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Effect of substituents on molybdenum triiodide complexes bearing PNP-type pincer ligands toward catalytic nitrogen fixation

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Molybdenum triiodide complexes bearing various substituted pyridine-based PNP-type pincer ligands are prepared and characterized by X-ray analysis. Their catalytic activity is investigated toward reduction of nitrogen gas into ammonia under ambinet reaction conditions.

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Ammonia is a typical and well-known raw material as nitrogen source of fertilizers, dyes, chemical fibres, and pharmaceuticals.¹ Recently, ammonia has attracted attention as energy and hydrogen carriers because ammonia has unique properties such as high energy density, low flammability, and no carbon content.² Therefore, development of a novel ammonia production process under mild reaction conditions is eagerly anticipated to replace the Haber-Bosch process as the industrial ammonia production requiring harsh reaction conditions. Since the first successful example discovered by Schrock and his coworker,³ catalytic ammonia production from molecular dinitrogen under mild reaction conditions using transition metal-dinitrogen complexes as catalysts has been developed for the last decade.4-7

In 2010, we found that dinitrogen-bridged dimolybdenum complex bearing PNP-type pincer ligands based on the pyridine skeleton worked as an effective catalyst toward ammonia production under ambient reaction conditions.⁸ Recently, we have improved the catalytic activity by the use of PPPtriphosphines and PCP-type pincer ligands based on the N-

heterocyclic carbene skeleton in place of the PNP-type pincer ligands.9,10 As an extensive study of our work,¹¹ we more recently found

that a molybdenum triiodide complex bearing the same PNPtype pincer ligand worked as a more effective catalyst toward catalytic nitrogen fixation, where up to 415 equiv of ammonia were produced based on the Mo atom of the catalyst,¹² than the dinitrogen-bridged dimolybdenum complex. Interestingly, this novel reaction system is proposed to proceed via direct cleavage of the nitrogen-nitrogen triple bond of the coordinated dinitrogen ligand on the dimolybdenum atoms.¹² This remarkable catalytic activity in the novel reaction system prompted us to prepare molybdenum triiodide complexes bearing various substituted PNP-type pincer ligands and investigate their catalytic activity toward ammonia production under ambient reaction conditions. As a result, we have found that the introduction of phenyl and ferrocenyl groups to the pyridine ring of the PNP-type pincer ligand substantially increased the catalytic activity. Herein, we have reported preliminary results.

According to the previous procedure,¹² we newly prepared a variety of molybdenum triiodide complexes bearing various substituted PNP-type pincer ligands. Treatment of [Mol₃(thf)₃] = tetrahydrofuran) with 2,6-bis(di-alkyl or (thf diphenylphosphinomethyl)pyridines bearing two alkyl and phenyl groups on the phosphorous atom and 2,6-bis(di-tertbutylphosphinomethyl)pyridines bearing substituents at the 4position of the pyridine moiety (R-PNPR', 1) in THF at 50 °C for 18 h gave the corresponding molybdenum triiodide complexes



Scheme 1 Synthesis of molybdenum triiodide complexes bearing various substituted PNP-type pincer ligands.^aRef 12

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[Mol₃(R-PNP^{R'})] (**2**; R = H, Ph, Me, MeO, ferrocenyl (Fc), and ruthenocenyl (Rc); R' = *t*-Bu, adamantyl (Ad), *i*-Pr, and Ph) in moderate to good yields (Scheme 1). All molecular structures except for **2b** were confirmed by X-ray analysis (see Supplementary Information).

The catalytic ammonia production was carried out according to the following procedure of our previous method using 2a as a catalyst.¹² To a mixture of **2b** as catalyst and 2,4,6-collidinium trifluoromethanesulfonate (48 equiv to the Mo atom of the catalyst; [ColH]OTf) as proton source in toluene was added a solution of decamethylcobaltcene (36 equiv to the Mo atom of the catalyst; $CoCp_{2}^{*}$ ($Cp^{*} = \eta^{5}-C_{5}Me_{5}$)) as reductant in toluene via a syringe pump at room temperature over a period of 1 h under atmosphere pressure of nitrogen gas, followed by stirring at room temperature for another 19 h. After the reaction, the amounts of ammonia (8.4 equiv based on the Mo atom of the catalyst) and molecular hydrogen (1.3 equiv based on the Mo atom of the catalyst) were determined by indophenol method¹³ and GC, respectively, where ammonia and molecular dihydrogen were obtained in 69% and 7% yields, respectively, based on the CoCp*₂ (Table 1, Entry 2). When 2c and 2d were used as catalysts in place of 2b, 5.6 equiv. and 1.9 equiv. of ammonia were produced based on the Mo atom of the catalysts, together with 4.0 equiv. and 7.0 equiv. of molecular hydrogen, respectively (Table 1, Entries 3 and 4). These results indicate that adamantyl, iso-propyl, and phenyl groups on the phosphorous atom of the PNP-type pincer ligands were less effective than tert-butyl group. Thus, molybdenum complex bearing tert-butyl groups on the phosphorous atom was found to work as the most effective catalyst.

Next, we investigated the nature of substituents at the 4postion of the pyridine ring in the PNP-type pincer ligand toward the catalytic nitrogen fixation. At first, we carried out reactions using 36 equiv of $CoCp_2^*$ as reductant and 48 equiv of [ColH]OTf as proton source in the presence of molybdenum triiodide complexes bearing substituents at the 4-postion of the pyridine ring in the PNP-type pincer ligand. However, unfortunately, we did not find a significant difference in the

Table 1 Molybdenum triiodide complexes bearing various

 functional groups catalyzed reduction of dinitrogen to ammonia^a

N ₂ + 6 Co + 6 OTf Catalyst toluene rt, 20h (1 atm) (36 equiv/Mo) (48 equiv/Mo)								
Entry	Catalyst	NH_3	NH ₃	H ₂	H ₂			
		(equiv) ^b	(%) ^c	(equiv) ^b	(%) ^c			
1 ^{<i>d</i>}	2a	10.9 ± 0.2	91 ± 2	0.2 ± 0.1	1 ± 1			
2	2b	8.4	69	1.3	7			
3	2c	5.6	46	4.0	22			
4	2d	1.9	16	7.0	39			
5	2e	11.5	94	0.2	1			
6	2f	10.3	88	0.3	2			
7	2g	7.6	63	1.6	9			

^aTo a mixture of molybdenum complex (0.010 mmol) and [ColH]OTf (0.48 mmol) in toluene (1 mL) was added a solution of $CoCp_{2}^{*}$ (0.36 mmol) in toluene (4 mL) at room temperature over a period of 1 h, followed by stirring at room temperature for another 19 h under N₂. ^bEquiv based on the molybudenum atom. ^cYield based on CoCp₂^{*}. ^dRef 12

Table 2 Molybdenum complexes bearing functional groups abnline 4-position of pyridine ring catalyzed reduction of dinitrogen to 4975K ammonia^a

N ₂ +			Catalyst toluene rt, 20h	2 NH₃	(+ H ₂)
(1 atm)	(360 equiv/Mo)	(480 equiv/Mo)			

Entry	Catalyst	NH ₃ (equiv) ^b	NH ₃ (%) ^c	H ₂ (equiv) ^b	H ₂ (%) ^c	
1	2a	66 ± 3	55 ± 2	31 ± 1	17 ± 1	
2	2e	90 ± 1	75 ± 1	27 ± 1	15 ± 0	
3	2f	59 ± 0	49 ± 0	61 ± 5	34 ± 3	
4	2g	24 ± 1	20 ± 1	103 ± 5	57 ± 3	
5	2h	83 ± 0	69 ± 1	44 ± 3	25 ± 2	
6	2i	75 ± 1	62 ± 1	30 ± 4	17 ± 2	
7	2a ^d	69	57	45	25	
8	2a ^e	65	54	53	29	
9	3e	87	73	19	11	
10	3h	59	49	65	36	

^aTo a mixture of molybdenum complex (0.002 mmol) and [ColH]OTf (0.96 mmol) in toluene (1 mL) was added a solution of CoCp^{*}₂ (0.72 mmol) in toluene (4 mL) at room temperature over a period of 1 h, followed by stirring at room temperature for another 19 h under N₂. ^bEquiv based on the molybudenum atom. ^cYield based on CoCp^{*}₂. ^dFeCp₂ (1equiv. to **1a**) was added. ^eRuCp₂ (1equiv. to **1a**) was added.



Fig. 1 IR absorbance of terminal dinitrogen ligand in dinitrogen-bridged dimolybdenum complexes.

amount of the produced ammonia under the same reaction conditions (Table 1, Entries 5–7). Based on these results, we used larger amounts of CoCp*₂ (360 equiv) as reductant and [CoIH]OTf (480 equiv) as proton source in the presence of the molybdenum triiodide complexes. Typical results are shown in Table 2. When **2e** was used as a catalyst, 90 equiv. of ammonia and 27 equiv. of molecular hydrogen, respectively, were produced based on the Mo atom of the catalyst (Table 2, Entry 2). For comparison, the amount of the produced ammonia using **2e** as a catalyst was substantially higher than that using **2a** as a catalyst (Table 2, Entry 1). On the other hand, when **2f** and **2g** were used as catalysts, only smaller amount of ammonia was produced than that using **2a** as a catalyst together with larger amount of molecular hydrogen (Table 2, Entries 3 and 4).

In our previous study,^{8b} we confirmed that Ph group and MeO group at the 4-postion of the pyridine ring in the PNP-type pincer ligand worked as electron-withdrawing and electrondonating groups, respectively, based on the comparison of the dinitrogen stretching frequency of the terminal dinitrogen ligand of the corresponding dinitrogen-bridged dimolybdenum complexes bearing the PNP-type pincer ligands (Figure 1). Both our previous result and the experimental results shown in Table 2 indicate that the presence of an electron-withdrawing group such as Ph group and an electron-donating group such as MeO group to the pyridine ring in the PNP-type pincer ligand increased and decreased the catalytic activity, respectively.

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Thus, the tendency of substituents to the pyridine ring of the PNP-type pincer ligands in **2** shown in Table 2 is in sharp contrast to that in dinitrogen-bridged dimolybdenum comprexes.^{8b}

Next, we carried out reactions in the presence of molybdenum triiodide complexes bearing Fc and Ru groups at the 4-postion of the pyridine ring in the PNP-type pincer ligand (**2h** and **2i**). The amounts of ammonia (83 and 75 equiv, respectively) using **2h** and **2i** as catalysts were higher than that using **2a** as a catalyst (Table 2, Entries 5 and 6). To obtain more information on the role of Fc and Ru groups to the catalysts, we confirmed no change in the amount of ammonia production when ferrocene and ruthenocene were added to the reaction using **2a** as a catalyst under the same reaction conditions (Table 2, Entries 7 and 8). These results indicate that the introduction of Fc and Rc groups to the pyridine ring of the PNP-type pincer ligand increased the catalytic activity.

In our previous study,^{8c} we confirmed that Fc and Rc groups at the 4-postion of the pyridine ring in the PNP-type pincer ligand did not work as electron-withdrawing groups, based on the comparison of the dinitrogen stretching frequency of the terminal dinitrogen ligand of the corresponding dinitrogenbridged dimolybdenum complexes bearing the PNP-type pincer ligands (Figure 1). To obtain more information on the property of Fc and Rc groups, cyclic voltammograms (CVs) of 2a, 2h, and **2i** were measured in THF with $[NBu_4]BAr^{F_4}$ (Ar^F = 3,5-(CF₃)₂C₆H₃) as supporting electrolyte. Typical results are shown in Table 3. The CV of 2a showed an irreversible electron oxidation wave at E_{pa} = +0.11 V vs FeCp₂^{0/+} assignable to Mo (III/IV) (Table 3, Entry 1). The CV of 2h showed an irreversible electron oxidation wave at E_{pa} = +0.13 V derived from Mo (III/IV) and a reversible one-electron oxidation wave derived from Fe (II/III) couple at $E_{1/2}$ = + 0.40 V vs. FeCp₂^{0/+} respectively (Table 3, Entry 2). Based on the CV of Fc-PNP^{t-Bu} (1h) reported in our previous study (Table 3, Entry 3),^{8c} complexation with molybdenum-triiodide led oxidation potential of Fc moiety at the pincer ligand to positive sift by + 0.29 V in 2h. Based on the CVs of 2a, 2h and 1h, we consider that an electronic interaction between the Mo centre and Fe centre in 2h may play an important role to increase the catalytic activity. As discussed in our previous work,^{8c} the direct interaction between the Mo centre and Fe centre may accelerate the reduction step in the catalytic ammonia production via an intramolecular electron transfer from the Fe centre of the Fc moiety to the active site of the Mo centre in the complex.

On the other hand, the CV of **2i** showed only one irreversible electron oxidation wave at $E_{pa} = +0.10$ V derived from Mo (III/IV) without the oxidation wave derived from Ru (II/III) of Rc group (Table 3, Entry 4). Based on the CV of Rc-PNP^{t-Bu} (**1i**) reported in our previous study,^{8c} where one irreversible oxidation wave was observed at $E_{pa} = +0.78$ V derived from Ru (II/III) (Table 3, Entry 5), we did not obtain any direct evidence to support an electronic interaction between the Mo centre and Ru centre in **2i**. Thus, unfortunately, we have not yet clarified the exact reason why the introduction of Rc group to the pyridine ring of the PNP-type pincer ligand increased the catalytic activity.



Fig. 2 Time profiles of ammonia production with **2a** (blue), **2e** (green) and **2h** (red) as catalysts. $CoCp_{2}^{*}$ (0.36 mmol; 180 equiv / Mo) and [CoIH]OTf (0.48 mmol; 240 equiv / Mo) was added a solution of catalyst (0.002 mmol) in toluene (5 mL) at room temperature.



Scheme 2 (a) Stoichiometric reduction of 2e and 2h with CoCp^{*}₂. Yield was determined by NMR. (b) Stoichiometric reaction of 3e and 3h with CoCp^{*}₂ and [ColH]OTf under Ar. Yield was determined by indophenol method

To verify the difference of the catalytic behavior of 2a, 2e, and **2h**, we monitored time dependence of ammonia formation using 360 equiv of CoCp*₂ and 480 equiv of [ColH]OTf. However, we did not observe any difference of the catalytic activity because the initial rate within 40 min from the start of the catalytic reaction was almost the same in all cases. Typical results are shown in the Supplementary Information (see Supplementary Information in details). Based on these experimental results, we modified the experimental procedure of the slow addition of a solution of CoCp*₂ over a period of 1 h to the reaction mixture to the addition of CoCp*₂ to the reaction mixture in one portion. The ammonia production finished within 5 min in all cases. Typical results are shown in Figure 2. Turnover frequencies (TOFs) for ammonia production using 2a, 2e, and 2h as catalysts, which are determined as mols of ammonia produced in initial 1 min per catalyst, were 5.6, 14 and 7.7 min⁻¹, respectively. These results indicate that the introduction of Ph and Fc groups to the pyridine ring of the PNPtype pincer ligand increased the reaction rate of ammonia production. Thus, the rate-determining step of the catalytic reaction described in this paper is not involved in protonation step but in reduction step.¹² At present, we consider that one of the reduction steps of cationic imido, amido, and ammonia complexes is the rate-determining step.

Finally, we carried out some stoichiometric reactions of 2e and 2h for comparison of the reactivity of 2e and 2h with that of **2a**. Reduction of **2e** and **2h** with 2.2 equiv. CoCp^{*}₂ in toluene at room temperature under an atmospheric dinitrogen gas gave the corresponding nitride complexes [MoI(N)(R-PNPt-Bu)] (3e: R = Ph; 3h: R = Fc) in 62% and 70% NMR yields, respectively (Scheme 2a). Both the nitride complexes were isolated, and the detailed molecular structure was confirmed by X-ray analysis (see Supplementary Information). Further stoichiometric reactions of the nitride complexes such as **3e** and **3h** with 3 equiv. of CoCp^{*}₂ and 4 equiv. of [CoIH]OTf under atmospheric pressure of argon gas gave ammonia in 59% and 86% yields based on the Mo atom of the complexes, respectively (Scheme 2b). Separately, we confirmed that both the nitride complexes 3e and 3h worked as the same effective catalysts toward ammonia production with 2e and 2h (Table 2, Entries 9 and 10). Based on the experimental results of the stoichiometric and catalytic reactions, we consider that ammonia production described in the presentviemanuscript proceeded via the same reaction pathway,1030/68270di925t cleavage of the nitrogen-nitrogen triple bond of the bridging dinitrogen ligand on the dimolybdenum atoms played a key role to afford the corresponding nitride complexes as reactive intermediates.12

In summary, we have newly prepared and characterized a series of molybdenum triiodide complexes bearing various substituted pyridine-based PNP-type pincer ligands. The introduction of Ph and Fc groups at the 4-position of the pyridine ring of the PNP-ligand as electron-withdrawing and redox active groups substantially increased the catalytic The former tendency is in sharp contrast to our activity. previous reaction system that the electron-withdrawing groups to the PNP-ligand of the dinitrogen-bridged dimolybdenum complexes decreased the catalytic activity.^{8b} However, the former tendency is consistent with that of our previous reaction system that iodide ligand as an electron-withdrawing group¹⁴ in the molybdenum complexes worked more effective catalysts than other halide ligands such as bromide and chloride ligands.¹² We believe that the achievement described in the present manuscript provides valuable information to improve the catalytic activity toward ammonia production under ambient reaction conditions.

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