thus, they reported that their  $[\text{HIPTN}_3\text{N}]\text{Mo}$  species was (1) accepting nitrogen from the atmosphere, (2) likely forming well-defined, isolable intermediates in a plausible theoretical catalytic cycle, and (3) converting between said intermediates.

In introducing the first well-defined catalytic system for nitrogen fixation with observable Chatt-type intermediates, Yandulov and Schrock demonstrated that catalytic nitrogen fixation likely is possible, thus motivating continued research in this field. Although their present system does not approach the turnover numbers and frequencies necessary for it to be industrially viable, it represents a validation of Chatt's preexisting theory and exhibits the potential of high oxidation state transition metals as well as sterically bulky ligands for nitrogen fixation purposes. Additionally, if other, more recent results are anything to go by, the problems of rate and efficiency are likely solvable: For example, Anderson et al. originally reported seven turnovers for a similar nitrogen fixation system, but follow up studies that further purified their reagents and also tinkered with the catalyst and

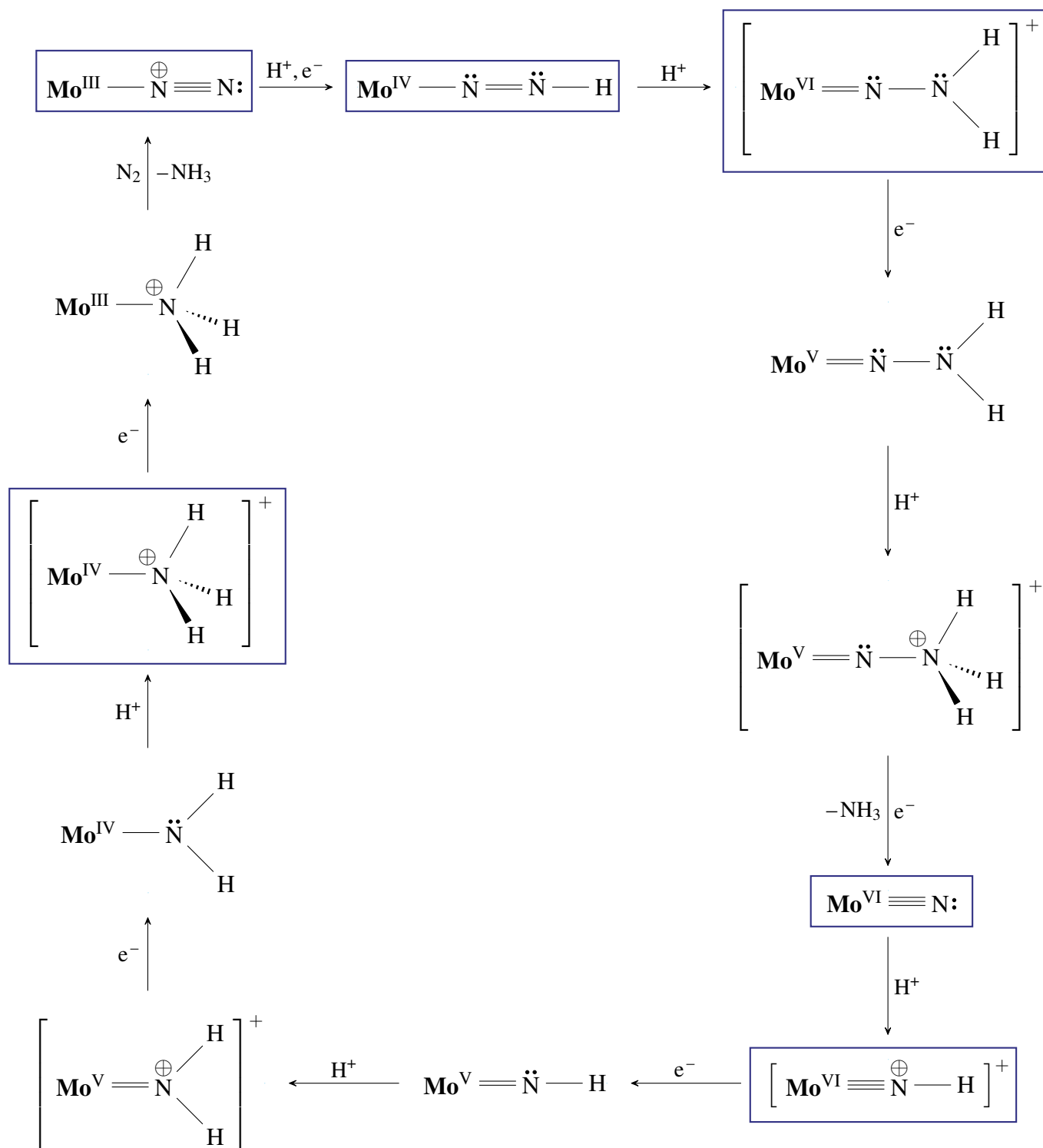


Figure 2: The mechanism. All boxed intermediates were isolated and characterized. The remaining intermediates are proposed to exist by Chatt, but have yet to be detected.

conditions brought the system up to nearly 100 turnovers<sup>[7]</sup>. However, a somewhat problematic hole in Yandulov and Schrock's results is their inability to characterize Chatt's other five proposed intermediates (see the unboxed species in Figure 2), especially considering the fact that they were able to characterize species as unstable and rare as the diazine adduct. Their verification of the interconvertibility of their characterized intermediates does support the existence of the other proposed intermediates, but it does not rule out the possibility of something else going on.

## References

- (1) Allen, A. D.; Senoff, C. V. *Chem. Commun.* **1965**, 621–622.
- (2) Yamamoto, A.; Kitazume, S.; Pu, L. S.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, 93, 371–380.
- (3) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, 301, 76–78.
- (4) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, 78, 589–625.
- (5) Yandulov, D. V.; Schrock, R. R.; Rheingold, A. L.; Ceccarelli, C.; Davis, W. M. *Inorg. Chem.*, 42, 796–813.
- (6) Yandulov, D. V., unpublished data.
- (7) Anderson, J. S.; Rittle, J.; Peters, J. C. *Nature* **2013**, 501, 84–87.