Dimension and bridging ligand effects on Mo-mediated catalytic transformation of dinitrogen to ammonia: Chain-like extended models of Nishibayashi's catalyst

Xiao-Lan Sheng [a], Enrique R. Batista [b], Yi-Xiang Duan [a], Yong-Hui Tian [a],*

[a] College of Life Sciences, Research Center of Analytical Instrumentation, Sichuan University, Chengdu, Sichuan 610064, PR China
[b] Theoretical Division, Los Alamos National Laboratory (LANL), Los Alamos, NM 87545, United States

ABSTRACT

Previous studies suggested that in Nishibayashi's homogenous catalytic systems based on molybdenum (Mo) complexes, the bimetallic structure facilitated dinitrogen to ammonia conversion in comparison to the corresponding monometallic complexes, likely due to the through-bond interactions between the two Mo centers. However, more detailed model systems are necessary to support this bimetallic hypothesis, and to elucidate the multi-metallic effects on the catalytic mechanism. In this work, we computationally examined the effects of dimension as well as the types of bridging ligands on the catalytic activities of molybdenum-dinitrogen complexes by using a set of extended model systems based on Nishibayashi's bimetallic structure. The polynuclear chains containing four ($[Mo]_4$) or more Mo centers were found to drastically enhance the catalytic performance by comparing with both the monometallic and bimetallic complexes. Carbide ($[:C\equiv C:]^{2-}$) was found to be a more effective bridging ligand than N_2 in terms of electronic charges dispersion between metal centers thereby facilitating reactions in the catalytic cycle. The mechanistic modelling suggests that in principle, more efficient catalytic system for N_2 to NH_3 transformation might be obtained by extending the polynuclear chain to a proper size in combination with an effective bridging ligand for charge dispersion.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Dinitrogen (N_2) is the most abundant molecule in earth's atmosphere. However, N_2 exists as an inert molecule due to its nonpolar nature and stability [1,2] making it difficult to participate in chemical reactions. Industrially, the conversion of dinitrogen to ammonia (NH_3) mainly relies on the Haber-Bosch process [3], which requires harsh reaction conditions (350–550 °C under the pressure of 150–350 atm) and is energy extensive. In contrast, nitrogenase enzyme can reduce N_2 to NH_3 at ambient temperature and pressure. It has been recognized that in the biological N_2 fixation systems, the dinitrogen reduction is accomplished on a cluster structure called iron–molybdenum cofactor [4–6].

Inspired by the biological systems, tremendous efforts have been devoted to the synthesis of metallocomplexes [7–15] facilitating dinitrogen reduction in the presence of electron and proton sources under ambient conditions. Chatt pioneered in the development of transition-metal dinitrogen complexes with well-defined

structures, and the first N_2 reduction to NH_3 was observed with quantitative conversion based on $[M(N_2)_2[PR_3]_4]$ (M = Mo or W; R = alkyl or aryl) complex [16,17]. Subsequently, the preparation of various transition-metal dinitrogen complexes and the transformation of the coordinated dinitrogen into nitrogenous compounds, especially NH_3, have been achieved at mild reaction conditions [18–26]. Although plenty of studies on the stoichiometric reactivity of transition metal-dinitrogen complexes have been reported, the cases for catalytic conversion from N_2 to NH_3 are rare [27–31]. In 2003, the first catalytic system of N_2 to NH_3 transformation under ambient conditions was prepared by Yandulov and Schrock [23] using a molybdenum complex as shown in Chart 1a, which is featured by a single metal center ($[HIPTN_3N]$-$Mo(N_2)$) supported by a triamidoamine ligand, where HIPT = {3,5-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$}. After that in 2011, the second Mo-containing system capable of catalytic conversion of N_2 into NH_3 was proposed by Nishibayashi and coworkers [24], from which a 23 equivalents of ammonia were obtained in terms of the catalyst (Chart 1b). In addition to the Mo-based catalysts, Anderson et al. proposed tris (phosphine)borane and tri(phosphine)alkyl supported iron complexes that could mediate the N_2 reduction to NH_3 in a catalytic

---

* Corresponding author.
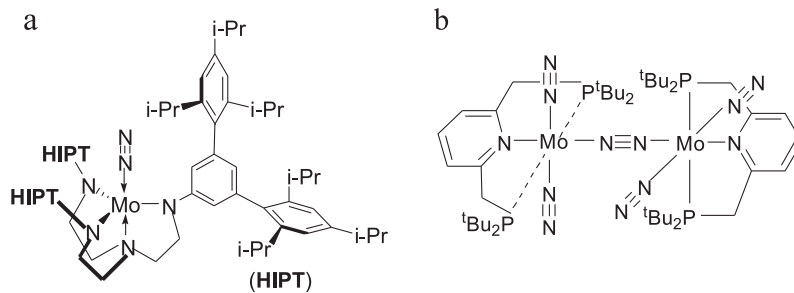 *E-mail address:* yonghuitian@scu.edu.cn (Y.-H. Tian).

a   b

Chart 1. Single-molybdenum (Schrock) and di-molybdenum (Nishibayashi) complexes.

mode [25,26,32,33]. Herein, we focus on the catalytic behaviors of Mo-based complexes, and hence a brief review is presented below about the reaction mechanism of the Mo-based homogeneous catalytic systems.

In Nishibayashi's catalytic system, a binuclear Mo-complex was used, which is featured by two Mo atoms bridged by a dinitrogen ligand (Chart 1b). Previous mechanistic studies [34–36] have shown that the reaction processes in Nishibayashi's bimetallic system and Schrock's monometallic system basically follow the similar reaction mechanism as originally proposed by Chatt. In this route called distal (or asymmetric) pathway, a nitride intermediate is produced with the release of a NH_3 as a result of sequential addition of H atoms on a single nitrogen atom of a terminal N_2 ligand. However, upon a closer comparative inspection of the above two Mo-complex catalysts, it can be recognized that they distinguish from each other mainly in two aspects. Firstly, the metal atom is in Mo(III) for Schrock's monometallic complex, in contrast to Mo(0) as in Nishibayashi's dimetallic complex. Secondly and also most importantly, the bimetallic complex is structurally characterized by two metal centers bridged with a dinitrogen ligand. Although the Schrock's mononuclear Mo(III) complex shows catalytic effect, the N_2 to NH_3 conversion is difficult for the Chatt's Mo(0) complexes, and only quantitative formation of NH_3 was achieved [37,38]. On the other hand, as in Nishibayashi's system, the bimetallic Mo(0)-complexes are capable of catalytically transforming N_2 into NH_3. In Nishibayashi's bimetallic Mo(0)-complex as shown in Chart 1b, the N_2 bridging ligand not only "mechanically" holds the two Mo(0) atoms forming a dimer, but also provides a channel between the two metal centers for electronic communication. According to recent theoretical studies [34,35], the bimetallic structure is likely to favor the charge delocalization on the two metal atoms upon proton addition on a terminal N_2 ligand. That explains why a bimetallic structure is necessary for the occurrence of catalytic dinitrogen reduction to ammonia in Nishibayashi's system. However, we envisage that the introduced electronic charges upon protonation are still very spatially confined in Nishibayashi's complex containing only two Mo atoms bridged by a N_2 ligand. The catalytic activity of Nishibayashi's bimetallic complex suggests that a chain-like extension by including more metal centers in polynuclear complexes would improve the catalytic performance of Mo-complexes for N_2 transformation to NH_3.

In this report, we carried out an extensive exploration of dimensional effect on the catalytic performance of Mo-complexes for dinitrogen reduction. For this purpose, we systematically investigated a series of model complexes containing multimetallic centers bridged by dinitrogen ligands structurally analogous to Nishibayashi's bimolybdenum catalyst. With the model systems, we intended to demonstrate how the chain length of Mo-complexes affected the catalytic behaviors and the energy profiles. Moreover, the effect of bridging ligands was inspected. We suggest that with a proper bridging ligand such as carbide [:C≡C:]$^{2-}$, a more effective electronic channel can be established between the adjacent metal centers, which may considerably facilitate the overall reactions in

terms of thermodynamics. The findings in this work may contribute to the mechanistic understanding of N_2 to NH_3 conversion catalyzed by organometallic complexes in homogeneous systems, and shed light on the principle for the design of efficient catalysts operated at ambient reaction conditions.

2. Computational methods

All geometries of the compounds in this paper were fully optimized with Becke's three parameter (B3) hybrid exchange functionals combined with Lee-Yang-Parr (LYP) correlation functionals (B3LYP) [39,40], which is implemented in Gaussian 09 [41]. The 6-31G(d,p) basis set was used for H, C, N, and P, while for Mo, the Stuttgart effective core potential and the corresponding basis set were employed [42]. The same theory level was used for the energy calculations based on the optimized geometries. Single-point energy calculations with larger basis sets and different functionals predicted basically the same reaction trends as for B3LYP/6-31G(d,p) as shown in Fig. S1 in the Supplementary Information (SI). In addition, solvation effect in dichloroethane [43,44] was accounted for using the solvation model based on density (SMD) scheme, in which the quantum mechanical charge density of a solute molecule interact with the solvent charges described by a continuum model [45,46].

The model complexes as described in Scheme 1 were constructed based on Nishibayashi's bimetallic complex (Chart 1b). It is noteworthy that the tertiary butyl groups (^tBu) of the tridentate pincer ligands as in the original Nishibayashi's complex (Chart 1b) were replaced with H atoms in the model structures to save computational cost, and the predicted trend of the calculated reaction energies should be very similar no matter H, or ^tBu is used [47]. In the model systems, we extended Nishibayashi's bimetallic complexes in one-dimension, and the polynuclear complexes thus obtained show a structural characteristic of a chain of metal centers bridged with N_2 ligands. The model structures are represented with a general formula as depicted in Scheme 1, where n refers to the number of repeat unit consisting of a metal center and a bridging N_2 ligand. For example, when n = 1 or 2, a dimer or trimer structure is obtained containing two or three metal centers, respectively. One notes that the **Mo** represents moiety composed of a Mo atom and a pincer ligand (Chart 1b). (See Scheme S1 and Fig. S2 in the SI for the detailed structures). The chain length effect was examined in a range from one to five metal centers, beyond which we found that the dimensional effect reached saturation as will be shown in the following sections. Note that the model compounds involved are merely used for the purpose of mechanis-
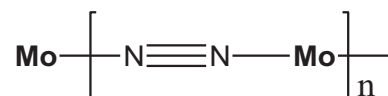
Scheme 1. Structure of the model polynuclear complex.