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Nitrogen cleavage and catalytic reactivity of a unique dinitrogen-bridged d^4-d^4 diarylamino-based PNP molybdenum complex

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One of the most important technol. inventions of the 20th century is Haber-Bosch process (HB) for synthesis of ammonia from atm. N_2. However, HB process is responsible for ca. 2% of global fossil fuel consumption and the co-production of commensurate amounts of CO_2. In this context, we are investigating mol. catalysts with the goal of developing electrocatalysts for the reduction of N_2 to ammonia. Reduction of N_2 using mol. catalysts has gained significant attention since Schrock's seminal report in 2003 and then a report by Nishibayashi in 2011. We have centered our approach on metal complexes that can bind and cleave N_2 via a bimetallic pathway, and then accept protons and electrons to yield NH_3. The Nishibayashi catalysts have been proposed, at least in some cases, to operate via dinitrogen-bridging Mo^{I} (d^5) fragments. Recent work by Schneider et al. demonstrates dinitrogen cleavage by Mo^{II} (d^4) fragments although the system failed to catalytically produce ammonia. Herein we describe the synthesis and characterization of a $(PNP)Mo^{IV}Br_3$ (1) complex (PNP = Ozerov's diaryl-based pincer ligand) which appears to undergo two-electron reduction to generate a four-coordinate $(PNP)Mo^{II}X$ (2-X) species (X = Br or I in the presence of added I^-). Under Ar atm., 2-Br dimerizes to afford a Mo-Mo quadruple-bonded complex $[(PNP)MoBr]_2$ (3). The same reduction under N_2 atmosphere leads to formation of a dinitrogen-bridged complex $[(PNP)Mo^{II}X]_2(\mu\text{-}N_2)$ (4-X) which is characterized by ^{1}H, ^{31}P and ^{15}N NMR, single crystal XRD and ESI-MS. $(PNP)MoBr_3$ (1) as well as the N_2-bridged species 4-I act as catalysts for the reaction of N_2 with reductants and acids to yield NH_3, suggesting that the bridging dinitrogen 4-I is cleaved to give the corresponding Mo^{V} nitride complex under the catalytic conditions. Using DFT, the barrier to cleavage of the N_2 bridged 4-I is calculated to be 24 kcal/mol. We are currently investigating the catalytic N_2 reduction and in particular, the cleavage of the dinitrogen-bridged species, using electrochem. methods.

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