Preparation and reactivity of a dinitrogen-bridged dimolybdenum-tetrachloride complex†

Kazuya Arashiba, Shogo Kuriyama, Kazunari Nakajima and Yoshiaki Nishibayashi*

A dinitrogen-bridged dimolybdenum-tetrachloride complex is prepared and reduced with Super-Hydride (LiBHEt₃) to afford the corresponding dimolybdenum-dinitrogen complex together with the formation of molecular dihydrogen. This reaction proceeds via the ligand exchange of the coordinated dihydrogen generated in situ with molecular dinitrogen.

The development of a nitrogen fixation system under mild reaction conditions is one of the most important subjects in chemistry.1 Quite recently, we have found another successful example² of the catalytic formation of ammonia from molecular dinitrogen under ambient conditions, where dinitrogen-bridged dimolybdenum-dinitrogen complexes work as an effective catalyst.³ In this reaction system, a sequential process of protonation and reduction is necessary to transform the coordinated molecular dinitrogen into ammonia at the molybdenum atom of the catalyst. Interestingly, a similar process may occur at the active site of nitrogenase to convert molecular dinitrogen into ammonia under ambient conditions.⁴

As the next stage of the previous work, we have focused on the development of the catalytic formation of ammonia from molecular dinitrogen and dihydrogen at ambient temperature and pressure.⁵,⁶ Previously, we have found the stoichiometric treatment of [MoCl₃(PNP)]₁ with 1 equiv. of KC₈ in THF at room temperature for 20 h under an atmospheric pressure of dinitrogen gave the dinitrogen-bridged dimolybdenum-tetrachloride complex [MoCl₄(PNP)]₂(μ-N₂) (2) in 64% yield (Scheme 1). No informative data on the structure of 2 were obtained from its NMR spectra due to the paramagnetism. Complex 2 exhibits μ-eff = 3.2 μB in THF-d₈ at 296 K (Evans NMR method), which is consistent with an S = 1 system (μ-eff = 2.83 μB) on each Mo atom. No Raman absorption attributable to the bridging N≡N stretch is observed at 1800–2100 cm⁻¹ for 2. Additionally, no IR absorption attributable to the terminal N≡N stretch is also observed for 2, in contrast to the value (1936 cm⁻¹) observed for

![Scheme 1](image-url)
These phenomena can be explained by the enhancement of the N–N π-bonding between the two nitrogen atoms of the bridging dinitrogen ligand. The reduction of 2 into 3 increases the population of the LUMO, which is responsible for the N–N π-bonding character. Similar phenomena were observed in a series of dinitrogen-bridged dimolybdenum complexes bearing bulky amido ligands developed by Cummins and co-workers. A more detailed molecular structure of 2 is determined by X-ray crystallographic study (Fig. 1). The molecular structure of 2 contains two [MoCl₂(PNP)] moieties bearing two chloride ligands in trans form. The two molybdenum atoms are bridged by one dinitrogen ligand in an end-on fashion with the almost linear Mo–N–N–Mo bonding. The two molybdenum fragments are twisted around the Mo–N–N–Mo axis with respect to each other away from the steric interaction between two PNP ligands: the torsion angle for C1(1)–Mo(1)–Mo(2)–Cl(3) is 96.73(2)°. As shown in Table 1, the bond distance of bridging-dinitrogen (N(1)–N(2) 1.169(3) Å) is slightly longer than that of 3 (N–N 1.146(4) Å), while the Mo–N(briding) distances in 2 (Mo(1)–N(1) 1.925(2) Å, Mo(2)–N(2) 1.927(2) Å) are shorter than that of 3 (Mo–N 2.024(3) Å). These results indicate that the N–N bond lengths of the dinitrogen-bridged dimolybdenum complexes 2 and 3 decrease as their Mo centers are reduced from Mo(2) to Mo(0). These phenomena can be explained by the enhancement of the N–N π-bonding between the two nitrogen atoms of the bridging dinitrogen ligand.

![Fig. 1 ORTEP drawing of 2. Thermal ellipsoids are shown at the 50% probability level.](image)

A cyclic voltammetric study of 2 reveals two reversible cathodic waves at −1.98 and −1.02 V and two quasi-reversible anodic waves at −0.06 and +0.17 V vs. Fe/Fe⁺, respectively.

A more detailed molecular structure of 2 is determined by X-ray crystallographic study (Fig. 1). The molecular structure of 2 contains two [MoCl₂(PNP)] moieties bearing two chloride ligands in trans form. The two molybdenum atoms are bridged by one dinitrogen ligand in an end-on fashion with the almost linear Mo–N–N–Mo bonding. The two molybdenum fragments are twisted around the Mo–N–N–Mo axis with respect to each other away from the steric interaction between two PNP ligands: the torsion angle for C1(1)–Mo(1)–Mo(2)–Cl(3) is 96.73(2)°. As shown in Table 1, the bond distance of bridging-dinitrogen (N(1)–N(2) 1.169(3) Å) is slightly longer than that of 3 (N–N 1.146(4) Å), while the Mo–N(briding) distances in 2 (Mo(1)–N(1) 1.925(2) Å, Mo(2)–N(2) 1.927(2) Å) are shorter than that of 3 (Mo–N 2.024(3) Å). These results indicate that the N–N bond lengths of the dinitrogen-bridged dimolybdenum complexes 2 and 3 decrease as their Mo centers are reduced from Mo(2) to Mo(0). These phenomena can be explained by the enhancement of the
molecular dihydrogen with molecular dinitrogen may be a key step to transform 2 into 3.\textsuperscript{9,10} In fact, unfortunately, we have not yet observed the formation of the dinitrogen-bridged dimolybdenum-bis(di-hydride) and bis(dihydrogen) complexes such as A and B by ESI-TOF-MS. However, when the reduction of 2 with LiBHEt\textsubscript{3} was carried out under an atmospheric pressure of argon, in place of dinitrogen, the formation of the dinitrogen-bridged dimolybdenum-dichloride-dihydride complex \([\text{Mo}]\text{[H]}\text{[Cl[PNP]}\text{]_2}\mu\text{[N}_2\text{]}\text{]}\text{ (4) was observed by ESI-TOF-MS from a reaction mixture after the reduction.}\textsuperscript{11}

Separately, we confirmed that only a small amount of 3 was observed by \textsuperscript{1}H NMR in the direct reduction of 1 with an excess amount of LiBHEt\textsubscript{3} in THF at room temperature for 20 h under an atmospheric pressure of dinitrogen. This result indicates that the stepwise reduction of 1 via 2 as a reactive intermediate into 3 provides a novel approach to the preparation of dinitrogen-bridged dimolybdenum-dinitrogen complexes. We believe that this process provides useful information to design the catalytic formation of ammonia from molecular dinitrogen and dihydrogen under mild reaction conditions.\textsuperscript{9,10}

Interestingly, we confirmed the formation of 2 from the oxidation of 3 with 4 equiv. of AgCl in THF at room temperature for 20 h under an atmospheric pressure of dinitrogen (Scheme 5). This is the reverse of the reductive transformation of 2 into 3. These results indicate that the bridging-dinitrogen ligand may be tightly coordinated to the two molybdenum atoms in 2 and 3 during the oxidation process.

In summary, we have prepared a novel dinitrogen-bridged dimolybdenum-tetrachloride complex bearing PNP-type pincer ligands and reduced the dimolybdenum-tetrachloride complex with Super-Hydride to form the corresponding dinitrogen-bridged dimolybdenum-dinitrogen complex together with molecular dihydrogen. We believe that the reduction of high oxidative molybdenum complexes with hydride species to regenerate the corresponding dinitrogen complexes is one of the most important steps to realize the catalytic formation of ammonia from molecular dinitrogen and dihydrogen under mild reaction conditions.\textsuperscript{12} Further studies on the preparation and reactivity of molybdenum- and iron-complexes bearing other pincer ligands are currently underway.\textsuperscript{13–15}

This work was supported by the Funding Program for Next Generation World-Leading Researchers (GR025). S.K. is a recipient of the JSPS Predoctoral Fellowships for Young Scientists.

Notes and references


11 ESI-TOF-MS (THF) of 4 \(1084\) (M).


13 We have recently found the first successful example of iron-catalyzed reduction of molecular dinitrogen under ambient reaction conditions; see: M. Yuki, H. Tanaka, K. Sasaki, Y. Miyake, K. Yoshihawa and Y. Nishibayashi, Nat. Commun., 2012, 3, 1254.

14 Quite recently, Peters and co-workers have reported the first successful example of the iron-catalyzed transformation of atmospheric pressure molecular dinitrogen into ammonia at \(78{^\circ}\text{C}\) J. A. Anderson, J. Rittle and J. C. Peters, Nature, 2013, 501, 84.