

## High oxidation state coordination chemistry with triamidoamine tungsten and molybdenum complexes

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**Abstract:** In this lecture I will focus on some recent developments in the chemistry of high oxidation state dinitrogen complexes with an emphasis on recent results involving triamidoamine molybdenum complexes.

The heterogeneous iron-catalyzed Haber-Bosch reduction of dinitrogen to ammonia at relatively high pressures (200-400 atm) and temperatures (350-650°C) was the first and most dramatic man-made catalytic reaction involving dinitrogen. Several decades later enzymes were discovered that reduce dinitrogen to ammonia and protons to dihydrogen in a process that consists of eight individual proton transfer and eight individual electron transfer steps (equation 1). The discovery of the first dinitrogen complex of a transition



metal by Allen and Senoff (ref. 1) raised the expectation that eventually we might be able to understand how to activate and reduce dinitrogen to ammonia using a transition metal complex as a catalyst under relatively mild conditions. However, controlling a catalytic reaction that involves the transfer of a minimum of 6 electrons and 6 protons (or three equivalents of dihydrogen) per dinitrogen molecule, and probably a large variety of intermediates, presents a significant challenge to the transition metal chemist. Reacting dinitrogen with small carbon-containing molecules (e.g., olefins or acetylenes) without forming ammonia first is at least equally challenging, if not more so.

A few years ago the structures of Mo/7Fe/10S nitrogenases from *Azotobacter vinelandii* (by Rees and his group (ref. 2)) and *Clostridium pasteurianum* (by Bolin and his group (ref. 3, 4, 5)) were solved and refined to relatively high resolution. The core (Fig. 1) contains a number of interesting structural features, among them the cuboidal Fe<sub>4</sub> and MoFe<sub>3</sub> units linked by inorganic sulfurs, the "cavity" of six irons in the center, the trigonal coordination geometry of the six core irons, and the six-coordinate molybdenum containing a coordinated histidine and a chelating homocitrate. Although this is a dramatic and long-awaited result, it should be remembered that the core is in one of several possible states. The structure therefore provides only tantalizing clues as to the *mechanism* by which dinitrogen is reduced. One of the main questions is whether molybdenum or iron, or perhaps both metals at different stages, are involved in binding dinitrogen and partially reduced (N<sub>2</sub>H<sub>x</sub>) species.

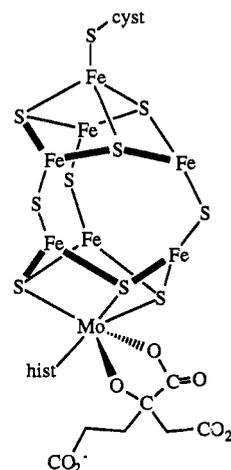
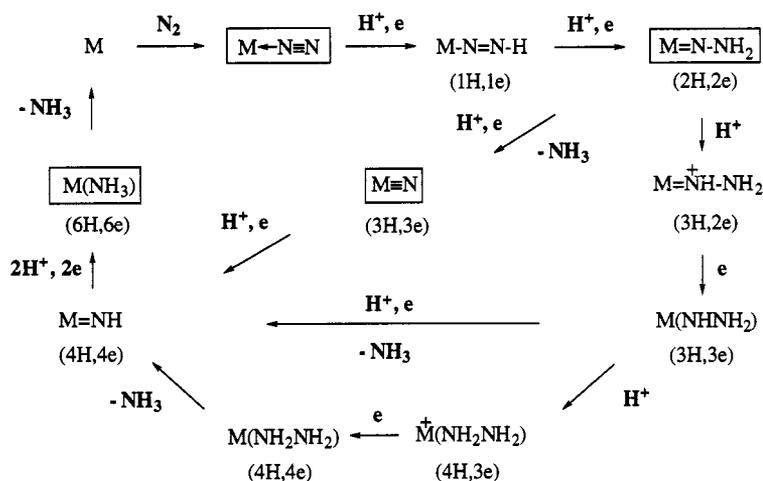


Fig 1. The Nitrogenase Core

A much-needed review of advances in the chemistry of dinitrogen complexes has appeared recently (ref. 6). Dinitrogen complexes are now known for all metals in groups 4 through 10 with the exception of palladium and platinum. Dinitrogen is most often found bound "end-on", but  $\mu$ -N<sub>2</sub> and multimetallic (e.g., M<sub>4</sub>N<sub>2</sub>) are also well-documented. A huge variety of "ancillary" ligands are found in dinitrogen complexes, from ammonia itself (as in [Ru(NH<sub>3</sub>)<sub>5</sub>(N<sub>2</sub>)]<sup>2+</sup>) (ref. 1), to phosphines (as in *trans*-Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>) (ref. 7), cyclopentadienyl ligands (as in [ZrCp\*<sub>2</sub>(N<sub>2</sub>)]<sub>2</sub>( $\mu$ -N<sub>2</sub>)) (ref. 8), and more recently, sulfur ligands such as the sulfur macrocycle, Me<sub>8</sub>[16]aneS<sub>4</sub>, in *trans*-Mo(N<sub>2</sub>)<sub>2</sub>(Me<sub>8</sub>[16]aneS<sub>4</sub>) (ref. 9). Significant advances have

been made in our understanding of reactions of bound  $N_2H_x$  ligands, especially  $[NNH_2]^{2-}$  ligands in molybdenum or tungsten  $M(dppe)_2$  complexes (ref. 6), and in what might be called "high oxidation state" dinitrogen chemistry, in which the metal (e.g., Mo or W) can be found in its highest possible oxidation state at some stage during a hypothetical dinitrogen reduction. The latter is the primary subject in this lecture.

Proposals for the reduction of dinitrogen to ammonia at a single metal (without a concomitant dihydrogen cycle) are shown in Scheme 1. Isolable transition metal complexes that contain the hydrazido(1-) ligand  $[M(NHNH_2)]$ , hydrazine  $[M(NH_2NH_2)]$ , or the parent imido ligand ( $M=NH$ ), are relatively rare compared to  $M(N_2)$ ,  $M=NNH_2$ ,  $M\equiv N$ , and  $M(NH_3)$  complexes. There is still considerable debate as to how dinitrogen might be reduced *most* readily. It is generally agreed that the most likely intermediate common to all *monometallic* pathways is a hydrazido(2-) complex,  $M=N-NH_2$ . Formation of a nitrido intermediate constitutes an increase in oxidation state of the metal by three, whereas for all other intermediates the metal oxidation state is increased by one or two.



Scheme 1. Proposed mechanisms of reduction of dinitrogen at a single metal center.

In contrast, the catalytic reduction of hydrazine to ammonia (a 2 proton, 2 electron process) is operationally simpler, and in fact has been observed in  $Cp^*MMe_3$  ( $M = Mo$  or  $W$ ;  $Cp^* = \eta^5-C_5Me_5$ ) systems (ref. 10, 11, 12), and more recently in systems that involve  $MoFe_3S_4$  catalysts (ref. 13, 14). It has long been known that hydrazine can disproportionate to ammonia and dinitrogen, and indeed  $[Ru(NH_3)_5(N_2)]^{2+}$  (ref. 1) was first prepared in a reaction that employed hydrazine.

An interesting question is to what degree the wide range of oxidation states available to Mo and W is an asset in binding and reducing dinitrogen in a controlled manner. Perhaps the simplest question to begin with is what is the minimal  $d^x$  configuration that would allow dinitrogen to be bound to a metal to give a dinitrogen complex in some significant concentration? "High oxidation state" dinitrogen chemistry actually has been in the literature for several years, although most has appeared in the past ten year period. With few exceptions (the most visible being  $[Zr(\eta^5-C_5Me_5)_2(N_2)]_2(\mu-N_2)$  (ref. 8, 15)), dinitrogen complexes of metals that have the  $d^2$  configuration are all  $M_2(\mu-N_2)$  complexes. Examples of structurally characterized  $M_2(\mu-N_2)$  complexes in group 5 include  $[TaCl_3(PBzPh_3)(THF)]_2(\mu-N_2)$  (ref. 16),  $[Ta(S-2,6-C_6H_3-i-Pr)_2_3(THF)]_2(\mu-N_2)$  (ref. 17),  $[Ta(O-2,6-C_6H_3-i-Pr)_2_3(THF)]_2(\mu-N_2)$  (ref. 17),  $[V(CH_2CMe_3)_3]_2(\mu-N_2)$  (ref. 18),  $[V(N-i-Pr)_2]_3(\mu-N_2)$  (ref. 19), and  $[Nb(NCy_2)_3]_2(\mu-N_2)$  (ref. 20). In group 6 examples include  $[Cp^*WMe_3]_2(\mu-N_2)$  (ref. 21),  $[Cp^*MoMe_3]_2(\mu-N_2)$  (ref. 22),  $[Cp^*MoMe_3]_2(\mu-N_2)[Cp^*WMe_3]$  (ref. 22),  $[Cp^*WMe_2(S-2,4,6-C_6H_2Me_3)]_2(\mu-N_2)$  (ref. 23), and  $[Cp^*WMe_2(OC_6F_5)]_2(\mu-N_2)$  (ref. 23).  $M_2(\mu-N_2)$  complexes in which M is in group 5 or 6 are characterized by long N-N (~1.28 Å) and short M-N (~1.80 Å) bonds, consistent with oxidation of each metal by two electrons, i.e., formation of "hydrazido(4-)" species,  $M=N=N=M$ , containing a linear, highly conjugated M-N-N-M  $\pi$  system. The conjugated  $\pi$  system in  $M=N=N=M$  species contribute to their relatively high stability and low reactivity. Attempts to protonate the dinitrogen in  $[Cp^*WMe_3]_2(\mu-N_2)$  in fact yielded methane and  $[Cp^*WMe_2X]_2(\mu-N_2)$  species where  $X = Cl$ , triflate,  $OC_6F_5$ ,  $SC_6F_5$ , or  $O_2CC_6F_5$  (ref. 23). While it seems clear that the  $d^2$  configuration is sufficient in group 5 to form an initial monometallic dinitrogen complex, and ultimately  $M_2(\mu-N_2)$  complexes, it is not

clear in group 6. For example the reduction of  $\text{Cp}^*\text{WMe}_3(\text{OTf})$  under dinitrogen to give  $\text{Cp}^*\text{Me}_3\text{W}=\text{N}-\text{N}=\text{WCp}^*\text{Me}_3$  (ref. 23) might involve a two electron reduction to give the  $d^3$  species, " $[\text{Cp}^*\text{Me}_3\text{W}]^-$ ", which reacts with dinitrogen to give " $[\text{Cp}^*\text{Me}_3\text{W}(\text{N}_2)]^-$ ", which subsequently reacts with  $\text{Cp}^*\text{WMe}_3(\text{OTf})$  to yield the observed product.

Reduction of several group 6  $\text{M}_2(\mu\text{-N}_2)$  complexes in the presence of a mild acid yields almost the theoretical amount of ammonia (1 equiv per M), but negligible hydrazine (ref. 24). The mechanism of splitting  $\text{N}_2$  and the nature of the resulting transition metal species are not known. However, since monomeric species such as  $\text{Cp}^*\text{Me}_3\text{W}=\text{NNH}_2$  and  $[\text{Cp}^*\text{Me}_3\text{Mo}(\eta^2\text{-N}_2\text{H}_4)]^+$  react under the same conditions to yield almost two equivalents of ammonia, two metals probably are not required. Furthermore, the observation that  $[\text{Cp}^*\text{Me}_3\text{W}(\eta^2\text{-N}_2\text{H}_4)]^+$  is reduced by one electron to give  $\text{Cp}^*\text{Me}_3\text{W}=\text{NH}$  and ammonia in virtually quantitative yield, along with the fact that hydrazine can be reduced relatively efficiently by  $[\text{Cp}^*\text{Me}_3\text{W}(\eta^2\text{-N}_2\text{H}_4)]^+$  plus a source of electrons and protons gave rise to the proposition that a single metal site is sufficient to split the N-N bond, that  $\eta^2$ -hydrazine complexes are crucial intermediates in the N-N bond splitting reaction, and that "hydrazido(4-)" species are thermodynamic sinks that probably should be avoided in a dinitrogen reduction system.

The frontier orbitals in  $\text{MCp}^*\text{Me}_3$  species consist of two nondegenerate  $\pi$  orbitals perpendicular to one another, and a  $\sigma$  orbital pointing in the same direction. The desire to explore other environments in which a " $2\pi, 1\sigma$ " set of frontier orbitals is available led to the synthesis of triamidoamine ( $[\text{RNCH}_2\text{CH}_2]_3\text{N}^{3-}$ ) complexes (Fig. 2). Main group compounds containing trialkoxoamine ligands are better known than compounds containing triamidoamine ligands (ref. 25), and transition metal complexes containing triamidoamine ligands were unknown four or five years ago. The syntheses of  $(\text{Me}_3\text{SiNHCH}_2\text{CH}_2)_3\text{N}$  (ref. 26) and its pentane-soluble trilithium salt (ref. 27) straightforwardly and on a large scale from inexpensive tris(2-aminoethyl)amine (tren) made the rapid development of transition metal triamidoamine chemistry possible. White, crystalline  $(\text{C}_6\text{F}_5\text{NHCH}_2\text{CH}_2)_3\text{N}$  is another substituted tren that can be prepared in excellent yield (by nucleophilic attack on hexafluorobenzene) (ref. 28). The fact that one of the linear combinations of three p orbitals on the equatorial nitrogen atoms is nonbonding with respect to the metal allows  $[(\text{RNHCH}_2\text{CH}_2)_3\text{N}]^{3-}$  ligands to donate a maximum of 12 electrons to a metal.

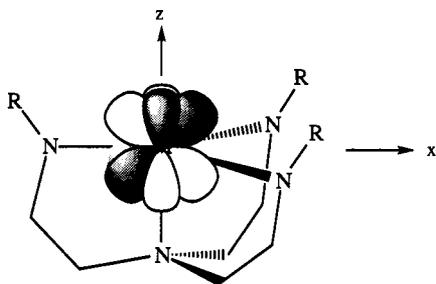


Fig. 2. The  $d_{xz}$ ,  $d_{yz}$ , " $d_{z^2}$ " frontier orbitals in a triamidoamine complex.

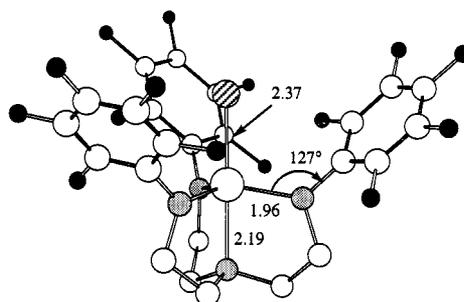
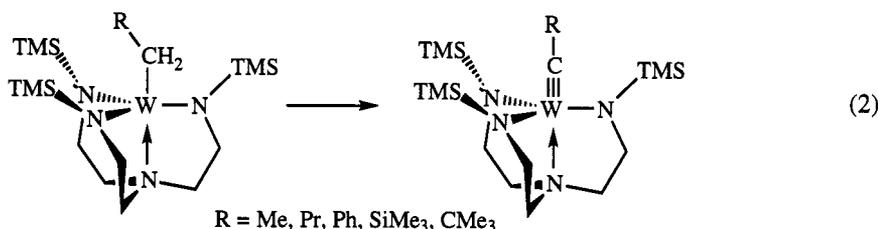
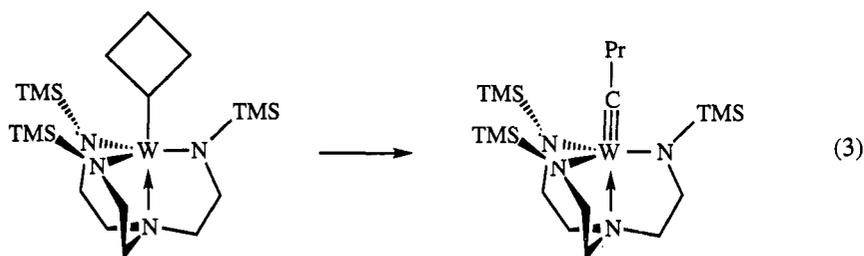


Fig. 3. The structure of  $[(\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2)_3\text{N}]\text{MoCl}$ .

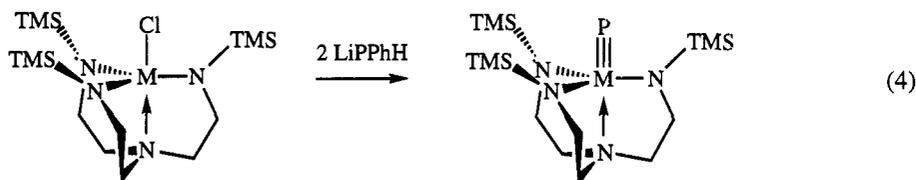
The first entries into group 6 chemistry consisted of reactions between  $\text{MCl}_4$  and  $\text{Li}_3[\text{N}_3\text{N}]$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ;  $[\text{N}_3\text{N}] = [(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]$ ) or mixtures of  $\text{NEt}_3$  and  $\text{H}_3[\text{N}_3\text{NF}]$  ( $[\text{N}_3\text{NF}] = [(\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2)_3\text{N}]$ ). The pseudotrigonal bipyramidal structures of  $[\text{N}_3\text{N}]\text{MoCl}$  (ref. 29) and  $[\text{N}_3\text{NF}]\text{MoCl}$  (Fig 3, ref 28) are similar, with  $\text{Mo}-\text{N}_{\text{equatorial}}$  bond lengths of 1.96-1.98 Å and  $\text{Mo}-\text{N}_{\text{axial}}$  bond lengths of 2.18-2.19 Å. The three substituents on the equatorial nitrogens create a three-fold symmetric pocket in which the axial chloride sits. Such  $d^2$  species are paramagnetic by virtue of the degeneracy of the  $d_{xz}$  and  $d_{yz}$  orbitals.



Some of the first experiments with  $[\text{N}_3\text{N}]\text{MCl}$  species consisted of alkylation reactions.  $[\text{N}_3\text{N}]\text{MoCl}$  can be alkylated to produce a variety of paramagnetic alkyl complexes, but  $[\text{N}_3\text{N}]\text{WMe}$  is the only alkyl complex of tungsten than can be observed and it is relatively unstable. All other tungsten alkyl complexes decompose in a variety of reactions that involve formal oxidation of the metal. Examples are shown in equations 2 and 3.



The obvious ease of formation and stability of the metal-carbon bond suggested that triple bonds to other elements might also be favorable. Indeed terminal phosphido complexes of both Mo and W can be prepared as shown in equation 4 ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) (ref. 30). The reaction is proposed to proceed via intermediate diamagnetic  $[\text{N}_3\text{N}]\text{M}(\text{PPh})$  species, the Mo version of which has been characterized



crystallographically. An X-ray study of  $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$  shows it to be a monomeric three-fold symmetric species in which the  $\text{W}\equiv\text{P}$  bond length is 2.16 Å. The magnitude of the coupling of P ( $\delta = 1080$  ppm) to W is unusually low (136 Hz), considering that W-P coupling even in simple  $\text{PR}_3$  complexes is often several hundred hertz. An analogous reaction between  $[\text{N}_3\text{N}]\text{MCl}$  and  $\text{LiAsHPh}$  gave  $[\text{N}_3\text{N}]\text{M}\equiv\text{As}$  species. An X-ray study of the Mo species (Fig. 4) showed the  $\text{Mo}\equiv\text{As}$  bond length to be 2.25 Å. Both  $[\text{N}_3\text{N}]\text{W}\equiv\text{P}$  and  $[\text{N}_3\text{N}]\text{W}\equiv\text{As}$  can be alkylated to give cationic linear phosphinidene and arsinidene complexes, respectively. An X-ray study of  $\{[\text{N}_3\text{N}]\text{W}=\text{AsMe}\}^+\text{OTf}^-$  showed the  $\text{W}=\text{As}$  bond length to be 2.25 Å (Fig. 5), the same as the  $\text{Mo}\equiv\text{As}$  bond length in  $[\text{N}_3\text{N}]\text{Mo}\equiv\text{As}$ . A molybdenum terminal phosphido complex has also been prepared from the reaction between  $\text{Mo}[\text{N}(\text{t-Bu})\text{Aryl}]_3$  and white phosphorus (ref. 31).

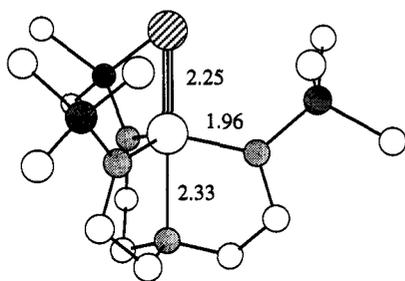


Fig. 4. X-ray Structure of  $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{Mo}\equiv\text{As}$ .

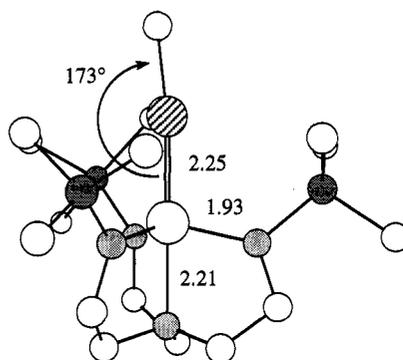
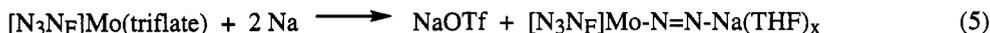


Fig. 5. X-ray Structure of  $\{[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{W}=\text{AsCH}_3\} \text{OTf}$ .

The discovery of Mo and W triamidoamine complexes made it possible to test the utility of a tetradentate *trianionic* ligand framework in dinitrogen chemistry, and to compare it with a *tetraanionic* ( $\text{MCp}^*\text{Me}_3$ ) framework, both of which have a  $2\pi, 1\sigma$  set of frontier orbitals. We anticipated that we might be able to reduce dinitrogen and break the N-N bond in some  $\text{N}_2\text{H}_x$  species to yield a  $[\text{N}_3\text{N}]\text{M}\equiv\text{N}$  species,

and that subsequent protonation and reduction of the nitrido species could regenerate the initial complex, thereby completing a catalytic cycle. The reduction of  $[\text{N}_3\text{N}_\text{F}]\text{Mo}(\text{triflate})$  by sodium amalgam (one equivalent) led to the formation of purple  $\{[\text{N}_3\text{N}_\text{F}]\text{Mo}\}_2(\mu\text{-N}_2)$  (ref. 28), which is paramagnetic by virtue of 10 electrons being present in the linear  $\text{Mo-N=N-Mo}$   $\pi$  system. This species is reduced readily to yield the same diamagnetic complex as is formed from  $[\text{N}_3\text{N}_\text{F}]\text{Mo}(\text{triflate})$  and two equivalents of sodium amalgam, as shown in equation 5. Therefore it is believed that the low spin version of " $\{[\text{N}_3\text{N}_\text{F}]\text{Mo}\}_2$ " is actually



the species that binds dinitrogen most rapidly, as the low spin  $e^4a^0$  orbital arrangement is optimal for backbonding to dinitrogen, and that  $[\text{N}_3\text{N}_\text{F}]\text{Mo-N=N-Na}(\text{THF})_x$  then reacts with  $[\text{N}_3\text{N}_\text{F}]\text{MoCl}$  to give  $\{[\text{N}_3\text{N}_\text{F}]\text{Mo}\}_2(\mu\text{-N}_2)$ . An alternative possibility is that  $d^3$  " $[\text{N}_3\text{N}_\text{F}]\text{Mo}$ " binds dinitrogen, and " $[\text{N}_3\text{N}_\text{F}]\text{Mo}(\text{N}_2)$ " is further reduced to give  $[\text{N}_3\text{N}_\text{F}]\text{Mo-N=N-Na}(\text{THF})_x$ . An X-ray study of the diamagnetic product of the reaction between  $[\text{N}_3\text{N}_\text{F}]\text{Mo-N=N-Na}(\text{THF})_x$  and  $i\text{-Pr}_3\text{SiCl}$  showed it to be the diazenido complex,  $[\text{N}_3\text{N}_\text{F}]\text{Mo-N=N-Si}(i\text{-Pr})_3$ , in which the N-N bond length is 1.22 Å, the Mo-N $_\alpha$  bond length is 1.777 Å, and the Mo-N-N angle is 171° (Fig. 6). The isolation of a two electron reduction product of dinitrogen in a relatively well-controlled reaction is extremely unusual. The isolation of  $\text{M=NNH}_2$  complexes, which are  $4e, 2\text{H}^+$  reduction products, has been much more common than isolation of diazenido complexes.

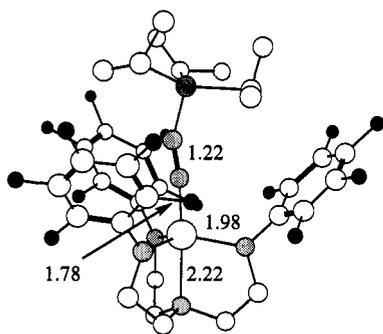


Fig. 6. The structure of  $[\text{N}_3\text{N}_\text{F}]\text{Mo-N=N-Si}(i\text{-Pr})_3$ .

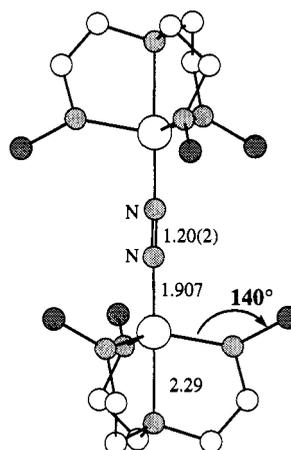
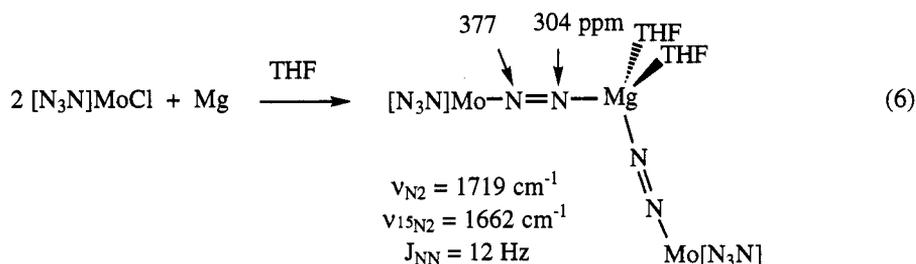


Fig. 7. The structure of  $\{[\text{N}_3\text{N}_\text{F}]\text{Mo}\}_2(\mu\text{-N}_2)$ .

Relatively early in the study of Mo chemistry it was found that an attempt to prepare " $[\text{N}_3\text{N}']\text{Mo}$ " ( $[\text{N}_3\text{N}'] = [(t\text{-Bu})\text{Me}_2\text{SiNCH}_2\text{CH}_2)_3\text{N}$ ) by treating  $\text{MoCl}_3(\text{THF})_3$  with  $\text{Li}_3[\text{N}_3\text{N}']$  led to the purple paramagnetic complex,  $\{[\text{N}_3\text{N}']\text{Mo}\}_2(\mu\text{-N}_2)$ , in low and irreproducible yield. An X-ray study (shown in Fig. 7 without Si substituents) revealed the  $\{[\text{N}_3\text{N}']\text{Mo-N=N-Mo}[\text{N}_3\text{N}']\}$  species to have an N-N bond length of 1.20 Å and an Mo-N bond length of 1.907 Å. A startling feature of the structure are the Mo-N-Si bond angles of 140°, which are approximately 15° larger than found in the vast majority of structures of  $[(\text{RNCH}_2\text{CH}_2)_3\text{N}]$  complexes, and which suggest a considerable degree of repulsive interaction between the two ends of the  $\text{Mo-N=N-Mo}$  molecule. This seems surprising in view of the fact that the link between the metals consists solely of dinitrogen, and suggests that hypothetical  $d^3$   $[\text{N}_3\text{N}']\text{Mo}(\text{N}_2)$  is likely to be a relatively high energy species, or that there is some kinetic barrier to loss of dinitrogen. Neither this  $\text{Mo}_2(\mu\text{-N}_2)$  species, nor what we presume to be the  $\text{C}_6\text{F}_5$  analog mentioned above, appears to cleave into two  $\text{Mo}\equiv\text{N}$  species, a formal 6 electron cleavage of dinitrogen by two  $d^3$  Mo fragments, a symmetric and attractively efficient method of cleaving dinitrogen that had never been observed.

The chemistry of " $[\text{N}_3\text{N}]\text{Mo}$ ," formed by reduction of  $[\text{N}_3\text{N}]\text{MoCl}$ , turns out to be rich, although preliminary results suggest that the system is complex, and that several paramagnetic species are formed (ref. 32). For example, reduction of  $[\text{N}_3\text{N}]\text{MoCl}$  in THF by one equivalent of sodium naphthalenide gives (*inter alia*) the paramagnetic  $d^3$  dinitrogen complex,  $[\text{N}_3\text{N}]\text{Mo}(\text{N}_2)$  ( $\nu_{\text{N}_2} = 1917 \text{ cm}^{-1}$ ), as confirmed in an X-ray study. In contrast, reduction of  $[\text{N}_3\text{N}]\text{MoCl}$  with magnesium under dinitrogen gave the diamagnetic

"magnesiodiazenido" complex shown in equation 6. Even under dinitrogen several other as yet unidentified complexes, are formed. It is believed that some of them arise from high spin or low spin "[N<sub>3</sub>N]Mo" in competition reactions. Further reaction of {[N<sub>3</sub>N]Mo(N<sub>2</sub>)<sub>2</sub>Mg(THF)<sub>2</sub>} with Me<sub>3</sub>SiCl yielded diamagnetic [N<sub>3</sub>N]Mo-N=N-SiMe<sub>3</sub>.



The dinitrogen chemistry of Mo took an unexpected turn recently with the discovery that a d<sup>3</sup>, trigonally symmetric triamido complex of Mo, Mo[N(t-Bu)Aryl]<sub>3</sub>, will react with dinitrogen to give paramagnetic purple {Mo[N(t-Bu)Aryl]<sub>3</sub>}<sub>2</sub>(μ-N<sub>2</sub>), and that {Mo[N(t-Bu)Aryl]<sub>3</sub>}<sub>2</sub>(μ-N<sub>2</sub>) will decompose cleanly to two equivalents of [N(t-Bu)Aryl]<sub>3</sub>Mo≡N in a first order reaction (ref. 33). This decomposition reaction is formally a 6 electron cleavage of dinitrogen with the 6 electrons coming from two Mo centers. It is surprising that [N(t-Bu)Aryl]<sub>3</sub>Mo(N<sub>2</sub>) has not yet been observed (cf. [N<sub>3</sub>N]Mo(N<sub>2</sub>)), and that [N<sub>3</sub>N]Mo-N=N-Mo[N<sub>3</sub>N] and [N<sub>3</sub>N<sub>F</sub>]Mo-N=N-Mo[N<sub>3</sub>N<sub>F</sub>] species do not decompose to known [N<sub>3</sub>N]Mo≡N and [N<sub>3</sub>N<sub>F</sub>]Mo≡N species, respectively. A theoretical study (ref. 34) suggests that the presence of a donor in the triamidoamine complexes creates a situation in which the cleavage reaction is endothermic. The fact that {Mo[N(t-Bu)Aryl]<sub>3</sub>}<sub>2</sub>(μ-N<sub>2</sub>) is paramagnetic, while [N(t-Bu)Aryl]<sub>3</sub>Mo≡N is diamagnetic has led to the suggestion that a distorted, diamagnetic form of {Mo[N(t-Bu)Aryl]<sub>3</sub>}<sub>2</sub>(μ-N<sub>2</sub>) is a required intermediate in the cleavage reaction. Further work will clearly be required in order to elucidate some of the more subtle features of 6 electron dinitrogen cleavage reactions of this general nature.

Although Mo and W high oxidation state dinitrogen chemistry is still in its infancy compared to dinitrogen chemistry involving lower oxidation state Mo and W species (ref. 6), several features of high oxidation state Mo and W dinitrogen chemistry discovered so far suggest that M(III) through M(VI) oxidation states can all be involved in a hypothetical dinitrogen reduction process. Although the "tetranionic" MCp\*Me<sub>3</sub> and the "trianionic" triamidoamine systems both contain 2π,1σ frontier orbital sets, there are important differences between the two. For example, side-on bonded intermediates can form more readily in the more open coordination sphere of a MCp\*Me<sub>3</sub> system, while in the triamidoamine system we have the opportunity to limit formation of μ-hydrazido(4-) species, as well as side-on bonded intermediates, and therefore to explore cleavage of the N-N bond via linear (diazenido(2-)) and nitrido intermediates. We hope to continue to synthesize new types of (often multidentate) ligands that will enforce coordination high oxidation state Mo and W geometries that are conducive to the binding and reduction of dinitrogen, and thereby to control the steric and electronic characteristics of the site at which dinitrogen binds.

Although we cannot yet utilize dinitrogen in a transition metal-catalyzed reaction in the manner that we utilize other small molecules, an enormous amount of progress has been made in the last several years. We now know that it should be possible to design a system in which dinitrogen can be reduced catalytically using electrophiles other than protons, e.g., the reduction of dinitrogen in the presence of Me<sub>3</sub>SiCl to give N(SiMe<sub>3</sub>)<sub>3</sub>. In fact this type of reaction already has been accomplished with some success (up to 25 turnovers) using Mo phosphine systems as catalysts (ref. 6), and there is every reason to suspect that an efficient process of this general type will be discovered soon.

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