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Effect of protonation on nitrogen splitting by a dinitrogen-bridged d4 -d4 diarylamino-based PNP molybdenum complex

By: Mandal, Souvik; Malakar, Santanu; Lease, Nicholas; Emge, Thomas J.; Hasanayn, Faraj; Goldman, Alan Stuart

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Ammonia production is critical to the well-being of society as the source of synthetic fertilizer, and it has great potential for energy storage and transportation. Unfortunately, the only com. process for ammonia synthesis is the Haber- Bosch process (HB) which is responsible for 2% of global fossil fuel consum ption and the co-production of commensurate amount of CO2 with the attendant contri bution to climate change. In this context, we are investi gating more sustainable synthesis of ammonia by reduction of N2 utilizing mol. catalysts, an approach that has gained significant attention since Schrock's seminal report in 2003. Our focus has been on dinitrogen reduction proceeding through bimetallic N2 cleavage.Herein we describe the synthesis and characte rization of a PNP-pincer-ligated Mo (IV) complex (PNP = Ozerov's diaryl-based pincer ligand), (PNP)MoIV X3 (1) (X= Cl, Br, I). Two-electron reduction under N2 atm leads to the formation of a dinitrogen-bridged complex [(PNP)MoII X]2 (m-N2) (4-X) which is only the third example of a fully charact erized dinitrogen complex with an 8-p-electron dimolybdenum system and the first to catalyt ically produce ammonia (TON = 6 equiv/ [Mo]) .Under thermal conditions, 4-I splits onto the corresp onding nitride (5-I) with an exptl. determined kinetic barrier of 29 kcal/mol while the kinetic barrier calculated with DFT is 30 kcal/mol. The nitride (5- I) can also be formed by photol ysis. Addition of two equivalent proton source to the dimer results in the rapid formation of a kinetic product which we propose to be the Mo-protonated dimer. Cleavage of the N2 bridge follows to yield a protonated nitride (6-I), which can also be formed directly by the reaction of the nitride (5- I) with one equivalent of proton. DFT calcul ations are in agreement with our observa tions, indicating that proton ation of Mo is followed by proton transfer to the N2 bridge, with the overall kinetic barrier to N2 splitting greatly lowered. We are currently investigating the structure of the initial protonation product. Investigation of the overall catalytic N2 reduction using electr ochem. methods is currently underway.

Conference

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