Catalytic Reduction of Dinitrogen to Ammonia by Use of Molybdenum−Nitride Complexes Bearing a Tridentate Triphosphine as Catalysts

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Ⓢ *Supporting Information*

ABSTRACT: Newly designed and prepared molybdenum−nitride complexes bearing a *mer*-tridentate triphosphine as a ligand have been found to work as the most effective catalysts toward the catalytic reduction of dinitrogen to ammonia under ambient conditions, where up to 63 equiv of ammonia based on the Mo atom of the catalyst were produced.

The transformation of dinitrogen into ammonia catalyzed by transition metal−dinitrogen complexes under mild reaction conditions is one of the most realizable approaches to develop the next-generation nitrogen fixation system in place of the Haber−Bosch process for industrial ammonia production.[1] Although the preparation of various transition metal−dinitrogen complexes and their stoichiometric transformation of the coordinated dinitrogen into ammonia have been thoroughly investigated,[2,3] only limited examples of the catalytic conversion of dinitrogen into ammonia using transition metal−dinitrogen complexes as catalysts under mild conditions are known.[4]

In 2003, Schrock and a co-worker reported the first example of the catalytic reaction of dinitrogen to give ammonia in the presence of a molybdenum−dinitrogen complex bearing a tetradentate triamidoamine ligand, where 8 equiv of ammonia based on the Mo atom were produced.[5] We recently found the second successful example of the Mo-catalyzed formation of ammonia from dinitrogen by using $[Mo(N_2)_2(PNP)]_2(\mu\text{-}N_2)$ (**1**) (PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) as a catalyst, where up to 12 equiv of ammonia based on each Mo atom of the catalyst (23 equiv based on the catalyst) were produced.[6] In this reaction system, the dinuclear structure of **1** plays an important role in exhibiting the catalytic ability.[7] In addition, some molybdenum−nitride complexes have been found to work as key reactive intermediates.[7] On the basis of the elucidated reaction mechanism, we have developed more effective catalysts by introducing an electron-donating group on the pyridine ring of the PNP ligand, where up to 26 equiv of ammonia based on each Mo atom of the catalyst (52 equiv based on the catalyst) were produced.[8] More recently, Peters and co-workers found the third successful example by using iron−dinitrogen complexes bearing triphosphineborane and

triphosphinealkyl moieties as ligands, where 7 equiv of ammonia based on the Fe atom were produced at −78 °C.[9−11]

On the basis of the findings achieved,[6−8] we envisaged the design of the novel complex $[Mo(N_2)_2(PPP)]_2(\mu\text{-}N_2)$ (**2**) (PPP = bis(di-*tert*-butylphosphinoethyl)phenylphosphine[12]) (Scheme 1). Our motivation for **2** is as follows. The phosphines

**Scheme 1. Molybdenum-Catalyzed Reduction of Dinitrogen to Ammonia under Ambient Conditions**
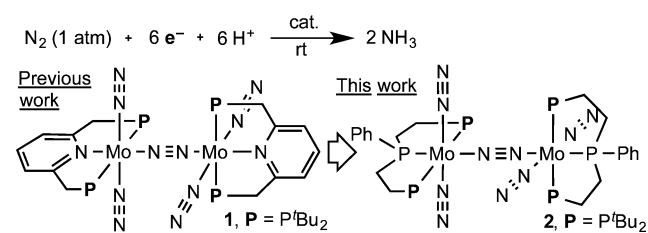
in PPP ligand have the advantages of lower Brønsted basicity and higher stability toward protonation in the catalytic reaction. In addition, the π-accepting ability of the PPP ligand can stabilize a variety of molybdenum complexes bearing a broad range of oxidation states of the Mo center during the catalytic reaction. As a result, molybdenum complexes bearing the PPP ligand have been found to work as the most effective catalysts, where up to 63 equiv of ammonia based on the Mo atom of the catalyst have been produced. The present catalytic activity is more than 5 times higher than that of the original complex **1**.[6] The result described in the present paper is the first successful example of catalytic nitrogen fixation using molybdenum complexes bearing only a triphosphine as an auxiliary ligand.

At first, we tried to prepare **2** by following the previous method for **1**.[6] However, we could not isolate **2** in pure form by reduction of $[MoCl_3(PPP)]$ (**3**) with reductants such as Na−Hg, KC$_8$, or CoCp*$_2$ (Cp* = η^5-C$_5$Me$_5$) under 1 atm N$_2$ in tetrahydrofuran (THF) at room temperature for 14 h, although a strong IR absorption derived from the terminal dinitrogen ligands was observed in all cases (Scheme 2).[13] Next, we tried to prepare

Scheme 2. Preparation of Molybdenum−Nitride Complexes Bearing the PPP Ligand
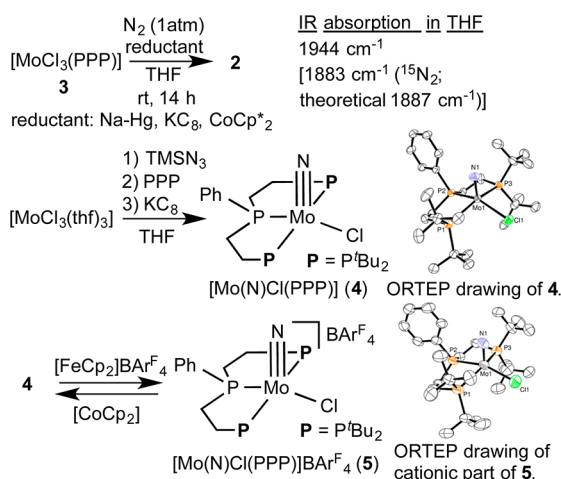
molybdenum−nitride complexes bearing the PPP ligand because molybdenum−nitride complexes bearing the PNP ligand have been found to work as effective catalysts, with catalytic activities almost the same as that of **1**.[7]

According to the previous method,[7] we prepared new neutral and cationic molybdenum−nitride complexes bearing the PPP ligand: $[Mo(N)Cl(PPP)]$ (**4**) and $[Mo(N)Cl(PPP)]BAr^F_4$ (**5**) (Ar^F = 3,5-bis(trifluoromethyl)phenyl), respectively. Treatment of $[MoCl_3(thf)_3]$ with Me_3SiN_3 at 50 °C, addition of PPP at 50 °C, and sequential reduction with KC_8 at room temperature gave **4** in 54% yield (Scheme 2). Oxidation of **4** with 1 equiv of $[FeCp_2]BAr^F_4$ (Cp = η^5-C_5H_5) at room temperature for 1 h afforded **5** in 81% yield (Scheme 2).[14] Interestingly, reduction of **5** with 1 equiv of cobaltocene ($CoCp_2$) at room temperature for 2 h gave **4** in 42% yield. The molecular structures of **4** and **5** were unambiguously determined by X-ray crystallographic analysis (Scheme 2).[15] Both complexes have a distorted square-pyramidal structure with *mer*-PPP. The electrochemical properties of **4** and **5** were estimated by cyclic voltammetry (CV). Typical results are shown in Table 1. CV of **4** revealed one reversible oxidation wave

Table 1. Electrochemical Data for Molybdenum−Nitride Complexes

complex	**4**	**5**	$[Mo(N)Cl(PNP)]$
$E_{1/2}{}^{a,b}$	−0.99 V	−	−1.25 V
$E_{1/2}{}^{a,c}$	−	−1.02 V	−

[a]Cyclic voltammetry in 0.1 M $[^nBu_4N]BF_4$/THF. Potential values are referenced to $FeCp_2{}^{0/+}$. [b]Oxidation potential. [c]Reduction potential.

assignable to Mo(IV/V) at −0.99 V. The $E_{1/2}$ value of **4** is higher than that of $[Mo(N)Cl(PNP)]$. On the other hand, CV of **5** revealed one reversible reduction wave assignable to Mo(IV/V) at −1.02 V, consistent with the redox behavior between **4** and **5**.

We carried out the catalytic reduction of dinitrogen to ammonia using **5** as a catalyst.[8] To a mixture of **5** and 2,6-lutidinium trifluoromethanesulfonate ($[LutH]OTf$) (48 equiv based on **5**) as a proton source in toluene was added a solution of $CoCp_2$ (36 equiv based on **5**) as a reductant in toluene via a syringe pump at room temperature over a period of 1 h, after which the resulting mixture was stirred at room temperature for another 19 h under 1 atm N_2. After the reaction, the formation of ammonia as well as dihydrogen was observed, the amounts of which were determined

by the indophenol method[16] and gas chromatography, respectively. Typical results are shown in Table 2. The yields of ammonia and dihydrogen were estimated on the basis of cobaltocene. In all cases, no formation of other products such as hydrazine was observed.

In the reaction using **5** as a catalyst, only a stoichiometric amount of ammonia based on the Mo atom of the catalyst was produced (Table 2, run 1). Using $CrCp^*_2$ in place of $CoCp_2$ as a reductant slightly increased the amount of ammonia (2.3 equiv based on the Mo atom; Table 2, run 2). When the catalytic reaction was carried out using $CoCp^*_2$, which has stronger reducing ability, 6.1 equiv of ammonia based on the Mo atom were produced (Table 2, run 3). This result indicates that **5** has catalytic activity toward ammonia formation.

The acidity of the proton source dramatically affected the catalytic activity of **5**. In fact, a lower amount of ammonia was produced when $[PicH]OTf$ (Pic = 2-methylpyridine), which has higher acidity than $[LutH]OTf$, was used as the proton source (Table 2, run 4). Use of $[ColH]OTf$ (Col = 2,4,6-trimethylpyridine), with lower acidity than $[LutH]OTf$, substantially increased the amount of ammonia (9.6 equiv based on the Mo atom; Table 2, run 5). Separately, we confirmed the direct conversion of dinitrogen into ammonia by using $^{15}N_2$ gas in place of normal $^{14}N_2$ gas.[15] The control experiments indicated that the use of both **5** and dinitrogen is essential to promote the catalytic reaction.[15]

The neutral complex **4** has catalytic activity similar to that of **5** under the present reaction conditions (Table 2, run 6). It is noteworthy that the formation of ammonia in 92% yield was observed together with dihydrogen in only 2% yield. In sharp contrast to the previous reaction system catalyzed by **1**,[8] the present reaction system by using **4** and **5** as catalysts can suppress the formation of dihydrogen as a side product.

Next, we investigated the reaction in the presence of a catalytic amount of **5** using larger amounts of $CoCp^*_2$ as a reducing reagent and $[ColH]OTf$ as a proton source under similar conditions. The detailed investigation of the reaction conditions is shown in the Supporting Information. To prevent the direct reaction of $CoCp^*_2$ with $[ColH]OTf$, we carried out the reaction by slow addition of a toluene solution of $CoCp^*_2$ over 10 h followed by stirring of the resulting mixture at room temperature for another 10 h. As a result, 63 equiv of ammonia based on the Mo atom (35% yield based on $CoCp^*_2$) were produced from the reaction with $CoCp^*_2$ (1.08 mmol; 540 equiv based on **5**) and $[ColH]OTf$ (1.44 mmol; 720 equiv to **5**) in the presence of **5** (0.002 mmol) as a catalyst in toluene at room temperature for 20 h, together with dihydrogen (28 equiv based on the Mo atom; 10% yield) (Scheme 3). This is the most effective catalytic reaction to date using transition metal−dinitrogen and related complexes as catalysts.

As shown in Table 1, the nature of the PPP ligand strongly affects the electrochemical properties of the molybdenum−nitride complexes. These electrochemical properties indicate that the reduction of molybdenum complexes bearing the PPP ligand proceeds more smoothly than that of molybdenum complexes bearing the PNP ligand. We consider the higher reactivity of the molybdenum complexes bearing the PPP ligand toward reduction to be one of the most important factors in promoting the catalytic reaction more smoothly. This electrochemical property prompted us to use **3** as a precursor, and it was found to have catalytic activity, as 6.4 equiv of ammonia based on the Mo atom were produced (Table 2, run 7). This unexpected catalytic reactivity is due to the unique property of the PPP ligand in **3**

Table 2. Molybdenum-Catalyzed Reduction of Dinitrogen to Ammonia under Ambient Conditions[a]

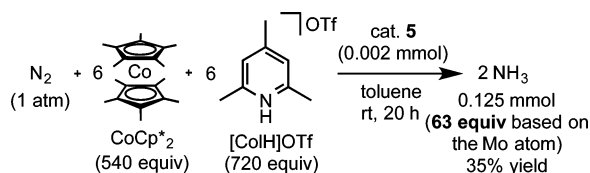$$N_2 + 6\,e^- + 6\,H^+ \xrightarrow[\text{rt}]{\text{cat.}} 2\,NH_3$$
(1 atm) (36 equiv)* (48 equiv)* *Based on the Mo atom of the catalyst.

run	cat.	reductant	proton source	NH₃ amount (equiv)[b]	NH₃ yield (%)[c]	H₂ amount (equiv)[b]	H₂ yield (%)[c]
1	5	CoCp₂	[LutH]OTf	1.8	15	10.5	58
2	5	CrCp*₂	[LutH]OTf	2.3	19	8.6	48
3	5	CoCp*₂	[LutH]OTf	6.1	51	0	0
4	5	CoCp*₂	[PicH]OTf	3.3	28	0.9	5
5	5	CoCp*₂	[ColH]OTf	9.6	80	1.1	6
6	4	CoCp*₂	[ColH]OTf	11.0	92	0.3	2
7	3	CoCp*₂	[ColH]OTf	6.4	53	1.7	9

reductant	$E_{1/2}$ (V)[d]	proton source	pK_a[e]
CoCp₂	−1.25	[LutH]OTf	6.77
CrCp*₂	−1.45	[PicH]OTf	5.97
CoCp*₂	−1.88	[ColH]OTf	7.48

[a]To a mixture of the catalyst (0.010 mmol) and proton source (48 equiv based on the catalyst) in toluene (1.0 mL) was added a solution of reductant (36 equiv based on the catalyst) in toluene (4.0 mL) at room temperature over a period of 1 h, followed by stirring at room temperature for another 19 h under 1 atm N_2. [b]Molar equivalents based on the Mo atom of the catalyst. [c]Yields based on the amount of reductant. [d]Electrochemical data ($E_{1/2}$ vs FeCp₂) for the reductants in MeCN with 0.1 M [$^nBu_4N$]BF₄.[17] [e]pK_a values of the proton sources in H_2O.[18]

Scheme 3. Molybdenum-Catalyzed Reduction of Dinitrogen to Ammonia under Ambient Conditions

$$N_2 + 6\,\underset{\text{CoCp*}_2}{Co} + 6\,\underset{[ColH]OTf}{} \xrightarrow[\text{toluene rt, 20 h}]{\text{cat. 5 (0.002 mmol)}} 2\,NH_3$$

(1 atm)   CoCp*₂ (540 equiv)   [ColH]OTf (720 equiv)   0.125 mmol (63 equiv based on the Mo atom) 35% yield

Scheme 4. Optimized Geometry of 2

2, P = P^{t}Bu₂

because [MoCl₃(PNP)] had no catalytic activity under the same reaction conditions. This result indicates that some reactive species such as **2** may be generated from the reduction of **3** with CoCp*₂ in the catalytic reaction.

Next, we monitored the time profile of the catalytic reaction using **5** as a catalyst. Typical results are shown in Figure 1,
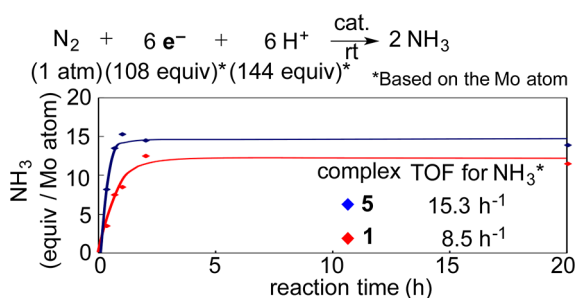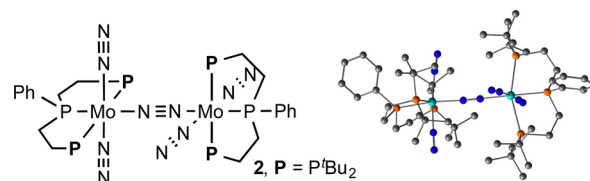

$$N_2 + 6\,e^- + 6\,H^+ \xrightarrow[\text{rt}]{\text{cat.}} 2\,NH_3$$
(1 atm) (108 equiv)* (144 equiv)* *Based on the Mo atom

complex	TOF for NH₃*
5	15.3 h⁻¹
1	8.5 h⁻¹

Figure 1. Time profiles of the formation of ammonia using **5** (blue) and **1** (red) as catalysts.

together with the time profile using **1** as a catalyst.[8] The catalytic formation of ammonia using **5** proceeded more rapidly than that using **1**, and the turnover frequency (TOF) for ammonia (determined as moles of ammonia per Mo atom produced in the initial 1 h) was 15.3 h⁻¹ compared with 8.5 h⁻¹ using **1**.[8] These results indicate that **5** has the highest performance in terms of not only the catalytic activity but also the rate of ammonia formation.

To get more information on the reaction pathway, we investigated the possibility of the formation of **2** by density functional theory calculations based on the molecular structures

of **4** and **5**. The optimized geometry of **2** (Scheme 4) is similar to that of **1**. For the terminal dinitrogen ligands in **2**, the N−N distance (1.140 Å) and the sum of the NPA charges[19] (−0.127) indicate that the dinitrogen ligands are moderately activated toward protonation in a similar manner as **1** (1.138 Å and −0.125).[7] The N−N stretching frequency of the terminal dinitrogen ligands in **2** was calculated to be 1947 cm⁻¹, which is very close to the absorption observed in the IR spectrum (Scheme 2). On the other hand, the energy of the bond between the Mo atom and the bridging dinitrogen is 13.6 kcal/mol. This value is substantially smaller than that for **1** (24.9 kcal/mol), and thus, the isolation of **2** from the reaction solution is expected to be difficult. As a result, we consider that the present catalytic reaction using **4** or **5** as the catalyst may proceed via **2** as a key reactive intermediate.

Finally, we carried out a stoichiometric reaction of **5** with 5 equiv of CoCp*₂ and 4 equiv of [ColH]OTf in toluene at room temperature for 20 h under 1 atm Ar, which afforded 0.77 equiv of ammonia based on **5** (77% yield). This result indicates that the nitrogen atom as a nitride ligand can be converted into ammonia under the catalytic reaction conditions. Unfortunately, we could not obtain the imide complexes from the reaction of **4** with 1 equiv of a proton source such as [PyH]OTf (Py = pyridine), [LutH]OTf, or [ColH]OTf. However, the formation of the dinitrogen-bridged dimolybdenum core bearing PPP ligands was detected by mass spectrometry from a reaction mixture of **4** with 4 equiv of CoCp*₂ and 5 equiv of [ColH]OTf in toluene at room temperature for 2 h under 1 atm N_2.[15] This result indicates that some dinitrogen-bridged dimolybdenum complexes bearing PPP ligands may be generated and work as key reactive intermediates of the catalytic reaction.

George and co-workers[20] and Tuczek and co-workers[21] previously used triphosphines and tetraphosphines as ligands to prepare highly reactive molybdenum−dinitrogen complexes. However, catalytic reactions have never been achieved using the molybdenum−dinitrogen complexes bearing triphosphines and tetraphosphines reported to date. In contrast, the present molybdenum−nitride complexes bearing the PPP ligand as only an auxiliary ligand have now been found to work as the most effective catalysts for nitrogen fixation. We believe that the meridional coordination mode of the PPP ligand to the Mo atom in **4** and **5** provides a suitable environment to the molybdenum complexes toward the catalytic reaction.[22] Further work is necessary to elucidate the reaction pathway in more detail.

In summary, we have found that newly designed and prepared molybdenum−nitride complexes bearing the PPP ligand work as the most effective catalysts for the catalytic reduction of dinitrogen to ammonia under ambient reaction conditions, producing up to 63 equiv of ammonia based on the Mo atom. This catalytic activity is more than 5 times higher than that of the original reaction system using **1** as a catalyst.[6] The results described here provide the first successful example of catalytic transformation using molybdenum complexes bearing only a triphosphine as an auxiliary ligand. We believe that the present findings provide useful information for the design of more effective catalysts.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental procedures, spectroscopic data, and X-ray data (CIF). 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 interest.

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(14) When PPh$_2$ groups were used in place of the P^{t}Bu$_2$ groups in the PPP ligand, we could not prepare the corresponding nitride complexes under the same reaction conditions.

(15) See the Supporting Information in details.

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