Dinitrogen comprises 79% of the earth's atmosphere. It is essential for the synthesis of nucleic acids and proteins which are required for all organisms.1,2 Unfortunately, molecular nitrogen is highly resistant toward either oxidation or reduction, to the extent that it is commonly used as an inert atmosphere for reactive chemicals.1-5 For dinitrogen to be most useful, it must be reduced to a form such as ammonia, which is currently performed effectively under ambient conditions only by the nitrogenase enzymes, and at very high temperatures and pressures by the Haber-Bosch process.2-5 The primary barrier to its reduction (at least in the gaseous phase) is the first hydrogenation step, as illustrated by the enthalpies of formation which follow:3

\[
\begin{align*}
N_2 + H_2 &\rightarrow N_2H_2 \quad \Delta H_f = +50.9 \text{ kcal/mol} \\
N_2H_2 + H_2 &\rightarrow N_2H_4 \quad \Delta H_f = -27.2 \text{ kcal/mol} \\
N_2H_4 + H_2 &\rightarrow 2NH_3 \quad \Delta H_f = -45.6 \text{ kcal/mol}
\end{align*}
\]

These values show that the overall reduction is energetically favorable, if the first step is overcome.

The isolation of [Ru(NH₃)₅N₂]²⁺ by Allen and Senoff in 1965 opened the door for dinitrogen coordination chemistry.7 This and other advances, such as the 1960 isolation of nitrogenase extracts, and the 1964 development of transition metal compounds capable of reducing dinitrogen, spurred a tremendous interest in the field of dinitrogen activation.6 A large number of dinitrogen reactions and complexes with transition metals have been discovered since 1965.1,4-6,8

Even with the amount of research on dinitrogen chemistry, no systems have been developed to compete effectively with the action of nitrogenase.¹ The chemistry of dinitrogen activation has expanded, providing many developments in the mechanism and structure of nitrogenase.²,3,9 Perhaps most interesting to modeling efforts has been structural data reported on the metal clusters found in nitrogenases.³,10 The Fe/Mo-cofactor proposed as the active dinitrogen reduction center is shown in Figure 1. While the cluster itself is known, the exact site of coordination and activation is not yet known.¹¹ Thus, synthetic efforts to model dinitrogen activation may be based on building clusters to closely model those found in nitrogenase, or in a looser sense, using structural principles learned from nitrogenase and previous dinitrogen chemistry to find a system that reduces dinitrogen but does not necessarily model nitrogenase.⁴
Efforts to closely model the clusters found within nitrogenase are based on Fe/Mo, V, Fe/S complexes. Synthesis of such clusters are done in an effort to model the entire Mo/Fe cofactor or structural units within the cofactor. In either case, definite models for the nitrogenase cofactor have proven elusive.

Other systems have been designed to explore dinitrogen activation that do not resemble the nitrogenase cofactor quite as closely. Recent reports include a system in which N₂ is bound by two trinuclear gold clusters. The N-N distance of 1.475(14)Å is longer than the single bond in hydrazine [1.454(20)Å], and significantly longer than free N₂ at 1.098(1)Å. Work using low-valent early transition metals has also produced cases of elongated N-N bonding, as well as examples of hydrogen addition to coordinated dinitrogen and dinitrogen cleavage to form nitride complexes.

The Zr complex with side-on bound dinitrogen illustrated in Figure 2A has an elongated N-N bond at 1.43(1)Å. It is found to react with molecular hydrogen in toluene to give the (m-h₂-N₂H)(m-H) complex shown in Figure 2B, as determined by NMR data and the crystal structure of an analogous compound with a [m-h₂-N₂(SiH₂₉Bu)](m-H) moiety. This reaction is unusual, as earlier complexes were noted to release N₂ upon reaction with H₂.

Dinitrogen cleavage by Mo(N(R)Ar₃)₃ (R = C(CD₃)₂Me, Ar = 3,5-C₆H₃Me₂) complexes as well as very recent reports of cleavage by Nb calix[4]arene complexes have given examples of structural systems which are capable of breaking the N-N bond. Although
it has been demonstrated that coordinated N2 can be reacted with H2 and cleaved to a nitride species, well-defined catalytic systems for N2 reduction at ambient conditions have not yet been achieved. Further research to deduce the structure of the active site of nitrogenase and to produce functioning synthetic models has been stimulated by these recent advances, with substantial progress still to be made.

References


