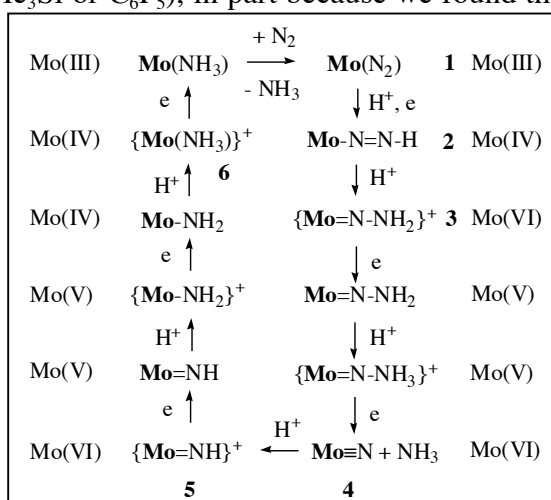


## 2. Catalytic Reduction of Dinitrogen under Mild Conditions

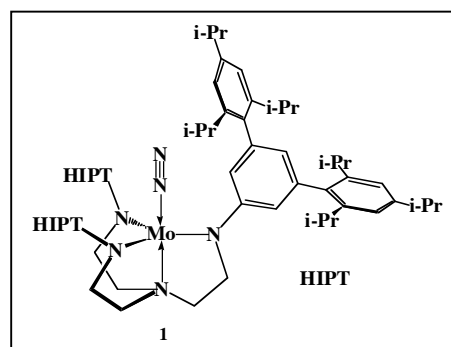
For the past several years we have been interested in the development of the chemistry of complexes that contain tetradentate triamidoamine ligands,  $[(RNCH_2CH_2)_3N]^{3-}$ , particularly from the point of view of activating and reducing molecular nitrogen to ammonia, especially with Mo complexes in which the molybdenum is in a relatively high oxidation state (Mo(III) - Mo(VI)). Carrying out the reduction of dinitrogen to ammonia with six electrons and six protons is an especially difficult task in view of the twelve or more intermediate species which are likely to be necessary intermediates, and one that had not been achieved catalytically in a *well-defined* manner in over 40 years of transition metal dinitrogen chemistry. In particular it was not known whether one metal is sufficient or more than one is required. Recently we have achieved the long sought goal of reducing dinitrogen catalytically at a single molybdenum center.

In the past decade we have been interested largely in Mo and W complexes that contain the triamidoamine ligand,  $[(RNCH_2CH_2)_3N]^{3-}$  ( $R = Me_3Si$  or  $C_6F_5$ ), in part because we found that dinitrogen can bind to a sterically protected  $d^3$  center to give  $[(Me_3SiNCH_2CH_2)_3N]Mo(N_2)$ , but also because unusual complexes that contain multiply bonded ligands in the trigonal binding cavity can be formed readily, e.g.,  $[(Me_3SiNCH_2CH_2)_3N]Mo\equiv P$ ,  $[(Me_3SiNCH_2CH_2)_3N]Mo\equiv As$ , and  $\{[(Me_3SiNCH_2CH_2)_3N]Mo=AsMe\}^+$ . Therefore, we envisioned dinitrogen being protonated and reduced at a single Mo center in a cycle analogous to that proposed by Chatt for Mo(0) and W(0) phosphine complexes, with the molybdenum varying in oxidation states between Mo(III) and Mo(VI) during this process (Scheme 1). However, we became convinced that Mo complexes that contain an arylated triamidoamine ligand ( $[(ArNCH_2CH_2)_3N]^{3-} = [ArN_3N]^{3-}$ ,  $Ar = aryl$ ) would be much more robust and also that formation of

complexes that contain a MoNNMo core would be prevented for steric reasons. This could be achieved effectively with the  $[HIPTN_3N]^{3-}$  ligand, where HIPT = 3,5-(2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (HexaisoPropylTerphenyl; see drawing of **1** above right). We then showed that many of the intermediates in a hypothetical monometallic reduction of dinitrogen could be prepared, all of which contain the same  $[HIPTN_3N]^{3-}$  ligand. These intermediates include paramagnetic  $Mo(N_2)$  (**1**;  $Mo = [HIPTN_3N]Mo$ ), diamagnetic  $Mo-N=N-H$  (**2**), diamagnetic  $\{Mo=N-NH_2\}\{BAr'_4\}$  (**3**;  $Ar' = 3,5-(CF_3)_2C_6H_3$ ), diamagnetic  $Mo\equiv N$  (**4**), diamagnetic  $\{Mo=NH\}\{BAr'_4\}$  (**5**), and paramagnetic  $\{Mo(NH_3)\}\{BAr'_4\}$  (**6**). Extensive <sup>15</sup>N labeling studies, NMR studies, and X-ray studies (of **1**, **4**, and **6** and **2**, **3**, and **5**) all reveal a trigonal pocket in which N<sub>2</sub> and its reduced products are protected to a dramatic degree by three 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub> rings clustered around it (see drawing of **1** above). Compounds **1** through **6** are among the thirteen or more that



Scheme 1. Proposed intermediates in the reduction of dinitrogen at a  $[HIPTN_3N]Mo$  ( $Mo$ ) center through the step-wise addition of protons and electrons.



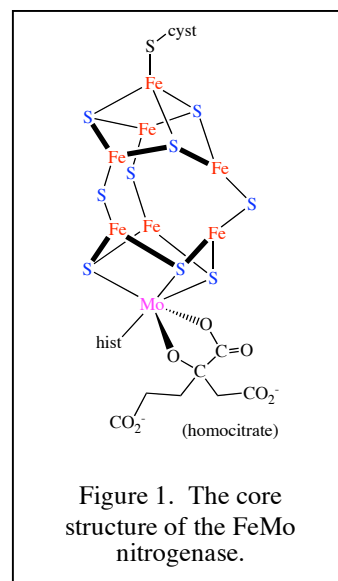
one might propose could take part in a catalytic reduction of end-on bound dinitrogen through the step-wise, alternating addition of six protons and six electrons (Scheme 1).

We have reported that dinitrogen in fact can be reduced catalytically by complexes **1**, **2**, **4**, or **6** in heptane if decamethylchromocene [ $\text{Cr}(\eta^5\text{-C}_5\text{Me}_5)_2 = \text{CrCp}^*_2$ ] is the reducing agent and  $\{\text{LutH}\}\{\text{BAr}'_4\}$  is the proton source. Heptane was chosen as the solvent in order to ensure that the concentration of sparingly soluble  $\{\text{LutH}\}\{\text{BAr}'_4\}$  in solution would be low, and  $\text{CrCp}^*_2$  was added with a syringe pump over a period of 6 hours in order to keep the concentration of  $\text{CrCp}^*_2$  low, thereby preventing predominantly formation of dihydrogen. It is also important that all cationic **Mo** derivatives in this family that we have isolated (e.g., **3**, **5**, or **6**, as  $\text{BAr}'_4^-$  salts) are soluble in alkane solvents. Sixteen runs on the scale of 36 equiv. of  $\text{CrCp}^*_2$  and 48 equiv. of  $\{\text{LutH}\}\{\text{BAr}'_4\}$  revealed that 7.56-8.06 equivalents of ammonia (63-66% yield) were formed. Only  $^{15}\text{N}$ -labeled ammonia was produced when the reduction was carried out under  $^{15}\text{N}_2$ .

There are several important features and implications of these findings. Foremost is the likelihood that dinitrogen is reduced at a sterically protected, *single* Mo center (Scheme 1), i.e., reduction of dinitrogen at two or more metal centers simultaneously is not required. Second, the oxidation state of Mo varies between Mo(III) and Mo(VI). The ability of molybdenum to vary its oxidation state over four levels is crucial for catalytic reduction. Third, catalytic reduction of dinitrogen has been achieved in an aprotic solvent environment and with a reducing agent that is considerably weaker than has been required in the past (e.g., sodium amalgam) for any reduction of dinitrogen. Fourth, although x-ray studies have focused attention on the six iron "cavity" in Fe/Mo nitrogenase as the site of dinitrogen reduction (Figure 1), this work suggests that reduction at the single Mo center should again be considered a strong possibility. In any case it is gratifying finally to reach the goal of catalytic reduction of dinitrogen by protons and electrons in a process that is relatively well-defined and that therefore can be studied systematically.

Forays into new types of ligand systems suggest that the catalytic reduction is extremely sensitive to small changes in ligand design, both steric and electronic. We have also shown that chromium, tungsten, and vanadium  $[\text{HIPTN}_3\text{N}]^{3-}$  systems do not reduce dinitrogen catalytically under conditions where Mo does. The reasons are that Cr(II) and Cr(III) do not bind dinitrogen, while tungsten(III) binds dinitrogen strongly, but will not release ammonia at the end. Tungsten(III) is also accessible only at an extremely low potential where hydrogen generation from protons and electrons is facile. Finally, the trianionic  $[\text{HIPTN}_3\text{N}]^{3-}$  ligand binds well to vanadium, but a  $3^-$  charge on the ligand requires that the overall charge on the intermediates in the V system be lower by one, i.e., the vanadium(V) nitride would be anionic instead of neutral; this low oxidation state is difficult to achieve with the reducing agents employed.

We are now focusing on the problematic diazenido species,  $\text{M-N=NH}$ , whose decomposition is believed to limit turnover in the unsuccessful systems. We have shown recently that Mo systems in which *one* of the three groups on the triamidoamine ligand is a somewhat smaller 3,5-disubstituted phenyl group are not successful as catalysts because the intermediate  $\text{Mo-N=NH}$  species is unstable under the reaction conditions, decomposing to  $\text{Mo(N}_2)$  and dihydrogen. This is only one of many ways to form dihydrogen, a wasteful product.



In this case the catalyst for dihydrogen formation is actually the Mo(N<sub>2</sub>) complex.

Future research will concentrate on the Mo system, new ligand systems, and mechanistic studies. In particular we will want to design ligands that are less likely to be removed from the metal, while still retaining the properties necessary for catalytic dinitrogen reduction. If possible, we will then take measures toward making the catalyst heterogeneous, using electrochemistry to provide electrons, and providing protons through the oxidation molecular hydrogen. Ultimately, we would like to demonstrate how to make dinitrogen reduction to ammonia relatively efficient.

The following papers are relevant to this area of chemistry (see publication list): 391, 395, 416, 417, 419, 426, 439, 443, 444, 447, 458, 474, 498, 499.