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Catalytic Reduction of Dinitrogen to Ammonia at a Single Molybdenum Center

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move terminal unaligned sequence from the output. The alignments were shuffled 10,000 independent times using the shuffle utility program in SQUID (www.genetics.wustl.edu/eddy/software/#squid). Runs of identical sequence aligned in all four species in the real alignments and the shuffled alignments were extracted and counted.
39. Six-mers are not statistically significant in the six-way comparisons and were therefore not tabulated; *n*-mers longer than 10 nt are quite rare in these comparisons.
40. Sequences of 100 shuffled multiple intergenic sequence alignments of sensu stricto species were extracted and combined with intergenic sequences from the two distantly related species. *n*-oligomers present in all species were identified in the real promoter sets and compared with those present in the shuffled data sets.
41. For example, essentially all of the 10-mers conserved in the sensu stricto species' sequences (considered because there is a high degree of confidence that they are not chance occurrences) that occur frequently in the genome (considered because those are likely to be functional) are known: 28 of 32 (present in alignments of sequences upstream of at least seven different genes) are accounted for by the following previously identified sequence motifs: eight variations of the PAC motif, seven variations of the RRPE motif, seven variations of a Ume6 binding site, two variations of the PACE motif (Rpn4 binding site), two variations of an Mbp1 binding site, and one each of the binding sites for Ndt80 and Reb1; the remaining four most frequent *n*-mers were simple A+T-rich sequences. Similarly, 94 of the 160 conserved 10-mers identified in the six-way sequence comparisons correspond to known sequence motifs (table S4), all of which occur upstream of genes known or likely to be regulated by the factor that binds to them. Of the remaining 66 conserved sequence motifs, 46 are A+T-rich, and 11 are immediately upstream of the translation initiation codon of genes encoding ribosomal proteins and thus may be translational regulatory sequences. This leaves only nine that are reasonable candidates for new regulatory sequences, four of which are conserved in the sequences upstream of several genes of similar function (the motifs marked with an asterisk in table S4).
42. We were surprised to find that only 15.7% of the 3523 multiple alignments of sensu stricto species promoters contain one of the seven sequences that have TATA element function (TATAA, TATATA, TATTTA, CATTTA, TTTAAT, TAATAA, TATAA) (*52*) conserved and aligned within 250 bp of the translational start codon. Even if the stringency of the search criteria is relaxed to allow for unaligned TATA boxes, promoters containing this sequence element are still in the minority: Only 42.8% of the sensu stricto species' promoters contain any one of the seven TATA sequences (*52*) anywhere within 250 bp of the translational start codon in all four orthologs. Furthermore, 142 promoters (4%) do not contain a TATA element in any of the four sensu stricto species. Thus, it appears that TATA-containing promoters are the minority in *S. cerevisiae*.
43. Because many of conserved *n*-mers are longer than the typical 6 to 8 bp that are required for a transcription factor to bind to DNA, we extracted all unique 6- to 8-mers from the longer conserved *n*-mers to test these for functional enrichment and coherent expression. Each unique *n*-mer had to be present in at least five different intergenic regions to test for the functional enrichment or coherent expression.
44. Functional enrichment was based on the Munich Information Center for Protein Sequences (MIPS) classification of *S. cerevisiae* genes. Functional enrichment and the associated *P* values were calculated as in (*53*).
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47. Expression coherence was calculated as described previously (*54*). Expression coherence was calculated for cell cycle (*55*), meiosis (*56*), methyl methanesulfonate (MMS) damage (*57*), sporulation (*58*), stress response (*59*), DNA damage (*60*), mitogen-activated protein kinase (MAPK) (*61*), and mitochondrial dysfunction (*62*) data sets.
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49. Using high-quality weight matrices for the binding sites of 23 transcription factors whose consensus binding sites are known, we identified: (i) all the occurrences of a particular binding site in the intergenic regions of *S. cerevisiae* using Patser (*34*), and then (ii) those occurrences that are conserved in the orthologous promoters in the other *Saccharomyces* species and/or are aligned in the CLUSTALW alignments of intergenic sequences of sensu stricto species. Sets of intergenic regions that bind to a particular DNA binding protein come from the data of Lee *et al.* at *P* value < 0.001 (*48*). The motif alignments for known transcription factor binding sites were generated by applying AlignACE (*33*) on the appropriate MIPS functional category.
50. Thirty-six *n*-mers are upstream of genes that are functionally enriched [18 from the sensu stricto sequence alignments and 18 from the six-way sequence comparisons (Table 1)], 52 *n*-mers are identified by coherent expression [39 from the sensu stricto sequence alignments and 13 from the six-way sequence comparisons (Table 2)], and 13 are from upstream of genes bound by a particular transcription factor [nine from the sensu stricto sequence alignments and four from the six-way sequence comparisons (Table 3)]. Twenty-two *n*-mers are found in more than one data set, leaving 79 conserved sequence motifs linked to a function.
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63. We thank E. Louis (University of Leicester) for invaluable advice on the *Saccharomyces* phylogeny, and for providing yeast strains; our Washington University colleagues M. Brent, J. Buhler, S. Eddy and members of his lab, S.-W. Ho, and G. Stormo, as well as E. Siggia (Rockefeller University) and R. Young (MIT) for advice and insightful comments on the manuscript. This project was funded by a grant from NIH (RO1 GM63803).

Supporting Online Material
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Figs. S1 to S3
Tables S1 to S4

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REPORTS

Catalytic Reduction of Dinitrogen to Ammonia at a Single Molybdenum Center

Dmitry V. Yandulov and Richard R. Schrock*

Dinitrogen (N_2) was reduced to ammonia at room temperature and 1 atmosphere with molybdenum catalysts that contain tetradentate $[HIPTN_3N]^{3-}$ triamidoamine ligands {such as $[HIPTN_3N]Mo(N_2)$, where $[HIPTN_3N]^{3-}$ is $[\{3,5\text{-}(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3NCH_2CH_2\}_3N]^{3-}$} in heptane. Slow addition of the proton source $[\{2,6\text{-lutidinium}\}\{BAr'_4]$, where Ar′ is $3,5\text{-}(CF_3)_2C_6H_3$] and reductant (decamethyl chromocene) was critical for achieving high efficiency (~66% in four turnovers). Numerous x-ray studies, along with isolation and characterization of six proposed intermediates in the catalytic reaction under noncatalytic conditions, suggest that N_2 was reduced at a sterically protected, single molybdenum center that cycled from Mo(III) through Mo(VI) states.

The reduction of dinitrogen (N_2) to ammonia (NH_3) by various nitrogenase enzymes is one of the most fascinating transition metal–catalyzed reactions in biology (*1*–*12*). Six electrons and six protons produce two equivalents of NH_3 per N_2 in discrete steps at 1 atm of ambient pressure and mild temperatures, with the aid of one or more transition metal centers (Fe, Mo, or V) within those nitrogenases. Although nitrogenases have been studied for decades (primarily the Fe/Mo nitrogenase), it is still not known today how they accomplish this feat.

With the discovery of the first N_2 complex of a transition metal in 1965 (*13*) came the hope that many N_2 complexes could be prepared and that an abiological catalytic reduction of N_2 at ambient pressure and temperature with protons and electrons at a well-defined transition-metal site would be forthcoming (*14*–*22*). Hundreds of N_2 complexes are now known, but only a few reports of the catalytic reduction of N_2 to NH_3 have appeared (*18*, *23*–*27*). No reduction of N_2 has been accomplished with a relatively mild reducing agent, and no system has revealed many details of the N_2 reduction steps. The

most mechanistically elaborated system that contains N_2 and reduced-N_2 ligands has been a series of W(0) and Mo(0) phosphine complexes (*14*–*16*, *21*). Although examples of almost all of the proposed intermediates for reduction of N_2 at a single metal center have been isolated, no catalytic reaction to give NH_3 [in the presence of protons and electrons (*28*)] that uses these relatively well-defined systems has been established since they were discovered more than 30 years ago.

We have been studying the chemistry of N_2 complexes for two decades, especially those of Mo and W (*29*), focusing on chemistry that we believe is relevant to N_2 reduction and that involves these metals in relatively high oxidation states [M(III) to M(VI)]. Recently, we prepared and began to explore the chemistry of Mo complexes that contain a triamidoamine ($[(ArNCH_2CH_2)_3N]^{3-}$ is $[ArN_3N]^{3-}$, where Ar is aryl) ligand (*30*, *31*). In order to prevent formation of what we believe to be relatively stable and unreactive bimetallic $[ArN_3N]$Mo-N=N-Mo$[ArN_3N]$ complexes, maximize steric hindrance in a monomeric species, and provide increased solubility of the complexes, we synthesized species that contain a $[HIPTN_3N]^{3-}$ ligand, where HIPT (hexa-iso-propyl-terphenyl) is 3,5-(2,4,6-i-$Pr_3C_6H_2$)$_2C_6H_3$ (Scheme 1) (*32*, *33*). Starting with **Mo**Cl (where **Mo** is $[HIPTN_3N]$Mo), we showed that we could prepare many intermediates in a hypothetical reduction of N_2, all of which contain the same $[HIPTN_3N]^{3-}$ ligand. These intermediates include paramagnetic **Mo**(N_2) (**1**); diamagnetic **Mo**-N=N-H (**2**); diamagnetic {**Mo**=N-NH_2}{BAr'_4}, where Ar′ is 3,5-$(CF_3)_2C_6H_3$ (**3**); diamagnetic **Mo**≡N (**4**); diamagnetic {**Mo**=NH}{BAr'_4} (**5**); and paramagnetic {**Mo**(NH_3)}{BAr'_4} (**6**). Extensive ^{15}N labeling studies, nuclear magnetic resonance (NMR) studies, and x-ray studies [of **1**, **4**, and **6** (*33*) and **2**, **3**, and **5** (*34*)] all reveal a trigonal pocket in which N_2 and its reduced products are protected to a marked degree by three 2,4,6-i-$Pr_3C_6H_2$ rings clustered around the pocket (Scheme 1). Compounds **1** through **6** are among the 13 or more that might take part in a catalytic reduction of end-on bound N_2 by the stepwise, alternating addition of six protons and six electrons (Fig. 1). The intermediates shown in Fig. 1, in which the oxidation state of the metal varies between Mo(III) and Mo(VI) (*29*), are analogous to those proposed originally by Chatt (*14*) for lower oxidation-state Mo and W phosphine complexes.

We also showed (*32*) that it is possible to prepare several compounds in high yield from others through the use of {2,6-lutidinium}{BAr'_4} as the proton source and cobaltocene as the electron source in C_6D_6. For example, the addition of 1.0 equivalent of {LutH}BAr'_4 and 2.0 equivalents of Co(η^5-$C_5H_5)_2$ ($CoCp_2$) in benzene to **Mo**(N_2) yields **Mo**-N=NH essentially quantitatively. [For $CoCp_2$, the reversible half-wave redox potential ($E^{0\prime}$) = –1.33 V versus $[FeCp_2]^{+/0}$ in CH_2Cl_2 (*35*).] This conversion is made possible by what is believed to be an initial protonation of an amido nitrogen [not the N_2 (*34*)] followed by an electron transfer, a type of proton-coupled electron transfer reaction (*36*). In the presence of 7.0 equivalents of {LutH}{BAr'_4} and 8.2 equivalents of $CoCp_2$, **Mo**(N_2) is converted in C_6D_6 into a mixture of compounds in which {**Mo**(NH_3)}{BAr'_4} is the major species (~60%). Although we found that {**Mo**(NH_3)}{BAr'_4} is not reduced to **Mo**(NH_3) by $CoCp_2$ in C_6D_6, {**Mo**(NH_3)}{BAr'_4} reacts with 3 equivalents of $CoCp_2$ in C_6D_6 to give an equilibrium mixture of {**Mo**(NH_3)}{BAr'_4} (90%) and **Mo**(N_2) (10%) after 18 hours in a sealed NMR tube. Therefore, it seemed plausible that an actual catalytic conversion of N_2 to NH_3 at a single metal center might finally be realized with a stronger reducing agent than $CoCp_2$, under the appropriate conditions.

Decamethylchromocene [Cr(η^5-$C_5Me_5)_2$, or $CrCp^*_2$] was chosen as the reducing agent on the basis of its demonstrated ability (in contrast to $CoCp_2$) to reduce {**Mo**(NH_3)}$^+$ completely to **Mo**(NH_3) in C_6D_6; $CrCp^*_2$ is a stronger reducing agent than $CoCp_2$ by 0.13 V in CH_3CN (*37*). However, initial experiments suggested that formation of **Mo**(N_2) from **Mo**(NH_3) under N_2 was relatively slow (minutes to hours). As expected, we found that $CrCp^*_2$ was oxidized rapidly by {LutH}{BAr'_4} in C_6D_6, in which {LutH}{BAr'_4} is soluble. Thus, it became apparent that, in order to achieve catalytic conversion of N_2 to NH_3 with any efficiency (in terms of electrons consumed), it would likely be necessary (i) to slow down the reaction between the proton source and the reducing agent relative to reactions that involve Mo species, and (ii) to allow sufficient time to convert **Mo**(NH_3) to **Mo**(N_2). Therefore, we felt that it would be most desirable to add {LutH}{BAr'_4} and $CrCp^*_2$ to the catalyst in solution at a slow, controllable rate, in order to maintain Mo intermediates in excess of both acid and reductant. The choice of heptane as the solvent ensured that the concentration of sparingly soluble {LutH}{BAr'_4} in solution would be low. (In contrast, all cationic **Mo** derivatives in this family that we have isolated, such as **3**, **5**, or **6**, as $BAr'_4{}^-$ salts, are soluble in alkane solvents.) The suspension was then stirred vigorously as a solution of $CrCp^*_2$ was added with a syringe pump, over a period of 6 hours. In order to be certain that all ammonia (in the gas phase, in solution, or as an ammonium salt) could be collected and measured accurately and with precision, we designed and constructed a self-contained glass reactor in which the reducing agent could be added by means of a magnetically driven syringe over a period of several hours. Great care was taken to purify solvents and reagents. We demonstrated that a reaction set up in a drybox in fact could be run outside the drybox with no significant change in result (*38*).

The results of several runs on the scale of 36 equivalents of $CrCp^*_2$ and 48 equivalents of {LutH}{BAr'_4} are listed in Table

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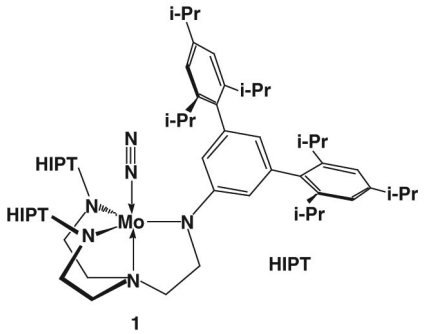

1

Scheme 1.

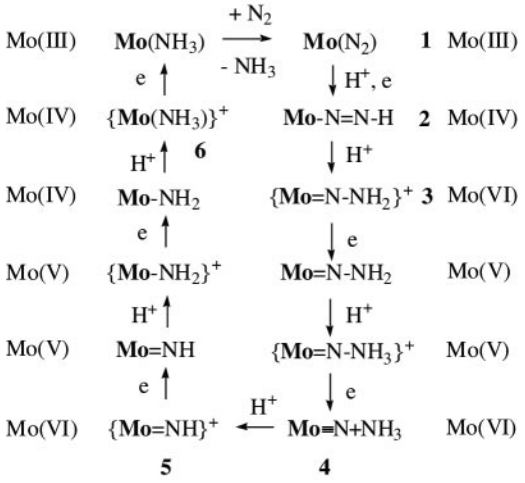

Fig. 1. Proposed intermediates in the reduction of dinitrogen at a $[HIPTN_3N]$Mo (**Mo**) center through the stepwise addition of protons and electrons.

1. Formation of 7.56 to 8.06 equivalents of NH_3 in the presence of four different Mo derivatives (**1**, **2**, **4**, or **6**; 16 runs total) suggests that NH_3 was formed catalytically with respect to Mo from N_2. In order to eliminate the remote possibility that the triamidoamine ligand and/or 2,6-lutidine or 2,6-lutidinium might serve as a nitrogen source for the NH_3, the reduction was carried out under $^{15}N_2$. The result was formation of 8.18 equivalents of $^{15}NH_4Cl$ with an ^{15}N isotopic enrichment that was indistinguishable from that of commercially available $^{15}NH_4Cl$ (>98% ^{15}N), according to its ^1H NMR spectrum in DMSO-d_6 (where DMSO is dimethyl sulfoxide) (Fig. 2). Addition of the reducing agent over 25 s (followed by stirring for 7 hours) resulted in a poorer yield of NH_3 (2.83 equivalents), which suggests that one or more side reactions, such as protonation of $CrCp^*_2$, takes precedence over N_2 reduction under these circumstances. Preliminary studies of the reduction of {**Mo**(NH_3)}{BAr'_4} under N_2 to give **Mo**(N_2) suggest that the slowest step in Fig. 1 is conversion of **Mo**(NH_3) to **Mo**(N_2), although the rate of addition of the reductant is believed to limit the rate of reduction in the experiments in which $CrCp^*_2$ is added over a period of 7 hours (Table 1). It is not yet known whether the reaction is limited to about four turnovers under the conditions we describe here or what species are present at the end of a reaction.

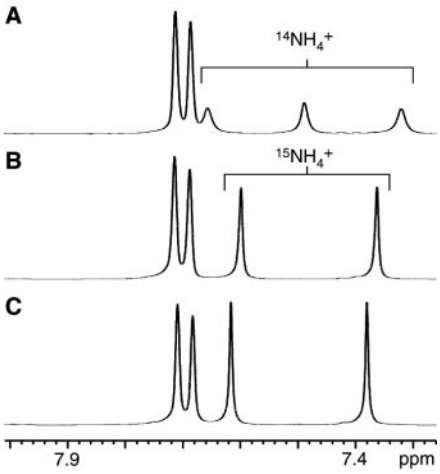

Fig. 2. ^1H NMR spectra (DMSO-d_6) of (**A**) the mixture of NH_4Cl and 2,6-LutHCl obtained from the reaction of **Mo**(N=NH) with 48 equivalents of {2,6-LutH}{BAr'_4} and 36 equivalents of $CrCp^*_2$ under an atmosphere of $^{14}N_2$, (**B**) the mixture obtained from the analogous reaction of **Mo**($^{15}N=^{15}NH$) under an atmosphere of $^{15}N_2$, and (**C**) authentic $^{15}NH_4Cl$ (>98% ^{15}N) in the presence of 2,6-LutHCl. ppm, parts per million.

To the best of our knowledge, the efficiencies (the yield of NH_3 relative to that expected by theory on the basis of reducing equivalents) of the most successful of these experiments (63 to 66%) are second only to that of Fe/Mo nitrogenase (75%). (Nitrogenases consume two or more reducing equivalents in side reactions that make H_2, although turnovers are essentially unlimited in nitrogenases in general.) Furthermore, the catalytic activity (with respect to Mo) is attained with the weakest reductant of all abiological systems that have been reported. [For $CrCp^*_2$, $E^{\circ\prime}$ can be estimated to be about –0.90 V versus the normal hydrogen electrode (NHE) (*35*); the reducing power of biological reducing agents is limited to about –0.46 V versus NHE (*2*). We consider it highly likely that N_2 is being reduced at a sterically protected, single Mo center and that the relevant oxidation states are Mo(III) to Mo(VI) (Fig. 1). In spite of x-ray studies that have focused attention on the seven-Fe cluster in Fe/Mo nitrogenase as the site of N_2 reduction (*12*), we believe that reduction of N_2 in Fe/Mo nitrogenase at the single Mo center, favored before the structure of Fe/Mo nitrogenase was elucidated through x-ray studies, again must be considered a strong possibility.

Table 1. The results of catalytic reduction of N_2. Unless otherwise indicated, all runs were done at 23° to 25°C and 1 atm of N_2, by dropwise addition with constant stirring of 10.0 mL of a solution of $CrCp^*_2$ in heptane (36 equivalents relative to Mo) at a rate of 1.7 ml per hour to a mixture of the Mo compound, 48 equivalents of {LutH}{BAr'_4} and 0.6 ml of heptane, followed by stirring for 1 hour. Ammonia was isolated as a mixture of solid NH_4Cl and 2,6-LutHCl and analyzed by the indophenol method (*38*–*40*). The theoretical yield is based on the amount of NH_3 possible with the reducing equivalents available. Numbers in parentheses in columns 2 and 4 are the standard deviations, σ. Equiv., equivalents; expt, experimental.

Mo compound	Equiv. NH_3 (expt/theory)	No. of runs	Yield NH_3, %
[$HIPTN_3N$]Mo(N_2) (**1**)	7.56 (11)/12	6*	63(1)
[$HIPTN_3N$]Mo(N=NH) (**2**)	7.73 (15)/12.33	4†	63(1)
[$HIPTN_3N$]Mo≡N (**4**)	7.97 (23)/12	3‡	66(2)
{[$HIPTN_3N$]Mo(NH_3)}{BAr'_4} (**6**)	8.06 (21)/12.67	3§	64(2)
[$HIPTN_3N$]Mo($^{15}N=^{15}NH$) under $^{15}N_2$	8.18/12.33	1‖	66
[$HIPTN_3N$]Mo(N_2)¶	2.83/12	1	24

*Two runs outside the drybox (7.54 and 7.62 equivalents), two runs inside (7.55 and 7.62 equivalents), and two runs inside in the dark (7.69 and 7.36 equivalents); average = 7.56 equivalents, σ = 0.11. †7.75, 7.93, 7.61, and 7.62 equivalents; average = 7.73, σ = 0.15. ‡8.22, 7.95, and 7.75 equivalents; average = 7.97, σ = 0.23. §8.08, 8.26, and 7.84 equivalents; average = 8.06, σ = 0.21. ‖>98% $^{15}NH_4Cl$ by ^1H NMR, as described in the text and Fig. 2. ¶$CrCp^*_2$ was added over a period of 25 s, followed by stirring for 7 hours.

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Supporting Online Material

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Materials and Methods
Fig. S1
References and Notes

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