

Recent Developments in Homogeneous Nitrogen Fixation.  
A Study of Reactive Intermediates.

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The goal of nitrogen fixation is to convert  $N_2$  gas, an inexpensive and abundant chemical, into  $NH_3$  gas. Ammonia is produced industrially to be used as a fertilizer, and produced biologically for amino acid biosynthesis. The reaction of  $N_2$  and three moles of  $H_2$  to give two moles of  $NH_3$  is favored thermodynamically by 16.65 kJ/mole [1]. The nitrogen triple bond must be cleaved, however, which makes the process kinetically unfavorable.

It has been possible to fix nitrogen industrially since 1913. The Haber-Bosch process uses an iron-oxide catalyst and a high pressure of  $N_2$  and  $H_2$  at high temperatures to accomplish the industrial synthesis of ammonia [2]. The desire for an alternative approach has spurred research into how nitrogen is fixed biologically.

Nitrogenases are the class of enzymes which convert  $N_2$  to  $NH_3$ , and are found in blue green algae, as well as rhizobium bacteria which have a symbiotic relationship with leguminous plants. Nitrogenases consist of two proteins: Component I contains a MoFe cofactor that binds the nitrogen, and Component II contains an FeS cofactor that transfers the six electrons necessary to reduce the dinitrogen. The diagram below describes how these two components interact to reduce  $N_2$  to  $NH_3$  via nitrogenase (Figure 1) [3]. It has generally been believed that molybdenum is necessary in the biological fixing of dinitrogen. Recently, however, this has been disproven by the discovery of nitrogenases which do not contain molybdenum. For example, an enzyme was discovered which is structurally identical to Mo-containing nitrogenases, but the molybdenum is replaced with a vanadium [4]. A second example, which is not as well characterized, is known to only contain iron and no other detectable transition metals [5].

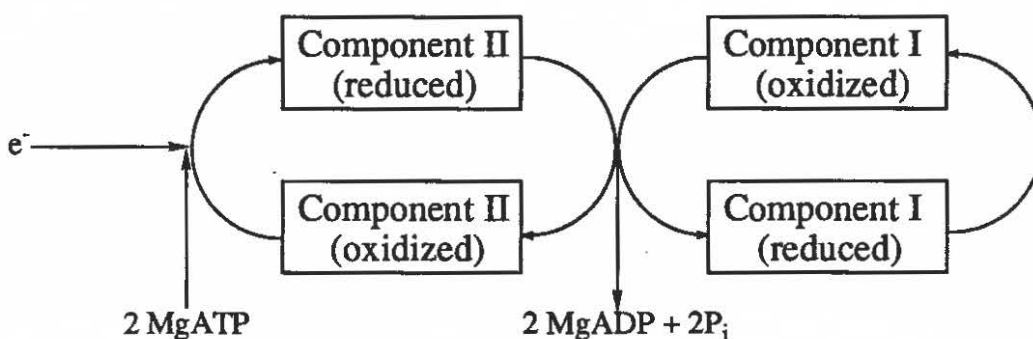


Figure 1

Much of the current research in nitrogen fixation has focused on understanding the chemistry of intermediates along the mechanistic pathway to ammonia using model systems. The diagram shown below gives a proposed mechanism, and demonstrates possible intermediates (Figure 2). A model bridging-diazene complex with biomimetic ligands has been synthesized which demonstrated how the diazene ligand could be stabilized via  $N-H \cdots S$  interactions in the active site of the enzyme [6]. Evidence for the hydrazido intermediate includes formation of hydrazine upon quenching of a working enzyme with either an acid or base [7].

To model the active site of nitrogenases, it is necessary to understand how  $N_2$  can be coordinated to a metal center. The majority of transition metal-dinitrogen complexes have  $N_2$  bound end-on to the metal, or in bimetallic systems the  $N_2$  is bridging end-on between two metals [8]. Since dinitrogen is isoelectronic with carbon monoxide, a correlation can be drawn between their bonding.

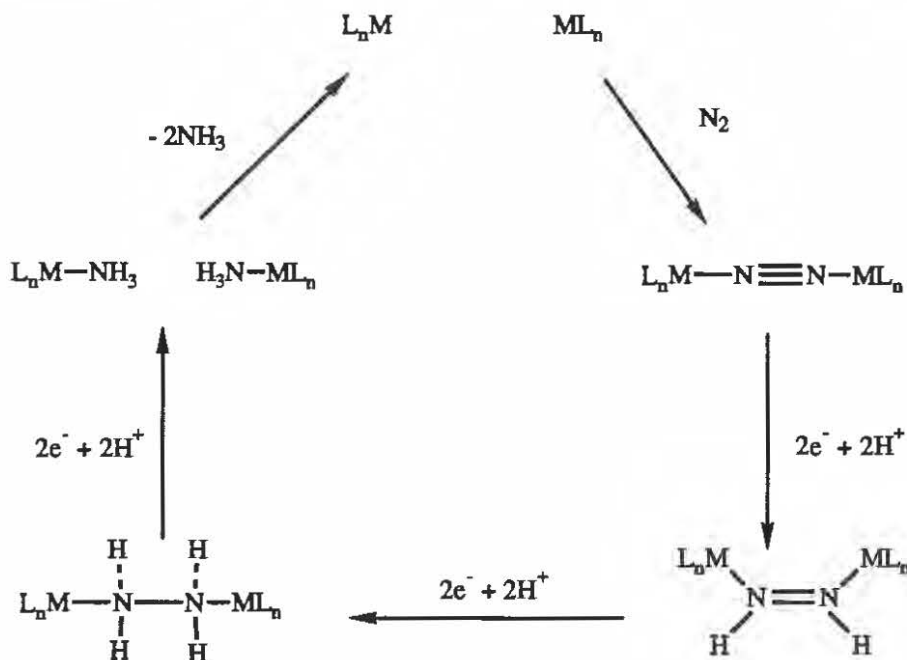


Figure 2

Dinitrogen is a  $\sigma$ -donor/ $\pi$ -acceptor ligand. Back-donation in most transition metal dinitrogen complexes where end-on binding is active do not weaken the  $N_2$  triple bond exceptionally well. A theoretical study, however, showed that in  $[Ni(PH_3)_2(N_2)]$  side-on binding of  $N_2$  is more energetically favorable than end-on binding, and better activates the  $N_2$  triple bond to conversion to  $NH_3$  [9]. Experimentally, though, there is only one example of side-on binding of  $N_2$ , and it yields less than 0.1% ammonia when reacted with a source of protons [10].

Chatt and Leigh have synthesized low-valent tungsten and molybdenum bis(dinitrogen) complexes which react with strong acids to form ammonia, often in high yields [11]. More recently, Graves has performed mechanistic studies of analogous complexes, and showed that the first 4 electrons necessary for reduction of  $N_2$  are obtained from the metal center, resulting in a hydrazido intermediate. Experimental evidence suggested that the next two electrons necessary for the formation of ammonia come from the disproportionation of two equivalents of the hydrazido intermediate [12]. This was demonstrated by synthesizing polymer-bound dinitrogen complexes, so that disproportionation reactions could be controlled [13].

Another approach to binding  $N_2$  to a metal center can be invoked if the metal center is electron deficient. High oxidation state metals have been shown to weaken the nitrogen-nitrogen bond via metal-ligand multiple bonding and produce some type of hydrazido intermediate [14]. Schrock has synthesized several examples of bimetallic and heterobimetallic dinitrogen complexes using molybdenum and tungsten. Protonation studies of these complexes in the presence of a sacrificial reducing agent produced ammonia in varied amounts, the best being

[MoCp\*Me<sub>3</sub>](μ-N<sub>2</sub>)[WCp\*Me<sub>3</sub>] (90% NH<sub>3</sub>, and traces of N<sub>2</sub>H<sub>4</sub>) [15]. In the search of a catalytic system for nitrogen fixation, Schrock has synthesized hydrazine and amino complexes in order to more fully understand the final step in the proposed mechanism: complete cleavage of the N-N bond in bound hydrazine. The tungsten-hydrazine complex catalytically reduces hydrazine to ammonia in greater than 90% yield [16].

Although a full understanding of the active site of nitrogenase has not been realized, research in the area of nitrogen fixation has progressed in the understanding of possible reactive intermediates. This has been accomplished through the synthesis and reaction chemistry of metal bound dinitrogen, diazene, hydrazido, hydrazine, and amino complexes. Ultimately, the goal of this research would be to develop a homogeneous system which may rival the Haber-Bosch process.

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