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Preparation and reactivity of molybdenum complexes bearing pyrrole-based PNP-type pincer ligand

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Molybdenum complexes bearing an anionic pyrrole-based PNP-type pincer ligand have been prepared and have been found to work as catalysts for the conversion of N_2 into NH_3 under ambient conditions.

Artificial nitrogen fixation to convert N_2 into NH_3 by using transition metal catalysts under ambient conditions has attracted attention as a candidate to develop small-scale reactor systems for convenient NH_3 production.[1,2] Entering the 21st century, catalytic conversion of N_2 into NH_3 has been reported for several homogeneous catalysts containing transition metals such as Ti,[3] V,[4] Mo,[5–7] Re,[8] Fe,[9,10] Ru,[11] Os,[11] and Co.[12] However, applicable pairs of reducing reagents with proton sources have been limited to metallocenes or KC_8 with the highly acidic Brookhart's acid ($[H(OEt_2)_2]BAr^F{}_4$, ($BAr^F{}_4$ = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate)) or conjugate acids of pyridine derivatives, amines, or a phosphine, responsible in part for the requirement of low temperatures (such as –78 °C) to inhibit the formation of side products such as H_2 from the direct reaction of reducing reagents with proton sources.

Very recently, our group has confirmed that SmI_2[13] can be used as the most effective reducing reagent so far to convert N_2 into NH_3 in combination with ethylene glycol or H_2O as a proton source, thus H_2O has become available for use in the artificial catalytic nitrogen fixation under ambient conditions.[14] Here, the turnover number (TON) and the initial turnover frequency (TOF) for the formation of NH_3 using SmI_2, H_2O, and a molybdenum complex bearing a carbene-based PCP-type pincer ligand as a reducing reagent, a proton source, and a catalyst, respectively, were found to be 4,350 equiv Mo^{-1} and 112.9 equiv min^{-1} Mo^{-1}, respectively, with both giving the best TON and TOF values among the artificial nitrogen fixation under mild reaction conditions, and the latter reaching to the TOF values reported for the bacterial nitrogen fixation.[15] In this catalytic system using SmI_2/H_2O, efficient reduction and protonation are proposed to proceed via the proton-coupled electron-transfer (PCET) process.[16] The SmI_2/H_2O pair can be also applicable to classical molybdenum dinitrogen complexes bearing monodentate or bidentate phosphines,[17] where stepwise six-electron reduction and sextuple protonation are proposed to occur onto the coordinated dinitrogen to afford 2 equiv of NH_3 per catalytic cycle (classical Chatt cycle),[18] but the catalytic activity is better for molybdenum complexes with *N*-heterocyclic carbene-based PCP-type or pyridine-based PNP-type pincer ligands, where direct cleavage of N≡N triple bond is proposed to proceed first in dinitrogen-bridged dimolybdenum complexes to afford the nitride species,[7,19–21] followed by presumable three-electron reduction and triple protonation to give 1 equiv of NH_3 per nitride species.

In order to investigate the electronic and steric effects of the pincer ligands on the catalytic reactivity and reaction pathways for the conversion of N_2 into NH_3, we have come to the idea to prepare and examine molybdenum complexes bearing an anionic pyrrole-based PNP-type pincer ligand.[22,23] Indeed, we have already achieved catalytic conversion of N_2 into NH_3 for pyrrole-based PNP-type pincer complexes of V,[4] Fe,[10] and Co.[12] Molybdenum complexes with azaferrocene-based PNP-type pincer ligands, where the anionic pyrrolide is coordinated to both Mo and FeCp* (Cp* = η^5-C_5Me_5) moieties, have been already prepared, but yielding only a stoichiometric amount of NH_3 even in catalytic conditions.[24]

Introduction of an anionic pyrrole-based PNP-type pincer ligand (**PNP** = 2,5-bis(di-*tert*-butylphosphinomethyl)pyrrolide) onto the molybdenum atom was achieved when the lithiated ligand Li**PNP** was treated with Mo(III) triiodo precursor $[MoI_3(thf)_3]$ in THF at room temperature to afford the Mo(III) diiodo complex [MoI_2(**PNP**)] (**1**) in 81% yield (Scheme 1). The effective magnetic susceptibility μ_{eff} determined by Evans method was found to be 1.4 μ_B for **1**, interpretable as the low-spin d^3 electronic configuration with an $S = 1/2$ spin state. The molecular structure of **1** was unambiguously determined by an X-ray analysis (Fig. 1a), which demonstrates that **1** has a distorted square pyramidal structure with a 5-coordinate geometry index value at $\tau_5 = 0.19$.[25]

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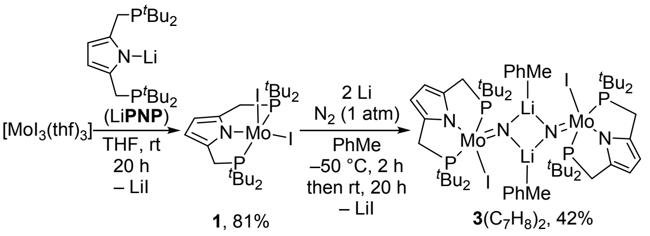
Next, we examined the reduction of **1** under an N_2 atmosphere to obtain the corresponding dinitrogen complexes. Indeed, treatment of **1** with KC_8 in THF under 1 atm of N_2 gave brown solid with an IR absorption band at 2060 cm^{-1}, attributable to the formation of a dinitrogen- and pyrrolide-bridged Mo(0)–Mo(I) mixed-valence coordination polymer $[(K(N_2)\{Mo(N_2)($**PNP**$)\}_2)_n]$ (**2**), which could not be isolated sufficiently pure (Scheme S2, ESI†). On the other hand, reduction of **1** with metallic lithium in toluene at –50 °C under 1 atm of N_2 afforded the dimeric 5-coordinate Mo(IV) nitrido complex $[\{Li(PhMe)MoI(N)($**PNP**$)\}_2]$ as diamagnetic brown solid (Scheme 1). (**3**$(C_7H_8)_2$) exhibited a new strong IR absorption band assignable to the coordinated Mo≡N nitrido vibration at 1063 cm^{-1}, comparable to the values reported for other 5-coordinate Mo nitrido complexes (948–1109 cm^{-1}) (Table S10, ESI†). In solution, **3**$(C_7H_8)_2$ gave a $^{31}P\{^1H\}$ NMR resonance at δ 95.7.



Scheme 1 Preparation of molybdenum diiodo and nitrido complexes bearing a pyrrole-based PNP-type pincer ligand with the cleavage of N_2.

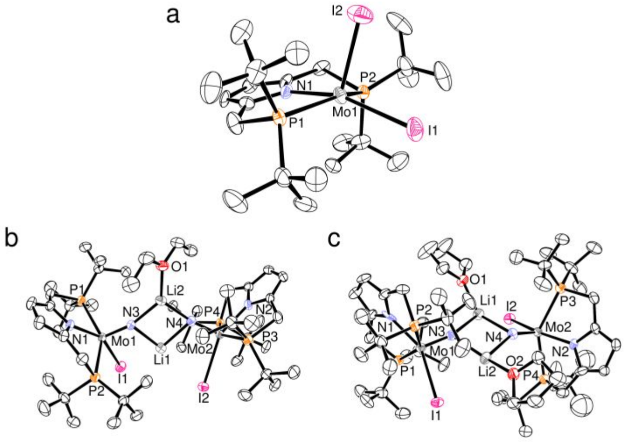
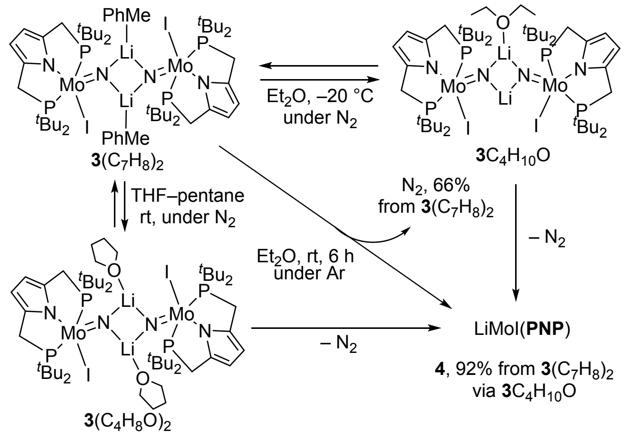


Fig. 1 ORTEP drawings of **1** (a), one of the two crystallographically independent residues of **3**$C_4H_{10}O$ (b), and **3**$(C_4H_8O)_2$ (c). Thermal ellipsoids are shown at the 50% level. Hydrogen atoms as well as uncoordinated solvate molecules, the other crystallographically independent residue of **3**$C_4H_{10}O$, and a minor disorder of **3**$(C_4H_8O)_2$ are omitted for clarity.

Detailed structures of $[Li_2L_n\{MoI(N)($**PNP**$)\}_2]$ (**3**L_n, L_n = $C_4H_{10}O$ or $(C_4H_8O)_2$) in solid state were eventually determined by X-ray analyses using crystals of $[Li_2(Et_2O)\{MoI(N)($**PNP**$)\}_2]\cdot 0.5Et_2O$ (**3**$C_4H_{10}O\cdot 0.5C_4H_{10}O$) (Fig. 1b) and $[\{Li(thf)MoI(N)($**PNP**$)\}_2]$ (**3**$(C_4H_8O)_2$ (Fig. 1c), obtained by further slow evaporation of diethyl ether solution of **3**$(C_7H_8)_2$ at –20 °C or from THF–pentane solution of **3**$(C_7H_8)_2$ at room temperature, respectively, in N_2 glovebox (Scheme 2). Both **3**$C_4H_{10}O$ and **3**$(C_4H_8O)_2$ have dimeric structures, where the two anionic Mo(IV) (iodo)(nitrido) moieties $\{MoI(N($**PNP**$)\}$ are linked with two cationic Li atoms bound to two μ_3-nitrido N atoms bridging one Mo and two Li atoms for each. One of the two Li atoms in **3**$C_4H_{10}O$ is additionally coordinated to an O atom of Et_2O to display a pseudo rotational C_2 symmetry around the Li···Li–O axis (Fig. 1b), whereas each of the Li atoms in **3**$(C_4H_8O)_2$ is additionally coordinated to a THF O atom to display a pseudo rotational C_2 symmetry around the vertical axis that passes through the center of the bridging Li_2N_2 core (Fig. 1c). Similar dimeric structure was previously reported for the 5-coordinate Mo(VI) nitrido complex bearing an anionic OCO-type pincer ligand bridged by Na(dmf) units.[26] The nitrido ligands in **3**$C_4H_{10}O$ or **3**$(C_4H_8O)_2$ possess the apical positions of distorted square pyramidal structures with an averaged τ_5 value at = 0.12±0.05 or 0.09±0.03, and with an averaged Mo≡N bond length at 1.677(4) or 1.678(7) Å, respectively, comparable to the values found for 5-coordinate Mo(IV), Mo(V), or Mo(VI) nitrido complexes bearing pincer ligands with τ_5 values at 0.001–0.26 and Mo≡N bond lengths at 1.63–1.73 Å (Table S9, ESI†). Further DFT calculations gave the estimation that the split of the dimer **3**$(C_4H_8O)_2$ to the corresponding monomeric nitrido complex $[Li(thf)MoI(N)($**PNP**$)]$ (**A**) at 298 K is endergonic (ΔG = +20.2 kcal mol^{-1}), demonstrating that that the dimeric structure is kept even in solution (Scheme S5, ESI†).



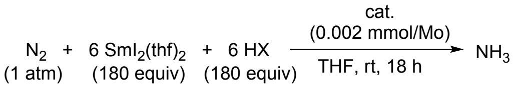
Scheme 2 Release of N_2 from the nitrido complex.

It must be noted that the dimeric nitrido complex **3**L_n, rather stable in non-polar solvents such as toluene or benzene, was found to be labile in O-donor solvents such as diethyl ether and THF, although crystals suitable for X-ray analyses were grown from these solvents. Indeed, crystals of **3**$C_4H_{10}O\cdot 0.5C_4H_{10}O$ and **3**$(C_4H_8O)_2$ are highly efflorescent, and further evaporation of solvents in N_2 glovebox led to the loss of the strong Mo≡N IR absorption to afford the Mo(I) compound LiMoI(**PNP**) (**4**) as a pale orange powder in 92% yield, where two nitrido ligands have been likely coupled to regenerate and liberate N_2, presumably assisted by the removal of lithium atoms more strongly bound to volatile O-donor solvents from the nitrido ligands (Scheme 2). **4** exhibited the effective magnetic susceptibility μ_{eff} at 1.3 μ_B, acceptable for the low-spin d^5 electronic configuration with an $S = 1/2$ spin state, and should have oligomeric structure where two or more Mo moieties are linked by the anionic pyrrole-based PNP ligand, for pyrrolide has been reported to work as a bridging ligand among Mo and

Li atoms,[27] and pyrrole-based PNP ligands themselves have been reported to work as bridging ligands via pyrrolide or phosphine moieties,[22,24,28] albeit fine crystals of **4** suitable for X-ray analyses have not been obtained. Formation of **4** has also been confirmed by elemental analyses, which have given the same results for those obtained by slow evaporation under 1 atm of N_2 and those obtained by vacuum drying. Furthermore, when **3**$(C_7H_8)_2$ was once dissolved in diethyl ether or THF and was further dried up, only compound **4** was obtained as the sole product, whereas the evolution of a stoichiometric amount of N_2 gas (66% based on **3**$(C_7H_8)_2$) was confirmed by stirring **3**$(C_7H_8)_2$ in diethyl ether at room temperature for 6 h under 1 atm of Ar (Scheme 2). Thus, the molybdenum complexes bearing the anionic pyrrole-based PNP-type pincer ligand has provided another example where both cleavage and formation of N_2 is observed in the same unit. This phenomena have been only observed for dimolybdenum[21,29] and multi-iron systems.[30] Further reverse reaction under 1 atm of N_2 to regenerate the nitrido complex **3**L_n from **4**, which is no longer dissolvable to toluene or benzene, has not been achieved.

With the new molybdenum PNP-type pincer complexes in our hands, catalytic nitrogen fixation under ambient conditions was next investigated (Table 1). When SmI_2, ethylene glycol, and **1** were used as a reducing reagent, a proton source, and a catalyst, respectively, for the conversion of N_2 into NH_3, 12 equiv of NH_3 were obtained based on the Mo atom of **1** (Table 1, entry 1). H_2O can also be used as a proton source to afford 11 equiv of NH_3 (Table 1, entry 2). On the other hand, $KC_8/[H(OEt_2)_2]BAr^F_4$ and $CoCp^*_2/[ColH]OTf$ (Col = 2,4,6-trimethylpyridine) pairs did not work as effective reagents for the nitrogen fixation catalyzed by **1** (Table S1, entries 3 and 4, ESI†). Both **3**$(C_7H_8)_2$ and **4** were also shown to work as the catalysts to convert N_2 into NH_3 under the employment of SmI_2 and ethylene glycol, but the yields of NH_3 were slightly worse (Table 1, entries 3 and 5), suggesting that the existence of Li cation gave a negative effect on the catalysis in spite of the positive effect on the isolation of the nitrido complexes **3**L_n.

Table 1 Catalytic reduction of N_2 into NH_3.[a]



$$\underset{(1\ \text{atm})}{N_2} + \underset{(180\ \text{equiv})}{6\ SmI_2(thf)_2} + \underset{(180\ \text{equiv})}{6\ HX} \xrightarrow[\text{THF, rt, 18 h}]{\substack{\text{cat.}\\(0.002\ \text{mmol/Mo})}} NH_3$$

entry	catalyst	HX	NH_3 (equiv/Mo)[b]
1	**1**	$HOCH_2CH_2OH$	12.2±1.0[c]
2	**1**	H_2O	11.2±0.7[c]
3	**3**$(C_7H_8)_2$	$HOCH_2CH_2OH$	6.9
4	**3**$(C_7H_8)_2$	H_2O	2.6
5	**4**	$HOCH_2CH_2OH$	7.3
6	**4**	H_2O	2.6

[a] A mixture of the molybdenum complex (0.002 mmol/Mo), $SmI_2(thf)_2$ (0.360 mmol), and HX (0.360 mmol, X = OCH_2CH_2OH or OH) in THF (5 mmol) was stirred at room temperature for 18 h under 1 atm of N_2. [b] Equiv of NH_3 based on the Mo atom of the catalyst after acid hydrolysis of the reaction mixture. [c] Average of three runs.

As shown in Scheme 1, stoichiometric reduction of **1** with Li under 1 atm of N_2 afforded the dimeric nitrido complex **3**L_n via the N≡N bond cleavage of the bridging N_2, with Li cation contributing to the stability of dimeric structure of **3**L_n in comparison to the corresponding monomeric structure (Scheme S5, ESI†). Thus, we have concluded that reaction pathway in the catalytic conditions using SmI_2 as a reducing reagent is similar to those proposed previously,[7] where the N≡N triple bond cleavage of the N_2-bridged species to afford the nitrido species is the key, but whether the nitrido species keeps dimeric or monomeric structure in catalytic conditions cannot be concluded at present because of the difference in reducing reagents between catalytic and stoichiometric conditions. In the catalytic conditions, two-electron reduction of **1** by SmI_2 under 1 atm of N_2 likely gives the Mo(I) N_2-bridged species, where the N≡N triple bond cleavage of the bridging N_2 occurs to afford the Mo(IV) nitrido species $\{MoI(N)(\mathbf{PNP})\}^-$ isoelectronic to **3**L_n. Further three-electron reduction and triple protonation per nitrido moiety by SmI_2/H_2O or ethylene glycol under N_2 presumably afford ammonia and Mo(I) species, where coordination of bridging N_2 occurs to regenerate the N_2-bridged species.

In summary, molybdenum complexes bearing an anionic pyrrole-based PNP-type pincer ligand have been newly prepared and characterized, and formation of the nitrido complex via the N≡N triple bond cleavage and regeneration of N_2 via the coupling of nitrido moieties are observed. The obtained complexes have been found to work as catalysts for the conversion of N_2 into NH_3 under ambient conditions, where the catalysis is proposed to proceed via the N≡N triple bond cleavage to afford the corresponding nitride species as a key step. As the nitrido species obtained by the N≡N triple bond cleavage have been recently considered as ones of the key reactive intermediates for the preparation of other N-containing compounds,[20,31] the nitrido complex obtained here provides another precursor for such catalytic or stoichiometric reactions. Further investigation on their reactivity is now in progress.

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Conflicts of interest

There are no conflicts to declare.

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Text for Table of Contents Entry

Molybdenum complexes bearing an anionic pyrrole-based PNP-type pincer ligand have been prepared and have been found to work as catalysts for the conversion of N_2 into NH_3 under ambient conditions.

(196 characters including spaces in total)

Graphical Abstract