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Organonitrogen Compounds

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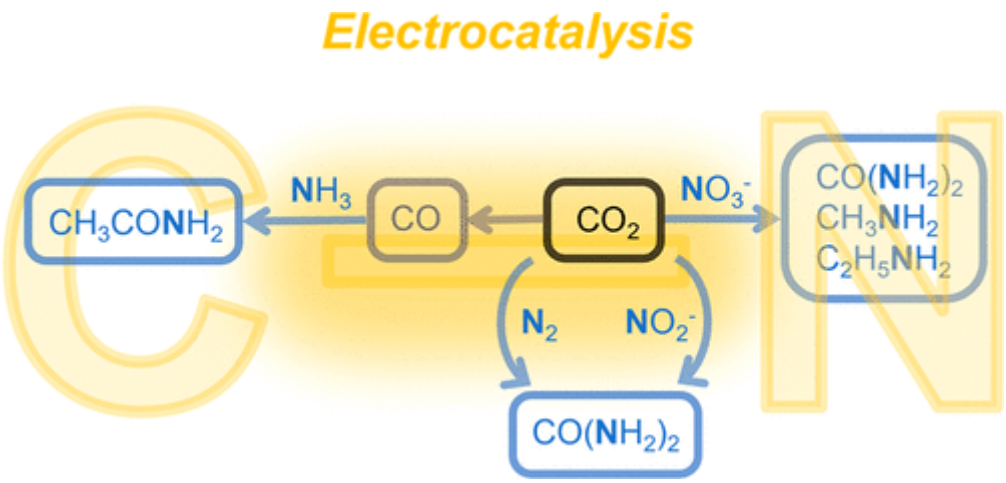
ABSTRACT: Since most DON compounds originate from release by living organisms or from degradation of dead organisms, input of DON to lakes and rivers does to a large extent reflect the chemical composition of biological matter. Thus, common DON compounds include free and protein-bound amino acids, amino sugars (from cell walls), and nucleotides (from RNA and DNA), but metabolites like urea and methylamines are also among frequently found DON compounds in freshwater. Other DON compounds may possibly be important in lakes and rivers, but have escaped detection because of low concentration. Many DON compounds are quickly utilized by microorganisms and this lowers their natural concentration to levels that are difficult to quantify by current analytical procedures. As an illustration, sensitive fluorescent techniques for analysis of amino acids have been available from around 1980 and have led to numerous data on amino acid concentrations in natural waters. In contrast, natural concentrations of, e.g., purine and pyrimidine monomers of nucleotides such as adenine and uracil are largely unknown due to lack of sensitive and reliable techniques for analysis of these compounds.

KEYWORDS- organonitrogen , dead organic nitrogen [DON], purine, pyrimidines, amino acid

I. INTRODUCTION

Given the limited product variety of electrocatalytic CO2 reduction reactions solely from CO2 and H2O as the reactants, it is desirable to expand the product scope by introducing additional reactants that provide elemental diversity. The integration of inorganic heteroatom-containing reactants into electrocatalytic CO2 reduction could, in principle, enable the sustainable synthesis of valuable products, such as organonitrogen compounds, which have widespread applications but typically rely on NH3 derived from the energy-intensive and fossil-fuel-dependent Haber–Bosch process for their industrial-scale production. In this Perspective, research progress toward building C–N bonds in N-integrated electrocatalytic CO2 reduction is highlighted, and the electrosyntheses of urea, acetamides, and amines are examined from the standpoints of reactivity, catalyst structure, and, most fundamentally, mechanism. Mechanistic discussions of C–N coupling in these advances are emphasized and critically evaluated, with the aim of directing future investigations on improving the product yield and broadening the product scope of N-integrated electrocatalytic CO2 reduction.[1,2,3]



II. DISCUSSION

Organonitrogen compounds are of vital importance to our lives. For almost all organonitrogen compounds, ammonia is only the feedstock as a nitrogen source. Ammonia is produced from dinitrogen (N_2) and dihydrogen (H_2) by the Haber-Bosch process, which consumes an enormous amount of energy. As an alternative method to convert N_2 into organonitrogen compounds under milder conditions, various stoichiometric reactions with transition metal complexes

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have been explored for the last 50 years. However, the field of catalytic formation of organonitrogen compounds directly from N_2 with transition metal complexes is still in its infancy. This short review summarizes strategies to achieve the direct synthesis of organonitrogen compounds from N_2 under mild reaction conditions using transition metal complexes ranging from stoichiometric reactions to catalytic reactions. various transition metal N_2 complexes or nitride complexes derived from N_2 undergoes N-functionalization reaction with carbon sources, and that in some cases synthetic cycles were established based on these stoichiometric reactions. Finally, the first catalytic formation of nitrogen–carbon bond containing compound (NCO^-) from N_2 mediated by the molybdenum complex was introduced. This was achieved by the extension of the synthetic cycle for NCO^- comprising two stoichiometric reactions (the fewest number of steps reported so far) that operates under similar and relatively mild conditions. NaNCO and KNCO are commercially important compounds applied in steel hardening, fine chemical synthesis, and the agrochemical industry with the world demand of 8000–10000 tonnes per year.[70] The direct and catalytic transformation of N_2 to useful nitrogen–carbon bond containing compounds under mild condition is a significant step forward from stoichiometric reactions. However, some points still need improvement: necessity of slow addition by syringe pump and low turnover number, as well as low atom economy. For further improvement of the catalytic reaction, optimization of reaction conditions including other combinations of the reagents should be considered to avoid side reactions. Since reducing agents and highly reactive carbon-centered electrophile coexisting in the current reaction system is generally incompatible with each other, exploration of milder reagents to selectively form organonitrogen compounds is required. It is also important to explore further about the reactivity of the metal complexes after nitrogen−carbon bond formation toward liberation of organonitrogen compounds from metal center. Compared to catalytic ammonia synthesis from N_2, attempts for direct and catalytic synthesis of organonitrogen compounds from N_2 have just begun. We hope that this concept will contribute to the discovery of more efficient catalytic systems for the synthesis of organonitrogen compounds under mild reaction conditions[4,5,6]

Dinitrogen (N_2), the main constituent of air, can be regarded as an easily accessible and unlimited precursor of nitrogen-containing compounds. However, we cannot use N_2 as a nitrogen precursor due to inertness of N_2 derived from its extremely strong triple bond (941 kJ/mol). Currently, the industrial use of N_2 totally relies on the Haber-Bosch process, which uses iron-based heterogeneous catalysts to produce ammonia (NH_3) from N_2 and hydrogen (H_2) under harsh reaction conditions (high temperature and pressure such as 400–500 °C, 150–250 atm).[1, 2] Subsequently, a significant amount of NH_3 produced by the Haber-Bosh process is used as a feedstock for value-added nitrogen-containing compounds. This industrial process, described as "making bread from air,"[3] is also known as an energy-intensive process that accounts for more than 1 % of the total energy consumed by human beings and emits an enormous amount of CO_2 when H_2 is produced by steam reforming.[4]

As an alternative method to convert N_2 under milder conditions, the use of transition metal complexes has been explored enthusiastically. The discovery of coordinated N_2 on transition metal complexes derived from hydrazine[5] or N_2 gas[6] demonstrated the potential of transition metal complexes to capture and activate N_2. Since then, stoichiometric or catalytic formation of nitrogen–hydrogen bonds to afford NH_3 using transition metal complexes with appropriate proton sources and reductants has been developed,[7] and turnover number of 60,000 has been achieved quite recently by the state-of-the-art catalyst.[8]

There has been also high motivation to directly convert N_2 into nitrogen-containing compounds other than NH_3 by forming nitrogen–non-hydrogen bonds, instead of nitrogen–hydrogen bonds, on transition metal complexes under mild reaction conditions, considering that a large part of produced NH_3 by the Haber-Bosch process is finally converted to nitrogen-containing compounds. Among them, the formation of nitrogen–carbon bonds to produce organonitrogen compounds is the most attractive approach because of their diversity and vital importance to our lives as biomolecules, medicines, and chemical fibers. In addition, development of such reactions contributes to reduce the number of reaction steps and to save a large amount of energy consumption upon NH_3 formation. To achieve this goal, the formation of nitrogen–carbon bonds at N_2 ligands or nitride ligands derived from N_2 on transition metal complexes has been intensively investigated as stoichiometric reactions. However, compared to the successful examples of catalytic formation of nitrogen–hydrogen bonds from N_2 to produce NH_3,[9] catalytic formation of nitrogen–carbon bonds to produce organonitrogen compounds is highly elusive and has not been achieved until recently.[10]

In this short review, the strategies are discussed to achieve the direct synthesis of organonitrogen compounds from N_2 under mild reaction conditions using transition metal complexes from stoichiometric to catalytic reactions.[11-13] First, early examples of the formation of nitrogen–carbon bonds from metal–N_2 and metal–nitride complexes are summarized. Then, synthetic cycles established based on these stoichiometric reactions are introduced. Finally, we

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demonstrate how to extend the synthetic cycles based on stoichiometric reactions to catalytic reaction to synthesize nitrogen–carbon bonds containing compound directly from N_2.

The first successful example of the formation of nitrogen–carbon bonds on dinitrogen (N_2) ligand was reported by Chatt and co-workers in 1972 (1).[14, 15] A tungsten N_2 complex bearing 1,2-bis(diphenylphosphino)ethane (dppe) ligands trans-$[W(N_2)_2(dppe)_2]$ (1) reacted with acyl chlorides as carbon-centered electrophiles to form the corresponding cationic acylhydrazide complex $[W(NNHCOR)(dppe)_2Cl]Cl$, where a proton was supplied from a trace amount of water in the system. The proton was removed by addition of Et_3N as a base to form acyldiazenide complexes $[W(NNCOR)(dppe)_2Cl]$. Protonation of $[W(NNCOR)(dppe)_2Cl]$ with HCl regenerated $W(NNHCOR)(dppe)_2Cl]Cl$. Chatt's and George's groups independently found the alkylation of molybdenum– or tungsten–N_2 complexes with alkyl halides under light irradiation to afford N-alkylated complexes.[16, 17] N,N-Dialkylhydrazide complexes of molybdenum or tungsten thus formed gave corresponding secondary alkyl amines in good yields upon treatment with $LiAlH_4$.[18]

Hidai and coworkers investigated a series of reactions of molybdenum and tungsten hydrazide complexes, prepared by protonation of the corresponding N_2 complexes, with various carbon-centered electrophiles (2).[19-21] Based on the findings, Hidai and coworkers reported a synthetic cycle starting from the tungsten–N_2 complex to release the corresponding pyrroles (3).[22, 23] Protonation of 1 with HBF_4 gave the cationic hydrazide complex $[W(NNH_2)(dppe)_2F]BF_4$ (2). The reaction of 2 with 2,5-dimethoxyfurane afforded the cationic pyrrolimide complex (3). Treatment of 3 with $LiAlH_4$ followed by quenching with MeOH gave the corresponding tetrahydride complex (4), pyrrole, and ammonia together with a small amount of N-aminopyrrole. Finally, 4 can be converted to the starting N_2 complex 1 by light irradiation under N_2 atmosphere.

N-arylation of coordinated N_2 with aryl halides to give aryldiazenide complexes via S_NAr-type reaction was reported by Hidai and coworkers.[24] A molybdenum–N_2 complex bearing tetradentate crown thioether ligand (5), which is more nucleophilic than its phosphine analogues, reacted with an aryl halide to give the corresponding aryldiazenide complex (4a). On the other hand, 5 was further converted to the corresponding hydrazide complex (6) by treatment with MeI at room temperature. As another example, Hidai and coworkers adopted the "bimetallic approach", where an anionic tungsten–N_2 complex $[^nBu_4N][W(N{=}C{=}S)(N_2)(dpe)_2]$ (7) reacted with $[Cr(p\text{-}FC_6H_4CO_2Me)(CO)_3]$ to give the corresponding aryldiazenide complex (4b).[25] The activation of arene with $Cr(CO)_3$ moiety is critical to achieve this unique reactivity, since 7 failed to react with non-coordinated $p\text{-}FC_6H_4CO_2Me$.

Quite recently, Xi and coworkers reported the stepwise functionalization of N_2 ligand on an anionic chromium complex bearing Cp* ligand $K[Cp^*Cr(depe)N_2]$ ($Cp^*=\eta^5\text{-}C_5Me_5$, depe=1,2-bis(diethylphosphino)ethane) with MeOTf to give a cationic dimethyl hydrazide complex $[Cp^*Cr(depe)(=NNMe_2)]OTf$ via a monomethyl diazenide complex $[Cp^*Cr(depe)(N{=}NMe)]$.[28]

In contrast to the addition of carbon-centered electrophiles to terminal N_2 ligand, Sellman and coworkers reported the reaction of a manganese–N_2 complex bearing a Cp ligand $[Cp(CO)_2Mn(N_2)]$ ($Cp=\eta^5\text{-}C_5H_5$) with phenyl lithium (PhLi) as a carbon-centered nucleophile to form the anionic diazenide complex $Li[Cp(CO)_2Mn(NPh{=}N)]$.[29] However, a recent study showed that the proposed reaction is unlikely to occur, and suggested that PhLi reacts with one of the CO ligands to provide an anionic acylcarbonyl dinitrogen complex $Li[Cp(CO)(N_2)MnCOPh]$, then it decomposed to give an anionic phenyl complex $Li[Cp(CO)_2MnPh]$, which was misassigned in the original literature as the anionic diazenide complex with nitrogen–carbon bond[7,8,9]

Holland and coworkers took a different approach to achieve the synthetic cycle for an aniline derivative from N_2 and arenes mediated by diketiminate-supported iron complexes, involving C−H activation of an arene as well as migration of an aryl group from the iron to the α-position of N_2 ligand as key steps (6).[31, 32]

As well as reactions of terminal N_2 ligands with carbon-centered reactants, the formation of nitrogen–carbon bonds on bridged N_2 ligands has been investigated. While N_2-bridged dihafnium[33] or discandium[34] complexes were reported to undergo alkylation with alkyl (pseudo) halides to give corresponding N-functionalized complexes, cycloaddition or insertion reactions of unsaturated organic molecules to bridged N_2 ligands on early transition metal complexes have been well investigated. Such reactivity offers synthetic methods complementary to that based on the addition of carbon-centered electrophiles to terminal N_2 ligand. Fryzuk and coworkers reported that the reaction of a N_2-bridged dizirconium complex bearing a diamido-bis(phosphine) ligand (8) with arylacetylene to form nitrogen–carbon bonds.[35] In this reaction, the formation of zircona-aza-cyclobutene intermediate through cycloaddition of alkyne across

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a zirconium–nitrogen bond is followed by cleavage of the zirconium–carbon bond by protonation with the second terminal alkyne to give the corresponding styryl-hydrazide complex (9, 7). Unfortunately, no release of organonitrogen compounds from complex 9 was observed at all.

Chirik and coworkers reported the preparation of a series of zirconium– and hafnium–N_2 complexes bearing cyclopentadienyl type ligands and their reactivities toward phenylisocyanate (8a)[36] and CO_2 (8b).[37, 38] Cycloaddition of zirconocene– and hafnocene–N_2 complexes proceeded smoothly to form nitrogen–carbon bonds. Subsequent silylation of the latter N-functionalized complexes with TMSI (TMS=Me_3Si) liberated the corresponding silyl-substituted hydrazine derivatives (8b).[37, 38] Kawaguchi and coworkers reported that a N_2-bridged dititanium complex underwent cycloaddition reactions with unsaturated compounds such as allene, isocyanate, and CO_2 to form nitrogen–carbon bonds[10,11]

III. RESULTS

As mentioned in the previous section, reactions of N_2 ligand with carbon-centered electrophiles typically result in formation of hydrazine derivatives retaining their nitrogen–nitrogen bond. Thus, development of other methods is desired to synthesize various types of organonitrogen compounds such as amine, amide, nitriles, and heterocycles without retaining nitrogen–nitrogen bond. The alternative method to directly synthesize organonitrogen compounds from N_2 is the use of terminal or bridged nitride ligands generated via cleavage of N≡N bond of N_2.[40]

Since the late 1960s, dinitrogen cleavage reactions and its application to the synthesis of organonitrogen compounds have been reported using titanium complexes under mild reaction conditions.[41-43] For example, Volpin and coworkers found the reaction of the titanium complex [Cp_2TiCl_2] with phenyl lithium at room temperature under the atmospheric to high pressure of N_2 to afford aniline in low yield.[41] However, these nitrogenous titanium complexes are ill-defined, and the reaction mechanisms of these reactions were unclear. Recently, the preparation of aniline derivatives from lithium nitride as a nitrogen source was reported by Shi and coworkers.[44]

In 1995, Cummins and coworkers reported the first successful example of N≡N bond cleavage using transition metal complexes under mild reaction conditions to give well-defined nitride complexes (9). The molybdenum complex bearing a tris(amide) ligand [Mo(N(^{t}Bu)(3,5-Xyl))$_3$] (10, 3,5-Xyl=3,5-dimethylphenyl) reacted with N_2 to give the corresponding N_2-bridged dinuclear molybdenum complex at −35 °C as a reactive intermediate, then cleavage of bridged N_2 ligand took place at room temperature to give the corresponding terminal nitride complex [Mo(N(^{t}Bu)(3,5-Xyl))$_3$] (11).[45]

Cummins and coworkers also reported the cleavage of N_2 ligand on the heterodinuclear niobium/molybdenum complex (12), which was generated from the corresponding molybdenum–nitride complex (13) and anionic niobium–nitride complex [Nb(N)(N(^{i}Pr)(3,5-Xyl))$_3$] (14).[46] Since these milestone works, the formation of terminal nitride complexes via direct cleavage of N_2 ligand with various transition metal complexes has been intensively studied. Other than the example of cleavage of N≡N bond using molybdenum complexes,[47, 48] N≡N bond cleavage reactions using tungsten[49] or rhenium[50, 51] complexes have been developed. The N≡N bond cleavage reactions are applied to the stoichiometric and catalytic synthesis of ammonia as reviewed comprehensively.[9, 40] In 2017, Nishibayashi and coworkers reported the catalytic ammonia formation under mild reaction conditions using molybdenum triiodide complex (15) via direct cleavage of bridged N_2 ligand and subsequent nitrogen−hydrogen bond formation (vide infra).[52]

These findings provide the opportunity to combine nitrogen fixation chemistry and nitrogen atom transfer chemistry in addition to the ammonia synthesis via nitrogen−hydrogen bond formation. Therefore, reactivity of the nitride ligands formed via N≡N bond cleavage with various carbon-centered electrophiles has been intensively examined.

Peters and coworkers reported the conversion of the nitride ligand on the molybdenum complex 11, prepared via direct cleavage of N≡N bond of N_2, into an organic amide by the reaction with trifluoroacetic anhydride at room temperature (10).[53] However, the amide ligand of the complex 11 decomposed to serve as a proton source in the reaction, thus preventing further application of this system into a synthetic or catalytic cycle.

In 2006, Cummins and coworkers reported a synthetic cycle for nitriles from N_2 including cleavage of N≡N bond as a key step, by the stepwise functionalization of 11 (11).[54] The cycle started with the reaction of 11 with TMSOTf and acyl chlorides to give the corresponding cationic acylimide complexes [Mo(NCOR)(N(^{t}Bu)(3,5-Xyl))$_3$]OTf (16,

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R=Me, ^{t}Bu, Ph). Sequential reduction and silylation of 16 afforded the ketimide complexes [Mo(NC(OTMS)R)(N(^{t}Bu)(3,5-Xyl))$_3$] (17), then treatment with zinc chloride gave the molybdenum chloride complex [MoCl(N(^{t}Bu)(3,5-Xyl))$_3$] (18) together with nitriles. Further reduction of 18 under a N_2 atmosphere regenerated 11 via cleavage of the N≡N bond of N_2.[12,13,14]

Cummins reported another synthetic cycle for the formation of nitriles based on the heterobimetallic dinuclear complex (20, 12).[55] Reduction of the complex 20 with Na/Hg afforded the anionic niobium–nitride complex Na[Nb(N)(N(Np)(3,5-Xyl))$_3$] (21) together with the neutral molybdenum–nitride complex [Mo(N)(N(Np)(3,5-Xyl))$_3$] via N≡N bond cleavage. Treatment of the anionic niobium complex 21 with acid chlorides gave the corresponding nitriles along with the niobium–oxo complex [Nb(O)(N(Np)(3,5-Xyl))$_3$] (22), where an isovalent N for (O)Cl metathetical exchange was driven by the formation of NaCl and a niobium–oxygen bond. Addition of Tf_2O to the oxo complex 22 and subsequent one electron reduction with $CoCp_2$ afforded the niobium monotriflate complex [Nb(OTf)(N(Np)(3,5-Xyl))$_3$] (24), which served as a precursor for the heterodinuclear complex 20.

In addition to molybdenum and niobium complexes bearing triamide ligands developed by Cummins and coworkers, transition metal complexes bearing pincer-type ligands have also shown to undergo cleavage of N≡N bond to give the corresponding terminal nitride complexes. In 2012, Schrock and coworkers found that the molybdenum diiodide complex bearing an anionic POCOP-type pincer ligand (25, POCOP=2,6-bis(di-tert-butylphosphinooxy)phenyl) can cleave N_2 upon reduction with Na/Hg to afford the corresponding anionic terminal nitride complex (26).[48] Mézailles and coworkers reported that the nitride complex 26 underwent nitride–alkyne cross metathesis reaction with internal alkynes to yield the corresponding nitriles. In this unique transformation, one electron oxidation of the intermediate with [Fc][BAr$^{F}_4$] (Ar^{F}=3,5-bis(trifluoromethyl)phenyl) plays a key role (13).[56]

Schneider and coworkers reported several synthetic cycles to afford nitriles and/or amides based on acylation of nitride complex derived from N_2 by using transition metal complexes bearing amide-containing PNP-type pincer ligands. Rhenium dichloride complex bearing PN^{amide}P^{tBu}-pincer ligand (28, PN^{amide}P^{tBu}=bis(di-tert-butylphosphinoethyl)amide) can cleave N_2 triggered by reduction with Na/Hg or $CoCp^*_2$ to give the corresponding rhenium–nitride complex (29), where a N_2-bridged dinuclear complex was proposed as a reactive intermediate.[51] The resultant nitride complex 29 reacted with MeOTf as a carbon-centered electrophile to afford the alkylimide complex 30, while protonation of 29 with HOTf proceeded at the amide ligand to give the corresponding cationic nitride complex (31, 14). Based on this reactivity, Schneider and coworkers established synthetic cycles to afford acetonitrile (15)[57] as well as benzonitrile from N_2.[58] Complex 29 was ethylated with EtOTf to afford the ethylimide complex (32) and subsequent deprotonation at the α-carbon in ethyl group gave the aldimide complex (33). Oxidation of 33 with N-chlorosuccinimide (NCS) afforded the rhenium trichloride complex 34 together with MeCN. Finally, reduction of 34 under N_2 atmosphere regenerated the starting nitride complex to complete the synthetic cycle.

Schneider and coworkers also found that the N_2 bridged dirhenium tetrachloro complex bearing an amine-type pincer ligand [{ReCl$_2$HPN^{amine}P^{iPr}}$_2$(μ-N$_2$)] (35, HPN^{amine}P^{iPr}=bis(diisopropylphosphinoethyl)amine) underwent photolytic splitting of N_2 to afford the corresponding nitride complex [Re(N)Cl$_2$HPN^{amine}P^{iPr}] (36).[50] By combining this photolytic N≡N bond cleavage with electrochemical approach, Schneider and coworkers achieved the 3-step (16)[50] and 2-step (17)[59] synthetic cycles to obtain benzamide and benzonitrile from the reaction of the rhenium–nitride complex with benzoyl halide.

Terminal nitride complexes formed via cleavage of N≡N bond can react not only with highly reactive carbon-centered electrophiles such as acid chlorides and alkylation agents as described above, but also with poorly reactive ones featuring multiple bonds such as CO, CO_2, and (hetero)cumulene.[13] In 2015, Sita and coworkers achieved molybdenum- or tungsten-mediated synthetic cycle to give TMSNCO from N_2, CO_2 and TMSCl (18).[60] Silylation of N_2-bridged dimolybdenum complex (40) under light irradiation gave the corresponding silylimide complex (41) and dichloro complex (42) via bis(μ-nitride-bridged) dimolybdenum complex generated via cleavage of N≡N bond. The imide–oxo metathesis of 41 with CO_2 yielded TMSNCO and the corresponding oxo complex (43). Deoxygenation of 43 with TMSCl generated 42, then reduction of 42 under a N_2 atmosphere regenerated the starting complex 40.[18,19]

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IV. CONCLUSION

In addition to CO_2, CO can be used as carbon-centered electrophiles to functionalize terminal nitride complexes. Kawaguchi and a coworker achieved a synthetic cycle mediated by vanadium complex to form potassium cyanate (KNCO) (19).[61] Reduction of a vanadium–tetrahydrofuran (THF) complex bearing a tridentate ONO-type pincer ligand [V(thf)ONO] (44, ONO=N-(4-methylphenyl)-2,6-bis-5-tert-butyl-3-methyl-6-phenoxymethyl)-4-tert-butylanilide) with KH under an atmospheric pressure of N_2 afforded the corresponding bis(μ-nitride)-bridged dinuclear complex (45) via cleavage of N≡N bond. 45 underwent structural rearrangement upon two-electron oxidation with benzoquinone to form the corresponding dinuclear vanadium complex with V≡N triple bonds (46). Upon reaction with CO, the vanadium isocyanate complex (47) was obtained. Subsequent ligand exchange with 2-butyne resulted in the release of KNCO and the formation of the corresponding alkyne complex (48). Further ligand exchange with THF regenerated the starting complex 44.

Schneider and coworkers investigated the reactivity of tungsten–nitride complex, formed via direct cleavage of N_2. Schneider and coworkers established a 7-step synthetic cycle to afford TMSNCO from N_2 and CO mediated by tungsten complex bearing an amide-containing PNP-type pincer ligand (20).[62] N_2-bridged ditungsten complex $[\{WClPN^{amide}P^{tBu}\}_2(\mu\text{-}N_2)]$ (49) reacted with CO to give the corresponding N_2-bridged ditungsten dicarbonyl dichloro complex $[\{W(CO)ClPN^{amide}P^{tBu}\}_2(\mu\text{-}N_2)]$ (50). Then, reduction of 50 afforded a N_2-bridged ditungsten dicarbonyl complex (51). Photolysis of 51 resulted in cleavage of N≡N bond to form the corresponding nitride carbonyl complex (52). The reaction of 52 with an atmospheric pressure of CO gave the corresponding isocyanate complex (53) via nitrogen−carbon bond formation. Upon treatment of 53 with TMSCl, tungsten chloro dicarbonyl complex (54) was formed together with TMSNCO. Oxidation of 54 with NCS under UV light irradiation afforded the trichloro complex (55), followed by regeneration of the starting complex 49 by reduction under atmospheric pressure of N_2.

Reactivity of bridged-nitride ligand formed via cleavage of N≡N bond with carbon-centered electrophiles is of interest along with that of terminal nitride complex. Except for uranium complexes reported by Mazzanti and coworkers, which underwent CO induced cleavage of N_2 to form the corresponding isocyanate complexes and cyanamide complex,[63] this reactivity is characteristic of group 4 or 5 transition metal complexes.

Chirik and coworkers intensively studied CO-induced nitrogen cleavage with concomitant nitrogen–carbon bond formation (21).[64] ansa-Hafnocene–N_2 complex (56) reacted with CO (4 atm, 1 atm, or 1 equiv.) to give the corresponding oxamidide complexes (57, 58) or isocyanate μ-imide complex (59). Free oxamide $H_2NC(O)$-$C(O)NH_2$ derived from N_2 and CO was obtained from reactions of the complexes 57 and 58 with an excess amount of HCl.

Hou and coworkers established a synthetic cycle for nitriles from N_2 mediated by a tetranuclear titanium hydride cluster (22).[65] The reaction of $[Cp'Ti(CH_2TMS)_3]$ (60, $Cp'=\eta^5\text{-}C_5Me_4SiMe_3$) with a mixture of H_2 and N_2 afforded the tetranuclear cluster (61). Cleavage of N≡N bond took place when 61 was treated with an atmospheric pressure of N_2 at 180 °C and mixed valent diimide dinitride cluster (62) was formed. The reaction of 62 with acyl chloride gave the corresponding nitriles together with the corresponding oxo complexes, and subsequent hydrolysis with HCl and ligand exchange with $TMSCH_2Li$ produced the starting complex 60.

Hou and coworkers also reported a synthetic cycle to give TMSNCO from N_2, CO_2, and TMSCl mediated by titanium complex (23).[66] Exposure of a N_2-bridged dititanium hydride complex (64) under an atmosphere of CO_2 at room temperature yielded the corresponding dioxo diisocyanate complex (65) via nitride oxo isocyanate complex as a reactive intermediate. Upon reaction of 65 with TMSCl at 55 °C, TMSNCO was formed together with TMS_2O and the mononuclear titanium trichloride complex (66). The reaction of the complex 66 with 3 equiv. of MeMgCl afforded the corresponding trimethyl titanium complex (67). Finally, hydrogenolysis of 67 with H_2 in the presence of N_2 afforded the starting complex 64 to complete the titanium-mediated synthetic cycle.

As shown in the previous sections, we overviewed the stoichiometric reactivity of N_2 complexes and nitride complexes derived from N_2 and their application to synthetic cycles for organonitrogen compounds. However, all of the synthetic cycles are only a combination of stoichiometric reactions. It should be well understood that it is quite difficult to achieve the catalytic reaction because of the low yield for each step and/or the use of incompatible reagents in the synthetic cycles. It is generally believed that the formation of nitrogen–carbon bonds is difficult and the use of highly reactive carbon-centered electrophiles that cause oxidative decomposition of the complexes is required. Furthermore,

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nitrogen–carbon bond containing moieties attached to the transition metal complexes are difficult to be liberated in many cases. Despite these many obstacles, we have achieved the first successful example of the catalytic and direct synthesis of an organonitrogen compound containing a nitrogen–carbon bond derived from N_2 with molybdenum–nitride complexes bearing pincer-type ligands as key intermediates. In this section, we introduce this interesting finding together with our research background.

As an extensive study of the development of catalytic nitrogen fixation using transition metal complexes, Nishibayashi and coworkers recently found the catalytic ammonia formation from N_2 under ambient reaction conditions using molybdenum triiodide complex bearing a pyridine-based PNP-type pincer ligand (15, 24a). In this reaction system, a molybdenum–nitride complex bearing a pyridine-based PNP-type pincer ligand (68) is formed via direct cleavage of bridged N_2 ligand, and subsequent formation of nitrogen–hydrogen bonds leads to the ammonia complex (69) which liberates free ammonia together with the nitride complex 68 (24b).[52, 67] More recently, Nishibayashi and coworkers found the use of SmI_2 as reductant and H_2O as proton source led to the remarkable catalytic activity toward ammonia formation from N_2 under ambient reaction conditions, where up to 60000 equiv. of ammonia were produced based on the molybdenum atom of the catalysts with a molybdenum turnover frequency of up to 800 equiv. min^{-1}.[8, 68] Based on the highly efficient catalytic cycle for the formation of ammonia from N_2, we have envisaged the formation of organonitrogen compounds from N_2 when carbon-centered electrophiles were used instead of proton source under the same reaction conditions. In order to achieve novel catalytic reactions for the formation of organonitrogen compounds, we first investigated stoichiometric reactions of molybdenum–nitride complexes in detail and then we tried to achieve the catalytic reactions based on information of the stoichiometric reactions.

We carried out stoichiometric reactions of molybdenum–nitride complex bearing PNP-type pincer ligand 68, prepared by the reduction of the corresponding molybdenum triiodide complex 15 under atmospheric pressure of N_2, with various carbon-centered electrophiles (25).[69]

Reactions with MeOTf, 2,2-diphenylacetyl chloride, and phenyl chloroformate at room temperature gave the corresponding N-functionalized complexes such as methylimide, acylimide, and carbamate complexes (70–72) in good to high yields, respectively. On the other hand, reactions with phenyl isocyanate and diphenylketene under the same reaction conditions afforded the corresponding acylimide complexes bearing a second electrophile attached at the benzylic position of the pincer ligand (73 and 74). In sharp contrast, no formation of nitrogen–carbon bonds at the nitride ligand on 68 was observed when benzoic anhydride and carbon monoxide were used as carbon-centered electrophiles. In both cases, only ligand exchange of iodide ligand occurred to give the corresponding nitride complexes (75 and 76).

Based on the stoichiometric reactions shown in 25, we investigated further reactions of the N-functionalized complexes. As a result, we observed an extremely unique reactivity of the carbamate complex 72. In fact, the reaction of the carbamate complex 72 with an excess amount of SmI_2 in THF at room temperature for 2 h gave the corresponding nitride complex 68 in 74 % NMR yield together with samarium species such as SmI_2(OPh) in 93 % NMR yield and SmI_2(NCO) in 75 % ion chromatography (IC) yield, respectively (26a). The ^{15}N-labelling experiments indicate that the nitrogen atom in the isocyanate moiety was derived from the nitride ligand. The result of the two kinds of stoichiometric reactions under similar reaction conditions suggests that it is possible to achieve the synthetic cycle for the formation of cyanate anion (NCO^-) from N_2 catalyzed by the molybdenum complexes bearing the PNP-type pincer ligand (26b).

When the atmospheric pressure of N_2 was reacted with 0.12 mmol of phenyl chloroformate (R=Ph) and 0.36 mmol of SmI_2 in the presence of 0.01 mmol of the molybdenum–nitride complex bearing PNP-type pincer ligand 68, only 0.45 equiv. of NCO^- were formed based on the molybdenum atom of the catalyst. The use of the combination of methyl chloroformate (R=Me) and molybdenum–nitride complex bearing PCP-type pincer ligand [Mo(N)I(PCP)] (77, PCP=1,3-bis(di-tert-butylphosphinomethyl)benzimidazol-2-ylidene), in place of phenyl chloroformate and 68, improved the amount of formed NCO^- to 0.74 equiv. based on the molybdenum atom. After the detailed investigation, we finally found the catalytic reaction of N_2 with SmI_2 and chloroformates in the presence of a catalytic amount of molybdenum–nitride complex bearing a PCP-type pincer ligand 77 in THF under ambient reaction conditions to give up to 9 equiv. of NCO^- based on the molybdenum atom of the catalyst in 75 % yield based on SmI_2 although slow addition of a THF solution of methyl chloroformate using syringe pump was necessary (27). This is the first successful example of catalytic and direct transformation of N_2 into nitrogen–carbon bond containing compound under ambient reaction conditions.

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To get more information on the reaction pathway, we isolated the molybdenum-isocyanate complex [Mo(NCO)ICl(PNP)] (78) from the reaction of the carbamate complex 72 with 1 equiv. of SmI_2 under 1 atm of Ar. Further reduction of the isocyanate complex 78 with an excess amount of SmI_2 under 1 atm of N_2 to afford the nitride complex 68 and NCO^- in 66 % and 75 % yields, respectively. DFT calculations based on the stoichiometric reactions support a proposed reaction pathway shown in 28. Interestingly, when we carried out reduction of the carbamate complex 72 with 1 equiv. of $CoCp^*_2$ under the same reaction conditions, another isocyanate complex [Mo(NCO)(OPh)Cl(PNP)] was obtained in 49 % yield. This experimental result indicates the importance of highly oxophilic samarium species to remove the phenoxy ligand from the isocyanate complex (28). Thus, the key to achieve the catalytic reaction is the interconversion between the carbamate and isocyanate complexes, enabled by the combination of high oxophilicity of samarium compounds and high reactivity of chloroformate esters bearing an alkoxy group as a leaving group.[20]

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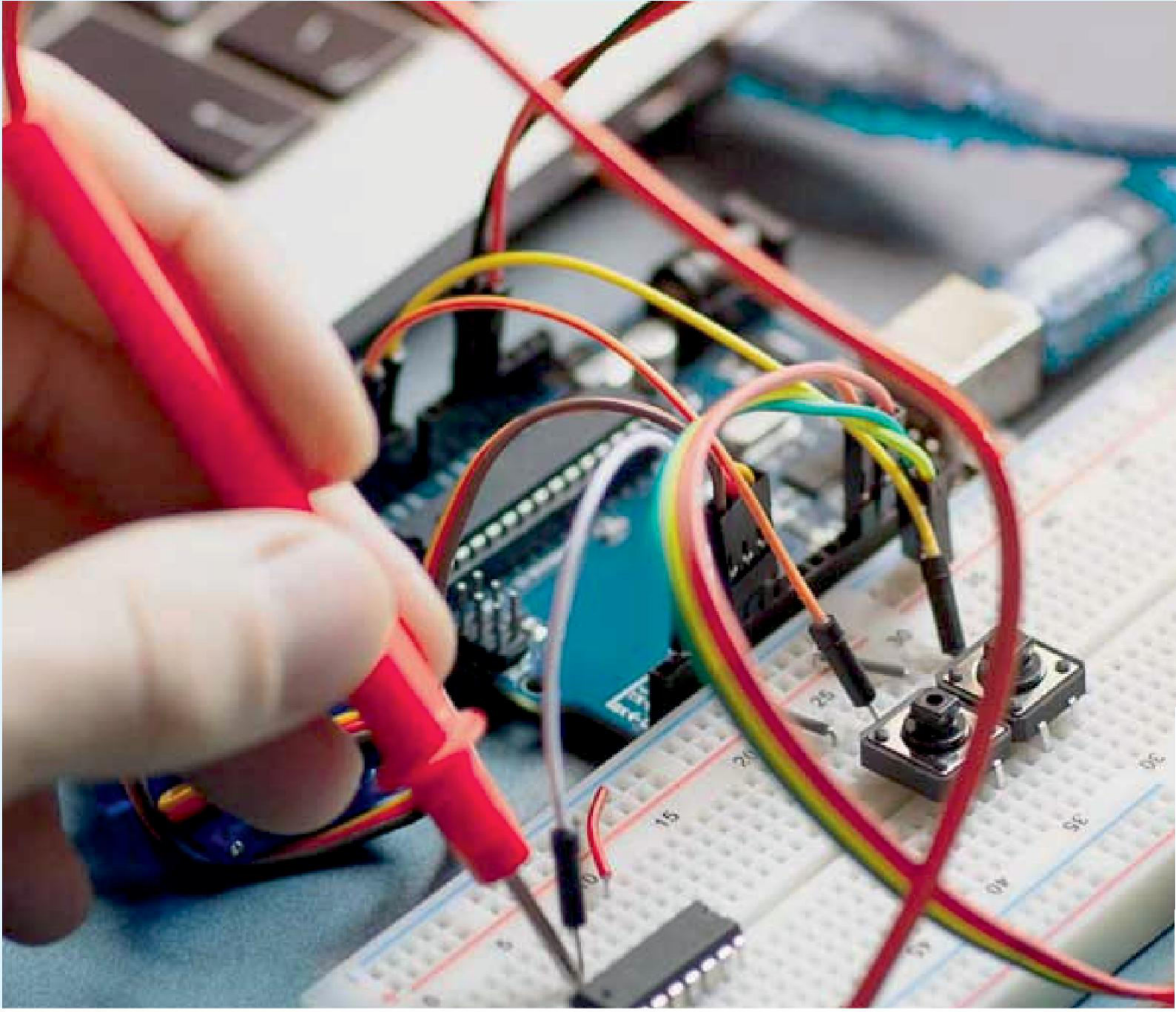

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