Chapter 1. Background and Context for the Development of Iron-Mediated Dinitrogen Reduction Chemistry
1.1. Introduction

Nitrogen fixation is the process by which one of the most inert molecules, N\textsubscript{2} (N≡N bond strength of 945.33 kJ mol\textsuperscript{-1}), is transformed into a bio-available nitrogen source, a principle component in proteins, nucleic acids, and other cellular constituents.\textsuperscript{1} Transition metal catalysts help drive the thermodynamically feasible hydrogenation of N\textsubscript{2} in both biological and industrial systems. Whereas biological ammonia production from N\textsubscript{2} occurs at ambient conditions through enzymatic action (Eq 1.1), the industrial hydrogenation of N\textsubscript{2}, exemplified in the Haber-Bosch system,\textsuperscript{2} requires extreme conditions (100-300 atm, 400-500 °C) in combination with Fe or Ru-based catalysts to drive ammonia production (Eq 1.2).

\begin{align*}
N_2 + 8H^+ + 8e^- + 16MgATP &\rightarrow 2NH_3 + H_2 + 16MgADP + 16P_i \quad (1.1) \\
N_2(g) + 3H_2(g) &\rightarrow NH_3(g) \quad (1.2)
\end{align*}

\[\Delta H^\circ = -46.2 \text{ kJ mol}^{-1}, \Delta S^\circ = -99 \text{ J mol}^{-1} \text{ K}^{-1}\]

In light of the operating conditions required for the industrial hydrogenation of N\textsubscript{2}, the realization of a competent dinitrogen reduction catalyst while adhering to the relatively mild conditions operable in nature is a truly formidable task. As such, nitrogen fixation is essential to sustaining life on this planet and has attracted intense scrutiny among the biology and chemistry communities for decades.\textsuperscript{3}

1.2. Biological N\textsubscript{2} reduction

Studying the function of nitrogenase is complicated due to the fact that substrate uptake does not occur unless the cofactor is fully loaded with electron and proton equivalents present during turnover conditions.\textsuperscript{4} While the isolated MoFe-protein
component of MoFe-nitrogenase exhibits nitrogenase activity in vitro, the presence of various cofactors (e.g., MgCl₂, ATP, hexose kinase), an excess of the obligatory electron-transfer Fe-protein, and NADH as an electron source are necessary for function, all of which severely hamper spectroscopic analysis of relevant intermediate states. Despite this inherent complexity, biochemical, spectroscopic, and crystallographic studies have revealed a great deal about nitrogenase enzymes.⁴ All nitrogenases feature a transition-metal based cofactor, which is the most likely site of N₂ binding. Three varieties of cofactors have been identified: iron and molybdenum (FeMo), iron and vanadium, and iron-only.⁵ FeMo was the first to be identified and is the most thoroughly studied enzyme of the nitrogenases (Figure 1.1).⁶,⁷ FeMo is comprised of an α₂β₂ tetramer that contains two polynuclear metal clusters, designated the P-cluster and FeMo-cofactor. The P-cluster likely participates in interprotein electron transfer, whereas the FeMo-cofactor is generally regarded as the site of substrate binding and reduction.⁷ Despite the structural determination of the FeMo cofactor, where dinitrogen binds in the FeMo-cofactor and how the enzyme functions is still yet unknown.⁸

![Figure 1.1. Picture of the FeMo-cofactor including an interstitial nitride.](image)
1.3. Biomimetic systems that model structure and function.

Designing well-defined transition metal complexes that can mimic the structure or function of nitrogenase are critical for gaining a mechanistic understanding of the enzyme. Biomimetic model design can be broadly split into two categories: cluster models and molecular models featuring a single metal site.

1.3.1 Cluster Models. The labs of Holm,\(^9\) and Coucouvanis,\(^{10}\) have prepared a veritable battalion of Fe\(_x\)S\(_x\) and MoFe\(_x\)S\(_x\) cluster assemblies in an attempt to replicate the structure of the FeMo-cofactor. While they have been successful in synthesizing a wide variety of iron-containing clusters, no systems have been described that adequately mimic the structure and function of the naturally occurring enzymes. Most synthetic strategies for the synthesis of multimetallic clusters rely heavily on self-assembly processes, yielding final structures that are often thermodynamically and kinetically inert. While certain substrate reactions have been realized using these elegant cluster systems (e.g., acetylene or hydrazine reduction), to our knowledge, none are known to bind and reduce N\(_2\).\(^{11}\)

1.3.2. Molecular Models. An alternative approach to the cluster synthesis strategy is to develop small molecule model systems where the immediate coordination environment of one or two metals can be rigorously controlled through choice of auxiliary ligands. The impetus for this approach is not to faithfully reproduce the cofactor structure, but to develop simplified models amenable to detailed spectroscopic investigation whereby different mechanistic proposals can be investigated.

Much of the biomimetic, molecular modeling effort has been focused on Mo-N\(_2\) complexes following the identification of the Mo center in the active site of nitrogenase.\(^{12}\)
Reduction of dinitrogen is a demanding multielectron redox process, requiring at least four oxidation states to be accessible for a single metal center to be functional. Historically, Mo has been shown to exhibit a much broader range of redox flexibility than Fe, and thus became an attractive target for designing model systems. A large number of Mo-model complexes have been synthesized that can facilitate the binding and activation of N₂. Two striking examples from this group involve the complete cleavage of the N—N triple bond using two Mo³⁺ complexes reported by Cummins (Figure 1.2), and the catalytic reduction of N₂ to ammonia reported at a single Mo center by Schrock (Scheme 1.3). Through judicious choice of ancillary ligands and the inherent redox flexibility in Mo, significant headway has been made in describing possible Mo-mediated mechanistic pathways for N₂ reduction at the FeMo-cofactor.

**Figure 1.2.** Dinitrogen cleavage by (Ar(R)N)₃Mo³⁺ complexes.
Figure 1.3. Dinitrogen reduction to ammonia at a single Mo center.

Considerably less attention has been devoted to developing N₂ reduction complexes employing iron.¹⁷ Notably, Leigh has reported that five-coordinate, phosphine supported Fe⁰-N₂ complexes (e.g., (Me₂P(CH₂)₂PMe₂)Fe⁰(N₂)) can be protonated to release small amounts of ammonia.¹⁷c,¹⁸ Zubieta and George reported that a related phosphine supported Fe⁰-N₂ (e.g., N((CH₂)₂PPh₂)₃Fe⁰(N₂)) complex can yield small amounts of hydrazine upon protonolysis.¹⁹ While these systems do yield trace-to-small amounts of amine products upon protonolysis, no intermediate species along the N₂-reduction pathway have been rigorously isolated and characterized. In a recent example, Holland reported that a bound dinitrogen ligand can be reduced in a stepwise fashion when complexed between two, three-coordinate iron centers (Figure 1.4).²⁰ Collectively, the work by these authors¹⁷-²⁰ demonstrate that iron can be adept at binding and activating N₂, while still providing isolable, well-characterized species. However, no iron-based system has been reported to support both weak π-acids (e.g., N₂) and strong π-base (e.g., NR²⁻, N₃⁻) type ligands.
1.3.3. Mechanistic Implications. The Mo-based model systems described above demonstrate that a Mo-centered mechanism (reduction scheme in Figure 1.3) for nitrogenase function is certainly feasible.\textsuperscript{14,15} The number of Mo-N\textsubscript{2} complexes\textsuperscript{13-15} far exceeds the number of Fe-N\textsubscript{2} complexes,\textsuperscript{17-20} and Mo has the redox flexibility required to mediate the multielectron processes in N\textsubscript{2} reduction. A limitation apparent in these systems is that once dinitrogen binds to a Mo center, the N\textsubscript{2} ligand becomes strongly activated, leaving the Mo center in a high oxidation state.\textsuperscript{14,15} Thus, strong reductants (e.g., Na\textsuperscript{0}, Cp\textsuperscript{*2}Cr) are often required to return the Mo center back to an oxidation state amenable to N\textsubscript{2} binding.\textsuperscript{15} During ammonia production, however, electrophilic reagents (e.g., H\textsuperscript{+}) are present and often not compatible with strong reductants. For this latter concern, late transition metals present an attractive alternative. If a single Fe site could efficiently bind and strongly activate N\textsubscript{2} like the Mo center in Schrock’s work,\textsuperscript{15} the high oxidation state products would be reduced much more easily and thus require weaker reductants to return to an oxidation state amenable to substrate uptake. The work of Leigh, Zubieta, George, and Holland demonstrates that Fe-based systems can bind and activate dinitrogen, fulfilling the requirement of the first half of the Chatt-cycle.\textsuperscript{17-20}
Progress then must be made to establish a framework where Fe exhibits the broad range of redox flexibility required for the latter half of the Chatt-cycle.

1.4. Tris(phosphino)borate ligands to support low-coordinate complexes.

An area of ongoing interest in the Peters group concerns the systematic preparation of pseudotetrahedral complexes that feature mid-to-late 3d ions (e.g., Fe, Co, Ni). Our particular interest concerns developing new, strong-field donor L₃ platforms that enable binding of π-acidic ligands (e.g., N₂, CO) and also strongly π-basic ligands (e.g., NR²⁻, N³⁻) in a fourth coordination site (i.e., L₃M-X where X is a π-acid or π-base). While later 3d systems that fulfill the first requirement are common, those that fulfill the latter requirement are rare. The historical incompatibility of pseudotetrahedral, later 3d ions with strongly π-basic ligands can be attributed to the high-spin ground state configurations that dominate this region of the periodic table. Complexes with strongly destabilized d-orbitals containing unpaired electrons are expected to be very reactive.

Using strong L₃ donor ligands with a borate unit embedded within the backbone of the ligand, 3d ions of the type L₃M=E are electronically accessible (L = P, M = Fe, Co; E = NR; d-count = 5, 6). Moreover, low-spin configurations are accessible even for d⁷ configurations in the absence of the strongly π-basic fourth donor ligand (e.g., low-spin [PhBP₃]CoI where [PhBP₃] = [PhB(CH₂PPh₂)₃]). A molecular orbital splitting diagram is presented in Figure 1.5 to rationalize the spin-states observed for Co¹¹ ions and the observed stability of [PhBP₃]M=NR species (M = d⁵ Fe, d⁶ Co).
The observed low-spin state for [PhBP₃]CoI is a consequence of the strong-field ligand donor strength of the [PhBP₃] anion and the ability of ligand to accommodate a Jahn-Teller distortion. The observed $C_s$ symmetry for [PhBP₃]CoI leaves its unpaired electron in an upper lying orbital of $d_{xz}$ or $(d_{yz})$ parentage. Removing one electron from the Co$^{II}$ species provides an orbital-splitting diagram for a Co$^{III}$ ion where the two unoccupied orbitals become degenerate. This configuration establishes [PhBP₃]Co$^{III}$ as an ideal platform to accept a divalent, strongly $\pi$-donating ligand.\(^{22a}\) This splitting diagram is also relevant for trivalent Fe complexes of the type [PhBP₃]Fe$^{III}$=NR.\(^{22b}\) In this instance, removal of one electron from the d⁶ Co$^{III}$ configuration would result in a low-spin, d⁵ configuration in which the unpaired electron resides in an orbital of non-bonding character. The isolation of stable imide complexes of Fe$^{III}$ lends credence to this molecular orbital description.\(^{22b}\) Although Fe$^{III}$ imide complexes are stable enough to be isolated; the complexes much more reactive than their 18 electron, Co$^{III}$ congeners.\(^{22b,28}\) The observed reactivity may be attributable to the metal-based radical of the 17 electron, Fe imide complexes. Despite the initial successes using the [PhBP₃] scaffold, ligand
1.5. Chapter Summaries.

In chapter two, the synthesis for a sterically encumbered, strong-field tris(diisopropylphosphino)borate ligand, \([\text{PhBP}^\text{Pr}_3]\) ([\text{PhBP}^\text{Pr}_3] = [\text{PhB(CH}_2\text{P}^\text{iPr}_2)_3]), is reported to probe aspects of its conformational and electronic characteristics within a host of complexes. To this end, the Tl(I) complex, \([\text{PhBP}^\text{Pr}_3]\text{Tl}\), was synthesized and characterized in the solid state by X-ray diffraction analysis. The Tl(I) complex was used to install the \([\text{PhBP}^\text{Pr}_3]\) ligand onto complexes of Fe, Co, and Ru. The spectroscopic, electrochemical, magnetic, and structural features of these complexes are compared with similar, previously described examples.

Chapter three describes the dinitrogen chemistry discovered using the \([\text{PhBP}^\text{Pr}_3]\) scaffold. Trigonally coordinated “\([\text{PhBP}^\text{Pr}_3]\text{M}\)” platforms (\(\text{M} = \text{Fe}, \text{Co}\)) support both \(\pi\)-acidic (\(\text{N}_2\)) and \(\pi\)-basic (\(\text{NR}\)) ligands at a fourth binding site. Methylation of monomeric \([\text{M}^0(\text{N}_2)^-]\) species successfully derivatizes the \(\beta\)-N atom of the \(\text{N}_2\) ligand and affords the diazenido product \([\text{M}^{11}(\text{N}_2\text{Me})]\). \(\text{M}^1(\text{N}_2)\text{M}^1\) complexes provide clean access to the chemistry of the “\([\text{PhBP}_3]\text{M}^{11}\)” subunit. For example, addition of \(\text{RN}_3\) to \(\text{M}^1(\text{N}_2)\text{M}^1\) results in oxidative nitrene transfer to generate \([\text{PhBP}^\text{Pr}_3]\text{M}=\text{NR}\) with concomitant \(\text{N}_2\) release.

Chapter four describes a tetrahedrally coordinated \(\text{L}_3\text{Fe}-\text{N}_x\) platform that accommodates both terminal nitride (\(\text{L}_3\text{Fe}^{11}=\text{N}\)) and dinitrogen (\(\text{L}_3\text{Fe}^1-\text{N}_2-\text{Fe}^1\text{L}_3\)) functionalities. The diamagnetic \(\text{L}_3\text{Fe}^{11}=\text{N}\) species featured has been characterized in solution under ambient conditions by multinuclear NMR (\(^1\text{H}, ^{31}\text{P}, \text{and } ^{15}\text{N}\)) and infrared
spectroscopy. The electronic structure of the title complex has also been explored using DFT. The terminal nitride complex oxidatively couples to generate the previously reported \( \text{L}_3\text{Fe}^{1-}\text{N}_2\text{Fe}^{1}\text{L}_3 \) species.

Chapter five describes the binding motifs, redox properties, and magnetic description for monomeric and dimeric dinitrogen complexes. The \([\text{PhBP}^{i}\text{Pr}_3]\) ligand can support a single iron or cobalt center in a pseudo-tetrahedral environment in which dinitrogen is bound in the fourth coordination site. Zero-valent metal-dinitrogen complexes have the general formula \([[\text{PhBP}^{i}\text{Pr}_3]\text{M(µ-N}_2\text{)]}_2[\text{Mg}^{2+}]]\), while bridging structures can also be obtained as neutral \([\text{M}^{I]}\text{—N}_2\text{—[M}^{I}]]\) or as anionic \([\text{M}^{I}]\text{—N}_2\text{—[M}^{0}]]\) species. The nature of the structural distortions observed in both \([\text{M}](\text{µ-N}_2)_2[\text{Mg}^{2+}]\) and \([\text{M}^{0}]\text{—N}_2\text{—[M}^{0}]]\) complexes are described. Magnetic data for the neutral and mixed-valence dimeric complexes show that they are ferromagnetically coupled.

Chapter six describes the coordination chemistry of group VIII metals featuring the bis(8-quinolinyl)amine (HBQA) ligand. The electrochemical behavior of several Fe, Ru, and Os complexes bearing the BQA ligand is reported and compared to related ligand platforms. Halide and phosphine ligand exchange reactions are examined from complexes of the type \((\text{BQA})\text{MX(PR}_3)_2\) \((\text{M} = \text{Ru, Os})\). Carbonyl and dinitrogen complexes of Ru and Os are prepared from halide abstraction from divalent Ru and Os precursors. The spectroscopic and structural features of these complexes are compared with similar, previously described examples.
References Cited


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