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Reduction of Dinitrogen to Ammonia Catalyzed by Molybdenum Diamido Complexes

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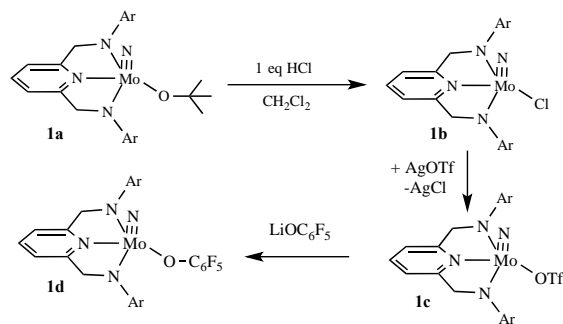
Supporting Information Placeholder

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, $[2,6-(\text{ArNCH}_2)_2\text{NC}_5\text{H}_3]^{2-}$ (Ar = 2,6-diisopropylphenyl), can be prepared from $\text{Li}_2[\text{Ar}_2\text{N}_3]$ 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°C and 22°C in a batch-wise manner with CoCp^*_2 as the electron source and $\text{Ph}_2\text{NH}_2\text{OTf}$ as the proton source. Up to ~ 10 equivalents 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 twelve intermediates in a "distal" reduction of dinitrogen were prepared and characterized and the proposed mechanism has been vetted through theoretical studies by primarily two groups.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-h} 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" (KC₈ and H(Et₂O)₂Barf at -78°C), it has been found recently that CoCp^*_2 and $\text{Ph}_2\text{NH}_2\text{OTf}$ are *more* effective than KC₈ and H(Et₂O)₂Barf.^{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 (PCET).⁶ 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 $\text{CoCp}^*_2/\text{Ph}_2\text{NH}_2\text{OTf}/\text{ether}/-78^\circ\text{C}$ 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 $[2,6-(\text{ArNCH}_2)_2\text{NC}_5\text{H}_3]^{2-}$ (Ar = 2,6-diisopropylphenyl) ligand.⁸

Deprotonation of $\text{H}_2[\text{Ar}_2\text{N}_3]$ with one equivalent of Li-*n*-Bu at -20°C followed by addition of $\text{Mo}(\text{N})(\text{O}-t\text{-Bu})_3$ 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 $[\text{Ar}_2\text{N}_3]\text{Mo}(\text{N})(\text{O}-t\text{-Bu})$ (**1a**; 65% yield) was isolated. $[\text{Ar}_2\text{N}_3]\text{Mo}(\text{N})(\text{O}-t\text{-Bu})$ (**1a**) 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. 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 contain consistent and correct elemental analyses of either despite multiple attempts.



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

An X-ray study of $\text{Mo}(\text{N})(\text{OC}_6\text{F}_5)$ (**1d**; Figure 1) showed it to be a distorted square pyramid ($\tau = 0.34^9$) with the nitride nitrogen in the apical position. The pentafluorophenoxide ligand is sandwiched between the two Ar groups on either side of it. This structure resembles that of

$[(t\text{-BuPOCOP})\text{Molybdenum}(\text{N})(\text{I})]^-$ ($\tau = 0.06$; $\text{Mo}\equiv\text{N} = 1.659(2) \text{ \AA}$),¹⁰ a square pyramidal diamagnetic $\text{Mo}(\text{IV})$ complex, and structures of Mo nitride complexes published by Nishibayashi^{4c,d} and Chirik.¹¹ An X-ray examination of crystals of **1a** showed that its structure is analogous to that of **1d**, although the solution is not of publishable quality.

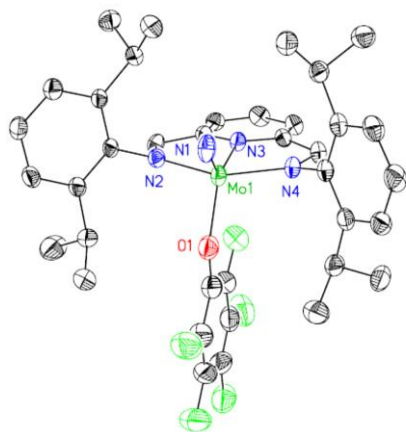


Figure 1. Ellipsoid drawing of $[\text{Ar}_2\text{N}_3]\text{Mo}(\text{N})(\text{OC}_6\text{F}_5)$; $\tau = 0.34$, $\text{Mo}\equiv\text{N} = 1.644(4) \text{ \AA}$, $\text{Mo}-\text{O} = 2.007(3) \text{ \AA}$, $\text{Mo}-\text{O}-\text{C} = 131.2(3)^\circ$.

An X-ray study of **1b** showed it to have a structure similar to that of **1d** with $\text{Mo}\equiv\text{N} = 1.664(4) \text{ \AA}$, $\text{Mo}-\text{Cl} = 2.41(3) \text{ \AA}$, and $\tau = 0.21$. 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 refined (see SI for details).

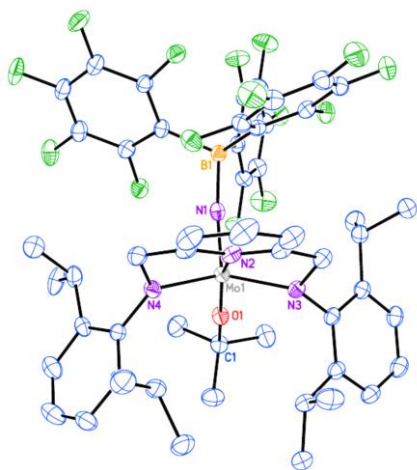


Figure 2. Ellipsoid drawing of $[\text{Ar}_2\text{N}_3]\text{Mo}[\text{NB}(\text{C}_6\text{F}_5)_3](\text{O}-t\text{-Bu})$ (**2a**); $\tau = 0.35$, $\text{Mo}\equiv\text{N} = 1.712(1) \text{ \AA}$, $\text{Mo}-\text{O} = 1.823(1) \text{ \AA}$, $\text{Mo}-\text{O}-\text{C} = 176.4(1)^\circ$, $\text{Mo}-\text{N}-\text{B}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

Addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to **1a** led to formation of the purple $\text{B}(\text{C}_6\text{F}_5)_3$ adduct, **2a**. An X-ray structure (Figure 2) showed that $\text{B}(\text{C}_6\text{F}_5)_3$ has added to the nitride in **1a** to give a distorted square pyramidal adduct ($\tau = 0.35$). The $\text{Mo}-\text{N}$ bond in **2a** ($1.712(1) \text{ \AA}$) is 0.07 \AA longer than the $\text{Mo}-\text{N}$ bond in **1d** ($1.644(4) \text{ \AA}$) and the $\text{Mo}-\text{O}$ distance ($1.823(1) \text{ \AA}$) is 0.18 \AA shorter than the $\text{Mo}-\text{O}$ bond in **1d** ($2.007(3) \text{ \AA}$). The large $\text{Mo}-\text{O}-\text{C}$ and $\text{Mo}-\text{N}-\text{B}$ angles are consistent with a relatively electrophilic metal in **2a** combined with steric interactions of the *t*-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 nitrido complexes that have been reported in the literature.¹² It should be noted that unlike **1a**, **2a** is relatively stable thermally at 22°C in the solid state or in benzene under N_2 .

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 equivalents 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 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 in the SI) produced 2.4-2.8 equivalents 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 batch-wise mode starting at -78°C followed by warming the reaction to 22°C .^{5b,7} These conditions yielded between 3.6 and 10.3 equivalents 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 equivalents 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 equivalents in runs 6-8 produced little additional ammonia. A reaction set up and incubated at 0°C (run 12) yielded less ammonia than at -78°C (runs 4 and 5).

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	$\text{H}^+(\text{eq})$	$\text{e}^-(\text{eq})$	$\text{NH}_3(\text{eq})$	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-¹⁵N	120	108 ^a	8.2	23
7	1a	140	108 ^a	10.3	29
8	1a-¹⁵N	140	108 ^a	9.8	27
9	1a-¹⁵N	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	

^a Initially 54 equivalents, then slow addition of another 54 equivalents as described in the SI. ^b Efficiency per e.

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} of ammonia isolated as ammonium chloride (see SI for details) as the analytical technique. 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 (except when **1b** was used) suggests that *some* ammonia is formed from atmospheric N₂.

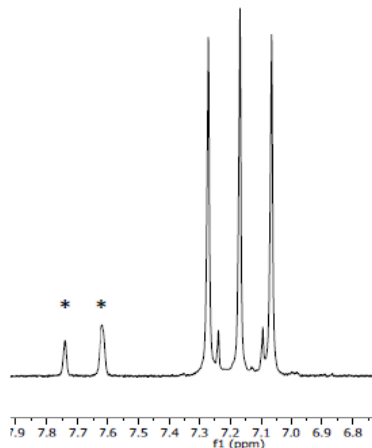


Figure 3. The proton NMR spectrum (in DMSO-d₆) of ¹⁴NH₄Cl (and ¹⁵NH₄Cl) derived from run 8 (* NaBarf standard).

At this stage we assume that the only other reduction product that is formed in the most successful reduction by CoCp*₂ and Ph₂NH₂OTf is molecular hydrogen, although it has not yet been identified and measured. We see no evidence in NMR spectra such as that in Figure 3 for formation of hydrazine.⁷ The lower pK_a of Ph₂NH₂OTf (3.2 in THF) versus NH₄⁺ (9.24 in water) suggests that acid is likely also to be consumed to form ammonium triflate, which removes NH₃ from any equilibrium between a Mo(NH₃) complex and a Mo(N₂) complex. Failure to produce more than ~10 equivalents of ammonia with larger amounts of reducing agent (runs 6-10) suggests that all catalytically active Mo ultimately is converted into an inactive form.

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 [HIPTN₃N]Mo(N₂) to [HIPTN₃N]Mo(N=NH) in benzene required both CoCp₂ 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 step-wise 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 [Ar₂N₃]Mo system also may be "non-innocent", as shown by Chirik in chemistry of Mo complexes that contain a diimine pincer ligand related to [Ar₂N₃]²⁻.¹¹ Interestingly, [NHNH₂]⁻ and hydrazine complexes of W(VI) that contain a ligand analogous to [Ar₂N₃]²⁻, *i.e.*, [(TosylNCH₂)₂NC₃H₃]W(NAr)(NHNH₂)(Cl) and {[(TosylNCH₂)₂NC₃H₃]W(NAr)(NH₂NH₂)(Cl)}OTf, are known,¹⁴ so an "alternating" mechanism in the [Ar₂N₃]Mo system may be more likely than the distal mechanism of reduction favored in the [HIPTN₃N]Mo system.

Studies aimed at determining the mechanism of nitrogen reduction starting with **1a** have not yet led to a conclusion. One possibility is that the *t*-butoxide ligand in **1a** is con-

verted into an OH or an oxo ligand through addition of a proton from Ph₂NH₂OTf at the nitride or at the *t*-butoxide oxygen. (It has long been known that many early metal alkoxides decompose to form ethers, carbonium ions, radicals, or in the case of *t*-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

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. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interests. LAW and TO contributed equally to this work.

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