Activation of Molecular Nitrogen: Coordination, Cleavage and Functionalization of N_2 Mediated By Metal Complexes

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Abstract: Recent developments in the activation and reactivity of coordinated dinitrogen are reviewed. Examples of weakly activated dinitrogen metal complexes, strongly reduced nitrogen-nitrogen bonds and N_2 cleavage reactions are discussed. Protonation reactions to form ammonia or hydrazido derivatives are covered along with processes in which nitrogen-boron, nitrogen-silicon or nitrogen-carbon bonds can form. Although this review builds on previous publications, a general introduction to this field is included.

Keywords: activation; coordination modes; dinitrogen; metal complexes; nitrogen fixation; reactivity

1 Introduction

1.1 Background

One of the challenges remaining in chemistry is the efficient utilization of molecular nitrogen, or dinitrogen, in the generation of complex nitrogen-containing products.[1–9] The use of N_2 as a feedstock is appealing for industrial use, as it is abundant, accessible and inexpensive. One can imagine a catalytic cycle in which dinitrogen and appropriate reagents could be combined to provide such materials as amines or *N*-heterocycles (Figure 1).

One of the barriers in generating such a cycle is the inertness of molecular nitrogen. Dinitrogen is a simple triply-bonded diatomic molecule that is very difficult to activate as reflected by its high ionization potential (15.058 eV), negative electron affinity (−1.8 eV) and high bond dissociation enthalpy (945 kJ mol^{-1}). The inertness of dinitrogen is not just due to its strong triple bond; carbon monoxide, which is isoelectronic with dinitrogen and undergoes a wide variety of chemical reactions,[10] has an even greater bond dissociation enthalpy (1076 kJ mol^{-1}), suggesting other factors must be responsible.

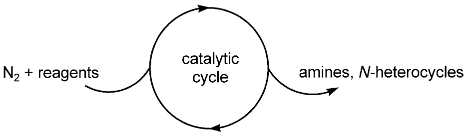


Figure 1. Conversion of molecular nitrogen into value added products mediated by a transition metal catalyst.

The orbital energies of N_2 provide a rationale for this inertness. The low energy highest occupied molecular orbital (HOMO; −15.6 eV) combined with the high energy lowest unoccupied molecular orbital (LUMO; 7.3 eV) disfavor electron transfer and Lewis acid-base reactions.[11,12] It is all of these intrinsic properties together that make N_2 unreactive. In fact, only one commercially successful process utilizes N_2 gas as a reagent.[13–15] The Haber–Bosch process involves the reaction of dinitrogen with three equivalents of H_2 gas over a promoted iron- or ruthenium-based catalyst to produce ammonia (Equation 1). This reaction is thermodynamically favorable under ambient conditions but high temperatures (400–550 °C) are required to give viable reaction rates and, as a result, the gases must be compressed to 100–300 atm to favor ammonia production. By providing a route to fixed nitrogen in the form of ammonia, used widely as fertilizer, Haber won the Nobel Prize in chemistry in 1918. Bosch developed the high-pressure techniques that made industrial ammonia synthesis feasible and was subsequently awarded the Nobel Prize in 1931.

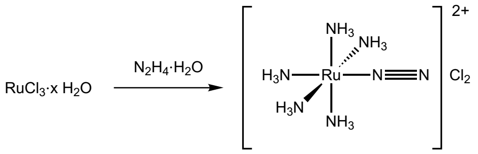
$$N_2\,(g) + 3\,H_2\,(g) \xrightarrow[\substack{100\text{–}300\text{ atm} \\ 400\text{–}550\ ^{\circ}\mathrm{C}}]{\text{metal catalyst}} 2\,NH_3\,(g) \qquad (1)$$

Michael Shaver was born in 1976 and is currently a Ph. D. candidate under Professor Michael D. Fryzuk at the University of British Columbia. He completed his B.Sc. (Hon.) at Mount Allison University under the supervision of Professor Stephen A. Westcott. He has been awarded NSERC Postgraduate Scholarships, the Killam Predoctoral Scholarship and the Li Tze Fong Fellowship to continue his studies. His research interests include transition metal catalysis, small molecule activation and novel organometallic research.

Michael Fryzuk completed his Ph. D. degree in 1978 at the University of Toronto under the direction of Professor Brice Bosnich; his thesis project involved the study of asymmetric hydrogenation using rhodium chiraphos and prophos catalyst precursors. He then spent one year as a National Research Council of Canada postdoctoral fellow in Professor John Bercaw's group at Caltech. In 1979 he accepted a position as assistant professor at the University of British Columbia, where he is currently professor of chemistry. From 1984 to 1987 he was a Fellow of the Alfred P. Sloan Foundation; in 1987 he was awarded an Alexander von Humboldt Fellowship. The University of British Columbia awarded him the Killam Research Prize in 1989. He has been the recipient of the Rutherford Medal in Chemistry (1990) awarded by the Royal Society of Canada and an E. W. R. Steacie Fellowship for 1990–92 awarded by the Natural Science and Engineering Research Council of Canada. In 1992 he was named the ALCAN Lecturer by the Canadian Society for Chemistry, and in that same year he was elected a Fellow of the Chemical Institute of Canada. In 1996, one of his published papers was given the Best Paper in Polyhedron Award. In 1997, Fryzuk was honored by being elected as a Fellow of the Royal Society of Canada. His research interests are in the activation of small molecules, particularly molecular nitrogen, by metal complexes.

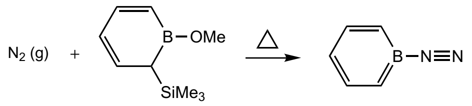
1.2 Coordination Chemistry of Dinitrogen

While the necessity of a transition metal-based catalyst in the Haber-Bosch system was known, it was not until 1965, with the synthesis of $[Ru(NH_3)_5N_2]^{2+}$, that interest in the coordination chemistry of dinitrogen to transition metals began (Equation 2).[16,17] While other systems including elemental lithium[18,19] under ambient conditions and thermolysis of borabenzene[20] have been shown to activate molecular nitrogen (Equations 3 and 4), complexes of the transition metals and lanthanide elements have dominated the field of dinitrogen coordination chemistry.



(2)

$$N_2\,(g) + 6\,Li\,(s) \xrightarrow[1\ atm]{25\ ^{o}C} 2\,Li_3N\,(s) \qquad (3)$$

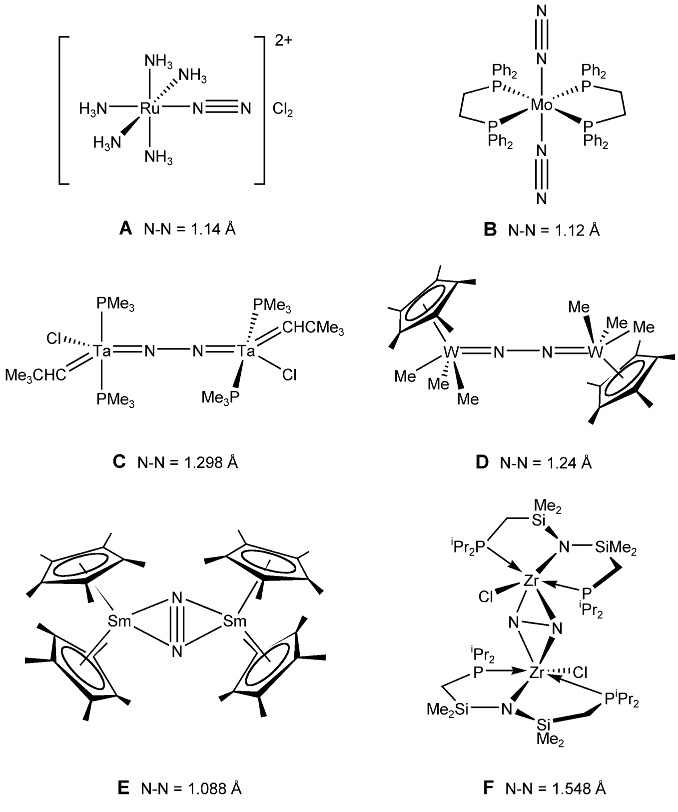


(4)

The Dewar–Chatt–Duncanson synergistic bonding model rationalizes the activation of a dinitrogen ligand in a transition metal complex. Simplistically, if dinitrogen is bound end-on to a single metal center, the filled N_2 non-bonding σ orbital forms a dative bond with empty metal d_{z2} or d_{x2-y2} orbitals. The filled d_{xz}, d_{yz}, or d_{xy} orbitals of the metal employ back-donation into the vacant π* of N_2, further stabilizing the metal-N_2 complex. This back-donation weakens the N–N bond, effectively activating the ligand towards further reactivity. Unfortunately, the stability of the N_2 lone pair, combined with the large HOMO-LUMO gap, minimizes overlap between metal and dinitrogen orbitals. As a consequence, dinitrogen is both a poor σ-donor and a poor π-acceptor, especially as compared to isoelectronic CO.

Strongly reducing early metals have the ability to activate coordinated dinitrogen further than synergistic bonding. By donating electrons into the N_2 unit, the dinitrogen bond order can be reduced; formalisms for reduction to an N=N double bond, $(N_2)^{2-}$, or an N–N single bond, $(N_2)^{4-}$, have been applied to describe many of these systems. These formalisms must not simply be taken at face value; while no controversies arise in mononuclear systems, in dinuclear dinitrogen complexes the situation is more complex. In many instances, an examination of the N–N bond length can correlate to the dinitrogen bond order and generally the greater the bond is lengthened from free N_2 (1.0975 Å), the greater the degree of dinitrogen activation. The infrared or Raman stretching frequency ν(N–N) is also often indicative of activation, with lower frequencies indicating longer N–N bonds. However, these experimental observations must be examined along with the formal oxidation state of the metal center; in many cases the results of these bond order determinations can be subject to interpretation. For instance, in the dinuclear dinitrogen alkylidene complex $\{Cl(PMe_3)_2 \cdot (CMe_3CH{=})Ta\}_2(\mu\text{-}N_2)$, **C**, the observed N–N bond length is 1.298 Å which is comparable to the N=N double bond in PhN=NPh (1.255 Å) and supports the presence of an $(N_2)^{2-}$ unit.[21] The complex, however, is better described as a diamagnetic Ta(V) species, which in turn implies the presence of an $(N_2)^{4-}$ unit. These controversies are usually limited to strongly activated dinuclear end-on bound dinitrogen complexes.

The metal complexes in Figure 2 illustrate three common bonding modes for the dinitrogen ligand. In general, dinitrogen bound in a terminal end-on fashion is not extensively activated as is shown in examples **A**[16,17] and **B**.[22] This terminal bonding mode is by far the most prevalent, especially in late metal chemistry. Greater activation can be achieved where dinitrogen bridges two metal centers. Back-donation also increases the basicity of the N–N unit; the donation from one metal renders it a better base to the second metal. Dinuclear end-on dinitrogen coordination is a particularly common mode for early transition metal dinitrogen complexes as the formation of strong multiple bonds to nitrogen ligands is facilitated by additional reduction from a second metal-nitrogen bond. This bonding mode is observed in examples **C**[21] and **D**.[23] The N–N bond lengths in complexes **C** and **D** are both similar to an N=N double bond. However, the presence of Ta(V) and W(VI) formal oxidation states respectively indicates $(N_2)^{4-}$ systems, and for this reason a single bond is drawn. The third common bonding mode is a side-on bound dinitrogen unit, as in structures **E**[24] and **F**.[25] In this bonding mode filled π-N_2 orbitals form an $M(\eta^2\text{-}N_2)M$ unit where one d orbital of σ-symmetry from each metal center interacts with the dinitrogen π system. This bonding mode is most commonly seen in dinuclear complexes of the early metals, and may be contingent on the lack of a second available d orbital appropriate for back-donation. Depending on available orbitals and steric congestion, activation can be quite weak, as in complex **E**, but extensive activation occurs in many of these systems; the exceedingly long N–N bond length of 1.548 Å in complex **F** is an example.



A N-N = 1.14 Å

B N-N = 1.12 Å

C N-N = 1.298 Å

D N-N = 1.24 Å

E N-N = 1.088 Å

F N-N = 1.548 Å

Figure 2. Examples of metal complexes exhibiting three different coordination modes for the dinitrogen ligand. The corresponding N–N bond lengths are given and show the breadth of activation that can be achieved with each bonding mode.

This review will focus on recent reports from the literature that document activation and functionalization of coordinated dinitrogen. In addition, studies that describe cleavage of the N-N bond will be presented.

2 Dinitrogen Activation

Much of the literature from the last decade on the coordination chemistry of dinitrogen has focused on the early transition metals, as they have the strongly reducing metal centers needed to provide highly activated systems.[1–9] Nevertheless, there are some recent reports on late metal systems, and it is useful to digress and examine some of these weakly activated dinitrogen complexes. For example, reduction of $[N_3N]ReCl$ ($[N_3N] = \{[(C_6F_5)NCH_2CH_2]_2NCH_2CH_2CH_2N(C_6F_5)\}$) with Na/Hg under an atmosphere of dinitrogen gives the mononuclear dinitrogen complex $[N_3N]Re(N_2)$.[26] The dinitrogen unit is only weakly activated; the N–N bond length of 1.087(4) Å corresponds to a triple bond, virtually identical to that of free N_2 (1.0976 Å).

The reaction of $CpRuCl(P)_2$ [$(P)_2$ = 1,2-bis(diisopropylphosphino)ethane (dippe), $(PEt_3)_2$, $(PMe^iPr_2)_2$] with $Na(BAr_4)$ [Ar = 3,5-bis(trifluoromethyl)phenyl] in fluorobenzene affords the dinitrogen complex $[CpRu(N_2)(P)_2][BAr_4]$. If dinitrogen is the limiting reagent, however, the dinitrogen-bridged complex $[\{CpRu(P)_2\}_2(\mu\text{-}N_2)][BAr_4]$ forms. The amount of dinitrogen available in the system determines whether the

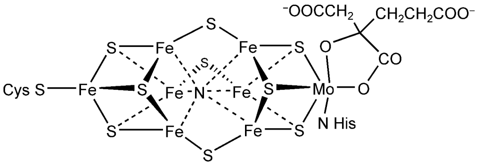


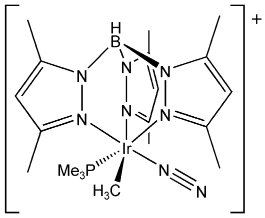
Figure 3. The metal-sulfido core (FeMo-cofactor) of the iron-molybdenum nitrogenase enzyme.

terminal or bridged ruthenium half-sandwich complexes form.[27] If the complex Cp*RuCl(dppm) is used instead of the Cp derivative, reactivity toward $NaBAr_4$ yields the cationic terminal dinitrogen complex $[Cp^*Ru(N_2)(dppm)][BAr_4]$ irrespective of the amount of molecular nitrogen.[28] The N_2 unit is bound more tightly and the generation of the bimetallic complex is much slower.

An interesting recent finding details the reaction of the acetonitrile complex $Ru(MeCN)(P^iPr_3)(N_2Me_2S_2)$ $[N_2Me_2S_2 = (SC_6H_4NMeCH_2)_2]$ with N_2 to form $Ru(N_2)(P^iPr_3)(N_2Me_2S_2)$.[29] The N_2 ligand binds end-on to the Ru center, and is not highly activated (1.110 Å). This finding is, however, important as it represents the first time dinitrogen has been bound to a metal thiolate core. The biological fixation of nitrogen takes place in nitrogenase enzymes that contain the FeMo-cofactor core.[30] This core has been crystallographically characterized[31,32] and, as is shown in Figure 3, contains an iron-sulfur motif in which molecular nitrogen is presumably converted to ammonia. Previous attempts at forming metal sulfide or metal thiolate dinitrogen complexes[33,34] were complicated by the formation of M–S–M bridges and oligo- or polynuclear complexes.[29] In the FeMo-cofactor, vacant binding sites are available due to steric strain and shielding from the surrounding enzyme.

The hydridotris(3,5-dimethylpyrazolyl)borate (Tp^{Me2}) iridium complex $(Tp^{Me2})(PMe_3)Ir(Me)OTf$ is isoelectronic with the iridium methyl complex, $Cp^*(PMe_3)Ir(Me)OTf$ ($Cp^* = C_5Me_5$; $OTf = OSO_2CF_3$), that has shown particular utility in C–H bond activation.[35] Exchange of the triflate leaving group for a more labile dinitrogen ligand, however, promoted the formation of the cationic iridium species thought to be responsible for C–H activation. The complex $(Tp^{Me2})(PMe_3)Ir(Me)N_2$, **G**, shows weak activation with a 1.095(6) Å N–N bond length. Of note, however, is that this complex represents the first structurally characterized example of a monomeric iridium dinitrogen complex (Figure 4).[36,37]

It is often beneficial that dinitrogen is a poor ligand. Dinitrogen can act as a dative ligand to stabilize a reactive metal fragment, as it stabilizes the cationic $[Tp^{Me2}(PMe_3)IrMe]^+$ fragment in the previous example. There are several recent examples where N_2 dissociation leads to enhanced reactivity. Reaction of the bridging-dinitrogen complex $Ru_2Cl_4(PP)_2(N_2)$ with phenyldiazomethane generates a benzylidene catalyst $RuCl_2(PP)(CHPh)$ $[PP = Cy_2P(CH_2)_4PCy_2]$ that is highly active in ring-opening metathesis polymerization (ROMP).[38] The dinuclear dinitrogen complex $\{RuCl_2(\eta^3\text{-}NN'N)\}_2(\mu\text{-}N_2)$ $\{NN'N = $ 2,6-bis[(dimethylamino)methyl]pyridine} also readily loses dinitrogen upon reaction with nitriles to form neutral or cationic ruthenium nitrile derivatives.[39]



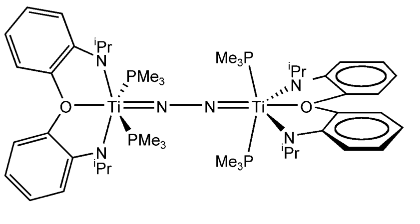
G N-N = 1.096 Å

Figure 4.

Early metals can have weakly activated dinitrogen ligands as well. The tantalum dinitrogen dimer $(Cp^*_2TaCl)_2(\mu\text{-}N_2)$ is prepared by reduction of Cp^*TaCl_2 with Na/Hg amalgam. This complex loses dinitrogen upon exposure to H_2 yielding $Cp^*_2TaH_2Cl$ isomers that were identified by *para*-hydrogen-induced polarization studies.[40] The complex *trans*-$[Mo(N_2)_2(dppe)_2]$ ($dppe = Ph_2PCH_2CH_2PPh_2$) can bind and activate such diverse substrates as *N*,*N*-dimethylformamide (dmf), nitriles, imines, isocyanides and alkynes[41] upon loss of N_2 as described in a recent review.[42]

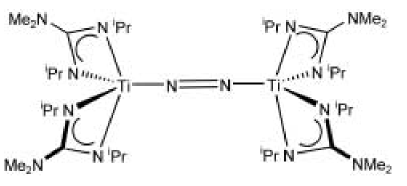
Of course, dinitrogen does not always dissociate so easily. An increase in activation is concomitant with a lengthening of the N–N bond and usually reduces the tendency for N_2 to dissociate. For example, decomposition of $[^iPr\text{-}NON]Ti(CH_2CHMe_2)_2$ in the presence of PMe_3 under dinitrogen affords the bridging dinitrogen complex $\{[^iPr\text{-}NON]Ti(PMe_3)_2\}_2(\mu\text{-}N_2)$, **H** (Figure 5), where $[^iPr\text{-}NON] = (^iPrN\text{-}o\text{-}C_6H_4)_2O$. This complex is similar to other titanium dinitrogen complexes with nitrogen-based ligands in that the N_2 unit is formally reduced to a hydrazido^{4-} moiety, although the N–N bond length is only 1.264(8) Å.[43] A similar titanium complex supported by guanidinate ligands has been prepared. The dinitrogen complex, $\{[(Me_2N)C(N^iPr)_2]_2Ti\}_2(N_2)$, **I** (Figure 6), is synthesized by reduction of the dichloride precursor, $[(Me_2N)C(N^iPr)_2]TiCl_2$. In this case, the N–N bond length and the paramagnetism of the complex support reduction to an $(N_2)^{2-}$ diazenido unit. The dinitrogen unit is still somewhat labile; it reacts with phenyl azide to give a titanium imido complex, pyridine *N*-oxide to give a bridging oxo complex and propylene sulfide to afford a bridging sulfido titanium dimer, all *via* loss of N_2.[44]

The paramagnetic $[Cp'''_2Zr]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}N_2)$ complex $[Cp''' = 1,3\text{-}(Me_3Si)C_5H_3^-]$ was recently reported. An N–N bond distance of 1.47(3) Å is observed.[45] Reaction of N_2 with a destabilized cyclometalated zirconocene hydride, produced from the elimination of $HCMe_3$ from



H N-N = 1.265 Å

Figure 5.

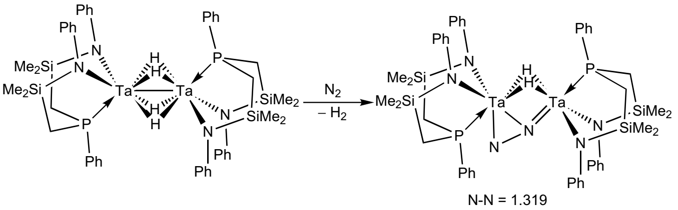


I N-N = 1.281 Å

Figure 6.

$Cp'''_2Zr(H)(CMe_3)$, gives the resultant complex. Strangely, the paramagnetism of the resultant complex implies an $(N_2)^{3-}$ unit, but this is not supported by requisite magnetics studies.

While all of the compounds discussed so far have shown either side-on or end-on bound dinitrogen, there are examples of a third type of coordination mode. The 'side-on end-on' coordination mode for the N_2 unit is observed in the complex $([NPN]Ta)_2(\mu\text{-}H)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}N_2)$ $\{[NPN] = (PhNSiMe_2CH_2)_2PPh\}$.[46] The tetrahydride $([NPN]Ta)_2(\mu\text{-}H)_4$ reacts under N_2 to form the symmetrically bonded dinitrogen complex. It is interesting that the generation of the complex does not require strong reducing agents as is characteristic of the preparation of many dinitrogen complexes. Rather, electrons from the reductive elimination of H_2 and the Ta–Ta bond present in the tetrahydride precursor provide the reducing power needed to activate N_2. While the end-on binding mode predominates for related group 5 systems, it is thought that the bridging hydrides make the asymmetric bonding mode energetically and sterically favorable. This is supported by the reaction of $([NPN]Ta)_2(\mu\text{-}H)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}N_2)$ with propene to generate $\{[NPN]Ta(CH_2CH_2CH_3)\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$, which has a symmetrically end-on bound dinitrogen fragment. As well, the isoelectronic complex $([NPN]NbCl)_2(\mu\text{-}N_2)$ was synthesized and also contains no bridging ligands and no asymmetric bonding mode.[47] This chemistry is summarized in Equations 5, 6 and 7. Similar bonding modes have been observed for the isoelectronic CO, NO^+ and CN^- ligands in bimetallic systems.[48–51] Related binding modes for N_2 have been found in polymetallic complexes of Ni with Li[52], and Co with K[53] and a trinuclear titanocene system.[54]



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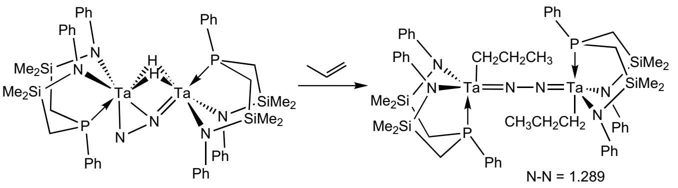

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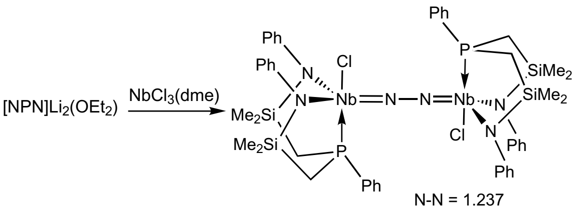

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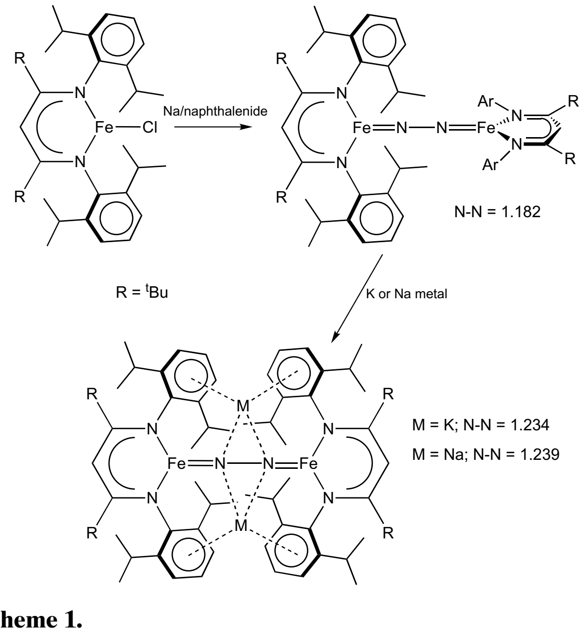
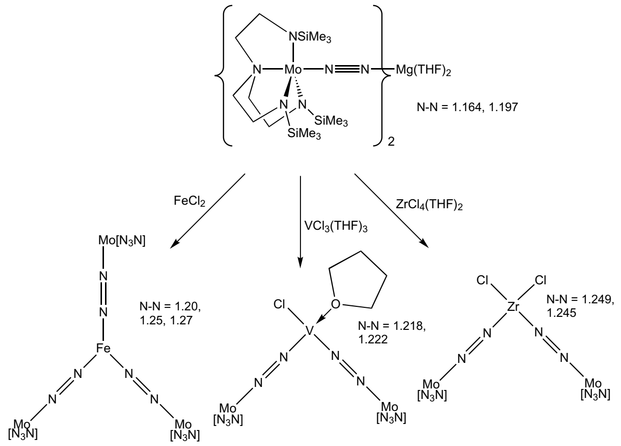
Another interesting study in activation utilizes a low-coordinate iron complex to promote the reduction of the dinitrogen bond. Using the β-diketiminato ligands as shown in Scheme 1, the complexes LFeNNFeL $[L = (\{2,6\text{-}(CH_3CHCH_3)C_6H_3\}NC(CMe_3)_2CH_2]$, K_2-[LFeNNFeL] and Na_2[LFeNNFeL] can be prepared *via* reduction of LFeCl. The N–N bond lengths for these



Scheme 1.



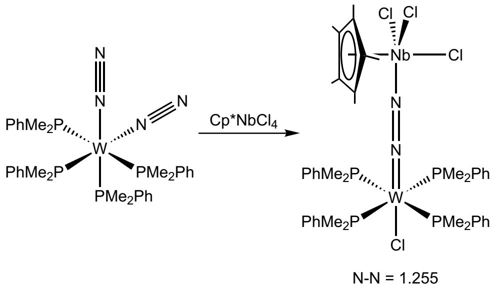
Scheme 2.

systems are 1.182(5) Å, 1.233(6) Å, and 1.239(4) Å respectively.[55] This is the first well-characterized example of an iron system in which there is lengthening of the N–N bond to such an extent.

There have also been recent advances in developing heterobimetallic complexes that contain activated dinitrogen. The magnesium-molybdenum dinitrogen complex $\{[N_3N]Mo(N_2)\}_2Mg(THF)_2$ $\{[N_3N] = (Me_3SiNCH_2CH_2)_3N\}$ can be used to prepare several other heterobimetallic dinitrogen complexes. Reaction of $\{[N_3N]Mo(N_2)\}_2Mg(THF)_2$ with $FeCl_2$ gives the trigonal planar $\{[N_3N]Mo(N{=}N)\}_3Fe$. Similarly, the complexes $\{[N_3N]Mo(N_2)\}_2VCl(THF)$ and $\{[N_3N]Mo(N_2)\}_2ZrCl_2$ are prepared by reaction with $VCl_3(THF)_3$ and $ZrCl_4(THF)_2$, respectively (Scheme 2). These complexes can be considered to have $\{[N_3N]Mo(N_2)\}^-$ units replacing the halide ligands.[56]

Treatment of Fe(por)(OTf) [por = octaethylporphyrinate, tetra(*p*-tolyl)porphyrinate] with $Re(N_2)\cdot(PMe_2Ph)_4Cl$ led to the heterobimetallic dinitrogen complex $[(por)Fe(N_2)Re(PMe_2Ph)_4Cl][OTf]$.[57] The bonding in this complex is similar to the previously published $(MeO)Cl_4Mo(N_2)Re(PMe_2Ph)_4Cl$;[58] the dinitrogen bond lengthens to 1.17 Å upon coordination to iron. Similarly, the reaction of Cr(por)(OTf) with $Re(N_2)(PMe_2Ph)_4Cl$ affords $[(por)Cr(N_2)Re(PMe_2Ph)_4Cl]$ [OTf]. These are the first heterometallic bridged dinitrogen complexes of iron(III) and chromium(III) porphyrins.

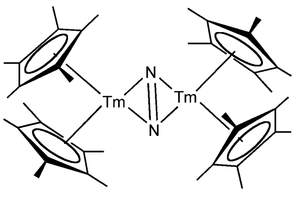
Reaction of the tungsten or molybdenum dinitrogen complexes *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ and *trans*-$[M(N_2)_2(dppe)_2]$ with $CpTiCl_3$, Cp_2MCl_2 (M = Ti, Zr, Hf), or Cp^*MCl_4 (M = Nb, Ta) yields numerous heterobimetallic dinitrogen complexes with cyclopentadienyl coligands. Crystal structures of $WCl(PMe_2Ph)_4(\mu\text{-}N_2)TiCpCl_2$ and $WCl(PMe_2Ph)_4(\mu\text{-}N_2)NbCpCl_3$ show M=N=N–M′ cores with N–N bonds activated compared to the terminally bonded systems. While most linkages were essentially linear, canting of the M–N=N–M′ bonds was observed in some systems. As well, dinitrogen methyl complexes were prepared from the above terminal dinitrogen complex reacting with $Cp_2ZrMeCl$, $TaMe_3Cl_2$ and $NbMe_2Cl_3$ forming $WCl(PMe_2Ph)_4(\mu\text{-}N_2)ZrCp_2Me$, $WCl(PMe_2Ph)_4(\mu\text{-}N_2)TaClMe_3$ and $WCl(PMe_2Ph)_4(\mu\text{-}N_2)NbCl_2Me_2$, respectively. Some of these systems could be protonated with inorganic acids to form hydrazine or ammonia. An example of these reactions, the synthesis of $WCl(PMe_2Ph)_4(\mu\text{-}N_2)NbCpCl_3$, is shown in Equation 8.[59]



(8)

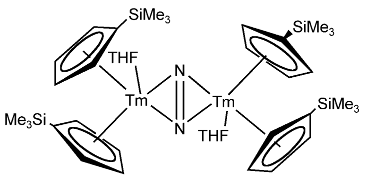
The emergence of numerous lanthanide and actinide dinitrogen complexes with reduced N–N bond orders has piqued interest in this area. For example, TmI_2, prepared directly from Tm and I_2, reacts with KC_5Me_5 in Et_2O under nitrogen to form $[(C_5Me_5)_2Tm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, **J** (Figure 7), in low yields. The complex contains side-on bound dinitrogen in a coplanar array with the two thulium centers. Control of the reaction can be improved by changing KC_5Me_5 with $KC_5H_3(SiMe_3)_2$. If the reaction is conducted with the monosubstituted silylcyclopentadienyl derivative, $KC_5H_4(SiMe_3)$, the resulting complex is not decomposed by THF, as in the previous cases, and the complex $\{[C_5H_4(SiMe_3)]_2Tm(THF)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, **K** (Figure 8), forms. The N–N bond lengths in these systems, 1.259(4) and 1.236(8) Å, respectively, indicate moderate activation.[60] An analogous product forms upon reaction of DyI_2 with $KC_5H_3(SiMe_3)_2$ under an atmosphere of dinitrogen, namely the complex $\{[C_5H_3(SiMe_3)_2]_2Dy\}_2(\mu\text{-}N_2)$, **L** (Figure 9). Preliminary crystallographic studies show a similar planar core to **J** and **K**, but the structure could not be refined.[61]

A new study details the preparation of amido and aryl oxide supported lanthanide dinitrogen complexes.[62]



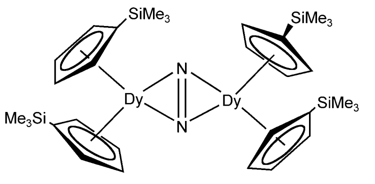
J N-N = 1.259 Å

Figure 7.



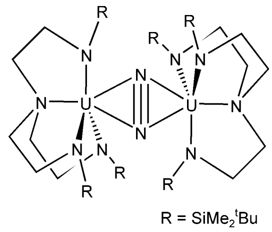
K N-N = 1.236 Å

Figure 8.



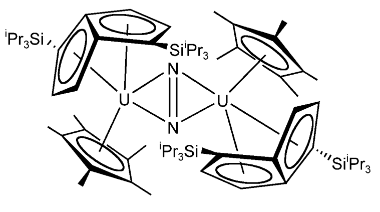
L

Figure 9.



M N-N = 1.109 Å

Figure 10.



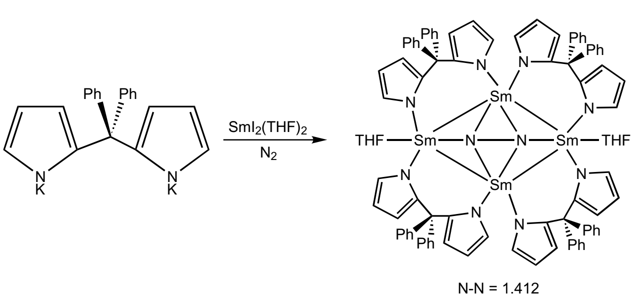
N N-N = 1.232 Å

Figure 11.

The synthesis of $\{[(Me_3Si)_2N]_2(THF)Tm\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ and $\{[(Me_3Si)_2N]_2(THF)Dy\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ was accomplished *via* addition of $NaN(SiMe_3)_2$ to $TmI_2(THF)_3$ and DyI_2, respectively. X-ray crystallography revealed the two complexes are isomorphous. The N-N distances are 1.264(7) Å and 1.305(6) Å, respectively, supporting the presence of an $(N_2)^{2-}$ moiety. Similarly, addition of $KOC_6H_3{}^tBu_2$ to NdI_2 gives $[({}^tBu_2C_6H_3O)_2(THF)Nd]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, with an N-N distance of 1.242(7) Å. The extensive dinitrogen chemistry with the strongly reducing Tm(II), Dy(II) and Nd(II) consistently supports the activation of dinitrogen to $(N_2)^{2-}$.

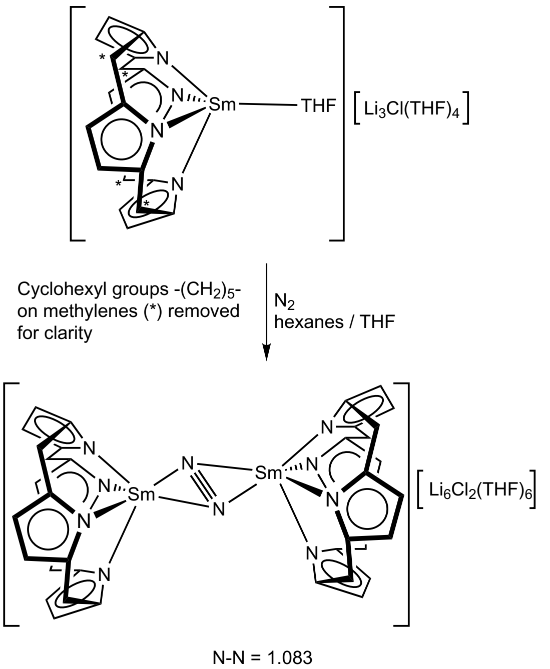
The synthesis of $\{U(NN'_3)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **M** **(**Figure 10), was accomplished simply by storing $U(NN'_3)$ $[NN'_3 = N(CH_2CH_2NSiMe_2{}^tBu)_3]$ under dinitrogen. Consistent with weak activation, ordination of N_2 is a reversible process in this system, and the molecule has a side-on $U(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)U$ core supported by π-back donation, but lacking significant dative N_2 to metal bonding, as supported by molecular orbital calculations. The bulky triamidoamine ligands prevent optimum overlap for N_2 activation so the N–N distance does not lengthen significantly from free N_2 and dinitrogen coordination is reversible.[63] A recent paper shows that uranium systems do have the potential to activate N_2 to a greater extent. The reaction of UI_3 with KCp* followed by $K_2[C_8H_4\{Si^iPr_3\text{-}1,4\}_2]$ affords $U(Cp^*)(\eta^8\text{-}C_8H_4\{Si^iPr_3\text{-}1,4\}_2)$. Under N_2, this complex coordinates and activates dinitrogen to form $\{U(\eta\text{-}Cp^*)(\eta\text{-}C_8H_4\{Si^iPr_3\text{-}1,4\}_2)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$, **N** (Figure 11). This complex exhibits an N–N bond length of 1.232 Å, showing significant activation compared to the N–N bond length in $\{U(NN'_3)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ of 1.109 Å.[64] This difference is surprising considering these two uranium dinitrogen complexes are isoelectronic, and shows how small structural changes can greatly affect dinitrogen coordination.

The most extensive lanthanide dinitrogen chemistry is that with samarium; these reactions continue to spur novel dinitrogen activation research. Samarium is able to accomplish a four electron dinitrogen reduction through the cooperative one electron oxidation of four metal centers. The reaction of $SmI_2(THF)_2$ with $K_2[Ph_2C(C_4H_3N)_2]$ yields $\{[\mu\text{-}Ph_2C(\eta^1\text{:}\eta^5\text{-}C_4H_3N)_2]Sm\}_4(\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}N_2)$ (Equation 9). The complex is composed of four $[Ph_2C(C_4H_3N)_2]Sm$ units arranged around a dinitrogen unit coordinated side-on to two samarium centers and end-on to the remaining samarium atoms. The N–N bond length of 1.412(17) Å is evident of extensive activation.[65] Performing the analogous reduction with the cyclohexyldipyrrolide dianion $[(CH_2)_5C(C_4H_3N)_2]^{2-}$ with Na in THF gives a similar dinitrogen complex, $\{[(CH_2)_5C(C_4H_3N)_2]Sm\}_4\cdot(THF)_2(\mu\text{-}N_2)[Na(THF)]_2\cdot 2\,THF$.[66] Reduction of the tetranuclear dinitrogen cluster $\{[1,1\text{-}(H_5C_3)_2(C_4H_3N)_2]\cdot Sm_4(THF)_2\}(\mu\text{-}N_2)$ with Na sand affords the linear polymeric divalent Sm complex $\{[1,1\text{-}(H_5C_3)_2(C_4H_3N)_2]_2\cdot Sm[Na(THF)]_2\}_n$. This reaction proceeds presumably through a tetranuclear intermediate and then loses two "Sm-N" units to create the polymeric structure.[67]



(9)

By using a divalent calix-tetrapyrrole samarium complex, $\{[(CH_2)_5]_4$-calix-tetrapyrrole$\}Sm(THF)[Li(THF)]_2$-$[Li(THF)_2](\mu\text{-}Cl)$, the dinitrogen complex $[\{[(CH_2)_5]_4$-calix-tetrapyrrole$\}Sm[Li(THF)]_3(\mu\text{-}Cl)]_2(\mu\text{-}N_2)\cdot 2THF$ is obtained, as shown in Equation 10. Further addition of calix-tetrapyrrole samarium complex produces a four-electron reduction of the coordinated dinitrogen, forming $[\{[(CH_2)_5]_4$-calix-tetrapyrrole$\}_2Sm_3Li_2](\mu N_2)$-$[Li(THF)_2]\cdot THF$.[68]



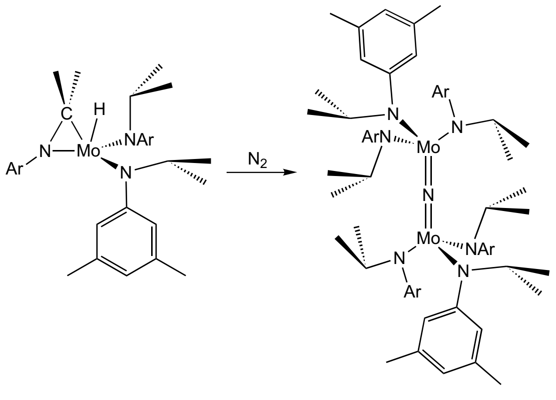
(10)

The breadth of these examples of dinitrogen activation shows a wide array of synthetically feasible metal dinitrogen complexes. Recent findings like the first metal thiolate dinitrogen complex, the side-on end-on coordination mode for molecular nitrogen, and the increasing number of heterobimetallic and lanthanide dinitrogen complexes show continuing advances in synthesizing dinitrogen complexes. Unfortunately, these examples are not based on activation for a purpose and merely represent a kind of trophy-collecting. A more important goal is the transformation of coordinated dinitrogen. This does not simply involve coordination of N_2, but implies the need for chemical change within the bound dinitrogen fragment. Activation of the N–N bond is the first step towards utilizing the abundant N_2 feedstock. The biological or industrial conversion of N_2 to ammonia requires the eventual cleavage of dinitrogen, but the coordination and activation of dinitrogen represents the preliminary step.

3 Dinitrogen Cleavage

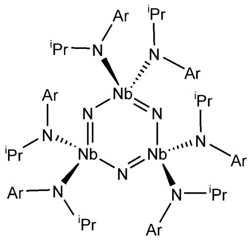
A particularly important study of the N_2 cleavage process by transition metals was provided by the serendipitous observation that the coordinatively unsaturated molybdenum complex $Mo[N(R)Ar]_3$ [$R = C(CD_3)_2CH_3$; $Ar = 3,5\text{-}C_6H_3Me_2$] activates the dinitrogen triple bond and eventually cleaves it. The reaction proceeds through a dinuclear end-on bridged N_2 intermediate $\{[N(R)Ar]_3Mo\}_2(\mu\text{-}N_2)$ at −35 °C and upon warming this product decomposes to the terminal nitride $Mo(\equiv N)[N(R)Ar]_3$.[69,70] Since this discovery, numerous other dinitrogen cleavage reactions have been reported. An isoelectronic vanadium system with a diamidoamine ligand set[71] and a niobium calixarene reduced with sodium[72,73] both support N–N bond cleavage reactions.

When preparation of the *N*-isopropylanilide derivative of $Mo[N(R)Ar]_3$ is attempted, the cyclometalated species $Mo(H)(\eta^2\text{-}Me_2C{=}NAr)(N[^iPr]Ar)_2$ forms, as shown in Equation 11. The reaction of this complex with dinitrogen gives the nitrido-bridged dimolybdenum complex $(\mu\text{-}N)[Mo(N[^iPr]Ar)_3]_2$ where the hydrido ligand has migrated back to carbon. Most likely, the formation of the terminal nitrido complex observed for the *tert*-butyl derivative is slow compared to combination with a second cyclometalated species to form the linear Mo=N=Mo core.[74]



(11)

As well, this $Mo[N(R)Ar]_3$ system can work in cooperation with niobium to afford N_2-scission. The niobium chloride $NbCl(N[^iPr]Ar)_3$ reacts with $Mg(THF)_2[N_2Mo(N[^tBu]Ar)_3]_2$ to form the dinitrogen bridged species $(N[^tBu]Ar)_3Mo{=}N{=}N{=}Nb(N[^iPr]Ar)_3$. This species does not spontaneously decompose to form the requisite Mo and Nb nitrides, but upon addition of KC_8 and the cation coordinator cryptand-222 liberates the niobium nitride $[K(cryptand\text{-}222)][N{\equiv}Nb(N[^iPr]Ar)_3]$. Interestingly, the addition of I_2 unexpectedly forms the niobazene trimer $\{(\mu\text{-}N)Nb(N[^iPr]Ar)_2\}_3$, **O** (Figure 12).[75]

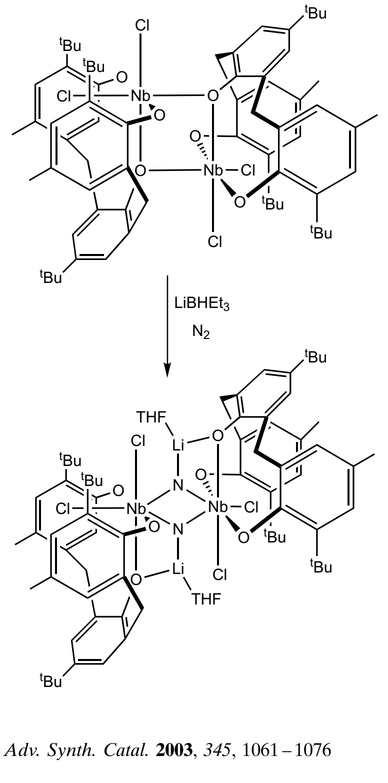


O

Figure 12.

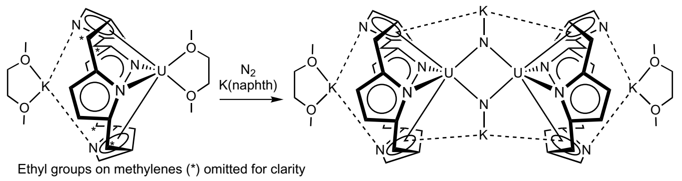
A molybdenum species isoelectronic to the tris(amido) molybdenum complex that is supported instead by three mesityl ligands has been reported. The complex $(Mes)_3Mo{=}N{=}N{=}Mo(Mes)_3$, formed from reaction of $MoCl_4 \cdot DME$ (DME = dimethoxyethane) and four equivalents of MesMgBr under N_2, is thermally stable unlike the triamido derivative. However, when exposed to UV light, $(Mes)_3Mo{=}N{=}N{=}Mo(Mes)_3$ splits dinitrogen and forms the bridging nitride complex $(Mes)_3Mo{=}N{=}Mo(Mes)_3$. This complex is presumably formed when the initially produced terminal molybdenum nitride attacks a bridged N_2 complex.[76]

A niobium complex supported by triaryl oxide ligands also displays the ability to split dinitrogen. Addition of an excess of $LiBHEt_3$ to $\{Nb(^tBu\text{-}L)Cl_2\}_2$ (Bu-L as shown in Equation 12) under N_2 gave $\{Nb(^tBu\text{-}L)(\mu\text{-}N) \cdot Li(THF)\}_2$.[77] It is suspected that the reaction proceeds through an $Nb^{III}(\mu\text{-}H)_2Nb^{III}$ dimer that binds and cleaves N_2 with the reductive elimination of H_2, a process known to generate dinitrogen complexes.[46,47,78,79]



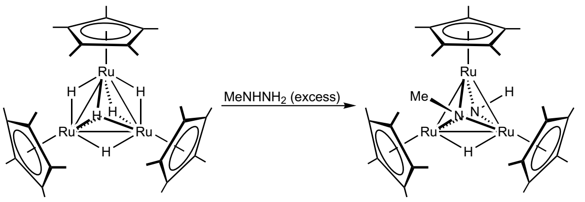
(12)

The first example of a lanthanide metal induced N–N bond scission was reported recently. The reaction of $UI_3(dme)_2$ with $K_4(Et_8\text{-calix-[4]-tetrapyrrole})$ ligand produces $[(Et_8\text{-calix[4]tetrapyrrole})U(dme)][K(dme)]$. Reduction of this complex with potassium naphthalenide under a nitrogen atmosphere affords the dinuclear μ-nitrido complex, $[\{K(dme)(calix[4]tetrapyrrole)U\}_2(\mu\text{-}NK)_2][K(dme)_4]$. This chemistry is shown in Equation 13.[80]



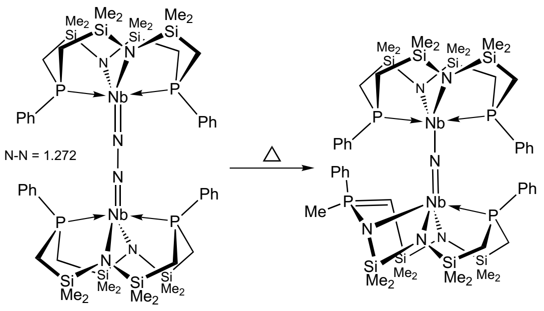
(13)

While not an example of dinitrogen conversion, nitrogen-nitrogen bond cleavage of hydrazine derivatives by a trinuclear pentahydride complex of ruthenium was recently reported. $(Cp^*Ru)_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ reacts with monosubstituted hydrazines $RHN\text{-}NH_2$ (R = Ph, Me) to give $(Cp^*Ru)_3(\mu_3\text{-}NR)(\mu_3\text{-}NH)(\mu\text{-}H)$, where the hydrazine bond has split and formed two bridging imido units, as shown in Equation 14. This complex indicates that polyhydride complexes can affect nitrogen cleavage; they offer reducing power *via* the reductive elimination of H_2.[81]

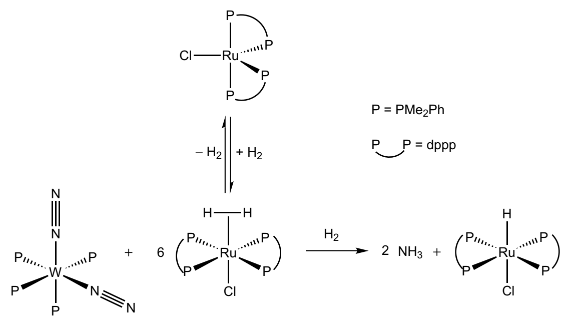


(14)

The final example of dinitrogen bond cleavage again employs a niobium based system. Reduction of $[P_2N_2]NbCl$ {where $[P_2N_2] = PhP(CH_2SiMe_2NSiMe_2 \cdot CH_2)_2PPh$} with KC_8 under a dinitrogen atmosphere generates the paramagnetic dinuclear dinitrogen complex $([P_2N_2]Nb)_2(\mu\text{-}N_2)$. Interestingly, thermolysis of this complex in toluene generates a bridging nitride species where one N atom from the activated N_2 inserts into the macrocycle backbone, forming the complex $[P_2N_2]Nb(\mu\text{-}N)Nb[PN_3]$ {where $[PN_3] = PhPMe(CHSiMe_2NSiMe_2CH_2P(Ph)CH_2SiMe_2NSiMe_2N)$}.[82] In this example, shown in Equation 15, N_2 has not only been cleaved, but also functionalized *via* incorporation into the macrocyclic ring. The formation of new N–P and N–Si bonds degrades the ligand, but shows that functionalization of coordinated nitrogen is possible in these cleavage processes.



(15)



Scheme 3.

The problem with developing a viable process coupling nitride formation with the production of useful nitrogen-containing materials is the inherent stability of the metal nitrides generated. Reactions of nitrides employ harsh reagents to affect moderate changes. In fact, in designing a catalytic cycle one must be careful not to employ activation by metal systems to too great an extent. If two metal centers reduce a dinitrogen fragment by three electrons each, converting $N \equiv N$ to 2 N^{3-}, these metals must be subsequently reduced themselves to close a catalytic cycle; an external source of reducing electrons is preferable.

4 Reactivity of Coordinated Dinitrogen

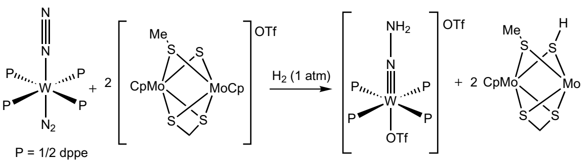
4.1 Formation of N–H Bonds from Coordinated Dinitrogen

If the synthesis of dinitrogen compounds is an arduous task, then finding controlled reactivities of the N_2 unit is even more challenging. By far the most studied reaction of activated N_2 involves protonation. Studies have focused on this reactivity because of the desire to mimic biological nitrogen fixation and to find a less energy intensive industrial synthesis for ammonia,[1,8] but the scope of these reactions is limited; only NH_3, N_2H_4 and free N_2 products can be produced. Many molybdenum N_2 complexes are easy to protonate. Compounds of the type $M(N_2)_2(PR_3)_4$ (M = Mo, W; $PR_3 = PMe_2Ph$, $PMePh_2$) can yield up to two equivalents of ammonia upon addition of acid. Even with intensive research in the past thirty years in this area, no well-defined homogeneous catalyst capable of the reduction and protonation of dinitrogen to ammonia has been found.[83–86] *Note added in proof*: A mononuclear molybdenum complex has been shown to catalytically convert N_2 to NH_3 (8 turnovers); see D. V. Yandulov and R. R. Schrock, *Science* **2003**, *301, 76.*

These N–H bonds can be produced through various routes. Often inorganic acids such as HCl or H_2SO_4 are added to group 6 dinitrogen complexes to afford N–H bonds. Acidic metal carbonyl hydrides such as $HCo \cdot (CO)_4$ prepared from $Co_2(CO)_8$ and H_2 can affect N–H bond formation on N_2 units coordinated to tungsten.[87] The cationic ruthenium complex $[CpRu(\eta^2\text{-}H_2) \cdot (dtfpe)][BF_4]$ {dtfpe = 1,2-bis[bis(4-trifluoromethylphenyl)phosphino]ethane} also protonates the activated N_2 in $W(N_2)_2(dppe)_2$, forming the requisite hydrazido complex.[88] Coordinated N_2 is transformed into ammonia by the action of hydrosulfido-bridged dinuclear iridium and iron complexes, which may mimic the protonation reactions in the metal-sulfido core of the nitrogenase enzyme.[89] In a rare case, N–H bonds can form by addition of H_2. The dinuclear zirconium complex $\{[P_2N_2]Zr\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ generates $\{[P_2N_2]Zr\}_2 \cdot (\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^2\text{-}NNH)$ upon exposure to H_2.[90,91] These protonation reactions have been discussed previously.[1,3]

Several new examples of protonation of metal N_2 complexes have arisen. The highly acidic $[RuCl(\eta^2\text{-}H_2)(dppp)_2][PF_6]$ [dppp = 1,3-bis(diphenylphosphino)propane] reacts stoichiometrically with *cis*-$W(N_2)_2(PMe_2Ph)_4$ to produce ammonia (Scheme 3). Yields of ammonia depend heavily on the geometry and electronics of the tungsten complex and the acidity of the ruthenium hydride used, and the reaction is by no means catalytic; the second hydride remains on ruthenium and is not transferred to nitrogen.[92,93]

The reaction of related tungsten complexes with sulfido-bridged dimolybdenum complexes under H_2 has been recently reported.[94] The bis(dinitrogen) complex *trans*-$W(N_2)_2(dppe)_2$ [dppe = 1,2-bis(diphenylphosphino)ethane] reacts with two equivalents of $[Cp'Mo(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SR)MoCp'][OTf]$ (Cp′ = C_5H_5, C_5H_4Me; R = H, Me; OTf = OSO_2CF_3) under H_2 to produce the hydrazido complex *trans*-$[W(OTf)(NNH_2)(dppe)_2]OTf$ and $Cp'Mo(\mu\text{-}S_2CH_2)(\mu\text{-}SH)(\mu\text{-}SR)MoCp'$. The heterolytic cleavage of H_2 occurs on the molybdenum sulfido complex, where one H atom is used for the N–H bond formation and the other H atom remains at the bridging sulfido ligand. Interestingly, if the complex *cis*-$W(N_2)_2(PMe_2Ph)_4$ is used with a large excess of the sulfido reagent and excess H_2, low yields of ammonia can be detected. If the hydrazido complex *cis*-$W(NNH_2)(OTf)(PMe_2Ph)_4$ is prepared prior to reaction, ammonia yields can be near quantitative. This chemistry is shown in Equations 16 and 17.



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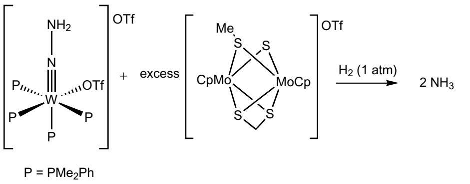

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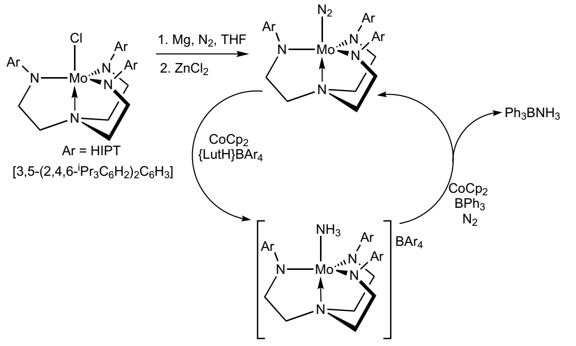


Scheme 4.

A comprehensive study of molybdenum and tungsten dinitrogen complexes with *trans* nitrile ligands was recently published.[95] This work complements previous studies on reduction pathways in Mo/W N_2, NNH, and NNH_2 complexes. DFT calculations on model systems $Mo(N_2)_2(dppe)_2$, $MoF(NNH)(dppe)_2$ and $[MoF(NNH_2)(dppe)_2]^+$ [dppe = 1,2-bis(diphenylphosphino)ethane], combined with observed vibration frequencies and force constants elucidated mechanistic details of dinitrogen protonation.[96,97] While many *cis* derivatives of molybdenum and tungsten dinitrogen complexes have shown higher activity than their *trans* analogues, the *trans* nitrile derivatives retain the *trans* ligand upon protonation to the corresponding NNH_2 complex and improve activity. The bis(dinitrogen) complexes exchange the second N_2 ligand with the counter-ion of the acid used for protonation. The new work reports the structure of $W(N_2)(NCEt)(dppe)_2$, the first tungsten dinitrogen nitrile complex having a P_4 ligand set, along with electronic, vibrational and DFT calculations on this and related complexes.[95] In these systems, the N_2 ligand is activated to a higher degree than the corresponding bis(dinitrogen) systems, making the first protonation step more facile. Further addition of protons is more difficult because the $N{-}NH_2$ ligand is less activated; in addition, the nitrile ligand becomes labile at this stage and this prevents formation of NH_3.

The V(II) pyrocatechol complexes first described in 1976 have the unique property of reducing nitrogen to ammonia in homogeneous protic media like water or alcohol.[98] In the polynuclear complex, several metals assist in activation and support the protonation of dinitrogen, however the mechanism of this process, specifically the number of vanadium ions in the polynuclear active center was unclear. A new report uses structural data on related systems and hyperfine EPR studies to show that a V_4 catechol unit is a possible active site for ammonia production.[99]

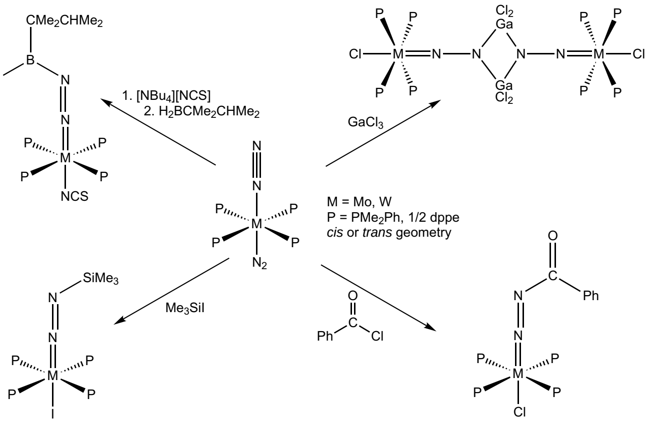
Finally, a new molybdenum system capable of affecting the conversion of dinitrogen into ammonia was reported.[100] The highly sterically encumbered molybdenum triamidoamine complex [HIPTN$_3$N]MoCl {[HIPTN$_3$N] = $[(HIPTNCH_2CH_2)_3N]^{3-}$; HIPT = hexaisopropylterphenyl; 3,5-(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$} can perform a diverse set of transformations. Reaction with NH_3 and $NaBR_4$ gives the corresponding cationic ammonia complex; reaction with TMS-N_3 affords the corresponding molybdenum nitride. This nitride can be reduced to the Mo=N−H imide by action of $HBAr_4$. If, however, cobaltocene is the chosen reductant, and {2,6-lutidinium}BAr_4 the proton source [[HIPTN$_3$N]-Mo(NH$_3$)]BAr$_4$ is produced. Addition of three equivalents of $CoCp_2$ and BPh_3 reforms the N_2 complex. These transformations are shown in Scheme 4.

The Haber–Bosch process is unlikely to be replaced. When Bosch converted Haber's bench-top ammonia synthesis to an industrial scale, great capital costs were incurred, but now that the infrastructure is in place, production of ammonia is relatively inexpensive. While a catalytic cycle that could bypass the high pressures and high temperatures required by this process would be beneficial, transforming dinitrogen into more valuable materials is more likely to find widespread applicability.

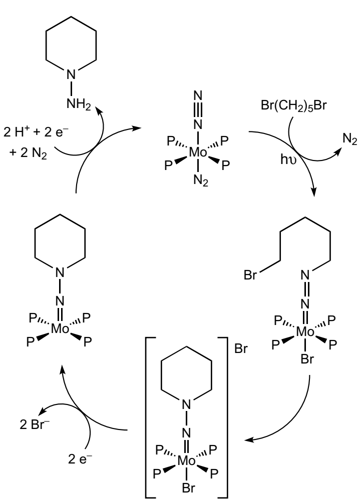
4.2 Formation of N−Element Bonds from Coordinated Dinitrogen

Development of a process to cheaply prepare high-value-added nitrogenous compounds directly from molecular nitrogen has become the 'holy grail' of modern dinitrogen activation research,[101] and thus many studies are examining the basic reactivity of activated dinitrogen. In the above protonation reactions, each proton source (inorganic acids, metal hydrides, metal thiols, protic media) can be thought of as an electrophile attacking the nucleophilic N_2 unit. In mononuclear end-on bound systems, polarization of the N_2 fragment induces nucleophilicity; in the corresponding dinuclear systems, the reduced $(N_2)^{2-}$ or $(N_2)^{4-}$ systems are inherently nucleophilic.

Many other electrophiles can react with coordinated N_2 such as RBH_2, $GaCl_3$, or $AlCl_3$ yielding new N−B,[102] N−Ga,[103] or N−Al[104] bonds. Nitrogen-carbon bond



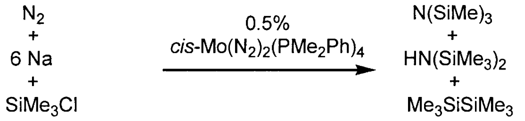
Scheme 5.



Scheme 6.

forming reactions are also known. Reaction of terminal tungsten dinitrogen systems with acyl chlorides or alkyl chlorides, for example, form N–C bonds.[105,106] These same systems can react with silyl iodides to afford silyldiazenido complexes.[107] Germyldiazenido complexes can be formed in much the same way.[108] This early reactivity is summarized in Scheme 5. Again, these reactions and others have been previously reviewed in several publications.[1,3]

It was mentioned that Si–N bonds could be generated by the action of silyl iodides on terminal N_2 molybdenum and tungsten complexes. This process can be made catalytic, albeit with low efficiency and low turnover numbers, by employing Me_3SiCl with an equimolar quantity of sodium metal under an atmosphere of N_2 with 5 mol % of a molybdenum dinitrogen complex, as shown in Equation 18.[109] Unfortunately, the harsh reagents required to facilitate this reaction are incompatible with one another; metallic sodium will react preferentially with Me_3SiCl to effect Si–Si bond formation. While the optimum yield for this reaction is only 37% relative to $N(SiMe)_3$ production, the simple proof of concept that the dinitrogen feedstock can be used to catalytically produce value-added products is notable.



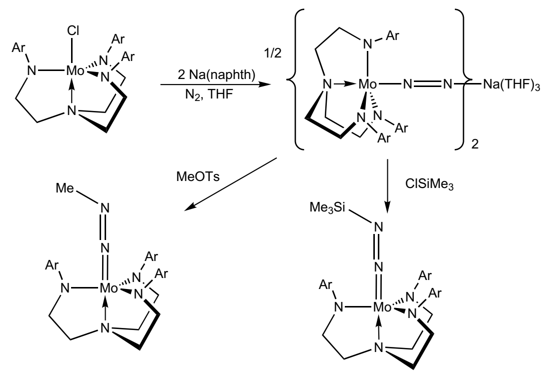
$$\begin{matrix} N_2 \\ + \\ 6\ Na \\ + \\ 6\ SiMe_3Cl \end{matrix} \xrightarrow[\qquad]{\begin{matrix}0.5\% \\ cis\text{-}Mo(N_2)_2(PMe_2Ph)_4\end{matrix}} \begin{matrix} N(SiMe)_3 \\ + \\ HN(SiMe_3)_2 \\ + \\ Me_3SiSiMe_3 \end{matrix} \qquad (18)$$

The reactivity of these molybdenum and tungsten systems can be expanded by prior protonation of the dinitrogen complexes. The resulting hydrazido derivatives can be used to generate heterocycles such as hydrazones, pyrroles, pyrazoles, pyridines and indoles. With control of reaction conditions, a synthetic cycle can be generated which makes this process quasi-catalytic; the reaction must be performed in a stepwise fashion in order to produce products catalytically. As an example, the preparation of *N*-aminopiperidine, employing irradiation of the sample to facilitate the transformation, is shown in Scheme 6.[110] There are many similar Mo and W systems to these that have been recently reviewed.[1,3]

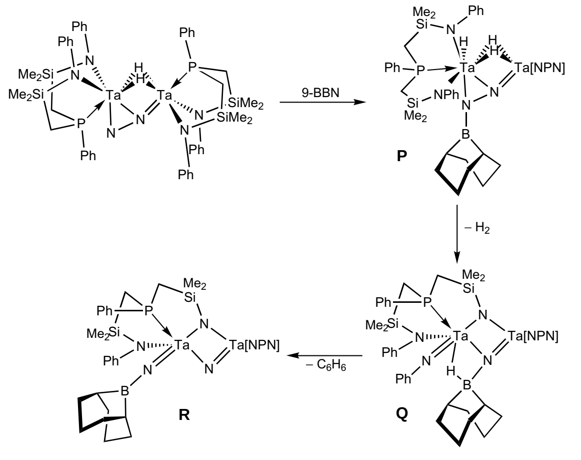
A recent report details the effect of sodium amalgam on the molybdenum-based cleavage reaction discussed earlier. Dinitrogen cleavage by $[NRAr]_3Mo$ systems was found to be accelerated by the presence of sodium amalgam *via* an intermediate $[(THF)_xNa][(N_2)Mo(NRAr)_3$. This intermediate could even be trapped by Me_3SiCl to form $(Me_3SiNN)Mo(NRAr)_3$, or by methyl triflate to give a cationic dimethylhydrazido product. Heterobimetallic systems were synthesized from reaction of the *in situ* generated intermediate and the corresponding metal chlorides.[111]

A related system also employs alkali metal activation of the coordinated dinitrogen unit to promote further reactivity. The reduction of $[N_3N]MoCl$ $\{[N_3N] = N(CH_2CH_2NSiMe_3)_3\}$ with Mg had already been shown to form $([N_3N]Mo{-}N{=}N)_2Mg(THF)_2$, which reacts with the strong electrophile Me_3SiCl to form a new N–Si bond.[112] A new report has shown that modifying the ligand with various aryl-based substituents changes the observed reactivity slightly. As shown in Scheme 7, the $[ArN_3N]MoCl$ can react with Na/naphthalenide under N_2 to afford $([ArN_3N]Mo{-}N{=}N)Na(THF)_3$ which reacts with Me_3SiCl and MeOTs to form new N–$SiMe_3$ and N–Me linkages stoichiometrically.[113]

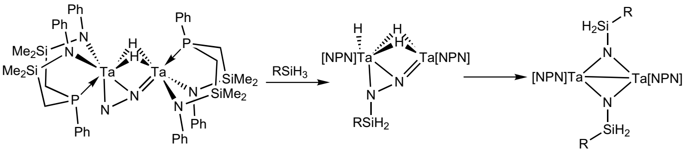
While the end-on dinitrogen complexes discussed above used alkali metals to promote reactivity, the slight polarity of the side-on end-on dinitrogen complex $([NPN]Ta)_2(\mu\text{-}H)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}N_2)$ $\{[NPN] = (PhNSiMe_2CH_2)_2PPh\}$ has also shown novel reactivity in two recent reports. The reaction of 9-BBN (9-borabicyclo[3.3.1]nonane) with the aforementioned dinitrogen complex proceeds first *via* addition of the B-H bond across a Ta-N bond to form $\{(NPN)Ta(H)\}(\mu\text{-}H)_2(\mu\text{-}N_2\text{-}BC_8H_{14})\{Ta(NPN)\}$ (**P**). Reductive elimination of the two remaining hydride ligands as H_2 provides the final two electrons required to split the N_2 unit. Silicon



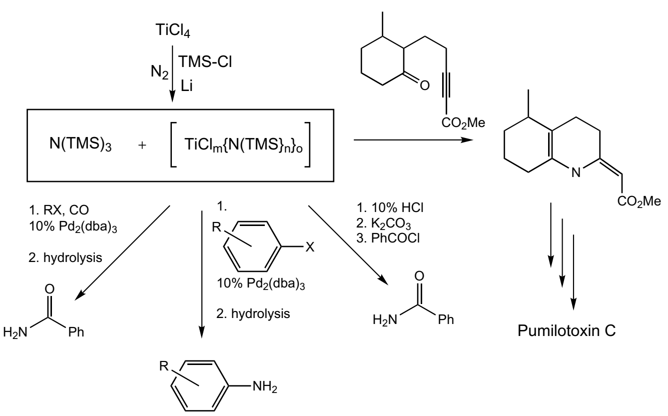
Scheme 7.



Scheme 8.



Scheme 9.



Scheme 10.

migration from the ligand to the bridging nitride gives an imide nitride species (**Q**) that loses benzene over time to afford the final product: an imido nitride (**R**) as shown in Scheme 8.[114] The involvement of the silicon in the ligand backbone inspired the reaction of primary silanes ($RSiH_3$; R = ^{n}Bu, Ph) with the side-on end-on dinitrogen complex. Similar to the reaction with boranes, Si–H addition across the Ta–N bond comprises the first step. Reductive loss of H_2 splits the N–N bond, and reaction with an additional silane affords the complex $\{[NPN]Ta\}_2(\mu\text{-}NSiH_2R)_2$ with two bridging silylimido units. The progression of this reaction is shown in Scheme 9.[115]

Even with the intensive studies conducted today, one of the more intriguing reactivities observed from molecular nitrogen was found in 1965, soon after the first dinitrogen complex was reported, and this chemistry has been slowly refined over the following years.[116,117] Systems based on titanium compounds such as Cp_2TiCl_2, Cp_2TiPh_2, $CpTiCl_3$ and others react with excess aryllithium reagents (PhLi, MeC_6H_4Li, etc.) and dinitrogen in ether to afford aromatic amines (NH_2Ph, $NH_2C_6H_4Me$) following hydrolysis. Diaryltitanocenes, Cp_2TiAr_2, react with excess Li, Na or Mg and also form the corresponding aromatic amines after hydrolysis. Much of this work had not been published in its entirety until a recent publication commemorating Professor Vol'pin's extensive contributions to the field of dinitrogen fixation.[118]

Any production of a value-added nitrogen-containing product must compete with already established industrial syntheses, but several recent publications have shown that dinitrogen activation can have true utility in the development of *new* synthetic strategies. The use of *in situ* prepared titanium dinitrogen complexes to synthesize *N*-heterocycles has shown surprising utility. The synthesis of a wide variety of heterocycles, such as indole, quinoline, pyrrole, pyrrolizine, and indolizine derivatives can be realized using an N_2-$TiCl_4$-Li-TMSCl system. These components added to the appropriate reagents *in situ* can afford the desired transformation.[119] In fact, the preparation of these heterocycles has been made catalytic; yields of indole derivatives were over 200% based on $TiCl_4$ when excess lithium and TMSCl were used. Interestingly, use of dry air as the nitrogen source gave nearly the same results as with molecular nitrogen.[120] New transformations brought about by this system continue to grow. For instance, non-substituted anilines can be synthesized *via* transmetalation of arylpalladium complexes with the *in situ* generated titanium dinitrogen complexes.[121] Tetrahydroindole derivatives have been synthesized using much the same route.[122] Amides have been synthesized by palladium-catalyzed carbonylation and nitrogenation. Reaction of the titanium dinitrogen fixing system with RX and CO in the presence of a Pd(0) catalyst gives the corresponding amides ($RCONH_2$) in good yields.[123] Most interestingly, however, is how many of these processes have found their way into more complicated syntheses. The syntheses of the natural products monomorine I,[124] (±)-lycopodine[121] and pumiliotoxine C[125] have all been developed from a dinitrogen feedstock. The broad chemistry accomplished by these systems is shown in Scheme 10.

5 Final Thoughts

Despite the flurry of activity and growth in dinitrogen activation and the chemistry promoted by it, there are still few processes whereby the use of N_2 as a feedstock is applicable to industrial syntheses. The preparation of dinitrogen complexes often requires strongly reducing conditions unsuitable for large scale syntheses. The few systems that show true potential in this regard are not fully understood from a mechanistic standpoint and oftentimes require stoichiometric amounts of dinitrogen complex. Still, while development of N_2 as an industrial feedstock is certainly an as yet unrealized goal, N_2 should now be considered a viable synthetic reagent. The significant recent advances documented here show the breadth of chemistry that dinitrogen can undergo and support the need for continued work in this area. It is hoped that this review will not only inspire current researchers to new chemical discoveries, but also drive others to employ molecular nitrogen as a synthon in their research.

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References

[1] M. D. Fryzuk, S. A. Johnson, *Coord. Chem. Rev.* **2000**, *200–202*, 379.
[2] M. Hidai, Y. Mizobe, *Pure Appl. Chem.* **2001**, *73*, 261.
[3] M. Hidai, Y. Mizobe, *Metal Ions In Biological Systems 39 (Molybdenum and Tungsten)*, **2002**, 121.
[4] M. Hidai, *Coord. Chem. Rev.* **1999**, *185–186*, 99.
[5] C. J. Pickett, *J. Biol. Inorg. Chem.* **1996**, *1*, 601.
[6] J. Chatt, J. R. Dilworth, R. L. Richards, *Chem. Rev.* **1978**, *78*, 589.
[7] T. A. Bazhenova, A. E. Shilov, *Coord. Chem. Rev.* **1995**, *144*, 69.
[8] M. Hidai, Y. Mizobe, *Chem. Rev.* **1995**, *95*, 1115.
[9] S. Gambarotta, *J. Organomet. Chem.* **1995**, *500*, 117.
[10] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, School of Chemistry, University of Leeds, U. K., **1997**.
[11] M. W. Chase, J. C. A. Davies, J. J. R. Downe, D. J. Frurip, R. A. McDonald, A. N. Syverue, *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. No. 1.
[12] R. A. Alberty, *J. Biol. Chem.* **1994**, *269*, 7099.
[13] J. Postgate, *Nitrogen Fixation*, Cambridge Press, Cambridge, **1998**.
[14] M. Appl, *Ammonia*, Wiley-VCH, Weinheim, **1999**.
[15] G. Ertl, in *Catalytic Ammonia Synthesis*, (Ed.: J. R. Jennings), Plenum Press, New York, **1991**.
[16] C. V. Senoff, *J. Chem. Ed.* **1990**, *67*, 368.
[17] A. D. Allen, C. V. Senoff, *J. Chem. Soc. Chem. Commun.* **1965**, 621.
[18] C. C. Addison, B. M. Davies, *J. Chem. Soc. A* **1969**, 1822.
[19] S. A. Kutolin, A. I. Vulikh, *Metod. Poluch. Khimich. Reakt. Prep.* **1967**, 52.
[20] G. Maier, H. P. Reisenauer, J. Henkelmann, C. Kliche, *Angew. Chem.* **1988**, *100*, 303.
[21] S. M. Rocklage, H. W. Turner, J. D. Fellmann, R. R. Schrock, *Organometallics* **1982**, *1*, 703.
[22] M. Hidai, K. Tominari, Y. Uchida, A. Misono, *J. Chem. Soc. Chem. Commun.* **1969**, 1392.
[23] M. B. O'Regan, A. H. Liu, W. C. Finch, R. R. Schrock, W. M. Davis, *J. Am. Chem. Soc.* **1990**, *112*, 4331.
[24] W. J. Evans, T. A. Ulibarri, J. W. Ziller, *J. Am. Chem. Soc.* **1988**, *110*, 6877.
[25] M. D. Fryzuk, T. S. Haddad, S. J. Rettig, *J. Am. Chem. Soc.* **1990**, *112*, 8185.
[26] N. C. Mosch-Zanetti, S. Kopke, R. Herbst-Irmer, M. Hewitt, *Inorg. Chem.* **2002**, *41*, 3513.
[27] H. Aneetha, M. Jimenez-Tenorio, M. C. Puerta, P. Valegra, K. Mereiter, *Organometallics* **2002**, *21*, 628.
[28] H. Aneetha, M. Jimenez-Tenorio, M. C. Puerta, P. Valerga, K. Mereiter, *Organometallics* **2003**, *22*, 1779.
[29] D. Sellmann, B. Hautsch, A. Rosler, F. W. Heinemann, *Angew. Chem. Int. Ed.* **2001**, *40*, 1505.
[30] J. B. Howard, D. C. Rees, *Chem. Rev.* **1996**, *96*, 2965.
[31] O. Einsle, F. A. Tezcan, S. L. A. Andrade, B. Schmid, M. Yoshida, J. B. Howard, D. C. Rees, *Science* **2002**, *297*, 1696.
[32] J. Kim, D. C. Rees, *Science* **1992**, *360*, 563.
[33] T. Yoshida, T. Adachi, M. Kaminaka, T. Ueda, *J. Am. Chem. Soc.* **1988**, *110*, 4872.
[34] J. R. Dilworth, J. Hu, R. M. Thompson, D. L. Hughes, *J. Chem. Soc. Chem. Commun.* **1992**, 551.
[35] B. A. Arndtsen, R. G. Bergman, *Science* **1995**, *270*, 1970.
[36] D. M. Tellers, R. G. Bergman, *J. Am. Chem. Soc.* **2000**, *122*, 954.
[37] D. M. Tellers, R. G. Bergman, *Organometallics* **2001**, *20*, 4819.
[38] D. Amoroso, G. P. A. Yap, D. E. Fogg, *Can. J. Chem.* **2001**, *79*, 958.
[39] I. del Rio, S. Back, M. S. Hannu, G. Rheinwald, H. Lang, G. van Koten, *Inorg. Chim. Acta* **2000**, *300–302*, 1094.
[40] D. C. Bregel, S. M. Oldham, R. J. Lachicotte, R. Eisenberg, *Inorg. Chem.* **2002**, *41*, 4371.

[41] H. Ishino, S. Kuwata, Y. Ishii, M. Hidai, *Organometallics* **2001**, *20*, 13.
[42] H. Seino, Y. Mizobe, M. Hidai, *Chem. Rec.* **2001**, *1*, 349.
[43] R. Baumann, R. Stumpf, W. M. Davis, L.-C. Liang, R. R. Schrock, *J. Am. Chem. Soc.* **1999**, *121*, 7822.
[44] S. M. Mullins, A. P. Duncan, R. G. Bergman, J. Arnold, *Inorg. Chem.* **2001**, *40*, 6952.
[45] J. A. Pool, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2003**, *125*, 2241.
[46] M. D. Fryzuk, S. A. Johnson, S. J. Rettig, *J. Am. Chem. Soc.* **1998**, *120*, 11024.
[47] M. D. Fryzuk, S. A. Johnson, B. O. Patrick, A. Albinati, S. A. Mason, T. F. Koetzle, *J. Am. Chem. Soc.* **2001**, *123*, 3960.
[48] J. A. Marsella, J. C. Huffman, K. G. Caulton, B. Longato, J. R. Norton, *J. Am. Chem. Soc.* **1982**, *104*, 6360.
[49] H. C. Aspinall, A. J. Deeming, S. Donovan-Mtunzi, *J. Chem. Soc. Dalton Trans.* **1985**, 2669.
[50] A. J. Deeming, S. Donovan-Mtunzi, *Organometallics* **1985**, *4*, 693.
[51] P. Legzdins, S. J. Rettig, J. E. Veltheer, J. J. Batchelor, F. W. B. Einstein, *Organometallics* **1993**, *12*, 3575.
[52] K. Jonas, *Angew. Chem. Int. Ed. Eng.* **1973**, *12*, 997.
[53] H. F. Klein, R. Hammer, J. Weiniger, P. Friedrich, G. Huttner, *Z. Naturforsch.* **1978**, *33b*, 1267.
[54] G. P. Pez, P. Apgar, R. K. Crissey, *J. Am. Chem. Soc.* **1982**, *104*, 482.
[55] J. M. Smith, R. J. Lachicotte, K. A. Pittard, T. R. Cundari, G. Lukat-Rodgers, K. R. Rodgers, P. L. Holland, *J. Am. Chem. Soc.* **2001**, *123*, 9222.
[56] M. B. O'Donoghue, W. M. Davis, R. R. Schrock, W. M. Reiff, *Inorg. Chem.* **1999**, *38*, 243.
[57] Q.-F. Zhang, J. L. C. Chim, W. Lai, W.-T. Wong, W.-H. Leung, *Inorg. Chem.* **2001**, *40*, 2470.
[58] M. Mercer, *J. Chem. Soc. Dalton Trans.* **1974**, 1637.
[59] H. Ishino, T. Nagano, S. Kuwata, Y. Yokobayashi, Y. Ishii, M. Hidai, *Organometallics* **2001**, *20*, 188.
[60] W. J. Evans, N. T. Allen, J. W. Ziller, *J. Am. Chem. Soc.* **2001**, *123*, 7927.
[61] W. J. Evans, N. T. Allen, J. W. Ziller, *Angew. Chem. Int. Ed.* **2002**, *41*, 359.
[62] W. J. Evans, G. Zucchi, J. W. Ziller, *J. Am. Chem. Soc.* **2003**, *125*, 10.
[63] P. Roussel, W. Errington, N. Kaltsoyannis, P. Scott, *J. Organomet. Chem.* **2001**, *635*, 69.
[64] F. G. N. Cloke, P. B. Hitchcock, *J. Am. Chem. Soc.* **2002**, *124*, 9352.
[65] T. Dube, S. Conoci, S. Gambarotta, G. P. A. Yap, G. Vasapollo, *Angew. Chem. Int. Ed.* **1999**, *38*, 3657.
[66] T. Dube, M. Ganesan, S. Conoci, S. Gambarotta, G. P. A. Yap, *Organometallics* **2000**, *19*, 3716.
[67] M. Canesan, M. P. Lalonde, S. Gambarotta, G. P. A. Yap, *Organometallics* **2001**, *20*, 2443.
[68] J. Guan, T. Dube, S. Gambarotta, G. P. A. Yap, *Organometallics* **2000**, *19*, 4820.
[69] C. C. Cummins, *Chem. Commun.* **1998**, 1777.
[70] C. E. LaPlaza, C. C. Cummins, *Science* **1995**, *268*, 861.
[71] G. K. B. Clentsmith, V. M. E. Bates, P. B. Hitchcock, F. G. N. Cloke, *J. Am. Chem. Soc.* **1999**, *121*, 10444.
[72] A. Zanotti-Gerosa, E. Solari, L. Giannini, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *J. Am. Chem. Soc.* **1998**, *120*, 437.
[73] A. Caselli, E. Solari, R. Scopelliti, C. Floriani, N. Re, C. Rizzolo, A. Chiesi-Villa, *J. Am. Chem. Soc.* **2000**, *122*, 3652.
[74] Y.-C. Tsai, M. J. A. Johnson, D. J. Mindiola, C. C. Cummins, *J. Am. Chem. Soc.* **1999**, *121*, 10426.
[75] D. J. Mindiola, K. Meyer, J.-P. F. Cherry, T. A. Baker, C. C. Cummins, *Organometallics* **2000**, *19*, 1622.
[76] E. Solari, C. D. Silva, B. Iacono, J. Hesschenbrouck, C. Rizzoli, R. Scopelliti, C. Floriani, *Angew. Chem. Int. Ed.* **2001**, *40*, 3907.
[77] H. Kawaguchi, T. Matsuo, *Angew. Chem. Int. Ed.* **2002**, *41*, 2792.
[78] B. Chaudret, J. Devillers, R. Poilblanc, *Organometallics* **1985**, *4*, 1727.
[79] C. Bianchini, A. Meli, F. Perruzini, F. Vizza, *Organometallics* **1989**, *8*, 2080.
[80] I. Korobkov, S. Gambarotta, G. P. A. Yap, *Angew. Chem. Int. Ed.* **2002**, *41*, 3433.
[81] Y. Nakajima, H. Suzuki, *Organometallics* **2003**, *22*, 959.
[82] M. D. Fryzuk, C. M. Kozak, M. R. Bowdridge, B. O. Patrick, S. J. Rettig, *J. Am. Chem. Soc.* **2002**, *124*, 8389.
[83] J. O. Dziegielewski, R. Grzybek, *Polyhedron* **1990**, *9*, 645.
[84] C. R. Dickson, A. J. Nozik, *J. Am. Chem. Soc.* **1978**, *100*, 8007.
[85] A. E. Shilov, *J. Mol. Catal.* **1987**, *41*, 221.
[86] M. Yu, L. P. Didenko, L. M. Kachapina, A. E. Shilov, A. K. Shilova, Y. T. Struchkov, *J. Chem. Soc. Chem. Commun.* **1989**, 1467.
[87] H. Nishihara, T. Mori, Y. Tsurita, K. Nakano, T. Saito, Y. Sasaki, *J. Am. Chem. Soc.* **1982**, *104*, 4367.
[88] G. Jia, R. H. Morris, C. T. Schweitzer, *Inorg. Chem.* **1991**, *30*, 593.
[89] Y. Nishibayashi, S. Iwai, M. Hidai, *J. Am. Chem. Soc.* **1998**, *120*, 10559.
[90] M. D. Fryzuk, J. B. Love, S. J. Rettig, V. G. Young, *Science* **1997**, *275*, 1445.
[91] H. Basch, D. G. Musaev, K. Morokuma, M. D. Fryzuk, J. B. Love, W. W. Seidel, A. Albinati, T. F. Koetzle, W. T. Klooster, S. A. Mason, J. Eckert, *J. Am. Chem. Soc.* **1999**, *121*, 523.
[92] Y. Nishibayashi, S. Takemoto, S. Iwai, M. Hidai, *Inorg. Chem.* **2000**, *39*, 5936.
[93] Y. Nishibayashi, S. Iwai, M. Hidai, *Science* **1998**, *279*, 540.
[94] Y. Nishibayashi, I. Wakiji, K. Hirata, M. R. DuBois, M. Hidai, *Inorg. Chem.* **2001**, *40*, 578.
[95] C. M. Habeck, N. Lehnert, C. Nather, F. Tuczek, *Inorg. Chim. Acta* **2002**, *337*, 11.
[96] N. Lehnert, F. Tuczek, *Inorg. Chem.* **1999**, *38*, 1659.
[97] N. Lehnert, F. Tuczek, *Inorg. Chem.* **1999**, *38*, 1671.
[98] N. P. Luneva, L. A. Nikonova, A. E. Shilov, *React. Kinet. Catal. Lett.* **1976**, *5*, 149.
[99] A. F. Shestakov, A. E. Shilov, *Kinetics and Catalysis* **2001**, *42*, 653.

[100] D. V. Yandulov, R. R. Schrock, *J. Am. Chem. Soc.* **2002**, *124*, 6252.
[101] M. D. Fryzuk, *Chem. Rec.* **2003**, *3*, 2.
[102] H. Ishino, Y. Ishii, M. Hidai, *Chem. Lett.* **1998**, 677.
[103] K. Takagahara, H. Ishino, Y. Ishii, M. Hidai, *Chem. Lett.* **1998**, 897.
[104] T. Takahashi, T. Kodama, A. Watakabe, Y. Uchida, M. Hidai, *J. Am. Chem. Soc.* **1983**, *105*, 1680.
[105] J. Chatt, A. A. Diamantis, G. A. Heath, N. E. Hooper, G. J. Leigh, *J. Chem. Soc. Dalton Trans.* **1977**, 688.
[106] J. Chatt, G. A. Heath, G. J. Leigh, *J. Chem. Soc. Chem. Commun.* **1972**, 444.
[107] M. Hidai, K. Komori, T. Kodama, D. M. Jin, T. Takahashi, S. Sugiura, Y. Uchida, Y. Mizobe, *J. Organomet. Chem.* **1984**, *272*, 155.
[108] H. Oshita, Y. Mizobe, M. Hidai, *J. Organomet. Chem.* **1993**, *456*, 213.
[109] K. Komori, H. Oshita, Y. Mizobe, M. Hidai, *J. Am. Chem. Soc.* **1989**, *111*, 1939.
[110] C. J. Pickett, G. J. Leigh, *J. Chem. Soc. Chem. Commun.* **1981**, 1033.
[111] J. C. Peters, J.-P. F. Cherry, J. C. Thomas, L. Baraldo, D. J. Mindiola, W. M. Davis, C. C. Cummins, *J. Am. Chem. Soc.* **1999**, *121*, 10053.
[112] M. B. O'Donoghue, W. M. Davis, R. R. Schrock, *Inorg. Chem.* **1998**, *37*, 5149.
[113] G. E. Greco, R. R. Schrock, *Inorg. Chem.* **2001**, *40*, 3861.
[114] M. D. Fryzuk, B. A. MacKay, S. A. Johnson, B. O. Patrick, *Angew. Chem. Int. Ed.* **2002**, *41*, 3709.
[115] M. D. Fryzuk, B. A. MacKay, B. O. Patrick, *J. Am. Chem. Soc.* **2003**, *125*, 3234.
[116] M. E. Vol'pin, V. B. Shur, R. V. Kudryavtsev, L. A. Prodayko, *J. Chem. Soc. Chem. Commun.* **1968**, 1038.
[117] M. E. Vol'pin, V. B. Shur, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, 1873.
[118] M. E. Vol'pin, V. B. Shur, E. G. Berkovich, *Inorg. Chim. Acta* **1998**, *280*, 264.
[119] M. Hori, M. Mori, *J. Org. Chem.* **1995**, *60*, 1480.
[120] M. Mori, K. Hori, M. Akashi, M. Hori, Y. Sato, M. Nishida, *Angew. Chem. Int. Ed.* **1998**, *37*, 636.
[121] K. Hori, M. Mori, *J. Am. Chem. Soc.* **1998**, *120*, 7651.
[122] M. Akashi, M. Nishida, M. Mori, *Chem. Lett.* **1999**, 465.
[123] K. Ueda, Y. Sato, M. Mori, *J. Am. Chem. Soc.* **2000**, *122*, 10722.
[124] M. Mori, M. Hori, Y. Sato, *J. Org. Chem.* **1998**, *63*, 4832.
[125] M. Akashi, Y. Sato, M. Mori, *J. Org. Chem.* **2001**, *66*, 7873.