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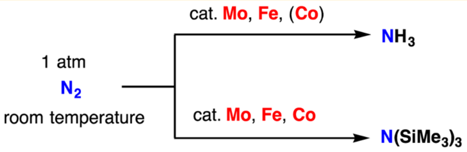
Recent Progress in Transition-Metal-Catalyzed Reduction of Molecular Dinitrogen under Ambient Reaction Conditions

Yoshiaki Nishibayashi*

Institute of Engineering Innovation, School of Engineering, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan

ABSTRACT: This paper describes our recent progress in catalytic nitrogen fixation by using transition-metal−dinitrogen complexes as catalysts. Two reaction systems for the catalytic transformation of molecular dinitrogen into ammonia and its equivalent such as silylamine under ambient reaction conditions have been achieved by the molybdenum−, iron−, and cobalt−dinitrogen complexes as catalysts. Many new findings presented here may provide new access to the development of economical nitrogen fixation in place of the Haber−Bosch process.



1. INTRODUCTION

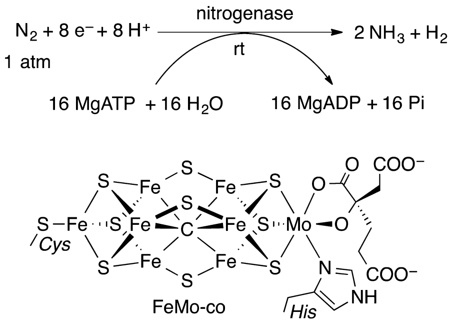
The development of nitrogen fixation, ammonia formation from molecular dinitrogen, under mild reaction conditions is one of the most important issues in the area of chemistry. Industrially, the Haber−Bosch process is the main method to produce ammonia from molecular dinitrogen and dihydrogen gases (Scheme 1).[1,2] The Haber−Bosch process now produces roughly 160 million metric tons of ammonia per year, but the process requires very drastic reaction conditions such as high temperature and pressure and spends at least 1−2% of the annual primary energy supply in the world. It is noteworthy that more than 90% of the total energy for industrial ammonia formation is consumed for the production of molecular dihydrogen as a raw material from fossil fuels, and more than 300 million metric tons of carbon dioxide are produced per year.[3]

Scheme 1. Industrial Haber−Bosch Process

$$N_2 + 3\,H_2 \xrightarrow[\text{200–500 atm, 500–600 °C}]{\text{cat. } Fe_3O_4/K_2O/Al_2O_3} 2\,NH_3$$

It is well-known that biological nitrogen fixation occurs at ambient temperature and pressure (Scheme 2),[4] in contrast to the energy-consuming Haber−Bosch process.[1] The exact reaction mechanism and reaction pathway have not yet been clarified[5] although the X-ray structure has recently been revealed for the active site of nitrogenase in FeMo cofactor.[4] In the biological nitrogen fixation system, molecular dinitrogen is coordinated and activated at the thiolated-bridged polynuclear complex and converted into ammonia via stepwise protonation and reduction. The biological nitrogen fixation is considered to be a prototype as an alternative method to the Haber−Bosch process for ammonia production under mild reaction conditions.

Scheme 2. Biological Nitrogen Fixation and the Active Site of Nitrogenase



molecular structure of the active site of nitrogenase

2. PREPARATION AND STOICHIOMETRIC REACTIVITY OF TRANSITION-METAL−DINITROGEN COMPLEXES

Since the discovery of a ruthenium-dinitrogen complex as the first transition-metal−dinitrogen complex,[6] a variety of transition-metal−dinitrogen complexes have been prepared (Scheme 3)[7,8] and the stoichiometric conversion of the coordinated dinitrogen into ammonia (NH_3) and/or hydrazine (NH_2NH_2) has been well examined aiming for the accomplishment of nitrogen fixation under mild reaction conditions. Especially, the molybdenum− and tungsten−dinitrogen complexes bearing four monodentate phosphines as ligands (**1** and **2**) have been most intensively studied (Scheme 4).[9,10] In this reaction system, the coordinated dinitrogen can be converted into ammonia and hydrazine under ambient reaction conditions by treatment with sulfuric acid and hydrochloric acid. A full reaction pathway for the protonation of the coordinated

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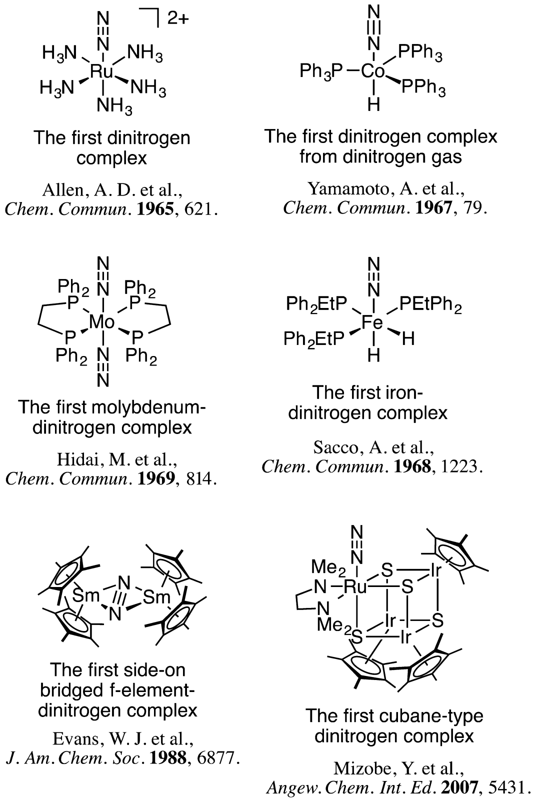
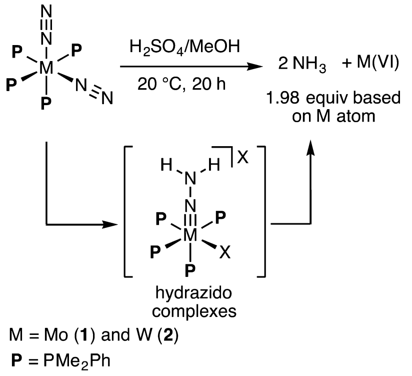
Scheme 3. A Variety of Transition-Metal–Dinitrogen Complexes



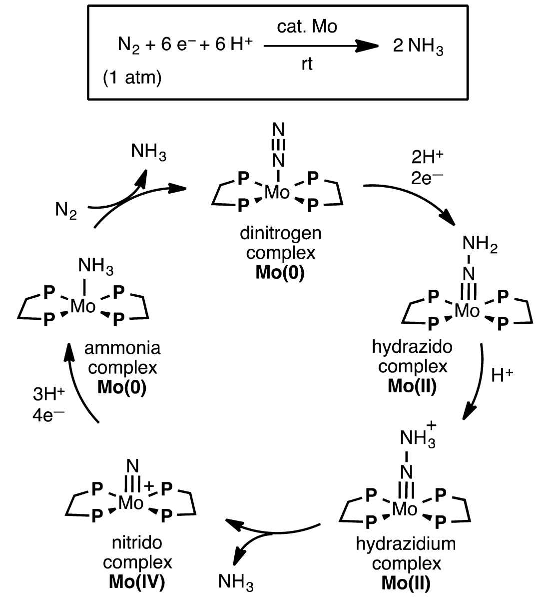
Scheme 4. Protonation of the Coordinated Dinitrogen on the Mo and W Complexes to Produce a Stoichiometric Amount of Ammonia



dinitrogen into ammonia has been proposed based on the reactivity of the isolated diazenido (MN=NH), hydrazido (MN–NH_2), hydrazidium (MN–NH_3), and nitride (M≡N) complexes as reactive intermediates. All of the electrons for the formation of ammonia were delivered from the central metals of the starting molybdenum– and tungsten–dinitrogen complexes. In fact, a higher valent molybdenum and tungsten species may be formed after the formation of a stoichiometric amount of ammonia (up to 2 equiv of ammonia based on the Mo and W atoms). As a byproduct, hydrazine (NH_2NH_2) was also formed in some cases, probably from the reaction of the reactive intermediate hydrazido complex with acids.[11]

In addition to the diazenido, hydrazido, hydrazidium, and nitride complexes derived from the corresponding dinitrogen complexes, imido (MNH), amido (MNH_2), and ammonia complexes (MNH_3) are also considered to be involved in the hypothetical catalytic cycle (Chatt cycle) for the catalytic nitrogen fixation (Scheme 5).[12] The Mo(0) and Mo(IV) complexes may be formed during the catalytic process. Recent investigation on the reaction mechanism of the biological nitrogen fixation by nitrogenase supports the formation of the hydrazine complexes as key reactive intermediates.[13] However, no hydrazine complex was involved in the proposed Chatt cycle, and rather the hydrazine complexes are formed as side-reactive intermediates. However, it was generally believed that the suitable choice of reducing reagents and a proton source may achieve the hypothetical catalytic cycle without any successful example until the report by Schrock and Yandulov in 2003.[14]

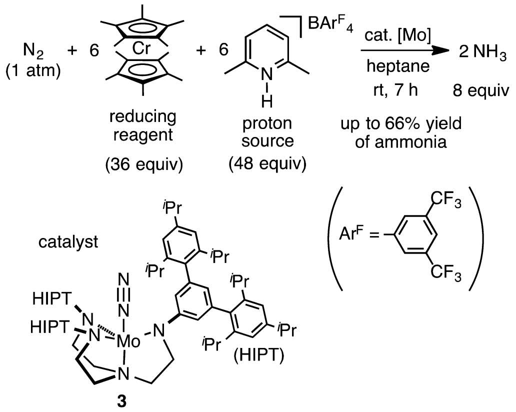
Scheme 5. Proposed Chatt Cycle for the Catalytic Ammonia Formation



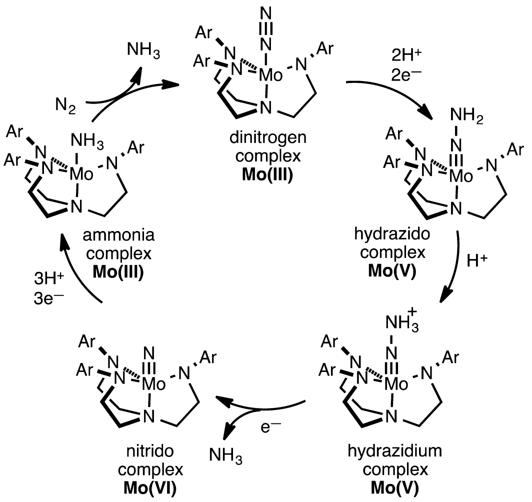
3. CATALYTIC FORMATION OF AMMONIA FROM MOLECULAR DINITROGEN BY USING TRANSITION-METAL–DINITROGEN COMPLEXES AS CATALYSTS

3.1. Molybdenum Triamidoamine System. In 2003, Schrock and Yandulov reported the molybdenum-catalyzed conversion of molecular dinitrogen into ammonia by using a molybdenum–dinitrogen complex bearing a triamidoamine as a ligand (**3**). Treatment of molecular dinitrogen with decamethylchromocene ($CrCp_2$*) as a reducing reagent and 2,6-lutidinium tetrakis[3,5-bis(trifluoromethyl)phenylborate] ([LutH]BAr_4^F; Ar^F = 3,5-bis(trifluoromethyl)phenyl)) as a proton source in the presence of the catalyst gave 8 equiv of ammonia based on the catalyst (Scheme 6).[14] Results of the isolation and characterization of key reactive intermediates and theoretical studies elucidated the detailed reaction pathway called the Schrock cycle (Scheme 7). In this cycle, the reaction proceeds via sequential addition of protons and electrons for the production of two ammonia molecules from one dinitrogen molecule.[14] As the proposed intermediates in the cycle, eight complexes were actually prepared and characterized spectroscopically. In addition, the corresponding nitrido complex bearing the same tridentate triamidoamine ligand showed a

Scheme 6. Catalytic Nitrogen Fixation Using Schrock Catalyst



Scheme 7. Schrock Cycle for the Catalytic Ammonia Formation

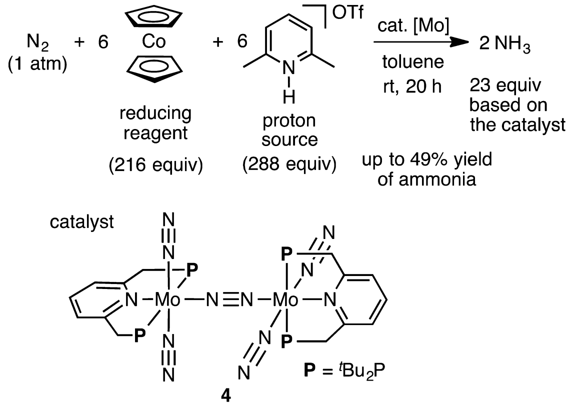


similar catalytic activity.[14] No great difference was observed between the Chatt and Schrock cycles involving the proposed complexes as reactive intermediates, while the main mechanistic difference from the Chatt cycle is that rather higher oxidation states of the central molybdenum atom are maintained in the Schrock cycle. Thus, in the Chatt cycle, the oxidation states of Mo(0) to Mo(IV) are proposed, while in the Schrock cycle, they are of Mo(III) to Mo(VI). In both catalytic cycles, no hydrazine complex is considered to be a key reactive intermediate. This proposal is consistent with the experimental result that only a small amount of hydrazine was formed in both reaction systems. Unfortunately, a higher catalytic activity has not been achieved despite the drastic modification of the original molybdenum complex.[14]

3.2. Molybdenum Tridentate Ligand System. *3.2.1. Molybdenum PNP-Pincer Ligand System.* In our extensive study on the development of the stoichiometric formation of ammonia from the coordinated molecular dinitrogen under mild reaction conditions,[15,16] we have recently found the molybdenum-catalyzed conversion of molecular dinitrogen into ammonia by using a dinitrogen-bridged dimolybdenum complex bearing tridentate PNP-type pincer ligands[17,18] (**4**) as a catalyst under ambient reaction conditions. In this reaction system, atmospheric molecular dinitrogen was catalytically converted into ammonia in the presence of both a reducing reagent and a proton source.[18] This is conisdered to be the second successful example of the catalytic nitrogen fixation under ambient reaction conditions.

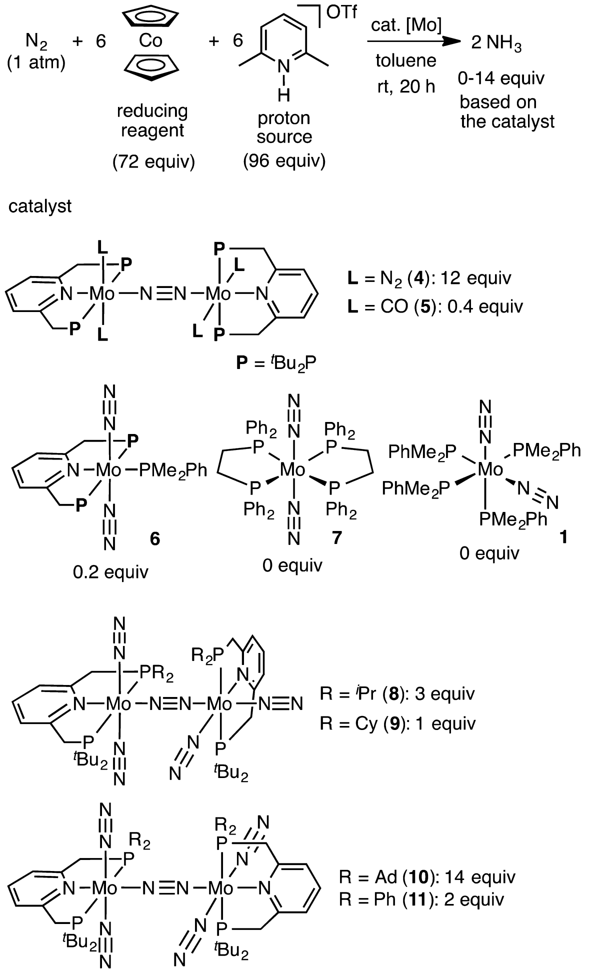
Thus, treatment of atmospheric molecular dinitrogen with cobaltocene ($CoCp_2$; 2.16 mmol) as a reducing reagent and 2,6-lutidinium trifluoromethanesulfonate ([LutH]OTf; 2.88 mmol) as a proton source in the presence of a catalytic amount of $[Mo(N_2)_2(PNP)]_2(\mu\text{-}N_2)$ **4** (0.01 mmol) in toluene at room temperature for 20 h gave ammonia (0.23 mmol) together with molecular dihydrogen (Scheme 8). In this reaction system, up to 23 equiv of ammonia were produced based on the catalyst (12 equiv based on the Mo atom of the catalyst).[18] When other molybdenum−dinitrogen complexes such as $[\{Mo(CO)_2(PNP)\}_2(\mu\text{-}N_2)]$ (**5**), $[Mo(N_2)_2(PNP)(PMe_2Ph)]$ (**6**), *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ **1**, and *trans*-$[Mo(N_2)_2(dppe)_2]$ (**7**) were used as catalysts in place of **4**, less than a stoichiometric amount of ammonia was formed in all cases (Scheme 9). These results indicated that only a dinitrogen-bridged dimolybdenum complex bearing a tridentate PNP-type pincer ligand **4** worked as an effective catalyst to accomplish an efficient performance on the catalytic nitrogen fixation.[18]

Scheme 8. Catalytic Nitrogen Fixation Using a Dinitrogen-Bridged Dimolybdenum Complex As a Catalyst under Ambient Conditions



To develop more effective catalysts, we attempted to prepare some molybdenum complexes bearing other types of PNP pincer ligands, where both phosphorus atoms have the same substitutents such as isopropyl and phenyl groups. However, according to the same method, we could not prepare the corresponding dinitrogen-bridged dimolybdenum complexes.[17] These results inspired us to prepare dinitrogen-bridged dimolybdenum complexes bearing unsymmetric PNP-type pincer ligands, where one phosphorus atom in the pincer ligand has two *tert*-butyl groups as substituents and the other has two other substituents such as *iso*-propyl, cyclohexyl, 1-adamantyl, and phenyl groups (Scheme 9).[19] In fact, the corresponding dinitrogen-bridged dimolybdenum complexes bearing these unsymmetric pincer ligands (**8**−**11**) could be prepared and characterized by X-ray analysis. Within these complexes, we found that only a molybdenum−dinitrogen complex bearing 2-(di-1-adamantylphosphino)methyl-6-(di-*t*-butylphosphino)methylpyridines as unsymmetric PNP-type pincer ligands (**10**) worked as an effective catalyst toward catalytic ammonia formation. In contrast, other molybdenum−dinitrogen complexes such as **8**, **9**, and **11** did not work as catalysts. In these cases, we observed the formation of only a

Scheme 9. Catalytic Nitrogen Fixation Using a Variety of Molybdenum–Dinitrogen Complexes As Catalysts under Ambient Conditions

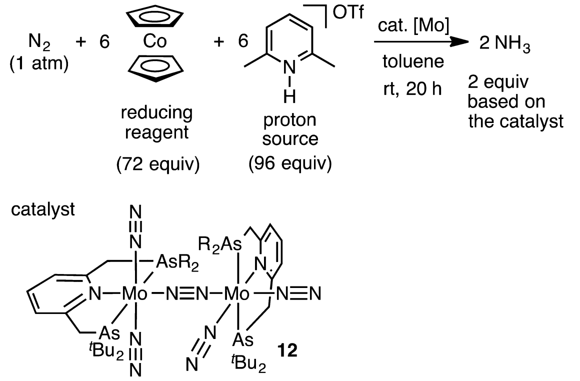


stoichiometric amount of ammonia based on the catalyst. These results showed that the kind of the PNP-type pincer ligands considerably affects the catalytic activity.

Next, we envisaged the use of an arsenic-containing ANA-type pincer ligand. In this case, phosphines in the PNP-type pincer ligand were substituted by arsines. It is well-known that arsines have a similar coordination mode to phosphines but also are more reluctant to oxidation, sterically bulkier, and poorer σ-donors and π-acceptors compared to phosphines. Therefore, the use of arsines in the pincer ligand might show different steric and electronic effects on coordination spheres from that of phosphines. Thus, we prepared the corresponding dinitrogen-bridged dimolybdenum complex bearing an arsenic-containing ANA-type pincer ligand (**12**), but unfortunately, this complex did not show any catalytic activity toward the catalytic nitrogen fixation (Scheme 10).[20] In this case, only 2 equiv of ammonia were produced based on the catalyst (1 equiv based on the Mo atom of the catalyst).

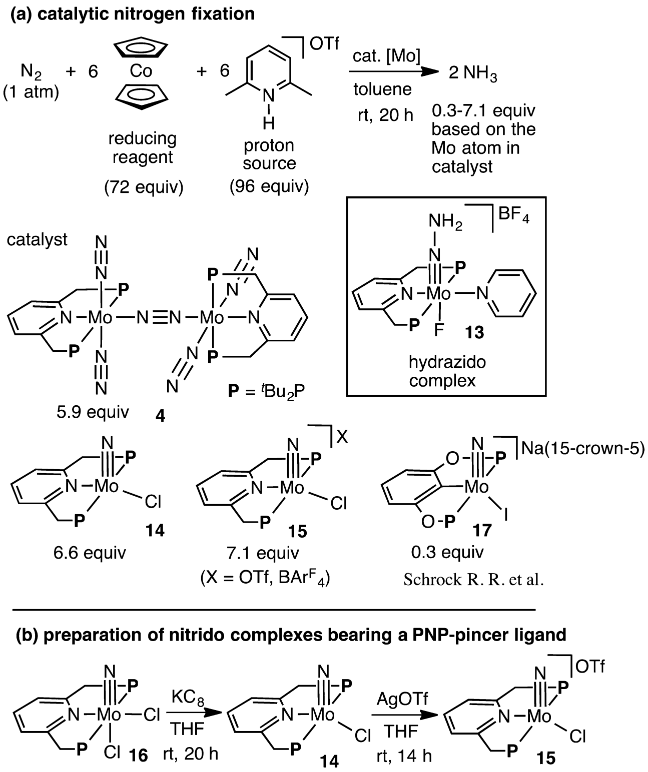
It is noteworthy that some transition-metal–nitrido complexes worked as key reactive intermediates in the stoichiometric conversion of the coordinated dinitrogen into ammonia.[21] To get more information on key reactive intermediates in our catalytic reaction, we newly prepared the mononuclear molybdenum–nitrido complexes bearing the PNP-type pincer ligand and examined their catalytic reactivity.

Scheme 10. Preparation and Reactivity of a Dinitrogen-Bridged Dimolybdenum Complex Bearing Arsenic-containing ANA-type Pincer Ligands



Previously, we already isolated and characterized the cationic mononuclear hydrazido complex $[Mo(\equiv N\text{-}NH_2)F(PNP)(pyridine)]BF_4$ (**13**), but this complex showed no catalytic activity.[18] We then newly prepared a neutral molybdenum(IV) nitrido complex $[Mo(\equiv N)Cl(PNP)]$ (**14**) and a cationic molybdenum(V) nitrido complex $[Mo(\equiv N)Cl(PNP)]X$ ($X =$ OTf and BAr_4^F; **15**) from the corresponding paramagnetic molybdenum(V) nitrido complex $[Mo(\equiv N)Cl_2(PNP)]$ (**16**), which were obtained by treatment of $[MoCl_3(thf)_3]$ with Me_3SiN_3 at 50 °C for 1 h and then the addition of a PNP pincer ligand at 50 °C for 4 h (Scheme 11).[21] These nitrido complexes **14** and **15** showed a similar catalytic activity to the corresponding dinitrogen-bridged dimolybdenum complex **4**.

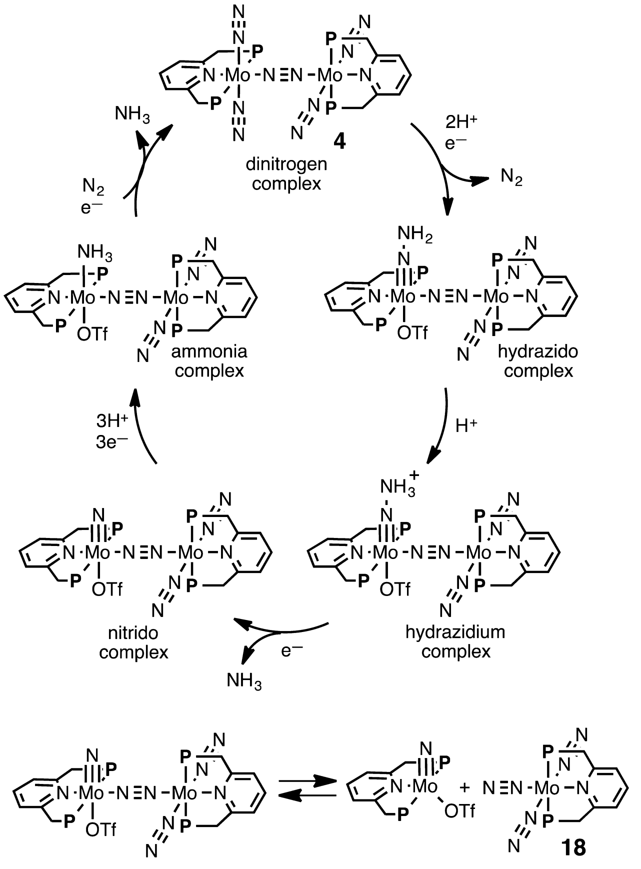
Scheme 11. (a) Catalytic Nitrogen Fixation Using Molybdenum–Nitrido Complexes As Catalysts under Ambient Conditions and (b) Preparation of Nitrido Complexes Bearing a PNP-Pincer Ligand



In contrast, we observed no catalytic activity of the molybdenum(V) nitrido complex **16**. We consider that the coordination of the second chloro ligand to the molybdenum center may prevent the transformation of **16** into the reactive species (Scheme 11).[21] Based on our finding, Schrock and co-workers prepared molybdenum−nitrido complexes bearing a PCP-type pincer ligand such as **17**, but we observed the formation of a stoichiometric amount of ammonia based on the catalyst when **17** was used as a catalyst under similar reaction conditions.[22]

To get more information on the reaction pathway of the catalytic ammonia formation by using the newly prepared molybdenum−nitrido complexes bearing a PNP-type pincer ligand (**14** and **15**), we also investigated the density functional theory (DFT) study. Both experimental and theoretical studies indicated that the dinitrogen-bridged dimolybdenum structure played an important role during the catalytic reaction. Previously, we have proposed a reaction pathway similar to the Chatt and Schrock cycle, where only a mononuclear molybdenum−dinitrogen complex (**18**) may work as a reactive intermediate.[18] However, based on the new findings of experimental and theoretical studies, we have withdrawn the original proposed reaction pathway. Instead of the original proposed reaction pathway, we proposed a novel reaction pathway, where the dinuclear structure involving the dinitrogen-bridged dimolybdenum−dinitrogen complex **4** plays a crucial role to exhibit catalytic activity for catalytic ammonia formation (Scheme 12).[21]

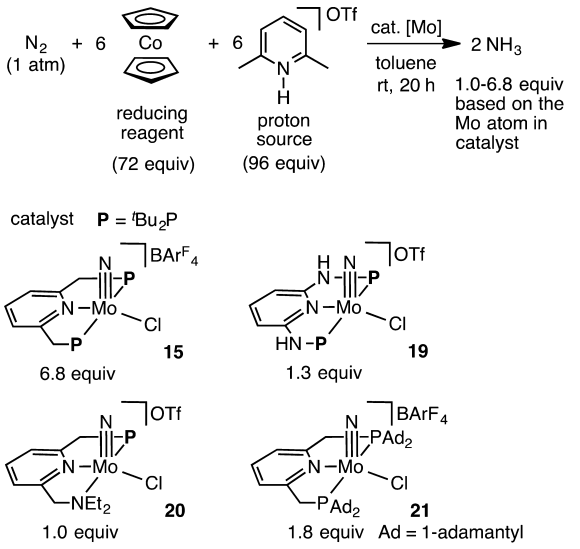
Scheme 12. Our Proposed Catalytic Cycle Using a Dinitrogen-Bridged Dimolybdenum Complex As a Catalyst



We have observed synergy between two molybdenum moieties linked with a bridging dinitrogen ligand at the protonation step of the coordinated dinitrogen ligand. A molybdenum moiety donates an electron to the other molybdenum moiety as the active site via the bridging dinitrogen ligand. As a result, a terminal dinitrogen at the active site is reductively activated to receive a proton. Thus, a mononuclear moiety of the dinuclear molybdenum-dinitrogen complex bearing the PNP-type pincer ligands works as a mobile ligand to the other molybdenum moiety as an active site. Experimentally, we observed the formation of both dinuclear nitrido and ammonia complexes bearing the dinitrogen-bridged dimolybdenum core $[\mathrm{Mo}(\equiv\mathrm{N})(\mathrm{OTf})(\mathrm{PNP})-\mathrm{N}\equiv\mathrm{N}-\mathrm{Mo}(\mathrm{N}_2)(\mathrm{PNP})]$ and $[\mathrm{Mo}(\mathrm{NH}_3)(\mathrm{PNP})-\mathrm{N}\equiv\mathrm{N}-\mathrm{Mo}(\mathrm{N}_2)_2(\mathrm{PNP})]$ by mass spectrometry from the catalytic and stoichiometric reactions of **4**.[21a] This experimental result supports the proposal of both dinuclear nitrido and ammonia complexes bearing the dinitrogen-bridged dimolybdenum core $[\mathrm{Mo}(\equiv\mathrm{N})(\mathrm{OTf})(\mathrm{PNP})-\mathrm{N}\equiv\mathrm{N}-\mathrm{Mo}(\mathrm{N}_2)_2(\mathrm{PNP})]$ and $[\mathrm{Mo}(\mathrm{NH}_3)(\mathrm{N}_2)(\mathrm{PNP})-\mathrm{N}\equiv\mathrm{N}-\mathrm{Mo}(\mathrm{N}_2)_2(\mathrm{PNP})]$ at the DFT calculation. This proposal is in sharp contrast to the common role of the dinitrogen-bridged dinuclear metal complexes bearing pincer ligands. It is well-known that the dinitrogen-bridged dinuclear metal complexes bearing pincer ligands worked only as precursors of mononuclear reactive metal species.[23]

As described above, the molybdenum−nitrido complexes such as **14** and **15** have been found to show a similar catalytic activity with the dinitrogen-bridged dimolybdenum−dinitrogen complex **4**. These results encouraged us to examine the catalytic activity of molybdenum−nitrido complexes bearing other pincer ligands, which were not prepared as the form of the corresponding dinitrogen-bridged dimolybdenum−dinitrogen complexes. We prepared a series of cationic molybdenum−nitrido complexes bearing a variety of pincer ligands (**19**−**21**) and examined their catalytic behavior toward the catalytic nitrogen fixation (Scheme 13).[24] Unfortunately, these newly prepared molybdenum−nitrido complexes showed no catalytic activity under the same reaction conditions. However, we believe that the present approach may realize the development

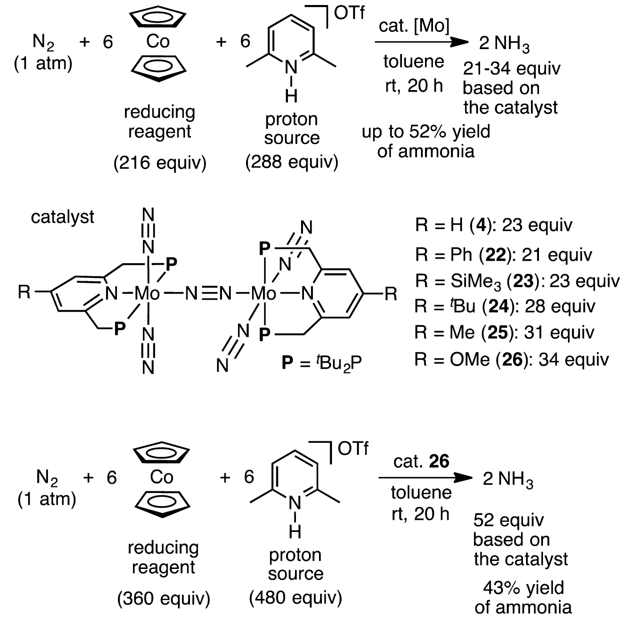
Scheme 13. Catalytic Nitrogen Fixation Using Molybdenum−Nitrido Complexes Bearing Various Pincer Ligands As Catalysts under Ambient Conditions



of new types of molybdenum complexes bearing a variety of ligands, which cannot be possible as the form of the corresponding dinitrogen-bridged dimolybdenum−dinitrogen complexes.

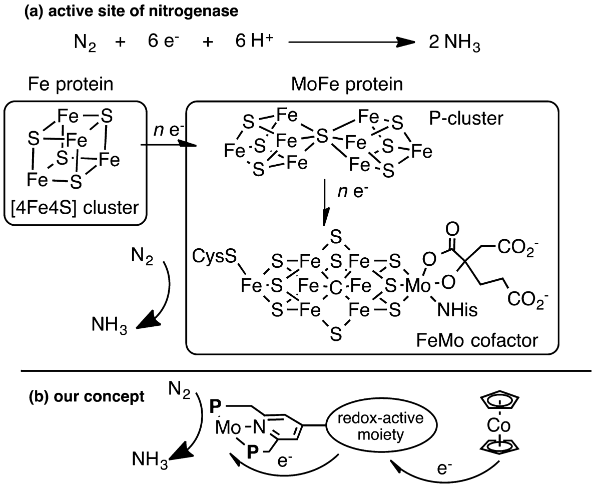
3.2.2. Molybdenum Substituted PNP-Pincer Ligand System. The proposed catalytic cycle shown in Scheme 12 encouraged us to design and prepare more effective dinitrogen-bridged dimolybdenum−dinitrogen complexes as catalysts. The theoretical finding in the catalytic reaction indicates that the first protonation to $[Mo(N_2)_2(PNP)]_2(\mu\text{-}N_2)$, **4**, is one of the rate-determining steps in the catalytic ammonia formation from molecular dinitrogen. Based on this finding, we envisaged the introduction of an electron-donating group to the pyridine ring of the PNP-pincer ligands might increase the back-donating ability of the molybdenum atom to the coordinated molecular dinitrogen. As a result, the electron-donating ability of the molybdenum center may accelerate the first protonation step of the coordinated dinitrogen ligand. We prepared a variety of substituted dinitrogen-bridged dimolybdenum−dinitrogen complexes (**22**−**26**),[25] after various substituents such as Ph, Me_3Si, ^{t}Bu, Me, and MeO groups were introduced to the 4-position of the pyridine ring of the PNP-pincer ligand. Then, we investigated the catalytic nitrogen fixation using newly prepared complexes as catalysts (Scheme 14).[25] In reactions using **22** and **23** as catalysts, 21 equiv and 23 equiv of ammonia were produced based on the catalysts, respectively. When **24** and **25** were used as catalysts, larger amounts (28 equiv and 31 equiv) of ammonia were obtained based on the catalysts, respectively. When **26** was used as a catalyst, moreover, 34 equiv of ammonia were formed based on the catalyst. The largest amount of ammonia was formed based on the catalyst when the most electron-donating group such as MeO moiety was introduced to the PNP-pincer ligands. These results indicate that the catalytic activity depends on the nature of the electronic and electrochemical properties of the substituent at the PNP-pincer ligand. Last, the use of a larger amount of $CoCp_2$ (360 equiv) and [LutH]OTf (480 equiv) gave 52 equiv of ammonia based on **26** (43% yield based on the cobaltocene).

Scheme 14. Catalytic Nitrogen Fixation Using Dinitrogen-Bridged Dimolybdenum Complexes Bearing a Variety of Substituted PNP Pincer Ligands As Catalysts under Ambient Conditions



As shown in biological nitrogen fixation in the Introduction, it is well-known that the active site of the nitrogenase in the FeMo cofactor receives electrons sequentially from P- and 4Fe4S-clusters adjacent to the FeMo cofactor to promote the reduction of the coordinated molecular dinitrogen into ammonia.[4,5] On the basis of the proposed reaction mechanism of nitrogenase, we envisaged that the presence of a ferrocene moiety as a redox active site to the pyridine ring of the PNP-pincer ligands in the dinitrogen-bridged dimolybdenum−dinitrogen complex. In this reaction system, the ferrocene moiety might work as a redox active site to accelerate the reduction processes in the catalytic nitrogen fixation via an intramolecular electron transfer from the iron atom of ferrocene to the active site of the molybdenum atom in the complex (Scheme 15). According to our proposal, we prepared and characterized a series of dinitrogen-bridged dimolybdenum−dinitrogen complexes bearing a metallocene group on the pyridine ring of the PNP-pincer ligands (**27**−**30**). The dimolybdenum−dinitrogen complex bearing ferrocene-substituted PNP-pincer ligands, **27**, has been found to work as the most effective catalyst toward the catalytic nitrogen fixation. In this reaction system, up to 45 equiv of ammonia were produced based on the catalyst (22 equiv of ammonia based on each Mo atom of the catalyst).[26] The catalytic activity of **27** is substantially higher than that of the original complex **4** under the same reaction conditions (Scheme 16).

Scheme 15. (a) Structure of the 4Fe4S Cluster, P-Cluster, and FeMo Cofactor of Nitrogenase and an Electron Flow toward FeMo Cofactor and (b) Our Concept for New Reaction System Using Mo Complexes Bearing a Redox-Active Moiety



In this reaction system, the electronic communication between the iron atom of the ferrocene moiety and the molybdenum atom of the dimolybdenum−dinitrogen complex played an important role to promote the catalytic nitrogen fixation more smoothly. In this reaction system, the ferrocene moiety worked as an intramolecular reductant toward the high-oxidation state of the molybdenum complexes such as hydrazido and hydrazidium complexes. In sharp contrast to the effect observed by the introduction of an electron-donating group such as methoxy moiety to the pyridine ring of the PNP-

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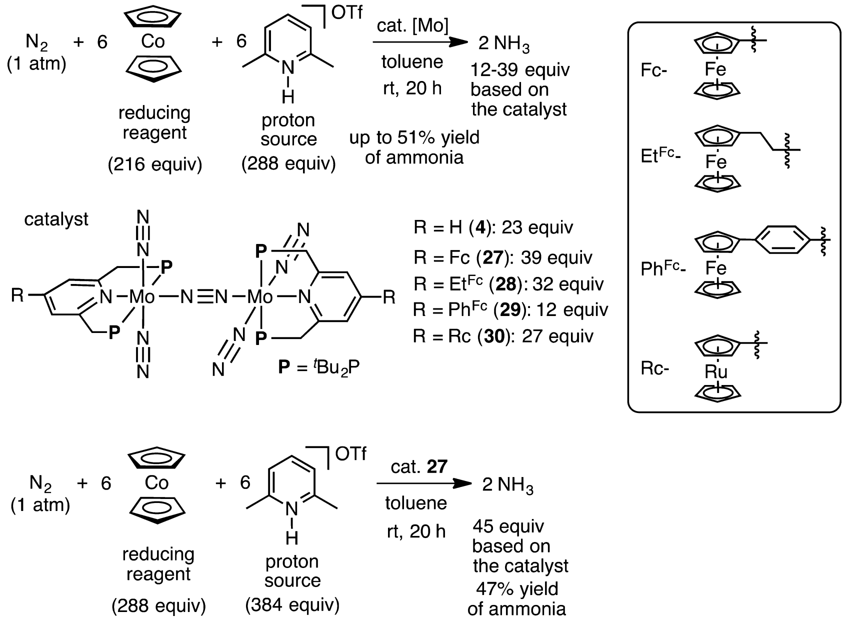
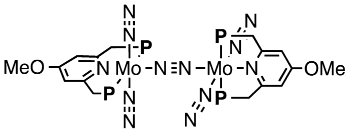
Scheme 16. Catalytic Nitrogen Fixation Using Dinitrogen-bridged Dimolybdenum Complexes Bearing Metallocene-substituted PNP Pincer Ligands As Catalysts under Ambient Conditions

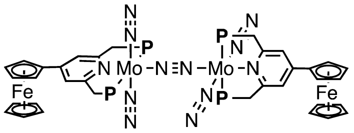


pincer ligand, the role of the ferrocene moiety to the pyridine ring of the PNP-pincer ligand is quite different (Scheme 17). In the former case, the electron-donating group accelerates the protonation step of the coordinated nitrogenous ligands on the molybdenum atom of the complexes in the catalytic nitrogen fixation. In the latter case, a ferrocene moiety accelerates the reduction step in the catalytic nitrogen fixation.

Scheme 17. Role of a Substituent to the PNP-Pincer Ligand toward the Catalytic Nitrogen Fixation



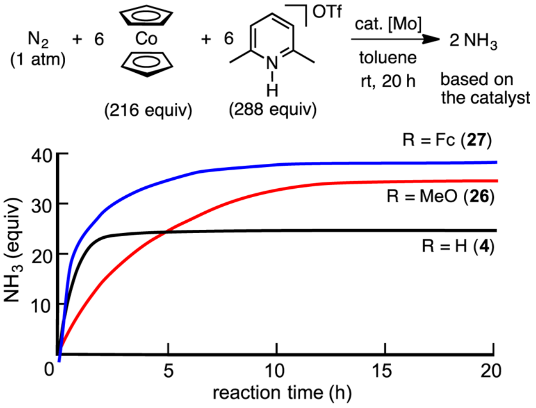
$[Mo(N_2)_2(4\text{-MeO-PNP})]_2(\mu\text{-}N_2)$ (**26**)



$[Mo(N_2)_2(4\text{-Fc-PNP})]_2(\mu\text{-}N_2)$ (**27**)

To get more information on the nature of the dinitrogen-bridged dimolybdenum−dinitrogen complexes bearing a variety of substituents to the PNP pincer liagnd, the time profile of catalytic reactions was monitored by using the dinitrogen-bridged dimolybdenum−dinitrogen complexes as catalysts. Typical results are shown in Scheme 18 together with the turnover number (TON) and the turnover frequency (TOF; TOF was determined by mols of ammonia produced in initial 1 h per catalyst) and yields for the formation of ammonia. When **4** and **26** were used as catalysts, the catalytic ammonia formation proceeded more slowly than that of **27** under the same reaction conditions.[9] In fact, the TOFs for the formation of ammonia using **4** and **26** as catalysts, 17 h^{-1} and 7 h^{-1}, respectively, were lower than that using **27** (23 h^{-1}). These results indicated that the dimolybdenum−dinitrogen complex bearing ferrocene-substituted PNP-pincer ligands **27** has a higher performance from the standpoint of both the catalytic performance (TON) and the rate for ammonia formation (TOF) in the catalytic nitrogen fixation.

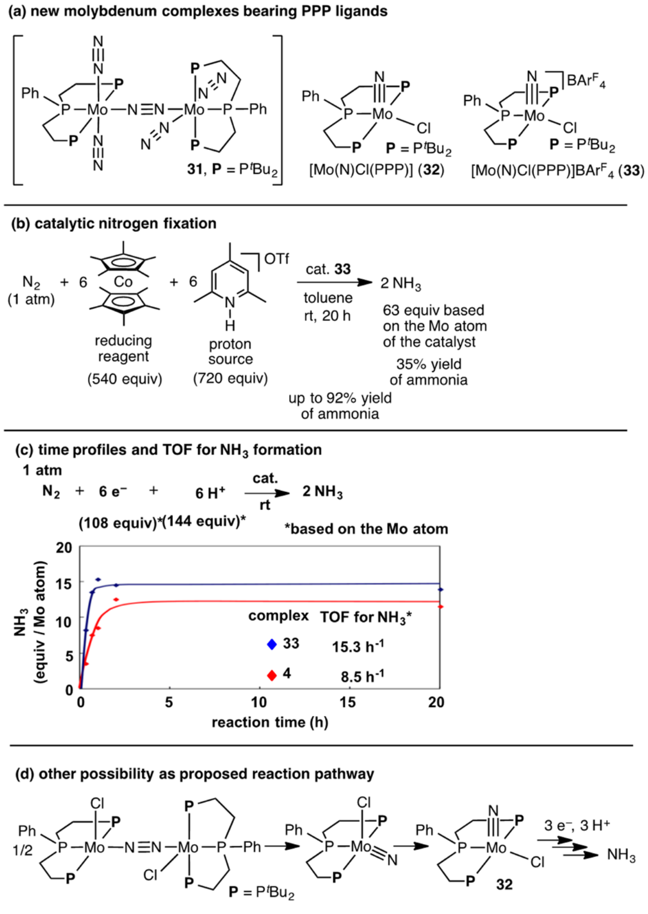
Scheme 18. Time Profiles, TON and TOF Values, and NH_3 Yields Using 4, 26, and 27 As Catalysts



complex	R	TON (NH_3)	TOF (NH_3) (h^{-1})	yield (NH_3) (%)
4	H	23	17	31
26	MeO	34	7	47
27	Fc	37	23	51

3.2.3. *Molybdenum Triphosphine System.* Based on our previous findings in the development of a catalytic nitrogen fixation system, we newly designed a novel dinitrogen-bridged dimolybdenum−dinitrogen complex bearing PPP ligands $[Mo(N_2)_2(PPP)]_2(\mu\text{-}N_2)$ (**31**; PPP = bis(di-*tert*-butylphosphinoethyl)phenylphosphine; Scheme 19), because the phosphines in PPP ligand have an advantage of lower Brønsted basicity and higher stability toward protonation in the catalytic reaction. In addition, the π-accepting ability of the PPP ligand can stabilize a variety of molybdenum complexes bearing

Scheme 19. (a) New Mo Complexes Bearing PPP Ligand, (b) Catalytic Nitrogen Fixation Using Molybdenum−Nitrido Complexes Bearing PPP Ligands As Catalysts under Ambient Conditions, (c) Time Profiles and TOF for NH_3 Formation Using 4 and 33 As Catalysts, and (d) Other Possibility As Proposed Reaction Pathway



a broad range of oxidation states of the Mo center in the catalytic reaction.

Although we have not yet succeeded in preparing the dinitrogen-bridged dimolybdenum−dinitrogen complex bearing PPP ligands **31**, we could prepare the neutral and cationic molybdenum−nitrido complexes bearing PPP ligand [Mo(N)-Cl(PPP)] (**32**) and [Mo(N)Cl(PPP)]BAr_4^F (**33**). When the nitrogen fixation was carried out in the presence of a catalytic amount of **33** by using larger amounts of $CoCp_2$* as a reducing reagent and [ColH]OTf as a proton source, up to 63 equiv of ammonia were produced based on the Mo atom (35% yield based on the $CoCp_2$*).[27] The catalytic activity of complex **33** is more than 5 times higher than that of the original complex **4**. This is so-far the most effective catalytic nitrogen fixation using transition-metal−dinitrogen and its related complexes as catalysts (up to 92% yield based on the $CoCp_2$*).

For comparison, we monitored the time profile of catalytic reactions by using **33** as a catalyst (Scheme 19). The catalytic formation of ammonia in the presence of a catalytic amount of **33** proceeded more smoothly than that of **4** under the same reaction conditions. In fact, the TOF for ammonia formation using **33** as a catalyst (15.3 h^{-1} based on the Mo atom) was higher than that using **4** (8.5 h^{-1}). These results also indicated that complex **33** has the highest performance from the standpoint of both the catalytic ability and the rate for ammonia formation.

Other researchers, George and co-workers[28] and Tuczek and co-workers,[29] previously used triphosphines and tetraphosphines as ligands to prepare a variety of molybdenum−dinitrogen complexes. However, the catalytic reaction has never been observed by using so-far reported molybdenum−dinitrogen complexes bearing triphosphines and tetraphsophines as auxiliary ligands. In contrast, our molybdenum−nitrido complex bearing a PPP ligand as only an auxiliary ligand, **33**, has now been found to work as the most effective catalyst for catalytic nitrogen fixation under ambient reaction conditions. The result shown in Scheme 19 provided the first successful example of catalytic transformation by using molybdenum complexes bearing only a triphosphine as an auxiliary ligand. We believe that the *mer*-coordination mode with a PPP ligand to the Mo atom in the complexes **32** and **33** provided a suitable environment for the molybdenum complexes toward the catalytic reaction.

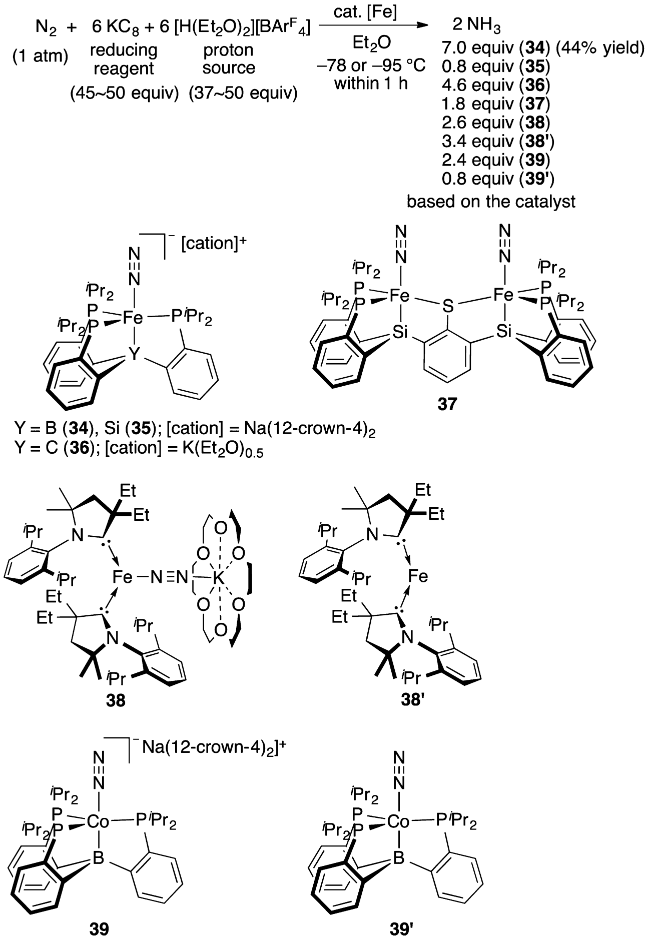
We have not yet clarified the reaction pathway for the catalytic nitrogen fixation using molybdenum−nitrido complexes bearing a PPP ligand such as **32** and **33** as catalysts. At present, we consider that the catalytic nitrogen fixation using **32** and **33** may proceed via a similar reaction pathway using the dinitrogen-bridged dimolybdenum−dinitrogen complex bearing a PNP pincer ligand **4** as a catalyst (Scheme 12). However, we cannot exclude another possibility such as the direct cleavage of the nitrogen−nitrogen triple bond of the bridging dinitrogen ligand of the dinitrogen-bridged dimolybdenum complexes, such as **31**, giving two nitride complexes (Scheme 19), which produce ammonia by sequential protonation and reduction. Further work is currently in progress to clarify the detailed reaction pathway.

3.3. Iron System.

In addition to two reaction systems using molybdenum−dinitrogen complexes as catalysts to produce ammonia from molecular dinitrogen under ambient reaction conditions, Peters and co-workers have found the third successful example of the catalytic system to produce ammonia by using iron−dinitrogen complexes as catalysts. Actually, the iron atom is known to be the important component element of the FeMo cofactor along with molybdenum. In this reaction system, an anionic iron−dinitrogen complex supported by tris(phosphine)borane (**34**) was used as a catalyst to reduce molecular dinitrogen into ammonia (7.0 equiv based on the catalyst) together with KC_8 as a reducing reagent and $[H(Et_2O)_2]BAr_4^F$ as a proton source at −78 °C under an atmospheric pressure of dinitrogen (Scheme 20).[30a] The reaction had to be carried out at sufficiently low temperature to avoid the direct reaction between the strong reducing reagent and the strong acid forming dihydrogen. Quite recently, an iron−hydrazido complex has been characterized as a reactive intermediate in the stoichiometric reaction.[30b]

When the boron atom of the tetradentate ligand was substituted for silicon (**35**),[31] only a stoichiometric amount of ammonia was obtained, while the introduction of an axial alkyl carbon to the tetradentate tris(phosphine) ligand (**36**)[32] gave a moderate result (4.6 equiv based on the catalyst; Scheme 20). These results revealed that the kind of element (B, C, Si) other than phosphine in a series of tetradentate ligands has a slight affect on dinitrogen activation. Quite recently, the preparation and reactivity of a thiolated-bridged diiron−dinitrogen complex (**37**) have been reported, where only a stoichiometric amount

Scheme 20. Catalytic Nitrogen Fixation Using Iron– and Cobalt–Dinitrogen Complexes As Catalysts



of ammonia was produced under the catalytic reaction conditions.[33]

More recently, an anionic two-coordinate iron–dinitrogen complex bearing two cyclic (alkyl)(amine)carbene ligands $[(CAAC)_2Fe(N_2)][K(18\text{-}c\text{-}6)]$ (**38**) has been found to work as a catalyst to produce ammonia (2.6 equiv based on the catalyst; Scheme 20), with its precursor $(CAAC)_2Fe$ (**38′**) working more effectively (3.4 equiv based on the catalyst).[34] As the recent structural study of the FeMo cofactor has suggested that a carbon atom coordinating to six iron atoms exists in its core,[4,5] the catalytic formation of ammonia using iron–dinitrogen complexes supported by an alkyl or a carbene carbon atom as the coordination atom can be regarded as a basic model for the biological nitrogen fixation performed by nitrogenase. Although the amount of produced ammonia has been still low and its reaction mechanism has not yet been clarified sufficiently, further investigation of nitrogen fixation using iron–dinitrogen complexes as catalysts should be valuable.

3.4. Cobalt System.

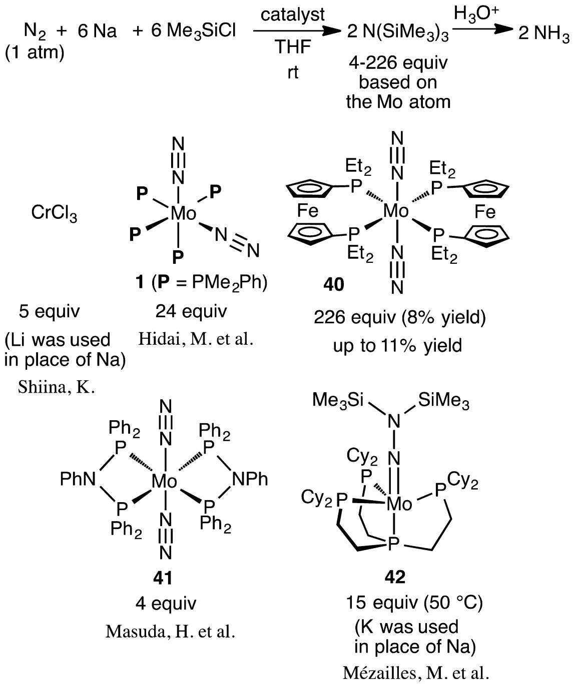
Quite recently, Peters and co-workers have reported the superstoichiometric reaction of molecular dinitrogen into ammonia under mild reaction conditions.[35] In this reaction system, up to 2.4 equiv of ammonia based on the Co atom of the complex were produced from an anionic cobalt–dinitrogen complex supported by tris(phosphine)-borane (**39**), although only 0.8 equiv of ammonia based on the Co atom of the complex were produced from the corresponding neutral cobalt–dinitrogen complex (**39′**; Scheme 20).

4. CATALYTIC FORMATION OF SILYLAMINE FROM MOLECULAR DINITROGEN BY USING TRANSITION METAL COMPLEXES AS CATALYSTS

4.1. Molybdenum System.

The approach for the catalytic tris(trimethylsilyl)amine $(N(SiMe_3)_3)$ formation from molecular dinitrogen is recognized as an alternative nitrogen fixation because $N(SiMe_3)_3$ can be readily transformed into ammonia quantitatively after acid hydrolysis (Scheme 21). In 1972, Shiina found the first example of the catalytic formation of $N(SiMe_3)_3$ from the reaction of molecular dinitrogen with Li as a reducing reagent and trimethylsilyl chloride (Me_3SiCl) in the presence of various metal salts such as $CrCl_3$ as catalysts. In this reaction, up to 5.4 equiv of $N(SiMe_3)_3$ were produced based on the catalyst.[36] However, we cannot exclude the possibility of the formation of lithium nitride (Li_3N) as a reactive intermediate. Later, Mori and co-workers reported similar conversion of molecular dinitrogen by using Li as a reducing reagent in the presence of titanium complexes such as $TiCl_3$, $TiCl_4$, and $Ti(O^iPr)_4$.[37] On the other hand, the molybdenum-catalyzed transformation of molecular dinitrogen into $N(SiMe_3)_3$ by using sodium (Na) as a reducing reagent was reported by Hidai and co-workers. In these cases, up to 24 equiv of $N(SiMe_3)_3$ were produced based on the catalyst.[38] On the basis of the experimental result of the formation of the silyldiazenido

Scheme 21. Catalytic Formation of Silylamine from Molecular Dinitrogen Using Molybdenum–Dinitrogen Complexes As Catalysts under Ambient Conditions



total chemical equation from N_2 to NH_3 in the present reaction system

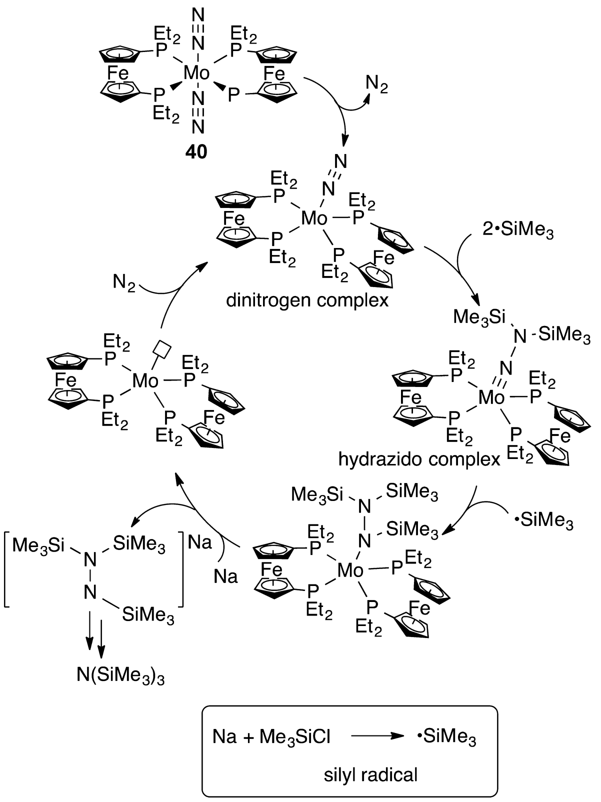
$$\begin{aligned} &N_2 + 6\,Na + 6\,Me_3SiCl \longrightarrow 2\,N(SiMe_3)_3 + 6\,NaCl \\ &2\,N(SiMe_3)_3 + 6\,H_2O \longrightarrow 2\,NH_3 + 6\,Me_3SiOH \\ &6\,Me_3SiOH \longrightarrow 3\,(Me_3Si)_2O + 3\,H_2O \\ \hline &N_2 + 6\,Na + 6\,Me_3SiCl + 3\,H_2O \longrightarrow 2\,NH_3 + 6\,NaCl + 3\,(Me_3Si)_2O \end{aligned}$$

complex from the reaction of the molybdenum dinitrogen complex bearing four dimethylphenylphosphine as ligands with trimethylsilyl iodide, Hidai and Mizobe proposed that the silyldiazenido complex worked as one of the key reactive intermediates in the catalytic reaction.[39]

We have recently reported the preparation and reactivity of molybdenum− and tungsten−dinitrogen complexes bearing two ferrocenyldiphosphines such as depf (1,1′-bis(diethylphosphino)ferrocene) as auxiliary ligands, *trans*-[M$(N_2)_2$(depf)$_2$] (M = Mo (**40**), W). In these complexes, an electron transfer from the Fe atom of a ferrocene unit to the metal centers may be expected to accelerate reduction of the coordinated nitrogenous ligands on the metal center.[40] In our continuous investigation on the catalytic formation of ammonia and ammonia equivalents from molecular dinitrogen by using transition-metal−dinitrogen complexes under mild reaction conditions,[40,41] we have more recently found that complex **40** worked as a highly efficient catalyst in catalytic formation of $N(SiMe_3)_3$ molecular dinitrogen (Scheme 21). In this reaction system, atmospheric molecular dinitrogen was catalytically converted into $N(SiMe_3)_3$ in the presence of Me_3SiCl and Na as a reducing reagent under ambient reaction conditions. In this case, up to 226 equiv of $N(SiMe_3)_3$ were produced based on the catalyst.[42]

On the basis of the study of the DFT calculation on the real reaction system collaborated with Prof. Yoshizawa's group, we proposed a reaction pathway shown in Scheme 22 for the formation of $N(SiMe_3)_3$. First, detachment of one of the coordinated molecular dinitrogens at the molybdenum center forms the corresponding five-coordinated complex as a reactive intermediate. The addition of 2 equiv of trimethylsilyl radical, which is generated from Na and Me_3SiCl, occurs at the terminal nitrogen atom in the five-coordinated complex to give the corresponding hydrazido complex. Then, the third trimethylsilyl radical attacks the nitrogen atom adjacent to the molybdenum center in the hydrazido complex to afford the corresponding four-coordinated complex. Last, the produced $Me_3SiNN(SiMe_3)_2$ moiety is released from the four-coordinated complex. Free $Me_3SiNN(SiMe_3)_2$ is further reduced into 2 equiv of $N(SiMe_3)_3$ under catalytic conditions. Then, the four-coordinated complex receives another molecular dinitrogen to create the starting five-coordinated complex. The result of the DFT calculation indicated that the addition step of the third trimethylsilyl radical to the molybdenum complex is rate-determining.

Scheme 22. Proposed Catalytic Cycle for Nitrogen Fixation Using a Molybdenum−Dinitrogen Complex Bearing Ferrocenyldiphosphine As a Catalyst

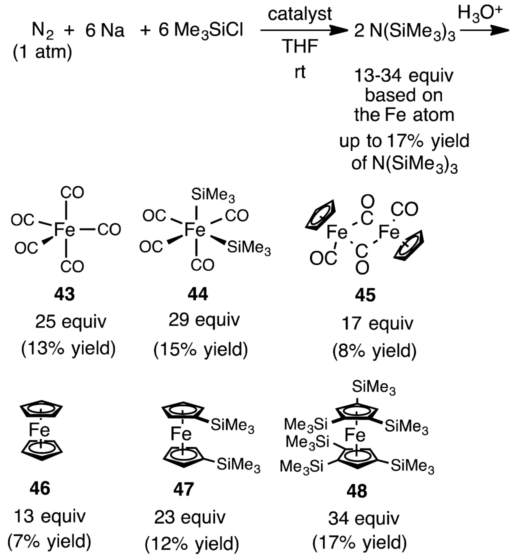


At present, we consider that the high catalytic activity of **40** is sterically controlled by the depf ligands not only by its bulkiness but also by the flexible bond between molybdenum and phosphine, which permits the molybdenum center to adopt various coordination modes. Some interaction between the molybdenum atom and the iron atom in ferrocene may be expected by considering the effectiveness of the depf ligand. However, unfortunately, we have not yet found any evidence to support our proposal shown in Scheme 22.

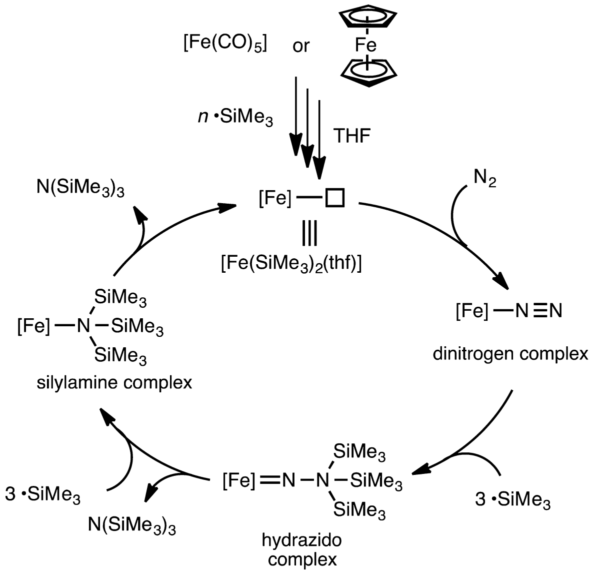
Recently, Masuda and co-workers have reported the preparation and characterization of several molybdenum−dinitrogen complexes bearing bis(diphenylphosphino)amines as ligands (**41**) and investigated their catalytic activity toward the formation of $N(SiMe_3)_3$ under ambient reaction conditions (Scheme 21).[43] Here, only a low catalytic activity (4 equiv based on the catalyst) has been found in the use of some molybdenum−dinitrogen complexes as a catalyst. More recently, Mézailles and co-workers have reported the reduction of molecular dinitrogen into $N(SiMe_3)_3$ by using molybdenum complexes bearing a bulky tetradentate phosphine as a ligand (**42**) under ambient reaction conditions (Scheme 21).[44] Although some reactive intermediates were isolated and characterized, the catalytic activity was moderate, where up to 15 equiv of $N(SiMe_3)_3$ were produced based on the Mo atom of the catalyst.

4.2. Iron System. As another approach, we have found that $Fe(CO)_5$ (**43**) promoted the catalytic conversion of molecular dinitrogen into $N(SiMe_3)_3$. Thus, with the reaction of Na and Me_3SiCl with atmospheric molecular dinitrogen in the presence of **43** in THF at room temperature for 20 h, 25 equiv of $N(SiMe_3)_3$ were formed based on the catalyst (Scheme 23).[45] When other solvents such as diethyl ether, 1,4-dioxane, 1,2-dimethoxyethane, benzene, and hexane were used, only a small amount of $N(SiMe_3)_3$ was observed in these cases. The experimental result obviously indicated that $Fe(CO)_5$ **43** worked as an effective catalyst only in THF. Other Fe carbonyl complexes such as $Fe(SiMe_3)_2(CO)_4$ (**44**) and $[CpFe(CO)_2]_2$ (**45**) were found to work as an effective catalyst. In addition to the Fe carbonyl complexes, ferrocene (**46**) also promoted the catalytic formation of $N(SiMe_3)_3$ under the same reaction conditions, where 13 equiv of $N(SiMe_3)_3$ were produced based on the catalyst. The introduction of trimethylsilyl moieties to the cyclopentadienyl ring of ferrocene as an electron-withdrawing group substantially enhanced the amount of $N(SiMe_3)_3$. In fact, 23 equiv of $N(SiMe_3)_3$ were produced based on the catalyst when $[\{\eta^5\text{-}C_5H_4(SiMe_3)\}_2Fe]$ (**47**) was used as a catalyst. Interestingly, $[\{\eta^5\text{-}C_5H_2(SiMe_3)_3\}_2Fe]$ (**48**) worked as the most effective catalyst. In this case, the largest

Scheme 23. Catalytic Formation of Silylamine from Molecular Dinitrogen Using Iron Complexes As Catalysts under Ambient Conditions



Scheme 24. Proposed Catalytic Cycle for Nitrogen Fixation Using an Iron–Dinitrogen Complex Bearing Trimethylsilyl Ligands As a Catalyst



amount of $N(SiMe_3)_3$ (34 equiv) was obtained based on the catalyst (Scheme 23).

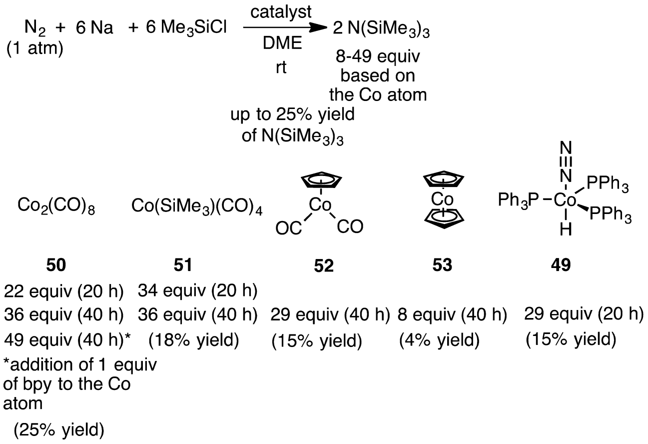
As shown in Scheme 23, Fe carbonyl complexes and ferrocenes have almost the same catalytic performance in the catalytic $N(SiMe_3)_3$ formation. On the basis of the result of the catalytic performance, we consider that common Fe complexes, generated *in situ* from Na, Me_3SiCl, and Fe species such as Fe carbonyl complexes and ferrocenes, worked as real catalysts. Separately, we consider that the trimethylsilyl radical, generated *in situ* from Na and Me_3SiCl, also played an important role in the catalytic $N(SiMe_3)_3$ formation from molecular dinitrogen. Based on the experimental results of the catalytic reaction and DFT calculations on the Fe–dinitrogen complexes, we proposed the reaction pathway for catalytic $N(SiMe_3)_3$ formation from molecular dinitrogen (Scheme 24). First, the reaction of Fe species with Na and Me_3SiCl under atmospheric pressure of molecular dinitrogen gives an Fe(II)–dinitrogen complex bearing two trimethylsilyl groups. A stepwise addition of three trimethylsilyl radicals to the distal N atom of the coordinated dinitrogen ligand in the dinitrogen complex proceeds to form a hydradizo complex. Then, the N–N bond cleavage of the hydradizo ligand in the complex occurs to afford the first silylamine. Simultaneously, a silylamine complex is formed after the addition of three further trimethylsilyl radicals. Finally, the silylamine complex liberates another $N(SiMe_3)_3$ to regenerate the starting Fe–dinitrogen complex bearing two trimethylsilyl groups. This is the first successful example of the Fe-catalyzed formation of $N(SiMe_3)_3$ from molecular dinitrogen under ambient conditions.

More recently, Peters and Ung reported the catalytic formation of silylamine from molecular dinitrogen by using a two-coordinated iron complex bearing two cyclic (alkyl)(amine)carbene ligands $[(CAAC)_2Fe]$, **38′**, as a catalyst, where up to 24 equiv of $N(SiMe_3)_3$ were produced based on the Fe atom of the catalyst.[34] In this system, the use of KC_8 as a reducing reagent was necessary to promote the catalytic reaction at room temperature. In fact, no catalytic reaction occurred at all when Na was used as a reducing reagent. The corresponding cationic complex $[(CAAC)_2Fe]BAr_4^F$ has been found to work as a slightly less effective catalyst under the same reaction conditions (19 equiv of $N(SiMe_3)_3$ based on the Fe atom of the catalyst). It is noteworthy that only a lower amount of $N(SiMe_3)_3$ (7 equiv of $N(SiMe_3)_3$ based on the Fe atom of the catalyst) was produced when the reaction was carried out at −78 °C in the presence of a catalytic amount of **38′**.

4.3. Cobalt System. Almost all the catalytic systems for the formation of ammonia and $N(SiMe_3)_3$ mentioned so far depended on the use of either Mo or Fe complexes as catalysts. Shilov and Bazhenova also previously reported the catalytic reduction of molecular dinitrogen into hydrazine by using a polynuclear Mo complex as a catalyst.[46] It is well-known that MoFe–nitrogenase promotes the reduction of molecular dinitrogen into ammonia under ambient reaction conditions, where the active site of the nitrogenase contains Fe and Mo atoms. These findings indicated that the reaction systems converting molecular dinitrogen catalytically into ammonia and ammonia equivalents under mild reaction conditions were limited only to the use of Mo and Fe complexes as catalysts.

As a promising candidate, we have paid attention to the use of Co complexes because Co is widely and cheaply used as an earth-abundant first row transition metal.[47] The complex $CoH(N_2)(PPh_3)_3$ (**49**) is known to be the first transition metal–dinitrogen complex directly derived from molecular dinitrogen under mild reaction conditions.[48] Despite the successful preparation of a cobalt–dinitrogen complex at the early stage, only a few examples of the stoichiometric transformation of the coordinated dinitrogen on the Co atom have been reported until now.[49] As an extensive study, we have quite recently found the cobalt-catalyzed transformation of molecular dinitrogen into $N(SiMe_3)_3$ under ambient reaction conditions. Typical results are shown in Scheme 25. Some Co carbonyl complexes such as $Co_2(CO)_8$ (**50**), $Co(SiMe_3)(CO)_4$ (**51**), $CpCo(CO)_2$ (**52**), and cobaltocene (**53**) have been found to work as effective catalysts toward the formation of $N(SiMe_3)_3$.[50] It is noteworthy that some cobalt–dinitrogen complexes such as $CoH(N_2)(PPh_3)_3$, **49**, have a similar catalytic activity with $Co_2(CO)_8$, **50**, under the same reaction conditions.[50] The use of 1,2-dimethoxyethane (DME) as

Scheme 25. Catalytic Formation of Silylamine from Molecular Dinitrogen Using Cobalt Complexes As Catalysts under Ambient Conditions

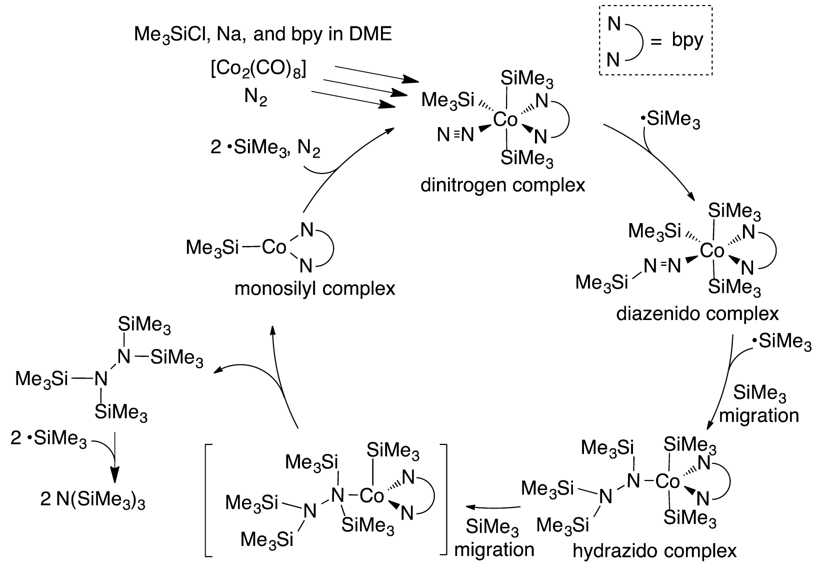


solvent was necessary to promote the catalytic reaction effectively. THF was found to be less effective than DME, but no formation of $N(SiMe_3)_3$ was observed in other solvents such as diethyl ether and 1,4-dioxane. Interestingly, the use of 1 equiv of 2,2′-bipyridine (bpy) to the Co atom of the catalyst **50** substantially increased the amount of $N(SiMe_3)_3$, where 49 equiv of $N(SiMe_3)_3$ were produced based on the Co atom of the catalyst (25% yield based on Na and Me_3SiCl), and this was revealed to be so far the most effective reaction system for the formation of $N(SiMe_3)_3$ from molecular dinitrogen by using Co complexes as catalysts. To the best of our knowledge, this seems to be the first successful example of the cobalt-catalyzed reduction of molecular dinitrogen under mild reaction conditions.

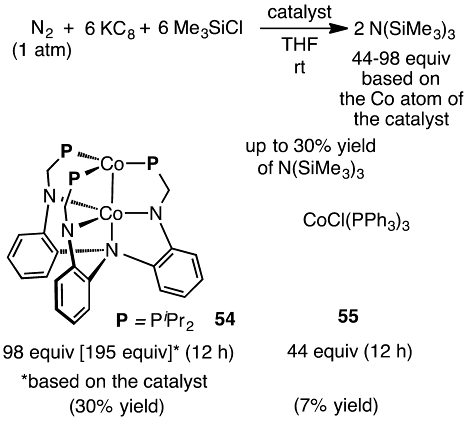
A plausible catalytic cycle for the cobalt-catalyzed transformation of molecular dinitrogen into $N(SiMe_3)_3$ in the presence of bpy is shown in Scheme 26.[50] First, a Co(III)−dinitrogen complex bearing three Me_3Si groups and bpy is generated *in situ* from Na, Me_3SiCl, bpy, and Co complexes. A Me_3Si radical adds to the diazenido complex followed by the migration of a Me_3Si moiety on the Co atom to the nitrogenous ligand to yield a hydrazido(1−) intermediate. Then, one of two Me_3Si ligands on the Co atom moves to the proximal N atom to form a hydrazine group. A temporarily generated hydrazine intermediate is spontaneously separated into a monosilyl intermediate and tetrasilylhydrazine. The hydrazine molecule can be readily transformed into two molecules of $N(SiMe_3)_3$ in the reaction solution. Finally, the introduction of two Me_3Si radicals and another dinitrogen molecule to the monosilyl complex results in regeneration of the starting Co−dinitrogen complex. Through the catalytic cycle, the bpy ligand is strongly bound to the Co atom of the complexes. The proposed reaction pathway, where the Co(III)−dinitrogen complex bearing three Me_3Si moieties and bpy is considered to work as a key reactive intermediate, was supported by the DFT calculation including the corresponding transition state in all steps of the catalytic cycle.

At the same time, independently, Lu and co-workers reported the first successful example of the cobalt-catalyzed reduction of molecular dinitrogen into $N(SiMe_3)_3$ under ambient reaction condition. A dicobalt complex bearing a trisphosphino(triamido)amine ligand (**54**) worked as an effective catalyst, where up to 98 equiv of $N(SiMe_3)_3$ were produced based on the Co atom of the catalyst (195 equiv based on the catalyst; Scheme 27).[51] In addition to the dicobalt complex, some Co complexes bearing phosphines as ligands such as $CoCl(PPh_3)_3$ (**55**) were also revealed to be good catalysts. In these reactions, the use of a large amount of KC_8 as a reducing reagent was necessary to achieve the high performance of the Co catalyst. Here, the activation of molecular dinitrogen may occur at a single Co site, and another Co moiety was considered to work as an electronic tuning ligand. Although the detailed DFT calculation supported a proposed reaction pathway from the coordinated dinitrogen into $N(SiMe_3)_3$ at the dicobalt complex **54**, the exact role of the second Co moiety in the dicobalt complex **54** has not yet been clear.

Scheme 26. Proposed Catalytic Cycle Using a Cobalt−Dinitrogen Complex Bearing Three Trimethylsilyl and bpy Ligands As a Catalyst



Scheme 27. Catalytic Formation of Silylamine from Molecular Dinitrogen Using a Dicobalt Complex As a Catalyst under Ambient Conditions



5. SUMMARY AND PERSPECTIVE

Recent progress in catalytic nitrogen fixation by using transition metal complexes as catalysts has realized not only the molybdenum-catalyzed reduction of molecular dinitrogen into ammonia and its equivalent, silylamine, under ambient reaction conditions but also the iron-catalyzed reduction of molecular dinitrogen into ammonia at a very low reaction temperature and silylamine under ambient reaction conditions. More recently, the chemistry of catalytic nitrogen fixation has also been expanding into the cobalt-catalyzed reduction of molecular dinitrogen into silylamine under ambient reaction conditions. Especially, in the molybdenum-catalyzed reaction, the use of sophisticated molybdenum complexes substantially increased the catalytic activity toward the direct formation of ammonia (up to 92% yield; 63 equiv of ammonia based on the Mo atom of the catalyst). However, we are sure that a real breakthrough is yet necessary and awaited for constructing a "post-Haber–Bosch process": a versatile and efficient synthetic method for the catalytic formation of ammonia from molecular dinitrogen under mild reaction conditions. For example, the development of more effective catalysts and the catalytic nitrogen fixation system using water as both a proton source and a sacrificed reducing reagent assisted with visible light is awaited. Recently, ammonia has been paid attention as a candidate of hydrogen carrier as well as fuel for vehicles. Toward this goal, chemists in this field should develop more sustainable transformation of molecular dinitrogen into ammonia without the use of fossil fuels.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ynishiba@sogo.t.u-tokyo.ac.jp.

Notes

The authors declare no competing financial interest.

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