

Recent Developments of Dinitrogen Activation on Metal Complexes and Clusters

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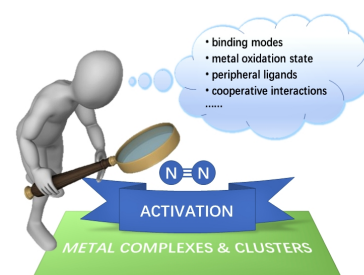
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ABSTRACT Dinitrogen (N₂) is the major component of the atmosphere and many factors bring about dinitrogen inertness with low reactivity. Dinitrogen activation on metal complexes and clusters under ambient condition is the long-standing goal in the modern chemistry. In this review, an attempt has been made to survey the mechanistic aspects of dinitrogen activation and functionalization based on different coordination binding modes of dinitrogen. Our goal is to provide a comprehensive survey of dinitrogen activation in order to guide the relevant research in the future.

Keywords: dinitrogen activation, binding mode, dinitrogen complex, metal cluster, synergistic mechanism



1 INTRODUCTION

Dinitrogen is the most abundant substance in the atmosphere, and its activation is a critical process for the life cycle on the earth. The transformations of N₂ into NH₃ and organonitrogen species are indispensable and essential for life. However, the process for cleavage and conversion of dinitrogen has been identified as a significant challenge.^[1] The high bond dissociation energy of the N≡N triple bond partly accounts for the thermodynamical difficulty. Lots of factors hindering dinitrogen activation mostly involve kinetics in nature. While the large HOMO-LUMO (the highest occupied molecular orbital – the lowest unoccupied molecular orbital) gap disfavors electron transfer, the low proton affinity makes direct protonation of dinitrogen extremely difficult under ambient conditions. Indeed, the high ionization potential, negative electron affinity, and non-polar strong bonds give rise to the inertness and low reactivity.^[2,3]

Qualitative Mulliken-Hund molecular orbital (MO) theory renders the familiar $(\sigma_s)^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^0(\sigma_{2p}^*)^0$ ground-state electron configuration for triple-bonded N₂. Inspired by Dewar-Chatt-Duncanson (DCD) σ -donor/ π -acceptor bonding model for alkene,^[4] dinitrogen activation can be classified into three categories as shown in Figure 1. Firstly, the lowest unoccupied molecular orbital (LUMO, π_{2p}^*) of N₂ can act as a Lewis acid site to accept electron density from an occupied metal d-orbital to form a π back-bond, or from external electrons undergoing a reduction reaction. Secondly, N₂ is able to bind as a Lewis base and donate electron density from the HOMO (σ_{2p}) into an unoccupied metal d -orbital, which results in the formation of a σ -type bond. Thirdly, the π_{2p} orbital of N₂ could also donate electron density to unoccupied metal d -orbitals, thus weakening the N≡N bond. In addition, the mixture of the above three ways to reduce or 'activate' the N≡N bond could be fulfilled in multi-metallic cluster systems.

The increase of the N-N bond length as well as the decrease of the N-N bond order, force constant, and stretching frequency are used to identify weakening of the N-N bond.^[5]

In general, dinitrogen activation on metal-based complexes and clusters can proceed either via *direct dissociative pathway* or *indirect associative pathway*.^[5] In the direct dissociative activation, the N≡N unit is directly dissociated into two N atoms, which is typically seen in systems with multiple active sites or strongly reducing early transition metals. In the associative activation, the N≡N triple bond is gradually weakened accompanied with the functionalization of N atoms by other agents (e.g. proton/electron, hydrogen, halides, etc.).^[6,7]

The industrial Haber-Bosch process converts N₂ and H₂ into NH₃ on Fe- or Ru-based heterogeneous metal catalysts under high-temperature and high-pressure operating conditions. The well-studied atomistic mechanism of the process is verified to be a direct N≡N dissociation process on multi-metallic active sites, involving the so-called **C7-site** of Fe(111) or Fe(211) surface or the **B5-site** of Ru(0001) step, which is the rate-determining step.^[8,9] However, biological nitrogen fixation occurs under ambient conditions, which is accomplished by multi-metallic clusters in the nitrogenase cofactors via the associative dinitrogen activation.^[10] Compared to the multifactorial active sites in the industrial and biological nitrogen fixation, it is instructive to perform mechanistic investigations on dinitrogen activation by model metal complexes and clusters using well-defined active sites.

Over the last half century, a series of metal complexes and clusters binding with dinitrogen were synthesized and identified, involving mono-nuclear or multi-nuclear metal active sites. This work is to provide an overview on mechanistic aspects of dinitrogen activation. We will briefly discuss the N₂ binding mode associated with the dinitrogen activation, and then discuss selected dinitrogen complexes based on different coordination

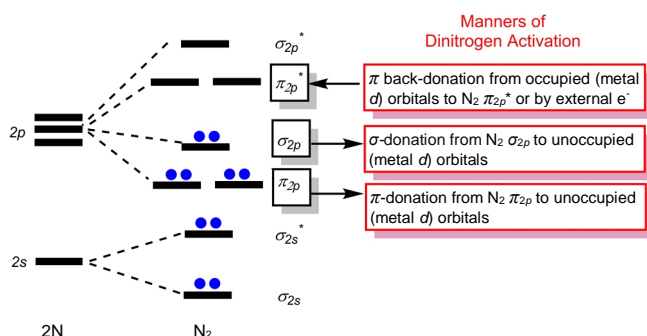


Figure 1. Schematic MO diagram involving dinitrogen activation.

binding modes. Representative examples and recent progress of dinitrogen activation on metal clusters will also be provided. At last, a perspective will be given on potential challenges in this field.

n COMMON MODES OF N₂ BINDING TO METALS

The dinitrogen coordination mode plays an essential role in dinitrogen activation.^[11] Comprehensive experimental and theoretical studies have demonstrated that dinitrogen can coordinate with the metal centers in terminal or bridging manners as summarized in Figure 2(a). Following the convention in coordination chemistry, when dinitrogen bridges metal sites, it is normally denoted as μ_n , where n is the number of bridged metals (μ_2 is usually abbreviated as μ). Based on the interaction between dinitrogen and each metal center, binding mode can be distinguished into “end-on” and “side-on”, which are represented as η^1 (one N-atom bounds to the metal) and η^2 (two N-atoms bound to the metal), respectively.^[10] For terminal dinitrogen bounded to a mononuclear transition metal, the side-on mode was found only in late transition metal complexes, while the end-on coordination mode was seen in mostly all existing mononuclear transition metal complexes.^[12] In multi-nuclear complexes or clusters, the binding mode of N₂ is richer, which is the combination of various active sites, as exemplified by the binding mode of N₂ in trinuclear complexes or clusters shown in Figure 2(b).

In weakly activated dinitrogen, one of the most typical bonding modes is mononuclear terminal end-on binding, which can be explained in a manner entailing σ -donation from the dinitrogen moiety to the metal, as well as some π back-bonding from the metal d orbitals to π^* -orbitals of dinitrogen. It is revealed that σ -donation is more crucial in this binding mode, while back-bonding plays a weaker role due to long $M \cdots N_2$ distance.^[13] Based on this generalization, the coordinated dinitrogen is best referred to as formally neutral and illustrated as $(N_2)^0$. Once the dinitrogen is strongly polarized, the terminal nitrogen is endowed with a formally negative charge, so that electrophilic attack by other agents can easily activate the unit of dinitrogen.^[5]

In order to strongly activate dinitrogen, a powerful reducing metal center is indispensable, which is most typically observed with the early transition metals, especially with low-valent ones.^[14] As the result of strongly reducing nature of the active metals with the availability of high-lying d -orbital electrons for π -back dona-

tion, the dinitrogen can be considered as $(N_2)^d$ ($d = -1$ to -4), which could be simply figured out by N-N stretching frequency and the N-N bond length. Additionally, most of compounds with strongly activated dinitrogen are not mononuclear, but the multi-nuclear cluster systems. Especially, each metal in dinuclear complexes utilizes two electrons to back-donate to the N₂ unit, leaving one of the N₂ π^* -orbitals complimentary to engage with another metal center, which facilitates the formation of dinuclear dinitrogen complex.^[15] Therefore, the metal oxidation state and coordination number greatly influence the activation of dinitrogen.^[16]

Additionally, the peripheral ligands of the metal site also play a significant role in determining the extent of N-N activation. Large differences in reactivity can arise from subtle modifications in

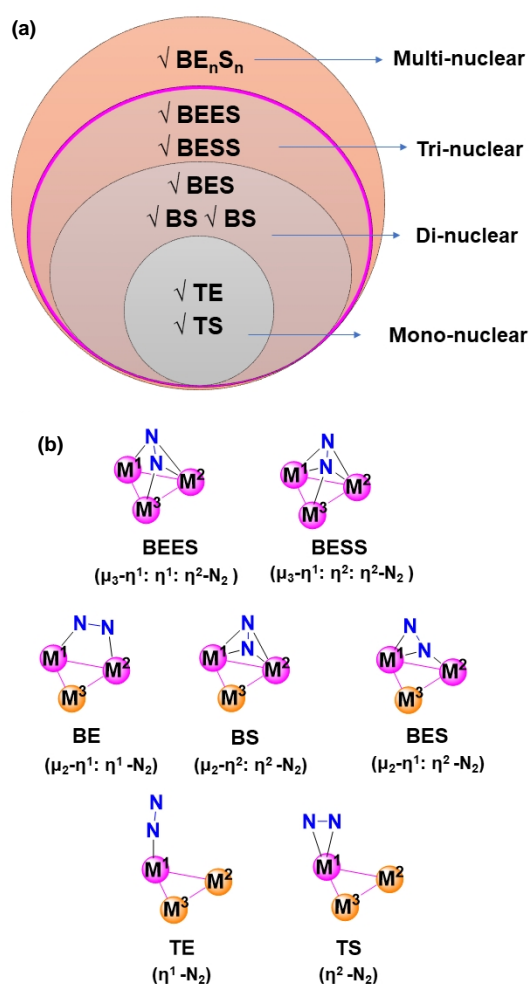


Figure 2. (a) Schematic illustration of the binding modes of N₂ on mono-nuclear or multi-nuclear complexes or clusters. (b) Schematic binding modes of N₂ in trinuclear complexes or clusters. Note that no distinction was made between single, double or triple bonds. The nomenclatures used in the text are the abbreviation for the coordination mode of “Terminal” (T), “Bridging” (B), end-on (E) and side-on (S). For instance, “BESS” stands for the bridging end-on/side-on/side-on binding mode. The pink balls stand for the dinitrogen active site in the metal complexes or clusters.

ligand electronic structure, steric geometry, and bite angle of peripheral ligands, among others.^[17] Typically, the geometric modifications are implemented using bulky peripheral ligands.^[18] For example, the addition of methyl groups to cyclopentadienyl ligands of bis(cyclopentadienyl)M (M = Zr, Hf) dimer affects the activation of dinitrogen, usually by forcing the two metal atoms apart to change the binding mode.^[19] Especially, a series of studies on hindered β -diketiminato complexes has revealed that a trigonal planar geometry at the metal results in the weakness of N-N bond on iron, cobalt, and nickel^[20] though these metals do not usually have sufficient back-bonding capacity to reduce dinitrogen. Similarly, the N-N bond activation can also be achieved by tetrahedral ligands,^[21] which induces strong π -back-bonding as explained by crystal-field analysis.^[22]

Moreover, the modifications of late transition-metal orbital energies caused by peripheral ligands with proper electron-withdrawing substituent groups can also promote the changes of N-N bond order in dinitrogen activation.^[23] The tri-nucleating macrobicyclic ligands could cause metal σ - and π -type frontier orbitals oriented toward the internal cavity of the cyclophane, providing the premise conditions for dinitrogen activation.^[24] In 2021, Murray and coworkers synthesized a 48-electron Co_3 cluster with mono-valent Co^I , $\text{Co}_3\text{L}^{\text{Et/Me}}$, in which electrons between the metal-metal bonding interaction assist in the cooperative activation of dinitrogen, and $\text{Co}_3\text{N}_2\text{L}^{\text{Et/Me}}$ is formed with a $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2$ coordination mode.^[25] Therefore, it is an effective method to utilize the geometric and electronic manipulation around a metal active center to modulate the extent of back-bonding and dinitrogen activation.

n N₂ ACTIVATION ON METAL COMPLEXES

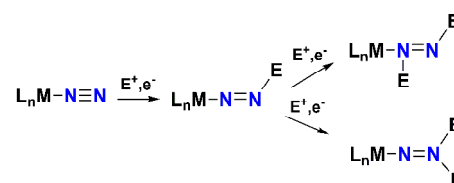
As the first characterized N₂ complex, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ was reported with the discovery of terminal end-on N₂ binding ($\eta^1\text{-N}_2$) in 1965.^[26] In this bound mode, the dinitrogen atoms and metal center are essentially collinear, which turns out to be most commonly observed for N₂. A number of different coordination modes of N₂ have since then be found, including the bridging end-on mode of $\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2$ diruthenium complex in 1968.^[27] The first bridging side-on N₂ complex, $[\text{Sm}(\text{C}_5\text{Me}_5)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)]$, was isolated in 1988, and asymmetric bridging end-on-side-on mode was realized in the dinitrogen complex $[(\text{NPN})\text{Ta}(\mu\text{-H})_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-N}_2)]$, where NPN is $\text{PhP}(\text{CH}_2\text{SiMe}_2\text{NPh})_2$.^[28,29] However, the major drawback of many of these systems was that it was difficult to separate the compounds from reaction products for the catalytic reuse.^[30] In 2003, a groundbreaking homogeneous catalytic ammonia production system was achieved using a well-defined tri(amido)amine Mo(III) complex reported by Schrock and coworkers.^[31] In 2011, the low-valent Mo-phosphine catalyst for ammonia production was reported by Nishibayashi and coworkers.^[32] In 2013, it was reported by Peters and coworkers that a tris(phosphine)borane iron complex was capable of binding and reducing dinitrogen to produce ammonia.^[33]

Significant progresses have been made in developing metal complexes for activating dinitrogen and reducing dinitrogen into ammonia. Based on both historical and recent studies, we summarize hereby various metal complexes that have been explored for dinitrogen activation and categorize these dinitrogen

metal complexes according to their different N₂ binding modes, and discuss the dinitrogen activation and functionalization mechanism accordingly.

We will begin with the terminal end-on mode, as shown in Figure 3(a). In this coordination mode, the distal N atom of the coordinated dinitrogen is nucleophilic and may react with various electrophiles.^[34,35] Typically, the electrophile is firstly added to the distal N atom, and the difunctionalized dinitrogen units can be generated by following a second addition to the same distal N atom or to the coordinated N atom.^[36] The dinitrogen unit in the terminal end-on N₂ complexes can undergo electrophilic functionalization to form ammonia, hydrazine or tris(trimethylsilyl)amine.^[37] A recent remarkable progress by the Peters group shows that low valent, trigonal Co and Fe complexes with terminal end-on N₂,^[21,38] can act as precursors for N₂ functionalization to catalytic nitrogen fixation.^[39,40] Depending on the various metals and its supporting apical ligand, degrees of N₂ activation make a difference based on the N-N stretching vibrational frequency $\nu(\text{N-N})$. The effective ligands for facilitating N₂ activation are continuously been developed, including the cyclic alkyl amino

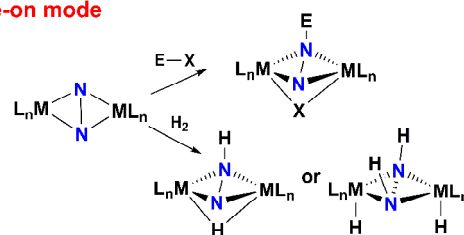
(a) Terminal end-on mode



(b) Bridging end-on mode



(c) Bridging side-on mode



(d) Bridging end-on side-on mode

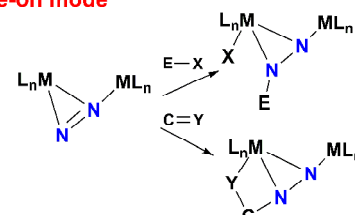


Figure 3. N₂ activation and functionalization mechanism based on different N₂ binding modes. Reproduced with permission from Ref.^[11] Copyright 2017, Nature Publishing Group.

carbene-based ligands^[441] and carbazole-based PNP-type pincer ligands.^[442]

In the bridging end-on mode of dinitrogen (Figure 3(b)), the electron densities of the two bridging N atoms are both reduced through coordination with metal atoms.^[443] However, further reduction to the formed metal nitride species is a productive route for the subsequent reaction,^[444] since the metal nitrides are easily attacked by electrophiles and nucleophiles. As shown in Figure 3(b), it is derived by the addition of electrons and cleavage of N-N bond involving the nitride formation and the bridging end-on mode can cause the formation of higher value organonitrogen derivatives.^[445] For example, bridging end-on N₂ complexes of group-7 metals can generate nitrides, with transformation of a (tBu₂PCH₂CH₂)₂N⁻ pincer-ligated dinitrogen dirhenium(II) complex into two Re(V) nitrides.^[444] The formation of nitrides was found in the group 5 metal dinuclear N₂ complex, [Nb(P₂N₂)₂(μ-N₂) (P₂N₂ = PhP(CH₂SiMe₂NSiMe₂CH₂)₂PPh), which can be considered as two Nb(IV) centers bound with a N₂⁴⁻ hydrazido ligand.^[446] In general, bridging end-on N₂ coordination to low-valent metals with the appropriate ligand design can ultimately give rise to nitrides.

The first bridging side-on N₂ complex is the disamarium species [Sm(C₅Me₅)₂](μ-η²:η²-N₂),^[447] in which N-N bond remains nearly unperturbed from free dinitrogen. Generally, the bridging side-on binding mode is usually found in lanthanides, actinides and early transition metals with the elongated N-N bond distance.^[448,449] Moreover, the side-on binding on alkali metals has been proved to enhance the back-donation by stabilizing the N₂ unit with negative charge.^[50] N₂ hydrogenation and functionalization available to the bridging side-on N₂ coordination are diverse as displayed in Figure 3(c). For example, the hydrogenation of [Zr(P₂N₂)₂](μ-η²:η²-N₂) produces the diazenido complex with a bridging hydrido ligand and an N-H bond.^[51] The corresponding generation of N-C and N-Si bonds undergoes the heterolytic bond cleavage with terminal arylalkynes and silanes, respectively.^[11] With the bridging side-on binding mode, a multimetallic uranium nitride complex is able to convert dinitrogen to ammonia and cyanate.^[52]

The widely studied end-on-side-on N₂ complex, [Ta(NPN)]-(μ-η¹:η²-N₂)(μ-H)₂ (NPN = PhP(CH₂SiMe₂NPh)₂), forms from the tetrahydride [Ta(NPN)]₂(μ-H)₄ and N₂.^[53] In the mode of the end-on-side-on, the geometry and charge distribution of N₂⁴⁻ unit are asymmetric with an activated N-N bond.^[54] The resulting reactivity of functionalization has shown to be extremely rich, especially for the electrophilic attack at the terminal N atom.^[55] The charge localization afforded by end-on-side-on N₂⁴⁻ binding provides different opportunities for bond formation with N atoms. Typically, the terminal N atom exhibits nucleophilic character, giving adducts with Lewis acids or bonding with main-group and C-centered electrophiles according to the mechanism as shown in Figure 3(d).

Furthermore, both theoretical and experimental studies indicated that extra metal centers promote dinitrogen activation.^[56,57] Particularly, low-coordinate complexes^[58] with three Fe atoms showed multi-metallic cooperation makes N-N bond cleavage thermodynamically feasible.^[59] Holland and coworkers developed

a series of multinuclear iron complexes to mimic the nitrogenase,^[60] and revealed that three-active iron(I) centers can engage with dinitrogen in both end-on/side-on/side-on (ESS) and end-on/end-on/side-on (EES) binding modes. The ESS binding mode can easily break the N-N bond without significant structural transformation, while the intermediate with the cleavage N-N bond is not thermodynamically stable. However, the negative charge on the two-coordinate nitride can be stabilized by a positively charged ion.^[61] Multi-metallic uranium-rhodium complex can be also used to initiate the cleavage of dinitrogen in the presence of KC₈.^[62] In the dinitrogen cleavage product, the uranium and rhodium adapted to the +IV and -I oxidation states, respectively. Jori and coworkers reported the cleavage of dinitrogen to nitrides by a uranium-potassium complex, in which the U(IV)/U(VI) tetrauranium cluster generates from successive one-electron transfer, resulting in N₂ cleavage and the formation of putative diuranium(V) bis-nitride. Noteworthy, cooperative potassium binding to the U-bound N₂⁴⁻ ligand facilitates dinitrogen cleavage during electron transfer.^[63] Followed by the “hydride electron reservoir” paradigm, Hou and coworkers suggested that the titanium/ruthenium hetero-multi-metallic hydride complexes can serve as a platform for dinitrogen activation.^[64]

n N₂ ACTIVATION ON METAL CLUSTERS

Metal clusters can be stabilized using peripheral ligands as discussed above. While most experimentally isolated metal clusters involving ligands, gas-phase clusters can provide model systems in understanding the fundamental N₂ activation and conversion mechanism. By using matrix isolation techniques, the bare metal clusters can be formed with the aid of thermal evaporation and laser-ablation technique.^[65,66] However, thermal evaporation is more suitable to study dinitrogen activation, which could avoid the dinitrogen cleavage prior to the interaction with the active centers.^[67]

Through the combination of experimental and theoretical studies, the mechanisms of metal cluster activation and cleavage of dinitrogen were extensively studied.^[68-72] The ligand-free Ti dimer can react with N₂ to give the cyclic bis-nitrido species Ti(μ-N₂)₂Ti without any significant activation barrier in just one step, in which the N≡N triple bond is completely cleaved.^[73] In reactions of N₂ with metal dimers, the interaction with N₂ in the end-on-side-on M₂(μ₂-η²:η¹-N₂) and bridging side-on M₂(μ₂-η²:η²-N₂) binding modes are revealed as two vital intermediates, in which the N≡N triple bond is significantly activated by the diatomic clusters Gd₂^[74] and Sc₂.^[75] The activation mechanism of N₂ on bare clusters M₂ (M = Gd, Sc, ...) provides important insights for understanding the mechanism of how N₂ is activated on low-valent metal clusters and surface and will be discussed in more details later.

Recently, He and coworkers reported a series of studies on dinitrogen activation by gas-phase multi-nuclear metal clusters, such as dinuclear carbide cluster anions Ta₂C₄⁻,^[69] and the trinuclear nitride cluster anions Ta₃N₃H_{0,1}.^[68] Additionally, N₂ binds to three metal atoms in the end-on/side-on/side-on (ESS) mode, and M₃(μ₃-η¹:η²:η²-N₂) is suggested in the feasible N≡N bond cleavage by trinuclear vanadium carbide cluster anions V₃C₄⁻.^[71]

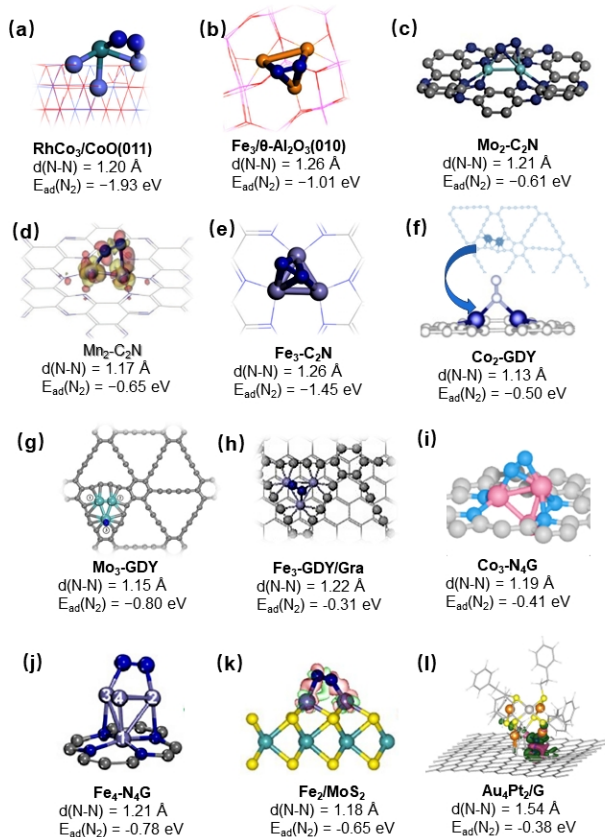


Figure 4. N₂ adsorption configuration on different surface single-cluster catalysts (SCCs) for ammonia synthesis. Reproduced with permission from Ref. [78-91] Copyright 2018, American Chemical Society; Copyright 2018, Nature Publishing Group; Copyright 2015, Elsevier; Copyright 2018, Royal Society of Chemistry; Copyright 2019, WILEY-VCH; Copyright 2020, MDPI; Copyright 2019, America Chemical Society; Copyright 2020, America Chemical Society; Copyright 2020, Royal Society of Chemistry; Copyright 2021, Elsevier; Copyright 2020, Tsinghua University Press; Copyright 2020, America Chemical Society; Copyright 2020, Nature Publishing Group and Copyright 2022, Royal Society of Chemistry.

Dinitrogen binds molecularly to the iron sites of Fe₅S_{2,3}⁻ in a common end-on coordination mode via an unprecedented back-donation interaction from the localized *d-d* bonding orbitals of Fe-Fe sites to the π* antibonding orbitals of N₂.^[76] The outstanding reactivity of heteronuclear metal cluster (FeV₂C₂⁻) toward N₂ benefits from the complementary cooperation of Fe and V atoms in the light of the geometric flexibility of the Fe-V-V ring as well as the electron-withdrawing and electron-donating capacity.^[77]

From dinitrogen activation on heterogeneously surface-supported metal clusters, we recently proposed that the singly dispersed bimetallic M₁A_n catalyst serves as a new surface single-cluster catalyst (SCC) for the biomimetic N₂-to-NH₃ thermal conversion.^[78] It is demonstrated that with isolated Rh₁Co₃ cluster on CoO(011) surface the preferred pathway indeed follows the analogous enzyme-catalyzed associative mechanism, in which a high degree of N₂ activation is embodied in a bridging

manner as shown in Figure 4(a), as well as the co-adsorption of N₂ and H₂ is followed by the alternating hydrogenation. The catalytic ability of M₁A_n catalyst arises from both the electronic effect of doped low-valent metal M that serves as a charge buffer and the complementary role of synergic metal atom A in catalysis. Similarly, the small Fe₃ clusters supported by θ-Al₂O₃(010) surface were found theoretically to undergo efficient N₂ activation as shown in Figure 4(b).^[79] The inert support has little electronic interaction with the Fe₃ cluster, and thus maintains Fe in an even more reduced state for metal-metal bonded Fe clusters.^[80] In this system, N₂ is firstly activated on the Fe₃ active center in an EES manner. The key role of multiple active sites in dinitrogen activation has been summarized in Figure 4(c-l).^[81-91]

Very recently, Luo and coworkers have demonstrated that graphdiyne supported TiCo₃@GDY also exhibits high activities via synergy effect, where the Co₃ cluster acts as the electron donor and the heteroatom serves as the single active site throughout the NRR process.^[92] Chen and coworkers have reported the ternary ruthenium complex hydrides Li₄RuH₆ and Ba₂RuH₆ as an alternative class of catalysts, composed of electron- and hydrogen-rich [RuH₆] anionic centers, for non-dissociative dinitrogen reduction.^[93,94] Dai and coworkers have designed an SCC of the Fe₄ cluster anchored to 2D GaS with the remarkable NRR performance, in which N₂ is completely activated in a side-on adsorption configuration. Therefore, multi-metallic clusters, which can be capable of performing collaborative reduction of the dinitrogen, provide an alternative strategy for the cleavage and transformations of dinitrogen, as well as pave the way for its future application in catalytic processes.^[95,96]

n THE SYNERGISTIC MECHANISM OF N₂ ACTIVATION

As the simplest and effective model for multi-nuclear active sites, dinuclear metal system could provide insights into the synergistic mechanism of electron rearrangements in dinitrogen activation. The strong interaction between the active centers and dinitrogen mainly results from the π back-donation from the metal centers to N₂. The triple bond of dinitrogen is weakened to a certain extent, in which electron density relocates from the metal-metal π

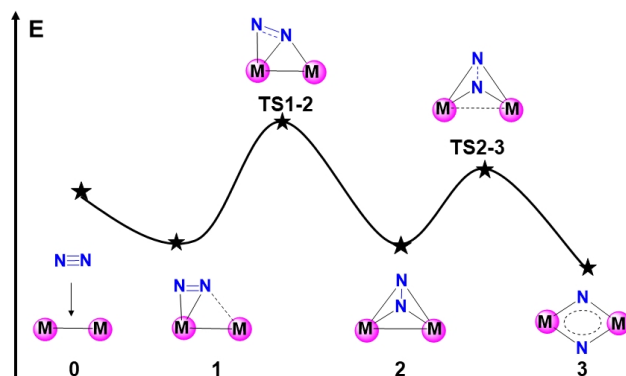


Figure 5. The synergistic mechanism of N₂ activation on the M₂-type site following the reduction of N-N bond-order from 3 to 0. Reproduced with permission from Ref. [74] Copyright 2007, WILEY-VCH.

bonding to the vacant antibonding orbitals of dinitrogen, and relatively weak donation of electron density from π bonds in dinitrogen to the vacant metal-metal empty orbitals could occur. From the view of geometric transformation, the approaching dinitrogen usually lies in the same plane as dinuclear metals, and end-on-side-on N_2 bonded manner **1** is favorable in the following dinitrogen activation as shown in Figure 5, which could be identified in structurally properly characterized systems.^[74,75] Along with the N-N bond distance elongated, the preferred isomer **2** with a nonplanar bridged-bonded C_{2v} symmetry could be rearranged from **1**. The end-on-side-on N_2 bonded model transfers to a double side-on ($\mu-\eta^2:\eta^2-N_2$) "butterfly" geometry. Finally, a planar cyclic $[M(\mu-N)_2M]$ isomer **3** with a completely cleaved N-N bond is trapped in the deep potential, exhibiting a slightly distorted planar square with D_{2h} symmetry. The process is accompanied by both partial donation of bonding electrons from N_2 to metal centers and π -back-donation from the metal centers to the antibonding π^* and σ^* orbitals of N_2 . It is suggested that interplay of occupied and empty d-orbitals at metal center dictates the reactivity of the dinuclear metal system with dinitrogen.^[74,75]

n CONCLUSIONS AND PERSPECTIVES

In this minireview, we have summarized the recent progresses of dinitrogen activation on metal complexes and clusters, including the species with peripheral ligands, bare metal clusters and surface single-cluster catalysts. As enzymatic active sites in nitrogenase rely upon all metal centers and the surrounding residues to work, the key design principles of redox versatility and cooperative dinitrogen activation by multiple proximal metal centers may be maintained in the metal complexes or clusters. In addition, dinitrogen coordination mode, metal oxidation state, coordination number, and peripheral ligands greatly influence the activation of dinitrogen.

Especially noteworthy is that the electronic coupling of the metal centers might trigger more accessible redox states than those of the individual component metals,^[97] and the rich redox character of a metal-metal bonded species might take part in cooperative interactions with dinitrogen. When metal remains in low oxidation state, the metal d -orbital energies are raised and the active site is more effective in reduction reaction. Therefore, it appears that the use of low-valent and multi-metallic systems, which are capable of performing cooperative activation of the dinitrogen, may provide a significant strategy for activating inert molecules like dinitrogen. In metal complexes and metal clusters, the steric factors provide the necessary quantum confinement effect, while the active sites offer selective redox ability for dinitrogen activation and subsequent conversion. Combination of robust support and highly active metal single-atom or single-clusters (including p -, d -, and even f -block metal clusters) may provide highly selective and effective catalysts for atomically precise heterogeneous catalysis.^[97,98]

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n COMPETING INTERESTS

The authors declare no competing interests.

n ADDITIONAL INFORMATION

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