Interplay between Theory and Experiment for Ammonia Synthesis Catalyzed by Transition Metal Complexes

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CONSPECTUS: Nitrogen fixation is an essential chemical process both biologically and industrially. Since the discovery of the first transition-metal–dinitrogen complex in 1965, a great deal of effort has been devoted to the development of artificial nitrogen fixation systems that work under mild reaction conditions. However, the transformation of chemically inert dinitrogen using homogeneous catalysts is still challenging because of the difficulty in breaking the strong triple bond of dinitrogen, and a very limited number of transition metal complexes have exhibited the catalytic activity for the direct transformation of dinitrogen into ammonia with low turnover numbers. To develop more effective nitrogen fixation systems, it is necessary to retrieve as much information as possible from the limited successful examples. Computational chemistry will provide valuable insights in the understanding of the reaction mechanisms involving unstable intermediates that are hard to isolate or characterize. We have been applying it for clarifying detailed mechanisms of dinitrogen activation and functionalization by transition metal complexes as well as for designing new catalysts for more effective nitrogen fixation.

This Account summarizes recent progress in the elucidation of catalytic mechanisms of nitrogen fixation by using mono- and dinuclear molybdenum complexes, as well as cubane-type metal–sulfido clusters from a theoretical point of view. First, we briefly introduce experimental and theoretical contributions to the elucidation of the reaction mechanism of nitrogen fixation catalyzed by a mononuclear Mo–trimidoamine complex. Special attention is paid to our recent studies on Mo-catalyzed nitrogen fixation using dinitrogen-bridged dimolybdenum complexes. A possible catalytic mechanism is proposed based on theoretical and experimental investigations. The catalytic mechanism involves the formation of a mononuclear molybdenum–nitride (Mo≡N) intermediate, as well as the regeneration of a dimolybdenum intermediate with the Mo–N≡N–Mo moiety. Comparison of the reactivity of di- and mononomolybdenum complexes suggests that the dimolybdenum structure is essential for the catalytic activity. synergy between the two Mo cores connected with a bridging N2 ligand is observed in the protonation of coordinated N2. Intermetallic electron transfer through the bridging N2 ligand reductively activates the coordinated N2 to be protonated. On the basis of the proposed catalytic mechanism, we used DFT calculations for rational design of dimolybdenum complexes serving as more effective catalysts for nitrogen fixation. Newly prepared dimolybdenum complexes with modified PNP-type pincer ligands exhibit greater catalytic activity than the original one.

INTRODUCTION

Nitrogen fixation, the reduction of atmospheric dinitrogen to ammonia, is one of the most important catalytic reactions in biology and chemistry. Since dinitrogen is chemically inert due to its extremely strong triple bond, both artificial and biological nitrogen fixation can proceed in the presence of metal-based catalysts. The Haber–Bosch process transforms N2 and H2 gases into ammonia on the surface of iron-based heterogeneous catalysts under harsh reaction conditions, where a huge amount of energy is consumed for the H2 production from fossil fuels such as natural gas.1 The development of an alternative to the Haber–Bosch process without the use of dihydrogen is still challenging because of the difficulty in breaking the strong N≡N triple bond of dinitrogen to synthesize ammonia under ambient reaction conditions with a homogeneous catalyst of high turnover number.

In contrast, biological nitrogen fixation as a part of the global nitrogen cycle is attained by the enzyme nitrogenase in certain bacteria at ambient temperature and pressure. Experimental studies of the Mo-containing nitrogenase revealed that its active site to reduce dinitrogen involves a double cubane-type iron–molybdenum cluster MoFe7S9C (FeMo cofactor; Scheme 1).2,3 Using eight pairs of proton and electron, FeMo cofactor

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converting dinitrogen to ammonia with the mandatory evolution of dihydrogen. Although the mechanism of biological nitrogen fixation has not completely been understood, a possible reaction pathway is proposed for N₂ transformation starting from a “Janus” E₁ intermediate, in which four protons and four electrons are accumulated in the FeMo cofactor and two of the hydrogens form [Fe–H–Fe] moieties.3

Since the discovery of [Ru(N₂)(NH₃)₅]²⁺ in 1965,4 a great number of well-defined transition-metal dinitrogen complexes have been prepared and the reactivity of coordinated N₂ ligand has been extensively investigated in a quest to discover a novel nitrogen fixation system that works under mild reaction conditions.5 However, there are only a few examples of the direct transformation of dinitrogen into ammonia catalyzed by transition-metal–dinitrogen complexes in the presence of proton and electron sources.6−10 In 2003 Yandulov and Schrock reported the first catalytic transformation of dinitrogen into ammonia under ambient conditions using Mo–triamidoamine complex 1 as a catalyst, where 8 equiv of ammonia was produced based on the catalyst, as shown in Scheme 2.8

Scheme 2. Nitrogen Fixation Catalyzed by a Mo−Triamidoamine Complex

Schrock and co-workers proposed a catalytic mechanism (the Yandulov−Schrock cycle) based on the isolation and observation of reactive intermediates.11,12 The validity of the proposed mechanism is supported by intensive theoretical studies on the energetics of the entire catalytic cycle.3−23

Nishibayashi and co-workers found the second example of Mo-catalyzed nitrogen fixation using a dinitrogen-bridged dimolybdenum complex bearing a PNP-type pincer ligand (2) under ambient reaction conditions, where 23 equiv of ammonia was produced based on the catalyst (Scheme 3).8 Detailed descriptions in this Account are devoted to the recent work for understanding this Mo-catalyzed nitrogen fixation system,24,25 which is a result of our synergistic relationship between theory and experiment in the chemistry of dinitrogen activation and transformation.26

More recently Peters and co-workers reported the first Fe-catalyzed direct transformation of dinitrogen into ammonia at −78 °C.10 In this system, an anionic iron−dinitrogen complex bearing tris(phosphine)borane produced 7 equiv of ammonia based on the catalyst. While a cationic Fe−N₃H₂ intermediate is spectroscopically characterized,17 theoretical approaches will provide a better insight into the Fe-catalyzed system, relevant to the biological nitrogen fixation.

Experimental and theoretical works on an alternative way to transform dinitrogen via photochemical activation of dinitrogen in dinitrogen-bridged bimetallic complexes should be described here.28−33 Floriani and co-workers reported the first photo-induced splitting of the bridging dinitrogen ligand in [Mo-(Mes)_3]_2(μ-N₂).28 Kirchner and co-workers theoretically proposed a photochemical activation scheme of a bridging dinitrogen ligand in bimetallic complexes using Sellmann-type FeII and RuII complexes as models.29 The π−π* excitation of the bridging dinitrogen ligand weakens its triple bond to yield a bent, diazene-like structure of the M−N−N−M moiety, which is prepared for the formation of diazene. Kunkely and Vogler reported that photoirradiation of a dinitrogen-bridged OsIII−OstII complex induces the reductive splitting of the bridging dinitrogen through MLCT excitation.30 Blank and co-workers performed pump–probe spectroscopy to investigate the photoexcitation dynamics of the dinitrogen splitting in the photolysis of [Mo(N[Bu]Ar)](μ-N₂).31 Furche, Evans, and co-workers have demonstrated photochemical activation of dinitrogen using rare-earth (M = Y, Lu, Dy) complexes bearing cyclopentadienyl ligands.32 DFT calculations were applied for rationalizing a low-energy charge transfer from one of the cyclopentadienyl ligands to the metal center, which leads to the binding and activation of dinitrogen by two metal units. More recently, we have found the cleavage and formation of dinitrogen in a single system assisted by molybdenum complexes bearing ferrocenylidiphosphine.33 In this system, a dimolybdenum μ-N₂ complex was split into two molybdenum−nitride complexes by photoirradiation, and the dimolybdenum complex was regenerated from the nitride complexes by oxidation.

NITROGEN FIXATION CATALYZED BY Mo−TRIAMIDOAMINE COMPLEXES

Yandulov and Schrock reported Mo-catalyzed nitrogen fixation using [HIPTN₃N]Mo(N₂) 1 under ambient reaction con-
HIPTN3N ligand can cause substantial errors in the calculated 
[HIPTN3N]Mo.

Coordinated N\(_2\) is converted to a nitride [Mo(≡N)] complex and an ammonia molecule by the stepwise addition of protons and electrons. Their experimental studies prompted computational approaches to clarify the mechanism of nitrogen fixation in the Mo–triamidoamine system.\(^ {13-23}\) Cao and co-workers first reported DFT calculations using a simplified model of 1, [PhN\(_3\)N]Mo(N\(_2\)).\(^ {15}\) They adopted NH\(_4^+\) and an iron–sulfur cluster as a pair of proton/electron sources. Studt and Tuczek\(^ {14}\) and Magistrato and co-workers\(^ {15}\) investigated the entire energy profile of the catalytic cycle using simplified models, [HN\(_3\)N]–Mo(N\(_2\)) and [PhN\(_3\)N]–Mo(N\(_2\)).

Later, this pathway was experimentally confirmed by Schrock and co-workers.\(^ {12}\) Tuczek and co-workers have recently conducted a large-scale calculation using the full [HIPTN3N]Mo catalyst for quantitative comparison with the available experimental data.\(^ {20}\) The use of the full Mo catalyst resulted in almost the same energetics as obtained earlier for the small model,\(^ {14}\) and the authors described that a larger model does not necessarily lead to an improvement in the calculated energetics. Lettner and Hölscher discussed the potential of transition metal complexes (M = Mo, Ru, Os) bearing a HIPT-substituted triamidoamine ligand as catalysts for reducing dinitrogen using dihydrogen as the reducing reagent.\(^ {22}\) They have also been pursuing the possibility of the transformation of dinitrogen into ammonia by dihydrogen catalyzed by transition metal complexes bearing various pincer ligands.\(^ {34}\)

Recent studies have attempted to computationally investigate the potential of 3 as a catalyst for nitrogen fixation.\(^ {37}\) DFT calculations demonstrated reductive activation of the N≡N bond in a model of 3, [[Ru(tmeda)](N\(_2\)) (Cp*Ir)(μ-S)\(_4\)] ([Ru(N\(_2\))]). Figure 2b presents a possible catalytic cycle of nitrogen fixation by [Ru]. The calculated cycle is based on the

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**Figure 1.** Yandulov–Schrock cycle for the transformation of dinitrogen into ammonia catalyzed by 1. [Mo] represents [HIPTN3N]Mo.

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**Figure 2.** (a) The structure of [[Ru(N\(_2\))(tmeda)](Cp*Ir)(μ-S)\(_4\)] 3. (b) Calculated catalytic cycle of nitrogen fixation by [[Ru(N\(_2\))(tmeda)](Cp*Ir)(μ-S)\(_4\)] ([Ru(N\(_2\))]). Energy changes in individual reaction steps are presented in kcal/mol, where protonation (red) and reduction (blue) steps are shown in different colors.
Yandulov–Schröck cycle, where LutH⁺ and CoCp*⁺ were adopted as proton and electron sources. Energy changes (ΔE) in the protonation steps were evaluated based on the equation

\[ [X] + \text{LutH}^+ \rightarrow [XH]^+ + \text{Lut} \]

where [X] is a neutral intermediate. The energy profiles of the reduction steps were calculated based on the equation

\[ [XH]^+ + [\text{CoCp*}] \rightarrow [X] + [\text{CoCp*}] \]

where [XH]^+ is a protonated intermediate. As shown in Figure 2b, almost all the reaction steps proceed in an exothermic way although the first protonation is endothermic by 17.8 kcal/mol. The calculated energy profile indicates that [Ru] can serve as a catalyst for nitrogen fixation if appropriate proton/electron sources are chosen.

Contrary to the promising DFT result, no experimental evidence has been found for the protonation of the N₂ ligand in 3. Mizobe and co-workers observed only catalytic evolution of H₂ followed by elimination of the N₂ ligand.56 This result suggests that the N₂ ligand in 3 is not sufficiently activated for functionalization. To pursue the possibility of the MIr₃S₄ core as a catalyst, we predicted the reactivity of dinitrogen complexes of MIr₃S₄ clusters \([\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Ru}, \text{Mo}, \text{W})\] with LutH⁺. Optimized structures and energy profiles of MIr₃S₄ clusters (M = Mo and W (in parentheses)). Relative energies and interatomic distances are given in kcal/mol and Å, respectively.

![Figure 3](image)

**Figure 3.** Optimized structures and energy profiles for the proton transfer from LutH⁺ to N₂ bound to (a) the RuIr₃S₄ cluster and (b) the MIr₃S₄ clusters (M = Mo and W (in parentheses)). Relative energies and interatomic distances are given in kcal/mol and Å, respectively.

The amount of negative charges on coordinated N₂ are also a useful criterion for judging the degree of N₂ activation.57 We found that MoIr₃S₄ and WIr₃S₄ cores particularly exhibit high N₂-activating ability. The N−N distance and N≡N stretching of \([\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Ru}, \text{Mo}, \text{W})\] are 1.150 (1.161) Å and 1952 (1889) cm⁻¹, respectively, indicating N₂-activating ability superior to \([\text{Ru}(\text{N₂})] \text{Cl}(\text{OTf})^-\) (1.128 Å and 2118 cm⁻¹). The NPA charges on the N₂ ligand are -0.33 and -0.49 in \([\text{Mo}(\text{N₂})]) and \([\text{W}(\text{N₂})])\), respectively, both of which are significantly more negative than that in \([\text{Ru}(\text{N₂})])\) (≈-0.10).

We next assessed the reactivity of \([\text{M}(\text{N₂})]) (\text{M} = \text{Ru}, \text{Mo}, \text{W}) with LutH⁺. Optimized structures and energy profiles for the protonation of the \(\text{N₂}\) ligand are presented in Figure 3. Protonation of the \(\text{N₂}\) ligand in \([\text{Ru}(\text{N₂})])\) would not proceed due to a high activation energy of 39.5 kcal/mol (Figure 3a), which agrees with the experimental result. On the other hand, the \(\text{N₂}\) ligand in \([\text{Mo}(\text{N₂})]) and \([\text{W}(\text{N₂})])\) is easily protonated (Figure 3b). Formation of the protonated complex requires very low activation energies for the Mo and W complexes (6.4 and 1.6 kcal/mol). All the results suggest that the MoIr₃S₄ and WIr₃S₄ clusters are best suited for the activation and protonation of the coordinated \(\text{N₂}\). After this prediction, Mizobe and co-workers synthesized a metal–sulfido cluster having the MoIr₃S₄ core. As a preliminary result, the Mo site binds CO, which is isoelectronic with N₂, whereby the CO ligand exhibited a \(\nu_{\text{CO}}\) band in an extremely low frequency region, 1725 cm⁻¹ for \([\text{Mo}(\text{Co})(\text{dppe}))\text{(Cp*Ir)}(\text{μ-} \text{S})]_\text{4}^{-}\) (dppe = Ph₂PCH₂CH₂PPh₂), in contrast to 1925 cm⁻¹ for \([\text{Ru}(\text{Co})(\text{dppe}))\text{(Cp*Ir)}(\text{μ-} \text{S})]_\text{4}^{-}\).

**NITROGEN FIXATION CATALYZED BY DINITROGEN-BRIDGED DIMOLYBDENUM COMPLEXES**

Nishibayashi and co-workers reported the Mo-catalyzed nitrogen fixation using dinitrogen-bridged dimolybdenum complex 2, as shown in Scheme 3.57 Dinitrogen was converted into ammonia at room temperature in the presence of \([\text{LutH}][\text{OTf}]) (\text{OTf} = \text{CF}_3\text{SO}_3^-) as a proton source and cobaltocene (CoCp₂) as a reducing reagent, where up to 23 equiv of NH₃ were produced based on the catalyst. We retrieved some pieces of information from the experimental results,9,23 to contemplate a possible catalytic cycle: (i) A CO-substituted dinitrogen-bridged dimolybdenum complex, \([\text{Mo}([\text{Co})(\text{PNP})])\text{(μ-N}_{\text{2}}]\)) \(_\text{2}^{-}\), produced less than a stoichiometric amount of ammonia. (ii) A mononuclear molybdenum complex, \([\text{Mo}(\text{N}_{\text{2}}))(\text{PNP})(\text{PMe}_{\text{2}}\text{Ph})]\) has no catalytic activity. (iii) The catalytic activity of 2 strongly depends on the counteranion of LutH⁺. The amount of produced ammonia was drastically decreased when [LutH]Cl and [LutH]BArF were used as proton sources. (iv) Mo–nitrile complexes, \([\text{Mo}([\text{N}])\text{Cl}(\text{PNP})])\) and \([\text{Mo}[\text{N}])\text{Cl}(\text{PNP})])\) OTF showed a similar catalytic activity to 2. Considering these findings, we developed a hypothesis in the DFT-based proposal: (a) Terminal \(\text{N}_{\text{2}}\) ligands are necessary for the catalytic reaction. (b) Dinuclear Mo–N₃ complexes are involved in the catalytic cycle. (c) Triflate (OTF⁻) that is the counteranion of LutH⁺ plays a role. (d) A dinuclear Mo complex is separated into mononuclear ones to afford a Mo–nitrile complex, \([\text{Mo}[\text{N}])\text{(OTF})\text{-}(\text{PNP})]\). We also assumed (e) the stepwise protonation and reduction of coordinated \(\text{N}_{\text{2}}\). A catalytic mechanism deduced from theoretical and experimental studies is summarized in Figure 4. The mechanism involves separation of a dinuclear Mo complex after sequential protonation/reduction of a terminal \(\text{N}_{\text{2}}\) ligand as well as regeneration of 2 linked with the exchange of ammonia for dinitrogen. Batista and co-workers independently proposed a remarkable role of dinuclear Mo complexes in the catalytic activity of 2.41

**Figure 5** presents detailed mechanisms for the transformation of dinitrogen into ammonia starting from 2. Activation energies of the proton transfer from LutH⁺ were evaluated for all protonation steps. Energy profiles of the reduction steps by CoCp₂ were calculated based on the equation \([XH]^+ + [\text{CoCp}_2] \rightarrow [X] + [\text{CoCp}_2]\)_³, where \([XH]^+\) is a protonated...
Figure 4. Proposed catalytic cycle of the transformation of dinitrogen into ammonia by dimolybdenum complex 2. The numbering of intermediates are given in Figure 5.

Figure 5. A possible reaction pathway starting from 2. Energy changes (activation energies) for individual reaction steps are presented in kcal/mol.
intermediate. Energy changes and activation energies (in parentheses) were calculated at the B3LYP** level of theory.

The catalytic cycle starts with the protonation of a terminal dinitrogen ligand in 2 to form \([\text{Mo}(\text{N}_2)(\text{NNH})-\text{N}==\text{N}==\text{Mo}(\text{N}_2)_2]\), A, where \(\text{Mo} = \text{Mo}(\text{PNP})\). The \(\text{N}_2\) ligand trans to the NNH group in A is then replaced by OTf\(^{-}\) (A \(\rightarrow\) B \(\rightarrow\) C; Figure 5a). Protonation and reduction of C afford a hydrazide(2-) complex \([\text{Mo}^{\text{OF}}(\text{NNH}_2)-\text{N}==\text{N}==\text{Mo}(\text{N}_2)_2]\), D. Reduction of \([\text{Mo}^{\text{OF}}(\text{NNH}_2)-\text{N}==\text{N}==\text{Mo}(\text{N}_2)_2]\), E, results in the formation of ammonia and \([\text{Mo}^{\text{OF}}(\text{N})-\text{N}==\text{N}==\text{Mo}(\text{N}_2)_2]\), F. Complex F is separated into two mononuclear complexes, a key intermediate \([\text{Mo}^{\text{OF}}(\text{N})-\text{N}]==\text{Mo}(\text{N}_2)_2]\, G, and \([\text{Mo}(\text{N}_2)_3]\), H (Figure 5b).

Figure 5c describes sequential protonation/reduction of G leading to ammine complex L. Coordination of dinitrogen to imide complex I gives a six-coordinate complex \([\text{Mo}^{\text{OF}}(\text{OF})-(\text{N}_2)(\text{NH})]\), J, and then the imide ligand is reduced to the ammine ligand to afford complex L. The catalytic cycle is completed by the regeneration of 2 linked with the exchange of the NH\(_3\) ligand for an incoming \(\text{N}_2\) molecule (Figure 5d). Reduction of L results in the elimination of OTf\(^{-}\). A five-coordinate complex \([\text{Mo}(\text{N}_2)(\text{NH})]\), M, couples with H\(^{+}\) generated from F to afford a dinuclear complex N. Finally, the NH\(_3\) ligand in N is replaced by dinitrogen to regenerate 2. Here we focus on two key steps in Figure 5a,b, (i) the protonation of a terminal \(\text{N}_2\) ligand in 2 and (ii) the formation of mononuclear molybdenum–nitride complex G.

Dinitrogen complex 2 has two possible reaction sites for the protonation, the terminal and bridging \(\text{N}_2\) ligands. The protonation of the bridging \(\text{N}_2\) ligand requires a high activation energy (\(E_a = 40.7\) kcal/mol) due to steric hindrance from tert-butyl groups in the pincer ligands. On the other hand, the protonation of a terminal \(\text{N}_2\) ligand is likely to occur (\(E_a = 8.4\) kcal/mol) although this reaction is endothermic by 6.5 kcal/mol. While proton detachment from the NNH group in A easily occurs (A \(\rightarrow\) 2; \(E_a = 1.9\) kcal/mol), the protonation of 2 prompts the elimination of the \(\text{N}_2\) ligand trans to the NNH group, where the reaction is 2.7 kcal/mol exothermic with an activation energy of 4.4 kcal/mol. After the \(\text{N}_2\) elimination, OTf\(^{-}\) occupies the vacant coordination site in B to cancel the electronic charge (B \(\rightarrow\) OTf\(^{-}\) \(\rightarrow\) C; \(\Delta E = -15.6\) kcal/mol). Totally, the first protonation process (2 \(\rightarrow\) C) is exothermic by \(11.8\) kcal/mol.

In the proposed mechanism in Figure 5, the formation of \([\text{Mo}^{\text{OF}}(\text{N})-\text{N}]==\text{Mo}(\text{N}_2)_2]\), G, is regarded as a key reaction step. Once the nitride intermediate F is formed, the bond energy between the Mo(=N) atom and the bridging \(\text{N}_2\) ligand is decreased to only \(4.4\) kcal/mol. The small Mo–N bond energy would rationalize the separation of F into the corresponding mononuclear complexes G and H. Experimentally, fragments assignable to \([\text{Mo}^{\text{OF}}(\text{N})-\text{N}]==\text{N}==\text{N}==\text{Mo}(\text{N}_2)_2]\) and \([\text{Mo}^{\text{OF}}(\text{N})-\text{N}]==\text{N}==\text{Mo}(\text{N}_2)_2]\) were observed by mass spectrometry from the stoichiometric reaction of 2 with [LutH]OTf.  

Here we would like to emphasize that the mononuclear Mo–N\(_2\) complex, \([\text{Mo}(\text{N}_2)_3]\), H, does not react with LutH\(^{+}\), and hence the dinuclear structure must be regenerated to start the next catalytic cycle. It may be strange because the NPA charges on a terminal \(\text{N}_2\) ligand, which is a good criterion for judging the degree of \(\text{N}_2\) activation, are almost identical in the di- and mononuclear Mo complexes (\(-0.12\) for 2 and \(-0.11\) for H). Why is a dimolybdenum structure connected with dinitrogen required for the protonation of \(\text{N}_2\) ligands? Figure 6a shows the distribution of the NPA charges in A. The sum of the NPA charges assigned to each Mo unit is calculated to be +0.66 for unit A and +0.34 for unit B, indicating that unit B donates 0.34 electron to unit A during the protonation of a terminal \(\text{N}_2\) ligand in unit A. This suggests that one Mo unit in 2 supports the other to accept a proton and stabilize the generated diazenide ligand by the intermetallic electron transfer.

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Synergy of the Mo centers through the bridging \(\text{N}_2\) ligand can be observed in the HOMO of 2 (Figure 6c). The HOMO of 2 is comprised of \(\pi\) orbitals of the two Mo atoms and a \(\pi\) orbital of the bridging \(\text{N}_2\) ligand. The bonding \(\pi\) orbital interacting...
with the metal d-orbitals is distorted due to the twisted connection of the two Mo units (the N₂−Mo−Mo−N₂ dihedral angle of −54.4°). The intermetallic electron transfer allows 2 to accept a proton at the first step of the nitrogen fixation.

The proposed catalytic mechanism prompted us to design more reactive dinitrogen-bridged dimolybdenum complexes as catalysts for nitrogen fixation. As shown in Figure 5a, the first protonation of a terminal N₂ ligand is energetically most unfavorable. We envisaged enhancing the electron-donating ability of the Mo centers to accelerate the first protonation process. Introduction of an electron-donating group to the pyridine ring of 2 is expected to intensify the back-donating ability of the metals to the N₂ ligands.

We evaluated the impact of introduction of electron-donating groups to the 4-position of the pyridine ring in the pincer ligand. Figure 7 describes energy profiles of the first protonation process calculated for 2a (R = H), 2b (R = Me), and 2c (R = OMe). The activation energies for the protonation of 2a (8.4 kcal/mol) are decreased to 7.4 kcal/mol for 2b and 7.0 kcal/mol for 2c. Methyl- and methoxy-substituted PNP ligands can accelerate the protonation of 2. The NPA charge on N₂ indicates reductive activation of the coordinated N₂ through an enhanced back-donation from Mo. We therefore expected that 2c would serve as an effective catalyst.

Nishibayashi and co-workers prepared a variety of substituted dimolybdenum complexes (2b−2f), in which substituents such as Me, MeO, Ph, Me₃Si, and tBu groups were introduced to the 4-position of the pyridine ring of the PNP-pincer ligand. The catalytic transformation of dinitrogen into ammonia were then examined using 2b−2f as catalysts (Scheme 4). In excellent accordance with the computational design, 2c produced the largest amount of NH₃ (34 equiv based on 2c). The use of a larger amount of CoCp₂ (360 equiv) and [LutH]OTf (480 equiv) gave 52 equiv of NH₃.

■ CONCLUDING REMARKS

We have summarized the synergetic relationships between computation and experiment in elucidating the mechanisms of nitrogen fixation catalyzed by transition metal complexes, the molybdenum−triadinoamine complex, the dinitrogen-bridged dimolybdenum complexes, and the cubane-type MIr₃S₄ clusters. In particular, DFT calculations in close liaison with experiments lead to the proposal of detailed reaction pathways for nitrogen fixation catalyzed by the dimolybdenum complex. The calculated mechanism tells us a crucial role of the dinuclear Mo−N≡N−Mo structure in the protonation of coordinated N₂. Intermetallic electron transfer via the bridging N₂ ligand stabilizes the generated diazenide (Mo−N≡NH) intermediate. Dimolybdenum complexes newly designed based on the theoretical findings exhibit higher catalytic activity than the original complex. We now have confidence that the mechanistic understanding and rational ligand design provided by theoretical calculations will further accelerate the development of metal-complex-catalyzed nitrogen fixation systems. Quite recently, we have found a new Mo-catalyzed nitrogen fixation system using molybdenum-nitride complexes bearing a triphosphine (PPP) ligand, [Mo(N)(PPP)Cl] and [Mo(N)- (PPP)Cl]BArF₄ as catalysts. The latter has the highest catalytic activity for nitrogen fixation, where 63 equiv of NH₃ were produced based on the Mo atom. Interestingly, no dinuclear complexes such as [Mo(N₂)ₓ(PPP)]ₜ(μ-N₂) have been isolated and characterized yet. We now have great interest in whether the formation of dinuclear complexes may be indispensable in the reaction pathway of the transformation of dinitrogen into ammonia.

■ AUTHOR INFORMATION

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Notes
The authors declare no competing financial interest.
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DEDICATION

Dedicated to the late professor Yasushi Mizobe of the University of Tokyo.

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