



South Europe–Japan Joint Forum on inorganic chemistry and its interfaces (Strasbourg, France, 17 & 18 October 2014)

## Molybdenum-catalyzed reduction of molecular dinitrogen into ammonia under ambient reaction conditions



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### ARTICLE INFO

#### Article history:

Received 10 December 2014

Accepted after revision 29 January 2015

Available online 17 June 2015

#### Keywords:

Ammonia  
Catalytic reaction  
Molecular dinitrogen  
Molybdenum  
Nitrogen fixation  
Protonation  
Reduction

### ABSTRACT

Synthesis of transition metal–dinitrogen complexes and stoichiometric transformations of their coordinated dinitrogen into ammonia and hydrazine have so far been well investigated in order to achieve a novel nitrogen fixation under ambient conditions. As an extension of our study, the dimolybdenum–dinitrogen complex bearing PNP pincer ligands has been found to work as an effective catalyst for the formation of ammonia from dinitrogen, where 52 equiv of ammonia are produced based on the catalyst (26 equiv of ammonia are produced based on the molybdenum atom of the catalyst). This is the most effective catalytic reaction system for the formation of ammonia from molecular dinitrogen catalyzed by transition metal–dinitrogen complexes as catalysts under ambient reaction conditions. Herein, we describe recent results concerning the catalytic reaction, including the proposed reaction pathway.

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### 1. Introduction

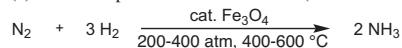
The development of a novel nitrogen fixation system is one of the most important subjects in chemistry. Industrially, ammonia is produced from molecular dinitrogen and dihydrogen by the use of the iron-based heterogeneous catalysts under harsh reaction conditions, such as high temperature and high pressure in order to activate molecular dinitrogen and to produce ammonia efficiently (Scheme 1) [1]. In sharp contrast to the energy-consuming Haber–Bosch process, biological nitrogen fixation is well known to occur under ambient reaction conditions. The precise reaction mechanism still remains unclear; however, an X-ray structural model has recently been reported for the active site of nitrogenase in FeMo-cofactor (Scheme 1) [2]. It is generally believed that molecular dinitrogen is coordinated and activated at these

multimetallic centers and converted into ammonia via a sequential process of protonation and reduction.

Since the discovery of the first transition metal–dinitrogen complex, a ruthenium–dinitrogen complex (Scheme 2) [3], the preparation of various transition metal–dinitrogen complexes and their stoichiometric reactivities have so far been well investigated toward the goal of the achievement of novel nitrogen fixation system under mild reaction conditions [4]. Especially, molybdenum– and tungsten–dinitrogen complexes have been most intensively studied, where the coordinated molecular dinitrogen can be converted into ammonia under mild reaction conditions by treatment with inorganic acids such as sulfuric acid (Scheme 2) [5,6]. In sharp contrast to the stoichiometric formation of ammonia from the transition metal–dinitrogen complexes, reactions of these transition metal–dinitrogen complexes with molecular dihydrogen under mild reaction conditions did not yield any ammonia at all. In this reaction system, the ligand exchange of the coordinated molecular dinitrogen with

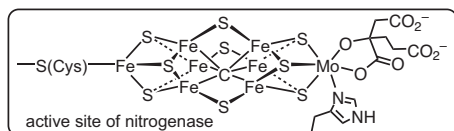
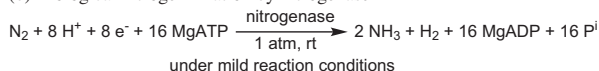
Email address: [ynishiba@sogo.t.u-tokyo.ac.jp](mailto:ynishiba@sogo.t.u-tokyo.ac.jp).

(a) Industrial production of ammonia (Haber-Bosch process)

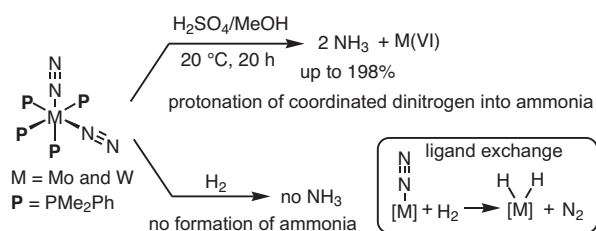
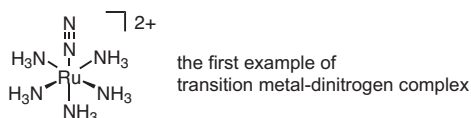


energy-consuming process under drastic reaction conditions

(b) Biological nitrogen fixation by nitrogenase



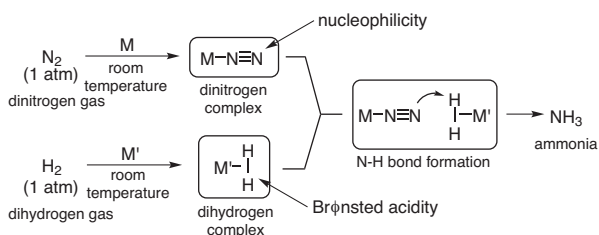
**Scheme 1.** a: industrial production of ammonia (Haber–Bosch process); b: biological nitrogen fixation by nitrogenase.



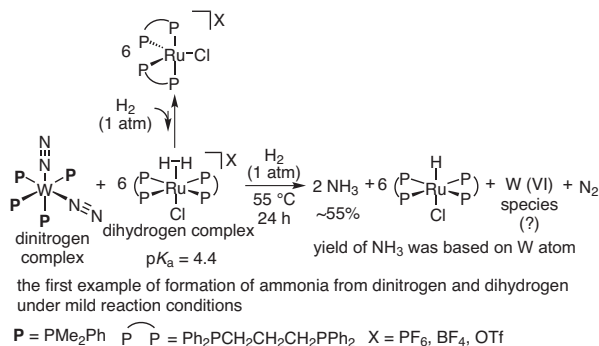
**Scheme 2.** Transition metal–dinitrogen complexes and their stoichiometric reactions.

molecular dihydrogen easily took place. As a result, no formation of ammonia was observed at all under these reaction conditions.

Based on these research backgrounds, we envisaged the direct reaction of the coordinated molecular dinitrogen with the coordinated molecular dihydrogen under mild reaction conditions. The terminal nitrogen atom of the coordinated dinitrogen on the transition metal complexes may attack the coordinated and electrophilic molecular dihydrogen to form nitrogen–hydrogen bonds, leading to the formation of ammonia (Scheme 3). After many trials, we evidenced the formation of ammonia through the reaction of tungsten–dinitrogen complexes with an excess amount of a ruthenium–dihydrogen complex at 55 °C for 24 h under 1 atm of molecular dihydrogen (Scheme 4) [7]. In this reaction system, only a stoichiometric amount of



**Scheme 3.** Concept for direct reaction of coordinated dinitrogen with dihydrogen.

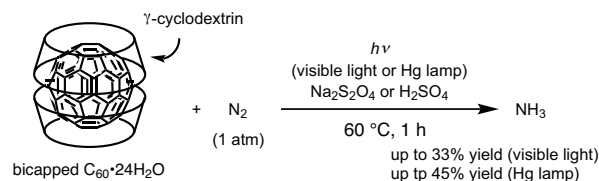


**Scheme 4.** Direct reaction of dinitrogen complex with dihydrogen complex.

ammonia was produced based on the tungsten atom. However, this is the first successful example of formation of ammonia from molecular dinitrogen and dihydrogen under mild reaction conditions [8]. This work was achieved when I was an assistant professor in the group of Prof. Masanobu Hidai at The University of Tokyo (1995–2000).

We also found a stoichiometric formation of ammonia by using a buckminsterfullerene bearing 2 equiv of  $\gamma$ -cyclodextrin as ligands. The reaction of the buckminsterfullerene molecule in water at 60 °C for 1 h under 1 atm of molecular dinitrogen under visible light gave a stoichiometric amount of ammonia based on the fullerene (Scheme 5) [9]. This work was achieved as a collaborative work with the group of Kyoto University Professor emeritus Zen-ichi Yoshida at Kinki University when I was an assistant professor in the group of Professor Sakae Uemura at Kyoto University (2000–2005).

In sharp contrast to many studies on the stoichiometric formation of ammonia from transition metal–dinitrogen complexes [4], there are only a few examples of catalytic transformation of molecular dinitrogen into ammonia by using transition metal–dinitrogen complexes as catalysts. In 2003, Prof. Schrock and a co-worker reported the first successful example of the catalytic conversion of molecular dinitrogen into ammonia under mild reaction conditions by using decamethylchromocene (CrCp\*<sub>2</sub>; Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>) as a reducing reagent and 2,6-lutidinium tetraarylborate ([LutH]BAR<sub>4</sub><sup>F</sup>; Ar<sup>F</sup> = 2,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) as a proton source in the presence of a transition metal–dinitrogen complex as a catalyst. In their reaction system, the molybdenum–dinitrogen complex bearing a triamido- and monoamine tetradentate ligand worked as an effective catalyst, where less than 8 equiv of ammonia were



**Scheme 5.** Nitrogen fixation assisted by biccapped C<sub>60</sub>.

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