

Reduction of Dinitrogen to Ammonia Catalyzed by Molybdenum Diamido Complexes

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S Supporting Information

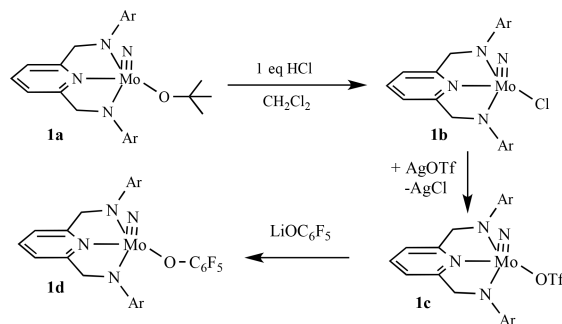
ABSTRACT: $[\text{Ar}_2\text{N}_3]\text{Mo}(\text{N})(\text{O}-t\text{-Bu})$, which contains the conformationally rigid pyridine-based diamido ligand, $[2,6-(\text{ArNCH}_2)_2\text{NC}_5\text{H}_3]^{2-}$ ($\text{Ar} = 2,6$ -diisopropylphenyl), can be prepared from $\text{H}_2[\text{Ar}_2\text{N}_3]$, butyllithium, and $(t\text{-BuO})_3\text{Mo}(\text{N})$. $[\text{Ar}_2\text{N}_3]\text{Mo}(\text{N})(\text{O}-t\text{-Bu})$ 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 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 $\sim 43\%$.

The catalytic reduction of molecular nitrogen to ammonia with protons and electrons under mild conditions¹ was first demonstrated with a molybdenum catalyst that contains a tren-based triamidoamine(3⁻) ligand ($[\text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{HIPT}))_3]^{3-}$ ($[\text{HIPTN}_3\text{N}]^{3-}$) where HIPT = 3,5-(2,4,6-triisopropylphenyl)₂C₆H₃).² 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.³ The reducing agent is CrCp^*_2 (decamethylchromocene), and the proton source is 2,6-LutidiniumBarf (Barf⁻ = $[\text{B}(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_4]^-$). The second reduction of molecular nitrogen under mild conditions was published in 2011.^{4a} The catalyst precursor in the first publication in this series is a bimetallic Mo(0) complex that contains a neutral “PNP pincer” ligand, 2,6-(*t*-Bu₂PCH₂)₂(NC₅H₃); CoCp_2 is the electron source, and 2,6-LutidiniumOTf (OTf = O₃S(CF₃)), the proton source. The actual catalytic cycle is likely to involve monomeric intermediates such as Mo(V) nitrides,^{4c,d} and several ligand variations have been explored.^{4b-i} 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.⁵ Although the original conditions are not “mild” (KC_8 and $\text{H}(\text{Et}_2\text{O})_2\text{Barf}$ at -78 °C), it has been found recently that CoCp^*_2 and $\text{Ph}_2\text{NH}_2\text{OTf}$ are more effective than KC_8 and $\text{H}(\text{Et}_2\text{O})_2\text{Barf}$.^{5b} Peters has proposed that CoCp^*_2 is itself protonated (on a cyclopentadienyl ring) to yield a cation that can function in a proton-coupled electron transfer (PCET⁶). An iron-catalyzed reduction of dinitrogen to hydrazine by CoCp^*_2 and $\text{Ph}_2\text{NH}_2\text{OTf}$ was reported in 2016.⁷ The $\text{CoCp}^*_2/\text{Ph}_2\text{NH}_2\text{OTf}/\text{ether}/-78$ °C conditions have been

shown to yield products derived only from atmospheric nitrogen in the two Fe catalyst systems.^{5b,7} We report here the catalytic reduction of dinitrogen to ammonia by a molybdenum complex that contains the $[2,6-(\text{ArNCH}_2)_2\text{NC}_5\text{H}_3]^{2-}$ ($\text{Ar} = 2,6$ -diisopropylphenyl) ligand.⁸

Deprotonation of $\text{H}_2[\text{Ar}_2\text{N}_3]$ with 1 equiv of $\text{Li}-n\text{-Bu}$ at -20 °C followed by addition of $\text{Mo}(\text{N})(\text{O}-t\text{-Bu})_3$ and a second equivalent of $\text{Li}-n\text{-Bu}$, 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 $[\text{Ar}_2\text{N}_3]\text{Mo}(\text{N})(\text{O}-t\text{-Bu})$ (**1a**; 65% yield) was isolated. $[\text{Ar}_2\text{N}_3]\text{Mo}(\text{N})(\text{O}-t\text{-Bu})$ (¹⁵N) (^{50%}-labeled; **1a**-¹⁵N) was prepared from 50% ¹⁵N-labeled $\text{Mo}(\text{N})(\text{O}-t\text{-Bu})_3$. The reaction between **1a** and HCl in diethyl ether yielded the chloride complex, $[\text{Ar}_2\text{N}_3]\text{Mo}(\text{N})(\text{Cl})$ (**1b**). Triflate (**1c**) and pentafluorophenoxide (**1d**) complexes also were prepared, as shown in Scheme 1.

Scheme 1. Syntheses of $[\text{Ar}_2\text{N}_3]\text{Mo}(\text{N})(\text{X})$ 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 $[\text{Ar}_2\text{N}_3]\text{Mo}(\text{N})(\text{OC}_6\text{F}_5)$ (**1d**; Figure 1) showed it to be a distorted square pyramid ($\tau = 0.34^9$) with the nitride in the apical position. The pentafluoro phenoxide ligand is sandwiched between the two Ar groups on either side of it. This structure resembles that of $[(t\text{-BuPOCOP})\text{Mo}(\text{N})(\text{I})]^-$ ($\tau = 0.06$; $\text{Mo}\equiv\text{N} = 1.659(2)$ Å),¹⁰ a square pyramidal diamagnetic Mo(IV) complex, and structures of Mo nitride complexes published by Nishibayashi^{4c,d} and Chirik.¹¹

An X-ray study of **1b** showed it to have a structure similar to that of **1d** with $\text{Mo}\equiv\text{N} = 1.664(4)$ Å, $\text{Mo}-\text{Cl} = 2.41(3)$ Å, and

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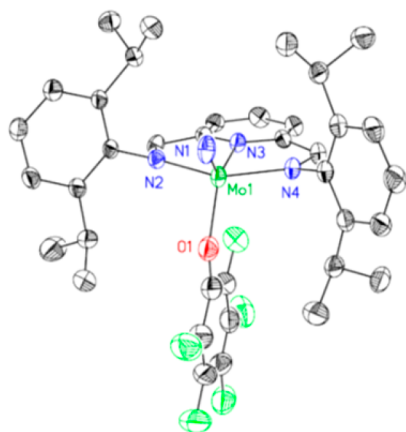


Figure 1. Ellipsoid drawing of $[\text{Ar}_2\text{N}_3]\text{Mo}(\text{N})(\text{OC}_6\text{F}_5)$; $\tau = 0.34$, $\text{Mo}\equiv\text{N} = 1.644(4)$ Å, $\text{Mo}-\text{O} = 2.007(3)$ Å, $\text{Mo}-\text{O}-\text{C} = 131.2(3)^\circ$.

$\tau = 0.21$. The crystal of **1b** that was chosen contained its cocrystallized bromide analog (~50%); the two compounds were successfully resolved in the study, and their structures were refined (see Supporting Information (SI) for details).

Because we could not obtain a high quality structural solution of **1a**, we added $\text{B}(\text{C}_6\text{F}_5)_3$ to **1a** to yield the purple $\text{B}(\text{C}_6\text{F}_5)_3$ adduct, **2a**, which is relatively stable thermally at 22 °C in the solid state or in benzene under N_2 . An X-ray structure of **2a** (Figure 2) showed that $\text{B}(\text{C}_6\text{F}_5)_3$ has added to the nitride

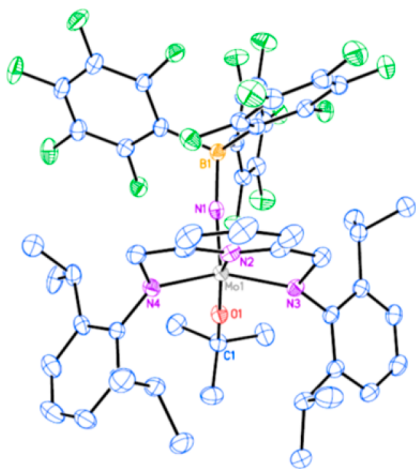


Figure 2. Ellipsoid drawing of $[\text{Ar}_2\text{N}_3]\text{Mo}[\text{NB}(\text{C}_6\text{F}_5)_3](\text{O}-t\text{-Bu})$ (**2a**); $\tau = 0.35$, $\text{Mo}\equiv\text{N} = 1.712(1)$ Å, $\text{Mo}-\text{O} = 1.823(1)$ Å, $\text{Mo}-\text{O}-\text{C} = 176.4(1)^\circ$, $\text{Mo}-\text{N}-\text{B} = 173.9(1)^\circ$.

in **1a** to give a distorted square pyramidal adduct ($\tau = 0.35$). 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 $\text{NB}(\text{C}_6\text{F}_5)_3$ unit with the Ar groups. The bond distances and angles in **2a** should be compared with those for other $\text{B}(\text{C}_6\text{F}_5)_3$ adducts of nitride complexes that have been reported in the literature.¹²

Attempts to reduce $^{14}\text{N}_2$ (at 1 atm) to ammonia using **1a–d** under conditions published for the $\text{Mo}[\text{HIPTN}_3\text{N}]$ system^{2a} revealed that only **1a** produced >2.0 equiv of ammonia (2.2), a result that most optimistically could be called catalytic; i.e., one

NH_3 is formed from the initial nitride and one NH_3 is formed from one-half of N_2 , with the other half of N_2 reforming the nitride. We then turned to batchwise reduction using **1a** with KC_8 and $\text{H}(\text{Et}_2\text{O})_2\text{Barf}$ 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 $\text{Ph}_2\text{NH}_2\text{OTf}$ as the acid in ether in a batchwise mode starting at -78 °C followed by warming the reaction to 22 °C.^{5b,7} 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

Table 1. Summary of Attempted Catalytic Reductions of N_2 by CoCp^*_2 and $\text{Ph}_2\text{NH}_2\text{OTf}$ in 7 mL of Ether at -78 °C

run	Mo	H^+ (equiv)	e^- (equiv)	NH_3 (equiv)	Eff^b
1,2	1a	48	36	4.4, 3.6	37, 30
3	1a	60	54	5.2	29
4,5	1a	108	54	7.9, 7.6	44, 42
6	1a - ^{15}N	120	108 ^a	8.2	23
7	1a	140	108 ^a	10.3	29
8	1a - ^{15}N	140	108 ^a	9.8	27
9	1a - ^{15}N	162	162	4.8	9
10	1a	322	162	5.4	10
11	1a	162	54	2.2	12
12	1a	108	54	2.5 (0 °C)	14
	1b	48	36	0	
	1c	108	54	1.3	
	1d	108	54	1.3	
	2a	108	54	1.2	

^aInitially 54 equiv, then slow addition of another 54 equiv as described in the SI. ^bEfficiency per e.

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.¹³ However, for convenience and accuracy we ultimately favored proton NMR spectra in $\text{DMSO}-d_6^{2a}$ (with NaBarf as a standard) of ammonium chloride as the analytical technique (see SI for details). For example, the mixture of $^{14}\text{NH}_4\text{Cl}$ and $^{15}\text{NH}_4\text{Cl}$ (from 50% ^{15}N -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 N_2 .

At this stage we have seen no evidence in NMR spectra such as that in Figure 3 for formation of hydrazine.⁷ The lower pK_a of $\text{Ph}_2\text{NH}_2\text{OTf}$ (3.2 in THF) versus NH_4^+ (9.24 in water) suggests that $\text{Ph}_2\text{NH}_2\text{OTf}$ is likely also to be consumed to form poorly soluble ammonium triflate, which effectively removes NH_3 from any equilibrium between a $\text{Mo}(\text{NH}_3)$ complex and a $\text{Mo}(\text{N}_2)$ 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.

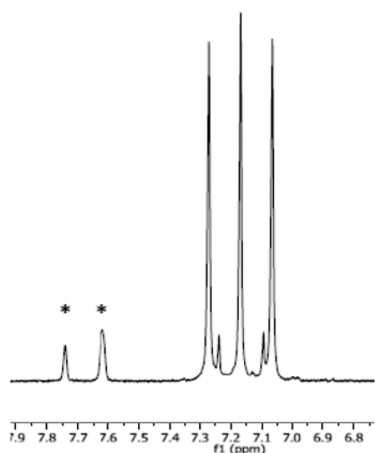


Figure 3. Proton NMR spectrum (in DMSO- d_6) of $^{14}\text{NH}_4\text{Cl}$ (and $^{15}\text{NH}_4\text{Cl}$) derived from run 8 (* NaBarf standard).

To date metallocenes 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^{2,4,5} or to hydrazine.⁷ It was noted that conversion of $[\text{HIPTN}_3\text{N}]\text{Mo}(\text{N}_2)$ to $[\text{HIPTN}_3\text{N}]\text{Mo}(\text{N}=\text{NH})$ in benzene required both CoCp_2 and lutidinium to be present at the same time,^{2f} which could be taken as evidence for some form of PCET in one or more steps in this and all other reductions,^{5b} but stepwise addition of a proton to a neutral complex followed by an electron to a positively charged complex could still be part of the overall mechanism of forming ammonia. The ligand in the $[\text{Ar}_2\text{N}_3]\text{Mo}$ system also may be “noninnocent”, as shown by Chirik in chemistry of Mo complexes that contain a diimine pincer ligand related to $[\text{Ar}_2\text{N}_3]^{2-}$.¹¹ Interestingly, $[\text{NHNH}_2]^-$ and hydrazine complexes of W(VI) that contain a ligand analogous to $[\text{Ar}_2\text{N}_3]^{2-}$, i.e., $[(\text{TosylNCH}_2)_2\text{NC}_5\text{H}_3]\text{W}(\text{NAr})(\text{NHNH}_2)(\text{Cl})$ and $\{[(\text{TosylNCH}_2)_2\text{NC}_5\text{H}_3]\text{W}(\text{NAr})(\text{NH}_2\text{NH}_2)(\text{Cl})\}\text{OTf}$, are known,¹⁴ so an “alternating” mechanism in the $[\text{Ar}_2\text{N}_3]$ Mo system may be more likely than the distal mechanism of reduction favored in the $[\text{HIPTN}_3\text{N}]\text{Mo}$ system.

Studies aimed at determining the mechanism of nitrogen reduction starting with **1a** have not yet led to a conclusion. The fact that **1a** is a catalyst precursor while **1c** is not suggests that either the *tert*-butoxide is intact throughout a catalytic cycle or, more likely, we propose, the *tert*-butoxide is converted into an OH or an oxo ligand upon addition of a proton from $\text{Ph}_2\text{NH}_2\text{OTf}$ to the nitride or to the *tert*-butoxide oxygen. (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.¹⁵) 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)

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Notes

The authors declare no competing financial interest.

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