Direct transformation of dinitrogen: synthesis of N-containing organic compounds via N–C bond formation
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ABSTRACT
N-containing organic compounds are of vital importance to lives. Practical synthesis of valuable N-containing organic compounds directly from dinitrogen (N₂), not through ammonia (NH₃), is a holy-grail in chemistry and chemical industry. An essential step for this transformation is the functionalization of the activated N₂ units/ligands to generate N–C bonds. Pioneering works of transition metal-mediated direct conversion of N₂ into organic compounds via N–C bond formation at metal-dinitrogen [N₂-M] complexes have generated diversified coordination modes and laid the foundation of understanding for the N–C bond formation mechanism. This review summarizes those major achievements and is organized by the coordination modes of the [N₂-M] complexes (end-on, side-on, end-on-side-on, etc.) that are involved in the N–C bond formation steps, and each part is arranged in terms of reaction types (N-alkylation, N-acylation, cycloaddition, insertion, etc.) between [N₂-M] complexes and carbon-based substrates. Additionally, earlier works on one-pot synthesis of organic compounds from N₂ via ill-defined intermediates are also briefed. Although almost all of the syntheses of N-containing organic compounds via direct transformation of N₂ so far in the literature are realized in homogeneous stoichiometric thermochemical reaction systems and are discussed here in detail, the sporadically reported syntheses involving photochemical, electrochemical, heterogeneous thermo-catalytic reactions, if any, are also mentioned. This review aims to provide readers with an in-depth understanding of the state-of-the-art and perspectives of future research particularly in direct catalytic and efficient conversion of N₂ into N-containing organic compounds under mild conditions, and to stimulate more research efforts to tackle this long-standing and grand scientific challenge.

Keywords: dinitrogen transformation, metal-dinitrogen complex, N–C bond formation, N-containing organic compounds

INTRODUCTION

As the most abundant constituent in Earth’s atmosphere (atm), dinitrogen (N₂) is the main nitrogen source of N-containing compounds on the Earth. Therefore, N₂ fixation and activation are essential both for nature and humans. Nevertheless, the high bond dissociation energy (942 kJ/mol) and large highest occupied molecular orbital (HOMO)—lowest unoccupied molecular orbital (LUMO) gap (10.82 eV) make N₂ exhibit extremely low reactivity and be regarded as an inert gas. Currently, the N₂ fixation and conversion in nature and industry mainly rely on two pathways, in which ammonia (NH₃) is the product [1]. In nature, nitrogenase metalloenzymes employ iron-sulfur clusters as the key cofactor (FeMo, FeV or FeFe cofactor) and water as the proton source to transfer N₂ into NH₃ at ambient temperature and pressure [2]. This biosynthetic NH₃ is a versatile precursor for the synthesis of N-containing organic compounds, such as amino acids and nucleic acids. Although the precise biological N₂ reduction mechanism is still controversial, spectroscopic and computational studies suggested the presence of an interstitial carbon atom at the center of the FeMo and FeV cofactors [3–5].
In industry, more than 170 million metric tons of NH3 is produced from the Haber-Bosch process annually, in which N2 reacts with dihydrogen (H2) under the harsh condition in the presence of iron or ruthenium catalysts. This NH3 synthesis process consumes 1–2% of the world’s annual energy supply along with the huge CO2 emission, due to the drastic reaction condition and the energy requirement for H2 production from fossil fuels and water [6]. As the main route of N2 fixation and transformation in industry, ~20% of NH3 produced from the Haber-Bosch process is used as the feedstock to produce N-containing chemicals, including higher-value N-containing organic compounds, like amines, nitriles, nitro and so on. To better understand the reaction mechanism of biological and industrial reduction of N2 into NH3, several catalytic systems including homogeneous molecular systems, electrochemical systems and heterogeneous systems have been studied for decades, and there are comprehensive reviews that readers may refer to [7–13].

Compared to NH3-based N2 fixation process, an alternative route of N2 fixation is the direct conversion of N2 into N-containing organic compounds under mild condition. This approach is always targeted because it provides the potential solution to developing a sustainable system with reduced fossil fuel requirements. The earliest study towards this goal began in the 1960s, when Vol’pin et al. discovered that the titanium species, for example, Cp2TiCl2 could react with PhLi under N2 to give aniline after hydrolysis [14]. However, further application of this reaction was hindered by the low yields and the lack of reaction details. During the same period, the first metal-dinitrogen (N2-M) complex [Ru(NH3)5(N2)]2+ was reported in 1965 [15]. After that, thousands of N2-M complexes have been documented [16]. The reactivity exploration reveals that the functionalization of the N2 ligands can also be fulfilled for some N2-M complexes [17]. Making N–C bonds from the reactions of transition metal N2 complexes with carbon-based reagents has received much attention in recent decades, although the catalysis system has not been realized [18,19].

This review will focus on the previous works regarding the transformation of N2 into organic compounds. In almost all of these works, the N–C bond formation steps are fulfilled upon the well-defined N2-M complexes with diversified coordination modes. This review is organized by the coordination modes of the N2-M complexes (to clarify, the N2-derived metal nitrides are also considered as a coordination mode of N2-M complexes) that are involved in the N–C bond formation steps, and each part is arranged in terms of the type of reactions between N2-M complexes and carbon-based substrates. The earlier works about one-pot synthesis of organic compounds from N2 via ill-defined intermediates are also introduced briefly in this review (Fig. 1).

**N–C BOND FORMATION VIA END-ON N2-M COMPLEXES**

End-on bond is the most prevalent bonding mode for N2-M complexes and the N2-M complexes with this binding mode have been known to assemble N–C bond for a long time. Main works were achieved via the reaction of end-on terminal N2-M complexes with alkyl or acyl halides and their analogues. N–C bond formations from the cycloaddition and insertion reactions of end-on-bridged N2-M complexes with imido-like N2 ligands have also been reported.
The strong electrophilic alkyl triflates and their analogues are often employed to functionalize the end-on N₂-M complexes because the N₂ ligands in these complexes feature a nucleophilic character by electron donation from the electron-rich metal centers. Peters et al. [20] and Greco and Schrock [21] reported that the methylation reaction occurs when the anionic end-on N₂-Mo complexes 1 and 3 are treated with methyl tosylate (MeOTs) to provide methyldiazenido complexes 2 and 4 (Scheme 1a and b). Additionally, 4 could further undergo N−C bond formation to furnish N,N-dimethylhydrazido complexes 5 by reaction with excess methyl triflate (MeOTf) or MeOTs (Scheme 1b).

Although many late-transition metal complexes with end-on N₂ ligands have been documented, reports on their reactivity toward electrophiles to make N−C bond are very rare. Peters et al. described that the anionic end-on terminal N₂-Mo complexes of Fe 6 and Co 8 react with MeOTs to give N-methylation species 7 and 9 (Scheme 2a) [22]. In 2016, the same group found that the modified N₂-Fe complex 10 bearing monoanionic tetradentate trisphosphinosilyl ligand can also be alkylated to afford N,N-dimethylated product 11 (Scheme 2b) [23].

There are only a few examples of N−C bond formation at N₂-M complexes by radicals. One example is the reactions of terminal end-on N₂-Mo, W complexes 12 with alkyl halides, driven by light (vide infra). Mechanism investigation reveals that the radicals in these reactions are generated in situ by the homolysis of the alkyl halides within the coordination sphere. The attacking of these alkyl radicals at the N₂ ligands provides 13. Furthermore, dialkylhydrazido complexes 14, 15 and 16 can also be obtained via alkylation of 13 or one-pot di-alkylation of 12 (Scheme 3a) [24,25]. It is noteworthy that if the diphosphine ligands in 12 are replaced by the monophosphine ligands, the corresponding N₂-Mo, W complexes fail to react with alkyl halides to assemble N−C bond. Another example that involves the radical mechanism is the N-functionalization of the terminal end-on N₂-Mo complex 17, which possesses higher reactivity than 12 (Scheme 3b) [26]. For instance, the treatment of 17 with BnBr or aryl iodide gives the N,N-dibenzylation product 18 or N-arylation complex 19, the latter of which can also be converted to the organo-hydrazido species 20 by further reaction with MeI. More intriguingly, when 17 is treated with MeI in toluene, the prospective product 21 is formed together with isolation of an unexpected product 22. A plausible mechanism is raised for the generation of 22 (Scheme 3c). The initial reaction between 17 and MeI results in iodine atom abstracting to afford intermediate A and the methyl radical, which would abstract an H-atom from toluene to yield benzyl radical. The latter reaction between A and benzyl radical gives the N-benzylhydrazido intermediate B, which can further react with MeI to afford the final product. The formation of 22 confirms...
Scheme 3. $N$-alkylation of end-on terminal $N_2$-$M$, $N_2$-$W$ complexes by in situ formed radicals. (a) $N$-alkylation of $N_2$-$M$, $W$ complexes supported by diphosphine ligands. (b) $N$-alkylation of $N_2$-$M$ complex supported by tetra-thioether ligand. (c) A plausible mechanism for the generation of 22.

the radical process of these $N$-alkylation reactions again.

$N$-alkylation by nucleophiles
For end-on terminal $N_2$-$M$ complexes, simple Lewis formulas could be used to depict their structures. As shown in Scheme 4a, the $N$ atom adjacent to the metal atom ($N_\alpha$) features positive charge and could be attacked by nucleophiles in theory. Surprisingly, there is only one example of this reactivity for $N_2$-$M$ complexes [27,28]. Sellman et al. found that an end-on terminal $N_2$-$Mn$ complex 23 reacts with methyl or phenyl lithium reagent at low temperature to give the $N_\alpha$-functionalized products 24, which could subsequently react with Meerwein reagent $Me_3OBF_4$ upon $N_\beta$ atom to afford 25. This azomethane complex would ultimately liberate free azomethane by pressuring with 100 bar of $N_2$ along with reforming $N_2$-$Mn$ complex 23. Thus, a synthetic cycle was raised for synthesis of azo-compound from $N_2$.

$N$-acylation
Besides alkyl halides, acyl chlorides are also used to functionalize end-on $N_2$-$M$ complexes. Chatt et al. found that the $N_2$-$M$, $W$ complexes supported by bidentate phosphines ligands react with acyl chloride to afford acyldiazenido complexes (Scheme 5) [29,30]. These $N$-acylation reactions possibly proceed through nucleophilic attacking of the $N_2$ ligands on the acyl carbons.

Cycloaddition and insertion
For some end-on-bridged $N_2$-$M$ complexes with strongly activated $N_2$ ligands, the imido-like structures make them able to undergo cycloaddition or insertion reactions with carbon-based
unsaturated substrates to assemble N–C bond.

In 2017, the reaction of an end-on bridging binuclear N2-Ti complex 27 with phenyllallene, tert-butyl isocyanate (tBuNCO) and CO2 was investigated by Kawaguchi et al., to provide N–C bond formation products (Scheme 6) [31]. Treatment of 27 with an excess of phenyllallene results in the formation of dititanium hydrazido complexes 28 and 29 as a mixture of isomers. The formation of 28 and 29 can be rationalized in terms of an initial [2+2] cycloaddition of phenyllallene with Ti=N bond in 27 to give the 4-membered titanacycle intermediates (two isomers), and the subsequent protonolysis of the Ti–C bonds in these intermediates to give the final products. Further studies indicate that the proton source in this reaction could be a second equivalent of phenyllallene, the ancillary ligands, or even adventitious impurities present in the reaction mixture. The reaction of 27 with tBuNCO also proceeds through a formal [2+2] cycloaddition reaction to afford 30. However, when 27 is introduced with an atm of CO2, the insertion of three molecules of CO2 into Ti = N bonds in 27 is achieved to furnish 31. By adding an excess amount of TMSCl, 31 could be converted to organic compound N3(TMS)(CO2TMS)3, which is unstable under the reaction condition and decomposes to two hydrazine derivatives [TMS(CO2TMS)N]2 and (TMS)3NN(CO2TMS)2 via decarboxylation.

The cycloaddition reactions between group 5 end-on N2-M complexes and carbon-based unsaturated bonds have also been observed. For example, N2-Nb complex 32 and N2-Ta complex 33 with diimido bridging N2 ligands are known to react with aldehyde and acetone to afford the corresponding ketazines (Scheme 7) [32,33].

**Scheme 6.** N–C bond formation from cycloaddition of end-on-bridged N2-Ti complex with phenyllallene, tBuNCO and CO2.

**Scheme 7.** N–C bond formation from the reactions of end-on-bridged N2-Nb, Ta complexes with aldehyde or acetone. (a) The reaction of N2-Nb complex with benzaldehyde. (b) The reaction of N2-Ta complex with acetone.

**N-protonation/carbonylation**

An alternative route for making N–C bond is the treatment of carbon-based substrates with the N-hydrogenated complexes derived from N2 because in some cases N-hydrogenation are more accessible than N-alkylation for end-on N2-M complexes. Seminal works about these transformations were finished by Hidai and others [25,34]. They reported that the N2-Mo, W complexes 34 and 12 supported by monophosphone or diphosphine ligand react with HX (X = Cl, Br and I) or HBF4 to afford the hydrazido complexes 35 and 36, which can act as the versatile precursors to construct N–C bond [25,35] (Scheme 8a). For instance, 35 could react with diphenylketene and phthalaldehyde to provide 37 and 38, while the reaction between 36 and succinyl chloride gives rise to 39. More intriguingly, these hydrazido complexes 35 and 36 are also reported to undergo a condensation reaction with ketones and aldehydes in the presence of catalytic amounts of acid to afford all kinds of diazoalkane.
N−C bond formation from the reactions of hydrazido Mo, W complexes with carbon-based reagents. (a) The reaction of N2-Mo, W complexes with HX (X = Cl, Br and I) or HBF4 to afford the hydrazido complexes. (b) Carboxylation of hydrazido complexes 35 and 36 to assemble N−C bond. (c) A synthetic cycle for synthesis of 1H-pyrrole from N2. The liberation of the N-containing organic compounds from these N-functionalized complexes has also been explored [36]. For example, when the cyclic hydrazido complex 42, produced from the reaction of 36 and the cyclic acetal of succinaldehyde, is treated with LiAlH4, the reductive destruction of 42 is observed to release 1H-pyrrole accompanied by the generation of the tetrahydride complex 43. Furthermore, this tetrahydride tungsten complex could be converted to the initial N2-W complex 12 under photolytic conditions to achieve a cycle (Scheme 8c) [37].

Involvement of photochemistry

Photochemistry is an emerging approach for the transfer of N2. The earliest observation of photocatalyzed N−C bond formation of N2-M complexes is of the reactions between end-on terminal N2-M complexes 12 and alkyl halides (Scheme 3a) [25]. In the case of N2-W complex, visible light or a tungsten-lamp is often necessary for these N-alkylation reactions. However, for the N2-Mo complex, it could react with alkyl bromide slowly in the dark. It is also reported that the N2 ligands in 12 are not evolved in the absence of the alkyl halides since irradiation of the N2-M complexes without organic halide caused no change. These results indicate the possibility of photo engaging in the assistance of alkyl radicals formation in these reactions [24].

Involvement of electrochemistry

Besides photochemistry, electrochemistry is another versatile method in the N2 conversion process. Although the direct involvement of electrochemistry in the N−C bond formation step has not been discovered, the electrochemical reduction of the N-alkylated complexes to release the final organic products has been developed. For example, the organohydrazido complexes 16, which is synthesized from the reaction of N2-M complexes 12 with 1,5-dibromopentane, undergoes electrochemical reduction at a Pt electrode in tetrahydrofuran (THF) under N2 by using [NBu4][BF4] as the electrolyte to liberate piperidine accompanied by the regeneration of N2-M complexes 12. According to the control experiment under the atmosphere of Ar or CO, a M(II) hydrazido intermediate is proposed in this piperidine releasing process. Based on these results, an electrochemical cycle to synthesize dialkylhydrazine from N2 was reported by Leigh et al. (Scheme 9) [38].

N−C bond formation via side-on N2-M complexes

The side-on bonding modes are often observed at group 3 and group 4 transition metal N2-M complexes. The N2 ligands in these side-on N2-M
complexes can be divided into neutral \( N_2 \), \( (N_2)^2^- \), \( (N_2)^3^- \) and \( (N_2)^4^- \), and the N–C bond formation usually takes place at side-on-bridged binuclear \( N_2 \)-M complexes with \( (N_2)^4^- \) moiety. Very recently, the N-functionalization of a \( (N_2)^3^- \)-Sc complex was also fulfilled.

**\( N \)-alkylation**

There are two reports about the reaction of group 4 side-on \( N_2 \)-M complexes with alkyl halides or their analogues to make N–C bond. One example was reported by Hirotsu et al. in 2007, in which the side-on-bridged \( N_2 \)-Hf complexes \( 44 \) with extremely activated \( (N_2)^4^- \) ligands can react with ethyl bromide (EtBr) to provide the N-ethylated products \( 45 \) (Scheme 10a) [39]. Controlled experiments indicate that this reaction is remarkably sensitive to the steric effects of the ancillary ligands. For example, when the R’ group in \( 44b \) is changed from Et to \( iPr \), the corresponding N-ethylation product could not be obtained. Besides, \( 45a \) and \( 45b \) fail to undergo further N-ethylation, even in the presence of excess EtBr. The other work is reported by the reaction of methyl triflate (MeOTf) with a hafnocene complex \( 46 \) that also bears side-on-bridging \( (N_2)^4^- \) ligand (Scheme 10b) [40]. This reaction offers a mixture of products and one of them is the \( N_2 \) ligand monomethylated product \( 47 \), which could be converted to the final organic compound \( N \)-methylhydrazine by treating with excess HCl. Besides, an unprecedented triflate hafnocene hydrazonato complex \( 48 \) is generated via a second N–C bond formation when additional MeOTf is added to \( 47 \).

Compared with the group 4 transition metals, rare-earth metal promoted direct conversion of \( N_2 \) into organic compounds attracts less attention. The only example of this topic was reported by Xi, Zhang et al. in 2019 (Scheme 11) [41]. Treatment of the \( (N_2)^3^- \)-bridged discandium complex \( 49 \) with MeOTf leads to the formation of \( N,N' \)-dimethylation discandium complex \( 50 \) in 43% yield. The yield of \( 50 \) can be improved via the treatment of \( 49 \) with MeOTf and potassium several times. Transformation of the \( (N_2Me_2)^2^- \) ligand into organic compounds could be accomplished by treatment of \( 50 \) with \( I_2 \), HCl, BnBr and acyl chloride to afford azomethane, 1,2-dimethylhydrazine and a series of tetra-substituted hydrazine derivatives, concomitant with the regeneration of the precursors of the \( N_2 \)-Sc complexes. Hence, a three-step synthetic cycle for scandium-mediated direct conversion of \( N_2 \) and carbon-based electrophiles to multi-substituted hydrazine derivatives could be realized. The insertion of a CO molecule into the Sc–N bond of \( 50 \) with further N–C bond formation is also observed to provide \( 51 \).

**Cycloaddition and insertion**

The group 4 side-on bridging \( N_2 \)-M complexes are known to undergo cycloaddition and insertion reactions with carbon-based reagents that contain \( C = X (X = N, O) \) bonds or \( C≡C \) bond, such as carbon dioxide (\( CO_2 \)), isocyanates (RNCO) or alkynes, owing to their imido-like reactivity. Compared with \( N \)-alkylation and acylation reactions, these cycloaddition and insertion reactions are more atom-efficient for \( N_2 \) functionalization,
because the formation of transition metal halides and inorganic salts as the by-products is avoided in these reactions. The earliest study of the cycloaddition reactions between group 4N2-M complexes and unsaturated bond to assemble N–C bond was finished by Fryzuk et al. via the reaction of side-on bridging N2-Zr complex 53 with arylacetylene (RC≡CH; R = Ph, 4-Me-C6H4 and 4-tBu-C6H4) (Scheme 12) [42]. The N-functionalization products 54 may result from a sequence of two successive steps: cycloaddition of alkyne across a Zr-N bond in 53 leading to the zircona-aza-cyclobutene intermediate D, which subsequently encounters Zr-C bond cleavage by protonation with another molecular terminal alkyne to yield 54. By elegant modulation of the substitutions on the multi-substituted Cp ligands, Chirik et al. accomplished a series of reactions of dinuclear N2-Zr, Hf complexes with isocyanates or CO2 to assemble N–C bond. N2-Hf complex 46 bearing tetramethylcyclopentadienyl (Cp4Me) ligands is reported to react with PhNCO to provide the initial product 56 via a possible intermediate 55. In the solution, 56 also reacts quickly with another molecule of ArNCO (Ar = Ph and p-MeC6H4) to afford 57, which could also be prepared directly from 46 (Scheme 13a) [43]. Besides, further studies indicate that another N-functionalization product 58, in which the same nitrogen atom is di-carboxylated, would be formed predominately when CO2 is bubbled into a solution of 46 (Scheme 13b) [44]. Subsequent reaction of 58 with TMSI gives rise to the generation of 59, which is known to liberate the corresponding hydrazine derivative (TMS)2NN(CO2TMS)2 by further reacting with excess TMSI. Unfortunately, the similar N-functionalization reactions of PhNCO and CO2 with zirconium congeners of 46 are unsuccessful, which is believed to be caused by the deleterious ligand-induced side-on, end-on isomerization of the (N2)4⁻ ligand. Hence, a [Me2Si]-bridged ansa-zirconocene N2 complex 60 with higher energy barrier for the side-on, end-on isomerization was designed and prepared to investigate the reactivity toward CO2 [45]. The treatment of 60 with CO2 leads to the immediate generation of 61, where N2-functionalization takes place at each N-atom. Organic compound N,N'-dicarboxylated hydrazine can be released from 61 by reacting with TMSI. Furthermore, a second N–C bond formation occurs when 61 is treated with MeOTf to provide 62, which is known to liberate region-specific hydrazine.

**Scheme 12.** N–C bond formation of side-on N2-Zr complex by reaction with alkyynes.

**Scheme 13.** N–C bond formation from the reactions of the side-on N2-Zr, Hf complexes with isocyanates and CO2. (a) The reaction of N2-Hf complex with PhNCO. (b) The reaction of N2-Hf complex with CO2. (c) The reaction of N2-Zr complex with CO2.
CO-induced $N_2$ scission and functionalization at side-on $N_2$-Zr and Hf complexes. (a) The reaction of $N_2$-Zr, Hf complexes and CO. (b) A plausible mechanism for this CO-induced $N_2$ scission and functionalization reaction.

X(COOMe)NN(COOMe)Me ($X = H, \text{TMS}$) by further reacting with $H_2O$ or TMSI (Scheme 13c). These results indicate that small modifications of the ligands will change the reactivity of the $N_2$-M complexes dramatically.

**CO-induced $N_2$ functionalization and cleavage**

Being isoelectronic with $N_2$, CO is an abundant and cheap diatomic molecule with BDE of 1 079 kJ/mol. Hence, the transformation of CO and $N_2$ into N–C bond is a challenge but a significant process. Until now, only two systems of CO-induced $N_2$ ligand scission and functionalization at $N_2$-M complexes have been developed, in which all of the $N_2$ ligands adopt side-on bridging coordination mode.

Following their earlier work on N–C bond formation from $N_2$-Zr and Hf complexes, Chirik et al. reported in 2010 the first example that treatment of the ansa-zirconocene and hafnocene $N_2$ complexes 60 and 63 with 4 atm or 1 atm of CO leads to the generation of the dinuclear oxamide complex 64 and 65 as two isomers [46,47]. Besides, when 63 is treated with less CO (1.5 equiv), a new product of imido-bridged dihafnium complex 66 could be isolated, in which the H-atom on the bridging imido is derived from the cyclometallation of the ‘Bu group (Scheme 14a). Protonolysis enables these products to release the corresponding N-containing organic compounds of free oxamide and isocyanic acid.

Density functional theory (DFT) calculations [48] and experimental results [49] reveal that the formation of 64 and 65 is assumed to be initiated by CO insertion into an Hf–N bond and followed by the retro [2+2] cycloaddition to provide the presumptive $\mu$-nitride species 67. The coordination and insertion of CO to the $\mu$-nitrido intermediate 67 results in the formation of 68, which was characterized by multinuclear nuclear magnetic resonance (NMR) spectroscopy at low temperature. 68 undergoes C–C bond formation via coupling of the terminal and bridging isocyanate units along with the loss of the terminal carbonyl ligand to give the final products (Scheme 14b).

More studies indicate that these CO-induced $N_2$ cleavage and functionalization reactions are also compatible with other zirconocene and hafnocene $N_2$ complexes. Therefore, a tetrametallic hafnocene oxamide complex 71 could be obtained via a dimeric hafnium intermediate 70 when the $N_2$-Hf complex 69 is treated with CO [50]. The transformations of these oxamidide complexes were also elaborated. Thermolysis of 71 at 110°C provides a $\mu$-oxo hafnocene complex 72 with both terminal cyanide and isocyanate ligands that undergoes preferential group transfer of the cyanide unit to liberate organonitriles of TMSCN or MeCN along with the generation of 73 by reacting with TMSI or MeOTf (Scheme 15a) [50]. Oxamidide complex 64 reacts with CO$_2$ and tBuNCO to give the formal [2+2] cycloaddition products 74 and 75 [51] (Scheme 15b). Additionally, various free $N,N'$-dialkyloxamide could be formed via stepwise $N$-alkylation of the oxamidide complex 76 and following protonolysis with HCl or ethanol (Scheme 15c).

The characterization and reactivity studies of the $\mu$-nitride intermediates were also developed (Scheme 16). Rapid bubbling of CO into $N_2$-Hf complex 69 at a low temperature produces a metastable dihafnecene nitride complex 79, which is characterized by IR and multinuclear NMR spectroscopy. This base-free $\mu$-nitride can react with various substrates [52–55]. For instance, the treatment of 79 with TMSI affords silylureate complex 80. This reaction is involved in the initial iodide ion abstraction to give a transient silyl cation and a formally anionic bridging nitride intermediate, whose nucleophilicity is increased by weakening the Hf–N multiple bonding. Hence, this intermediate could undergo nucleophilic attacking of the nitride group to the terminal isocyanate moiety to form the ureate core, which is then trapped by the silyl cation to yield 80. Besides, when 79 is treated with cyclooctyne, monosubstituted allenes and isocyanates, the formal [2+2] cycloaddition reactions occur to
Scheme 15. N−C bond formation of CO- and N$_2$-derived oxamide complexes. (a) Thermolysis of oxamide complex 71. (b) The reaction of oxamide complex 64 with CO$_2$ and tBuNCO. (c) N-alkylation of the oxamide complex 76 to afford $N,N'$-dialkyloxamides.

afford 81, 84 and 85, respectively. The alkyne and isocyanates products are kinetically unstable at elevated temperature and engage in additional N−C bond formations to give 82 and 86. Complex 82 could be converted to a binuclear complex 83 with two bridging carbodiimyl ligands by reacting with TMSCl. The μ-oxo complex 86 can liberate N-containing organic compound of carbodiimide along with the generation of dihafnium oxo complex 73 by reacting with MeOTf. In contrast, exposure of the nitride complex 79 to another heterocumulene of CO$_2$ provides μ-oxo bis(isocyanate) complex 87, resulting from deoxygenation of CO$_2$ accompanied by N−C bond formation. Furthermore, the Hf−nitride bond in 79 also engages in the insertion of cyclohexynitrile (CyCN) to provide 88, which can continue reacting with another molecule of CyCN to afford bridging ureate-type complex 89 via additional N−C bond formation (Scheme 16).

The other system of CO-induced N$_2$ scission and functionalization was discovered by Mazzanti et al. using uranium complexes. A side-on-bridged binuclear N$_2$-U complex 90 with μ-nitride ligands reacts with CO to provide the oxo/cyanated diuranium complex 91 accompanied by releasing of potassium cyanate (KCN), which is formed from the reaction of nitride unit with CO [56] (Scheme 17a). To understand the role of the bridging nitride in these transformations, a similar N$_2$-U complex 92 with bridged μ-oxo ligand was synthesized and its reactivity toward CO was also investigated [57]. The reaction between 92 and CO immediately results in the generation of cyanamido bridged complex 93 with retaining the μ-oxo moiety via both cleavages of N−N single bond and C≡O triple bond (Scheme 17b). DFT calculation indicates that the different reactivity of 90 and 92 is attributed to the different bonding nature of the N$_2$ ligands, in which the μ-nitride is involved in the binding and resultant activation of N$_2$, but the μ-oxo is not.

Scheme 16. N−C bond formation of CO- and N$_2$-derived Hf-nitride complexes.
Scheme 17. CO-induced N₂ scission and functionalization at side-on N₂-U complexes. (a) The reaction between CO and N₂-U complex 90 with μ-nitrido ligand. (b) The reaction between CO and N₂-U complex 92 with μ-oxo ligand.

Scheme 18. N-alkylation of side-on-end-on N₂-Ta complex by BnBr.

N—C BOND FORMATION VIA SIDE-ON-END-ON N₂-M COMPLEXES

The side-on-end-on bound mode is much less common relative to the aforementioned two coordination modes in N₂-M complexes. All of the work regarding the making of N—C bond from N₂-M complex with this bonding mode were finished by Fryzuk et al. by employing a binuclear N₂-Ta complex.

N-alkylation

In 2001, the N-alkylation of the side-on-end-on bridging binuclear N₁-Ta complex 94 was developed to afford N-benzylation product 95 in high yield by reaction with benzyl bromide (BnBr) (Scheme 18) [58]. This reaction was similar to the N-alkylation reaction of the side-on N₂-Zr complexes 44 (Scheme 10a).

Cycloaddition and insertion

Besides, this side-on-end-on N₂-Ta complex 94 was also reported to undergo [2+2] cycloaddition reaction by treating with heteroatom 1,2-cumulenes (Scheme 19a) [59]. For example, the reaction between 94 and N,N' diphenyl carbodiimide results in the formation of 96. However, when carbon disulfite or isothiocyanates are added, the N-functionalization product 97 is generated concomitant with the N—N bond scission. In the case of tert-butyl isothiocyanate (tBuNCS), the generated intermediate 98 would further undergo N—Si bond formation at elevated temperature to give 99. As depicted in Scheme 19b, the formation of 97 and 98 can be rationalized by the following mechanism. The initial [2+2] cycloaddition reactions between 94 and the C=S bond of the substrates give intermediate E, followed by reductive elimination of H₂ to provide a transient intermediate F that contains a Ta—Ta bond. The Ta—Ta bond in F would trigger the N—N bond cleavage to afford the final products.

N—C BOND FORMATION VIA METAL NITRIDES

The complete reduction of N₂-M complexes might cleave the N—N bond of the N₂ ligands to give metal nitrides. In the most terminal metal nitrides, the strong metal—nitrogen bonds result in these nitrides often exhibiting weak nucleophilicity and just reacting with high-energy species such as alkyl triflates and acyl chlorides to assemble N—C bond. However, some bridging nitrides derived from N₂ can also react with other carbon-based substrates, like MeI and CO, to form N—C bond.
In 2007, Kawaguchi et al. reported the reaction between MeI and bis(μ-nitrido) dinobiium complex 101, which is prepared from the tetra(μ-hydride) dinobiium precursor 100 (Scheme 20) [60]. Stepwise methylation of 101 by MeI yields mono-imido 102 and bi-imido 103, the latter of which could also react with excess pyridine to give terminal imido 104, which reacts with CO$_2$ to generate 105 and 106 through further N−C bond formation. A plausible mechanism for this process was raised by the authors. A [2+2] cycloaddition of 104 with CO$_2$ followed by extrusion of methyl isocyanate (MeNCO) results in the formation of a terminal oxo species that dimerizes to give 106. Meanwhile, the generated MeNCO would also undergo [2+2] cycloaddition with another molecule of 104 to form 105 [61].

Cummins et al. found that the terminal molybdenum nitride 108 synthesized from the three coordination Mo(III) complex 107, undergoes N-alkylation by reacting with MeI to provide 109 (Scheme 21) [62].

Another example of making N−C bond from metal nitrides was fulfilled by Schneider et al. in 2016. The reactions between ROTf (R = Me, Et and Bn) and a terminal rhenium nitride 111, which is prepared from the reduction of the dichloride precursor 110 with sodium amalgam or CoCp$^*$, give the N-alkylation complexes 112 (Scheme 22) [63–65]. Further studies suggest that the nitriles (RCN) can be liberated by deprotonation and oxidation of 112 via the ketimido intermediates 113, accompanied by the generation of trichloride complex 114, which could also be reduced by sodium amalgam to afford the starting material 111. According to these results, a full synthetic cycle for synthesis of nitriles from N$_2$ with moderate isolated yields was established (Scheme 22).

Because the group 8–10 N$_2$-derived nitrides are rare, the N-functionalization of these nitrides is hardly observed. One exception was reported by Holland et al., who employed an unprecedented trinuclear iron nitride 116 to achieve this transformation. This nitride complex 116, obtained from the reduction of the chloride precursor 115 with precisely equivalent KC$_8$ under N$_2$ atmosphere, can react with MeOTs and 18-crown-6 (18-C-6) to give the methylimido complex 118 via a presumptive two-coordinate nitride 117 with higher reactivity (Scheme 23) [66].

**N-acylation**

The N-acylation of N$_2$-derived nitride has also been investigated. For example, the N-acylation
products 119 are obtained when 108 is treated with acyl chlorides in the presence of additives, such as [TMS(py)][OTf] and iPr3SiOTf. Furthermore, when the N-acylated products 119 react with magnesium anthracene (MgC14H10) and trimethylsilyl triflate (TMSOTf) in one pot, it would be converted to the trimethylsiloxy-substituted ketimide 121 via the intermediates of 120. Further reaction of 121 with SnCl3 or ZnCl2 affords the corresponding organic nitriles commitment with the generation of molybdenum chloride complex 122, a precursor of the trisamide molybdenum complex 107. In consequence, an efficient synthetic cycle that can directly convert N2 to nitrile was accomplished (Scheme 24) [67].

**N-acylation/elimination**

In addition to simple N-acylated products, the reactions between N2-derived metal nitrides and acyl chlorides also afford nitriles proceeded through N-acylation and subsequent elimination in formal. Hou et al. discovered that the reaction of titanium trialkyl complex 123 with N2 and H2 results in a novel diimide/tetrahydride complex 124. This complex can react with N2 at elevated temperature to provide a tetranuclear diimide/dinitride complex 125 that can further react with a series of acyl chloride to afford the corresponding nitriles in high yield (Scheme 25) [68]. Based on the experimental and computational results, the authors think that the functionalization of the imide ligands is prior to the nitride groups in these reactions. Furthermore, by treatment of the crude reaction mixture with HCl, the titanium trichloride complex 127 is isolated, which could be easily converted to 123 by reacting with TMSCH2Li. Hence, a synthetic cycle of titanium-promoted synthesis of nitriles direct from N2 was proposed (Scheme 25).

Another synthetic cycle for providing organic nitriles from N2 was developed by Cummins et al. via a niobium nitride intermediate (Scheme 26) [69]. An end-on bridging heterodinuclear N2-M complex 129, prepared from the reaction of the niobium triflate complex 128 and the aforementioned N2-Mo
complex 1, could undergo N₂ ligand scission to form anionic niobium nitride 130 along with the formation of molybdenum nitride 108, when 129 is treated with sodium amalgam. Treatment of 130 with acyl chloride results in releasing of nitriles accompanied by the generation of the niobium oxo complex 131. By treating with triflic anhydride, this oxo complex 131 can be converted to a bistriflate complex 132 that could be reduced to the initial compound 128 to finish the cycle.

**Redox-coupled N-atom transfer**

In comparison with N-alkylation or acylation and subsequent reduction, a more efficient route to transfer the nitride into organic compounds is the transformation of nitride-N atom into an incoming substrate with concurrent metal reduction. In 2014, Kawaguchi et al. reported the redox-coupled N-atom transformation of a V-nitride (Scheme 27) [70]. Reduction of the V(III) complex 133 by KH under N₂ results in a split of the N₂ to provide the μ-nitride V(IV) complex 134, which could be oxidized to V(V) nitride compound 135 via reacting with p-benzoquinone. When 135 is treated with CO or 2,6-xylidilocyanide in the presence of [2.2.2]-cryptand, the N-atom transformation of the substrates is observed concomitant with the formation of 136. The contact-ion-pair complex 137 could also be isolated from the reaction of 135 and CO. Although the extrusion of the cyanate or carbodiimide ligand in 136 are not easy, the contact-ion-pair 137 readily undergoes ligand exchange with 2-butyne to liberate potassium cyanate (KNCO) with the formation of the alkyne adduct 138. Additionally, 138 is facilely converted into the starting complex 133 upon dissolving in THF. Hence, a synthetic cycle for direct conversion of N₂ and CO into KNCO was completed. However, achieving the catalytic process of this synthetic cycle remains elusive due to the incompatibility of the individual steps in this cycle, such as the requirement of solvents in the N—C bond formation step and KNCO releasing step being different.

**N-silylation/imido transfer**

Besides N-hydrogenated intermediates, N₂-derived N-silylated complexes are also good precursors to make N—C bond. For instance, a cycle of Mo- and W-promoted synthesis of isocyanates from N₂ via a silyl-imido intermediate was established (Scheme 28) [71]. Photolysis of the end-on bridging N₂-Mo, W complexes 140 leads to the generation of nitride intermediates via N—N bond cleavage (vide infra), which would be trapped in situ by TMSCl to afford silyl-imido complexes 141. When TMSCl is replaced by Ph₃SiCl, Me₃CCl or Me₃GeCl, the similar reaction could also take place to provide the corresponding imido complexes. Besides, the organic compound TMSNCO could be obtained concomitant with the formation of the mono-nuclear oxo complexes 142 by treatment of 141 with CO₂. These oxo complexes 142 are known to react with additional TMSCl to regenerate the dichloride complexes 139 that are the precursors of the N₂-M complexes 140.

**Metal-ligand cooperative N-atom transfer**

Metal-ligand cooperative N-atom transfer is also an efficient strategy because of the avoiding of extra protons and electrons. Recently, a
metal-ligand cooperative N-atom transfer of a Re-nitride was reported by a cooperative $2 H^+ / 2 e^-$ transfer of the pincer ligand (Scheme 29) [72]. This Re-nitride complex 144, which is generated from photo-promoted cleaving of the end-on bridging binuclear $N_2$-Re complex 143 \((\text{vide infra})\), could react with benzoyl chloride to afford benzamide \((\text{PhCONH}_2)\), benzonitrile \((\text{PhCN})\) and benzoic acid \((\text{PhCOOH})\) along with the formation of trichloride Re complexes 145, in which the pincer ligand is oxidized to an imine-type ligand. The producing of PhCN and PhCOOH is caused from the reaction of the initially formed benzamide with excess benzoylchloride in the crude.

**Involvement of photochemistry**

Besides photo-promoted radical generation, another pathway of the photochemistry participating in $N_2$ transformation is the direct photolytic splitting of $N_2$ ligands into nitrides, which could further engage in N-atom transfer. Two examples of this method have been reported. In the first example, irradiation of the above-mentioned end-on bridging $N_2$-Mo, W complexes 140 over several days by medium-pressure Hg lamps lead to the generation of two metal nitrides 146 and 147 (Scheme 30a). Furthermore, when 140 are photolyzed in the presence of excess TMSCl, the terminal silylimido complexes 141 are obtained in moderate yield with the formation of dichloride complexes 139 (Scheme 29) [71]. The other example involves the photolysis of an end-on-bridged $N_2$-Re complex 143 that has abnormal thermal-stability, to provide the aforementioned Re-nitride 144 (Scheme 30b) [72]. It is noteworthy that the photo source of this reaction could be Xe(Hg) lamp \((\lambda > 305 \text{ nm})\) or a 390 nm LED lamp.

**Involvement of electrochemistry**

Electrochemical $N_2$ reduction is an alternative to chemical $N_2$ reduction for the synthesis of $N_2$-M complexes. This approach has been utilized to regain the $N_2$-Re complex 143 to achieve a cycle (Scheme 31) [72]. Schneider et al. found that in the controlled potential electrolysis experiment, the trichloride Re complexes 145 formed from the reaction of Re-nitride with PhCOCl, could be converted to the $N_2$-Re complex 143 via electrolyzing at $E = -1.65 \text{ V}$ for 8 h in the presence of proton source of 2,6-dichlorophenol (DCP) and subsequently electrolyzing at $E = -1.85 \text{ V}$ for 5 h under $N_2$. Thus, a three-step cycle for the synthesis of PhCONH$_2$/PhCN from $N_2$ was established, in which the creative approaches of metal-ligand cooperation and photo- and electrochemistry were all used.

**N–C Bond Formation via Uncharacterized $N_2$-M Intermediates**

Compared to the above works, the earlier reports about the conversion of $N_2$ into organic compounds were achieved by one-pot reactions of ill-defined...
Scheme 32. Ti-promoted transformation of N₂ into amines via ill-defined intermediates. (a) The reaction of Cp₂TiCl₂ with aryllithium reagents under N₂ to afford aromatic amines. (b) The reaction of diaryltitanocenes Cp₂TiAr₂ with alkali or alkaline metal under N₂ to afford aromatic amines. (c) Synthesis of organic amines from the reaction between ketones and a supposed titanium nitride species.

N₂ complexes or their derivatives with carbon-based substrates and followed by hydrolysis. In this section, some examples of this method were introduced briefly.

The initial works of transition metal promoted direct conversion of N₂ into organic compounds were reported more than 50 years ago, when Vol’pin and Shur et al. developed two systems for transformation of N₂ into aromatic amines mediated by titanium species [14,73]. In the first system, several aromatic amines are obtained when Cp₂TiCl₂ is treated with excess of aryllithium (aryl = Ph, m- and p-MeC₆H₄) reagents under N₂ pressure of 80–100 atm and followed by hydrolysis (Scheme 32a). When the aryllithium in these reactions is replaced by alkyl- or alkali metal (Li, Na and Mg) and N₂ (100 atm) (Scheme 32b). Although plenty of effort has been made, the detailed mechanisms of these works are yet unclear.

Meanwhile, a related work was reported in 1970 by van Tamelen and Rudler, who succeeded in the synthesis of organic amines from the reaction between ketones and a supposed titanium nitride species prepared through the reaction of Cp₂TiCl₂ with magnesium under N₂ (Scheme 32c) [74].

Additionally, Mori et al. achieved incorporation of N₂ into organic compounds via the N-silylation titanium complexes 148, which were prepared from the one-pot reaction of titanium species (TiCl₄ or Ti(O_iPr)₄), Li and TMSCl under N₂ or dry air (1 atm) [75]. Although the precise components and structures of 148 have not been determined so far, they are considered to contain XTi = NTMS, X₂TiN(TMS)₂ (X = Cl, OPr) and N(TMS)₃.

Scheme 33. Ti-promoted N—C bond formation via ill-defined N-silylation titanium species. (a) Preparation of N-silylation titanium complexes 148 from one-pot reaction of TiCl₄ or Ti(O_iPr)₄ with Li and TMSCl under N₂ or dry air. (b) The reaction between 148 and keto-carbonyl compounds to afford nitric heterocycles. (c) Palladium-catalyzed synthesis of aryl- or allyl-amines and amide derivatives from 148 and aryl or allyl halides in the absence or the presence of CO (Scheme 33).

CONCLUSION AND OUTLOOK

Direct transformation of N₂ into N-containing organic compounds is of fundamental and practical significance. In the past 60 years, the area of direct incorporation of N₂ into N—C bond effectuated
many great achievements. Relative to the traditional methods of assembling N–C bond via N-alkylation of N₂-M complexes, more atom-efficient approaches, such as cycloaddition, insertion and redox-coupled N-atom transfer for making N–C bond have been developed and received more attention in recent years. By the delicate design, some synthetic cycles about direct conversion of N₂ into organic compounds have also been developed. In these cycles, photo- and electrochemistry are sometimes used to prepare the N₂-M complexes, cleave the N–N bond or release the final products. However, all of these reactions are stoichiometric and the catalytic system for the direct introduction of N₂ into organic compounds has not been realized yet. The main factors that prevent these complete synthetic cycles from becoming a catalytic process are the rigorous reaction conditions of the N–C bond formation and N-containing organic compounds releasing steps in these cycles, which are incompatible with the preparation steps for N₂-M complexes. Hence, developing milder systems are imperative. Besides, new reaction types also need to be explored. In this context, we think the following fields can be considered in the future.

New reaction systems

So far, most N–C bond formation occurs at N₂-M complexes of group 4–6 transition metals. Exploring other metal promoted N–C bond formation is an attractive topic. Besides, the multi-metal synergistically promoted N₂ activation and functionalization also need to be studied. Toward this end, the design of new types of ligands should be considered.

New reaction types

Reductive elimination, an essential step in catalytic amination reactions, has not been found to take place at N₂-derived N-containing transition metal complexes. This process should be explored in future because it provides an efficient approach to assemble N–C bond concomitant with regaining the N₂-M complexes or their precursors. Additionally, other intriguing reaction modes, such as the [4+2] cycloadditions of N₂ ligands and insertion of N₂ into metal–carbon bond should also be investigated.

Polynuclear metal species cooperative N₂ scission and functionalization

Stimulated by the previous works on multinuclear Ti, Fe complexes-promoted N₂ cleavage and N–C bond formation [66,68], the strategy to realize synergistic N₂-splitting and subsequent functionalization using polynuclear metal complexes should be further explored. Additionally, recent reports on gas-phase polynuclear metal clusters-mediated N₂ scission and subsequent N–C bond formation deserve further attention [79,80].

Main group elements promoted N–C bond formation

The recent report about N₂ reduction by borylenes from Braunschweig et al. suggests the potential of boron mediated formation of N–C bond from N₂ [81]. Besides, some calculation results indicate that the direct reactions of boron or carbene with N₂ are also permitted in some cases. For example, Li and Schaefer et al. designed a new molecular system for nitrogen reduction, involving a 2,3′-bipyridine-anchored, end-on-bridging dinitrogen complex of the Me₂B–BMe₂ intermediate by theoretical calculations [82]. Zhu et al. designed a metal-free dinitrogen activation system based on the boron and NHC carbene system [83]. These results offer inspiration for future work on p-block elements promoting or catalytic conversion of N₂ into organic compounds.

Analogue of PCET: lessons from N₂-to-NH₃ catalysis system

Very recently, Nishibayashi et al. achieved a remarkable N₂-to-NH₃ process via a molybdenum-catalysis system. By using the samarium diiodide (SmI₂) as the reductant and alcohol or water as the proton sources, the total turnover number (TON) of this reaction reaches up to 4350 with 91% yield of NH₃. Further studies reveal that a proton-coupled electron-transfer (PCET) process, in which O–H bonds in water or alcohols are weakened by coordination to SmI₂, is the key to this high reactivity [84]. Inspired by this, a similar process of C–X (X = O, Cl, Br, I) bonds coordinated to a relevant reductant to weaken the C–X bonds, which could be named as carbocation-coupled electron-transfer (CCET) should also be studied. This CCET process may offer a path forward for developing catalysis systems that incorporate N₂ into amines via successive alkylation of a N₂-derived nitride.

Photochemistry

Limited complexes capable of N₂ photoactivation are currently known, and the underlying photophysical and photochemical processes after light absorption are largely unresolved. Light can induce the
split of N≡N bond in the M-N₂ complexes and the resulting nitride complexes are typically reactive. Hence, the following N–C formation reaction should be possible. Besides, the excitation into N–N π * orbitals is also possible, which can lead to a weakened π bond, and hence a following N–C formation directly from M-N₂* and carbon-based substrates including CO, CO₂ might be possible.

**Electrochemistry**

Previous work indicates that electrochemical reduction could release final organic compounds along with regeneration of N₂-M complexes. This stimulates us to create an electrochemical reduction system, in which the electrolyzation step is compatible with the N–C bond formation step. Besides, the recent report of N₂ and CO₂ coupling to produce urea, which was conducted by an electrocatalyst consisting of PdCu alloy nanoparticles on TiO₂ nanosheets, suggests that designing a new solid catalyst to incorporate N₂ into high-value N-containing product beyond NH₃ should also be attractive [85].

**Heterogeneous catalysis systems**

Although the industrial Haber-Bosch process produces NH₃ over the surface of heterogeneous solid-state catalysts, a similar process, in which a heterogeneous catalyst catalyzes or promotes direct transformation of N₂ into organic compounds, has not been reported in literature. Development of the new systems, where the merits of the homogeneous molecular systems and the heterogeneous systems are rationally combined, is a promising approach toward the goal.

**Via N-protonation or silylation intermediates**

The strategy of conversion of N₂ into organic compounds via the N-silylation and N-protonation complexes can be further extended. As an example, converting the less active M-N₂ complexes into M-N–Si/H species in situ followed by catalytic reaction with carbon-based substrates, might result in various valuable organic compounds being synthesized.

In a word, with combined efforts from cross-disciplines the dream of direct catalytic and efficient conversion of N₂ into N-containing organic compounds under mild conditions is believed to be attainable in the future.

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