Development of catalytic nitrogen fixation using transition metal–dinitrogen complexes under mild reaction conditions

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PERSPECTIVE

Development of catalytic nitrogen fixation using transition metal–dinitrogen complexes under mild reaction conditions

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This paper describes our recent progress in catalytic nitrogen fixation using transition metal–dinitrogen complexes as catalysts. Our research group has recently developed novel reaction systems for the catalytic transformation of molecular dinitrogen into ammonia and hydrazine using molybdenum–, iron–, cobalt– and vanadium–dinitrogen complexes under mild reaction conditions. The new findings presented in this paper may provide a new approach to the development of economical nitrogen fixation to replace the energy-consuming Haber–Bosch process.

1. Introduction

The Haber–Bosch process is an industrial method that involves fixing nitrogen from the air. At the time of its development, the process was referred to as a method for "making bread from air".[1] In the Haber–Bosch process, ammonia is synthesised from nitrogen and hydrogen gases under the extreme reaction conditions of high temperature and high pressure using iron-based catalysts.[2] Although about 100 years have passed since the development of the process at the beginning of the 20th century, almost the same method is essentially still used today (Fig. 1(a)). It is pointed out that if the Haber–Bosch process had not been developed, the human population would have remained at about half the present population.[3] It should be noted that human beings incorporate ammonia as a nitrogen source and synthesize amino acids and proteins in the body using ammonia as a nitrogen source. Therefore, it is an important challenge for scientists to develop an energy-saving nitrogen-fixation method to replace the Haber–Bosch process, which currently requires large-scale manufacturing plants and fossil fuels. Recently, reactions with higher efficiency under more moderate conditions have been developed using alternative catalysts to the Haber–Bosch process.[4] However, hydrogen gas, derived from fossil fuels, is still used as a raw material in these reactions. Therefore, there is still room for improvement in industrial processes to produce ammonia.

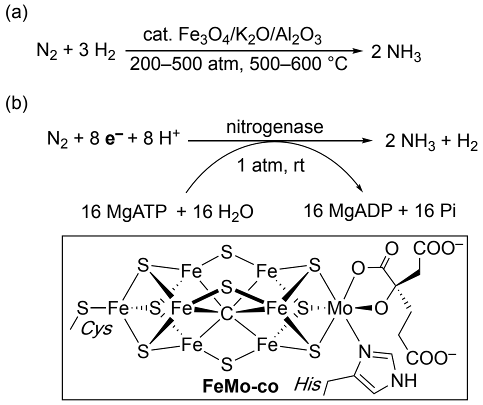

Fig. 1 (a) Industrial Haber–Bosch process. (b) Biological nitrogen fixation and structure of the active site (FeMo-co) of nitrogenase.

In contrast to the industrial ammonia synthesis method of the Haber–Bosch process, the nitrogen-fixing enzyme nitrogenase has the ability to convert nitrogen gas to ammonia under considerably mild reaction conditions, e.g. at room temperature under atmospheric pressure (Fig. 1(b)).[5] Recently, it was discovered that the structure of the active site in nitrogenase is a carbon-centred organometallic complex composed of sulfur-bridged iron and molybdenum.[6] Total synthesis of the skeleton of the active site having this unique structure in inorganic chemistry has also been studied as an interesting research subject.[7] However, focusing on the specific function of nitrogenase, we consider that the additional important research subject is to develop molecular catalysts with the function of nitrogenase that directly lead to the development of the next-generation nitrogen fixation under milder conditions.

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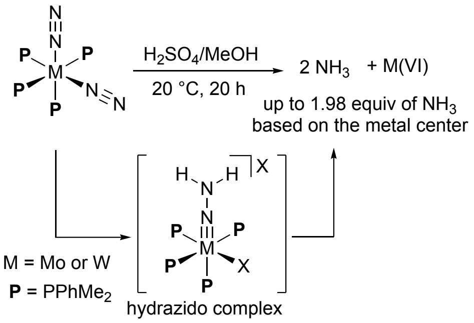

Fig. 2 Stoichiometric formation of ammonia by the protonation of dinitrogen complexes with Brønsted acids.

Since first initial study of a ruthenium–nitrogen complex where dinitrogen was found to be coordinated to the transition metal was reported in 1965, many studies have been conducted on the synthesis of various transition metal–dinitrogen complexes and their chemical reactivities.[8] Among these studies, special interest has been focused on the chemical reactivities of molybdenum–dinitrogen and iron–dinitrogen complexes contained in the active site of nitrogenase. The molybdenum–dinitrogen complex was synthesised and isolated for the first time by Hidai and co-workers.[9] The first breakthrough in ammonia synthesis was reported in 1975. When molybdenum– and its congener tungsten–dinitrogen complexes having four monodentate phosphines are reacted with sulfuric acid at room temperature, ammonia was produced via intermediate called hydrazide–complexes in which the terminal nitrogen atom of dinitrogen molecule coordinated to the metal was protonated (Fig. 2).[10] Unfortunately, all the nitrogen atoms of the produced ammonia comes from the dinitrogen molecule that is originally coordinated to the metal, and the electrons necessary for the reduction of dinitrogen are supplied from the central molybdenum or tungsten to which the dinitrogen is coordinated. To develop catalytic nitrogen fixation systems, it is necessary to supply the electrons necessary for the reduction of dinitrogen molecule from exogenous reductants and to complete the catalyst cycle for regenerating the corresponding dinitrogen complexes. Many designs to attain such catalytic cycles have previously been proposed. However, the realisation of such a catalytic reaction is extremely difficult because it contains multiple steps that need to be controlled (at least 13 steps) where conflicting reactions, i.e. protonation (oxidation) and reduction, proceed alternately (Fig. 3). Therefore, nearly 40 years have passed to achieve catalytic nitrogen fixation under mild reaction conditions since the first report of the isolation of dinitrogen complexes.‡

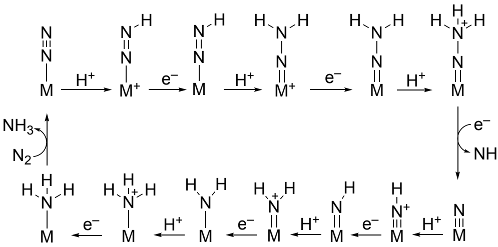

Fig. 3 A plausible catalytic cycle from dinitrogen into ammonia.

2. Catalytic nitrogen fixation using transition metal–dinitrogen complexes

2-1. Catalytic nitrogen fixation using molybdenum–dinitrogen complexes

In 2003, the first catalytic ammonia-producing reaction was achieved using transition metal–nitrogen complexes as molecular catalysts. Schrock and a co-worker reported that two or more equivalents of ammonia corresponding to the stoichiometric amount per catalyst molecule are produced when nitrogen gas is reacted with a reductant and a proton source at room temperature under atmospheric pressure in the presence of a molybdenum–dinitrogen complex containing a triamide–monoamine tetradentate ligand (**A**) (Fig. 4).[11] The amount of ammonia produced was up to 8 equivalents per catalyst molecule. Thus, the catalytic reaction is not efficient, but they realised the long-term goal of developing a catalytic ammonia-producing reaction. Although they succeeded in elucidation of the detailed reaction mechanism by the isolation of key intermediates and verification of the reactivity, they unfortunately did not succeed in developing more highly active reaction systems.

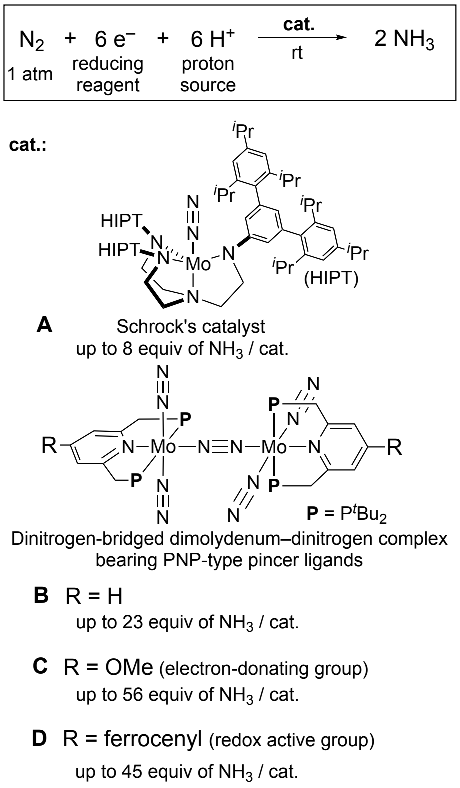

Fig. 4 Catalytic formation of ammonia by using molybdenum–dinitrogen complexes as catalysts.

In our laboratory, we designed and synthesised a dinitrogen-bridged dinuclear molybdenum complex bearing a PNP-type pincer ligand containing a pyridine skeleton (**B**). When the reaction was performed in the presence of a catalytic amount of **B** as a catalyst, ammonia exceeding the stoichiometric amount was produced under ambient reaction conditions.

When cobaltocene was used as a reductant, up to 23 equivalents of ammonia per catalyst molecule were produced, greatly exceeding the catalytic ability reported by Schrock and co-workers (Fig. 4). Our results achieved the catalytic ammonia-producing reaction using transition metal–dinitrogen complexes as catalysts as the second successful example.[12]

In a collaborative effort with Yoshizawa, Tanaka and co-workers, through theoretical calculations we revealed that the catalytic reaction proceeds via a reaction path that overturns the conventional common knowledge (Fig. 5).[13] Since the binding energy between the bridged dinitrogen and the metal is low (dinitrogen-bridged dinuclear complexes are unstable in solution), they easily convert to the corresponding mononuclear complexes. However, in the case of dinitrogen-bridged dinuclear molybdenum complexes having PNP-type pincer ligands, the binding energy between the bridged dinitrogen and molybdenum is relatively high. Therefore, the complexes maintain a dinuclear structure even in solution. It was suggested that the protonation of the terminal dinitrogen, which is the first step of the catalytic reaction, proceeds with respect to the dinitrogen-bridged dinuclear complexes. In fact, we confirmed that no protonation occurs in mononuclear molybdenum–dinitrogen complexes generated from the dinitrogen-bridged dinuclear molybdenum complex by DFT calculation. Thus, the catalytic reaction proceeds with maintaining the structure of the dinitrogen-bridged dinuclear molybdenum skeleton. Also, we observed the formation of dinitrogen-bridged dinuclear nitride complexes and ammonia complexes in the catalytic reaction system. We believe that this experimental result supports our proposed reaction pathway.

The catalytic cycle presented in Fig. 5 likely consists of stepwise protonation and reduction processes. However, the possibility that the reaction proceeds in the process of the proton-coupled electron transfer (PCET) cannot be not excluded. To promote each step in the protonation in the catalytic reaction, we revealed that the catalytic activity can be almost doubled by introducing electron-donating groups (**C**) such as methyl groups and methoxy groups onto the pyridine ring of the PNP-type pincer ligands (Fig. 4).[14] Meanwhile, in order to promote the reduction step, the introduction of redox-active ferrocene onto the pyridine ring of the PNP-type pincer ligands resulted in approximately doubled catalytic activity (**D**) (Fig. 4).[15] These results suggest that further improvement of the catalytic activity may be possible by introducing PNP-type pincer ligands that have both electron- donating and redox-active properties. At present, unfortunately we have not yet succeeded in developing pincer ligands with such properties.

2-2. Catalytic nitrogen fixation using molybdenum complexes with new tridentate ligands

In the abovementioned ammonia-producing catalytic reaction, the main cause of the catalytic deactivation was that the PNP-type pincer ligands dissociate from molybdenum. We actually observed only dissociated PNP-type pincer ligands in the solution after the completion of the catalytic reaction.

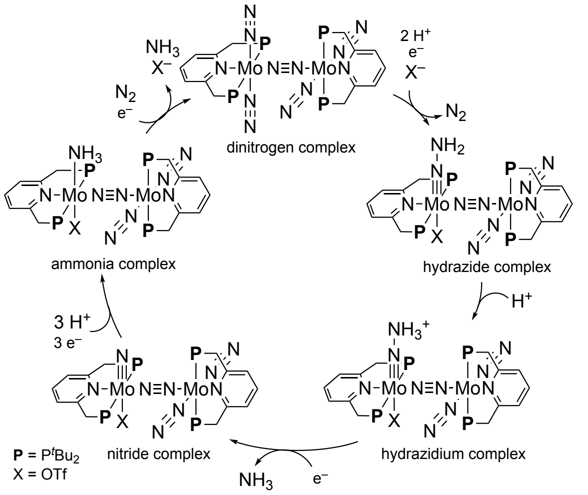

Fig. 5 Proposed reaction pathway for the catalytic conversion of dinitrogen into ammonia using a molybdenum–dinitrogen complex bearing a PNP-type pincer ligand as a catalyst.

Based on these experimental results, we attempted to design new tridentate ligands to replace the PNP-type pincer ligands.

First, we designed PPP (triphosphine)-type tridentate ligands in which the pyridine part in the PNP-type pincer ligand is substituted by a soft base, phosphine[16] (**E**) (Fig. 6). We expected that this complex would become stable because of the increased capability of back donation from the metal to the phosphine. Next, we designed PCP-type pincer tridentate ligands in which the pyridine part of the PNP-type pincer ligand is substituted by *N*-heterocyclic carbene (NHC) that has stronger electron-donating properties than phosphine[17] (**F**) (Fig. 6). We expected that the protonation proceeds more rapidly with the stability of the complex because the binding energy between the NHC and the metal becomes higher than that between pyridine and the metal. Based on molecular design, we actually synthesised the corresponding complexes and verified their catalytic ability. As a result, we demonstrated that both complexes show the expected improvement in their catalytic activities.[16,17] In particular, in the catalytic reaction using dinitrogen-bridged dinuclear molybdenum complexes having PCP-type pincer ligands, up to 230 equivalents of ammonia per catalyst molecule were produced.[17] This result indicates that the catalytic activity of this complex exhibits higher by one order of magnitude. Although we have not yet succeeded in clarifying the detailed reaction mechanism, we consider that the catalytic reaction using this complex proceeds through a mechanism similar to that using the complex with the PNP-type pincer ligands. We consider that one of the main factors in improving the catalytic activity is that the PCP-type pincer ligand from the molybdenum atom of the complex is blocked from being dissociated. Actually, we did not observe any dissociated PCP-type pincer ligands in the solution after the catalytic reaction.

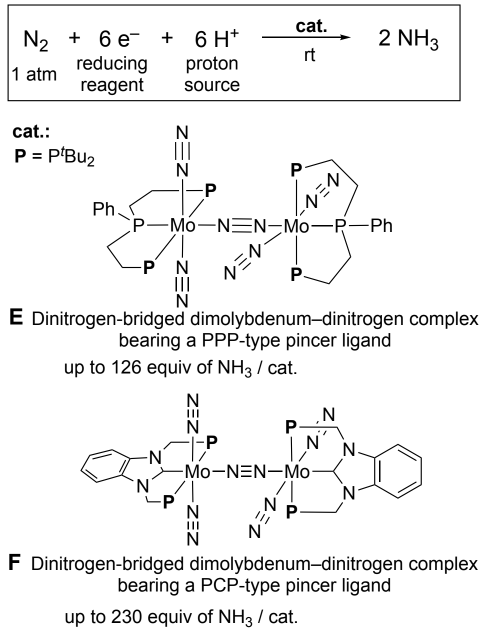

Fig. 6 Catalytic formation of ammonia by using molybdenum–dinitrogen complexes bearing PPP- or PNP-type pincer ligands as catalysts.

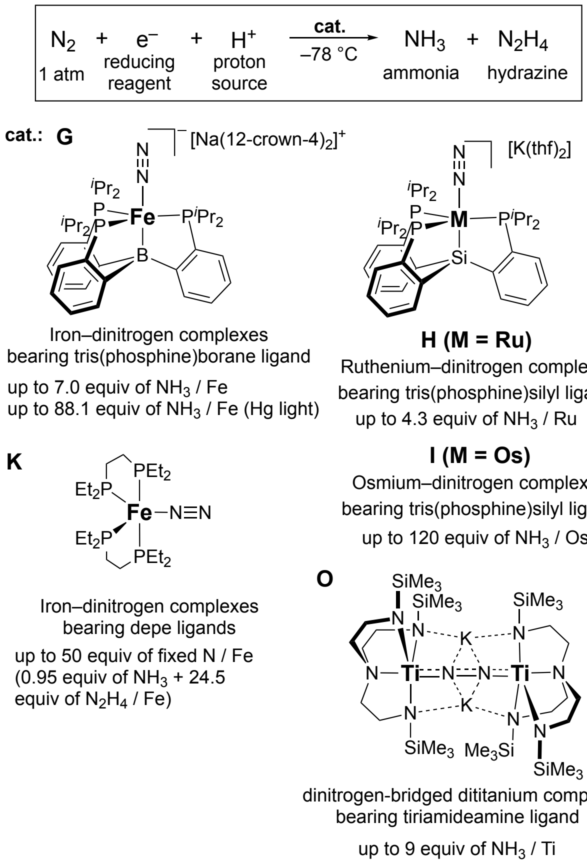

Fig. 7 Catalytic formation of ammonia and hydrazine by using iron, rutenium, osmium and titanium complexes as catalysts.

2-3. Catalytic ammonia- and hydrazine-producing reactions using iron–, cobalt– and vanadium–nitrogen complexes

In addition to the molybdenum–dinitrogen complexes, catalytic reactions using an iron–dinitrogen complex as catalysts, which is one of the key elements present in the structure of the active site of the nitrogen-fixing enzyme nitrogenase, have also developed. In 2013, the first catalytic ammonia-producing reaction using iron–dinitrogen complexes was achieved. Peters and co-workers reported that 7 equiv of ammonia per catalyst molecule are produced when nitrogen gas is reacted with a reductant and proton source at −78°C in the presence of an iron–dinitrogen complex with a tetradentate ligands (**G**) (Fig. 7).[18a-18c] In their experiments, the reaction was performed at −78°C to avoid the evolution of hydrogen gas due to the direct reaction between highly reductive KC_8 and proton sources with high acidity. More recently, Peters and co-workers found that the use of ruthenium– and osmium–dinitrogen complexes (**H** and **I**, respectively) as catalysts produced 4.3 equiv and 120 equiv of ammonia based on per catalyst.[18d]

After the preparation of iron–dinitrogen complexes bearing azaferrocene-based PNP-type pincer ligand and their reactivity,[19] our research group newly designed and synthesised an iron–dinitrogen complex with an anionic PNP-type pincer ligand containing a pyrrole skeleton (**J**) and succeeded in developing a catalytic ammonia/hydrazine-producing reaction using this complex as a catalyst (Fig. 8). This reaction system is the first successful example where hydrazine is directly produced from nitrogen gas using a transition metal–nitrogen complex as a catalyst.[20] After our work was reported, it was also reported that hydrazine was produced with high selectivity using an iron–dinitrogen complex with two diphosphine ligands (**K**) as a catalyst, while investigating different types of proton sources (Fig. 7).[21] Very recently, our research group also succeeded in slightly improving the catalytic activity by introducing substituents onto the pyrrole ring of anionic PNP-type pincer ligands.[22] At present, the amount of ammonia per catalyst molecule produced in the iron-based catalytic reaction is not so much as that produced in the molybdenum-based reaction.[18,20-24] However, we also obtained new results that lead to the elucidation of the mechanism of nitrogenase, such as the direct generation of hydrazine from nitrogen gas. This experimental result provides interesting features not found in the reaction system using molybdenum catalyst.

Furthermore, focusing on cobalt which is not included in the structure of the active site of the nitrogen-fixing enzyme nitrogenase but which can be easily obtained with a base metal, we succeeded in developing catalytic ammonia-producing reaction using a cobalt–dinitrogen complex having an anionic PNP-type pincer ligand containing a pyrrole skeleton (**L**) as a catalyst (Fig. 8).[25] The catalytic activity of this complex was found to be almost the same as that of the iron–dinitrogen complex **J**. Hence, the development of a catalyst with a high activity is a subject for future research. The reaction system featuring the cobalt–dinitrogen complex is the first successful example of catalytic nitrogen-fixing reaction using cobalt complexes.[25,26]

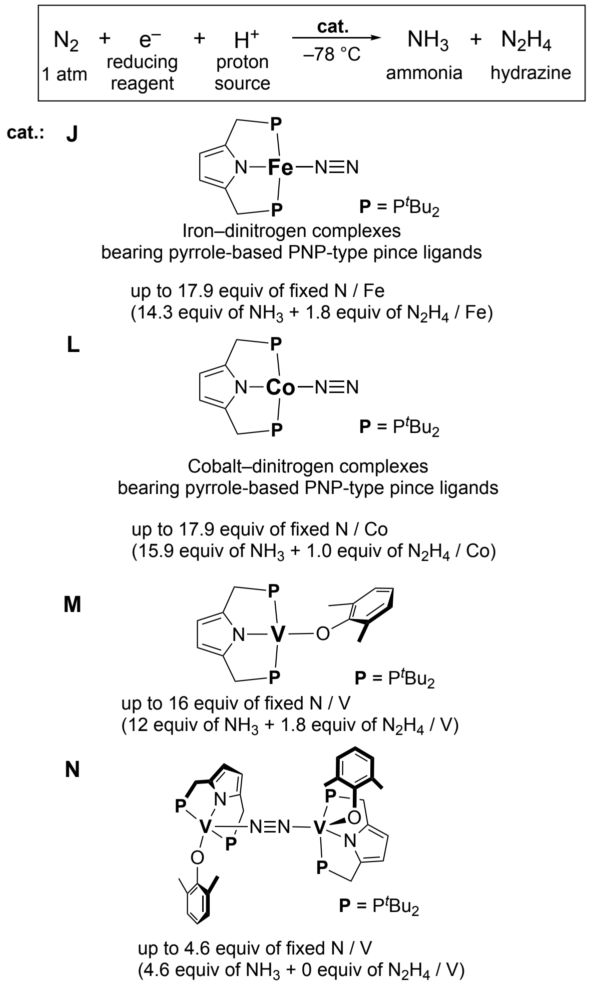

Fig. 8 Catalytic formation of ammonia and hydrazine by using iron, cobalt and vanadium complexes bearing pyrrole-based PNP-type pincer ligands as catalysts.

Very recently, our research group succeeded in developing the catalytic ammonia-producing reaction using vanadium complexes, which is the last key element[27] that exists in the active site of the nitrogen-fixing enzyme nitrogenase because there are three different types of nitrogenases whose active sites contain MoFe, VFe, and all Fe moieties.[5] A vanadium complex having both an anionic PNP-type pincer ligand containing a pyrrole skeleton and a phenoxide ligand (**M**) was newly designed and synthesised, and when this was used as a catalyst, ammonia and hydrazine were catalytically produced (Fig. 8). Although it was found that the catalytic activity of the vanadium complex is in the same order as those of the iron- and cobalt-complexes, this reaction system represents the first successful example of a catalytic nitrogen-fixing reaction using a vanadium complex.[28] On the other hand, vanadium complexes without phenoxide ligands did not show any catalytic activity. We also succeeded in synthesising the corresponding dinitrogen-bridged dinuclear vanadium complex (**N**), and confirmed that it has the same level of catalytic activity as that of mononuclear vanadium complex **M**. We believe that the anionic mononuclear dinitrogen complex worked as active species in this catalysis. Similar active species are proposed in the iron- and cobalt-complexes.

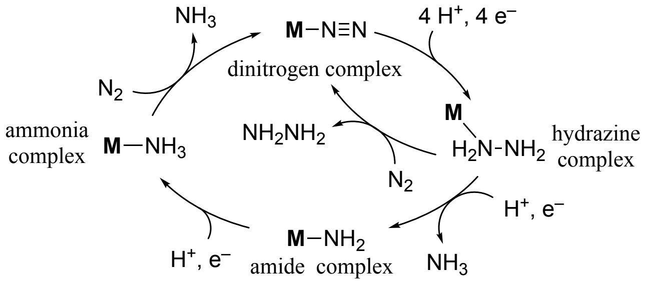

Fig. 9 Proposed reaction pathway for catalytic conversion of dinitrogen into ammonia and hydrazine using iron, cobalt, and vanadium complexes as catalysts.

At around the same time as we reported the reaction system using the vanadium complex, catalytic ammonia- and hydrazine-producing reactions using the dinitrogen-bridged dinuclear titanium-nitrogen complex (**O**) were reported (Fig. 7). In their work, ammonia was produced as the main product and they observed that the amount of ammonia produced was up to nine equivalents per titanium atom.[29] At the same time, our group tried to develop the titanium– and zirconium–catalysed reactions, however, unfortunately, only stoichiometric amounts of ammonia and hydrazine being obtained in both cases.[30]

As described above, our research group has succeeded in developing three types of catalytic ammonia- and hydrazine-producing reaction systems using iron, cobalt, and vanadium complexes as molecular catalysts. Particularly, for the reaction system using the vanadium complex, the results are especially interesting in that early transition metals are often used as catalysts. However, compared with the reaction systems using the molybdenum complex as a catalyst, there are many problems that need to be solved in the reaction systems using these three transition metal (Fe, Co, and V) complexes, e.g., the reactions need to be conducted at ultra-low temperature such as -78 °C. In these reaction systems, in contrast to the reaction system using a molybdenum complex, mononuclear dinitrogen complexes work as reactive active species. The results of theoretical calculations also support our presumed reaction mechanism.[31] The proposed reaction mechanism is shown in Fig. 9. The elucidation of the detailed reaction mechanism is now in progress.

2-4. A new catalytic reaction based on cleavage of N≡N triple bonds

In the process of investigating the abovementioned more active catalytic ammonia-producing reaction using the molybdenum complex, it was revealed that molybdenum triiodide complex with PNP-type pincer ligands containing pyridine skeleton (**P**) has extremely high catalytic activity. We achieved up to 830 equivalents of ammonia production, using highly reductive decamethylcobaltocene as a reductant and low acidity collidine-conjugate acid as a proton source (Fig. 10(a)).[32] The catalytic activity of this system was ca. 40 times higher than that using the aforementioned dinitrogen-bridged dinuclear molybdenum complex **B** (the ammonia production of which was up to 23 equivalents).

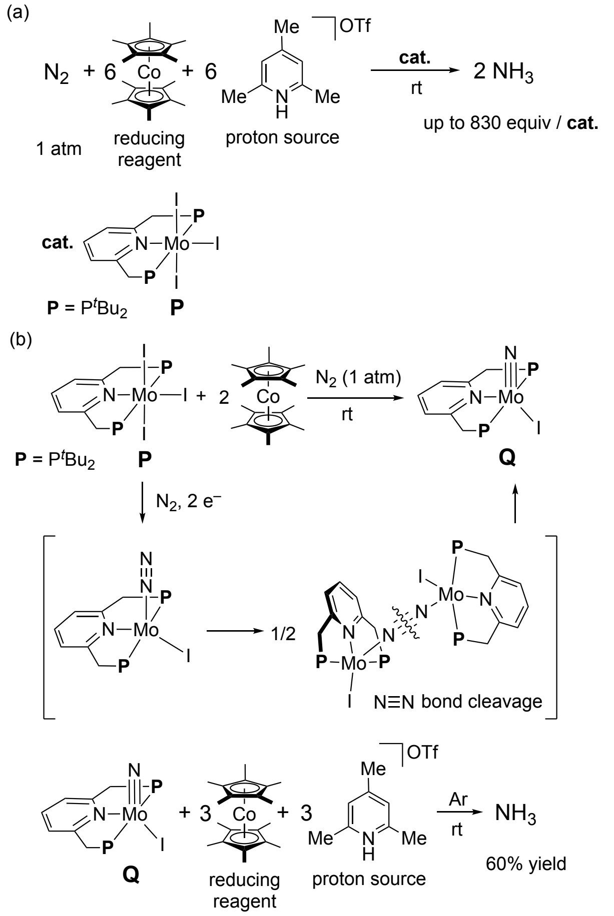

Fig. 10 (a) Catalytic formation of ammonia by using a molybdenum triiodide complex bearing a PNP-type pincer ligand as a catalyst.
(b) Stoichiometric transformation of the molybdenum triiodide complex into the corresponding nitrido complex.

It has the same PNP-type pincer ligand, but the ammonia formation rate and the reaction order as well are greatly different between the case of using the molybdenum triiodide complex **P** as the catalyst and the case of using the dinitrogen-bridged dinuclear molybdenum complex **B** as the catalyst. These results suggest that the reaction mechanisms of these two catalytic reactions are possibly different. When the molybdenum triiodide complex **P** was reacted with an excess amount of the reducing agent at room temperature under a nitrogen gas atmosphere, contrary to initial expectation that the dinitrogen-bridged dinuclear molybdenum complex **B** was generated, the molybdenum nitride complex (**Q**) was immediately produced (Fig. 10(b)). The formation of the nitride complex **Q** is based on the cleavage of the N≡N bond of dinitrogen molecules bridged on Mo(I) which is two-electron reduced from Mo (III) derived from molybdenum triiodide complex **P**. Separately, we confirmed that ammonia is produced from nitride complex **Q** under catalytic reaction conditions (Fig. 10(b)). Therefore, it is presumed that this reaction proceeds via a new catalytic cycle, which is different from the conventional catalytic cycle of ammonia-producing reactions. In other words, it seems that extremely high catalytic activity could be achieved by passing through a new catalytic cycle with the cleavage of the N≡N bond of the dinitrogen molecule as a key. Based on our experimental results and theoretical calculations carried out in collaboration with Yoshizawa, Tanaka and co-workers, a newly presumed catalytic cycle is shown in Fig. 11.[32]

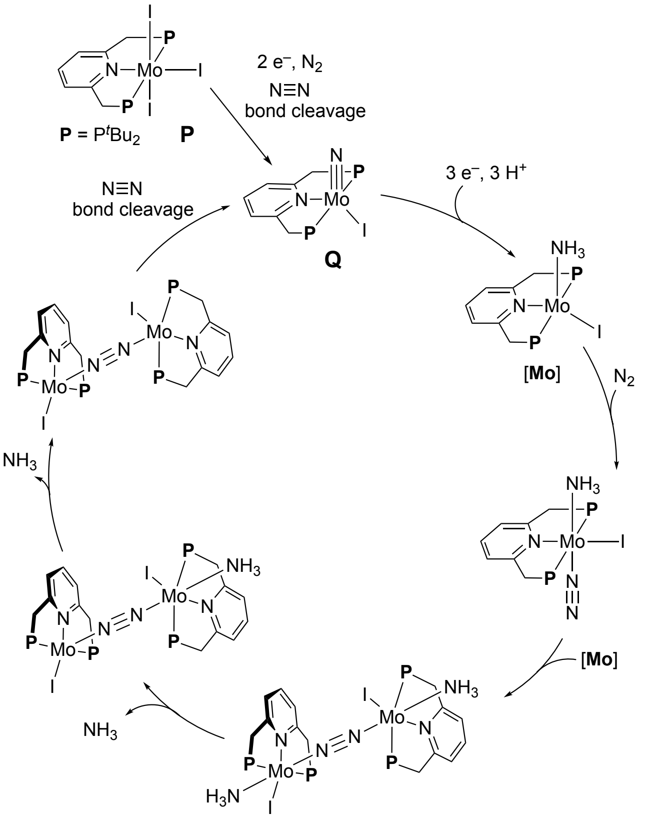

Fig. 11 Proposed reaction pathway for catalytic conversion of dinitrogen into ammonia via direct cleavage of dinitrogen using a molybdenum triiodide complex bearing a PNP-type pincer ligand as a catalyst.

The key factor that determines the reaction pathways whether the cleavage of the N≡N triple bond occurs initially or not is the presence/absence of iodine. Actually, from different experiments, we confirmed that when an equivalent amount of iodine I_2 is added to the dinitrogen-bridged dinuclear molybdenum complex **B** showed extremely high catalytic activity comparable to that of molybdenum triiodide complex **P** and nitride complex **Q**. The results of the theoretical calculations reveal that the cleavage of the N≡N triple bond proceeds only with dinitrogen bridged to Mo(I)–Mo(I) complex, whereas the triple bond cleavage does not proceed with dinitrogen bridged to Mo(0)–Mo(0) or Mo(II)–Mo(II) complexes. It is quite interesting that the reaction mechanism can be simply controlled by the presence/absence of additives.

3. Conclusions

This Perspective covers the development of catalytic nitrogen-fixing reactions using transition metal complexes, focusing on the progress in our research group. It should be noted that we could not review all of the results in this area, including the recent progress in the catalytic silylamine-producing reaction from dinitrogen[33] due to space limitations.

A series of research results indicate that dinitrogen molecular is chemically inert (the binding energy of the N≡N triple bond is 220 kcal/mol and is one of the most inactive chemical bonds). Therefore, we are convinced that our results present a breakthrough that may lead to a new era where dinitrogen can be catalytically converted to ammonia under ambient reaction conditions.[34,35] From the viewpoint of practical application, it is expected that catalytic ammonia-producing reactions using more inexpensive and easy-to-obtain materials such as alcohol and water can be realized in the near future.[36] We expect that our research results will greatly contribute to the further progress of nitrogen-fixing reactions using molecular catalysts.[37]

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

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Notes and references

‡ Previously Shilov and co-workers reported that the reaction of dinitrogen with reductant in protic media in the presence of a catalytic amount of a molybdenum complex afforded hydrazine together with a small amount of ammonia.[38] In this system, however, the detailed mechanism and the catalytically relevant species such as a dinitrogen complex have remained unclear.

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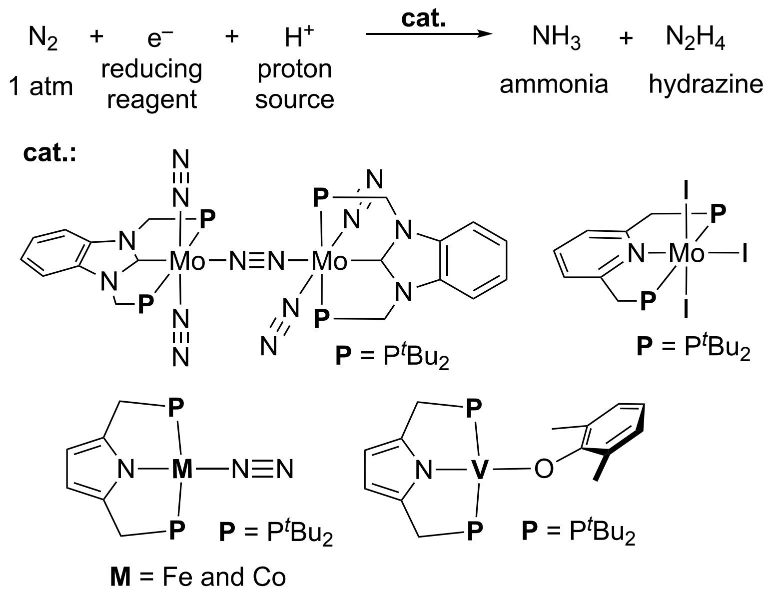
N2 1 atm
+
e⁻ reducing reagent
+
H⁺ proton source
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NH3 ammonia
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N2H4 hydrazine
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P = PᵗBu2
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P = PᵗBu2