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Coordination Chemistry Reviews
200–202 (2000) 379–409

COORDINATION CHEMISTRY REVIEWS

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The continuing story of dinitrogen activation

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Received 21 September 1999; accepted 7 January 2000

Contents

Abstract

This review attempts to survey the recent literature concerning the coordination chemistry and the reactivity patterns of metal–dinitrogen complexes. In order that this work may stand

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PII: S0010-8545(00)00264-2

alone, a certain amount of background information is included; however, the emphasis is on synthesis and reactivity patterns of recently discovered dinitrogen complexes. In addition, some effort is made to discuss new trends in dinitrogen chemistry as well as to point out underdeveloped topics in this area.

Keywords: Dinitrogen; Nitrogen; Nitrogen fixation; Nitrogenase; Metal complexes

1. Introduction

Molecular nitrogen (N_2) surrounds us as the major component of the atmosphere here on Earth. We breathe this molecule constantly, but because of its extreme inertness, dinitrogen is not involved in our metabolism. However, nitrogen is an essential element in the chemistry of life, and the initial source of all nitrogen in organisms is molecular nitrogen. Only a few organisms are capable of utilizing this plentiful source of nitrogen. The process by which N_2 is incorporated into biological systems is referred to as nitrogen fixation and involves the nitrogenase enzymes that contain a metal–sulfido cluster at the active site. The recent X-ray crystal structure [1] of one such enzyme cofactor has inspired increased interest in the mechanism by which nitrogenase converts N_2 to ammonia. Since the discovery of the first dinitrogen complex, $[(H_3N)_5Ru(N_2)]^{2+}$, in 1965 [2,3], the coordination chemistry of this simple molecule has flourished, and dinitrogen compounds of almost every transition element have been prepared. Some of this early coordination chemistry of N_2 was aimed at modeling what was believed to be the active site of nitrogenase. Additionally, there is continued interest in developing new kinds of reactivities for coordinated N_2 in an attempt to achieve a different goal; the discovery of new catalytic processes for the fixation and functionalization of dinitrogen. In this review, an attempt will be made to update two reviews, published in 1995 [4,5], with recently published work that details synthetic aspects of dinitrogen coordination chemistry as well as current reactivity studies of dinitrogen complexes. In addition, some ideas for future study will be presented.

1.1. Industrial importance of dinitrogen

At the turn of the last century, the imminent need for a source of fixed nitrogen became apparent, as natural sources of nitrogen compounds, used largely for fertilizers, were being depleted [6]. Three processes were developed that utilize a highly abundant feedstock: dinitrogen gas (N_2). The Birkeland–Eyde arc process [7,8] generates nitric acid via electric discharge into an oxygen–nitrogen mixture (Eq. (1)). The electric arc furnace required to overcome the activation barrier to this reaction proved too expensive to operate and has rendered this process obsolete. The Frank–Caro cyanamide process utilizes calcium carbide, CaC_2, which reacts with nitrogen under harsh conditions ($\sim 1000°C$) to generate CaNCN (Eq. (2)) [7,9].

Birkeland–Eyde arc process

$$2N_2(g) + 5O_2(g) + 2H_2O(l) \xrightarrow{\text{electric arc furnace}} 4HNO_3(l);$$
$$\Delta H^\circ = -30.3 \text{ kJ mol}^{-1} \tag{1}$$

Frank–Caro cyanamide process

$$CaC_2(s) + N_2(g) \xrightarrow{1000°C} CaNCN(s) + C(s) \tag{2}$$

The Haber–Bosch process, which has proven the most successful commercially, reacts N_2 gas with three equivalents of H_2 gas over a metal catalyst to produce ammonia (Eq. (3)) [7,10,11]. While this reaction is exothermic and thermodynamically favored under ambient conditions, the feedstock gases must be compressed to several hundred atmospheres to favor ammonia production at the high temperatures currently required. A catalyst that could perform this reaction at lower temperatures, and therefore lower pressures, would be economically advantageous; advancements in this area have been made using a Ru-based catalyst on graphite [12] instead of an Fe-based catalyst.

Haber–Bosch process

$$N_2(g) + 3H_2(g) \xrightarrow[\sim 200 \text{ atm, } 400°C]{\text{metal catalyst}} 2NH_3(g)$$
$$\Delta H^\circ = -46.2 \text{ kJ mol}^{-1}, \ \Delta S^\circ = -99 \text{ J mol K}^{-1} \tag{3}$$

1.2. Biological importance of dinitrogen

The ability of some organisms to fix atmospheric N_2 was first demonstrated in 1886. In contrast to the high-temperature industrial processes described above, the biological fixation of N_2 by nitrogenase-type enzymes is accomplished at ambient temperature and pressure, albeit utilizing a reaction that requires an electron source (Eq. (4)) [13–15]. While a relatively low reduction potential is achieved, this is an energy intensive process, requiring sixteen equivalents of MgATP.

$$N_2 + 8H^+ + 8e^- + 16MgATP \xrightarrow{\text{nitrogenase}} 2NH_3 + H_2 + 16MgADP + 16PO_4^{3-} \tag{4}$$

The three known types of nitrogenase enzyme differ in the make-up of their active sites; although the most common contain a combination of Fe and Mo centers, FeV and Fe only enzymes have also been identified. The refinement of the molecular structure of the FeMo cofactor of a nitrogenase enzyme [1], depicted in Fig. 1, has provided some clues to the mechanism of nitrogenase, and has provoked much speculation on the nature of the binding site and mode of binding of N_2 [16–22]. The initial binding of dinitrogen is now believed by most to occur at the Fe centers, rather than at Mo, which appears coordinatively saturated. The complexity of the nitrogenase enzymes makes modeling active sites and elucidating the mechanism of dinitrogen reduction a daunting task.

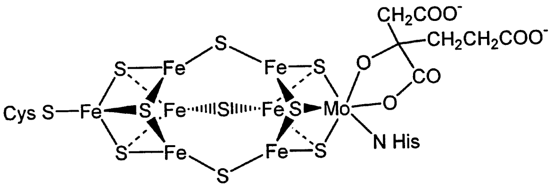


Fig. 1. Schematic of the FeMo cofactor of FeMo nitrogenase.

1.3. Perspective

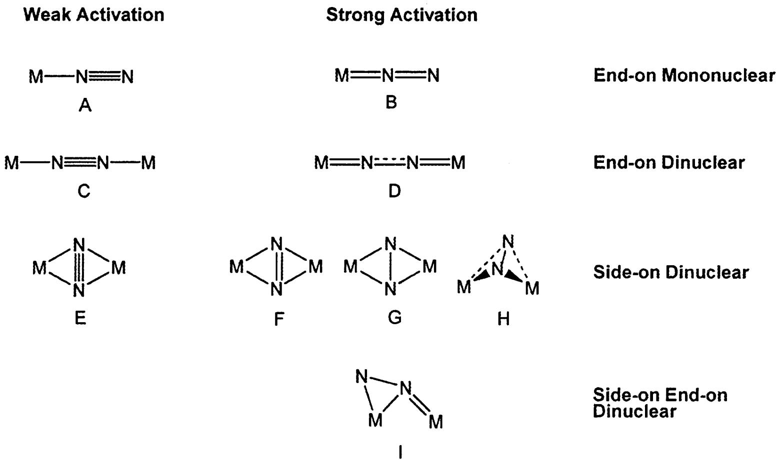
While the Haber–Bosch process differs substantially from the biological fixation of dinitrogen, both of these processes involve the activation of N_2 by a transition metal-containing catalyst. Numerous efforts have been made to develop synthetic metal-based catalysts to functionalize molecular nitrogen under mild conditions [23,24]. Although some progress has been made in this area, many of the systems remain intriguing curiosities and are commercially impractical [4,5,25,26].

The limited reactivity of dinitrogen and the harsh conditions required to convert N_2 into useful nitrogen-containing compounds are in contrast with the reactivities of other small molecules. The gases CO, H_2, O_2 and ethylene undergo a variety of reactions catalyzed by transition metals under relatively mild conditions and therefore find use in a number of industrial processes [27]. The catalytic activation of molecular nitrogen to produce nitrogen-containing compounds under mild conditions remains one of the loftier goals in chemistry.

2. The nature of the metal–dinitrogen bond

The dinitrogen molecule is poorly suited to act as a ligand. Compared to isoelectronic CO, it is both a poorer σ-donor and a weaker π-acceptor, is more difficult to reduce, and lacks a dipole moment. Nevertheless, dinitrogen compounds have been prepared for almost every transition metal. The bonding mode of N_2 is highly dependent on the metal center(s), metal oxidation state, and the ligand environment used. Some of the simplest mononuclear and dinuclear bonding modes that have been observed for dinitrogen to transition metals are shown in Scheme 1.

The bonding of N_2 to a metal can be categorized by the ability of the metal center(s) to reduce or ‘activate’ the N–N bond, via donation of electron density into the π^*-orbitals of the dinitrogen moiety. The degree of back-bonding is typically measured by the weakening of the N–N bond, observed both from the increase in the bond length (typically determined by X-ray crystallography) compared to free N_2, and from the decrease of the N–N stretching frequency (from infrared and Raman spectroscopy). A comparison of N–N bond lengths and stretching frequencies of some organic compounds is given in Table 1, along with some examples of dinitrogen complexes. In the following section we describe some new dinitrogen compounds, categorizing them as either weakly or strongly activated [28].



Scheme 1.

2.1. Weak activation

The majority of dinitrogen compounds contain a dinitrogen moiety that is not significantly elongated from free N_2, and the dinitrogen can be considered only weakly activated. The most common bonding mode for weakly activated dinitrogen is mononuclear end-on, bonding mode A in Scheme 1. End-on bonding can be described in a manner similar to that commonly invoked for CO, involving both σ-donation from the N_2 moiety to the metal and π back-bonding from the metal to the two orthogonal N_2 π^*-orbitals, as shown in Fig. 2. It has been suggested that in this binding mode, σ-donation is more important, with back-bonding occurring to a lesser degree [32]. In accordance with this generalization, the N–N bond length is typically less than 1.12 Å, and therefore the coordinated N_2 is best described as formally neutral, which can be depicted as $(N_2)^0$. Although little activation occurs

Table 1
N–N bond lengths and stretching frequencies for N–N triple, double, and single bonds, as well as a selection of dinitrogen compounds

Compound	N–N bond length (Å)	N–N stretching frequency (cm^{-1})
N_2 gas	1.0975	2331
PhN=NPh	1.255	1442
H_2N–NH_2	1.460	1111
$CpFe(dippe)(N_2)^+$ [29]	1.13(1)	2112
$\{[(Me_3SiNCH_2CH_2)_3N]Mo\}_2(N_2)Mg(THF)_2$ [30]	1.195(13)	1719
$\{[^iPr_2PCH_2SiMe_2)_2N]Zr(OAr)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ [31]	1.528(7)	751

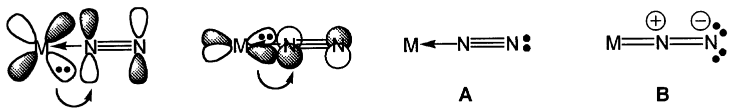
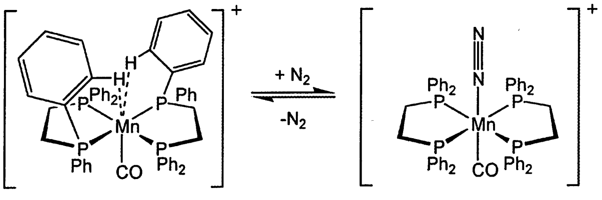


Fig. 2. Synergistic bonding in end-on dinitrogen complexes involves σ-donation from the N_2 unit to the metal and π-back-bonding from two orthogonal metal orbitals to the π*-orbitals of the N_2 moiety. This back-bonding can also be described by the contribution of resonance structure **B** to the σ-bonded structure **A**.

in terms of the formal reduction of N_2, in some cases the dinitrogen will undergo reactions such as protonation, as described in Section 3; more often, no chemical activation is observed.

Mononuclear end-on bound dinitrogen compounds are most commonly seen in 18-electron complexes with strong-field ligands. While coordinative unsaturation is necessary to form dinitrogen compounds, the ease with which unsaturation can be generated is remarkable for the late transition metals. For example, $Re(PMe_3)_5Cl$ spontaneously ionizes in ethanol to yield the dinitrogen compound $[Re(PMe_3)_5N_2]$-Cl [33]. Recent examples of related reactions include the piano-stool complex $TpRu(Ph_2PCH_2CH_2NMe_2)Cl$ which reacts with $NaBPh_4$ to precipitate NaCl and produce the dinitrogen compound $[TpRu(Ph_2PCH_2CH_2NMe_2)N_2]^+$ [34]. Similarly, Cl^- abstraction in the related piano-stool complex CpRu(dippe)Cl generates the 18-electron dinitrogen compound $[CpRu(dippe)_2N_2]^+$; $[Cp^*Ru(dippe)_2N_2]^+$ is prepared in a similar manner [35]. In comparison, the isoelectronic Fe species $[CpFe(dippe)N_2]^+$ is in equilibrium with the 16-electron paramagnetic species $[CpFe(dippe)]^+$ in solution, demonstrative of the weaker binding of N_2 to the first row transition metals. The more electron rich and sterically bulky $[Cp^*Fe(dippe)]^+$ does not bind dinitrogen at all [29].

Another example of a first row transition element that weakly binds N_2 is provided by $[Mn(CO)(dppe)_2(N_2)]^+$. This compound is in equilibrium in solution with the electron deficient $[Mn(CO)(dppe)_2]^+$ (Eq. (5)), which is stabilized by two agostic interactions with the supporting dppe ligands [36,37].

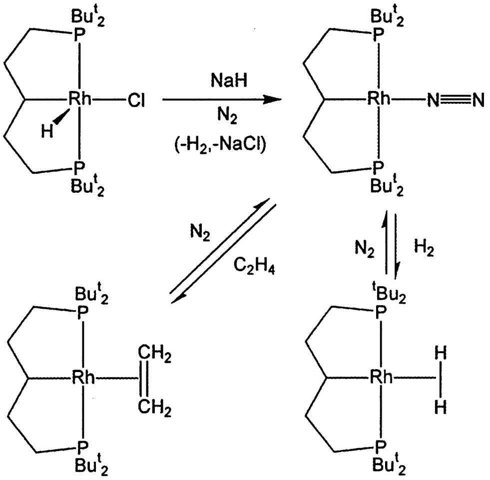


(5)

A similar reaction has been reported for the coordinatively-unsaturated cationic Ru(II) hydride, $[RuH(MeDuPHOS)_2]^+$; the preparation of this complex under N_2 results in the formation of the dinitrogen complex $[Ru(N_2)H(MeDuPHOS)_2]^+$, which is unstable and loses N_2 readily [38]. Examples of unsaturated complexes that bind N_2 in the absence of better donors abound; for example, the reduction of $FeCl_2(depe)_2$ (depe = $Et_2PCH_2CH_2PEt_2$) generates the dinitrogen complex

$Fe(N_2)(depe)_2$, which is formed from the transient 16-electron coordinatively unsaturated Fe(0) derivative $Fe(depe)_2$ [39].

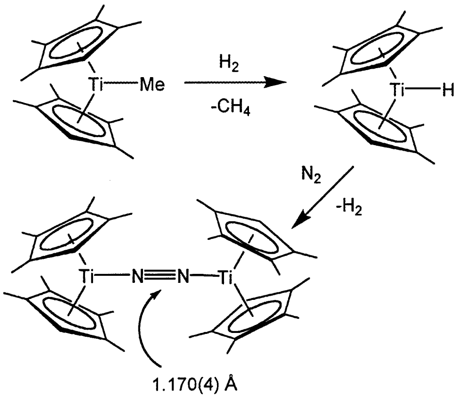
T-shaped 14-electron complexes of Rh(I) can also bind N_2. As shown in Scheme 2, reaction of excess NaH with the Rh(III) hydrido-chloride under N_2 generates the 16-electron square-planar dinitrogen complex stabilized by the PCP pincer ligand. By examination of the equilibria shown in Scheme 2, it was shown that the H_2 binds more strongly than N_2, which in turn binds more strongly than ethylene. This equilibrium with ethylene is remarkable, since ethylene is a much better π-acceptor than N_2; this phenomenon is probably a consequence of the steric bulk of the ancillary ligand disfavoring ethylene coordination [40]. In a related system, the formation of an N_2 complex affects an insertion process [41].



Scheme 2.

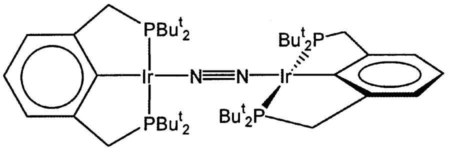
Hydrides can be used to generate dinitrogen compounds. Photolysis of $[(Ph_2PCH_2CH_2)_3P]RuH_2$ under dinitrogen generates $[(Ph_2PCH_2CH_2)_3P]RuN_2$ via a cyclometalated intermediate [42]. The reaction of $ReH_7(PPh_3)$ with sterically bulky HSC_6H_2-2,4,6-$^i Pr_3$ generates $Re(SC_6H_2\text{-}2,4,6\text{-}^iPr_3)_3(PPh_3)(N_2)$, which is a 14-electron complex, not counting possible π-donation from the thiolate ligands. Utilizing the less bulky 2,6-$Me_2C_6H_3SH$ ligand, no dinitrogen compound is produced; instead, an agostic interaction occurs with one of the Me substituents on the thiolate [43].

A similar reaction has been observed with a titanium hydride, and is very sensitive to the steric bulk of the ligand. Titanium(III) hydrides stabilized by bulky, substituted cyclopentadienyl ligands are known; for example, reaction of $(C_5Me_5)_2TiR$ with H_2 generates $(C_5Me_5)_2TiH$, and similarly, hydrogenolysis of $(C_5Me_4Ph)_2TiR$ gives $(C_5Me_4Ph)_2TiH$, which has been structurally characterized [44]. However, when the slightly less bulky tetramethylcyclopentadienyl ligand is used, the corresponding titanium hydride, $(C_5Me_4H)_2TiH$, reacts with N_2 to produce the dinuclear dinitrogen complex $[(C_5Me_4H)_2Ti]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)$ and one equivalent of H_2 [45] (Scheme 3). In contrast, both of the aforementioned pentasubstituted cyclopentadienyl titanium(III) hydride derivatives, $(C_5Me_5)_2TiH$ and $(C_5Me_4Ph)_2$-TiH, are unreactive towards N_2 [44]. A possible rationalization is that the less bulky ancillary ligands allow easier disproportionation of the Ti(III) hydride to form Ti(II) and Ti(IV) species that subsequently react with N_2. The N_2 bond in this example is only moderately activated, with an N–N distance of 1.170(4) Å. Likewise, the N_2 moiety is weakly bound, and this complex loses N_2 under vacuum.



Scheme 3.

Related to the Rh(I) chemistry shown in Scheme 2 is a recent study in which a related pincer-type PCP complex of Ir(III) was found to catalyze dehydrogenation of hydrocarbons. In the presence of N_2, however, this reaction was inhibited via the formation of the dinitrogen-bridged dinuclear species $[C_6H_3\text{-}2,6\text{-}(CH_2P^tBu_2)_2Ir]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$, **1**. The factors that favor dinuclear complexes over mononuclear complexes in weakly activated dinitrogen compounds are unclear; a subtle combination of steric, electronic and entropic effects are anticipated. Solubility differences may also determine whether the mononuclear or dinuclear complex is isolated. Because many of these late transition metal complexes already have four electrons in appropriate metal π-orbitals for back-bonding, the formation of dinuclear complexes does not greatly increase the back-bonding to the coordinated N_2. The N_2 bond length in complex **1** is 1.176(13) Å, only slightly longer than in related mononuclear compounds. The stability of this complex, and its ability to inhibit catalysis, has been attributed to the perpendicular arrangement of the two bulky PCP ligands, which encapsulates the $Ir_2(\mu\text{-}N_2)$ core of the dinitrogen complex [46].



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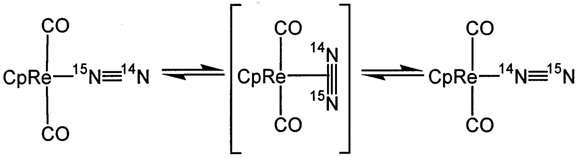
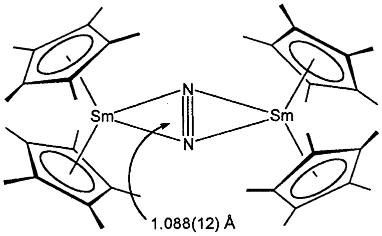
Another example of a dinuclear end-on N_2 complex with weak activation is provided by $[(depe)(CO)Mo]_2(\mu\text{-}N_2)$; the X-ray structure indicates that the N–N bond length is 1.127(5) Å. Once again, it is unclear why this mode of bonding occurs instead of the more common mononuclear mode [47].

No example of the mononuclear side-on bonding mode has been structurally characterized in the solid state; in mononuclear systems, the zirconium(III) system $Cp_2Zr(CH_2CMe_3)(\eta^2\text{-}N_2)$ is still the only complex for which there is spectroscopic evidence of side-on bound N_2 [48]. This bonding mode is considered less favorable for the late transition metals [32]. However, an elegant labeling study has shown that an end-to-end rotation of bound N_2 occurs in $CpRe(CO)_2(N_2)$ and related compounds via a nondissociative intramolecular process; these results imply the intermediacy of a side-on N_2 complex, shown in Scheme 4 [49,50].



Scheme 4.

A dinuclear side-on mode of $(N_2)^0$ coordination has been observed with Lewis acidic and coordinatively-unsaturated lanthanide and actinide complexes. When $(\eta^5\text{-}C_5Me_5)_2Sm$ is exposed to N_2, the dinuclear side-on bridged complex $[(\eta^5\text{-}C_5Me_5)Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**2**) can be crystallized [51]. The unsaturated $(\eta^5\text{-}C_5Me_5)_2Sm$ fragment binds N_2 rather weakly, based on NMR experiments. In addition, the N_2 can be removed from the dinuclear complex both in solution and in the solid state under vacuum.



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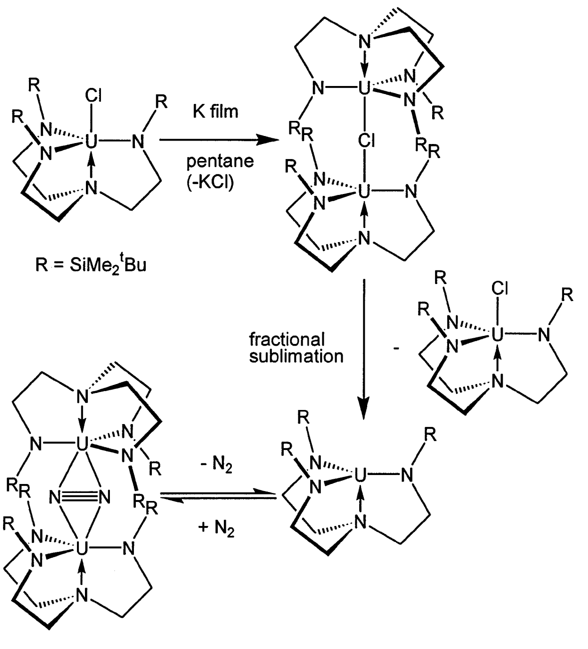
A similar coordination mode of dinitrogen has been observed with uranium. Reduction of $[N_3N']UCl$ with potassium ($[N_3N'] = N(CH_2CH_2NSi^tBuMe_2)_3$) generates the mixed-valent (III/IV) dimer $([N_3N']U)_2(\mu\text{-}Cl)$, from which $[N_3N']U$ can be sublimed. Under 1 atm of dinitrogen, conversion to the $([N_3N']U)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ is complete (Scheme 5). As with the previous example, the N–N bond length of 1.109(7) is essentially the same as free dinitrogen, and under vacuum the bound dinitrogen is readily removed. The reduction step is very sensitive to the substituent



Scheme 5.

on the amide ligands; using $SiMe_3$ in lieu of Si^tBuMe_2 resulted in no reaction with potassium, whereas the $SiPh_2Me$ substituent lead to dark intractable products [52,53].

A side-on dinuclear mode of bonding has been reported [54] for N_2 with lithium in the dication $[\{(THF)_3Li\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]^{2+}$. The N_2 moiety is formally neutral in this interpretation, and the unusual preference for N_2 binding to Li^+ in the presence of THF was explained as a result of crystal packing. An alternative explanation has been proposed; the ion previously described as a dication, $[\{(THF)_3Li\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]^{2+}$, may in fact be a monocation, $[\{(THF)_3Li\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]^{+}$, containing $(N_2)^{1-}$ [55].

2.2. Strong activation

Strong activation of the N–N bond requires a strongly reducing metal center and is most commonly observed with the early transition metals. Because of the strongly reducing nature of these metals, the N_2 unit can be considered $(N_2)^{2-}$ or $(N_2)^{4-}$. The formalism used is determined by the N–N bond length, N–N stretching frequency, and the apparent oxidation state of the metals; in many cases these factors are inconclusive, and subject to interpretation.

The majority of compounds containing strongly activated dinitrogen are not mononuclear, and they are rarely 18-electron complexes. Dinuclear complexes prevail, and the end-on bridging (μ-η^1:η^1) bonding mode, shown as D in Scheme 1, is the most common. This preference for dinuclear complexes suggests that the initially formed mononuclear dinitrogen complexes are more susceptible to attack by another coordinatively unsaturated metal species than is dinitrogen itself [56]. There are two ways to rationalize this trend for the early transition metals. The first is that the early transition elements are hard metals that form strong multiple bonds to hard ligands such as nitrogen, so additional reduction of the dinitrogen unit by a second metal strengthens both metal–nitrogen bonds. The second factor is that the ease of reduction of the dinitrogen molecule increases as the N–N bond order decreases. Thus, coordinated N_2 is easier to further reduce than uncoordinated N_2. Indeed, a comparison of the dissociation energies of the N–N bond for N≡N (946 kJ mol^{-1}), HN=NH (414 kJ mol^{-1}), and $H_2N–NH_2$ (159 kJ mol^{-1}) suggests that the cleavage of the first N–N bond is the most difficult [57]. In many cases each metal only has two electrons available to back-donate to the N_2 unit, leaving one of the N_2 π^*-orbitals free to interact with another metal center, which would favor dinuclear dinitrogen complex formation.

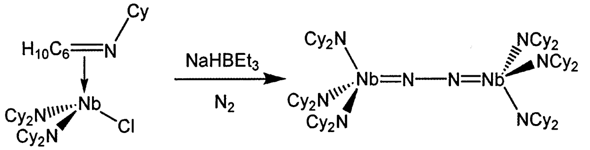
The ancillary ligands play a key role in the formation of strongly activated N_2 complexes; large differences in reactivity can result from subtle changes in ligand sterics, electronics and bite angle. For example three different vanadium(II) complexes with strikingly different characteristics were prepared using three amidinate ligand precursors ([CyNC(H)NCy]Li, [CyNC(Me)NCy]Li, and $[Me_3SiNC(Ph)NSiMe_3]Li$). The first (and smallest) ligand formed a $(CyNC(H)NCy)_2V(TMEDA)$ complex that, when heated, eliminated TMEDA to give a ligand-bridged metal–metal bonded system. The methyl-substituted ligand did not result in a dimer, but instead produced the $[CyNC(Me)NCy]_2V(THF)_2$ adduct that eliminated THF on heating and then disproportionated to form $[CyNC(Me)NCy]_3V$, a V(III) species. The largest ligand formed a $[Me_3SiNC(Ph)NSiMe_3]_2V(THF)_2$ species as well, but in this case, loss of THF on heating yielded a dinitrogen compound $\{[Me_3SiNC(Ph)NSiMe_3]_2V\}_2(\mu\text{-}\eta^1{:}\eta^1\ N_2)$ [58].

Although the N–N bond length of 1.235(6) Å for the above N_2 complex implies activation to a $(N_2)^{2-}$ ligand, this N_2 is weakly coordinated and easily displaced by THF. Ready displacement of N_2 despite significant elongation of the N–N bond is common for the first row transition metals [59]; although the first row early transition metals are reducing enough to bind N_2, this reducing power often just balances the entropic disadvantage of this reaction.

Vanadium(III) complexes are also known to form dinitrogen complexes, and ligand design is of key importance. For example, $[(Me_3Si)PhN]_3V(THF)$ loses THF to form an intractable solid. However, using the chelating amide $CH_3C[(CH_2)N(^iPr)]_3$, a dinitrogen complex, $\{CH_3C[(CH_2)N(^iPr)]_3V\}_2(\mu\text{-}N_2)$, is formed. Despite having a similar N–N bond length to the previous vanadium(II) example (1.257(6) Å), in this case the N_2 moiety is firmly bound [60].

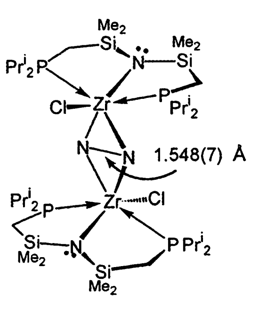
The end-on mode of bonding is also favored by the other group five elements. The reduction of the cyclometalated Nb(V) species $(Cy_2N)_2NbCl(\eta^2\text{-}CyN{=}C_6H_{10})$ using $NaHBEt_3$ produces $[(Cy_2N)_3Nb]_2(\mu\text{-}\eta^1{:}\eta^1\ N_2)$, as shown in Eq. (6). This compound is the first niobium dinitrogen complex formed from direct reaction with

N_2 gas, and has a long N–N distance of 1.34(1) Å. As is typical of the more strongly reducing second and third row early transition elements, the formally $(N_2)^{4-}$ unit is firmly bound, and is not displaced by donor solvents [61].



(6)

Several examples of the dinuclear side-on (μ-η^2:η^2) mode of bonding have been reported. The dinuclear side-on zirconium dinitrogen complexes utilizing chelating amidophosphine ligands shown in **3**,**4** and **5** were generated by the reduction of the corresponding Zr(IV) chloride precursors. The long bond lengths imply that dinitrogen has been reduced to $(N_2)^{4-}$, and in fact in some cases the N–N bond is longer than that of hydrazine. In two cases the $Zr(N_2)Zr$ core is found to be planar, however, with the $2,6\text{-}Me_2C_6H_3O^-$ ligand the $Zr(N_2)Zr$ core is hinged [31,62,63].



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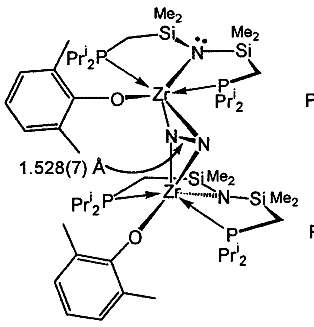

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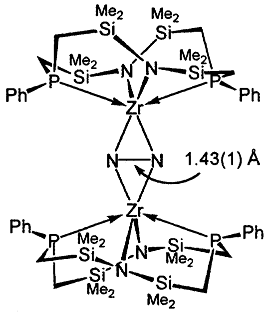
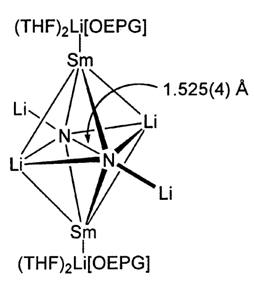


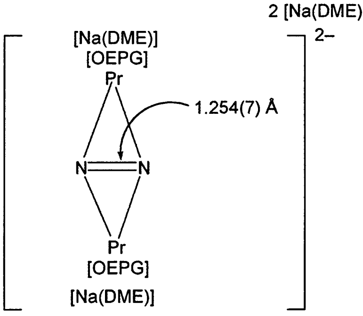
5

A long N–N bond of 1.525(4) Å was also observed in a mixed lithium–samarium octoethylporphyrinogen [OEPG] system, containing an N_2 side-on bound to two samarium atoms, as well as coordinated to four lithium atoms, **6**. Compound **6** was obtained by reducing a mixture of $SmCl_3(THF)_3$ and $[OEPG]Li_2(THF)_4$ with one equivalent of lithium, producing an unidentified Sm(II) compound, which then reacted with dinitrogen to yield the formally Sm(III) dinitrogen complex. This reaction is intriguing because the two samarium centers provide only one electron each, yet the final N_2 unit has been reduced to $(N_2)^{4-}$, based on the N–N bond length; four samarium centers must have been involved in the overall reduction, but the second samarium product has not been identified [64].



6

Related to the above lithium–samarium dinitrogen complex are paramagnetic derivatives of praseodymium and neodymium stabilized by the octaethylporphyrinogen ancillary ligand [65]. In these complexes, sodium salts are used in their preparation, and sodium is used as the reducing agent. Depending on the solvent of crystallization, interaction of the Na^+ ion with the bridging, side-on dinitrogen unit can be observed. The N–N bond distances are similar: 1.254(7) Å for the dianionic Pr(III) derivative, **7**, and 1.234(8) Å for the neutral Nd(III) complex, **8**. Unlike the related samarium system, **6**, only a two-electron reduction of the N_2 unit is implied from these bond lengths.



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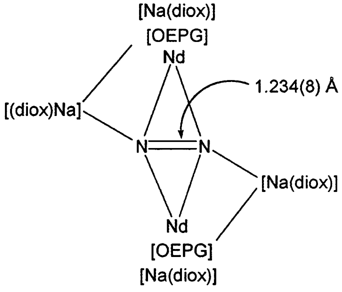
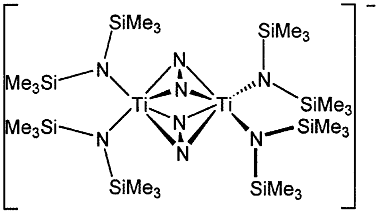


8

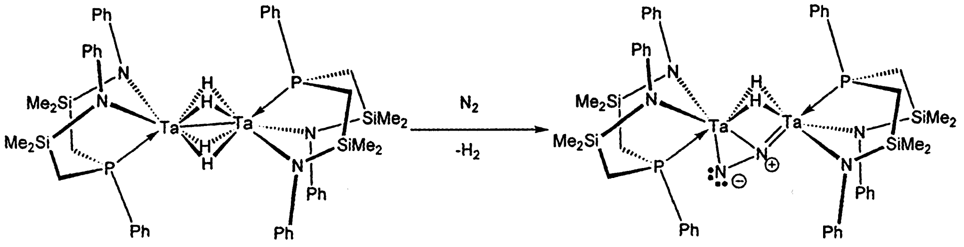
A titanium system containing two side-on bridging dinitrogen units has been described. The Ti(I)/Ti(II) mixed valent complex shown in **9** has a very long N–N bond distance of 1.379 Å, considering that a total of only five electrons are available for donation to both N_2 units [66].



9

The molecular orbitals involved in the dinuclear side-on versus dinuclear end-on bonding mode of dinitrogen have been reported [67,68]. The side-on mode involves the interaction of only one d-orbital of π symmetry per metal center; the unavailability of a second orbital of π symmetry of appropriate energy may be of importance in certain cases where this mode of bonding is observed. Regardless of molecular orbital considerations, this bonding mode appears more often in sterically and electronically unsaturated complexes of the more electropositive elements [69], which perhaps indicates that the increase in electrostatic interactions on going from end-on to side-on bonding is also important for these elements.

While the dinuclear side-on bound mode of bonding has not yet been observed for any complex of a Group V or VI transition metal, a side-on end-on dinuclear mode (μ-η^1:η^2) has been characterized with tantalum, and is shown in Eq. (7). The N–N bond distance is relatively long at 1.319(6) Å [70].



(7)

A related dinitrogen complex involving four titanium centers has been characterized by X-ray crystallography. One molecule found in the unit cell is shown in Fig. 3(a). Owing to a co-crystallized molecule in the crystal lattice, and few other methods of characterization, the charge of this complex is ambiguous; it may be uninegative. The bonding in the complex can be simplified by considering it an adduct of the complex shown in Fig. 3(b) [71]. The common feature between the tantalum and titanium complex that contain this similar end-on side-on dinuclear mode of bonding is a bridging ligand, which controls the distance between the two metals, in the case of the tantalum example the hydrides, and in the titanium example the linked fulvalene ligand. This restriction likely impedes the formation of the more frequently observed end-on binuclear binding mode, and may have relevance to the binding of N_2 in nitrogenase, which contains bridging sulfide ligands.

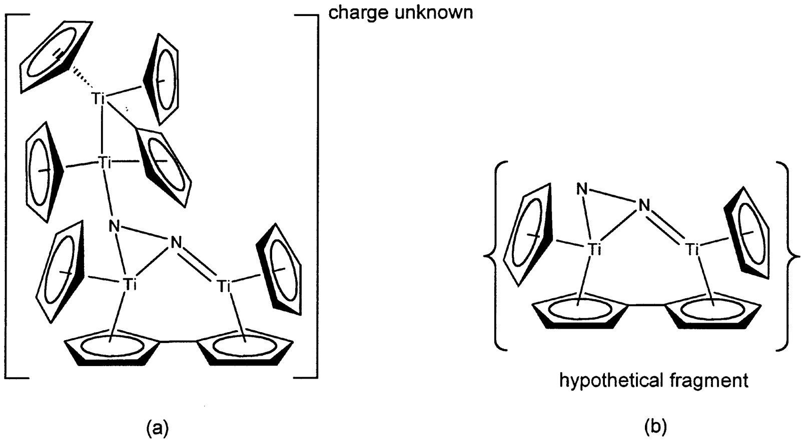
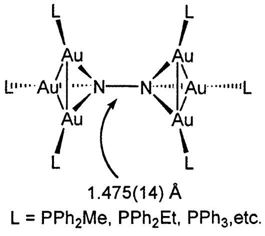


Fig. 3. The dinitrogen complex shown in (a) co-crystallized with Cp_2Ti(diglyme). The charge on the individual fragments is unknown; the dinitrogen complex may be uninegative. Removal of a fragment known to form a THF adduct produces the hypothetical fragment shown in (b), which resembles the bonding mode shown in Eq. (7).

Aside from its bonding mode, the reaction by which the tantalum dinitrogen compound shown in Eq. (7) is formed is not common for the early transition metals; the dinuclear tantalum(IV) tetrahydride eliminates hydrogen and binds dinitrogen. This reaction is interesting because no strong reducing agent, such as an alkali metal, is required to strongly activate the N–N bond [70].

One final polynuclear complex should be mentioned, though this derivative is strictly a hydrazine complex, due to its mode of preparation. The bonding of six gold(I) cations to the $(N_2)^{4-}$ unit produces **10**, in which Au–Au interactions are important [72]. This species might provide clues as to how many Fe atoms could interact with reduced dinitrogen in nitrogenase.



10

3. Reactivity of bound dinitrogen

In the past, a large importance was placed on the synthesis of dinitrogen compounds, and the bonding of the dinitrogen moiety. With the exception of protonation reactions, relatively few other reactivities were reported. This is possibly because the numbers of systems that react in a controlled manner with functionalization of the N_2 unit are scarce. In recent years increasing emphasis has been placed on expanding the reactivity of coordinated dinitrogen.

3.1. Reactions with electrophiles

In strongly activated dinitrogen complexes, the N_2 unit is formally described as $(N_2)^{2-}$ or $(N_2)^{4-}$, so it comes as no surprise that it is often susceptible to electrophilic attack. In the case of weakly activated end-on dinitrogen complexes, depending on the degree of back-bonding (and therefore the contribution of resonance structure B in Fig. 2) the dinitrogen unit is expected to be polarized to some degree with the terminal nitrogen bearing a formally negative charge. Electrophilic attack is therefore expected to take place at this terminal nitrogen.

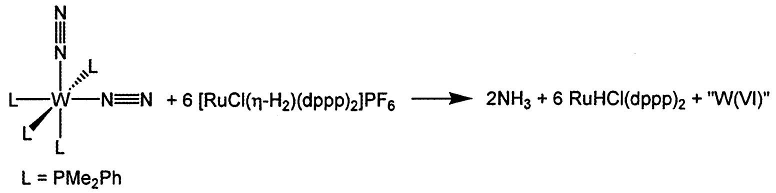
3.1.1. Protonation studies

By far the most studied reaction of coordinated N_2 with an electrophile involves the reaction with H^+. This is not surprising given the anticipated relevance to biological nitrogen fixation (Eq. (4)). As shown in Eq. (8), the products that can result even under very mild protonation conditions are NH_3, N_2H_4 and free N_2; the other possible product, N_2H_2, is not stable and disproportionates to N_2 and N_2H_4.

$$L_nM{-}N{\equiv}N \xrightarrow{\text{excess H}^+} \left\{\begin{array}{l}NH_3\\ H_2NNH_2\\ N_2\end{array}\right. \qquad (8)$$

For some time it was believed that molybdenum was the active site for ammonia production in the nitrogenase enzyme, so the protonation of molybdenum dinitrogen compounds appeared particularly relevant, especially because in some cases ammonia was produced. For example in complexes of the type $M(N_2)_2(PR_3)_4$ ($M = Mo$, W; $PR_3 = PMe_2Ph$, $PMePh_2$), protonation leads to NH_3 (up to two equivalents) and liberation of N_2 (one equivalent) [5].

A recent advance in the stoichiometric production of ammonia via a protonation sequence was the report that cationic dihydrogen complexes could be used as the acid [73]. The η^2-H_2 complex is acidic, and the source of the dihydrogen ligand is molecular hydrogen, so this reaction represents the overall formation of ammonia from N_2 and H_2 (Eq. (9)) Unfortunately, this process requires a stoichiometric amount of the metal–dihydrogen complex, as the remaining hydride formed from the heterolytic cleavage of H_2 is not transferred to give a true hydrogenation of N_2.

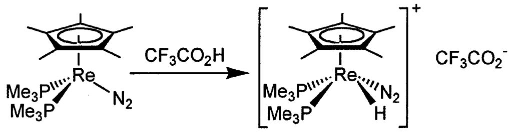


(9)

The use of thiolate complexes (L_nM–SH) as the source of protons has also been reported [74]. This can be viewed as a model of the nitrogenase enzyme since proton transfer to some form of coordinated dinitrogen from protonated sulfido units has been suggested [16,17,22].

The reported protonation of iron dinitrogen compounds to produce ammonia may be of similar biological relevance, though currently both the protonation mechanism and the nature of the dinitrogen compound, prepared by the deprotonation of an $Fe(II)(N_2)H^+$ intermediate, remain unknown [39,75].

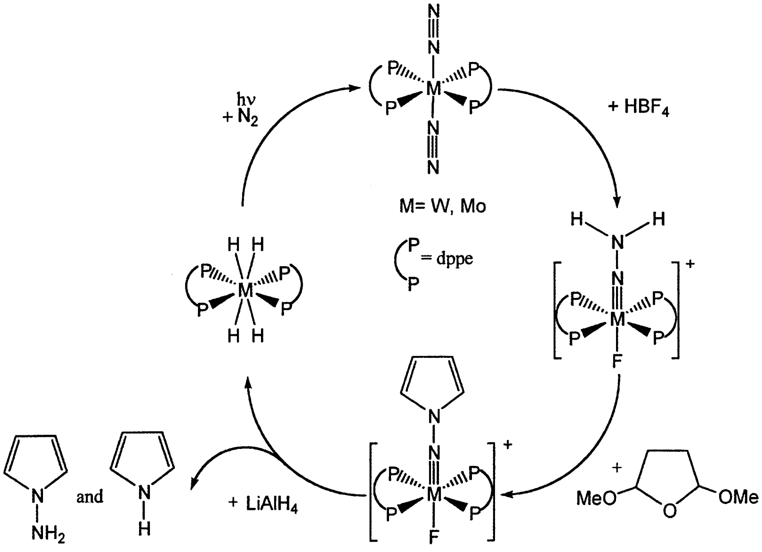
Protonation studies have revealed some interesting features of the complicated chemistry of bound dinitrogen. Studies have shown that there is not always a correlation between the structure of a dinitrogen compound (e.g. the degree of back-bonding) and the production of N_2H_4 or NH_3 on protonation; the ability of the metal to transfer electrons to the dinitrogen moiety during the protonation sequence is also relevant. Furthermore, the protonation of dinitrogen compounds under acidic conditions is frequently affected by temperature, solvent, choice of counteranion, and concentration of acid, indicating that in many cases the mechanism may be complicated [59]. Many side reactions might be expected under harsh acidic conditions, particularly if the ancillary ligands are themselves sensitive to protonation. The metal center may also be more susceptible to protonation than coordinated N_2. An example where a protonated metal species is isolable is provided by the electron rich compound $(C_5Me_5)Re(PMe_3)_2(N_2)$, shown in Eq. (10) [76].



(10)

The nitrogenase enzyme is much more complex than these simple model systems, and both the site of reduction and the binding mode of dinitrogen in the active site of the enzyme are unknown. The nitrogenase enzyme behaves in a catalytic manner with a mild reducing potential, two conditions that no model system has yet emulated. Currently, theoretical and often speculative [22,77,78] approaches to studying the protonation mechanism in nitrogenase appear more amenable to study than experimental models [16–18,20,79].

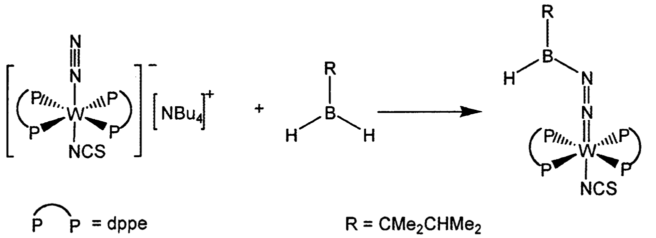
Protonated dinitrogen compounds have also been used to further functionalize dinitrogen. For example, the protonation of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with two equivalents of HCl generates the hydrazido complex *cis*,*mer*-$[WCl_2(NNH_2)(PMe_2Ph)_3]$, which undergoes a number of condensation reactions to form organonitrogen derivatives [80–83]. Besides hydrazone type derivatives, heterocycles such as pyrroles, pyrazoles, pyridines and indoles can be prepared. An example of a possible catalytic cycle derived from the observed reactivity is shown in Scheme 6. This area has recently been reviewed [84].



Scheme 6.

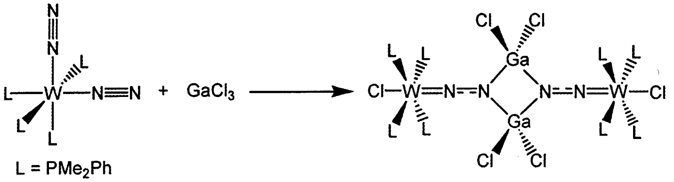
3.1.2. Reactions with other electrophiles

Similar to protonation reactions, complexes of the type *trans*-$W(N_2)_2(dppe)_2$ have been shown to react cleanly with a number of electrophiles; reaction with acyl chlorides to generate N–C bonds have been known for some time [85,86]. A related N–C bond forming reaction is a photochemical reaction with alkyl halides [85]. Recently, the reactivity of these systems has been expanded to include N–B forming reactions as shown in Eq. (11); the second product of this reaction is presumably $[NBu_4]^+[BH_3(CMe_2CMe_2H)]^-$ [87].



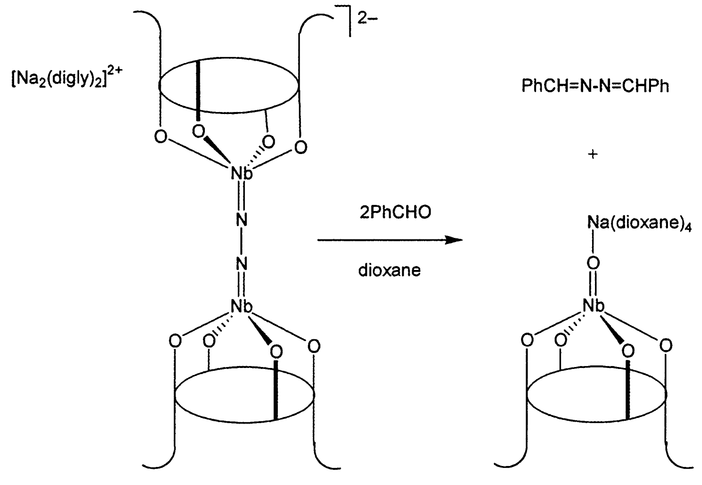
(11)

Gallium–nitrogen bonds have also been accessed by electrophilic attack. In the example shown in Eq. (12), the N–N bond distance of 1.32(2) Å is intermediate between single bond and double bond character [88]. Similar complexes have previously been prepared with trivalent aluminum [89].



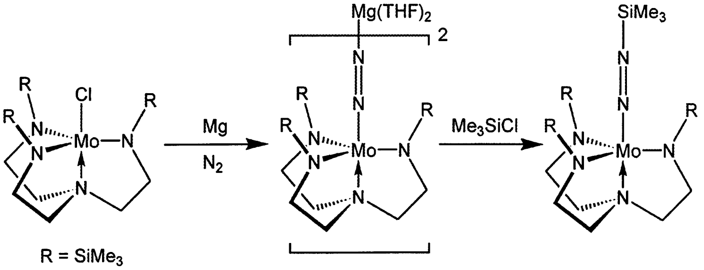
(12)

Double-bond metathesis reactions are also known for strongly activated dinuclear end-on complexes. For example, the dinuclear end-on Nb(III) dinitrogen complex, stabilized by calix[4]arene tetraanion, reacts with benzaldehyde to produce a metal–oxo compound and PhCH=N–N=CHPh, as shown in Eq. (13) [90].



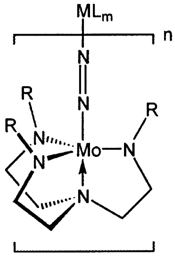
(13)

The reduction of the Mo(IV) complex [N_3N]MoCl, where [N_3N] = N(CH_2CH_2-$NSiMe_3$)$_3$, with magnesium generates the formally $(N_2)^{2-}$ species {[N_3N]-Mo–N=N}$_2$Mg(THF)$_2$, which reacts with the strong electrophile Me_3SiCl, as shown in Scheme 7. Reactions with other electrophiles produce side products from the reactivity of the ligand amido donors [30].



Scheme 7.

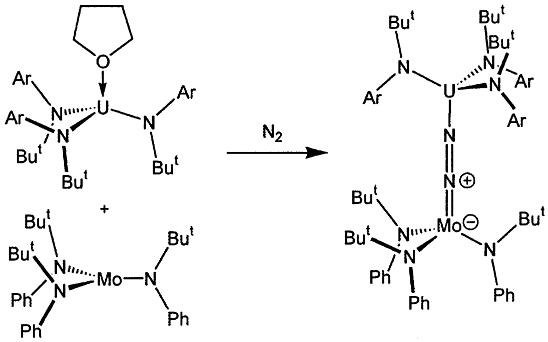
The reactivity of {[NN_3]Mo–N=N}$_2$Mg(THF)$_2$ with electrophiles has been exploited to synthesize heterodinuclear dinitrogen compounds of Zr(IV), V(IV), V(III) and Fe(III), shown in Scheme 8. For example, by varying the stoichiometry of the reaction between {[N_3N]Mo–N=N}$_2$Mg(THF)$_2$ and $ZrCl_4(THF)_2$ up to three chloride ligands can be replaced by {[N_3N]Mo–N=N}$^-$. With metals that are more easily reduced, the reactivity is complicated by redox reactions. Thus the Fe(III) compound {[N_3N]Mo–N=N}$_3$Fe is produced from the Fe(II) starting material $FeCl_2$, with the concomitant production of Fe^0 metal. Attempts to produce other late transition metal heterodinuclear N_2 complexes from the reaction of {[N_3N]Mo–N=N}$_2$Mg(THF)$_2$ with $MCl_2(PPh_3)_2$ (M = Ni or Pd) instead resulted in oxidation of the N_2 complex to produce [N_3N]Mo(N≡N). Heating [N_3N]Mo(N≡N) irreversibly forms the dinuclear N_2 complex {[N_3N]Mo}$_2$(μ-η^1:η^1-N_2) [91,92].



n = 3; ML_m = Fe, VCl, ZrCl
n = 2; ML_m = Fe(dmpe), VCl(THF), $ZrCl_2$
n = 1; ML_m = $ZrCl_3(THF)_2$

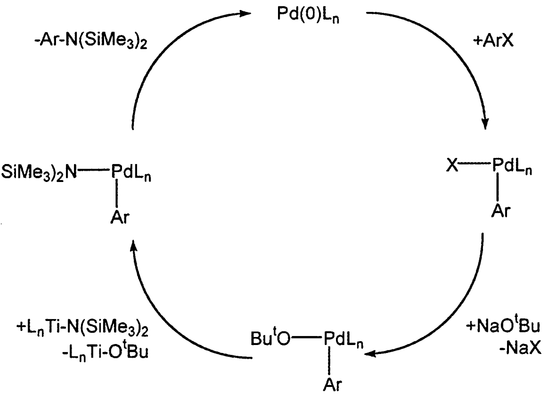
Scheme 8.

A heterodinuclear N_2 complex of uranium and molybdenum was prepared from a 1:1 mixture of $U(N[R]Ar)_3(THF)$ and $Mo(N[^tBu]Ph)_3$, as shown in Eq. (14). The compound $\{Mo(N[^tBu]Ph)_3\}_2(\mu\text{-}N_2)$ is known, and a likely mechanism of formation of the heterodinuclear complex involves the trapping of $(N_2)Mo(N[^tBu]Ph)_3$ by $U(N[R]Ar)_3(THF)$ faster than with another equivalent of $Mo(N[^tBu]Ph)_3$ [93].



(14)

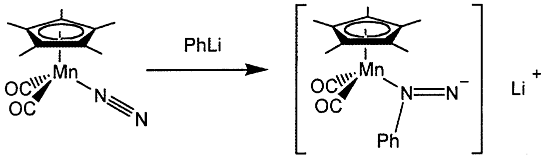
While there are still few examples of heterobimetallic dinitrogen complexes, two unique metal centers could contribute different reactivities in the functionalization of N_2. This has been demonstrated by a system involving two separate metal centers, an early metal, Ti, and a late metal, Pd. The reduction of $Ti(O^iPr)_4$ by Li in the presence of N_2 and Me_3SiCl produces nitrogen containing titanium compounds. When added to a solution containing a catalytic amount of $Pd_2(dba)_3$, and $P(o\text{-tolyl})_3$ in the presence of NaO^tBu and an aryl chloride, primary and secondary aryl amines were produced [94]. A possible reaction mechanism is shown in Scheme 9, and is related to the palladium catalyzed reaction of aryl chlorides with ammonia. The proposed mechanism of the N–C bond forming step involves a reductive elimination in this case, however, the overall reactivity is of activated N_2 with an electrophile.



Scheme 9.

3.2. Reactions with nucleophiles

Although less common then the reaction with electrophiles, the reaction of dinitrogen compounds with nucleophiles has been known for some time; Eq. (15) shows that the reaction of PhLi with $CpMn(CO)_2(N{\equiv}N)$ proceeds by nucleophilic attack at the nitrogen bound to manganese, which has a formally positive charge [95,96].



(15)

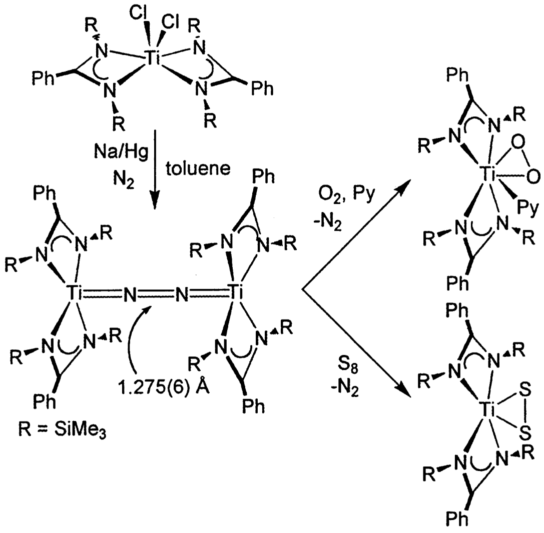
A similar mechanism of C–N bond formation has been proposed in the reaction of dinuclear titanium dinitrogen complexes with aryllithium and lithium. Following hydrolysis of the reaction mixture both aromatic amines and ammonia are produced. The formation of C–N bonds is only reported for aryllithium reagents; alkyl amines were not prepared by this method. While this reactivity has been known for some time, only recently have the details been reported [97,98]. The mechanism of this reaction, however, remains unclear, though it has been proposed that C–N bond formation occurs by nucleophilic attack of PhLi at N_2 in a dinuclear titanium N_2 complex. Several aspects of the reactivity complicate the mechanism, including the formation of benzyne complexes in the reaction mixture. No example of a fully characterized reaction of a dinuclear N_2 complex with a nucleophile has been reported.

3.3. Displacement of coordinated N_2

While not a useful reaction for the functionalization of dinitrogen, the displacement of dinitrogen from a metal can provide a useful route to other low-valent complexes. The reaction of $\{[PhC(NSiMe_3)_2]_2Ti\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ with O_2 or S_8 occurs with loss of N_2, as shown in Scheme 10; the N_2 complex behaves as a source of Ti(II) [99–101].

Dinitrogen complexes have also been used as reactive low-valent precursors for the late transition metals. Dinitrogen is readily displaced from the dinuclear complex $\{[2,6\text{-}(Me_2NCH_2)_2(C_5H_3N)]RuCl_2\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ by alkenes to generate the corresponding mononuclear alkene complexes, and reaction of the N_2 complex with $PhC{\equiv}CH$ results in the formation of a vinylidene complex [102]. The reaction of *trans*-$Mo(dppe)_2(N_2)_2$ with PhCH=NPh eliminates N_2 and C_6H_6 to produce the isocyanide complex $Mo(dppe)_2(N_2)(C{\equiv}NPh)$ [103]. A ruthenium dinitrogen complex, which activates the C–H bond of a thiophene after thermal displacement of the N_2 unit, has also been reported [104].

In many complexes, dihydrogen can replace the coordinated dinitrogen. A correlation between the stability of dihydrogen compounds and N–N stretching



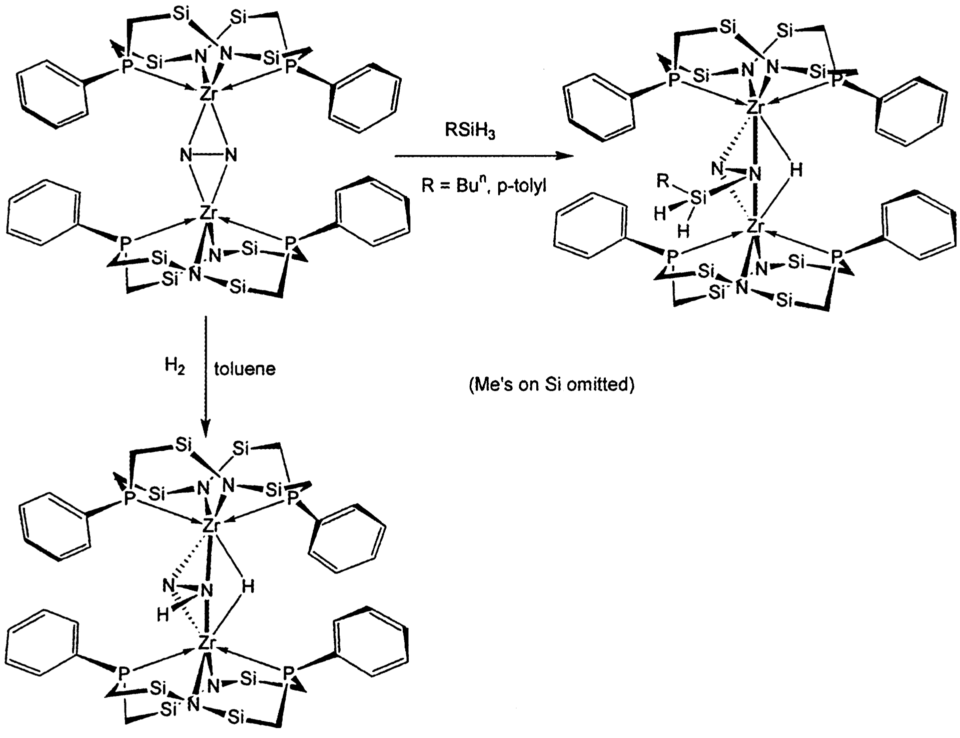
Scheme 10.

frequencies has been proposed; if $\nu(N_2)$ falls in the range 2060–2160 cm^{-1} then the corresponding dihydrogen compound is expected to be stable. When a lower $\nu(N_2)$ is observed, the back-bonding is expected to be large enough to generate a dihydride. A number of late metal–dinitrogen compounds have been characterized exclusively to determine if dihydrogen complexes could be accessible [105]. Some exceptions to this proposed $\nu(N_2)$ criteria for dihydrogen complexes have been reported [106].

3.4. Hydrogenation

The Haber–Bosch (Section 1.1) process reacts N_2 with H_2 under harsh conditions to generate NH_3. The reaction of transition metal N_2 complexes with H_2 instead results in either no reaction or the loss of N_2 producing metal hydrides or dihydrogen complexes (Section 3.3). In contrast to the displacement reaction, the side-on dinitrogen complex $\{[P_2N_2]Zr\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ reacts with H_2 to generate a species with a bridging hydride and a N–H bond. The solution and the solid-state structures confirm that H_2 has been activated and a new N–H bond has been formed. A similar sequence occurs with silanes to generate species with *N*-silyl groups; both reactions are shown in Scheme 11 [63,107].

These two similar transformations are new reactions for coordinated dinitrogen. The overall reaction with H_2 can be viewed as the hydrogenation of a metal–nitrogen bond. It is also possible to view this reaction as an example of electrophilic reactivity; the dihydrogen moiety is heterolytically cleaved, the H^+ protonates the N_2 unit, and the H^- forms a bridging hydride. Considered in this manner, this reaction is related to that shown in Eq. (9), except that in this case one complex



Scheme 11.

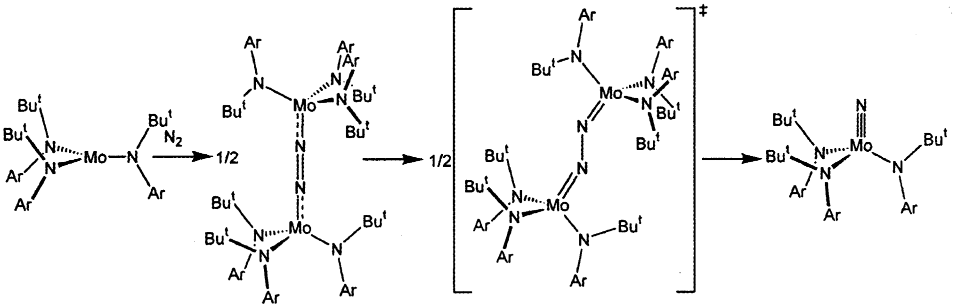
performs the dual roles of binding dinitrogen and activating dihydrogen. The hydrogenation of the N–N bond in a dinitrogen complex, involving the formation of two N–H bonds from the addition of H_2 to a dinitrogen complex to produce a diazene complex has not yet been accomplished; a recent theoretical study suggests that this reaction is thermodynamically feasible [108].

3.5. Dinitrogen bond cleavage

The reaction of N_2 gas with alkaline earth metals, Be, B, Al, and Si forms nitrides, though most require heating; with Li this reaction proceeds at room temperature to form Li_3N. Many transition metals also form nitrides when heated with N_2, including Sc, Y, lanthanoids, Hf, Zr, V, Cr, Mo, W, Th, Ur, and Pu. This process, referred to as nitriding, can be made catalytic in some cases. For example, a mixture of $TiCl_4$, $AlCl_3$ and metallic aluminum produces more than 200 mol of ammonia per mole of titanium after hydrolysis. A species formulated as $C_6H_6{\cdot}TiCl_2{\cdot}2AlCl_3$, a catalyst for the nitriding of aluminum, also reacts with dinitrogen in the absence of aluminum to give a nitride complex [109,110]. The cleavage of the N≡N triple bond on the surface of the metal catalyst is also considered the first step in ammonia formation in the Haber–Bosch process.

Despite these precedents, well characterized transition metal complexes, which are capable of cleaving the N≡N bond have only recently been discovered.

The use of bulky amide ligands has allowed for the preparation of coordinatively unsaturated molybdenum complexes of the formula $Mo[N(R)Ar]_3$ ($R = C(CD_3)_2CH_3$; $Ar = 3,5\text{-}C_6H_3Me_2$) [111,112]; the steric bulk of the ligands prevents strong metal–metal multiple bond formation typical for coordinatively unsaturated Mo(III) [113]. Cooling $Mo[N(R)Ar]_3$ under N_2 at − 35°C for several days produced the dinuclear end-on bridged N_2 intermediate $\{[N(R)Ar]_3Mo\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ (Scheme 12). At 28°C this species decomposes in a first-order process to generate the Mo(VI) nitride complex Mo(≡N)[N(R)Ar]. This process has been examined in detail, and the activation parameters and ^{15}N-isotope effect are known. Calculations as well as symmetry considerations suggest a 'zigzag' transition state in the N–N bond cleaving step [114,115].

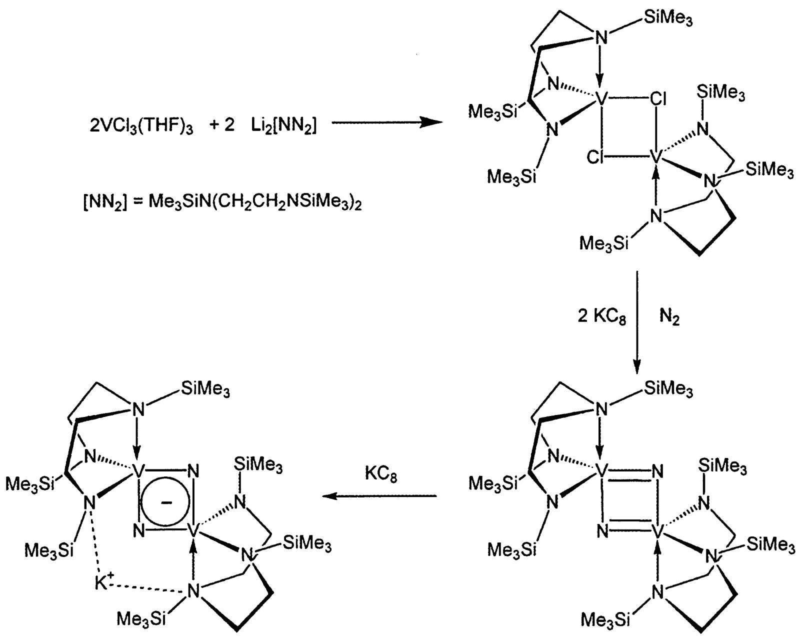


Scheme 12.

Dinitrogen cleavage should also be plausible using isoelectronic Group V elements in oxidation state two. This has been demonstrated using a vanadium system stabilized by a tridentate silylated diamidoamine ligand (Scheme 13) [116]. Reduction of the V(III) chloride-bridged dimer with KC_8 under N_2 leads to the formation of a dinuclear nitride species with an N···N separation of 2.54 Å. Further reduction can be effected to generate a mixed-valence V(IV)/V(V) anion with a reduced N···N separation of 2.44 Å.

Another example of a Group V metal assisting in the cleavage of dinitrogen uses calix-4-arenes, described as models for metal oxide surfaces, with niobium(V) [90]. A dianionic dinitrogen complex is formed by reduction to Nb(III) using sodium, with a very long N–N bond of 1.390 Å. Further reduction to Nb(II) forms a dinuclear system with bridging nitrides (Scheme 14).

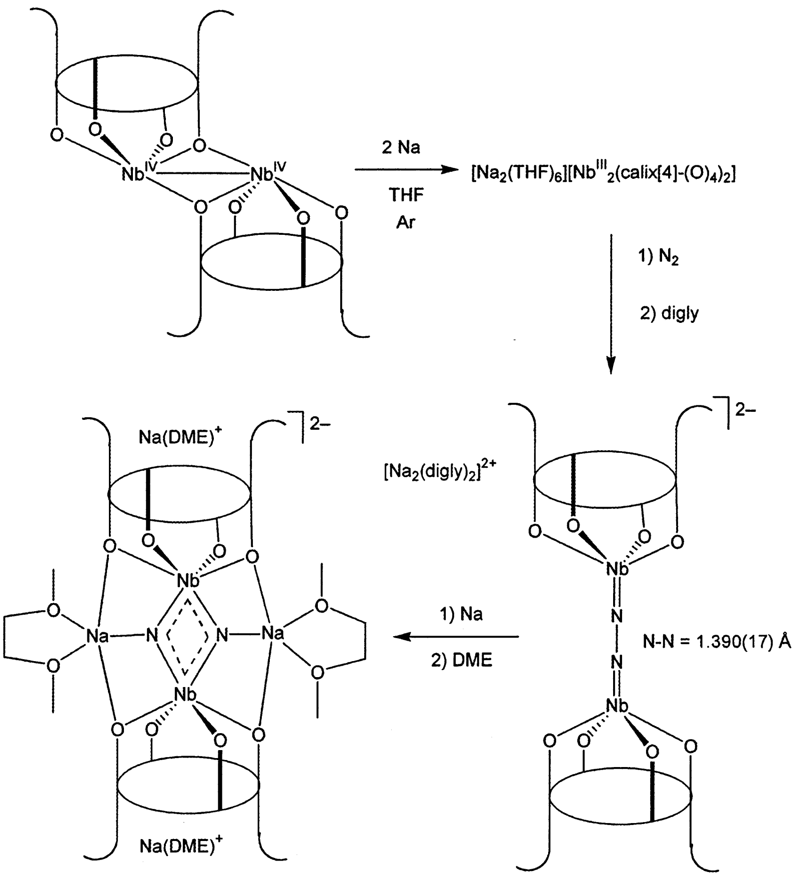
The requirements for N≡N bond cleavage are: (1) metal centers that form strong multiple bonds to nitrogen, such as Group V and Group VI metals; (2) metal centers that are in an appropriate oxidation state to provide a total of six electrons to N_2. However, meeting these requirements does not guarantee N≡N bond cleavage will occur. The complex $\{[(^tBuMe_2SiNCH_2CH_2)_3N]Mo\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ is known not to cleave dinitrogen, and calculations on model compounds indicate that this reaction is endothermic; this has been attributed to the *trans* influence of



Scheme 13.

the amine ligand weakening the Mo–N bonds [114]. The use of purely σ-donor ligands such as mesityl also seems to disfavor N≡N bond cleavage. The complex $[(Mes)_3V]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)$ can be reduced to $[(Mes)_3V]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)^{2-}$, where the two electrons are not transferred to the N_2 unit (as required to promote bond cleavage) but instead reside on the metal centers [117]. The reverse reaction, N–N bond formation from metal nitrides, has been known for some time with the late transition metals. A recent example is the reduction of $[Os(VI)(tpm)Cl_2(N)]^+$ to form the neutral dinuclear complex $[(tpm)Cl_2Os]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)$ [118,119].

To the extent that activation of N_2 can be measured by N–N bond lengthening upon coordination, complete cleavage of the N–N bond would appear to be the ultimate example of N_2 activation. However, its utility in the functionalization of dinitrogen has yet to be demonstrated. Clearly a driving force for the cleavage of the strong N≡N bond and formation of the nitride Mo(≡N)[N(R)Ar] is the formation of a comparably strong M≡N bond. It has been suggested that regeneration of the Mo(III) precursor to generate a catalytic cycle should prove possible by coupling dinitrogen cleavage with inter-metal nitrogen atom transfer reactions [120]. While not as common as oxygen atom transfer, metal-mediated nitrogen atom-transfer is known [121–123].



Scheme 14.

3.6. Diazenido and hydrazido functionalization and bond cleavage

Numerous dinitrogen complexes have now been prepared, and some show controlled reactivity, forming bonds to carbon and other elements. The reactivities of the resulting diazenido and hydrazido ligands are of importance to the exploration of catalytic processes. To develop a catalytic process reactions must be devised that can remove the functionalized dinitrogen moiety and leave the metal center in a useable form. Unlike direct cleavage of the N≡N bond, many examples of cleavage of the N–N bond after functionalization are known. Examples utilizing W and Mo have already been given in Section 3.1.1. Utilizing cobaltocene as a reducing agent cleaved the N–N bond in tungsten (1-pyridinio)imido complexes [124]. Related N–N bond cleavage in titanium (1-pyridinio)imido complexes has also been reported [125].

The transformation of dinitrogenous substrates has also been reported for bimetallic centers [126,127]. A catalytic cycle for the electrochemical reduction of PhN=NH to $PhNH_2$ and NH_3 at a $(CpMo)_2(\mu\text{-}SMe_3)$ core is proposed from the observed reactivity.

4. Future trends

Numerous examples of dinitrogen complexes are now documented, with varying degrees of activation, and in a number of bonding modes. The challenges in the goal of functionalizing dinitrogen are now no longer simply in generating dinitrogen complexes, but in observing new reactivities that are of potential use in catalytic cycles. Little progress has been made towards the goal of creating catalytic processes similar to those available for other small molecules such as CO and C_2H_4. While a number of catalytic cycles have been observed, none are currently thought of as commercially interesting; most rely on costly strong reducing agents to generate the dinitrogen complexes, and the resulting reactivity with electrophiles offers few benefits compared to the use of cheaply available NH_3, which also reacts with electrophiles. Methods other than harsh alkali metal reductions are required to generate dinitrogen complexes if a process is to be economically viable; this is chiefly a problem with the early metals, as the majority of their dinitrogen complexes are made in this manner. The early metals also suffer the disadvantage of forming strong bonds to nitrogen in the functionalized products, making a catalytic cycle that does not involve both electrophiles and reducing agents difficult to imagine. The late transition metals, while frequently not requiring as harsh reducing conditions as the early metals to generate dinitrogen complexes, often fail to demonstrate significant activation and reactivity of bound dinitrogen. However, because late transition metals generally form weaker bonds to nitrogen, the removal of functionalized dinitrogen from these complexes may be more feasible. If more reactive late transition metal–dinitrogen complexes are desirable, perhaps they will be generated as polynuclear species, containing many metal centers (similar to nitrogenase), that might provide increased reactivity while maintaining a relative ease in the recovery of nitrogenous products.

Whereas other small molecules such as CO, alkenes and alkynes undergo migratory insertion into metal–alkyl, metal–hydride and metal–acyl bonds, the same transformation has never been observed for N_2. The reaction of alkenes and alkynes with dinitrogen complexes generally results in the displacement of the coordinated N_2 unit and the incorporation of the π-ligand. The formation of C–N bonds via reaction of these unsaturated molecules with N_2 has not yet been observed, and would be of great interest, because of the thermodynamic driving force provided by these C–C multiple bonds.

5. Conclusion

There have been significant recent advances in the area of dinitrogen research. Reactivities that were believed impossible are now well documented. Nevertheless, much remains to be accomplished. It is hoped that this review will assist in guiding research into the new millenium.

Acknowledgements

Thanks to both the NSERC of Canada, and the PRF, administered by the American Chemical Society for funding in the form of research grants. Thanks also to the NSERC of Canada for financial support in the form of a postgraduate scholarship for S.A. Johnson, as well as the University of British Columbia for a University Graduate Fellowship.

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