Chapter 1

INTRODUCTION

Introductory remarks often begin, predictably, with an introduction to a subject matter. In this instance however I would like to begin with an introduction to the style and purpose of the document to follow, before setting the stage for our players (e.g., nitrogen gas and electricity). In preparing to write this thesis I am forced to address the question of purpose. Keeping in mind that I find myself in a fortunate and perhaps atypical state in which the vast majority of my five years\(^1\) of research at Caltech has found its way into the published literature in the form of peer-reviewed journal articles. What purpose then is my thesis to serve, that is not already served by a perusal of my published works? After some deliberation on this question I have come across the following thoughts: i. almost every project which concludes in publication also encompasses some experimental results which, though of potential interest to a specialized reader, are not suited to publication (usually due to a lack of concrete interpretation or in some cases due to only a tangential relation to the main conclusion(s) of the project) in a thesis these results might be given light ii. as this paragraph surely gives evidence to, I have a tendency to elaborate and even to editorialize, habits which are rightly suppressed in compositions for the scientific literature iii. one component of research, which I believe is of great value, especially to researchers at the beginning of their career, is an accounting of the thought process (dare I say method?) that leads to scientific discovery. Of these thoughts the first is an obvious “correct” answer to the dilemma of purpose, the second is something of a metaphorical carrot (a treat to myself which might
encourage me in the writing process, though perhaps to the detriment of any reader brave enough to wade through my rambling), and the third, to my current thinking, may be the most valuable information that I might provide to my most likely future audience, which is to say some few overzealous new students to join Jonas’ group in the next five or so years. I have settled on the following approach then, with each chapter (excluding this first) I shall recount a project, this will involve the reproduction of a manuscript describing scientific discovery, experimentation, and conclusions; I shall endeavor where possible to include additional experimental results and interpretation; additionally I shall begin each chapter with an account (to be set in italics) of one or more processes that contributed to the work discussed, which will hopefully contain useful lessons for new researchers. The sorts of lessons which might be conveyed in a candid discussion with one’s advisor or colleague but that are generally not included in a published report.²

1.1 Background

The reduction of nitrogen (N₂) to ammonia (NH₃) (a reaction referred to herein both as nitrogen fixation and the nitrogen reduction reaction, abbreviated N₂RR) is a critical reaction for sustaining life on this planet.³ This transformation is known to be effected biologically by nitrogenase enzymes and synthetically in a number of chemical systems, including the massive-scale industrial hydrogenation of N₂ mediated by the Haber-Bosch process.⁴ In the Haber-Bosch process, H₂ and N₂ gas are dissociatively adsorbed at the surface of an Fe-based heterogeneous catalyst to give surface bound hydrides and nitrides, these surface bound species recombine to form sequential N-H bonds, ultimately giving rise to NH₃. (Scheme 1.1).⁵
Scheme 1.1: Mechanism (above) and net reaction (middle) of N₂ fixation by the Haber-Bosch process and the net reaction of N₂ fixation by nitrogenase (bottom) showing limiting 1:1 stoichiometry of H₂ production (vide infra).

\[
\begin{align*}
\text{H}_2(g) & \rightleftharpoons 2 \text{H} \text{(ad)} \\
\text{N}_2(g) & \rightleftharpoons \text{N}_2 \text{(ad)} \\
\text{N} \text{(ad)} + \text{H} \text{(ad)} & \rightleftharpoons \text{NH} \text{(ad)} \\
\text{NH} \text{(ad)} + \text{H} \text{(ad)} & \rightleftharpoons \text{NH}_2 \text{(ad)} \\
\text{NH}_2 \text{(ad)} + \text{H} \text{(ad)} & \rightleftharpoons \text{NH}_3 \text{(ad)} \\
\text{NH}_3 \text{(ad)} & \rightleftharpoons \text{NH}_3 \\
\text{N}_2 + 3\text{H}_2 & \xrightarrow{\Delta \text{Fe catalyst}} 2\text{NH}_3 \quad \Delta H = -92.4 \text{ kJ/mol N}_2
\end{align*}
\]

Despite this reaction being exothermic (\(\Delta H = -46.2 \text{ kJ/mol of NH}_3\)), the Haber-Bosch process requires forcing conditions to attain reasonable rates of NH₃ production, (typical Haber-Bosch reactor operating conditions: temperatures \(\geq 200^\circ\text{C}\) and pressures \(\geq 400 \text{ atm}\)).⁶ This industrial process is sufficiently energy intensive, and performed on such a massive scale, as to constitute \(~2\%\) of the global energy demand.⁷ The biological N₂ to NH₃ transformation as performed by nitrogenase enzymes is known to occur at ambient temperature and 1 atm of N₂ (Scheme 1.1).⁸ Although considering the consumption of 16 equiv Mg(ATP) per molecule of N₂ fixed (two Mg(ATP) per reducing equivalent) in this process as well as the generation of at least some H₂ (1 equiv of H₂ produced per equiv of N₂ fixed has been demonstrated as a limiting stoichiometry⁴,⁹) the energetic efficiency of the processes may in fact be similar. Frustratingly, intimate understanding of the mechanism(s) of nitrogen
fixation as performed in biological systems, has remained elusive; presenting an ongoing opportunity for the inorganic and organometallic communities to expound a basic understanding of nitrogenous coordination chemistry and reactivity.

Some (of the many) notable advances in this field, prior to the beginning of the work described in this thesis,\textsuperscript{10} include coordination, cleavage, or functionalization of N\textsubscript{2} or NxHy ligands relevant to nitrogen fixation at Mo,\textsuperscript{11,12} W,\textsuperscript{11} Fe,\textsuperscript{13,14} Ti,\textsuperscript{15} Zr,\textsuperscript{16} V,\textsuperscript{17} and Co\textsuperscript{18} metal centers. Additionally, rare examples of direct conversion of N\textsubscript{2} to NH\textsubscript{3} by molecular systems have been demonstrated. For instance the treatment of Fe\textsuperscript{19} and Co\textsuperscript{20} dinitrogen compounds with acid has been shown to liberate modest yields of NH\textsubscript{3} (≤ 0.21 mol NH\textsubscript{3}/mol complex), while Chatt et al. demonstrated that the treatment of a W dinitrogen compound with acid has yielded stoichiometric yields of NH\textsubscript{3} (~2.0 mol NH\textsubscript{3}/mol complex),\textsuperscript{21} Chirik et al. have also demonstrated the generation of ~15% NH\textsubscript{3} from a Zr dinitrogen complex in the presence of H\textsubscript{2} at elevated temperatures.\textsuperscript{22} Interestingly, a mere handful of examples of complexes capable of mediating the catalytic conversion of N\textsubscript{2} to NH\textsubscript{3} in the presence of acid and electron sources have been reported, all utilizing complexes of W, Mo, or Fe.

Building on the early work by Chatt et al. (vide supra) that demonstrated the ability of phosphine ligated W-N\textsubscript{2} complexes to yield stoichiometric NH\textsubscript{3} upon treatment with acid\textsuperscript{21} (a reaction in which the W(0) metal center is presumably oxidized to W(VI) degradation products in order to provide the requisite 6 e\textsuperscript{-}), Pickett and Talarmin demonstrated the conversion of trans-[W(N\textsubscript{2})\textsubscript{2}(dppe)\textsubscript{2}] (dppe = bis(diphenylphosphino)ethane) to trans-[W(NNH\textsubscript{2})TsO(dppe)\textsubscript{2}]\textsuperscript{+} (NNH\textsubscript{2} = hydrazido(2-), TsO = p-toluenesulfonate) upon treatment with p-toluenesulfonic acid, and further showed that trans-[W(NNH\textsubscript{2})TsO(dppe)\textsubscript{2}]\textsuperscript{+} could be
reduced by a mercury pool electrode at -2.6 V (vs Fe/Fc⁺) in the presence of N₂ to regenerate trans-[W(N₂)₂(dppe)₂] (85-95% yield) with concomitant generation of NH₃ (22-24% yield) establishing cyclic (though not catalytic) conversion of N₂ to NH₃ by W with protons and reducing equivalents (Scheme 1.2).²³

In later work Schrock et al. demonstrated that a triamidoamine Mo system, [HIPTN₃N]Mo(N₂) ([HIPTN₃N]₃⁻ = \{3,5-(2,4,6-(Pr₃C₆H₂)₂C₆H₃NCH₂CH₂\}_₃N\}₃⁻) (Figure 1.1, A) could mediate the catalytic conversion of N₂ to NH₃ when treated with [2,6-lutidinium][BArF₄] over ~6 hours in the presence of (Cp*)₂Cr at room temperature (~7.5 equiv NH₃ produced per Mo).²⁴

**Scheme 1.2:** Cyclic electrosynthesis of NH₃ from N₂ by a W system

![Scheme 1.2](image-url)
Figure 1.1: [HIPTN₃N]Mo(N₂) (A) and six independently synthesized [HIPTN₃N]Mo-NₓHᵧ ligand complexes (B), complexes in green were shown to catalyze N₂ to NH₃ conversion. The [Mo(N₂)₂(PNP)]₂(μ-N₂) pincer complex (C) was also reported to catalyze N₂ to NH₃ conversion. D schematically shows the Chatt or distal vs. alternating mechanisms for sequential protonation and reduction of N₂ bound at a single metal center to generate 2 equiv NH₃, each step represents delivery of one proton and one electron to the nitrogenous ligand, it should be noted that in addition to these mechanisms hybrid pathways are also possible.
A particularly interesting feature of this research was the ability to isolate and characterize six proposed intermediates (Figure 1.1, B), and to demonstrate catalytic competency from four of these, which strongly suggests that this reaction follows a Chatt\textsuperscript{11} (or “distal”) type mechanism (Figure 1.1, D). Nishibayashi et al. later reported a PNP-ligated Mo system (Figure 1.1, C) capable of generating 12 equiv of NH\textsubscript{3} from N\textsubscript{2} per Mo metal center, in this case utilizing [2,6-lutidinium][OTf] (OTf = trifluoromethanesulfonate) and the weaker reductant Cp\textsubscript{2}Co, also at room temperature.\textsuperscript{25}

**Scheme 1.3:** Catalytic N\textsubscript{2} conversion to NH\textsubscript{3} by [Na(12-crown-4)\textsubscript{2}][(P\textsuperscript{3}B)Fe(N\textsubscript{2})] (A) and [K(Et\textsubscript{2}O)\textsubscript{0.5}][(P\textsuperscript{3}C)Fe(N\textsubscript{2})] (B)
More recently, our group has reported that a tris(phosphine)borane ligated Fe complex, [Na(12-crown-4)2][(P3B)Fe(N2)] (P3B = tris[2-(diisopropylphosphino)phenyl]borane), is capable of catalytically converting N2 to NH3 upon treatment with KC8 and [H·OEt2][BARF4] at -78°C (~7 equiv NH3 generated per Fe, Scheme 1.3, A).26 Similar reactivity can be observed for the structurally related tris(phosphine)alkyl complex [K(Et2O)0.5][(P3C)Fe(N2)], which is also competent for catalytic N2 to NH3 conversion when treated with KC8 and [H·OEt2][BARF4] at -78°C (~4.6 equiv NH3 generated per Fe, Scheme 1.3, B).27

A key structural feature of the (P3B)Fe and (P3C)Fe systems is flexibility of the M-axial ligand interaction, which is postulated to facilitate N2 fixation by allowing the metal center to sample geometries ranging from trigonal bipyramidal to tetrahedral, in turn giving access to d-orbital manifolds that stabilize the alternately π-basic or π-acidic nitrogenous ligands that may be encountered during catalysis (Figure 1.2). For example the Fe center in [Na(12-crown-4)2][(P3B)Fe(N2)] adopts a trigonal bipyramidal geometry (Figure 1.2, A) providing available filled dxz and dyz orbitals for π back donation into the N2 π* orbitals, facilitating N2 binding and activation. Whereas in the imide complex (P3B)Fe(NAr) (Figure 1.2, B), the Fe center adopts approximate tetrahedral geometry to facilitate M-N multiple bonding with empty dxz and dyz orbitals.28
Figure 1.2: Qualitative ligand field splitting diagrams for TPB ligated Fe complexes adopting trigonal bipyramidal geometry (A) or pseudo-tetrahedral geometry (B) to stabilize π acidic and π basic ligands respectively. Flexibility of the Fe-B interaction is critical in facilitating this geometric variability.

Thus at the beginning of this research (and indeed still today) there remain many interesting questions relating to N$_2$RR. Questions of particular interest that will be (at least in part) addressed in the following chapters include: i) what mechanisms allow N$_2$RR (for instance at a single metal center) in turn what chemical properties of a catalyst enable or enhance this reactivity ii) how can selectivity for N$_2$RR over hydrogen evolution be accomplished iii) can electrocatalytic N$_2$RR be demonstrated by a molecular catalyst considering how few catalysts are known for this chemistry?
1.2 REFERENCES

1 I do not count my first half year at Caltech (before I joined Jonas’ group) to my research total bringing my count down from five and one half years (total residency time).

2 To this end I may need to attribute some idea or innovation to an individual other than myself, that is to say one of my many wonderful colleagues and collaborators. As my understanding of the origin of ideas within a group of close collaborators and also my memory are not infallible, I shall try to be vague in these cases to avoid offering affront.


10 The discussion here treats with the state of the art of nitrogen fixation at the time this thesis work began, circa 2013, thus setting the stage for the earlier projects discussed in the first chapters, more recent developments and citation appear throughout the later chapters with additional discussion.


