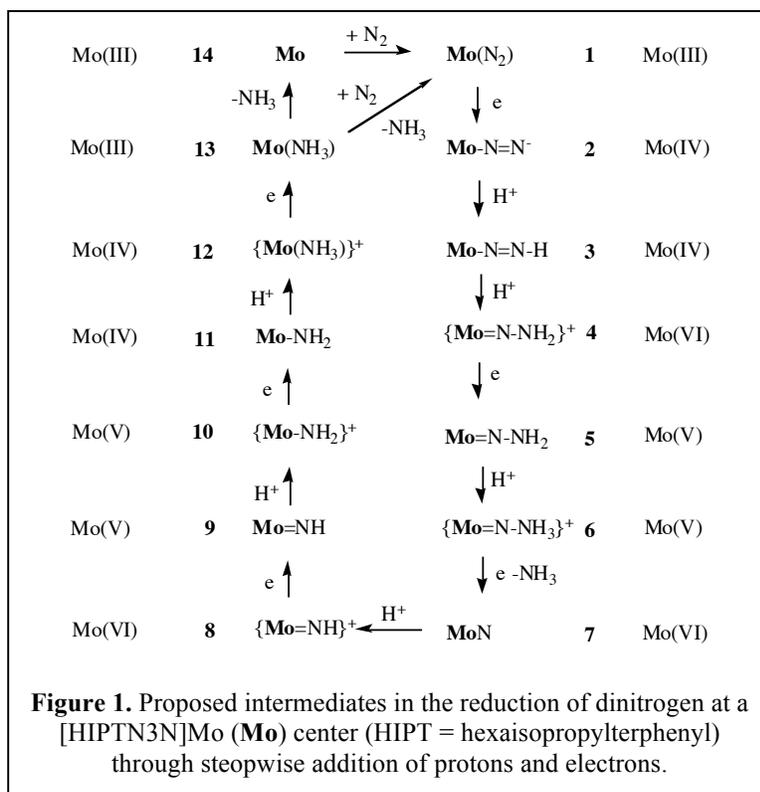


Catalytic Reduction of Dinitrogen to Ammonia with Molybdenum under Mild Conditions

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We have designed molybdenum complexes that will reduce dinitrogen selectively and catalytically to ammonia at 1 atm and room temperature using protons and electrons (~66% yield, ~4 turnovers).¹ The most successful catalysts contain the [HIPTN₃N]³⁻ ligand, where HIPT = 3,5-(2,4,6-i-Pr₃C₆H₂)₂C₆H₃ (HexaIsoPropylTerphenyl). This ligand was designed to prevent formation of relatively stable and unreactive [ArN₃N]Mo-N=N-Mo[ArN₃N] complexes, maximize steric protection of a metal coordination site in a monometallic species, and provide increased solubility in nonpolar solvents. Eight of the intermediates in a hypothetical "Chatt-like" reduction of dinitrogen (Figure 1) were prepared and characterized. These include paramagnetic **Mo(N₂)** (**Mo** = [HIPTN₃N]Mo), diamagnetic [**Mo(N₂)**], diamagnetic **Mo-N=N-H**, diamagnetic [**Mo=N-NH₂**]BAR'₄ (Ar' = 3,5-(CF₃)₂C₆H₃), diamagnetic **Mo≡N**, diamagnetic [**Mo=NH**]BAR'₄, paramagnetic [**Mo(NH₃)**]BAR'₄, and paramagnetic **Mo(NH₃)**. Several isolated species were employed to reduce dinitrogen catalytically to ammonia in heptane. The proton source is [2,6-dimethylpyridinium][BAR'₄] or [2,4,6-trimethylpyridinium][BAR'₄] and the reductant is decamethyl chromocene. Ammonia is formed selectively (no hydrazine is detected) with an efficiency of 55-65% in electrons. The remaining reducing equivalents are used to form dihydrogen. Both ammonia and dihydrogen (especially) are inhibitors of dinitrogen reduction.² Although **MoH₂** is formed readily in the presence of ammonia, it is unstable with respect to a heterolytic cleavage of dihydrogen.³ The amount of dinitrogen that can be reduced under the conditions employed is limited in large part because the [HIPTN₃N]³⁻ ligand is removed from the metal in the presence of protons and reducing agent.



The reduction of dinitrogen is exceedingly sensitive to the steric crowding around provided by the triamidoamine ligand system. Molybdenum complexes that contain

"hybrid" ligands, [(HIPTNCH₂CH₂)₂NCH₂CH₂NAryl]³⁻, where the Aryl group is significantly less sterically demanding than HIPT, are considerably less successful for catalytic N₂ reduction.⁴ When Aryl = 3,5-(CF₃)₂C₆H₃, for example, no turnover is observed. Evidence suggests that in this case the Mo-N=NH intermediate is catalytically decomposed to MoN₂ and hydrogen by the conjugate base (lutidine) of the acid employed as the proton source for dinitrogen reduction. Decomposition of Mo-N=NH species therefore are becoming a focus of our attempts to understand the details of catalytic dinitrogen reduction. In the parent system both bimolecular or unimolecular decomposition of **Mo**-N=NH are relatively slow for steric reasons.

It will be difficult, but not impossible, to find a way to develop a practical method of reducing dinitrogen at room temperature and pressure using molybdenum catalysts. Current research is aimed at the synthesis of a ligand that is resistant to loss from the metal through protonation of the amido nitrogens and to the development of electrochemical methods of reducing dinitrogen.

References

¹ (a) Schrock, R. R. *Acc. Chem. Res.* **2005**, *38*, 955-962. (b) Schrock, R. R. *Angew. Chem. Int. Ed.* **2008**, *47*, 5512-5522.

² Hetterscheid, D. G. H.; Hanna, B. S.; Schrock, R. R. *Inorg. Chem.* **2009**, *48*, 8569-8577.

³ Kinney, R. A.; Hetterscheid, D. G. H.; Hanna, B. S.; Schrock, R. R.; Hoffman, B. M. *Inorg. Chem.* **2010**, *49*, 704-713.

⁴ Weare, W. W.; Schrock, R. R.; Hock, A. S.; Müller, P. *Inorg. Chem.* **2006**, *45*, 9185-9196.