Reduction of Dinitrogen to Ammonia Catalyzed by Molybdenum Diamido Complexes

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ABSTRACT: \( [\text{Ar}_2\text{N}_3]\text{Mo(N)}(\text{O-}t\text{-Bu}) \), which contains the conformationally rigid pyridine-based diamido ligand, \( [\text{Ar}_2\text{N}_3]\text{Mo(N)}(\text{O-}t\text{-Bu}) \), can be prepared from \( \text{H}_2[\text{Ar}_2\text{N}_3] \), butyllithium, and \( t\text{-BuO}_2\text{Mo(N)}(\text{Ar}_2\text{N}_3) \). \( \text{Ar}_2\text{N}_3 \) serves as a catalyst or precursor for the catalytic reduction of molecular nitrogen to ammonia in diethyl ether between −78 and 22 °C in a batchwise manner with \( \text{CoCp}_2 \) as the electron source and \( \text{Ph}_2\text{NH}_2\text{OTf} \) as the proton source. Up to 10 equiv of ammonia can be formed per Mo with a maximum efficiency in electrons of ~43%.

The catalytic reduction of molecular nitrogen to ammonia with protons and electrons under mild conditions was first demonstrated with a molybdenum catalyst that contains a tren-based triamidosamine (3−) ligand \((\text{N}([\text{CH}_2\text{CH}_2\text{N}-(\text{HIPT})])\text{Mo(N)}(\text{O}−t\text{-Bu}))\). The maximum oxidation state of molybdenum in the catalytic cycle is proposed to be Mo(VI) (in a nitrido complex), and the lowest is Mo(III) (in an ammonia or dinitrogen complex). Eight of the proposed 12 intermediates in a “distal” reduction of dinitrogen were prepared and characterized, and the proposed mechanism has been vetted through theoretical studies. The reducing agent is \( \text{CrCp}_2^* \) (decamethylchromocene), and the proton source is 2,6-LutidiiumBarf \( (\text{Barf} = \text{B}(3,5-(\text{CF}_3)\text{C}_6\text{H}_3)) \). The second reduction of molecular nitrogen under mild conditions was published in 2011. The catalyst precursor in this first publication in this series is a bimetallic Mo(0) complex that contains a neutral “PNP pincer” ligand \( ([\text{N}([\text{CH}_2\text{CH}_2\text{N}-(\text{HIPT})])\text{Mo(N)}(\text{O}−t\text{-Bu})]) \). The actual catalytic cycle is likely to involve monomeric intermediates such as Mo(V) nitrides, and several ligand variations have been explored. The third catalytic reduction of dinitrogen to ammonia is catalyzed by an iron complex in which the ligand scaffold is a tetradentate neutral trisphosphine “tripodal” ligand. Although the original conditions are not “mild” (KC₈ and \( \text{H}([\text{Et}_2\text{O}])\text{Barf} \) at −78 °C), it has been found recently that \( \text{CoCp}_2^* \) and \( \text{Ph}_2\text{NH}_2\text{OTf} \) are more effective than \( \text{KC}_8 \) and \( \text{H}([\text{Et}_2\text{O}])\text{Barf} \). Peters has proposed that \( \text{CoCp}_2^* \) is itself protonated (on a cyclopentadienyl ring) to yield a cation that can function in a proton-coupled electron transfer (PCET). An iron-catalyzed reduction of dinitrogen to hydrazine by \( \text{CoCp}_2^*/\text{Ph}_2\text{NH}_2\text{OTf/ether} \) at −78 °C conditions have been shown to yield products derived only from atmospheric nitrogen in the two Fe catalyst systems. We report here the catalytic reduction of dinitrogen to ammonia by a molybdenum complex that contains the \( [\text{2,6-}(\text{ArNCH}_2)\text{NC}_6\text{H}_3]^2− \) ligand.

Deprotonation of \( \text{H}_2[\text{Ar}_2\text{N}_3] \) with 1 equiv of Li-\( n\)-Bu at −20 °C followed by addition of \( \text{Mo(N)}(\text{O}-t\text{-Bu}) \) and a second equivalent of Li-\( n\)-Bu, and ultimately heating the reaction mixture to 90 °C for ~20 h resulted in formation of a dark-colored mixture from which purple pentane-soluble \( [\text{Ar}_2\text{N}_3]\text{Mo(N)}(\text{O}-t\text{-Bu}) \) was isolated. \( [\text{Ar}_2\text{N}_3]\text{Mo}^1\text{(O}-t\text{-Bu}) \) (50%-labeled; 1a; 65% yield) was isolated. \( [\text{Ar}_2\text{N}_3]\text{Mo}^1\text{(O}-t\text{-Bu}) \) (50%-labeled; 1a; 65% yield) was isolated. \( [\text{Ar}_2\text{N}_3]\text{Mo}^1\text{(O}-t\text{-Bu}) \) (50%-labeled; 1a; 65% yield) was isolated. The reaction between 1a and HCl in diethyl ether yielded the chloride complex, \( [\text{Ar}_2\text{N}_3]\text{Mo(N)}(\text{Cl}) \) (1b). Triflate (1c) and pentfluorophenoxide (1d) complexes also were prepared, as shown in Scheme 1.

Scheme 1. Syntheses of \( [\text{Ar}_2\text{N}_3]\text{Mo(N)}(X) \) Complexes

Compounds 1a and 1c appear to be unstable at 22 °C in the solid state or in solution over a period of 24 h, and we did not obtain consistent and correct elemental analyses of either despite multiple attempts.

An X-ray study of \( [\text{Ar}_2\text{N}_3]\text{Mo(N)}(\text{OC}_6\text{F}_5) \) (1d; Figure 1) showed it to be a distorted square pyramid \((\tau = 0.34)\) with the nitride in the apical position. The pentafluoro phenoxide ligand is sandwiched between the two Ar groups on either side of it. The structure resembles that of \( [\text{[t-BuP(O)COP]}\text{Mo(N)}(1)]− \) \((\tau = 0.06; \text{Mo} = 1.659(2) \text{Å}) \), a square pyramidal diamagnetic Mo(IV) complex, and structures of Mo nitride complexes published by Nishiyabashi and Chirik.

An X-ray study of 1b showed it to have a structure similar to that of 1d with Mo = 1.664(4) Å, Mo−Cl = 2.41(3) Å, and...
The Mo–N bond in 2a (1.712(1) Å) is 0.07 Å longer than the Mo–N bond in 1d (1.644(4) Å), and the Mo–O distance (1.823(1) Å) is 0.18 Å shorter than the Mo–O bond in 1d (2.007(3) Å). The large Mo–O–C and Mo–N–B angles are consistent with a relatively electrophilic metal in 2a combined with steric interactions of the tert-butoxide and NB(C₆F₅)₂ unit with the Ar groups. The bond distances and angles in 2a should be compared with those for other B(C₆F₅)₃ adducts of nitrilo complexes that have been reported in the literature.

Attempts to reduce ¹⁴N₂ (at 1 atm) to ammonia using 1a–d under conditions published for the Mo[HİPTN₃N] system revealed that only 1a produced >2.0 equiv of ammonia (2.2), a result that most optimistically could be called catalytic; i.e., one NH₃ is formed from the initial nitride and one NH₃ is formed from one-half of N₂, with the other half of N₂ reforming the nitride. We then turned to batchwise reduction using 1a with KCl and H(ETO₃)₂BARf at ~78 °C. These runs (see Table S2 in the SI) produced 2.4–2.8 equiv of ammonia. Finally, we explored CoCp*₂ as the reductant and Ph₂NH₂OTf as the acid in ether in a batchwise mode starting at ~78 °C followed by warming the reaction to 22 °C.⁴ These conditions yielded between 3.6 and 10.3 equiv of ammonia (runs 1–10 in Table 1) when 1a was the initial complex; complex 1b produced no ammonia, and complexes 1c, 1d, and 2a produced less than 2.0 equiv of ammonia. The efficiency of the reduction to ammonia in terms of electrons maximized at ~43% (runs 4 and 5), then dropped when more reducing agent was added (runs 6, 7, 8), and dropped further in runs 9–11; clearly the second 54 equiv in runs 6–8 produced little additional ammonia. A reaction set up and incubated at 0 °C (run 12) instead of at ~78 °C yielded less ammonia (runs 4 and 5).

Ammonia was quantified initially using the indophenol method. However, for convenience and accuracy we ultimately favored proton NMR spectra in DMSO-d₆ (with NaBARf as a standard) of ammonium chloride as the analytical technique (see SI for details). For example, the mixture of ¹⁴NH₄Cl and ¹⁵NH₄Cl (from 50% ¹⁵N-labeled 1a) from run 8 is shown in Figure 3. These results provide no information as to how much of what compound is formed from 1a that is part of the catalytic cycle. What is clear is that 1b, 1c, 1d, and 2a technically all fail as catalyst precursors, even though formation of more than 1.0 equiv of ammonia from 1c, 1d, and 2a suggests that some ammonia is formed from atmospheric N₂.

At this stage we have seen no evidence in NMR spectra such as that in Figure 3 for formation of hydrazine. The lower pKₐ of Ph₂NH₂OTf (3.2 in THF) versus NH₃⁺ (9.24 in water) suggests that Ph₂NH₂OTf is likely also to be consumed to form poorly soluble ammonium triflate, which effectively removes NH₃ from any equilibrium between a Mo(NH₃) complex and a Mo(N₂) complex. Failure to produce more than ~10 equiv of ammonia with larger amounts of reducing agent (runs 6–10) suggests that all catalytically active Mo ultimately is converted into an inactive form.

Table 1: Summary of Attempted Catalytic Reductions of N₂ by CoCp*₂ and Ph₂NH₂OTf in 7 mL of Ether at ~78 °C

<table>
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<tr>
<th>run</th>
<th>Mo</th>
<th>H⁺ (equiv)</th>
<th>e⁻ (equiv)</th>
<th>NH₃ (equiv)</th>
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<td>54</td>
<td>7.9, 7.6</td>
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<tr>
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<td>1a</td>
<td>150</td>
<td>108⁺⁺</td>
<td>8.2</td>
<td>23</td>
</tr>
<tr>
<td>5</td>
<td>1a</td>
<td>150</td>
<td>108⁺⁺</td>
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<tr>
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<td>108⁺⁺</td>
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<td>162</td>
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<td>54</td>
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<tr>
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<tr>
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<td>108</td>
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<td>1.2</td>
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*Initially 54 equiv, then slow addition of another 54 equiv as described in the SI. ²Efficiency per e.
Communication

Mo system may be more likely than the distal mechanism of dinitrogen reduction. It was noted that conversion of $\text{[HIPTN}_3\text{N}][\text{Mo(N}_2\text{)}]$ to $\text{[HIPTN}_3\text{N}][\text{Mo(N=NH)}]$ in benzene required both CoCp$_2$ and lutidinium to be present at the same time, which could be taken as evidence for some form of PCET in one or more steps in this and all other reductions, but stepwise addition of a proton to a neutral complex followed by an electron to a proton NMR spectrum (in DMSO-$d_6$) of $^{15}\text{NH}_4\text{Cl}$ derived from run 8 (* NaBarf standard).

To date metalloenes and nitrogen-based acids have been most successful as the reducing agent and proton source, respectively, in the Mo- and Fe-catalyzed reductions of nitrogen to ammonia in systems described so far, or to hydrazine. It has long been known that many early transition metal alkoxides decompose to form ethers, carbonium ions, radicals, or, in the case of tert-butoxide, isobutene. Formation and survival of an oxo and/or a hydroxo ligand, or both, in a catalytic cycle would be a surprising twist in the continuing story of catalytic dinitrogen reduction.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b04800.

Crystallographic data (CIF)
Crystallographic details for the X-ray structural studies, experimental details for the synthesis of all new compounds, and a detailed description of all catalytic runs (PDF)

REFERENCES


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**Notes**

The authors declare no competing financial interest.

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