Dinitrogen Coordination Chemistry: On the Biomimetic Borderlands

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1. Introduction

1.1. On the Borderlands

Biological nitrogen fixation by the nitrogenase enzymes has long been a touchstone for dinitrogen chemists.[1,2] Both the enzymatic reduction and protonation of N_2 mediated by these metalloenzymes (eq 1)[3,4] and the industrial hydrogenation of N_2 exemplified by the Haber−Bosch process (eq 2)[5−7] employ transition metal-based catalysts to accelerate the thermodynamically feasible production of ammonia.

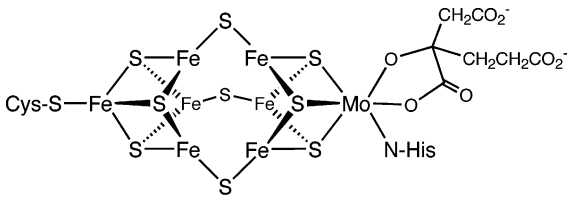
$$N{\equiv}N + 8H^+ + 8e^- + 16MgATP \rightarrow 2NH_3 + H_2 + 16MgADP + 16P_i \quad (1)$$

$$N{\equiv}N_{(g)} + 3H_{2(g)} \xrightarrow[\substack{100-300\ atm\\ 400-500\ °C}]{Fe\ or\ Ru\ catalyst} 2NH_{3(g)} \quad (2)$$

$$\Delta H° = -46.2\ kJ\ mol^{-1}, \quad \Delta S° = -99\ J\ mol^{-1}\ K^{-1}$$

These two processes are the major connections between the atmospheric reservoir of inorganic nitrogen atoms and the biosphere, where nitrogen is an essential element to all life.[8] As a result of the important roles metals play in these processes, comparisons to nitrogenase and the Haber−Bosch process are ubiquitous in the literature of transition metal dinitrogen complexes. Nitrogenase binds dinitrogen and other substrates, it reduces bound substrates using electrons provided by other metal clusters, it allows for protonation of reduced N atoms, it produces H_2 as a reaction byproduct, and it releases fixed nitrogen as ammonia. The mechanistic details of this catalytic process remain unclear.

The most common nitrogenase enzyme employs an iron−molybdenum−sulfur cluster (the FeMo-cofactor) as the principal catalytic agent at its active site.[9] Although two other similar enzyme types ("iron−vanadium" and "iron-only", where Mo is replaced by V or Fe) are also known to exist,[10] in this discussion "nitrogenase" refers to the common type. Extracted from purified protein with acid[11] or from cellulose-bound protein with DMF or NMF after treatment with bipyridyl,[12] isolated FeMo-cofactor has the composition Fe_7S_9Mo(homocitrate). The first X-ray crystal structure of the nitrogenase enzyme from *Azotobacter vinelandii* in 1992 allowed characterization of its FeMo-cofactor to 2.7 Å resolution.[13] The original FeMo-cofactor structure (**1**) contained a number of surprises, including a variety of possible N_2 binding sites and six three-coordinate iron sites deployed around the cofactor's center. This discovery stimulated research on both the synthetic and enzymologic sides of biomimetic dinitrogen chemistry.



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Although this important structural revelation was a watershed moment in the study of nitrogenase, the central question of how the molecular events in the nitrogen fixation process are orchestrated remains unanswered despite 12 years of intensive research. For inorganic chemists, the biomimetic imperative focuses on synthesis of model complexes that can help to describe the structure and function of metal sites in metalloenzymes.[14−16] Synthetic analogues have been extremely useful in clarifying other bioinorganic systems such as the oxygen-binding metalloenzymes,[17] but the study of nitrogen fixation continues to challenge this paradigm.[18] In the time since the

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Bruce MacKay was born in Saskatoon, Canada, but was raised in nearby Medicine Hat. After running a small but vigorous bicycle shop there for four years, he completed a B.Sc. (Hons.) in chemistry and biology at the University of British Columbia. A positive experience in his undergraduate research project with Professor Michael Fryzuk led him to begin his Ph.D. studies in 1999. He is a Natural Sciences and Engineering Research Council of Canada scholar (PGS-A and -B) and UBC Graduate Teaching Award winner whose research interestes are in small-molecule activation, catalysis, and novel molecular transformations using metal hydride reagents. He enjoys cycling, playing tennis with his wife, Jodi, and meddling in departmental affairs when he is not in the lab or at home.

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 postodoctoral 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 the E. W. R. Steacie Fellowship for 1990–1992, awarded by the Natural Sciences 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.

FeMo-cofactor's structure was elucidated, no genuine structural/functional nitrogenase mimic has yet been prepared. The exact nature of the metal−dinitrogen interactions when N_2 is bound at the FeMo-cofactor and the mechanism by which it is activated and converted are still completely unknown.

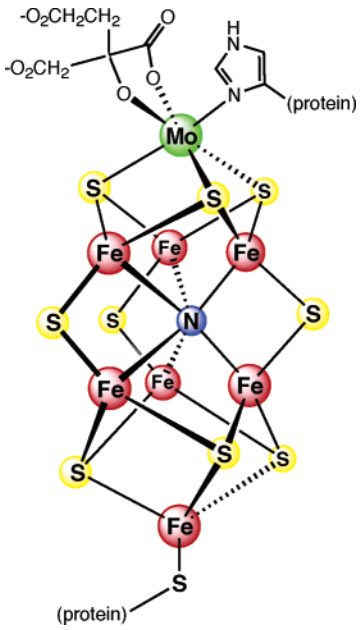


Figure 1. Structure of the FeMo-cofactor including an interstitial nitride.

Since the original FeMo-cofactor structure was uncovered, mutually exclusive models[19] have been advanced proposing N_2 coordination at Mo[20] or Fe, where the cofactor-N_2 contact is at a pair of Fe atoms,[21] at a square face of four Fe atoms,[22,23] or within the "cage" of six Fe atoms.[24] Each of these postulates has deficiencies, and all are challenged by a recent finding[25] indicating that a previously unsuspected interstitial six-coordinate atom, most likely nitrogen (blue atom in Figure 1), occupies this cavity, bridging the six "coordinatively unsaturated" iron atoms, which are now understood to be tetracoordinate. This conclusion rationalizes previous ESEEMS observations,[26] and it has also been supported by theoretical studies.[27] A recent combined ENDOR/ESEEMS study[28] has established that the central atom does not exchange with dinitrogen-derived atoms during catalysis. The presence of this nitrido ligand has many implications for the atomic events in nitrogen fixation. Clearly, current research is yielding surprises that highlight the interdependence of nitrogenase research and transition metal dinitrogen chemistry, and therefore many of us who investigate dinitrogen coordination chemistry feel we are working on the borderlands of bioinorganic chemistry.

1.2. Scope

This review seeks to provide an overview of selected current results from the synthetic side of dinitrogen coordination chemistry that are potentially significant under the biomimetic imperative. It is apparent from the number, variety, and scope of recent reviews impacting this area that the topic spans many subdisciplines in chemistry and biology. Dinitrogen chemistry of the transition metals has been reviewed thoroughly in 1995[29,30] and updated recently.[31] Nitrogenase itself been extensively reviewed from the enzymologic standpoint,[32,33,9] and reviews specific to vanadium[34,35] and molybdenum[36,37] enzyme systems

and the difficulties of preparing valid model systems[18] have recently been published. Kinetic[4] and thermodynamic[38] aspects of nitrogenase have been reviewed, as has the puzzling constitutive evolution of H_2.[39,40] Herein we will concern ourselves with well-characterized transition metal complexes involving either one or two metals, leaving the promising chemistry of cubanes, metal clusters, and structurally accurate polymetallic FeMo-cofactor analogues and theoretical treatments to the appropriate specific reviews elsewhere in this issue. Since the nitrogenase systems contain iron, vanadium, and molybdenum, synthetic dinitrogen complexes of these elements and their congeners will constitute the bulk of this review. For the sake of completeness, some other surprising results are included.

2. Dinitrogen Chemistry

2.1. Properties as a Ligand

Dinitrogen is generally inert to reaction, and therefore it is widely used to protect against contamination by unwanted dioxygen and moisture in chemical synthesis and the food industry. The chemical inertia that makes catalysts necessary for ammonia production from N_2 is related to intrinsic properties of the molecule. First, it is nonpolar with tightly bound σ and π electrons, and therefore it is a poor ligand. As a consequence, N_2 forms complexes reluctantly, and the field of dinitrogen chemistry is considerably less developed than that of the isoelectronic CO ligand. To extend the comparison to CO, N_2 is both a weaker σ donor and a poorer π acceptor,[41] and although there are now several examples of complexes involving more than one dinitrogen unit, migratory insertion reactions for N_2 are still unknown. Second, the triple bond in dinitrogen is extremely strong (944 KJ mol^{-1}); therefore, N−N bond cleavage is difficult, and most simple organonitrogen compounds are endothermic despite their stability.[42] Finally, the large HOMO−LUMO gap means N_2 is reluctant to accept or lose electrons, making redox reactions with dinitrogen difficult despite the fact that nitrogen displays a range of stable oxidation states in its compounds.

2.2. Metal–Dinitrogen Interactions

The first dinitrogen complex[43] was derived from hydrazine, which highlights the serendipitous nature of dinitrogen complex synthesis. Subsequent studies fundamental to the field of dinitrogen chemistry established synthetic methods, bonding and activation modes, and preliminary reactivity patterns for N_2 complexes. Dinitrogen complexes of nearly every transition metal and many lanthanides and actinides are now known. The mode of M_n-N_2 bonding varies with the metal, the oxidation state, and the choice of ancillary ligands. It is worth noting here that dinitrogen complexes involving sulfur-based ancillary ligands are rare despite the presence of sulfide ligands in FeMo-cofactor.[44] The common modes for bonding of dinitrogen to transition metals are illustrated in Figure 2, and for comparison the more

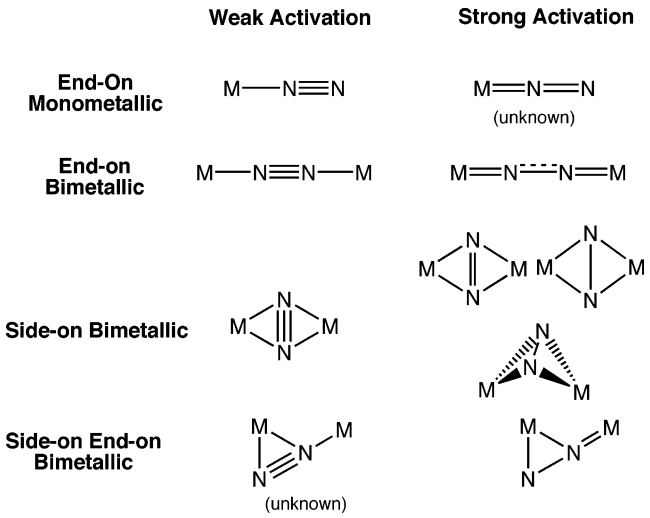


Figure 2. Dinitrogen binding modes in monometallic and bimetallic complexes.

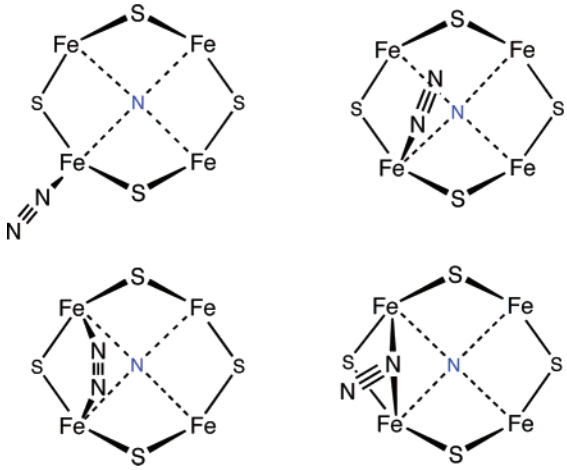


Figure 3. Favorable binding modes for N_2 at the FeMo-cofactor, given an interstitial nitride.

likely bonding arrangements predicted for the FeMo-cofactor in a theoretical consideration[27] of the interstitial nitride are shown in Figure 3.

Dinitrogen's N−N bond is frequently elongated or "activated" in its complexes. Activation is generally attributed to reduction of N−N bond order via the donation of reducing electrons from metal orbitals of appropriate symmetry into molecular orbitals that are antibonding with respect to dinitrogen, rather than to withdrawal of electron density from N−N bonding orbitals. Many such activated dinitrogen complexes display subsequent reactivity patterns at the N_2 unit that can lead to its functionalization, further activation, and complete N−N bond cleavage. These are the broad goals of synthetic dinitrogen activation. Activation is usually quantified by crystallographic measurement of N−N internuclear distances or by N−N stretch frequencies measured using IR or Raman spectroscopy. Free $N_{2(g)}$ has a bond length of 1.0975 Å and $\nu_{NN} = 2331\ cm^{-1}$, while azobenzene (PhN=NPh) shows a 1.255 Å bond length and $\nu_{NN} = 1442\ cm^{-1}$ and hydrazine shows a 1.460 Å bond length and $\nu_{NN} = 1111\ cm^{-1}$.[45−51] Very often the level of activation is correlated to a "formal reduction" by an integer number of reducing equivalents—the activated N_2 moieties are therefore commonly re-

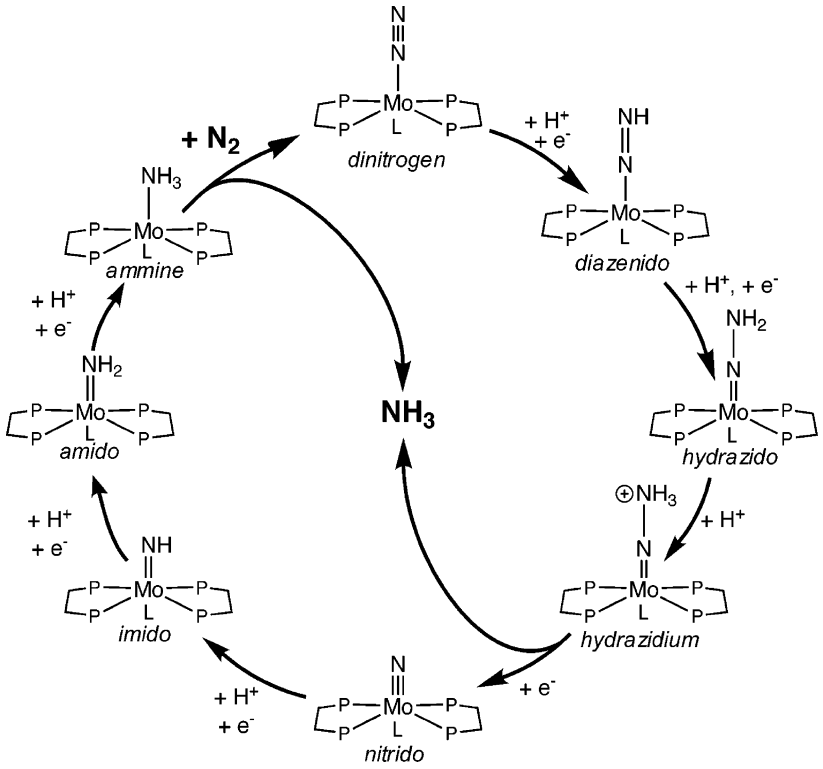


Figure 4. The Chatt cycle for nitrogen fixation on a Group 6 metal.

ferred to by names derived from analogous organic nitrogen compounds, viz., diazene for HN=NH, hydrazine for H_2N-NH_2, diazenido for N_2^{2-}, hydrazido for N_2^{4-}, and nitrido for the final result of overall N−N bond cleavage (see section 2.3 for further details). In some complexes the metal−dinitrogen orbital interactions are complicated, and therefore some caution is required in strictly correlating activation and N−N bond length.

The general methods of synthesizing dinitrogen complexes from N_2 can be broken very roughly into three broad areas: (1) displacement of a weakly bound ligand or an agostic interaction by N_2, (2) spontaneous coordination of N_2 at a vacant site within the coordination sphere, and (3) reduction of metal complexes to give transient low-valent metal fragments that bind and activate N_2.

2.3. Current Paradigms—The Chatt Cycle and Reductive Cleavage

Despite the polymetallic nature of the FeMo-cofactor, one of the most successful models for protonation of coordinated dinitrogen to NH_3 is based on a monometallic dinitrogen complex of a group 6 metal supported by a set of four ancillary phosphine ligands (chelating or not), which can be formulated as $[(P)_4M(N_2)L]$ (M = Mo or W, L = a monodentate ligand including N_2). Fundamental work established variants with different monodentate or chelating phosphines, and explored their reactivities with externally supplied reducing equivalents and protons to produce a variety of observable fixed nitrogenous intermediates and free nitrogen compounds. The "Chatt cycle", named for Joseph Chatt, founder of the Nitrogen Fixation Laboratory at Sussex, is shown in Figure 4.[52] Formation of hydrazine and/or ammonia upon protonation has become a standard reactivity test for reduced N_2 moieties in dinitrogen coordination chemistry[2] (diazene, HN=NH, conproportionates readily to ammonia and hydrazine in solution although it can be generated transiently and trapped). However, although protonation of coordinated N_2 is still an important line of inquiry, current interests in dinitrogen coordination chemistry have grown to include use of these intermediate reduced and functionalized $(N_2)^{n-}$ units for other reaction schemes such as N atom transfer and N−heteroatom bond formation.

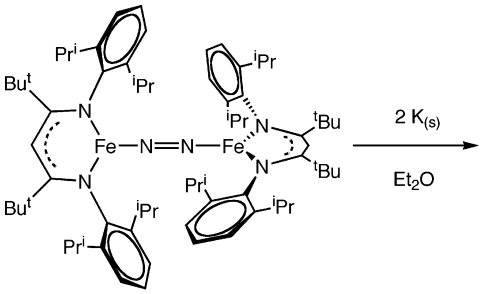
Another important recent trend in dinitrogen chemistry is the mediation of N−N bond cleavage events by high oxidation-state metal centers. Since the seminal work of Cummins,[53] systems demonstrating this approach have offered insight into ideal conditions for metal−dinitrogen binding and the mechanism of dinitrogen reduction and cleavage. These systems achieve N−N bond scission spontaneously using built-in reducing power or alkali metal co-reductants, and they have given insight into the operant reaction mechanism by providing well-defined intermediates and avenues for kinetic studies. Complexes featuring nitrido ligands are also available as end products, and their chemistry may now become important to our understanding of nitrogenase. In an earlier review of nitrogenase, Rees once observed that "if N_2 is not broken, it cannot be fixed" [54]—in light of his recent discovery of a central ligand in the FeMo-cofactor, the formation of nitrido and other nitrogenous ligands from coordinated N_2 and the ensuing reactivities of these species are important areas for consideration.

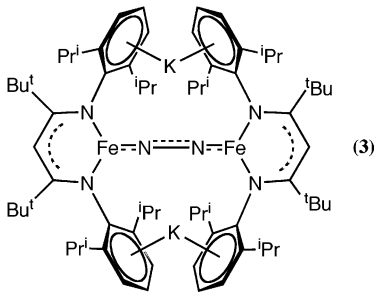
3. Complexes of the Group 8 Metals

3.1. Iron

Iron is the most abundant and utilized transition metal in the biosphere, and for many years its presence in all three nitrogenase enzyme types and in other redox-active enzymes was strong circumstantial evidence of a key role in biological dinitrogen fixation.[55] In addition, a common form of Haber−Bosch catalyst is potassium-promoted porous iron.[56] Synthetic iron dinitrogen complexes generally show end-on bound N_2 units that are weakly activated since many are formally Fe(0) and lack significant polarization at the N_2 unit, although the observation of dinitrogen fixation in solution by these complexes[57] implies that strong activation is not a requirement for fixation.

A linear dinuclear dinitrogen complex of iron supported by sterically demanding anionic β-diketiminato ligands has been prepared by the reduction of the (diketiminato)iron(II) chloride under N_2.[58] Crystallographic analysis shows an N−N bond of 1.182(5) Å, which represents atypical elongation for an iron N_2 complex. A dianionic derivative prepared by reaction with 2 equiv of potassium, shown in eq 3, shows further N−N bond elongation to 1.239(4) Å.

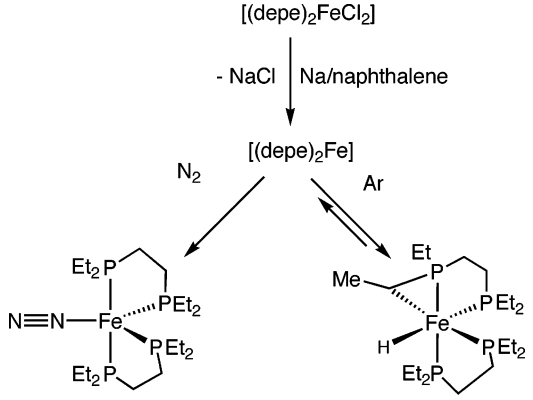




(3)

Theoretical considerations suggest that these two reducing equivalents occupy an MO of antibonding character with respect to N_2, and thus the second step in this stepwise reduction greatly increases activation. In the solid state, the alkali metal cation associates with the ligand aryl groups in a manner reminiscent of earlier work on a vanadium system[59] (see Scheme 6 in section 5.1 below). A thorough exploration of the Mössbauer and EPR properties of the parent chloride and its methyl and tolylamido derivatives and comparison to observed isomer shifts and quadrupole splittings for isolated FeMo-cofactor allowed the authors to make comparisons for these measurements based on geometry and coordination number.[60] However, since FeMo-cofactor is now known to contain a central bridging ligand that raises the coordination number of the six central iron atoms, these comparisons may be less valid than originally supposed.

Scheme 1



Ligand selection plays a subtle role in directing the reactivity of iron phosphine dinitrogen complexes. Iron prefers to bind dinitrogen rather than dihydrogen in these complexes, evident from the observation that N_2 can displace H_2 from cationic *trans*-[(dppm)$_2$Fe(H)(η^2-H$_2$)]$^+$ (where dppm = $Ph_2PCH_2PPh_2$).[61] Solution NMR kinetics experiments in which H_2 was displaced by a variety of other ligands established the relative rates of replacement as MeCN > N_2 > C_2H_4 ∼ pyridine, establishing a slight kinetic preference for the N_2 ligand. The IR spectrum of this dinitrogen complex exhibits $\nu_{NN} = 2116$ cm^{-1}, indicative of weak activation. The weakly activated end-on dinitrogen moiety in [(depe)$_2$Fe(N_2)] (where depe = $Et_2PCH_2CH_2PEt_2$) is in the equatorial plane of a trigonal bipyramidal coordination geometry. The N−N bond length is 1.139(13) Å, and the associated IR stretch is 1955 cm^{-1}. This complex arises from sodium reduction of [(depe)$_2$Fe(Cl_2)],[62] which gives a cyclometalated compound in the absence of N_2. This species also appears to prefer N_2 as a ligand, in that the addition of N_2 reverses the cyclometalation by forming [(depe)$_2$Fe(N_2)].[63] This is shown in Scheme 1. In contrast to the previous example, the dinitrogen ligand of this formally iron(0) complex can be displaced by CO, CS_2, and H_2—upon protonation the hydrido chloride complex *trans*-[(depe)$_2$FeH(Cl)] forms quantitatively as N_2 is lost. A further equivalent of HCl gives the dichloride starting material and H_2 gas.

By comparison, the related cationic hydride complex [(dmpe)$_2$FeH(N_2)]$^+$ (where dmpe = $Me_2PCH_2CH_2PMe_2$) undergoes successive protonation and reduction in protic media to give low yields of ammonia but no hydrazine.[64] After loss of ammonia, the resulting Fe(II) complex is reduced and reprotonated to a dihydrogen complex, [(dmpe)$_2$FeH(H_2)]$^+$, which reacts with N_2 via loss of H_2 to give a cationic dinitrogen complex. The putative Fe(0) dinitrogen complex [(dmpe)$_2$Fe(N_2)] that is available by deprotonation is not likely to be the derivative that leads to ammonia formation.[65] Deprotonation of [(dmpe)$_2$FeH(N_2)]$^+$ is expected to give the dmpe homologue of [(depe)$_2$Fe(N_2)], which has been shown not to yield ammonia on protonation, and therefore the nature of the intermediate that is protonated in this system

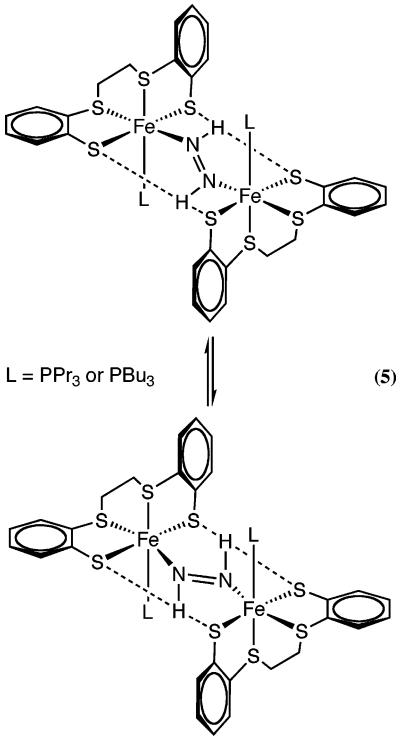
remains unknown. The equilibrium observed between $[(CO)_2(Et_3P)_2Fe(N_2)]$ and linear bridging dinuclear $[(CO)_2(Et_3P)_2Fe]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)$[66] may imply the possibility of bimetallic intermediates in this scheme (note that the linear bridging $\mu\text{-}\eta^1\text{:}\eta^1$ mode is prevalent in the coordination chemistry of dinitrogen and henceforth this designation is implied for bridging systems unless otherwise specified). In any case, a system that produces NH_3 in protic media using biologically accessible oxidation states is undeniably significant. This cycle is distinct from the Chatt cycle, wherein N_2 displaces ammonia and not H_2. The dihydrogen complex $[(dmpe)_2FeH(H_2)]^+$ can react with a molybdenum dinitrogen complex via ligand exchange as outlined in eq 4.[67] Hydridic intermedi-

$$2[(dmpe)_2Fe(H_2)]^+ + [(dppe)_2Mo(N_2)] \xrightarrow[THF]{Ar} 2[(dmpe)_2FeH(N_2)]^+ + [(dppe)_2MoH_4] \quad (4)$$

ates have been proposed to explain the evolution of H_2 in the nitrogenase reaction,[68] and the observation that $[(dmpe)_2FeH(N_2)]^+$ reacts with CO_2 and CS_2 via insertion into the Fe−H bond[69] (rather than by loss of N_2) suggests that a reactive hydride species that is still competent to bind N_2 is possible.

Protonation of Fe(0) complexes supported by a C_{3v}-symmetric (NP_3) chelating ligand (where (NP_3) = $N(CH_2CH_2PPh_2)_3$) gives hydrazine and a small amount of ammonia. Oddly, the neutral iron(0) complex $[(NP_3)Fe(N_2)]$ is initially prepared by the deprotonation of cationic $[(NP_3)FeH(N_2)]^+$—the neutral complex is then treated with excess HBr in protonation experiments. The N−N bond is 1.102(13) Å in the cationic hydride complex, which has $\nu_{NN} = 2090\ cm^{-1}$ as compared to $\nu_{NN} = 1967\ cm^{-1}$ in the neutral complex.[70] A more complicated pentadentate nitrogen−sulfur ligand supports an iron hydrazine complex, which can be reacted with dioxygen to give bimetallic $[(NS_4)Fe]_2(\mu\text{-}HN{=}NH)$. This diazene complex is stabilized by internal N−H···S hydrogen bonds. Although the hydrazine moiety in the starting complex is not derived from dinitrogen, this is an example of the stabilization of putative intermediates in the nitrogenase reaction by an iron−sulfur complex.[71] This work has recently been extended using a tetradentate ($^{tp}S_4$) ligand (where ($^{tp}S_4$) = $(S\text{-}o\text{-}C_6H_4\text{-}SCH_2CH_2S\text{-}o\text{-}C_6H_4\text{-}S)^{2-}$), leading to trapping of *trans*-diazene.[72] Observation of an equilibrium, shown in eq 5, between two diastereomers of the analogous dinuclear diazenido complex is reported.[73] The contribution of diazene-ligand H···S hydrogen bonding to total coordination energy is estimated at 20%.[74,75] These interactions are also expected to vary with the oxidation state of the metal, implying that stepwise reduction of the complex contributes to structural change.

Dinitrogen complexes of iron in a variety of oxidation states, all derived from reduction of the Fe(II) complex [(PhBP$_3$)FeCl] (where $PhBP_3^-$ = $PhB(CH_2P^iPr_3)_3^-$), have been reported.[76] When reduced with Mg(0), the parent chloride complex gives a heterobimetallic dinitrogen complex that loses the N_β−Mg interaction upon alkylation at N_β with MeOTs



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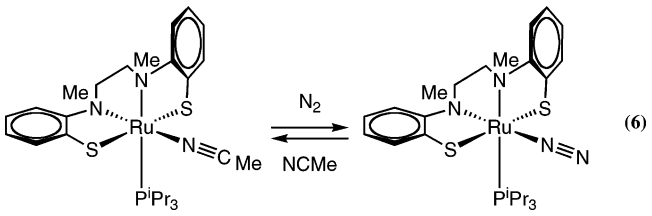
or the addition of crown ether. A linear homobimetallic neutral dinitrogen complex results from reduction with Na/Hg. This complex tolerates further reduction with Na and can also react with alkyl azides to give C_{3v}-symmetric imido complexes via loss of N_2. Similar complexes of cobalt are also reported.

An experiment proposed to model "prebiotic" dinitrogen fixation employs H_2S as a reductant and proton source over an iron sulfide surface.[77] Low yields of ammonia are reported, indicating that iron/sulfur compounds are competent to fix nitrogen even in the absence of complicated protein coligands.

3.2. Ruthenium and Osmium

Like iron, ruthenium is a catalyst component for some Haber−Bosch systems. Although ruthenium is not found in biological systems,[78] it has a role in biomimetic chemistry in that dinitrogen and related complexes of ruthenium are often more stable than their iron congeners, and therefore ruthenium has been a synthetic workbench for those attempting to model iron−dinitrogen interactions and stabilize reactive intermediates.[75] For example, although iron−sulfur complexes are often reluctant to bind N_2, [(SNNS)(P^{i}Pr$_3$)Ru(NCMe)] (where (SNNS) = $(S\text{-}o\text{-}C_6H_4\text{-}N(Me)CH_2CH_2N(Me)\text{-}o\text{-}C_6H_4\text{-}S)^{2-}$) reacts spontaneously with dinitrogen, wherein N_2 reversibly displaces acetonitrile to form the linear monometallic N_2 complex [(SNNS)(P^{i}Pr$_3$)Ru(N_2)], as shown in eq 6. This complex has an N−N bond length of 1.110(4) Å,[44] which indicates slightly greater activation than the mononuclear iron dinitrogen complexes already cited. The ($^{tp}S_4$) ligand cited in the last section was initially developed and deployed successfully on Ru, leading to synthesis and crystallographic characterization of dinuclear complexes containing either bridging diazene or hydrazine fragments.[79]



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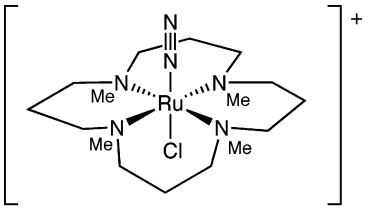
As in the coordination chemistry of iron, N_2 can displace H_2 ligands from ruthenium, leading to weakly activated complexes.[80] $[(Ph_2PCH_2CH_2)_3P)RuH_2]$ can be photolyzed to a cyclometalated intermediate that reverses its cyclometalation to bind N_2[81] in a manner analogous to a previously cited iron complex (see Scheme 1). N_2 can reversibly displace H_2 from $[(Tp)(dppe)Ru(H_2)]^+$ (where Tp is the scorpionate ligand hydrotris(pyrazolyl)borate) to form a weakly activated cationic dinitrogen complex of ruthenium.[82] A different synthetic methodology and replacement of the bisphosphine ligand with a chelating phosphineamine gives $[(Tp)(Ph_2PCH_2CH_2NMe_2)Ru(N_2)]^+$, which has an N−N bond length coincidentally exactly equal to that of free N_2.[83] The $[(Tp)(Ph_2PCH_2CH_2NMe_2)Ru]^+$ fragment reversibly coordinates a number of σ donors, and the order of complex stabilities is vinylidene > CO > N_2 > NCMe > H_2O ∼ acetone > $CF_3SO_3^-$. Reduction of $[(TMC)RuCl_2]Cl$ (where (TMC) is the macrocyclic polyamine tetramethyl-1,5,9,13-tetraazacyclohexadecane ligand) with Zn gave cationic *trans*-$[(TMC)Ru(N_2)Cl]^+$ (**2**), which apparently shows N−N bond shortening to 1.005(10) Å.[84] The kinetics of this system's N_2 uptake ability has been explored.[85] Pincer dinitrogen complexes of Ru generally display weak activation[86] and can easily lose their N_2 ligands in ligand substitution reactions.[87,88]



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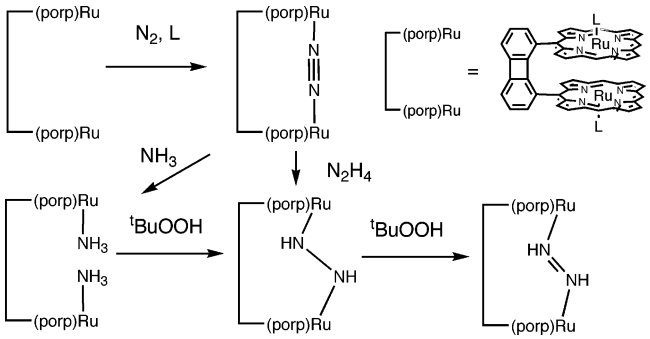
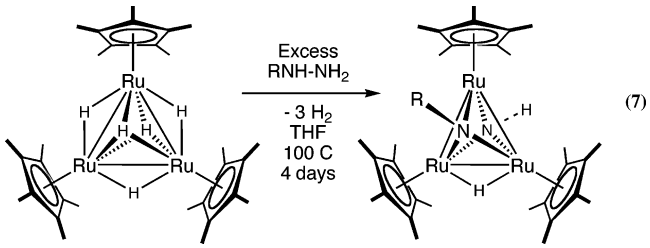
Although they are not related to nitrogenase, porphyrin-based ligands have an undeniable place in biomimetic inorganic chemistry, and the discovery of a cofacial diporphyrin complex of ruthenium capable of binding dinitrogen, diazene, hydrazine, or 2 equiv of ammonia is an interesting example of ruthenium dinitrogen chemistry.[89] The parent dinitrogen complex can also be synthesized by ligand substitution with the dihydrogen complex.[90] The system, shown in Scheme 2, supports a series of two-electron oxidations between these species, effecting the overall oxidation of 2 equiv of NH_3 to N_2. Unfortunately, reversing this formation of N_2 from ammonia is beyond the reach of this system. The electrochemical characterization of these species suggests that this system is not competent to catalyze N−N bond cleavage via a reductive pathway due to the strength of the final N−N bond of hydrazine,[89] but observation of this series of coordinated intermediates is important.

Scheme 2



A trimetallic ruthenium pentahydride cluster supported by Cp* ligands reacts with substituted hydrazines $RNH-NH_2$ (R = Ph, Me), as shown in eq 7.[91]



(7)

This reaction proceeds via elimination of hydride ligands as dihydrogen prior to N−N bond cleavage. One of the resulting imido fragments then migrates to the opposite face of the $(Cp^*Ru)_3$ core, prior to another H_2 elimination. In addition to the formation of H_2, this result is potentially significant to nitrogenase in that two M_3 triangles (connected by a single and likely nitrogenous ligand) are found in FeMo-cofactor, although neither the fates of the hydrides and the hydrazine protons in this system nor the route of ammonia extrusion in the natural system are yet known. The cluster also reacts with azobenzene.

Osmium supports little dinitrogen chemistry. A monomeric cationic dinitrogen complex $[(RPh_2P)_4Os(N_2)H]^+$ (where R = OMe or OEt) is obtained from reaction of $[(RPh_2P)_4Os(H)_2]$ with methyl triflate under N_2.[92] The end-on anionic dinitrogen complex $[(NH_3)_5Os(N_2)]^{2+}$ can be photoisomerized to give a metastable isomer that is currently the only crystallographically characterized monometallic side-on dinitrogen complex.[93] Osmium nitrido complexes are currently of some synthetic interest,[94,95] and have been employed to demonstrate the reductive coupling of an osmium nitride with a molybdenum nitride to form N_2 in the formal reverse of reductive cleavage.[96] In a reaction that is the formal reverse of another process of interest, the osmium(IV) nitride complex $[(tpy)OsCl_2(\equiv N)]^+$ (where tpy = terpyridyl) can be oxidized to a hydrazido complex in the presence of amines, and eventually to the neutral dinuclear dinitrogen complex $[(tpy)OsCl_2]_2(N_2)$.[97,98]

4. Complexes of the Group 6 Metals

4.1. Chromium

The dinitrogen chemistry of chromium is not very rich. One example in which a biomimetically signifi-

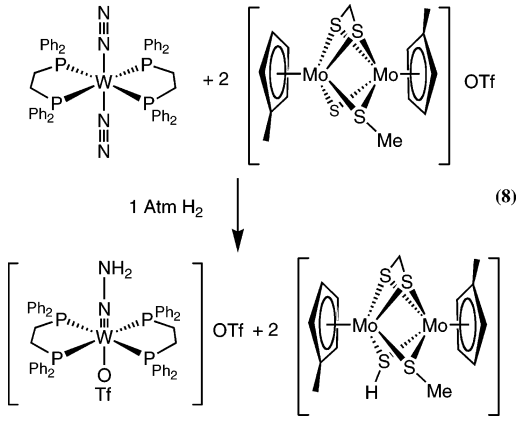
cant ligand plays a role is a porphyrin complex of chromium with a triflate ligand, which reacts via loss of triflate with $[(PhMe_2P)_4Re(N_2)Cl]$ to produce a linear bridging heterobimetallic dinitrogen complex.[99] The IR spectrum of the resulting species shows the N−N stretch at 1887 cm^{-1}, 33 cm^{-1} lower than in the rhenium starting material. However, if the same experiment is performed using [(porp)Fe(OTf)], the N−N stretch is 1803 cm^{-1}, indicative of greater N−N activation upon coordination to iron than to chromium. The four-coordinate nitride $[(R(Ar)N)_3Cr{\equiv}N]$ has been prepared by deoxygenation of NO rather than by methods paralleling the $[(R(Ar)N)_3Mo]$ dinitrogen chemistry, which will be addressed in detail in section 4.2.[100] This chromium compound does not display reactivity at the nitrido moiety.

4.2. Molybdenum and Tungsten

These two metals are by far the most azophilic of the transition series, and their dinitrogen chemistries are roughly similar, with some exceptions. As in iron N_2 chemistry, early work was based on octahedral complexes of the general formulation $[(P)_4M(N_2)(L)]$ or $[(P{-}P)_2M(N_2)(L)]$, where P is a phosphine donor, P−P is a bisphosphine, and L (in cis or trans geometry[101]) is one of many other ligands including dinitrogen. The preparations and properties of these complexes have been widely reviewed, and new variants are still being developed.[102,103]

Protonation of N_2 coordinated to Mo(0) or W(0) is a mature reaction path with extensive chemistry[104,105] in which research is ongoing.[106] Complexes with monodentate tertiary phosphines generally give more ammonia on protonation, and the bidentate phosphine analogues frequently stabilize protonated hydrazido ligands. A geometric selectivity is observed in that the cis bis-dinitrogen complexes yield substoichiometric amounts of ammonia while the trans complexes yield the hydrazido product. Chelating phosphines favor hydrazine production, while monodentate phosphine complexes tend to produce more ammonia. Electrophilic attack at the terminal nitrogen of the weakly activated N_2 moiety is more likely,[107] although the extent to which this occurs depends on the degree of back-bonding in the complex and therefore on the other ancillary ligands. Bridging hydrosulfido complexes of Fe and Ir have recently been employed as proton sources.[108] The reaction of a dimeric molybdenum μ-sulfido complex with H_2 generates an acidic −SH moiety which gives NH_3 when reacted with *cis*-$[(P{-}P)_2W(N_2)_2]$ but stops at a protonated hydrazido ligand when reacted with *trans*-$[(P{-}P)_2W(N_2)_2]$, as shown in eq 8.[109]

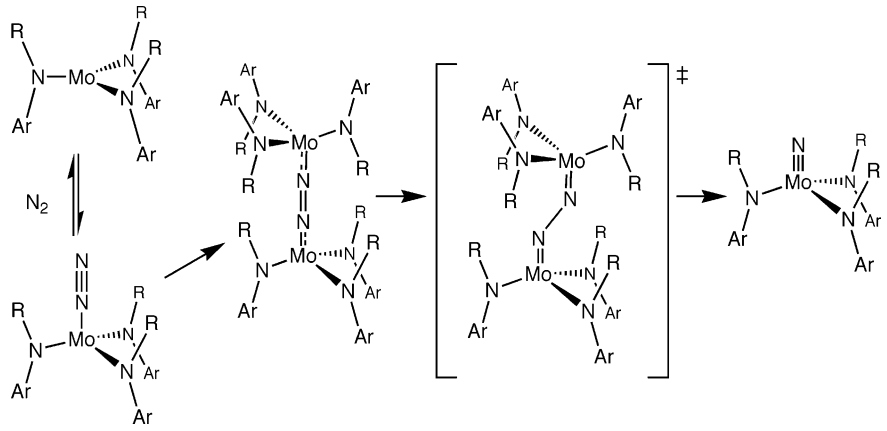
The dependence of the extent of N_2 activation on the nature of the other ligand L in *trans*-$[(dppe)_2W(N_2)(L)]$ has been explored[110] with the result that L = NCEt gives higher N−N activation than L = N_2. However, protonation of the dinitrogen unit to a hydrazido ligand $(N{-}NH_2)^{2-}$ induces lability in the nitrile, highlighting the importance of ancillary ligand interactions. Vibrational spectroscopy of ^2H and ^{15}N isotopomers of $[(dppe)_2W(N_2)_2]$ and the protonated complexes $[(dppe)_2W(NNH)F]$ and $[(dppe)_2W(NNH_2)F]^+$ shows M−N bond strength increasing synergistically with a decrease in N−N bond strength, and also suggests that the monoprotonated intermediate exists as an equilibrium between metal-protonated and nitrogen-protonated forms.[111] The majority of ligand-to-metal charge-transfer responsible for dinitrogen reduction occurs in the first protonation,[112] perhaps facilitating the second protonation by increasing the charge density on the terminal N and allowing it to interact with the second electrophile. Study of the third protonation, giving the hydrazidium complex $[(depe)_2W(NNH_3)F]^{2+}$, shows a bond order of one in the reduced $N{-}NH_3$ moiety and a triple bond between W and N. Cleavage of the remaining N−N bond is thought to be a high-barrier event with $\Delta H^{\ddagger} > 168$ KJ mol^{-1},[113] which supports the general observation that bisphosphine $[(P{-}P)_2M(N_2)L]$ complexes of Mo and W often stop at hydrazine in protonation schemes while monodentate $[(P)_4M(N_2)L]$ complexes yield ammonia.



(8)

A recent finding shows that cationic dihydrogen complexes of Ru are sufficiently acidic to protonate the N_2 moiety of $[(dppp)_2W(N_2)_2]$[114,115] (where (dppp) = $Ph_2PCH_2CH_2CH_2PPh_2$), although the stoichiometry treats each ruthenium complex as 1 equiv of H^+. The hydrazido complexes derived from the protonation of $[(P)_4M(N_2)L]$ and $[(P{-}P)_2M(N_2)L]$ precursors are themselves substrates for reaction schemes aimed at formation of N-heterocycles. These areas have been reviewed recently.[1,105] The dinitrogen moiety of this type of complex has been reacted with a number of Group IV and V metals supported by mixed Cp, chloride, and methyl ligands to generate a series of linear bridging dinitrogen complexes which can be generally formulated as $[Cl(P)_4M](\mu\text{-}N_2)[Cp_nM'Cl_mMe_x]$ (where M = Mo, W, M′ = Ti, Zr, Hf, Nb, Ta, and *m*, *n*, and *x* are various integers).[116] The resulting heterobimetallic complexes are isostructural across the metal−dinitrogen moiety, which displays activation to $(N_2)^{2-}$, and the bridging complexes supported by monodentate phosphines display typical reactivity, undergoing protonation to substoichiometric amounts of ammonia with trace evolution of hydrazine. The Mo(0) analogue of the previously discussed $[(NP_3)Fe(N_2)]$ complex binds two dinitrogen molecules—its formulation is *cis*-$[(NP_3)Mo(N_2)_2]$ and it gives 0.4 mol of NH_3 and 0.2 mol of hydrazine per mole of complex on protonation with HBr.[70]

Scheme 3



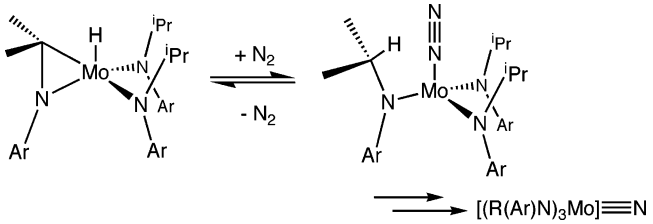
Addition of carbonyl ligands changes the N_2 binding characteristics of Mo and W. Treatment of *trans*-$[(depe)_2Mo(N_2)_2]$ with CO gives the bimetallic linear molybdenum complex *trans*-$[(CO)(depe)_2Mo]_2(\mu\text{-}N_2)$.[117] This latter complex can lose N_2 if refluxed in xylene under argon. However, the resulting monometallic complex is stabilized by a weak agostic interaction with a ligand ethyl group and readily reacquires N_2 in solution even when N_2 is present in trace amounts. The bridging dinitrogen complex only forms with alkyl substituents on P, and when (dppe) is employed only the monometallic terminal dinitrogen complex is observed, presumably due to steric effects. A mixed carbonyl−phosphine complex of tungsten stabilized by an agostic interaction with an isopropyl group also binds dinitrogen when it is present, giving the bridging bimetallic complex *trans*-$[(CO)_3(P^iPr_3)_2W]_2(N_2)$ at the expense of the agostic interaction.[118]

Cummins and co-workers first reported the spontaneous reductive cleavage of N_2 by neutral complexes of the general formulation $[(R(Ar)N)_3Mo]$ in 1995 (where R = alkyl and Ar = aryl, especially 3,5-$(CH_3)_2C_6H_3$).[53] This process is shown in Scheme 3. Designed as a $3e^-$ reducing agent for small-molecule activation,[119] this system benefits from favorable edge interactions between the three aryl groups which enforce a C_{3v} symmetry, resulting in an aryl "bowl" and an alkyl "pocket" on opposite sides of the metal. Dinitrogen binds reversibly in the alkyl pocket.

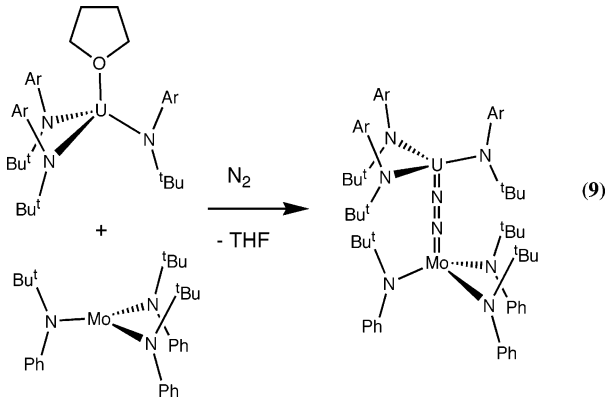
Both the initial monometallic binding of N_2 and the formation of the dimeric species $[(R(Ar)N)_3Mo](\mu\text{-}N_2)[Mo(N(Ar)R)_3]$ are low-barrier events that require spin-state changes as the N−N bond order changes. The N−N bond order in the linear bimetallic species is estimated at slightly greater than two by Raman spectroscopy and EXAFS.[120] The first-order process of N−N bond cleavage proceeds via a rate-limiting zigzag transition state[121] that relates to cleavage of the last N−N bond, rather than the preceding reductions. A ^{15}N isotope effect is observable in this system, and reductive cleavage is subject to steric constraints. Since various combinations of R and Ar are available, a thorough exploration of this dependence has been performed. When R = isopropyl, a tautomeric equilibrium with a cyclometalated molybdenum hydride is observable, as shown in Scheme 4.

The cyclometalated species does not undergo the insertion chemistry typical of early metal hydrides.

Scheme 4

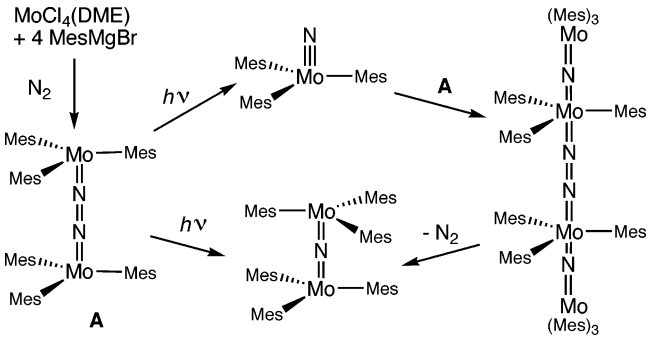


It is worth noting that similar chemistry on Nb has not led to any dinitrogen chemistry to date, despite successful syntheses of niobium analogues of the metallaaziridine hydride.[122,123] The molecular structure of the cyclometalated Mo complex has been established by a neutron diffraction study, and this form acts as a "masked" source of $[(R(Ar)N)_3Mo]$[124] which interacts with N_2 to produce four-coordinate $[(R(Ar)N)_3Mo{\equiv}N]$. However, when R = adamantyl, no N−N cleavage reaction ensues, presumably because the additional bulk of the adamantyl group prevents formation of the bridging bimetallic intermediate. The bound dinitrogen complex can accept electrons from external sources—anions of the monomeric intermediate $[(R(Ar)N)_3Mo(N_2)]$ can be prepared with suitable reductants, and these anions can be trapped by reaction with TMSCl (where TMS = $SiMe_3$), giving $[(R(Ar)N)_3Mo(-N{=}NTMS)]$ even when R = adamantyl. The kinetics of N_2 binding and cleavage are greatly improved by the presence of N-heterocyclic bases or KH in THF[125] and by catalytic amounts of Na/Hg amalgam.[126] Equation 9 shows how bimetallic dinitrogen complexes of U and Mo have been prepared from this system,[127] as have complexes featuring bridging nitrido ligands (see section 5.2). An R = isopropyl derivative of $[(R(Ar)N)_3Mo]$ reacts with Mg to give the reduced salt $([(R(Ar)N)_3Mo]\mu\text{-}N_2)_2Mg$, which is a synthon that has been used to prepare a heterodinuclear complex by metathesis with $[(R(Ar)N)_3NbCl]$, as will be discussed in section 5.2. The $[(R(Ar)N)_3Mo]$ system prefers to cleave the N−N bond even when N_2O is used as a substrate.[128] The nitrido species has exhibited intermetal N atom transfer,[129] and formation of trifluoroacetamide when treated with the anhydride of trifluoracetic acid.[130] The limited reactivity of this species may be due to combined effects of steric protection by the alkyl pocket and the strength of the M≡N bond.[131]



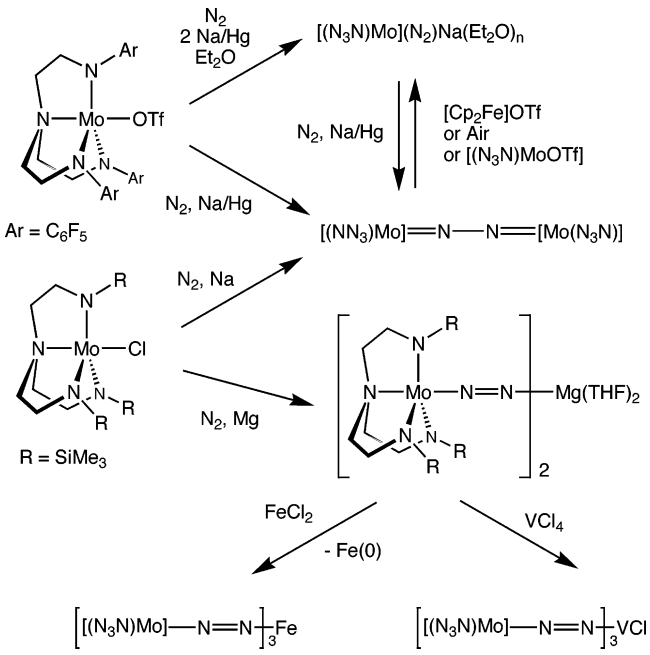
A related system using three-coordinate Mo supported by mesityl (Mes, or 2,4,6-$Me_3C_6H_2$) ligands[132] has enabled the four-electron reduction of N_2 to a thermally stable bridging hydrazido ligand contained in $[(Mes)_3Mo]_2(\mu\text{-}N_2)$. In contrast to the numerous examples of stable bimetallic linear dinitrogen complexes already discussed, this species can be photolyzed in the presence of N_2 to generate bridging and terminal nitrido species, postulating the existence of a linear Mo_4N_4 array, as shown in Scheme 5. Photolysis of Mo[133] and W[134] dinitrogen complexes has also been reported.

Scheme 5



Schrock and co-workers have previously established a cycle for protonation and reduction of N_2 bound to a $[Cp^*MMe_3]$ species (M = Mo or W) that is a good match for the Chatt cycle except for a protonation of the metal-bound N_α of $M{=}N{-}NH_2$ that may lead to a proposed η^2-hydrazine intermediate prior to N−N bond scission. This chemistry has been summarized recently.[36] Schrock has been exploring dinitrogen chemistry supported by a trianionic (N_3N) "triamidoamine" ligand (where $(N_3N)^{3-} = ((RNCH_2CH_2)_3N)^{3-}$ and R = an array of alkyl, silyl, aryl, and fluoroaryl substituents) on Mo and W. The initial report[135] of a rational synthesis of $[(N_3N)Mo(N_2)]$ includes characterization of the bridging dimolybdenum species $[(N_3N)Mo]_2(\mu\text{-}N_2)$ which can be reduced to $[(N_3N)Mo](\mu\text{-}N_2)NaL_n$ (L_n = ether in various amounts). A variant complex of molybdenum based on a tridentate $(MeN_2N)^{2-}$ ligand (where $(MeN_2N)^{2-} = (MeN(CH_2CH_2NC_6F_5)_2)^{2-}$) was not competent to activate dinitrogen.[136] The bridging molybdenum dinitrogen complex $[(N_3N)Mo]_2(\mu\text{-}N_2)$ reacts with trialkyl halides of Si and Sn to give new N−Si and N−Sn bonds. A different preparative regime beginning with $[(N_3N)MoCl]$[137] allows synthesis of the heterometallic magnesium salt $([(N_3N)Mo]\mu\text{-}N_2)_2Mg(THF)_2$ which reacts with $FeCl_2$ to give a heterometallic dinitrogen complex of Fe and Mo via concomitant reduction of some $FeCl_2$ to Fe(0). This magnesium salt can be used in metathesis schemes with VCl_4 and $ZrCl_4$ to replace up to three chlorides with $[(N_3N)Mo(N_2)]$ fragments, although reactions attempted with more easily reduced metal halides were complicated by redox chemistry. Some of this chemistry is summarized in Scheme 6.

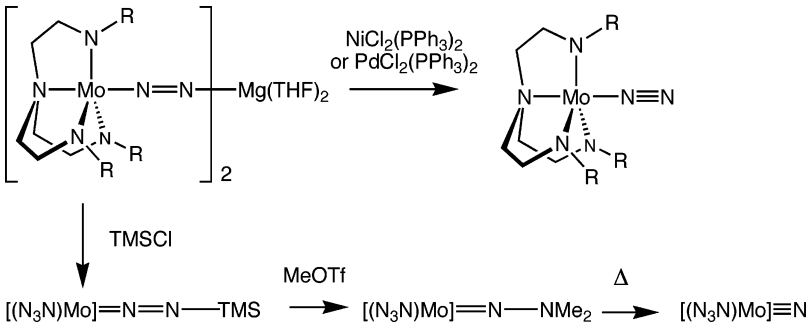
Scheme 6



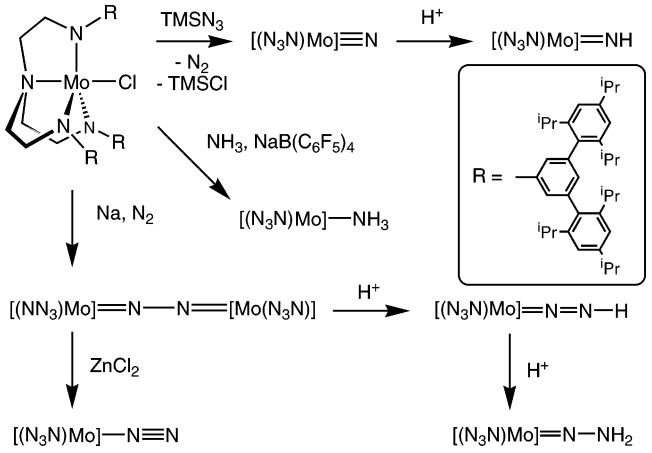
Neutral $[(N_3N)Mo(N_2)]$ can also be obtained from the magnesium adduct by application of $PdCl_2(PPh_3)_2$ or $NiCl_2(PPh_3)_2$,[138] as can $[(N_3N)Mo(N{=}N\text{-}TMS)]$ by reaction with TMSCl. This species undergoes N-alkylation with MeOTf to give $[(N_3N)Mo(=N\text{-}NMe_2)]$, although control of this reaction is imperfect in that some ligand amide methylation is observed. $[(N_3N)Mo(N_2)]$ dimerizes via loss of N_2 if heated for extended periods, indicating the thermodynamic stability of $[(N_3N)Mo]_2(\mu\text{-}N_2)$.[139] The nitrido species $[(N_3N)Mo{\equiv}N]$ is available via decomposition of $[(N_3N)Mo(=N\text{-}NMe_2)]$ or by reaction of the parent chloride with azides, as shown in Scheme 7, and efforts to functionalize or liberate nitrido ligands from the complex were initially unproductive.[140] Electrochemical data are available for $[(N_3N)MoCl]$ complexes with varying ligand R groups, and cyclic voltammetry suggests that the barrier to reduction increases as does the electron-donating ability of the (N_3N) ligand aryl group.[141] Furthermore, the rate at which chloride is lost in the reduced species indicates that these $[(N_3N)MoCl]$ complexes are not ideal candidates for catalytic regimes. Analogous W complexes were irreversibly reduced in this study.

The most recent generation of these complexes employs sterically demanding 3,5-bis(2,4,6-triisopropylphenyl)phenyl (HIPT) substituents on the (N_3N) framework.[142,143] The parent molybdenum(IV) chlo-

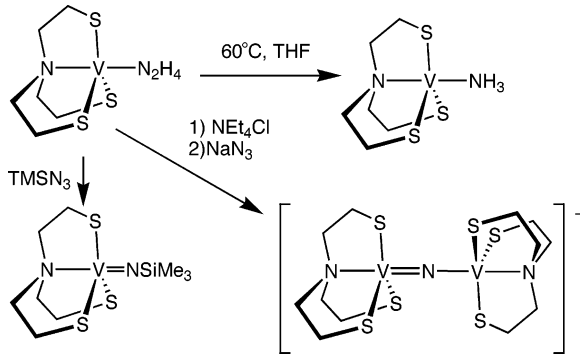
Scheme 7



Scheme 8



Scheme 9



ride complex [(N$_3$N)MoCl] is easily prepared, and the chloride resides in a well-protected pocket roughly 7 Å deep, trans to the central amine donor. This (HIPT)-substituted [(N$_3$N)MoCl] synthon is the starting point for synthesis of a number of complexes that contain nitrogenous species of interest to this discussion. Reaction of this species with $TMSN_3$ gives the nitride [(N$_3$N)Mo≡N], which can be protonated to form [(N$_3$N)Mo=NH]$^+$. The chloride ligand can also be removed with NaB(3,5-(F$_3$C)$_2$C$_6$H$_3$)$_4$ in the presence of ammonia to give [(N$_3$N)Mo(NH$_3$)]. Upon treatment with 1 equiv of Mg in the presence of N_2, [(N$_3$N)MoCl] forms the insertion product [(N$_3$N)Mo]-(μ-N$_2$)MgCl. This species can be protonated to [(N$_3$N)-Mo(N=NH)] and further to [(N$_3$N)Mo(=NNH$_2$)]$^+$, or oxidized by $ZnCl_2$ to give free neutral [(N$_3$N)Mo(N$_2$)]. Scheme 8 summarizes these interconversions. The bulk of the three (HIPT) substituents precludes dimerization via loss of N_2. Many of these putative intermediates from the nitrogenase reaction are subject to reduction using cobaltocene synergistically with 2,6-lutidinium tetraarylborate as a proton source, and therefore a scheme of stepwise protonations and reductions that parallels the Chatt cycle and Schrock's earlier work with [Cp*WMe$_3$] has evolved. Judicious choice of kinetically compatible reducing agents and proton sources has allowed modest catalytic cycling of this complex under N_2.[144] Steric protection by the extremely large HIPT groups appears central to preventing the formation of bimetallic species and allowing reduction of the cationic ammonia complex to a complex that is capable of undergoing a ligand displacement reaction with N_2 to regenerate the initial dinitrogen complex.

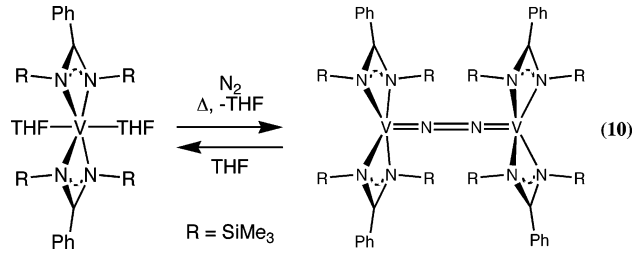
5. Complexes of the Group 5 Metals

5.1. Vanadium

The discovery of vanadium nitrogenase prompted research into the coordination chemistry of vanadium as a functional model of this enzyme subtype. Model systems of V(II) have recently been reviewed.[145] A key finding in the evolution of synthetic vanadium dinitrogen chemistry is that gels containing hydroxides of V and Mg, or "soups" of V(II) with catechols,[146] are capable of nitrogen fixation at high pH. Mononuclear and dinuclear bridging vanadium dinitrogen complexes are known, as are mononuclear complexes with two N_2 ligands. Protonation of bridging dinitrogen complexes of vanadium typically evolves ammonia and free N_2.[147]

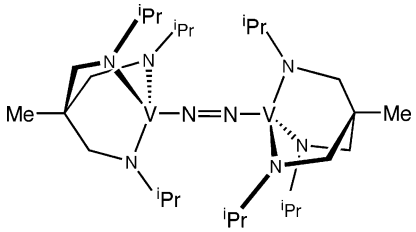
Group 5 metals in the higher oxidation states often act as strong activators in dinitrogen chemistry, although V is not as strongly reducing as Nb or Ta and therefore vanadium does not always bind N_2 irreversibly. In a system that is isoelectronic to the neutral [P$_4$Mo(N$_2$)L]-type systems described previously, a vanadium(III) precursor is reduced in the presence of various phosphines and dinitrogen to give anionic complexes of the type [P$_4$V(N$_2$)L]$^-$, where L can be N_2, in cis and trans configurations.[148] These complexes lose N_2 under even slightly reduced pressure. The cis form is more labile to ligand substitution reactions, and the complexes yield 0.25 equiv of ammonia and small amounts of hydrazine on protonation with HBr. A tridentate trianionic $(S_3N)^{3-}$ ligand (where $(S_3N)^{3-} = (N(CH_2CH_2S)_3)^{3-}$) does not enable direct entry into dinitrogen chemistry on vanadium but does allow preparation of a hydrazine complex [(S$_3$N)V(N$_2$H$_4$)][149] and subsequent reactions which lead to coordinated ammine, nitrido, and imido moieties, as shown in Scheme 9.

The amidinate ligand $(Me_3SiNC(Ph)NSiMe_3)^-$ supports synthesis of the V(II) species $[(Me_3SiNC(Ph)NSiMe_3)V(THF)_2]$, which forms $[(Me_3SiNC(Ph)NSiMe_3)V]_2(\mu\text{-}N_2)$ via loss of THF upon heating. The N−N bond is 1.235(6) Å, characteristic of significant reduction. However, this is a reversible process, as the monometallic THF complex forms again on dissolution in THF, as shown in eq 10.[150] The same group



(10)

has employed a tridentate ligand strategy on V(III) to synthesize $([(Me(CH_2N^iPr)_3)V]_2(\mu\text{-}N_2)$ (**3**), which shows increased activation (N−N = 1.257(6) Å) and does not lose N_2, in contrast to the previous example.[151] The same report describes synthesis of the V(III) complex $[(Me_3Si(Ph)N)_3V(THF)]$, which features THF bound in the aryl "bowl" of the complex. This complex sponsors no dinitrogen chemistry when THF is removed.

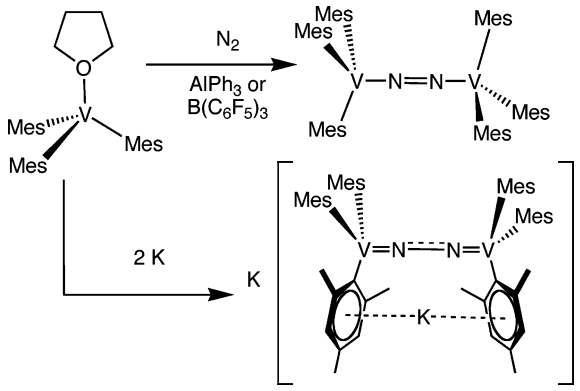


3

Two other three-coordinate vanadium complexes show reactivities similar to that of the amidinato system. Treatment of $VCl_3(THF)_3$ with 3 equiv of neopentyllithium (NpLi) under N_2 gives diamagnetic $[(Np)_3V]_2(\mu\text{-}N_2)$, which readily loses N_2.[152] Only the alkyl groups react to protonation, and no ammonia or hydrazine is observed. Under N_2, $[(Mes)_3V(THF)]$ reversibly loses THF to $AlPh_3$ or $B(C_6F_5)_3$ to give diamagnetic $[(Mes)_3V]_2(\mu\text{-}N_2)$, which can be reduced in a stepwise fashion with alkali metals to give anionic $M_n\{[(Mes)_3V]_2(\mu\text{-}N_2)\}$ (where M = Na or K and one or more Mes−M π interactions exist), as can be seen in Scheme 10.[153] This compound is also attainable without the addition of the Lewis acid via reduction of the original tetrahydrofuranate under N_2,[59] indicating that this reduction manifold is accessible from both V(II) and V(III). The anionic complexes give 20−38% hydrazine and traces of ammonia on protonation, while the neutral dinitrogen complex quantitatively loses N_2 when protonated.

A recent result concerns the reaction of a nitride of vanadium with electrophiles. The sodium salt of the nitrido complex $[L_3V{\equiv}N]^-$ reacts with CS_2 or CO_2 to give NaNCS or NaNCO and the corresponding sulfido- or oxovanadium species by extrusion from an intermediate featuring a nitrido−carbon bond,[154] as shown in Scheme 11. Despite the fact that this N

Scheme 10



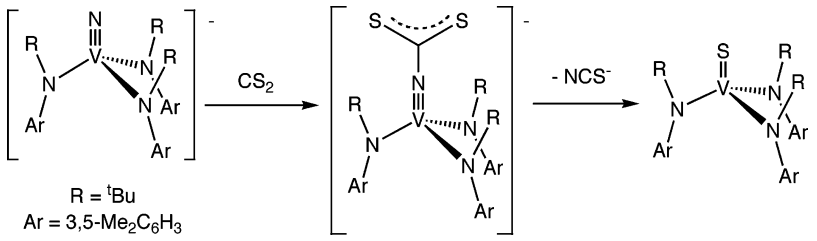
atom derives from inorganic azide and not dinitrogen, the removal of a nitrido ligand from a metal complex is noteworthy in both the synthetic and biomimetic contexts.

A vanadium(III) system reminiscent of the $[(N(R)Ar)_3Mo]$ and $[(N_3N)Mo]$ systems previously discussed has been shown to reductively cleave N_2.[155] The dimeric diamidoamine complex of V(III), $[(N_2N)VCl]_2$ (where $(N_2N)^{2-} = (Me_3SiN(CH_2CH_2NSiMe_3)_2)^{2-}$), can be reduced using 1 equiv of potassium graphite per V under N_2 to give a transient V(II) species that is d^3 and therefore isoelectronic to the Mo systems. This species binds and activates dinitrogen in solution to give $[(N_2N)V]_2(\mu\text{-}N)_2$. The diamagnetic product features a rectangular V_2N_2 motif with V−N distances of 1.769(10) and 1.862 Å, and an N−N separation of 2.50(2) Å, suggesting the complete cleavage of dinitrogen to two bridging nitrido ligands. Both N atoms in the dimer originate from the same N_2 molecule, and theoretical considerations[156] suggest a side-on intermediate. Reduction of $[(N_2N)VCl]_2$ using an excess of potassium graphite or of nitride $[(N_2N)V]_2(\mu\text{-}N)_2$ with $Ag[BPh]_4$ allows isolation of paramagnetic $M([(N_2N)V]_2(\mu\text{-}N)_2)$ (M = K or Ag), as shown in Scheme 12. The final reduced product shows slightly tighter bonding in the V_2N_2 core but greater than 3 Å separation between one V and one of its former amine ligands, suggestive of a mixed-valent d^1 V(V)−V(IV) dimer. This species is a minor product in the one-electron reductions of the starting chloride complex, suggesting that the reduced dinitrogen complex reacts with available equivalents of reducing agents faster than does the parent chloride complex.

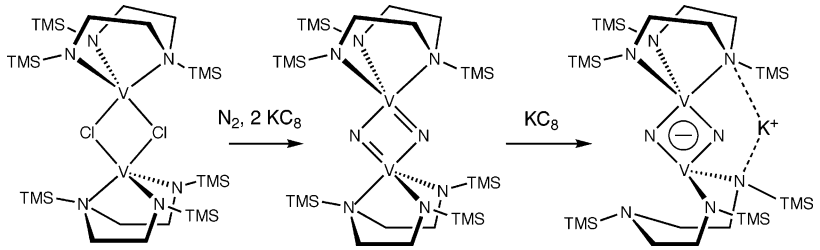
5.2. Niobium and Tantalum

These two elements are entirely nonbiological, and yet their dinitrogen chemistries are varied and worth brief examination. Strong activation is typical of both metals, and early work was dominated by linear hydrazido moieties.[157−159] A recent result employs a calix(4)arene-supported Nb═Nb metal−metal bonded species to activate N_2.[160] The resulting linear diazenido complex accepts additional external reducing equivalents, facilitating complete N−N bond cleavage and rearrangement to a Nb_2N_2 square, as shown in eq 11. The core of this structure is a common motif for group 5 nitrides, reminiscent of the motif observed in a previously cited vanadium system and illustra-

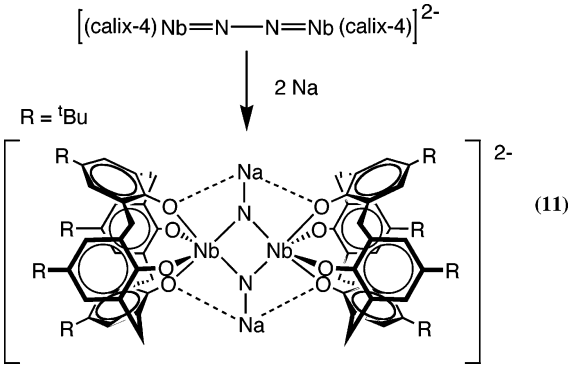
Scheme 11



Scheme 12

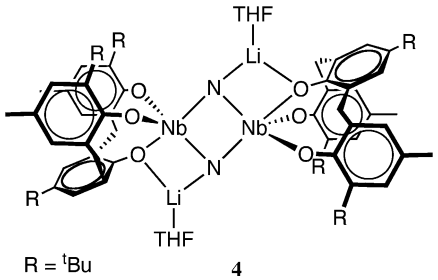


tive of another manner in which metals can mediate overall N−N bond cleavage.



(11)

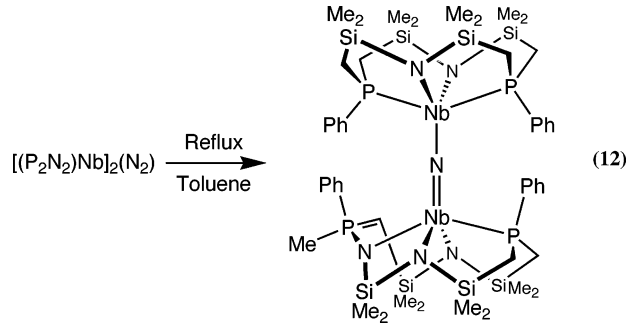
In a similar study employing a tridentate tris(aryloxide) ligand, treatment of the aryloxo-bridged $[(ArO)_3NbCl]_2$ dimer with excess $LiBHEt_3$ results in complex **4**, featuring bridging niobium nitrides with inclusion of lithium atoms in the resulting scaffold.[161]



4

Although direct entry into niobium dinitrogen chemistry based on $[(R(Ar)N)_3Nb]$ species has not yet been attained, the previously cited complex $([(R(Ar)N)_3Mo](N_2))_2Mg$ reacts via salt metathesis with $[(R(Ar)N)_3NbCl]$ to give a dinuclear anion, a monomeric anionic niobium nitride, and finally a niobazene cyclic trimer after reaction with I_2.[162]

A linear bimetallic paramagnetic dinitrogen complex of Nb supported by the $(P_2N_2)^{2-}$ macrocycle (where $(P_2N_2)^{2-} = (PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh)^{2-}$) can be prepared by reduction of $[(P_2N_2)NbCl]$ under N_2.[163] The dinitrogen complex can be thermolyzed to a bridging nitrido species at the expense of one (P_2N_2) ligand, which undergoes considerable rearrangement instigated by the insertion of the other N atom into a Si−C bond, as shown in eq 12.



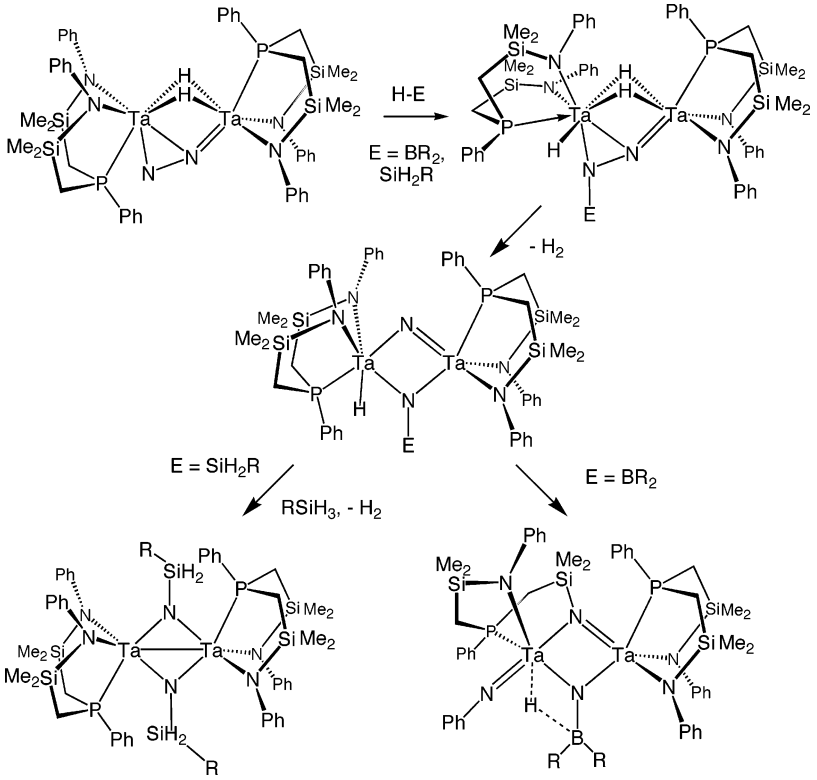
(12)

Analogous tantalum complexes have not yet been synthesized, but a tridentate $(NPN)^{2-}$ ligand (where $(NPN)^{2-} = ((PhNSiMe_2CH_2)_2PPh)^{2-}$) allows synthesis of a dinuclear dinitrogen complex featuring the unusual side-on end-on bonding mode,[164] which is yet another possibility for N_2 binding at the FeMo-cofactor. This bonding mode gives substantial polarization to the dinitrogen moiety, and the complex displays equally unusual reactivity patterns, including the ability to undergo hydroboration[165] and hydrosilylation[166] reactions. Subsequent spontaneous reactions involve the reductive loss of bridging hydrides as H_2, leading to N−N bond scission and the evolution of reactive nitrido ligands, as summarized in Scheme 13.

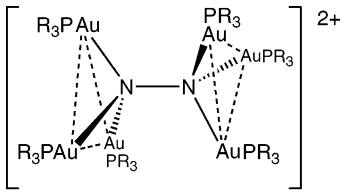
6. Other Notable Dinitrogen Complexes

The following are offered as recent synthetic examples from the other transition metals which present facets of dinitrogen chemistry that are of current interest. The N_2 unit of a hydrazine-derived family of dicationic hexametallic gold N_2 complexes of composition $[LAu]_3(N_2)[AuL]_3^{2+}$ (L = various tertiary phosphines) resides in a metal−N_2 motif reminiscent of the trigonal prism of iron atoms at the FeMo-cofactor, with Au−Au interactions mediating the

Scheme 13



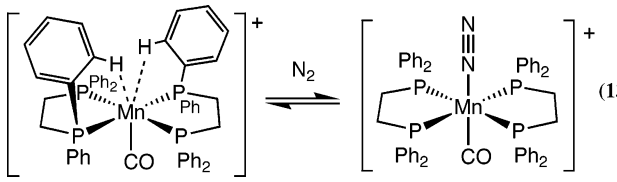
geometry in the place of bridging sulfide ligands,[167] as in the generalized complex **5**. One of these complexes gives excellent yields of ammonia on protonation.



5

Rhenium complexes exhibit some dinitrogen chemistry. The thiolate complex $[(Ph_3P)(ArS)_3Re]$ forms nitrile and isocyanide adducts with different aryl substituents but will bind N_2 only when Ar = 2,4,6-(^{i}Pr)$_3$C$_6$H$_2$.[168] $[(Ph(OEt)_2P)_3ReCl_3]$ reacts with substituted hydrazines via conproportionation to give $[(Ph(OEt)_2P)_4Re(N_2)Cl]$, cationic $[(Ph(OEt)_2P)_3Re(N_2)_2]^+$, and cationic alkyldiazenido derivatives.[169] A family of $[(R_3P)(N{-}N)Re(N_2)]^+$ cations (where N−N = a chelating diamine) have been characterized, one of which shows an N−N bond length of 1.13(1) Å.[170] Reduction of $[(N_2N'N)ReCl]$ (where $(N_2N'N)$ = an unsymmetric triamidoamine ligand) under N_2 gives $[(N_2N'N)Re(N_2)]$, which shows little activation (the N−N bond is 1.087(4) Å) and no additional reactivity despite the similarity of the ligand−metal environment to systems previously discussed.

The electron-deficient complex $[(dppe)_2Mn(CO)]^+$ exists in equilibrium with the weakly activated dinitrogen complex *trans*-$[(dppe)_2Mn(CO)(N_2)]^+$. The five-coordinate complex is stabilized by agostic interactions with ortho protons of two ligand phenyl groups, and therefore this is another extreme example of dinitrogen displacing a weaker donor (an agostic H), as shown in eq 13.[171]



(13)

Group 4 metals support an extensive but essentially nonbiological dinitrogen chemistry. Recent work has featured nitrogen-donor ligands. The diamagnetic bimetallic guanidinate complex $[((Me_2N)C(N^i{-}Pr)_2)_2Ti]_2(\mu{-}N_2)$ has an N−N bond length of 1.28(1) Å, indicating considerable activation to the $(N{=}N)^{2-}$ diazenido level and some delocalization of the remaining electrons through the Ti−N=N−Ti core.[172] The dinitrogen unit in this complex is displaced by nucleophiles such as phenyl azide, which gives the monometallic phenylimido complex. Benzamidinate ligands give isostructural results (N−N = 1.275(6) Å).[173] Figure 5 compares these complexes, both of which are prepared by reduction of a dichloride precursor.

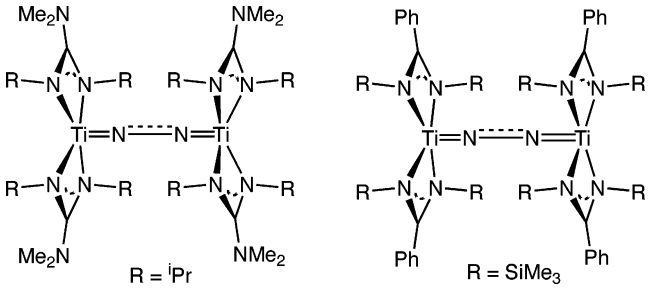
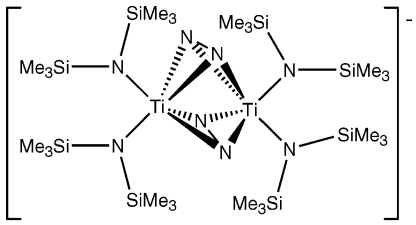


Figure 5.

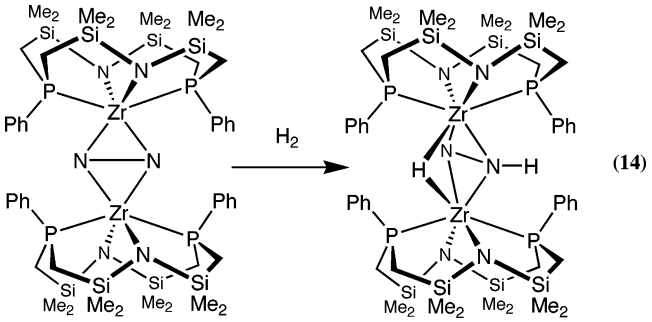
A tridentate diamido (NON) ligand ((NON) = (^{i}PrN-*o*-C_6H_4)$_2$O) supports the more strongly activated [(NON)(Me_3P)Ti]$_2$(μ-N_2), in which the N−N bond length is 1.264(8) Å.[174] This complex is derived from a diisobutyl precursor. Among the many outcomes of the reaction between TMS_2NLi and $TiCl_2$-$(TMEDA)_2$ is the anionic complex [$(TMS_2N)_2Ti]_2$-(μ-η^2:η^2-$N_2)_2^-$ (**6**), in which each Ti is bound to six N atoms. This paramagnetic mixed-valent complex



6

displays a pair of strongly activated N_2 moieties (N−N = 1.379(21) Å) which is of interest since an overall reduction by five electrons is suggested by the stoichiometry. A recent result on Zr may also bear on odd-number reductions—a disubstituted Cp″ (where Cp‴ = 1,3-$(Me_3Si)_2C_5H_2^-$) ligand has led to isolation of the side-on bound paramagnetic complex [Cp'''_2-$Zr]_2$(μ-η^2:η^2-N_2), which shows an N−N bond distance of 1.47(3) Å.[175]

Side-on bimetallic zirconium dinitrogen complexes supported by amidophosphine ligands have been prepared.[176] These complexes show substantial N−N elongation and undergo reactions with silanes and H_2[177] that lead to the formation of new bonds to dinitrogen-derived atoms. A representative example of this chemistry supported by the (P_2N_2) macrocyclic ligand is illustrated in eq 14.



(14)

7. Outlook and Future Considerations

In this review, we have tried to present recent findings in dinitrogen coordination chemistry that are relevant to the nitrogenase reaction in the broadest sense. By concentrating on the N_2 chemistry of those metals that are active in nitrogenase enzymes, namely iron, molybdenum, vanadium, and their congeners, it is hoped that at some future point this information may help develop an understanding of how nitrogenase functions by detailing some of what we understand about metal−dinitrogen interactions in simpler systems. It is likely, however, that before this can happen, some breakthroughs on the biological side will be necessary. Because nothing is known about the details of the binding of N_2 to the FeMo-cofactor and its subsequent transformation to ammonia, any attempts to try and relate results from the synthetic side to the biological side are fraught with difficulty. Uncovering the FeMo-cofactor structure has raised more questions in transition metal chemistry than it has answered, and dinitrogen coordination chemistry continues to be an empirical and often refractory pursuit governed by serendipity. It is true, however, that much beautiful chemistry has been discovered and more is likely from both sides. Once nitrogenase is unraveled, it will be interesting to go back and assess just how biomimetic all of this exciting synthetic chemistry actually was.

8. Acknowledgments

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