Nitrogen Fixation

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Photolytic N_2 Splitting: A Road to Sustainable NH_3 Production?**

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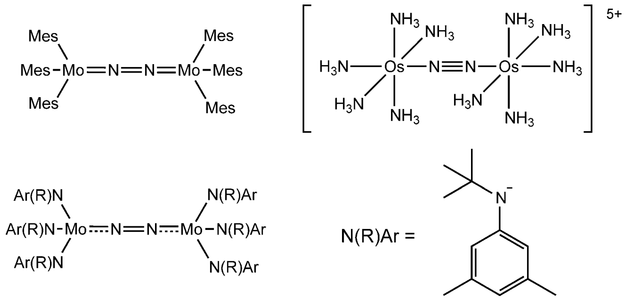
molybdenum · nitrogen fixation · photochemistry · radicals · reaction mechanisms

*Dedicated to Professor
Bradford B. Wayland*

As dinitrogen is the most abundant gas in our atmosphere, its functionalization is attractive, both from a synthetic perspective and as a potential energy storage vector. However, N_2 cleavage and functionalization at ambient conditions remains an extremely challenging topic. The nonbasic, nonpolarized neutral molecule does not easily form additional bonds, the strong $N\equiv N$ bond is difficult to cleave, and the 10.82 eV energy difference between its HOMO and LUMO makes it rather difficult to reduce N_2.[1] Taking it further, the conversion of N_2 into ammonia involves a kinetically complex proton-coupled six-electron reduction process. In the Haber–Bosch process the dinitrogen molecule is cleaved at surface iron atoms, and then reacted further with dihydrogen to form ammonia. However, the requirement of high pressure and temperature leads to a high energy consumption, and hence scientists have dreamed for many years of systems which tolerate milder reaction conditions. Some bioinspired examples of homogeneous catalysts are reported to convert dinitrogen electrochemically into ammonia. They operate by stepwise protonation and reduction steps, and thereby mimic nitrogen fixation by the enzyme nitrogenase.[2] However, these systems not nearly rival the heterogeneous Haber–Bosch process. Hence, an alternative pathway in which the N–N bond is first thermally[3] or photochemically cleaved before functionalization, seems an interesting approach.

Photochemical N–N bond cleavage has thus far received only limited attention. Examples of photolytic N_2 cleavage have been previously reported for molybdenum[4] and osmium[5] (Scheme 1), but recently the groups of Yoshizawa and Nishibayashi have pushed the field a step further by providing an example of photolytic N_2 cleavage leading to a reactive nitrido complex which can be subsequently converted into ammonia (0.37 equiv).[6] This conversion is the first example of ammonia formation from a nitride produced by light-induced cleavage of dinitrogen.



Scheme 1. Previously reported examples of systems capable of cleaving N_2 photolytically.

The authors applied the dinuclear pentamethylcyclopentadienyl molybdenum dinitrogen complex **1** (Scheme 2), which bears a ferrocenyl diphosphine ligand and contains an (end-on) bridging dinitrogen ligand. The complex **1** can exist in three different redox states: **1**, **1**$^{+}$, and **1**$^{2+}$. Counterintuitively, the bridging dinitrogen ligand is most preactivated in the dicationic two-electron oxidized species **1**$^{2+}$. This unusual behavior can be understood with a simplified Hückel representation of the 10e Mo-N-N-Mo π system of **1** (Scheme 2A). While the two SOMOs of **1** have both N–N bonding and Mo–N antibonding character, the two lower lying (doubly occupied) orbitals have Mo–N bonding and N–N antibonding character. As a result, successive oxidation of **1** to **1**$^{+}$ and **1**$^{2+}$ increases the Mo–N bond order, but weakens the N–N bond. DFT calculations are in agreement with this model.

Surprisingly, photolysis of **1**, having the least activated N–N bond, using visible light ($\lambda > 400$ nm), led to selective formation of the nitrido complex **2** (Scheme 2B), while irradiation of the more activated species **1**$^{+}$ and **1**$^{2+}$ resulted in nonselective photolysis, thus producing a complex mixture of compounds. Based on TD-DFT calculations the authors speculate that an electronic transition at $\lambda = 495$ nm, associated with loss of electron density between the two nitrogen atoms, facilitates the observed N–N splitting. However, considering the thermal stability of **1**$^{+}$ and **1**$^{2+}$, this seems to be only a partial explanation.

The authors not only report on the photochemical splitting of N_2, but also demonstrate that the resulting nitrido complex **2** is still a reactive compound. Oxidation of **2** to **2**$^{+}$ results in N–N coupling to generate **1**$^{2+}$. Hence, this molybdenum system can both cleave and form N_2, a feature which was only reported once before in a homogeneous system.[7] Furthermore, oxidation of **2** in the presence of 1,4-cyclo-

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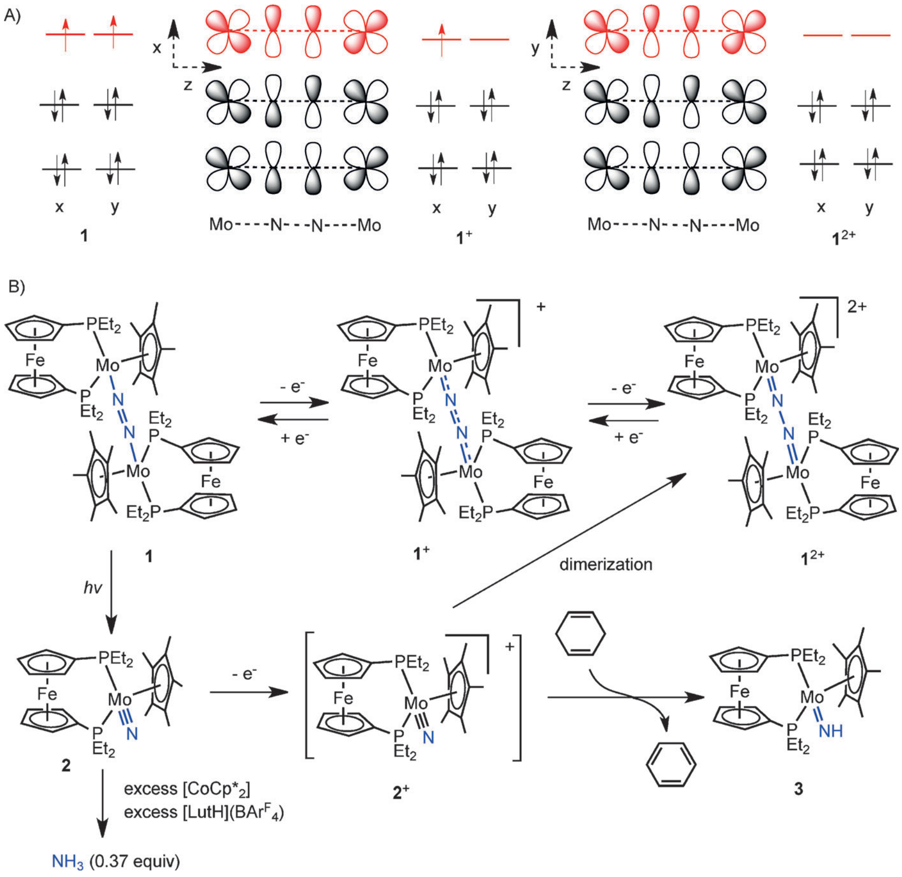
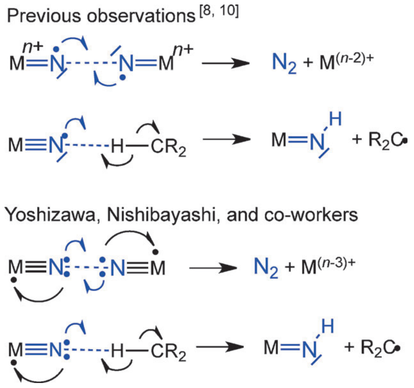


Scheme 2. A) Simplified Hückel representation of the Mo-N-N-Mo π system in **1**, $\mathbf{1}^+$, and $\mathbf{1}^{2+}$. B) Photochemical N–N splitting in **1** to produce the nitrido complex **2**. Reduction of **2** under acidic conditions leads to NH_3 formation. Oxidation of **2** to $\mathbf{2}^+$ induces hydrogen abstraction and N–N coupling.

hexadiene as a hydrogen atom source results in formation of a mixture of the imido complex **3** and $\mathbf{1}^{2+}$ (Scheme 2B). Quite surprisingly, protonation of **2** with [LutH]($BAr^F{}_4$) yields the same mixture of the imido complex **3** and dinuclear N_2-bridged complex $\mathbf{1}^{2+}$, and is difficult to understand mechanistically.

To investigate the mechanism of the N–N coupling reaction,[7–9] Yoshizawa, Nishibayashi, and co-workers calculated the SOMO of the proposed intermediate $\mathbf{2}^+$, which is the one-electron oxidized form of the nitrido complex **2**. Surprisingly this intermediate possesses negligible nitridyl radical ($^{\bullet}N^{2-}$) character. More than 90% of the spin density of $\mathbf{2}^+$ is located at the molybdenum atom. This characteristic contrasts with recently reported nitridyl radical complexes of titanium, rhodium, and iridium (Scheme 3), which have significant spin density at the nitrogen atom.[9,10] The rhodium and iridium nitridyl radical complexes undergo fast radical-type N–N coupling, but do not react with 1,4-cyclohexadiene.[9] The titanium complex does undergo hydrogen-atom transfer (HAT) reactivity, thus producing a Ti=NH imido complex.[10] The complex $\mathbf{2}^+$ undergoes both types of reactions despite having negligible nitridyl radical character (Scheme 3). This reactivity seems to underline Mayer's postulate that HAT is mainly determined by the relative E–H bond strengths rather than discrete spin density at the hydrogen-accepting element.[11] In contrast, **2** does not undergo N–N coupling, but does after oxidation to $\mathbf{2}^+$. This reactivity suggests that the N–N coupling proceeds by a radical process which requires at least some radical density in proximity to the coupling nitrogen atoms (Scheme 3).



Scheme 3. Radical-type N–N coupling and HAT reactivity of nitrido and nitridyl radical complexes.

Interestingly, subjecting **2** to an excess of [LutH]($BAr^F{}_4$) and [$CoCp^*_2$] resulted in the formation of ammonia, albeit in low yield (0.37 equiv; Scheme 2B). Other metal nitrides have been reported to yield ammonia, but were not derived from N_2.[12] Such examples were only reported for a niobium[13a] and iron complex.[13b] Overall, this system contributes to ongoing efforts of achieving nitrogen fixation under mild, ambient, and environmentally friendly conditions. Supplying additional energy to break the N–N bond in a photochemical manner avoids the need to use extremely powerful reducing agents, and is an important step forward. Future efforts should focus on improving ammonia yields, regeneration of the dinitrogen complex, and the use of cheaper reagents to convert the nitride into ammonia or other synthetically useful amines. Especially the use of H_2 to convert the nitride into ammonia would make the overall process attractive,[12b] and perhaps even economically viable.

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