

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

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

Cite this: *Chem. Commun.*, 2013, **49**, 11215Received 11th September 2013,
Accepted 8th October 2013

DOI: 10.1039/c3cc46946h

www.rsc.org/chemcomm

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.

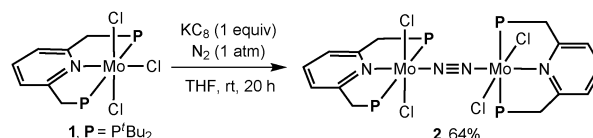
The development of a nitrogen fixation system under mild reaction conditions is one of the most important subjects in chemistry.¹ Quite recently, we have found another successful example² of the catalytic formation of ammonia from molecular dinitrogen under ambient conditions, where dinitrogen-bridged 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 formation of ammonia from the reaction of a tungsten-dinitrogen complex with an excess amount of ruthenium-dihydrogen complex under mild reaction conditions.⁶ After the reaction, a ruthenium-hydride complex was observed together with high oxidative tungsten species without nitrogenous ligands. To achieve the catalytic formation of ammonia as the next nitrogen fixation, in place of the Haber-Bosch process,⁷ the ruthenium-hydride species should reduce the high oxidative tungsten species to regenerate the corresponding tungsten-dinitrogen complex. However, unfortunately, the tungsten species can not

be reduced with the ruthenium-hydride species or with other hydride species such as LiBHET₃.⁶

As the first stage of the development of the catalytic formation of ammonia from molecular dinitrogen and dihydrogen under mild reaction conditions, we envisaged the reaction of the high oxidative molybdenum complexes with hydride species to regenerate the corresponding dinitrogen complexes as starting catalytic species. In this reaction, the high oxidative molybdenum complexes can be reduced into the corresponding dinitrogen complexes, where the ligand exchange of the coordinated dihydrogen with molecular dinitrogen may be involved as a key step to regenerate the corresponding dinitrogen complexes. Herein, we describe the preparation of the dinitrogen-bridged dimolybdenum-tetrachloride complex bearing a PNP-type pincer ligand and the reduction of the dimolybdenum-tetrachloride complex with Super-Hydride (LiBHET₃) to afford the corresponding molybdenum-dinitrogen complex together with the formation of molecular dihydrogen.

Treatment of [MoCl₃(PNP)]³ (**1**:PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) 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 [MoCl₂(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 μ_B in THF-*d*₈ at 296 K (Evans NMR method), which is consistent with an *S* = 1 system (μ_{eff} = 2.83 μ_B) 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 Preparation of a dinitrogen-bridged dimolybdenum-tetrachloride complex bearing PNP pincer ligand (**2**).

Institute of Engineering Innovation, School of Engineering, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo, 113-8656, Japan. E-mail: ynishiba@sogo.t.u-tokyo.ac.jp; Fax: +81-3-5841-1175

† Electronic supplementary information (ESI) available. CCDC 953144. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc46946h



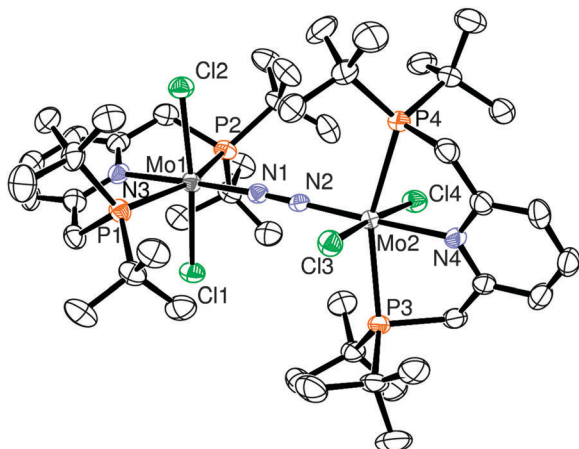


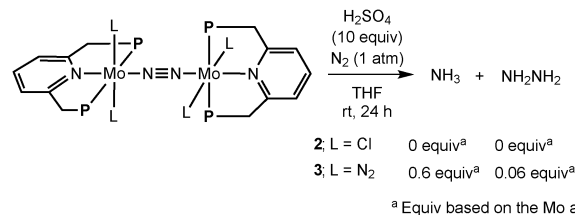
Fig. 1 ORTEP drawing of **2**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1–N1 1.925(2), Mo2–N2 1.927(2), Mo1–N3 2.192(2), Mo2–N4 2.197(2), N1–N2 1.169(3), Mo1–N1–N2 177.1(2), Mo2–N2–N1 177.9(2), P1–Mo1–P2 157.59(3), P3–Mo2–P4 156.94(3), Cl1–Mo1–Cl2 173.41(3), Cl3–Mo2–Cl4 174.64(3).

$[\text{Mo}(\text{N}_2)_2(\text{PNP})]_2(\mu\text{-N}_2)$ (**3**).³ 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. Fc/Fc^+ , respectively.

A more detailed molecular structure of **2** is determined by X-ray crystallographic study (Fig. 1). The molecular structure of **2** contains two $[\text{MoCl}_2(\text{PNP})]$ 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 Cl(1)–Mo(1)–Mo(2)–Cl(3) is $96.73(2)^\circ$. 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(bridging) 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(II) to Mo(0). These phenomena can be explained by the enhancement of the

Table 1 Comparison of the metrical parameters of **2** and **3**

	2 (L = Cl)	3 (L = N ₂)
Distances (Å)		
N–N(bridging)	1.169(3)	1.146(4)
Mo–N(bridging)	1.925(2) and 1.927(2)	2.024(3)
Mo–N(pyridine)	2.192(2) and 2.197(2)	2.182(3)
Angles (°)		
Mo–N–N	177.1(2) and 177.9(2)	178.9(2)
P–Mo–P	157.59(3) and 156.94(3)	157.07(4)
L–Mo–Mo–L	96.73(2)	61.41(9)

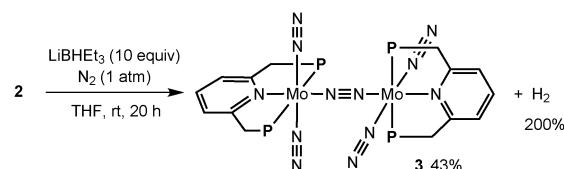


Scheme 2 Protonation of dinitrogen-bridged dimolybdenum complexes (**2** and **3**).

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.⁸

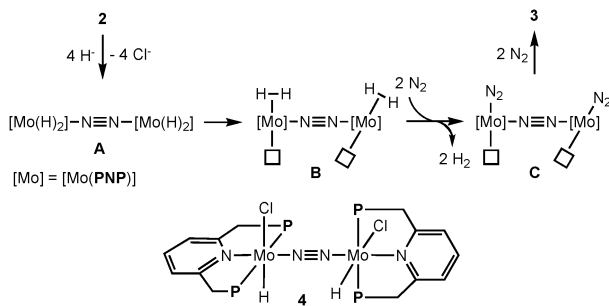
Next, the novel dinitrogen-bridged dimolybdenum-tetrachloride complex **2** was applied as a catalyst toward the catalytic reaction of molecular dinitrogen to form ammonia under ambient conditions.³ Unfortunately, **2** did not work as an effective catalyst toward the catalytic reaction. This result prompts us to investigate the stoichiometric reactivity of the coordinated dinitrogen ligand toward the protonation. The reaction of **2** with an excess amount of sulfuric acid in THF at room temperature for 24 h did not result in the formation of ammonia and hydrazine at all (Scheme 2). This result suggests that the bridging-dinitrogen moiety in **2** may be less reactive toward the protonation than the terminal dinitrogen ligands in **3**, where the formation of stoichiometric amounts of ammonia and hydrazine (0.6 equiv. of ammonia and 0.06 equiv. of hydrazine based on the Mo atom in **3**, respectively) was observed under the same reaction conditions.³

Next, we investigated the reduction of **2** with an excess amount (10 equiv.) of LiBHET₃ in THF at room temperature for 20 h under an atmospheric pressure of dinitrogen to afford **3** in 43% isolated yield together with the formation of molecular dihydrogen in 200% GLC yield (2 equiv. based on **2**) (Scheme 3). Separately, we confirmed the almost complete consumption of **2** by ESI-TOF-MS. Based on the result of the formation of molecular dihydrogen, we consider the following proposed reaction pathway leading to the formation of **3** (Scheme 4). At first, a dinitrogen-bridged dimolybdenum-tetrahydride complex (**A**) may be formed from the reaction of dimolybdenum-tetrachloride complex **2** with LiBHET₃ and then the dinitrogen-bridged dimolybdenum-tetrahydride complex **A** is converted into the dinitrogen-bridged dimolybdenum-bis(dinitrogen) complex (**C**) via a dinitrogen-bridged dimolybdenum-bis(dihydrogen) complex (**B**) as a key intermediate. The ligand exchange of the coordinated

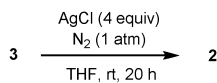


Scheme 3 Reduction of **2** with Super-Hydride to form a dinitrogen-bridged dimolybdenum-dinitrogen complex (**3**).





Scheme 4 Proposed reaction pathway from **2** to **3** via dimolybdenum-tetrahydride and -bis(dihydrogen) complexes.



Scheme 5 Oxidation of **3** with AgCl to form **2**.

molecular dihydrogen with molecular dinitrogen may be a key step to transform **2** into **3**.^{9,10} In fact, unfortunately, we have not yet observed the formation of the dinitrogen-bridged dimolybdenum-bis(dihydride) and bis(dihydrogen) complexes such as **A** and **B** by ESI-TOF-MS. However, when the reduction of **2** with LiBHET₃ was carried out under an atmospheric pressure of argon, in place of dinitrogen, the formation of the dinitrogen-bridged dimolybdenum-dichloride-dihydride complex [Mo(H)Cl(PNP)]₂(μ-N₂) (**4**) was observed by ESI-TOF-MS from a reaction mixture after the reduction.¹¹

Separately, we confirmed that only a small amount of **3** was observed by ¹H NMR in the direct reduction of **1** with an excess amount of LiBHET₃ 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.^{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.¹² Further studies on the preparation and reactivity of molybdenum- and iron-complexes bearing other pincer ligands are currently underway.^{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

- For recent reviews, see: (a) S. Hinrichsen, H. Broda, C. Gradert, L. Söncksen and F. Tuczek, *Annu. Rep. Prog. Chem., Sect. A*, 2012, **108**, 17; (b) Y. Nishibayashi, *Dalton Trans.*, 2012, **41**, 7447; (c) K. C. MacLeod and P. L. Holland, *Nat. Chem.*, 2013, **5**, 559; (d) M. D. Fryzuk, *Chem. Commun.*, 2013, **49**, 4866; (e) Y. Tanabe and Y. Nishibayashi, *Coord. Chem. Rev.*, 2013, **257**, 2551.
- (a) D. V. Yandulov and R. R. Schrock, *Science*, 2003, **301**, 76; (b) R. R. Schrock, *Acc. Chem. Res.*, 2005, **38**, 955; (c) R. R. Schrock, *Angew. Chem., Int. Ed.*, 2008, **47**, 5512.
- (a) K. Arashiba, Y. Miyake and Y. Nishibayashi, *Nat. Chem.*, 2011, **3**, 120; (b) K. Arashiba, K. Sasaki, S. Kuriyama, Y. Miyake, H. Nakanishi and Y. Nishibayashi, *Organometallics*, 2012, **31**, 2035; (c) E. Kinoshita, K. Arashiba, S. Kuriyama, Y. Miyake, R. Shimazaki, H. Nakanishi and Y. Nishibayashi, *Organometallics*, 2012, **31**, 8437.
- Nitrogen Fixation*, ed. M. W. Ribbe, Human Press, New York, 2011.
- (a) J. A. Pool, E. Lobkovsky and P. J. Chirik, *Nature*, 2004, **427**, 527; (b) M. M. Rodriguez, E. Bill, W. W. Brennessel and P. L. Holland, *Science*, 2011, **334**, 780; (c) T. Shima, S. Hu, G. Luo, X. Kang, Y. Luo and Z. Hou, *Science*, 2013, **340**, 1549.
- (a) Y. Nishibayashi, S. Iwai and M. Hidai, *Science*, 1998, **279**, 540; (b) Y. Nishibayashi, S. Takemoto, S. Iwai and M. Hidai, *Inorg. Chem.*, 2000, **39**, 5946; (c) Y. Nishibayashi, I. Wakiji, K. Hirata, M. R. DuBois and M. Hida, *Inorg. Chem.*, 2001, **40**, 578.
- Ammonia Synthesis Catalysis: Innovation and Practice*, ed. H. Liu, World Scientific, Beijing, 2013.
- J. J. Curley, T. R. Cook, S. Y. Reece, P. Müller and C. C. Cummins, *J. Am. Chem. Soc.*, 2008, **130**, 9394.
- For a review, see: J. Ballmann, R. F. Munhá and M. D. Fryzuk, *Chem. Commun.*, 2010, **46**, 1013.
- (a) M. Hidai, K. Tominari and Y. Uchida, *J. Am. Chem. Soc.*, 1972, **94**, 110; (b) L. Archer and T. A. George, *Inorg. Chem.*, 1979, **18**, 2079; (c) R. Pierantozzi and G. L. Geoffroy, *Inorg. Chem.*, 1980, **19**, 1821.
- ESI-TOF-MS (THF) of **4** 1084 (M).
- J. D. Gilbertson, N. K. Szymczak and D. R. Tyler, *J. Am. Chem. Soc.*, 2005, **127**, 10184.
- 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. Yoshizawa and Y. Nishibayashi, *Nat. Commun.*, 2012, **3**, 1254.
- 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 $-78\text{ }^{\circ}\text{C}$: J. A. Anderson, J. Rittle and J. C. Peters, *Nature*, 2013, **501**, 84.
- For recent examples of molybdenum-dinitrogen complexes bearing other types of ligands, see: (a) T. Miyazaki, Y. Tanabe, M. Yuki, Y. Miyake, K. Nakajima and Y. Nishibayashi, *Chem.-Eur. J.*, 2013, **19**, 11874; (b) Y. Tanabe, S. Kuriyama, K. Arashiba, Y. Miyake, K. Nakajima and Y. Nishibayashi, *Chem. Commun.*, 2013, **49**, 9290.

