

Photoactivation of Dinitrogen by Molybdenum Complexes

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One of the great challenges in modern synthetic chemistry is the functionalization of dinitrogen (N_2). Nitrogen atoms are critical for the majority of manufactured chemical compounds (e.g. pharmaceuticals, fertilizers, and explosives). However, the most abundant nitrogen source, N_2 , is extremely inert under ambient conditions. While the industrial Haber-Bosch process utilizes a heterogeneous iron catalyst to functionalize N_2 to ammonia (NH_3), this process consumes large amounts of energy. Nature overcomes the inertness under ambient conditions using bacterial nitrogenase enzymes that contain an [Fe-Mo] active site to effectively convert N_2 into NH_3 .¹ While it would be useful to synthetically functionalize N_2 directly under ambient conditions, several decades of work have shown this to be difficult.²

The most successful systems use transition metal compounds to bind and activate N_2 .² Synthetic catalytic routes have drawn inspiration from the nitrogenase active site for the synthesis of Fe- and Mo-based complexes for N_2 cleavage (**Fig. 1**).³ Molybdenum in particular has shown much success as a metal center for nitrogen fixation catalysts. However, these systems usually require large excesses of reducing agents and acid for conversion.²⁻³ Therefore, investigations into methods for further activating these N_2 -Mo complexes have been undertaken.

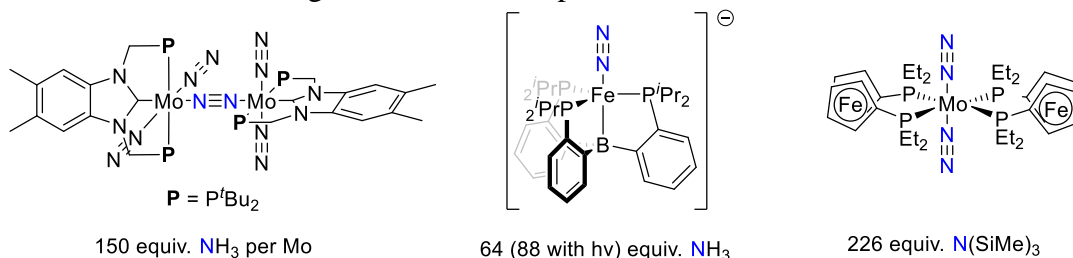


Figure 1 – Examples of most efficient synthetic catalysts for nitrogen fixation.

Photochemical activation is an attractive method for accessing high-energy reactive species of the N_2 -Mo complexes and potentially avoid the need for adding strong or excess reducing agents.⁴ Photoactivation of N_2 using metal complexes was first discussed by Fischler and von Gustorf.^{4a} They postulated that for an end-on M- N_2 complex, a d-d transition would preferentially weaken the M- N_2 bond while a MLCT transition to the N-N π^* orbital would weaken the N-N bond, leading to reactive metal-nitrides or -imidos.

Several photoactivated dinitrogen-molybdenum complexes have been synthesized in the past 20 years.^{3,4b} The first such example was demonstrated by Floriani and coworkers, showing that a bridging Mo-N-Mo complex forms upon photoexcitation of a μ - N_2 -[MoL₃]₂ complex (L = mesityl) (**Fig. 2a**).⁵ Recently, another [μ - N_2 -Mo₂] complex bearing ferrocenyldiphosphine from the Nishibayashi group was able to undergo photoactivated cleavage under ambient to afford Mo-nitride complexes (**Fig. 2b**).⁶ These and many similar [μ - N_2 -Mo₂] systems result in terminal Mo-nitride complexes, which are reactive with numerous substrates.⁷⁻⁸ There has also been work on trapping the photoactivated complexes with electrophiles other than H^+ . Sita and coworkers have established a chemical procedure that traps photoactivated [μ - N_2 -Mo₂] dimers with R_3ECl (E = C, Si, Ge) to form a terminal Mo-imido complex that can also be converted to form isocyanates (**Fig. 2c**).⁹ The starting material can be regenerated through reduction of the resulting L_nMoCl_2 complex under N_2 atmosphere. This trapping of the photoactivated nitrogen atoms with electrophiles could

serve as a template for establishing productive chemical cycles for other photoactivated $[\mu\text{-N}_2\text{-Mo}_2]$ systems.

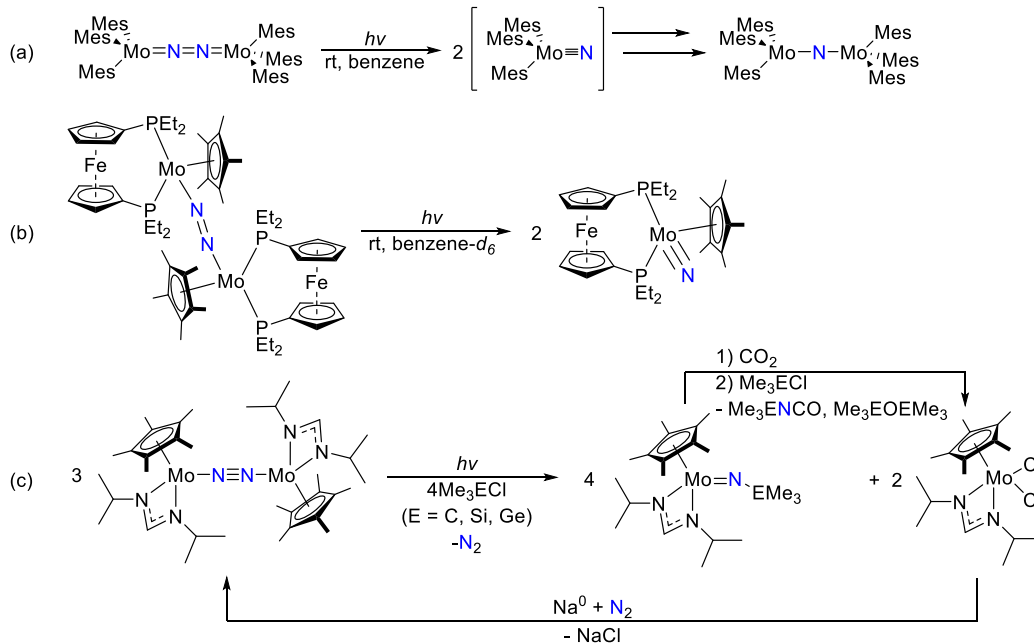


Figure 2 – Examples of photoactivation of $[\mu\text{-N}_2\text{-Mo}_2]$ complexes.

The photoactivation of $[\mu\text{-N}_2\text{-Mo}_2]$ complexes¹⁰⁻¹¹ have also been studied using transient spectroscopy, which probes short-lived reactive states generated by photochemical excitation. Blank and coworkers performed transient absorption spectroscopy on an isolable $\mu\text{-N}_2\text{-[MoR}_3\text{]}_2$ intermediate ($\text{R} = \text{N}(t\text{-Bu})(3,5\text{-C}_6\text{H}_3\text{Me}_2)$) that cleaves the N-N bond and Mo-N bond equally upon photoexcitation.¹⁰ They found that there is a short-lived triplet excited state that undergoes internal conversion (IC) and vibrational relaxation (VR) back down to the ground state (**Fig. 3**). The low cleavage yield results from the fast relaxation to the ground state. While only one other transient study on $[\mu\text{-N}_2\text{-Mo}_2]$ complex has been done,¹¹ both were characterized to have short excited-state lifetimes, with key structural distortions and electron density on the $\text{N}_2\text{-Mo}_2$ core, and relaxation processes in competition with bond dissociation.

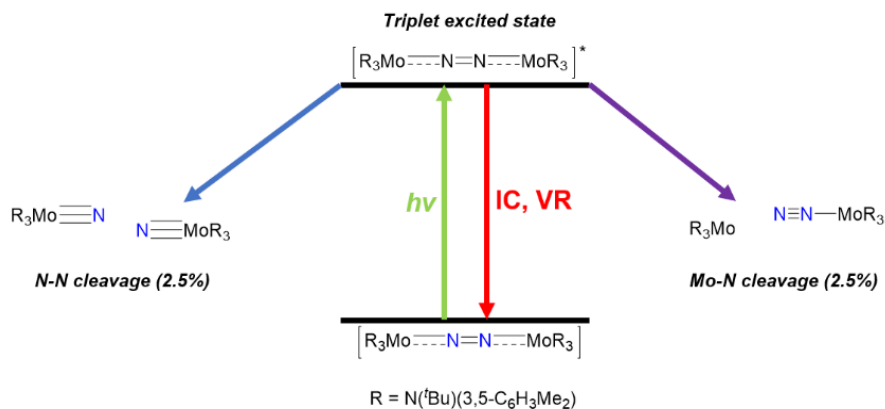


Figure 3 - Photochemical excitation of the isolable $[\mu\text{-N}_2\text{-Mo}_2]$ intermediate.

While advances have been made in photoactivating N₂-Mo complexes, there are several key challenges present. The photoactivated complexes have yet to reach the efficiency of current synthetic catalysts and still require similar amounts of strong reducing agents or acids.^{2-3,8} While foundational transient spectroscopy and computational studies have been performed, further work is necessary for mapping out the underlying photochemical mechanisms and maximizing the yield of productive metal-nitrogen products; for example, targeting specific excitation wavelengths may improve yields of N-N bond cleavage. Additional methods for improving desirable reactivity should include modifying the supporting ligands to promote desired structural distortions and electron density in the N₂-Mo core .

References:

1. Burgess, B.K.; Lowe, D.J. Mechanism of Molybdenum Nitrogenase. *Chem. Rev.* **1996**, *96*, 2983–3012.
2. (a) Fryzuk, M.D.; Johnson, S.A. The continuing story of dinitrogen activation. *Coord. Chem. Rev.* **2000**, *200-202*, 379-409; (b) Stucke, N.; Flöser, B.M.; Weyrich, T.; Tuzcek, F. Nitrogen Fixation Catalyzed by Transition Metal Complexes: Recent Developments. *Eur. J. Inorg. Chem.* **2018**, *12*, 1337–135
3. Burford, R.J.; Fryzuk, M.D. Examining the relationship between coordination mode and reactivity of dinitrogen. *Nat. Rev. Chem.* **2017**, *1*, 1-13.
4. (a) Fischler, I.; von Gustorf, E.K. Chemische und biologische Aspekte der Fixierung und Reduktion molekularen Stickstoffs. *Naturwissenschaften* **1975**, *62*, 63 –70; (b) Krewald, V. Dinitrogen photoactivation: status quo and future perspectives. *Dalt. Trans.* **2018**, *47*, 10320-10329.
5. Solari, E.; Da Silva, C.; Iacono, B.; Hesschenbrouck, J.; Rizzoli, C.; Scopelliti, R.; Floriani, C. Photochemical Activation of the NN Bond in a Dimolybdenum-Dinitrogen complex: Formation of a Molybdenum Nitride. *Angew. Chem. Int. Ed.* **2001**, *40*, 3907-3909.
6. Miyazaki, T.; Tanaka, H.; Tanabe, Y.; Yuki, M.; Nakajima, K.; Yoshizawa, K.; Nishibayashi, Y. Cleavage and Formation of Molecular Dinitrogen in a single system assisted by Molybdenum Complexes Bearing Ferrocenyldiphosphine. *Angew. Chem. Int. Ed.* **2014**, *53*, 11488-11492.
7. Smith, J. M. Reactivity of Transition Metal Nitride Complexes. In *Progress in Inorganic Chemistry*; Karlin, K.D., Ed.; John Wiley & Sons, Inc.: Hoboken, New Jersey, 2014; Volume 58, Chapter 6.
8. Arashiba, K.; Kinoshita, E.; Kuriyama, S.; Eizawa, A.; Nakajima, K.; Tanaka, H.; Yoshizawa, K.; Nishibayashi, Y. Catalytic Reduction of Dinitrogen to Ammonia by Use of Molybdenum-Nitride Complexes Bearing a Tridentate Triphosphine as Catalysts. *J. Am. Chem. Soc.* **2015**, *137*, 5666-5669.
9. Keane, A.J.; Farrell, W.S.; Yonke, B.L.; Zavalij, P.Y.; Sita, L.R. Metal-Mediated Production of Isocyanates, R₃N=C=O from Dinitrogen, Carbon Dioxide, and R₃ECl. *Angew. Chem. Int. Ed* **2015**, *54*, 10220-10224.
10. Huss, A.S.; Curley, J.J.; Cummins, C.C.; Blank, D.A. Relaxation and Dissociation Following Photoexcitation of the (μ-N₂)[Mo(N[t-Bu]Ar)₃]₂ Dinitrogen Cleavage Intermediate. *J. Phys. Chem. B* **2013**, *117*, 1429–1436.
11. Rafiq, S.; Bezdek, M.J.; Koch, M.; Chirik, P.J.; Scholes, G.D. Ultrafast Photophysics of a Dinitrogen-Bridged Molybdenum Complex. *J. Am. Chem. Soc.* **2018**, *140*, 6298–6307.