SYNTHESIS AND CHARACTERIZATION OF TRI-COBALT (II) AND –IRON (II) COMPLEXES AND THEIR POTENTIAL APPLICATION FOR N₂ ACTIVATION

By

JEONG AH LEE

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To my family, fiance’, mentor and friends, I couldn’t have done this without you.
Thank you for all of your support along the way
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<tr>
<td>ATP</td>
<td>Adenosine triphosphate</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
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<tr>
<td>CSD</td>
<td>Cambridge structure database</td>
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<tr>
<td>PDB</td>
<td>Protein data bank</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
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<tr>
<td>DHA</td>
<td>9,10-dihydroanthracene</td>
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<tr>
<td>DIW</td>
<td>Deionized water</td>
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<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
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<td>ENDOR</td>
<td>Electron-nuclear double resonance</td>
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<tr>
<td>EPR</td>
<td>Electron spin resonance</td>
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<tr>
<td>FeMoco</td>
<td>Iron-Molybdenum cofactor</td>
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<tr>
<td>FT-IR</td>
<td>Fourier transform infrared</td>
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<td>HBAr\textsuperscript{f}</td>
<td>([3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_4\text{B}]\text{[(Et}_2\text{O})_2\text{H}])</td>
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<td>LT</td>
<td>Lowe-Thorneley</td>
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<tr>
<td>NADH</td>
<td>Nicotinamide adenine dinucleotide hydride</td>
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<tr>
<td>NHE</td>
<td>Normal hydrogen electron</td>
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<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
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<tr>
<td>SQuID</td>
<td>Superconducting quantum interference device</td>
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<td>TEMPO</td>
<td>1-hydroxy-2,2,6,6-Tetramethylpiperidine</td>
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<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
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SYNTHESIS AND CHARACTERIZATION OF TRI-COBALT (II) AND –IRON (II) COMPLEXES AND THEIR POTENTIAL APPLICATION FOR N\textsubscript{2} ACTIVATION

By

Jeong Ah Lee

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Chair: Leslie J. Murray
Major: Chemistry

This document describes the synthesis of trinuclear (β-diketiminate)cobalt(II) complexes, Co\textsubscript{3}Cl\textsubscript{3}L and Co\textsubscript{3}Br\textsubscript{3}L, bearing nacanc ligand capable of preorganizing a trimetallic cluster in which each metal center is coordinated by a β-diketiminate arm. Through the different binding modes of anions in these clusters, the flexibility of ligand was elucidated by the interaction between multiple factors, steric demands, metal ions, and halide anions. N\textsubscript{2} reduction reactions of these tri-cobalt clusters with reducing agents were attempted, affording low yield of ammonia from the indophenol test. Tri(amido)tricobalt(II) complex, Co\textsubscript{3}(NH\textsubscript{2})\textsubscript{3}L, was synthesized and its acid hydrolysis was attempted. We compared yields on ammonia after acid hydrolysis of tricobalt reduction products and Co\textsubscript{3}(NH\textsubscript{2})\textsubscript{3}L in order to examine the potential of release of N\textsubscript{2} derived ligands.

Also, synthesis of sulfide-bridged triiron clusters of the type Fe\textsubscript{3}S\textsubscript{(3-x)}Br\textsubscript{x}L (where 1<x<3) is attempted as a preliminary work in order to model a tetrairon-sulfide fragment of FeMoco. Iron-sulfide project is considered to provide the open coordination site to N\textsubscript{2} and we got some promising data from IR spectra and ESI-MS.
CHAPTER 1
DINITROGEN ACTIVATION AT BIOLOGICAL AND SYNTHETIC IRON CENTERS

Metal clusters constitute the active sites of a number of metalloenzymes, which catalyze essential multielectron redox reactions involving small molecule substrates, such as N₂, O₂, and CO.¹⁻² These metal clusters are assembled from late first row transition metals, such as the sulfide-bridged tetracopper cluster in nitrous oxide reductase, the NiFe₄S₄ cluster in carbon monoxide dehydrogenase, and the Fe₇S₉Mo cofactor in nitrogenase (Figure 1-1).³⁻⁴ Features which are common to these enzymes are: (i) the active sites consist of polynuclear metal centers, (ii) the multielectron redox reactions take place by either a single or a series of multielectron redox steps, and (iii) each metal center is coordinatively unsaturated, which allows substrates to bind directly to the metal cluster cofactor. In addition, each metal center in the cofactor is typically in a weak ligand field and is consequently in a high or intermediate spin state, which provides a facile mechanism to engender reactivity into activated substrates.

A hallmark of these multielectron redox reactions, which are catalyzed by metalloenzymes, is that the reactions are either thermodynamically or kinetically unfavorable depending on the substrate. For example, standard reduction potential (E° vs. NHE) of CO₂ to CO is -0.53 V, which indicates this reaction is thermodynamically unfavorable,⁵ whereas reduction of N₂ to NH₃ is thermodynamically favored (E° vs. NHE = 0.55 V) but the activation barrier is large. Specifically for dinitrogen, the high activation barrier is associated with the strong π bonds in N≡N, with cleavage of the first requiring 130 kcal/mol.⁶ Whereas biological systems have developed discrete molecular clusters capable of catalyzing these reactions at low overpotentials (i.e., catalysis operates at or near the thermodynamic minimum), synthetic chemists have yet to replicate this type of reactivity ex vivo. A prime example of this benefit is the biological versus industrial process for N₂ fixation to NH₃; the iron-molybdenum cofactor
(FeMoco, Figure 1-3) of nitrogenase catalyzes this reaction under ambient conditions whereas the Haber-Bosch process requires high temperatures and pressures. Computational studies carried out on the enzymatic clusters point towards a strongly cooperative pathway, whereby the redox requirements for these multielectron redox reaction are shared over the entire metal cluster.\textsuperscript{7} In these studies, dinitrogen and dihydrogen are proposed to bind to the surface of the iron-based Mittasch catalyst to generate adsorbed N and H atoms, which combine to generate ammonia. The proposed bridged binding mode of dinitrogen to the iron atoms on the (111) face of crystals suggests the simultaneous participation and cooperation of multiple metal centers in the cleavage of dinitrogen.\textsuperscript{8} Surprisingly, the Haber-Bosch ammonia synthesis for industrial nitrogen fixation consumes more than 1\% of the annual global energy supply which contrasts the biological process.\textsuperscript{9-10} Consequently, lowering the energetic cost of abiotic nitrogen fixation through the design of new catalysts will lead to lower greenhouse gas emissions and mitigate global warming, which is considered to be one of the greatest concerns for human health in the coming decades.\textsuperscript{11} We hypothesize that by understanding the factors that control and determine cooperativity between metal ions within clusters and the relationship of those effects to reactivity, we will be able to design and develop metal cluster catalysts for these reactions that require lower energy demands that current methods. Surprisingly, few synthetic systems have been reported in which electronic and steric effects are correlated to cluster reactivity.

The biological nitrogenase is a two-component system composed of the MoFe protein, which provides the active site for substrate binding and reduction, and the electron-transfer Fe protein. The biological reductant NADH primes the metal cluster for dinitrogen reduction and MgATP is also required for the reaction. Fe protein and MoFe protein associate and dissociate in a catalytic cycle involving sequential single electron transfer from NADH to FeMoco mediated
by the Fe protein and MgATP hydrolysis. In biological dinitrogen reduction, the MoFe protein contains two P-clusters, key components of the electron transfer dimension of reactivity, which are called Fe₈S₇, and Fe protein has Fe₄S₄ cluster, also involves in electron transfer for dinitrogen reduction (Figure 1-2). It has been reported that N₂ reduction occurs at the main catalytic site, FeMoco (Figure 1-3), through electron transporters, Fe₈S₇ and Fe₄S₄.

Substantial progress has been made in understanding the structure and nature of reactive intermediates of FeMoco, primarily through spectroscopic studies on native and site-directed variants of the MoFe protein as well as on model complexes. In the current proposed mechanism for the dinitrogen reduction, N₂ binds to a face of FeMoco and is subsequently protonated and reduced to afford two equivalents of ammonia. The nature of the cluster (i.e., protonation state and presence of metal hydrides) that initially binds and the coordination mode of N₂ remain unclear and recent computational work by Dance suggests that N₂ binds in a bridging fashion to the metal cofactor (Figure 1-4). Recent studies have suggested that the tetrairon face comprised of Fe2, Fe3, Fe6, and Fe7, which are linked by two μ₂-S²⁻ and two μ₃-S²⁻ ligands is the site in FeMoco at which dinitrogen binds and is subsequently reduced (Figure 1-4). According to this proposed mechanism, the reduced form of the cluster contains protonated sulfide ligands and iron-hydride centers immediately prior to N₂ coordination. Dinitrogen binds in a bridging fashion, and protons are subsequently transferred from the sulfide bridges to the N₂ ligand. Subsequently, hydride transfer from the Fe centers to the bound N₂-derived ligand results in scission of the N–N bond and formation of two equivalents of ammonia. Therefore, it has been presumed that the sulfur ligand is able to be a trigger of N₂ reduction reaction because it acts as H⁺ acceptor which facilitates an intramolecular proton transfer to bound N₂.
The iron centers in FeMoco are coordinatively unsaturated, and therefore have an accessible coordination site for substrate binding and activation (Figure 1-3). Indeed, the crystal structure of the CO inhibited form of the MoFe protein demonstrates the possible dynamic nature of the cluster to access low coordinate iron centers to bind substrates; one bridging sulfide dissociates from the cluster to generate an open coordination site on two iron centers, which is the site of CO binding. This concept of low valent and low coordinate iron centers as sites for dinitrogen reduction has been recently extended to synthetic systems. Holland and coworkers demonstrated that sulfide-bridged dinuclear iron(II) complex from self-organized or fragment condensation of pre-synthesized clusters can react with ammonia and with substituted hydrazines. In a similar vein, Peters and coworkers demonstrated that dinuclear iron complexes containing Fe–S–Fe linkages readily bind dinitrogen upon reduction.

The Lowe-Thorneley (LT) kinetic model for nitrogenase function described the kinetics of transformations among catalytic intermediates (denoted En) where n is the number of electrons and protons delivered to MoFe protein. Recent studies in which intermediate states were isolated temporally using rapid-freeze-quench and characterized by ENDOR spectroscopy demonstrated that N2 reduction requires activation of the MoFe protein to the E4 state (Figure 1-4). In this state, the cofactor is reduced by four electrons as well as accommodating four protons of which two are proposed to be hydrides that bridge Fe atoms and the remaining two are protons bound to inorganic sulfide ligands. From these studies, Hoffman, Seefeldt, and Dean have proposed that low-valent iron centers within the cluster are generated through reductive elimination of dihydrogen from the cofactor, and that this low-valent iron center is the reactive site for dinitrogen binding and activation (Figure 1-4). This mechanism contrasts the computational work reported by Dance in Figure 1-5 (i.e., hydride ligands are transferred to the
activated \( \text{N}_2 \) derived ligand); therefore, differentiating the structural motifs capable of binding and weakening the triple bond in dinitrogen such as hydride bridged \textit{versus} low valent iron centers is an important target for synthetic modeling chemists.

The stoichiometric transformation of coordinated dinitrogen in transition metal-dinitrogen complexes into ammonia and/or hydrazine has been widely investigated with the goal of achieving nitrogen fixation under ambient conditions. A number of approaches have been developed for \( \text{N}_2 \) reduction using molecular complexes. Catalytic systems are known for the low valent molybdenum complexes, which are inspired by the single Mo cation in the iron-molybdenum cofactor, and the low valent iron-containing complexes. Until recently, molybdenum complexes have been the more successful for dinitrogen functionalization and catalytic reduction. Shilov and Schrock reported catalytic reductions to ammonia using decamethylchromocene (CrCp\(^{\ast}\)) as the reducing agent and 2,6-lutidinium-Bar’\(^4\) \((\{\text{LutH}\}\{\text{Bar’}_4\})\) as the proton source,\(^{21,22}\) and Shiina, Hidai and Mizobe reported catalytic reduction of dinitrogen to silylamines and organonitrogen compounds later.\(^{23,24}\) Recently, Nishibayashi reported that a molybdenum-dinitrogen complex bearing two ancillary ferrocenyldiphosphine ligands could be reduced by the one-electron redox couple in ferrocene, thereby using a milder reductant to prime the \( \text{N}_2 \) reduction reaction.\(^{25}\) Moreover, they reported that the reactions of dinuclear molybdenum-dinitrogen complex supported by a PNP-type pincer ligand with lutidinium triflate as the proton source and cobaltocene as a stoichiometric reductant to afford ammonia in good yields.\(^{26,27}\) In addition, some polynuclear metal clusters containing tantalum and zirconium are reported systems where the metal-ion cooperativity plays an important role in hydrogenation and cleavage of dinitrogen reactions.\(^{28,29}\) Since iron is a common component of both FeMoco and the Mittasch catalyst in the Haber-Bosch process, significant
effort has focused on synthetic iron complexes for the reduction of dinitrogen. Peters and coworkers demonstrated that the synthesized mononuclear low-valent iron complexes catalytically perform the reduction of dinitrogen to ammonia using H(OEt₂)-[B(3,5-(CF₃)₂-C₆H₃)₄] as a proton source and KC₈ as the reducing agent (Scheme 1-1).³⁰

In a similar vein, Holland and coworkers reported a family of multinuclear low-valent iron complexes with β-diketiminate ligands, some of which contain a diazenide-bridged cluster resulting from N–N bond weakening, and some of which contain a nitride-bridged cluster resulting from N–N bond cleavage. In this system, dinitrogen activation is proposed to result from the steric constraints imposed by the ligands; that is, reduced steric bulk on the aryl substituents and on the β-diketiminate arms allows for close approach of multiple centers to activate and cleave N₂ (Scheme 1-2). For these β-diketiminate complexes, redox cooperativity appears essential for scission of the N₂ triple bond as compared to coordination (Scheme 1-2).²⁰,³¹-³⁴

Density functional theory (DFT) calculations were performed to probe the role of cooperativity between iron β-diketiminate fragments and potassium cation promoters in dinitrogen activation.³⁵ The results demonstrated that at least three iron fragments are needed to cleave the triple bond of dinitrogen and also provided evidence that the potassium cation aids in lowering the activation barrier by further activating the N₂ fragment for π-back donation by the iron centers. From the experimental and theoretical studies, Holland and Cundari and coworkers suggested that the dinitrogen activation in these complexes arise from the unusual low-coordinate geometry at iron, which gives high-energy, singly occupied d orbitals that transfer electron density into the π* orbitals of dinitrogen.³⁶

To probe redox cooperativity in a rational and designed manner, Holland and coworkers developed two macrocyclic dinucleating β-diketiminate ligands in which the spatial relationship
between iron centers in the dinuclear complexes.\textsuperscript{36} However, these ligands systems afforded significant flexibility, precluding cooperative activation of substrates, the frontier orbitals of the metal centers were oriented in opposite directions in the dimetallic complexes. Similarly, the effect of metal identity on the reactivity of diketiminate complexes has also been investigated. Specifically, reduction of the monometallic cobalt(II) and nickel(II) diketiminate complexes under a dinitrogen atmosphere affords the dicobalt(I) or dinickel(I) dinitrogen-bridged complexes (Scheme 1-3).\textsuperscript{37} Further reduction of these complexes with KC\textsubscript{8} results in incorporation of K\textsuperscript{+} cations to yield the analogous complexes to the dinitrogen-bridged diiron products in A and B in Scheme 1-2. In these complexes, the N\textsubscript{2} ligands bridges in a linear \(\mu-1,2\) fashion, which contrasts the dichromium(I) analog in which a \(\mu-\eta^2: \eta^2\) is observed.

In addition, the work by Powers and coworkers indicates that low-coordinate transition metal complexes can be protected by increasing the steric bulk on the periphery of the ligand.\textsuperscript{38-39} As mentioned above, work by Holland and Peters has demonstrated that three- and four-coordinate transition metals bind dinitrogen so strongly that the dinitrogen complexes have unusually weak N-N bonds because of back-bonding from the metal into the \(\pi^*\) orbitals of dinitrogen, which shifts the electron density onto the dinitrogen unit.\textsuperscript{40-44} To explore how redox cooperativity influences small molecule activation as well as other multielectron redox reactions, an ideal framework would permit the designed assembly of a multimetallic complex in which the electronic environment of each metal center can be controlled. In this vein, a designed ligand approach would provide superior predictive control of metal-metal interactions and cluster electronic structure as compared to self-assembled clusters. Both approaches have led to compounds that model the active sites of metalloenzymes and have provided key insights into coordination environment of each metal center and reaction mechanisms of the biological
counterparts. However, self-assembly provides limited control of the coordination environment of each metal center, the spatial arrangement and relative disposition of the metal ions and their frontier orbitals, and the separation between metal centers in the clusters. In contrast, designed ligand architectures can generate metal clusters with predictable cluster nuclearity and coordination environment of each site. A ligand-based approach to cluster synthesis has been explored by a number of research groups such as those of Betley, Agapie, and Holm. This thesis describes the use of a macrobicyclic ligand to template the assembly of a trimetallic cluster and to simultaneously provide steric protection for the metal centers.

β-diketiminate units are well known to be proficient in stabilizing low-coordinate late transition and main group metals. In case of 3d-transition metals, the iron, cobalt, nickel, and copper clusters with macrocyclic binucleating β-diketiminate ligands have been synthesized. Importantly, there is substantial precedence for the reactivity of the monometallic diketiminate complexes with a variety of substrates including dinitrogen, carbon dioxide, and dioxygen. In a number of these reports, the reactant metal diketiminate complexes activate substrates to afford multimetallic products, which is strong evidence for a cooperative mechanism for substrate activation. We therefore designed ligands wherein the metal diketiminate fragments were preorganized prior to substrate binding, thereby programming and harnessing redox cooperativity in a rational manner. Recently, our group reported the synthesis of a tri-iron clusters housed within a macrobicyclic ligand in which each metal center is ligated by the two N-donor atoms in a given diketiminate arm. Moreover, reduction of this complex with KC₈ under a dinitrogen atmosphere affords a complex in which N-atom ligands – derived from N₂ – which bridge the iron centers (2 in Scheme 1-4). This species was characterized by X-ray
crystallography and NMR spectra for the acid hydrolyzed complex synthesized under either $^{14}\text{N}_2$ or $^{15}\text{N}_2$ confirm reduction of atmospheric dinitrogen. This cluster represents the first example of a designed metal cluster capable of N\textsubscript{2} reduction, and the reactivity is unique as compared to the monometallic systems. Using the same ligand, our group isolated a tricopper(I)-dinitrogen complex, which is the first structurally characterized example of dinitrogen coordinated to a copper(I) center. The N\textsubscript{2} ligand is bound in either a $\mu$-$\eta^1\cdot\eta^2\cdot\eta^1$ (75 % occupancy) and $\mu$-$\eta^1\cdot\eta^1\cdot\eta^1$ (25 % occupancy) fashion (1 in Scheme 1-4).\textsuperscript{67} Together with the reported dinitrogen reduction at iron, this result provides strong evidence of the unusual selectivity afforded by our ligand architecture; in the tricopper complex, solvent is rigorously excluded as a potential ligand and the metal centers bind N\textsubscript{2} as it is the only available ligand with the appropriate sterics in the reaction mixture to be accommodated within the central cavity.

Building on those reports, the research reported here sought to explore how the metal identity influence both redox cooperativity and dinitrogen activation wherein the synthesized clusters are supported by this macrobicyclic ligand. Specifically, there are no prior reports of cleavage of the N\textsubscript{2} triple bond using any late 3\textit{d} transition metal ion other than iron, and our target was to evaluate whether the constraints (\textit{viz.} spatial and electronic) placed by our ligand could turn on N\textsubscript{2} reduction in tricobalt clusters upon reduction. Concomitant with this line of inquiry, this thesis also focused on the synthesis of sulfide-bridged triiron clusters of the type $\text{Fe}_3\text{S}_{(3-x)}\text{Br}_x\text{L}$ (where $1 \leq x \leq 3$) in order to model a fragment of the tetrairon face of the iron-molybdenum cofactor.\textsuperscript{14} One goal of these complexes was to use the electronic coupling within the cluster afforded by the sulfide donors to access N\textsubscript{2} reduction using milder reducing agents.
Figure 1-1. Structures of active centers of (left) tetra-Cu in nitrous oxide reductase, (middle) Ni-Fe in carbon monoxide dehydrogenase, and (right) Fe in nitrogenase. Made with Pymol using PDB: 3SBQ, 1WUI, and 4WES.

Figure 1-2. Structure of the docked Fe protein and MoFe protein. Made with Pymol using PDB:2AFK.
Figure 1-3. Atomic structure of the FeMoco of molybdenum-dependent nitrogenase. 

Figure 1-4. E₄ state of FeMoco and dinitrogen reduction through elimination of dihydrogen. Made with Pymol and Chemdraw using PDB: 1M1N.
Figure 1-5. Key steps and intermediates in the full mechanism proposed for the hydrogenation of N₂ to 2 NH₃ through introduction and migration of H atoms.¹²

Scheme 1-1. Cooling a solution of Fe catalyst in Et₂O at -78 °C followed by the addition of 40 equivalents of KC₈ and then 38 equivalents of H(OEt₂)·[B(3,5-(CF₃)₂-C₆H₃)₄] leads to the formation of 4.6 equivalents of NH₃.  

\[
\begin{align*}
\text{N}_2 \text{ (1 atm)} & \quad + \\
\text{xs KC}_8 & \quad \quad \text{Cat.} \\
\text{xs HBAf}_2(\text{EtO})_2 & \quad \text{-78°C, Et}_2\text{O} \\
\end{align*}
\]

\[
\quad \rightarrow 4.6 \text{ equivalents of NH}_3
\]

cat. = [Na(12-crown-4)]⁺
Scheme 1-2. Iron complexes with varying steric bulk give different N₂ products upon reduction with KC₈.³¹

Scheme 1-3. Binding of dinitrogen by low coordinate cobalt and nickel complexes.³⁷
Scheme 1-4. Synthesis of Cu$_3$(N$_2$L) ($\mu$-$\eta^1$:$\eta^2$:$\eta^1$ coordination mode) and Fe$_3$(NH$_x$L)$._{66,67}$
CHAPTER 2
TRINUCLEAR COBALT(II) CHEMISTRY

Introduction

Nitrogen fixation has been the subject of extensive investigation over recent decades. A successful artificial fixation is the Haber-Bosch process which supplies ammonia for fertilizers that support a significant fraction of the world’s crops. This process requires a potassium-promoted iron catalyst called the Mittasch catalyst to lower the barrier for the interconversion between dinitrogen and dihydrogen, and ammonia, with the reaction conditions favoring NH₃ production by employing high temperatures and pressures. During the Haber-Bosch process dinitrogen and dihydrogen are proposed to coordinate to the iron surface of the catalyst, followed by cleavage of the substrate bonds and recombination of N and H atoms to liberate ammonia.⁶⁹ In contrast to the energy-intensive conditions of the Haber-Bosch process, biological nitrogen fixation is catalyzed by the nitrogenase family of enzymes, which operate under ambient conditions. This family of enzymes utilizes an iron-sulfur cofactor wherein the identity of one metal center varies between Fe, Mo, or V. The most extensively studied and most effective (as determined by turnover number and frequency data) members of this enzyme family employ the molybdenum-containing cluster, Fe₇S₉Mo, which is known as the iron-molybdenum cofactor or FeMoco (Figure 2-1).⁷⁰ Given the disparity between the biological and industrial reaction conditions, significant research effort has focused on developing a detailed mechanistic understanding the catalytic N₂ reduction at FeMoco.

Recent EPR and ENDOR studies by Hoffman and Seefeldt suggested the E₄ state of the cluster is first generated by reduction with four electrons and concomitant inclusion of four protons (Figure 2-2).⁷¹ In particular, the four protons are proposed to exist as a combination of two metal hydrides and two protonated sulfide bridges. A key result of these experiments is the
observation that the E4 state liberates one equivalent of H₂ either prior to or concomitant with N₂ binding. These hydrogen atom or proton equivalents therefore function in two capacities: first, to generate a low valent iron center capable of π-backbonding to a dinitrogen ligand, and second, to provide H-atom or proton equivalents to the bound N₂ to aid in N–N bond scission. Based on these studies as well as others carried out on enzyme variants with site-directed mutations, a number of proposed mechanisms confirm N₂ binding and subsequent reduction to diazene to the tetrairon face of FeMoco, with the cluster remain intact during the catalytic cycle. However, recent crystallographic data reported by Rees and coworkers suggests that sulfide donors within the cluster may be labile. In the structural solution of the CO inhibited enzyme, the CO ligand bridges two iron centers that constitute the tetrairon face and displaces a sulfide donor from the cluster. Surprisingly, reactivation of the enzyme results in a reinsertion of the sulfide ligand and displacement of CO. This result provides an important insight into possible fluxional processes that may occur during catalysis by FeMoco and a reminder that the structural data reflects only static pictures of the cluster.¹⁵ To complement these biochemical approaches and to provide chemical evidence for proposed intermediates, we have designed and synthesized multimetallic complexes in an effort to understand the chemical transformations involved during N₂ reduction at this metal cluster cofactor.

Mono- and multinuclear assemblies of iron are reported to be capable of dinitrogen activation in molecular systems. Holland and coworkers reported that reduction of a (β-dimetiminato)iron(II) complex with KC₈ in the presence of dinitrogen afforded a mixed-valent tetrairon(II/III) cluster in which three of the iron centers are bridged by a two nitride donors (one is μ₃ and the other μ₂) and the assembly incorporates two K⁺ cations.⁷² Interestingly, varying the alkali reductant to either an Na or Rb source resulted in subtle differences in the cluster
composition and extent of $N_2$ activation, specifically; the use of metallic Na affords a mixed valent di(nitride)triiron complex whereas Rb generates a structure analogous to the KC₈ product (Scheme 2-1 A). In addition, increased equivalents of either Rb or Cs do not result in $N_2$ activation, but afford trimetallic complexes containing linear bridging $N_2$ donors (Scheme 2-1 B). Based on these data, subtle steric and electronic effects have been proposed as important in controlling the assembly of the requisite metal cluster for dinitrogen activation. In a similar vein, Peters and coworkers reported the synthesis of a family of mononuclear low-valent iron complexes which catalytically reduced dinitrogen to ammonia (4.6 equivalents) using H(OEt₂)-[B(3,5-(CF₃)₂-C₆H₃)₄] as a proton source and KC₈ as the reductant (Scheme 2-1 C). This catalytic cycle is proposed to traverse only monoiron intermediates, but the presence of multimetallic transients cannot be rigorously excluded. Nonetheless, there are important parallels that can be drawn from the results reported by the Holland and Peters groups. In these systems, the metal centers in the initial mononuclear compounds are coordinatively unsaturated, and therefore have an accessible coordination site for substrate binding and activation. These monoiron complexes are first reduced to iron(I) or iron(0) with the reduced metal center engaging in $N_2$ activation. In contrast to these systems, however, biological dinitrogen fixation occurs at a multiiron cluster in which the cluster – containing seven iron atoms and one molybdenum center – undergoes four electrons, which is substoichiometric as compared to the complexes reported by Peters and Holland and suggests cooperative reactivity with $N_2$ in the E4 state of the cluster. Moreover, neither synthetic system can directly interrogate the role of or tune and control metal-ion redox cooperativity during dinitrogen reduction.

Since early reports of the employment of monoanionic β-diketiminates, also known as “[nacnac]” ligands, being used to stabilize first row transition metal complexes, these versatile
ligands have been used extensively to support metal centers with various oxidation states across the periodic table.\textsuperscript{62} Even though designed ligands may be synthetically challenging and reported in low yields, we aimed to design a multinucleating macrobicyclic ligand framework containing β-diketiminate units with the consideration of advantage of pre-organized ligands and build this architecture based on ease of synthesis (Figure 2-3). In regard with the overall structure of the ligand, three β-diketimine arms as struts and two arene linkers were able to build an inner cavity for metal coordination (Figure 2-4). The coordination sites employed are β-diketiminate units which are strong σ-donor ligands. Three β-diketiminate units were chosen in order to bring three metal centers into close proximity so that activation of substrates may potentially occur via cooperation of the metal centers and the tri-ethyl benzene rings were employed to preferentially place the trisamine groups on one face of the aryl ring and contribute to the high yields seen in the synthesis of H\textsubscript{3}L (Figure 2-4).\textsuperscript{73}

A condensation reaction of 1,3,5-tri(aminomethyl)-2,4,6-triethylbenzene\textsuperscript{74} with 2,4-pentanedione-2,2-(ethylene glycol) monoketal\textsuperscript{75} afforded the desired macrobicyclic tris(β-diketiminate) ligand, H\textsubscript{3}L, in about 65 % yield, as described in Scheme 1.\textsuperscript{73} Enamine/imine tautomerism is a commonly observed feature of β-diketimimates because of the stabilized hydrogen bonding of the proton of the enamine by the lone pair of the adjacent imine nitrogen atom, leading to the bond delocalization of the NCCCN backbone.\textsuperscript{76} Only one species was shown in \textsuperscript{1}H-NMR spectroscopy of the free ligand, H\textsubscript{3}L, demonstrating that the tautomerism of the β-diketiminate units and the rotations of the ethyl groups on the arene rings take place on the the NMR time scale, however, X-ray diffraction data of solid-state structure revealed that all of the six nitrogen atoms have protons with different partial occupancies, providing further
evidence for the electron delocalization in β-diketiminate units because of the enamine/imine tautomerism.\textsuperscript{73}

The ligand, H\textsubscript{3}L, was designed in order to possess the following features: (1) the six ethyl groups on the arene rings provide steric protection to the internal cavity of the ligand, and so can limit the size and shape of incoming substrates, (2) the orientation of the β-diketiminate chelate through arene caps can orient the position of metal centers within the nacnac arms towards the internal empty cavity, and (3) the two arene linkers define the metal-metal distances. The features of the ligand are affected by the volume of the internal cavity and oxidation state of metal centers. Furthermore, these features correlate highly with the reactivity with substrates.

Using this ligand, we recently reported a trinuclear (β-diketiminato)iron complex as the first designed multinuclear complex capable of activating dinitrogen upon reduction (Scheme 2-2).\textsuperscript{66} Here, reaction of nitride-bridged iron complex, Fe\textsubscript{3}(NH\textsubscript{x})\textsubscript{3}L, with excess HCl afforded ammonia in 30 % yield and it showed both intra- and intermolecular redox cooperativity towards cleavage of dinitrogen.

Consistent with our result, Cundari and Holland reported a detailed density functional theory (DFT) calculation on the interactions and extent of activation of N\textsubscript{2} as a function of nuclearity of the self-assembled cluster. These studies demonstrated that at least three iron centers are required to cleave the triple bond of dinitrogen, and that association of alkali cations aids in bond activation.\textsuperscript{35} In the system reported by our group, we were unable to isolate intermediates to confirm an intermolecular-only or a mixed intra- and inter-cluster mechanism for N\textsubscript{2} activation. To date, iron is the only late 3\textit{d} transition metal that has been reported as active for dinitrogen cleavage. For example, reduction of the cobalt(II) analog of Holland’s (nacnac)iron(II) complex results only in coordination of N\textsubscript{2}, although substantial π-backbonding
is observed as evident from vibrational spectroscopy.\textsuperscript{37} We reasoned that a substitution of iron for cobalt in our macrobicyclic ligand followed by subsequent reduction under an N\textsubscript{2} atmosphere could provide insight into the mechanism of N\textsubscript{2} reduction in our trimetallic system. One possibility is that similar cleavage of dinitrogen would occur, which would suggest that our designed approach affords enhanced cooperativity as compared to the mononuclear compounds. Alternatively, such a reaction would generate N\textsubscript{2} bridged cobalt clusters (e.g., hydrazide or diazenide) for which the structures and composition of products might support an intra-cluster cooperative step in the N\textsubscript{2} reduction reaction (e.g., Co\textsubscript{3}(N)L) or solely intermolecular events (e.g., K\textsubscript{2}(N)\textsubscript{2}[Co\textsubscript{3}Br\textsubscript{2}L\textsubscript{2}]) (Scheme 2-3). To that end, this chapter focuses on the synthesis, characterization, and the reactivity with dinitrogen upon reduction of two tricobalt clusters, Co\textsubscript{3}Cl\textsubscript{3}L and Co\textsubscript{3}Br\textsubscript{3}L.

**Experimental Methods**

**General Consideration.** All reactions were performed under dry, air free conditions using either a dinitrogen-filled Innovative Technologies glove box, and argon-filled MBraun Unilab glove box, or standard Schlenk techniques. Solvents were either purchased anhydrous and used as received (Sigma-Aldrich) or extracted from an Innovative Technologies solvent purification system. Anhydrous CoCl\textsubscript{2} and CoBr\textsubscript{2} were purchased from Sigma-Aldrich, washed with diethyl ether, and dried over SOCl\textsubscript{2} or SOBr\textsubscript{2} and dried under reduced pressure overnight prior to use. Potassium graphite (KC\textsubscript{8}) was synthesized from mixing the potassium metal and graphite and stirring at 150 °C under argon atmosphere overnight, causing the formation of shiny gold brown powder. NMR spectra were recorded on a 500 MHz Inova spectrophotometer with the spectra referenced to the residual protonated solvent signal, 3.58 ppm for THF-\textit{d}\textsubscript{8} and 6.97, 7.01 and, 7.09 ppm for Toluene- \textit{d}\textsubscript{8}. Deuterated solvents were purchased from Cambridge Isotope Labs and dried by standard methods as described elsewhere.\textsuperscript{77} Infrared spectra were
recorded in a nitrogen-filled glove box as solids on a Bruker Alpha FTIR with an ATR diamond crystal stage using the Oprus 7.0 software package. UV/VIS spectra were recorded on a Varian Cary 50 UV/VIS spectrophotometer using screw-top quartz cuvettes with a 1 cm path-length. Cyclic voltammetry was performed under a nitrogen atmosphere using a standard three electrode setup. Electrodes were purchased from either BASi, Inc. or CH Instruments, Inc. Potential sweeps were controlled by a Princeton Applied Research Versastat ll potentiostat. EPR measurements were recorded on a Bruker Elexsys E580 with a Bruker 4116DM resonator. Data was collected in the field from 50 to 7050 G with the following parameters for (1): temperature = 5 K, power = 6.30 × 10^{-2} mW, frequency = 9.269 GHz, modulation frequency = 100.00 kHz, modulation amplitude = 10.00 G, and gain = 60 dB and for (2): temperature = 5 K, power = 6.30 × 10^{-2} mW, frequency = 9.269 GHz, modulation frequency = 100.00 kHz, modulation amplitude = 10.00 G, and gain = 60 dB. Elemental analyses were performed by Complete Analysis Laboratories, Inc (Parsippany, NJ). All other reagents were purchased from Sigma-Aldrich and used without further purification.

**X-Ray Crystallography.** X-Ray Intensity data were collected at 100 K on a Bruker DUO diffractometer using Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.54178 Å) from an ImuS power source, and an APEXII CCD area detector. Raw data frames were read by the SAINT³ program and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces. The structures were solved and refined in SHELXTL6.1, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic
thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms unless otherwise stated.

**H₃L (1).** 1, 3, 5-trisaminomethyl-2, 4, 6-triethylbenzene and 2,4-pentanedione-2,2-(ethylene glycol) monoketal were synthesized according to a previous report.⁷⁴,⁷⁵ A Mixture of 2,4-pentanedione-2,2-(ethylene glycol) monoketal (3.10 g, 20.6 mmol) and 1,3,5-tris(amonomethyl)-2,4,6-triethylbenzene (3.43 g, 18.8 mmol) in methanol (100 ml) were placed in a round-bottomed flask and stirred at reflux for two days. The product was formed as white precipitate which was collected by glass frit (F). Traces of solvent and water formed from the reaction were removed under reduced pressure at 60 ºC. Single crystals of this free ligand suitable for X-ray diffraction analysis were grown by slow evaporation of dichloromethane (3.01 mg, 66 % yield).

**Co₃Cl₃L (2).** A solution of benzyl potassium (183 mg, 1.36 mmol) in 4 ml of THF at -40 ºC was added dropwise to a solution of 1 (300 mg, 0.43 mmol) in 10 ml of THF at -40 ºC over a period of 15 minutes. The solution turned dark purple and was stirred for an hour. The solvent was removed under reduced pressure and anhydrous CoCl₂ (199 mg, 1.36 mmol) was added to the residue. Toluene (18 ml) was added and the reaction was stirred for 1 hour at room temperature and then overnight at 95 ºC to afford a deep brown solution. After cooling, the solution was filtered to remove precipitated KCl. The filtrate volume was reduced to approximately 12 ml, filtered, and cooled to -40 ºC for a period of two days which resulted in the formation of fine precipitate of 2 as reddish brown powder. The precipitate from cold toluene was dried under reduced pressure and dissolved in THF (10 ml). Then the solution was setup pentane (5 ml) diffusion to THF (1 ml). The diffusion vial was at room temperature for 2 days, causing the formation of dark red blocks. (242 mg, 42 % yield). Elemental analysis for
C\textsubscript{45}H\textsubscript{63}N\textsubscript{6}Cl\textsubscript{3}Co\textsubscript{3}: % Calculated C, 48.93; H, 5.75; N, 7.61; % Found C, 48.88; H, 5.82; N, 7.55. IR: 2963 (m), 2909 (m), 1519 (s), 1413 (s), 1384 (s), 1326 (s), 1214 (m), 1066 (s), 1016 (s), 937 (m), 935 (m), 741 (s) cm\textsuperscript{-1}

\textbf{Co\textsubscript{3}Br\textsubscript{3}L (3).} A solution of benzyl potassium (183 mg, 1.36 mmol) in 4 ml of THF at -40°C was added dropwise to a solution of \textbf{1} (300 mg, 0.43 mmol) in 10 ml of THF at -40°C over a period of 15 minutes. The solution turned dark purple and was stirred for an hour. The solvent was removed under reduced pressure and anhydrous CoBr\textsubscript{2} (335 mg, 1.36 mmol) was added to the residue. Toluene (18 ml) was added and the reaction was stirred for 1 hour at room temperature and then overnight at 95 °C to afford a deep brown solution. After cooling, the solution was filtered to remove residual benzyl potassium and precipitated KBr. The filtrate volume was reduced to approximately 12 ml, filtered, and cooled to -40 °C for a period of two days which resulted in the formation of fine precipitate of \textbf{3} as purple/brown powder. The precipitate from cold toluene was dried under reduced pressure and dissolved in THF (10 ml). Then the solution was setup pentane (5 ml) diffusion to THF (1 ml). The diffusion vial was at room temperature for 2 days, causing the formation of reddish purple blocks. (199 mg, 58 % yield). Elemental analysis for C\textsubscript{45}H\textsubscript{63}N\textsubscript{6}Br\textsubscript{3}Co\textsubscript{3}: % Calculated C, 55.65; H, 6.54; N, 8.65; % Found C, 54.11; H, 6.48; N, 8.01. IR: 2928 (m), 2890 (m), 1520 (s), 1452 (w), 1431 (s), 1389 (s), 1370 (s), 1319 (s), 1292 (w), 1270 (w), 1028 (m), 1021 (s), 944 (m), 770 (m), 739 (s), 730 (w), 470 (m)

\textbf{Co\textsubscript{3}(NH\textsubscript{2})\textsubscript{3}L (4).} A sodium amide (NaNH\textsubscript{2}, 59 mg, 1.40 mmol) was added to the solution of \textbf{2} (420 mg, 0.43 mmol) in 8 ml of THF. The solution changed color to dark green from brick red after 1 day stirring at room temperature. The reaction was stirred for one more day at room temperature. After mixing, the solution was filtered to remove residual sodium chloride which is
light gray fine powder by filter paper. The dried filtrate re-dissolved in 14 ml of toluene for 2 hours for extraction and then filtered through celite plug to remove yellowish precipitate. Toluene was removed under reduced pressure. The dried filtrate re-dissolved in 10 ml of THF and the diffusion vial from hexane to THF was at room temperature for 3 days, causing the formation of bright green blocks. (300 mg, 78 % yield). IR: 3391 (w), 2961 (m), 2922 (m), 2865 (m), 1603 (w), 1521 (s), 1460 (m), 1427 (m), 1398 (s), 1371 (m), 1325 (s), 1283 (w), 1253 (w), 1235 (w), 1212 (w), 1068 (m), 1014 (s), 944 (w), 891 (w), 790 (m), 772 (s), 723 (s), 691 (m), 633 (w), 575 (w), 512 (s), 477 (w), 463 (m).1

**Indophenol test.** The indophenol test was carried out on samples of 4 and products from the reduction reactions of 2 or 3 by potassium graphite (KC₈) or other reducing reagents under dinitrogen using the general procedure outlined below. To a frozen solution of samples (around 3 mg) in toluene (4 ml) was added HCl in diethyl ether (2.0 M, 200 μL, 0.40 mmol), which resulted in an immediate color change from dark brown to sky blue. The mixture was warmed to room temperature and stirred overnight, after which all volatiles were removed under reduced pressure at room temperature. The sky blue colored residue was dissolved in a phosphate buffer solution (50 mM, pH 7.01, 5 mL), filtered through a syringe filter (0.45 μm) into a 10 mL volumetric flask. The flask was filled to the 10 mM mark on the flask using rinsate from the syringe filter. Ammonia was quantified using the indophenol method as previously published.79 A standard curve was generated using mixtures of NH₄Cl and 2 or 3.

**Formation of NH₄Cl.** The following procedure was performed to assay for the formation of NH₄Cl using 4 in an inert gas-filled glove box. A solution of 4 in THF was cooled to – 40 °C to which HCl in diethyl ether (2.0 M) was added dropwise. A pale blue suspension was immediately formed, allowed to warm to room temperature, and stirred overnight. Then the
suspension was filtered through toluene-rinsed Celite, and all volatiles were removed under reduced pressure. The resulting pale blue residue was dissolved in $d_6$-DMSO for $^1$H-NMR. $^1$H NMR for NH$_4$Cl (500 MHz, DMSO-$d_6$): δ 7.15 (t, $J$=51 Hz).

**Vanillin test.** The vanillin test was carried out on sample of 4 and products from the reduction reaction of 2 and 3 by KC$_8$ or other reducing reagents under N$_2$ using the general procedure outlined below. To a frozen solution of samples (3.5 mg) in toluene (4 ml) was added HCl in diethyl ether (2.0 M, 200 µL, 0.40 mmol), which resulted in an immediate color change from dark brown to sky blue. The mixture was warmed to room temperature and stirred overnight, after which all volatiles were removed under reduced pressure at room temperature. The sky blue colored residue was dissolved 3 ml of deionized water (DIW) and this solution was placed in a 10-ml calibrated flask and 3 ml of the vanillin solution (A 2 % m/V solution was prepared in 25 % ethanol) were added. The flask was stoppered tightly and placed in a water-bath at about 40 °C for 15 min, after which it was removed from the bath and allowed to cool to room temperature, Then, 1 ml of 2.5 M sulphuric acid was added, the volume was made up to the mark with DIW and the flask was set aside, for 10 min for full colour development. The absorbance of the yellow dye is measured at 400 nm using DIW as a reference.\textsuperscript{80}

**Results and Discussion**

**Synthesis and Characterization of a tri(μ-chloro)tricobalt(II) complex, 2.** The synthesis of the target complex Co$_3$Cl$_3$L was previously achieved by our group, however, additional characterization and improved synthetic conditions were necessary for the proposed research and were the initial focus of this project. The change of crystallization conditions from vapor diffusion of pentane into a THF solution of 2 to a recrystallization from cold toluene solution at -35°C resulted in reproducibly good yields of pure 2 as a microcrystalline powder (75%). Single crystals suitable for X-ray diffraction were grown using the original synthetic
protocol (Figure 2-5). In that structure solution, the three cobalt(II) ions are coordinated by the nacnac N-atom donors and bridged by three \( \mu_2 \)-chlorides with the metal and halide ions arranged in a planar hexagonal core, which is an unprecedented structure type for cobalt halide clusters. For example, Sobota and coworkers reported a \( \text{Co}_3\text{Cl}_3 \) cluster which adopts a chair-like conformation with the three chloride ions below the plane of the \( \text{Co}_3 \) plane. The bond angles around each cobalt center are consistent with those of other reported (nacnac)Co\( ^{II} \) complexes and indicate a pseudotetrahedral geometry at each Co\( ^{II} \); for example, the \( \text{N}1-\text{Co}1-\text{N}2, \text{N}1-\text{Co}1-\text{Cl}1, \text{N}2-\text{Co}1-\text{Cl}1, \text{N}1-\text{Co}1-\text{Cl}3, \) and \( \text{Cl}1-\text{Co}1-\text{Cl}3 \) angles are \( 102.7(1)^\circ, 106.1(1)^\circ, 106.5(1)^\circ, 105.4(1)^\circ, \) and \( 127.6(1)^\circ \) with gives a calculated \( \tau_4 \) value of 0.90 for Co1 (where a perfect tetrahedron is 1.00 and square planar is 0.00). The average Co-N distances, which range from 1.940(3) to 1.948(3) Å, are shorter by 0.028 Å than those in \( [\text{L}^\text{Me}\text{Co}]_2(\mu_2-\text{Cl})_2(2,4-\text{bis}(2,6-\text{diisopropylphenylimido})-3\text{-pentyl}) \) and nominally longer (0.04 Å) than the average distance in \( \text{L}^{\text{Bu}}\text{CoCl} \) (\( \text{L}^{\text{Bu}} = 2,2,6,6\text{-tetramethyl}-3,5\text{-bis}(2,6\text{-triisopropylpyenylimide})\text{hept}-4\text{-yl} \) reported by Holland and co-workers. These minor observed differences in bond distance could arise from the contrasting steric constraints imposed by the cyclophane ligand as compared to those enforced by the 2,5-diisopropylphenyl substituents on the diketiminate N-atoms and the tert-butyl substituents on the nacnac backbone in the monometallic compounds.

Figure 2-6 shows the absorption spectra of \( \mathbf{2} \) in the ultraviolet and visible (UV-vis) radiation range; these data were reproducible with \( \lambda_{\text{max}} = 321 \text{ nm, 425 nm, 458 nm, and 500 nm} \) (Figure 2-7). Using Beer’s Law and spectra collected over a range of solution concentrations (viz. 0.01, 0.015, 0.0175, 0.02, 0.17, 0.20, and 0.25 mM) in toluene, the extinction coefficients at 321 and 500 nm were determined \( 45(4) \times 10^3 \text{ M}^{-1}\text{cm}^{-1} \) and \( 2700(20) \text{ M}^{-1}\text{cm}^{-1} \), respectively. These magnitudes of these values are consistent with the higher energy absorption as a charge
transfer band and likely metal-to-ligand based on prior reports in mononuclear nacnac complexes and the lower energy feature as a d-d transition.  

The room temperature magnetic susceptibility was determined for 2 by the Evans method using a crystalline sample of 2 (Figure 2-8). The calculated \( \mu_{\text{eff}} \) value of 6.2(1) \( \mu_B \) was determined by both the frequency difference between the two tetramethylsilane resonances, and between the trace protonated solvent in the capillary insert and the solution of 2 (\( \Delta \nu = 145.63 \) Hz). Using the spin-only approximation, this effective magnetic moment lies between \( S = \frac{5}{2} \) (5.916 \( \mu_B \)) and \( S = 3 \) (6.928 \( \mu_B \)). Each cobalt(II) ion in 2 is predicted to adopt a high spin configuration with three unpaired electrons (\( S_{\text{Co}} = \frac{3}{2} \)) based on prior reports of related monometallic compounds. This comparison, however, should be used as a general guide and taken cautiously as the spin-only approximation may have limited utility given the expected unquenched orbital angular momentum of the cobalt(II) ions in this ligand environment. Nonetheless, the value is lower than that expected for three non-interacting cobalt centers, which suggests that the metal centers in 2 couple antiferromagnetically. This type of coupling scheme would be consistent with results for the related trinuclear complexes, such as Fe\(_3\)Br\(_3\)L and Mn\(_3\)Br\(_3\)L, which all exhibit antiferromagnetic exchange interactions. A broad isotropic signal centered at \( g = 2.04 \) is observed in X-band EPR spectra of 2 collected in 2-methyltetrahydrofuran at 5 K, which would be expected for an \( S_{\text{T}} = \frac{1}{2} \) ground state for the cluster (Figure 2-9). To gain a more detailed understanding of the strength of the interactions between the metal centers, variable temperature magnetic susceptibility data will be necessary; these experiments, however, are beyond the scope of this thesis.

**Synthesis and Characterization of a (\( \mu_2\)-bromo)(\( \mu_3\)-bromo)(bromo)tricobalt(II) complex, 3.** Prior to this thesis, the synthesis of the target complex Co\(_3\)Br\(_3\)L had also been
accomplished in our group. As for 2, however, additional characterization and improved synthetic conditions were necessary for the proposed research and were the initial focus of this project. The change of crystallization conditions from vapor diffusion of hexanes into a THF solution of 3 to a recrystallization from cold toluene at -35°C resulted in reproducibly good yields of crystalline 3 (78%). Single crystals suitable for X-ray diffraction were grown using the original synthetic protocol and crystallization conditions (Figure 2-10).81 In that structure solution, each cobalt(II) ion is coordinated by the two nacnac N-atom donors of a given ligand arm, and each bromide donor adopts a distinct coordination mode (terminal, µ2, and µ3). The structure type observed for this complex mirrors the reported structures of Fe3Br3L and Mn3Br3L.73 As noted in those compounds, the CoII centers in 3 lie out of the NCCCN plane of β-diketiminate by 0.27(4) – 0.58(4) Å. All Co–Br bond lengths in 3 are comparable and range from 2.490 (5) Å to 2.373 (5) Å, despite the different observed coordination modes. Focusing on the metal coordination within the nacnac arm, we also observe similar Co–N distances between 2 and 3 as might be expected. As might be anticipated from the greater distortion in 3 relative to 2, the coordination geometries are further from an idealized tetrahedral geometry with τ4=0.89 for Co1, 0.87 for Co2, and 0.86 for Co3 (Figure 2-10).82

In addition to the differences in the metal coordination environments for 3 as compared to 2, we also observe a significantly larger dihedral angle of 7.5° between two cyclophane arene rings in 3 whereas a significantly smaller one of 0.57(9)° is measured for 2. In our discussion of the structures of the triiron(II) and trimanganese(II) analogs of 3, we suggested that the structure is determined by the balance between the size of the halide and the electronic preference of the metal center, as manifested by the N···N distance in each nacnac arm and the consequent tuning of the cavity between the two ethyl ligands. Indeed, comparison of 2 and 3 provide evidence in
support of this hypothesis; for a given transition metal cation where the N–M–N bite angle preference is presumably held constant, the smaller anion (viz. chloride) affords a more symmetric and less distorted complex, whereas the complex with the larger anion is significantly more distorted. Again, we cannot completely exclude crystal packing effects or selective crystallization of one structure type over another in a given system, and other physical methods that report of the solution structure of these complexes will be invaluable.

The flexibility observed for the ligand was initially surprising, but indicates that there is sufficient plasticity to allow substrate entry and possible product egress during reactions. Moreover, target substrates such as dinitrogen may be readily held in different binding modes depending on the extent of bond activation. These results from 2 and 3 suggested that these types of clusters can be regarded as selective anion receptors from the interaction between the following factors; (1) the steric effect of the cavity interior and the ethyl substituents on the arene linkers, (2) the coordination preferences of the metal ions used, and (3) size of the halide anions.

Figure 2-11 shows the absorption spectra of 3 in the ultraviolet and visible (UV-vis) radiation range; these data were reproducible with $\lambda_{\text{max}}=331$ nm, 344 nm, 442 nm, and 505 nm (Figure 2-12). Using Beer’s Law and spectra collected over a range of solution concentrations (viz. 0.005, 0.010, 0.015, 0.150, 0.175, and 0.20 mM) in toluene, the extinction coefficients at 331 and 505 nm were determined $44(4) \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ and $3300(55) \text{ M}^{-1}\text{cm}^{-1}$, respectively. As noted above, these values are consistent with the higher energy absorption as a charge transfer band and likely metal-to-ligand based on prior reports in mononuclear nacnac complexes and the lower energy feature as a $d$-$d$ transition. The similar absorption spectra and extinction coefficients for 2 and 3 are expected given that the predicted weak coupling interactions afforded
by the halide bridges lead to an approximate treatment of the cluster as three monometallic centers.

The room temperature magnetic susceptibility of a crystalline sample of 3 was determined using the Evans method (Figure 2-13). The calculated $\mu_{\text{eff}}$ value of $6.9(1) \, \mu\text{B}$ was determined by both the frequency difference between two tetramethylsilane resonances, and between the trace proton-solvent in capillary insert and the solution of 3 ($\Delta \nu = 145.63$ Hz). Using the spin-only approximation, this effective magnetic moment compares favorably with an $S = 3$ ($6.928 \, \mu\text{B}$) system. Each cobalt(II) ion in 3 is predicted to adopt a high spin configuration with three unpaired electrons ($S_{\text{Co}} = 3/2$) based on prior reports of related monometallic compounds.$^{73}$

As noted above for 2, the spin-only approximation does not include any effects arising from the unquenched orbital angular momentum typically observed for high or intermediate spin cobalt(II) ions. Here again, the value is lower than that expected for three non-interacting cobalt centers, which suggests that the metal centers in 3 couple antiferromagnetically, an observation that is consistent with the data recorded for Fe$_3$Br$_3$L, Mn$_3$Br$_3$L, and 2.$^{73}$ A silent X-band EPR spectra of 3 was collected in 2-methyltetrahydrofuran at 5 K, and is consistent with an integer value of $S_T$ ground state for the cluster (Figure 2-14). SQuID measurements would certainly provide greater information on the metal-metal interactions as mediated by the bromide bridges; these experiments however are beyond the scope of this thesis.

**Synthesis and Characterization of tri(μ-amido)tricobalt(II), 4.** Reaction of sodium amide with 2 afforded by simple salt metathesis the corresponding putative tri(μ-amido)tricobalt(II) complex 4 in reasonable yield as green blocks (Scheme 2-4). Preliminary characterization including unit cell determination and decomposition analysis (vide infra) of this complex agrees with the proposed composition. Structurally, the complex is proposed to contain
a hexagonal cluster similar to the \([\text{Co}_3\text{Cl}_3]^{3+}\) core of \(2\) and the \([\text{Fe}_3(\text{NH}_2)_3]^{3+}\) in the reported iron analog.\(^{66}\)

IR spectroscopy supports the isolated product contains an amide functional group through the presence of N-H stretch at 3391 cm\(^{-1}\) (Figure 2-15). This feature is at comparable energy with the stretching modes reported for the other cobalt-bound N-H functionalities and to other complexes with \(\mu\text{-NH}_2\) ligands including the amide-bridged triiron cluster reported by previously by our group.\(^{88,89,90}\)

Using the indophenol assay\(^{88}\) to quantify the ammonia released after acid hydrolysis of cobalt amide complex, we obtained quantitative yields of \(\text{NH}_3\) per proposed \(\mu\text{-NH}_2\) ligand in the synthesized cobalt amide complex. The yield was determined using an empirically determined value for the extinction coefficient for indophenol under our experimental conditions. This yield is distinct from our prior reports in the analogous \(\text{Fe}_3\) complex for which only 30\% of the amide ligands were detected after protonolysis. The cause of this discrepancy remains unclear, but electronic effects may contribute to the lower yield, such as differences in ligand substitution kinetics during protonation and release of metal-amide fragments from our cyclophane ligand as previously suggested.\(^{73}\) Addition of excess HCl in Et\(_2\)O to a solution of 4 in THF afforded \(\text{NH}_4\text{Cl}\), which was characterized by \(^1\text{H}\)-NMR spectroscopy in \(d_6\)-DMSO (Figure 2-16). A triplet at 7.15 ppm with \(J = 51\) Hz agrees with the expected coupling of \(^{14}\text{N}\) \((I = 1)\) to the \(^1\text{H}\)-nuclei in \(\text{NH}_4\text{Cl}\). The chemical shift and coupling constant are comparable with \(\text{NH}_4\text{Cl}\) released upon protonolysis of \(\text{Fe}_3(\text{NH}_2)_3\text{L}\).\(^{90}\)

**Indophenol Assay of 2 and 3 with Various Reductants in the Presence of \(\text{N}_2\).** Using complexes 2 and 3, dinitrogen reduction was attempted under an \(\text{N}_2\) atmosphere with various reducing reagents. As mentioned in Chapter 1, Holland and coworkers have reported the
reduction of N₂ upon addition of KC₈ or alkali metals to solutions of low-coordinate iron complexes supported by bulky β-diketiminate ligands. These reactions afforded either the diazenido-bridged diiron complexes or the mixed-valent (μ₃-nitrido)(μ₄-nitride) tetrairon dipotassium cluster (Scheme 2-5).³¹ The treatment of nitride-bridged mixed-valence iron complex with 100 molar equivalents of ethereal HCl produced ammonia in 42 ± 2 % yield (Scheme 2-6).⁹¹ This experiment demonstrates that iron-based β-diketiminate complexes can cleave the N≡N triple bond, which can be protonated to afford ammonia upon addition of acid.

Analogous to their work on Fe-based systems, Holland and coworkers reported the synthesis of a mono-cobalt (II) complex with bulky β-diketiminates (same as L¹ in Scheme 2-5) and their conversion to the dinitrogen-bridged dicobalt(I) complex, B in Scheme 2-5, upon stoichiometric reduction under a dinitrogen atmosphere (Scheme 2-7).³⁷ X-ray crystallography supports the assignment of a N≡N ligand with minimal activation of the triple bond based on an N–N bond distance of 1.139(2) Å. Addition of excess KC₈ to complex A resulted in greater activation of the N₂ ligand and formation of complex C. In addition, alkali cations were incorporated within the structure and coordinated to the reduced N₂ fragment. The observed N–N bond distance is dependent on the identity of the alkali cation with values of 1.211(3)Å for Na⁺ and 1.241(7)Å for K⁺. Based on these observations, the alkali cation was proposed to be a key requirement for further activation of N₂ by polarizing the N–N bond to promote back-bonding interactions from the reduced Co centers.³⁷ Recently, our lab isolated Fe₃(NHₓ)₃L (x=1 or 2) from the reaction of Fe₃Br₃L with 6 equivalents of KC₈ under N₂ atmosphere, which releases ~30 % of theoretical ammonium halide upon addition of acid (Figure 2-17).⁶⁶

KC₈ (6.15 equivalents) were added to 2 or 3 in dried, degassed, and dinitrogen-saturated toluene at -95 °C to yield a dark red (2-6) or (3-6) solution, respectively. Reddish black block
crystals were isolated from a vapor diffusion into toluene in 10 % yield. Removal of the solvent under reduced pressure yielded crude product, which was further characterized to determine if N\textsubscript{2} activation indeed occurred. Infrared spectra on the corresponding products are displayed in Figure 2-18.

First, the indophenol test was used to assay ammonia release upon protonolysis of the product complexes. Assuming a composition similar to that of Fe\textsubscript{3}(NH\textsubscript{x})\textsubscript{3}L (x=1 or 2), the yield of ammonia was determined to be 10(0.5)% for 2-6 and 15(0.7)% for 3-6. As a control, solutions of 2 and 3 were treated with HCl and no ammonia was observed using this assay. The low yields of the ammonia precluded characterization by \textsuperscript{1}H-NMR, and therefore, experiments were not performed using \textsuperscript{15}N\textsubscript{2}.

These determined values are lower than that for the triiron congener, and led us to consider that weakening of the N≡N bond occurs – similar to the compounds reported by Holland – rather than complete scission. The reported stretching frequencies of N-N bond on M-N\textsubscript{2}-M complexes vary between 1400 and 1850 cm\textsuperscript{-1}, with lower values corresponding to greater activation of N\textsubscript{2}.\textsuperscript{37} In comparison, our group isolated a N\textsubscript{2}-adduct trinuclear copper complex which has N-N stretch at 1952 cm\textsuperscript{-1} by resonance Raman spectroscopy.\textsuperscript{67} In the infrared spectra of products 2-6 and 3-6, no absorptions are observed that can be readily assigned to an activated N\textsubscript{2} ligand. However, further experiments will be required including resonance Raman spectroscopy to rule out this possibility given the strong ligand vibrations in this spectral window and the difficulty observing the N\textsubscript{2} vibration in a related tricopper(I)-dinitrogen complex. A vanillin test,\textsuperscript{89} which is a quantitative and qualitative analysis test to detect hydrazine, was performed on compound 2-6 and 3-6. We reasoned that this test may also provide a method to detect diazene, as that product is expected to rapidly disproportionate in acidic media to yield
hydrazine. No hydrazine was detected in acid hydrolyzed products of 2-6 and 3-6, indicating that only minimal N₂ activation occurs upon reduction of the tricobalt complexes. Unfortunately subsequent control experiments where solutions of 2 or 3 were treated first with aqueous hydrazine and then acidified also gave negative results in the vanillin test.

In an effort to increase the yield of ammonia released, reductions of 2 and 3 with varying molar equivalents (3, 4, 8 and 9) of KC₈ in presence of N₂ were performed to generated the corresponding products (Figure 2-19).

We observed an almost linear increase in the ammonia released upon protonolysis with increasing reducing equivalents as assayed by the indophenol test for reductions using the chloride-bridged complex 2 (Figure 2-20). In contrast, a large increase in ammonia released is observed in the samples of 3 between 4 and 6 equiv of KC₈ followed by a decrease after 8 equiv. of the reductant. This result, though preliminary, could suggest that loss of the halide upon reduction, which is expected to be more facile for 3, could play a role in the reduction kinetics and reactivity of the reduced species.

The trend from the indophenol test on the series of products from increasing reducing equivalents differs from our previous result with the triiron(II) congener. Specifically, ammonia release from that system was maximized at 6 equiv. KC₈. We were intrigued by the positive correlation between equivalents of reductant and detected ammonia and speculated that 2 could be a competent catalyst for homogenous dinitrogen fixation under conditions similar to those reported by Peters and coworkers (Figure 2-21).³⁰,⁹²

Therefore, [(3,5-(CF₃)₂C₆H₅)₄B][(Et₂O)₂H] (HBArif) was used as a proton source with KC₈ as the reductant. In these experiments, 1 and 3 equiv. of HBArif were added to solutions of 2 (1 equiv.) with either 1 or 3 equiv. of KC₈ added under an N₂ atmosphere. However, an
immediate color change from dark red to violet was observed upon addition of the proton source to the reaction mixtures, independent of the number of equivalents of acid or reductant present. FT-IR spectra were collected on the crude filtrates from these reactions, both of which were isolated as light violet oils (Figure 2-22). In these spectra, absorptions indicative of the free-ligand (e.g., 1619 cm⁻¹) are readily apparent as well as vibrations associated with the ‘BArf anion. This result is not unexpected insofar as the trimetallic complexes of this ligand have been previously demonstrated to readily demetallate in the presence of weak acids (e.g., acetonitrile) and decomposition upon exposure to strong acids, such as HBArf likely out-competes N₂ activation.

One possible reason for the low observed yields of ammonia upon reduction of 2 and 3 is that demetallation results in transient ammonia-ligated metal centers that are substitutionally inert and may not be observed chemically in our assay. For example, the reduction reaction products may contain cobalt(III) rather than cobalt(II) centers; the former is anticipated to be substitutionally inert if low spin and in an octahedral environment, whereas the latter is always predicted to be labile based on Taube’s correlation. The presence of CoIII centers may therefore preclude detection of some percentage of the N-derived ligands in the reaction products. With this effect in mind, the reduction products were treated with 3 equivalents of KC₈ under an Ar atmosphere in toluene and the products then subjected to the indophenol assay. No increases were observed to the yield of ammonia as compared to the as-isolated reaction products. Similarly, we postulated that over-reduction of the reactive centers may occur in deference to reduction of starting complexes 2 and 3; that is, partially reduced complexes or reduced cluster with bound N₂ may be more easily reduced as compared to the halide-bridged tricobalt(II) compounds. In an effort to control the distribution of oxidation states in the reaction mixture,
KC₈ was added in a stepwise fashion over the course of several hours to a solution of 2 to yield needle-like crystals upon cooling a hot benzene solution of the putative reduction product to room temperature. The yield of ammonia from the indophenol test was 10(1)% – again, based on a predicted formula of three imide donors – as compared to 1.6(0.2)% when the reductant is added as one addition. This yield is greater, however, compared to the reduced N₂ bound di-iron complex reported by the Holland group or mixed valence tri-iron complex from our group.⁶⁶,⁷² The vanillin test, which can detect formed hydrazine, was performed to detect bound diazenide or hydrazide, however, nothing was detected. In contrast with FT-IR data of crude filtrate from diverse equivalents of KC₈ reduction reactions, two vibrations were observed at 3456 cm⁻¹ and 3660 cm⁻¹, and attributed to O-H stretches which are presumed to be from water or hydroxide contamination in either reactants or on the glass surface (Figure 2-23).

In the case of our analogous iron chemistry, the N-H vibrations of Fe₃(NH₃)₃L and Fe₃(NH₂)₃L are observed at similar energy, viz. 3397 and 3398 cm⁻¹ respectively.⁹⁰ Initially, the vibration at 3456 cm⁻¹ in spectra of products from the reduction 2 and 3 was tentatively assigned as an N-H stretching mode in N-adduct cobalt complex. However, the N-H stretches in 4 were observed at 3391 cm⁻¹, indicating that either the vibration at 3456 cm⁻¹ does not correspond to an NH₃ donor, or that the protonation state of the bridging nitrogen atom has a significant effect on the energy of this absorption. The latter scenario seems unlikely given the similarity between the energy of reported NH and NH₂ stretching modes in cobalt complexes.⁹⁴,⁹⁵ A new absorption at 570 cm⁻¹ is observed in IR spectra of the reduction product as compared to 2. This feature corresponds reasonably well with reported Co–O stretching modes in oxo-bridged cobalt clusters, such as those at 663 and 572 cm⁻¹ in Co₃O₄ cubic structures.⁹⁴,⁹⁵ The presence of O-H peak vibration at 3660 cm⁻¹ suggest the product of N₂ reduction reaction of trinuclear cobalt
complexes is extremely air and moisture sensitive and may be reacting with trace water molecules on the glass surface of the reaction flask or in the solvent. In an effort to limit water contamination all glassware was silylated and solvents was dried over sodium metal prior to use. However, this treatment had no effect on the yield of ammonia or composition of the final product based on IR spectroscopy.

For the triiron system, a Fe₃(NHₓ)₃L (x=1 or 2) was isolated as the product of N₂ activation reaction. In order to determine whether the solvent was acting as a proton source or H-atom source, deuterated solvents were used. However, no changes were observed in the IR spectra, and specifically, there was not a loss of intensity or shift in the assigned N–H vibration. Similarly, addition of dihydroanthracene or d₄-dihydroanthracene to the reaction had no effect on the product yield or the N–H vibration. In light of this result, it was proposed that, if C–H activation was occurring, the intramolecular reaction with one of the benzylic protons on the ligand would likely be favored. In addition, attempts to isolate intermediates in the reduction reaction by limiting the equivalents of reductant also proved unfruitful; the only observable products by IR spectroscopy and X-ray crystallography were the starting tri(bromide) complex and the tri(amide/imide) cluster.⁹⁰ Informed by these results in our triiron system in which intermediates containing hydrazide or diazenide donors could not be isolated and the possibility of H-atom or H⁺ transfer reactivity, we considered that intermediate(s) in generated upon reduction of 2 or 3 might demonstrate similar reactivity and that the yield of ammonia might be improved by either adding an H-atom or Lewis acid source to the reduction reactions or the reaction products. 9,10-dihydroanthracene (DHA) and 1-hydroxy-2,2,6,6-Tetramethylpiperidine (TEMPOH) were used as H-atom sources (Figure 2-24). In addition, various Lewis acids including trimethylsilyl triflate, trimethylsilyl chloride, methyl triflate, camphorsulfonic acid,
and boron trifluoride diethyl etherate, were added to the crude filtrate from reduction reaction. These modifications to the reaction however had no effect and hitherto, the isolation of a tricobalt-dinitrogen or evidence for appreciable N₂ reduction in the cobalt systems remain challenging.

Our group isolated the crystal which is potassium metal- and N₂-bound dimer of trinuclear iron complexes from N₂ reduction reaction (Figure 2-25). The crystal was isolated from pentane diffusion into a toluene solution of crude filtrate from the reduction of 2 with 6 equiv. of KC₈ in presence of N₂. In this complex, the halves of the dimer are held together by potassium cations that form cation-π interactions with the β-diketiminate ligands. This coordination mode of potassium cations is similar to the reported alkali metal bound N₂ reduced iron, cobalt, and nickel complexes from Holland group.⁷,⁹⁶ Here, the partial occupancy (4%) of iron atoms which are coordinated in a η₆ fashion to the benzene caps in the internal cavity is observed. This shift of the iron atoms from the nacnac arms to the internal face of the aromatic caps is generally observed in all reduction reaction products, independent of the reaction atmosphere (e.g., N₂ or Ar) or of the reductant used (e.g., Na or K/C₁₀H₈, K(β₃), or KC₈), but is not present in products of salt metathesis reactions (e.g., Fe₅(NH₂)₃L and Fe₅(OMe)₃L).⁴⁰,⁴²,⁶⁴ A similar shift has been reported for mononuclear (nacnac)cobalt(I) complexes and supports our hypothesis that a transient iron(I) center is formed upon reduction. Given the observed dimer in the reduction reactions for our iron system, we speculated that addition of excess alkali cations to the reduction reactions of 2 and 3 could effectively stabilize the N₂ activation products and improve yields and favor isolation of crystalline products. Simply, we interpreted the observed dimeric hexairon compound in equilibrium with two monomeric complexes, each with one coordinated K⁺ cation, with subsequent loss of K⁺ ultimately leading to the major NHₓ.
containing product. Therefore, addition of excess of alkali cations would effectively shift the equilibrium to the dimeric state and potentially favor isolation of a N\textsubscript{2} adduct of the tricobalt complex (Scheme 2-8).

Four equiv. of KC\textsubscript{8} was added to compounds 2 or 3 in the presence of 10 equiv. of different alkali-metal reagents (KCl, KI, NaI, and NaCl) under an N\textsubscript{2} atmosphere using the same protocol as described above. Single crystals from vapor diffusion into THF were isolated, and their unit-cells were determined. The unit cell was not similar to the iron dimer with potassium bridges (Figure 2-25), but instead, closer to the Fe\textsubscript{3}(NH\textsubscript{x})\textsubscript{3}L (x=1 or 2) compound which has three amine or imine ligands from the cleavage of N-N bond between metals. This result is very promising because 4 was already verified to release protonated NH\textsubscript{3}, NH\textsubscript{4}\textsuperscript{+}, by indophenol test. Additional characterization and its conversion test to ammonia are ongoing.

**Conclusion**

N\textsubscript{2} reduction reactions were attempted using 2 and 3 with various molar equivalents of reducing reagents in the presence of dinitrogen. The yields on ammonia from the indophenol test of the tricobalt reduction products were markedly low, 15\%, and hydrazine was not detected using the vanillin test. We validated that the low yields did not arise from the incomplete release of N\textsubscript{2} derived ligands; acid hydrolysis of 4 in toluene quantitatively releases all bound amide donors using the indophenol assay, and we have excluded (at least preliminarily) that substitution kinetics are a significant factor. Future experiments are required to probe the effect, if any, of the identity of the reducing agent as well as isotopic labelling studies to probe the initial products of reduction of the trinuclear cobalt complexes under N\textsubscript{2}.

In conclusion, two trinuclear (β-diketiminate)cobalt complexes (2 and 3) were synthesized and characterized by various analytical methods, including FT-IR, UV-vis, Evans method, and X-ray crystallography. Reduction of 2 and 3 with KC\textsubscript{8} under a dinitrogen
atmosphere was attempted and the presence of terminally reduced N-atom ligands was
determined using the indophenol assay. In addition, a tri(amido)tricobalt(II) complex, 4, was
synthesized and its preliminary characterization is included here.
Figure 2-1. The proposed iron-molybdenum cofactor (FeMoco) of dinitrogen for N₂ fixation.

Figure 2-2. Proposed mechanism of E₄ intermediate in dinitrogen fixation with the Fe2, 3, 6, and 7 face of FeMoco.¹⁴

Figure 2-3. Synthetic method of the macrobicyclic tris(β-diketiminate) ligand (left) and Crystal structure of H₃L (right). Hydrogen atoms have been omitted for clarity with the exception of the β-diketiminate protons in H₃L. C and N atoms are represented by gray and blue spheres, respectively.⁷³
Figure 2-4. Pre-organized ligand framework by platform and strut parts.

Figure 2-5. Crystal structure of 2. The pentane solvent molecule co-crystallized with the complex in an asymmetric unit and carbon-bound hydrogen atoms were omitted for clarity. Co, Cl, C, and N atoms are represented by violet, green, gray, and blue spheres, respectively.
Figure 2-6. The UV/VIS spectra of the 2 in toluene with concentration of 0.01 mM, 0.015 mM, 0.0175 mM, and 0.02 mM. The inset is UV/VIS spectra of the 2 in toluene with 0.17 mM, 0.2 mM, and 0.25 mM.

Figure 2-7. Plot of absorption of solutions of 2 in toluene at 321 (left) and 500 nm (right) as a function of concentration. Data were fit to a linear function with the y-intercept freely determined. $R^2 = 0.995$ (left) and 0.999 (right).
Figure 2-8. $^1$H-NMR of 2 crystals in $d_8$-THF with capillary.

Figure 2-9. X-band EPR spectrum of 2 collected at 5 K and as a glass in 2-methyltetrahydrofuran, $g \approx 2.04$
Figure 2-10. Crystal structure of 3. The THF solvent molecule co-crystallized with the complex in an asymmetric unit and carbon-hound hydrogen atoms were omitted for clarity. Co, Br, C, and N atoms are represented by violet, green, gray, and blue spheres, respectively.

Figure 2-11. The UV/VIS spectra of the 3 in toluene with concentration of 0.005 mM, 0.01 mM, and 0.015 mM. The inset is UV/VIS spectra of the 3 in toluene with 0.15 mM, 0.175 mM, and 0.2 mM.
Figure 2-12. Plot of absorption of solutions of 3 in toluene 331 nm (left) and 505 nm (right) as a function of concentration. Data were fit to a linear function with the y-intercept freely determined. R²=0.997 (left) and 0.999 (right).

Figure 2-13. ¹H-NMR of 3 crystal in d₈-THF with capillary.
Figure 2-14. X-band EPR spectra of 3 collect at 5 K and as a glass in 2-methyltetrahydrofuran.

Figure 2-15. Infrared spectra of 4 crystal.
Figure 2-16. The UV-vis spectra of indophenol test of 4 crystal. The sample solution using 4.2 mg of 4 (black). The three-fold diluted sample solution of 4.2 mg of 4 (red).

Figure 2-17. The $^1$H-NMR spectra of 4 with excess HCl in diethyl ether.
Figure 2-18. Structure of $\text{Fe}_3(\text{NH}_x)_3\text{L}$ ($x=1$ or 2). The pentane solvent molecule co-crystallized in $\text{Fe}_3(\text{NH}_x)_3\text{L}$ and hydrogen atoms have been omitted for clarity, except for the bridging nitrogen-bonded ones in $\text{Fe}_3(\text{NH}_x)_3\text{L}$. Fe, C, and N atoms are represented by orange, gray, and blue spheres, respectively.
Figure 2-19. IR-spectra of the products from the reaction of 6.15 equiv. of KC₈ with 2 (top) and 3 (bottom).
Figure 2-20. The overall reaction network of indophenol test using crude filtrate from the reduction reaction of 2 or 3 with diverse equivalents of KC₈ under N₂ atmosphere.
Figure 2-21. Plot of NH₃ yield against equivalents of KC₈.

\[
\begin{align*}
\text{N}_2 & \quad (1 \text{ atm}) \\
+ \quad & \quad \text{xs KC}_8 \\
+ \quad & \quad \text{xs HBARf}_4(\text{Et}_2\text{O})_2 \\
\xrightarrow{\text{Cat.} \quad -78^\circ \text{C, Et}_2\text{O}} & \quad 4.6 \text{ equivalents of NH}_3 \\
\end{align*}
\]

Figure 2-22. Cooling a solution of Fe catalyst in Et₂O at -78 °C followed by the addition of 40 equivalents of KC₈ and then 38 equivalents of [H(Et₂O)₂][BARf₄] leads to the formation of 4.6 equivalents of NH₃.³⁰
Figure 2-23. FT-IR spectrum of the crude filtrate from HBArf added N₂ reduction reaction.

Figure 2-24. Infrared spectra of crystal from 3.15 eq. of KC₅ added N₂ reduction reaction. A whole spectra (left) and zoomed in spectra (right).
Figure 2-25. The structure DHA and TEMPOH.⁹⁷

Figure 2-26. The X-ray data of N₂ reduced dimer (top) and the expended data (bottom), Fe, C, K, and N atoms are represented by orange, gray, green, and blue spheres, respectively.
Scheme 2-1. The synthesized iron complexes for N$_2$ fixation.$^{30,72}$

A.  

\[
\begin{align*}
[L^3\text{Fe}(u-\text{Cl})_2] & \quad \xrightarrow{2 \text{ eq. of } M	ext{Cl}, \text{M=Na, K, or Rb}} \quad N_2 \quad \xrightarrow{\text{K, Na, Rb}} \quad \text{NH}_3 \quad \xrightarrow{\text{xs HCl}} \quad \text{NH}_3 \\
\text{Ar}=2,6\text{-dimethylphenyl}
\end{align*}
\]

B.  

\[
\begin{align*}
[L^3\text{Fe}(u-\text{Cl})_2] & \quad \xrightarrow{4 \text{ eq. of } \text{KCl}} \quad \text{N}_2 \quad \xrightarrow{\text{cat. } \text{Na}(12\text{-crown-4})_2} \\
\end{align*}
\]

C.  

\[
\begin{align*}
\text{N}_2 (1 \text{ atm}) & \quad + \quad \text{xs KC}_8 \\
\text{N}_2 & \quad + \quad \text{xs HBA}_{4}(\text{Et}_2\text{O})_2 \\
\text{cat. } \text{H}_{2} \text{Pp}_{2} & \quad \xrightarrow{-78^\circ \text{C}, \text{Et}_2\text{O}} \quad 4.6 \text{ equivalents of } \text{NH}_3
\end{align*}
\]

Scheme 2-2. The synthesis of trinuclear iron-amide complex and indophenol result.$^{66}$

\[
\begin{align*}
\text{H}_3\text{L} & \quad 1) \ 3.15 \text{ eq BrK} \\
\text{Br}_2\text{K} & \quad 2) \ 3.30 \text{ eq FeBr}_2 \\
\text{Fe}_2\text{Br}_3\text{L} & \quad \xrightarrow{\text{N}_2} \\
\text{Fe}_3\text{Br}_3\text{L} & \quad \xrightarrow{\text{xs. HCl}} \quad 30(2) \% \text{ of } \text{NH}_3
\end{align*}
\]
Scheme 2-3. The proposed structures of N$_2$ reduced trinuclear cobalt complexes.

\[ \text{Co}_3(\text{N}_2)\text{L} \]

\[ \text{K}_2(\text{N}_2)(\text{Co}_3\text{Br}_2\text{L})_2 \]


\[ \text{Co}_3(\text{Cl}_2)\text{Cl} \quad \text{+ 3.5 eq of NaNH}_2 \quad \text{THF} \quad 2 \text{ days @ RT} \quad \text{67%} \]
Scheme 2-5. Iron complexes with varying steric bulk give different N\textsubscript{2} products upon reduction with KC\textsubscript{8}\textsuperscript{31}.

A. 2

\[
\begin{array}{c}
\text{L}^{1}\text{FeCl} \\
\text{Bu}^\text{Bu}
\end{array}
\xrightarrow{4 \text{ eq. of KC}_8} \quad \begin{array}{c}
\text{Bu}^\text{Bu} \\
\text{Bu}^\text{Bu}
\end{array}
\]

\[
\begin{array}{cc}
\text{N} & \text{N} \\
\text{Fe} & \text{Fe} \\
\text{N} & \text{N}
\end{array}
\]

\[
\text{N}_2
\]

\[+ 2\text{KCl}\]

B. 4 eq. of KC\textsubscript{8}

\[
\begin{array}{c}
\text{N} & \text{N} \\
\text{Fe} & \text{Fe} \\
\text{N} & \text{N}
\end{array}
\]

\[
\text{Cl} \quad \text{Cl}
\]

\[
\begin{array}{c}
\text{N} & \text{N} \\
\text{Fe} & \text{Fe} \\
\text{N} & \text{N}
\end{array}
\]

\[
\text{K} \quad \text{K}
\]

\[
\text{N}_2
\]

\[+ 2\text{KCl}\]

C. 2 eq. of KC\textsubscript{8}

\[
\begin{array}{cc}
\text{N} & \text{N} \\
\text{Fe} & \text{Fe} \\
\text{N} & \text{N}
\end{array}
\]

\[
\text{Cl} \quad \text{Cl}
\]

\[
\begin{array}{c}
\text{N} & \text{N} \\
\text{Fe} & \text{Fe} \\
\text{N} & \text{N}
\end{array}
\]

\[
\text{K} \quad \text{K}
\]

\[
\text{N}_2
\]

\[+ \text{KCl}\]

\[
\text{Ar}=2,6\text{-dimethylphenyl}
\]

Scheme 2-6. The reaction of nitride-bridged iron product with H\textsubscript{2} produces NH\textsubscript{3} in 42 ± 2 % yield\textsuperscript{91}.

\[
\begin{array}{c}
\text{N} & \text{N} \\
\text{Fe} & \text{Fe} \\
\text{N} & \text{N}
\end{array}
\]

\[
\text{Cl} \quad \text{Cl}
\]

\[
\begin{array}{c}
\text{N} & \text{N} \\
\text{Fe} & \text{Fe} \\
\text{N} & \text{N}
\end{array}
\]

\[
\text{K} \quad \text{K}
\]

\[
\text{N}_2
\]

\[+ \text{excess H}_2 \text{ toluene}
\]

\[2\]

\[
\begin{array}{c}
\text{N} & \text{N} \\
\text{Fe} & \text{Fe} \\
\text{N} & \text{N}
\end{array}
\]

\[
\text{H} \quad \text{H}
\]

\[
\begin{array}{c}
\text{N} & \text{N} \\
\text{Fe} & \text{Fe} \\
\text{N} & \text{N}
\end{array}
\]

\[
\text{K} \quad \text{K}
\]

\[
\text{N}_2
\]

\[+ 2\text{NH}_3 + 2\text{KCl}\]

\[
\text{Ar}=2,8\text{-dimethylphenyl}
\]
Scheme 2-7. Binding of nitrogen by low-coordinate cobalt.\textsuperscript{37}

\begin{align*}
\text{tBu} & \quad \text{N} \quad \text{N} \quad \text{Co-Cl} \quad \text{tBu} \\
\text{tBu} & \quad \text{N} \quad \text{N} \quad \text{Co-Cl} \quad \text{tBu}
\end{align*}

\begin{align*}
& \xrightarrow{1 \text{ eq. of } \text{KC}_8, \text{N}_2} \text{tBu} \quad \text{N} \quad \text{N} \quad \text{Co} \quad \text{N} \quad \text{N} \quad \text{tBu} \\
& \quad \frac{1}{2} \text{KCl} \quad \text{tBu} \quad \text{N} \quad \text{N} \quad \text{Co} \quad \text{N} \quad \text{N} \quad \text{tBu}
\end{align*}

\begin{align*}
\text{tBu} & \quad \text{N} \quad \text{N} \quad \text{Co-Cl} \quad \text{tBu} \\
\text{tBu} & \quad \text{N} \quad \text{N} \quad \text{Co-Cl} \quad \text{tBu}
\end{align*}

\begin{align*}
& \xrightarrow{\text{excess } M', \text{N}_2} \text{tBu} \quad \text{N} \quad \text{N} \quad \text{Co} \quad \text{N} \quad \text{N} \quad \text{tBu} \\
& \quad \frac{1}{2} \text{KCl} \quad \text{tBu} \quad \text{N} \quad \text{N} \quad \text{Co} \quad \text{N} \quad \text{N} \quad \text{tBu}
\end{align*}

\[ M' = \text{Na, K} \]

Scheme 2-8. The proposed mechanism of reduced N\textsubscript{2} adduct cobalt complex with potassium cation.

\begin{align*}
\text{N} \quad \text{Cl} \quad \text{Co} \quad \text{Cl} \quad \text{Co} \quad \text{N} \quad \text{Cl} \quad \text{Co} \quad \text{Cl} \\
\text{Co(II)}_3\text{Cl}_3\text{L} + 4 \text{KC}_8 + \text{N}_2 & \quad \longrightarrow \quad \text{Co(II)}\text{Co(III)}_2(\text{N}_3)_2\text{LK} + 3 \text{KCl} + 4 \text{C}_8
\end{align*}
CHAPTER 3
TRINUCLEAR IRON SULFIDE COMPLEX

Introduction

Several key steps and intermediates for reduction of dinitrogen to ammonia by the iron-
molybdenum cofactor in nitrogenase were introduced in Chapter 1. In particular, Hoffman and
Seefeldt trapped and characterized the E₄ intermediate – for which the proposed structure is
depicted in Figure 3-1 – of the native and other less active variants (generated by site-directed
mutagenesis) of the enzyme. This state is generated by the four-electron, four-proton reduction
of the oxidized resting state of the cofactor, and is proposed to undergo the reductive elimination
of H₂ to generate low-valent Fe center(s) which coordinated substrate (Figure 3-2).

In particular, computational studies such as those reported by Dance, point to the
tetrairon face or one part of the “iron belt” of FeMoco constituted by Fe2, 3, 6, and 7 as the locus
for substrate binding and where H atom equivalents (e.g., H⁻ and H⁺ on Fe and S, respectively).
ENDOR and other EPR methods corroborate the reaction site as the tetrairon face, as substrate
gating effects were observed when the residues proximal to this face were mutated to larger,
more encumbered ones. One proposed computational mechanism however disputes reductive
elimination of iron-hydrides as the event that activates the cluster for N₂ binding, and instead
invoke hydride transfer events to substrate at later points of the reaction. Evidently, an important
aspect of the reactivity of FeMoco is the ability of the iron and sulfide functionalities to bind
hydrides and protons, respectively. However, only a handful of synthetic iron-sulfur clusters are
known that contain coordinated hydrides and there are no synthetic examples that reduction
of iron sulfur clusters leads to protonation of bridging sulfides. The latter is surprising as the use
of sulfides as stores for protons to balance iron-sulfur cluster reduction is widely proposed in the
chemical community. Fundamentally then, there is a gap in our basic understanding of the
reactivity and properties of iron-sulfur clusters in the context of proton and hydride management, which is critical to develop clearer mechanistic insight into dinitrogen reduction by FeMoco as well as the function of these clusters in electron transfer processes.

In addition to understanding hydride and proton management by FeMoco, one aspect of the structure of FeMoco is unprecedented in synthetic cluster chemistry: only $\mu_2$-sulfides connect the Fe centers in the iron belt. Tatsumi and co-workers reported iron-sulfur clusters of similar nuclearities to FeMoco, but the sulfide bridges in the synthetic complexes are cap the tetrairon face rather than the edges as in FeMoco. Indeed, a CSD search reveals that edge-capping sulfides are not observed in any synthetic iron-sulfur cluster with nuclearities greater than two. One proposed consequence of the edge vs. face capping sulfides is that the former allow access to the metal centers, presumably for $N_2$ and hydride coordination. We predicted that our pre-organized macrobicyclic ligand framework would allow access to this structural motif as well as provide the structural stability to observe protonation the sulfide or accommodate hydride donors. We have previously synthesized an all ferric [3Fe-3S] cluster. There are no available coordination sites however in that species, precluding any understanding of the role of both hydride and sulfide donors on $N_2$ activation. Therefore, the work reported here aims to extend that initial work towards the synthesis of the structurally-related [3Fe-2S] and [3Fe-1S] clusters. This chapter introduces the preliminary results of synthesis and characterization of trinuclear iron-sulfur complex, [3Fe-2S]. The initial targets are complexes which contain one halide donor, with the expectation that this donor can either be removed by reduction or by reaction with hydride transfer reagents, such as KEt$_3$BH.

**Experimental Methods**

**General Consideration.** All reactions were performed under dry, air free conditions using either a dinitrogen-filled Innovative Technologies glove box, and argon-filled MBraun
Unilab glove box, or standard Schlenk techniques. Solvents were either purchased anhydrous and used as received (Sigma-Aldrich) or extracted from an Innovative Technologies solvent purification system. Anhydrous FeBr₂ was purchased from Acros Organics and dried further under an N₂ stream at 220 °C under vacuum overnight. NMR spectra were recorded on a 500 MHz Inova spectrophotometer with the spectra referenced to the residual protonated solvent signal, 3.58 ppm for THF-d₈ and 6.97, 7.01 and, 7.09 ppm for Toluene- d₈. Deuterated solvents were purchased from Cambridge Isotope Labs and dried by standard methods as described elsewhere. Infrared spectra were recorded in a nitrogen-filled glove box as solids on a Bruker Alpha FTIR with an ATR diamond crystal stage using the Opus 7.0 software package. Elemental analyses were performed by Complete Analysis Laboratories, Inc (Parsippany, NJ). Electrospray mass spectra were collected by direct injection into an Agilent 6120 TOF spectrometer at a gas temperature of 150 °C and fragmentation voltage of 120 V on solution samples prepared in a nitrogen atmosphere glovebox and transported in Hamilton gastight samples-lock syringes. All other reagents were purchased from Sigma-Aldrich and used without further purification.

**X-Ray Crystallography.** X-Ray Intensity data were collected at 100 K on a Bruker DUO diffractometer using Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.54178 Å) from an ImuS power source, and an APEXII CCD area detector. Raw data frames were read by the SAINT³ program and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces. The structures were solved and refined in SHELXTL6.1, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic
thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms unless otherwise stated.

**H₃L (1).** 1, 3, 5-trisaminomethyl-2, 4, 6-triethylbenzene was synthesized according to a previous report.²⁴ 2,4-pentanedione-2,2-(ethylene glycol) monoketal was synthesized according to a previous literature report.²⁵ A mixture of 2,4-pentanedione-2,2-(ethylene glycol) monoketal (3.10 g, 20.6 mmol) and 1,3,5-tris(amonomethyl)-2,4,6-triethylbenzene (3.43 g, 18.8 mmol) in methanol (100 ml) were placed in a round-bottomed flask and stirred at reflux for two days. The product was formed as white precipitate which was collected by glass frit (F). Traces of solvent and water formed from the reaction were removed under reduced pressure at 60 °C. Single crystals of this free ligand suitable for X-ray diffraction analysis were grown by slow evaporation of dichloromethane (3.01 mg, 66 % yield). 1 was synthesized according to a previous report.²³

**Fe₃Br₃L (2).** A solution of benzyl potassium (549 mg, 4.10 mmol) in 12 ml of THF at -40°C was added dropwise to a solution of 1 (300 mg, 0.43 mmol) in 10 ml of THF at -40°C over a period of 15 minutes. The solution turned dark purple and was stirred for an hour. The solvent was removed under reduced pressure and anhydrous FeBr₂ (900 mg, 4.17 mmol) was added to the residue. Toluene (55 mL) was added and the reaction was stirred for 1 hour at room temperature and then overnight at 80 °C to afford a deep red solution. After cooling, the solution was filtered to remove residual benzyl potassium and precipitated KBr. The filtrate volume was reduced to approximately 40 mL, filtered, and cooled to -40 °C for a period of two days which resulted in the formation of crystalline Fe₃Br₃L as red/brown crystals that were x-ray quality. A second crop of crystals was obtained by repeating the toluene crystallization procedure (761 mg,
Elemental analysis for C₄₅H₆₃N₆Br₃Fe₃: % Calculated C, 49.35; H, 5.80; N, 7.67; % Found C, 49.30; H, 5.84; N, 7.61.

**Results and Discussion**

**Synthesis and Characterization of Trinuclear Iron-Sulfur Complexes, Fe₃(S)₂BrL.**

Our group has reported the synthesis of 2 which has three bromide ligands, μ, μ₃, and terminal coordination mode. Recently, we synthesized tri(μ₂-sulfide)triiron(III) cluster, Fe₃S₃L, by treating 2 with 3 equiv. of sodium triphenylmethylthiolate in THF at room temperature. The solid-state structure of Fe₃S₃L shows that three ferric centers are coordinated to each β-diketiminate arm of the ligand, and linked by three sulfide ligands. The planar arrangement of the iron-sulfur cluster is unprecedented in synthetic chemistry and a consequence of the strict steric constraints imposed by the ligand. Interestingly, the cluster in this complex is structurally very similar to the initially reported but incorrect structure for a ferredoxin isolated from *Azotobacter vinlandii.*

Three iron(III) metals afford a planar hexagonal conformation with three sulfide ligands (Figure 3-3). The oxidation state of iron centers was confirmed by Mössbauer spectroscopy.

Building from this synthetic approach, we reasoned that cluster with a lower sulfide content could be accessed through careful control of the reaction conditions. These synthetic reactions are proposed and attempted using 2 (Scheme 3-1). The approaches take advantage of the lability of the metal-halide bonds and the stronger iron-sulfur interactions. Many reactions have been attempted and are on progress of characterization in Scheme 3-1. Reactions with disulfide reagents (Na₂S₂ and [K(18-crown-6)]₂[S₂]) were envisioned to afford controlled delivery of two S-atom donors per cluster; we anticipated that substitution of two halides with S₂²⁻ would be concomitant with metal oxidation and S–S bond cleavage to afford the corresponding Fe₃⁺Fe²⁺(S)₂BrL, Scheme 3-1 (A).
For the reaction of equiv. of Na₂S₂ or 2 equiv. of NaSCPh₃ and 2 in THF, the color of the mixture changed from brick red to dark green. IR spectra and ESI data of crude filtrate from these reactions are promising in comparison when compared to those data for the triiron tri(μ₂-sulfide). In the IR spectra of the reaction products, Fe-S, Fe-N, and C-N vibrations of this complex are shifted to higher energy but not are distinct from those in Fe₃S₃L. Fe₃S₃L¹⁰⁰ has more shifted vibrations at 1519, 1428, 1386, 1322, and 1010 cm⁻¹ than isolated compounds (Fe^{III}_2Fe^{II}(S)_2BrL) which has vibrations at 1521, 1432, 1391, 1330, and 1014 cm⁻¹ from the vibrations from H₃L at 1550, 1485, 1433, 1367, and 1026 cm⁻¹ (Figure 3-4).⁷³

We expect that the change of oxidation state of iron metals from all ferric in the trisulfide compound to a mixed valent cluster in these products would afford stronger Fe-N interactions and weaker C-N interactions, relatively, which would be directly manifested by higher (Fe-N interactions) and lower (C-N interactions) energy vibrations for the isolated compounds versus the trisulfide. In the high resolution ESI mass spectra collected in positive mode, the peak observed at m/z 951.23 can be assigned to be [Fe₃S₃L]⁺ although this assignment is not unambiguous as adventitious water in the instrument lines could generate oxo-containing complexes, such as [Fe₃S₂O₂L]⁺ (Figure 3-5).¹⁰⁰ Importantly however, we observed an ion envelope with a maximum at m/z 998.18, which corresponds to a parent ion [Fe₃S₂BrL]⁺. This envelope could be readily simulated using the natural abundances of the respective isotopes of the elements present in the complex, which strongly supports the successful synthesis of this species. We note that this ion envelope was not observed in crude reaction mixtures from the synthesis of the trisulfide complex, which suggests that it does not arise from complex decomposition under our MS conditions. Recently, needle reddish black crystals were isolated
from vapor-diffusion crystallizations and the characterization of this crystalline product is the aim of future work.

In addition to reaction of formally two equivalents of S\(^{-}\) with \textbf{2} using disulfide and Ph\(_3\)CS\(^{-}\), we also speculated that we could take advantage of the formation of strong Si–O (452 kJ/mol) and Si–N (355 kJ/mol) bonds to transfer an S\(^{2-}\) from (Me\(_3\)Si)\(_2\)S (293 kJ/mol) to Fe\(_3\)(OMe)\(_3\)L and Fe\(_3\)(NH\(_2\))\(_3\)L\textsuperscript{.104} These two precursor complexes can be easily synthesized by salt metathesis of Fe\(_3\)Br\(_3\)L with sodium methoxide and sodium amide and their characterization and synthesis previously reported by our group (Figure 3-6)\textsuperscript{.101} To access a similar halide containing complex as in the routes investigated above, further derivatization using Me\(_3\)SiCl or Me\(_3\)SiBr will be performed. The proposed reaction schemes are depicted in Scheme 3-2. These synthetic routes are the subject of future work on this project.

There have been some studies which investigated the synthesis of partial sulfide iron complex using Fe\(_3\)(OMe)\(_3\)L or Fe\(_3\)(NH\(_2\))\(_3\)L mentioned above (Scheme 3-2).

**Conclusion and Outlook**

The attempt of synthesis of [3Fe-2S] and [3Fe-1S] complexes will continue with diverse sulfide reagents, starting trinuclear iron complexes, and reaction conditions to provide open coordination site to dinitrogen. We expected that the coordinated halide groups can activate as better leaving groups than the coordinated sulfur ligand to iron metal centers in [3Fe-2S] and [3Fe-1S] clusters when KC\(_8\) is added. The synthesis and characterization of [3Fe-2S] and [3Fe-1S] clusters need to be accomplished, and then the reactivity towards N\(_2\) will be examined by conducting reduction of the resulting complexes under a dinitrogen atmosphere with various reductants such as KC\(_8\), alkali metals, or alkali metal/naphthalene mixture. This research will contribute one more step in understanding the function of sulfur atoms in FeMoco for the reduction of dinitrogen. Based on the proposed mechanism of dinitrogen fixation on iron-sulfur
active site in FeMoco of nitrogenase, our group is focusing on the synthesis of sulfide-bridged triiron complexes, with the expectation that these compounds will act as isolated fragments of the biological cluster and demonstrate reactivity towards dinitrogen at lower overpotential. Here, we have reported the preliminary attempts to synthesize [3Fe-2S] and [3Fe-1S] clusters using a variety of S-transfer reagents. From IR spectra and low resolution ESI/MS data, access to the di(sulfide) complex Fe₃S₂BrL appears possible and will be further explored. Additional characterization will be required, including the X-ray crystal structure. The reaction of this species with dinitrogen under reducing conditions is likely to provide insight into the fluxionality of iron-(μ₂-sulfide) linkages in FeMoco and the role, if any, that plays in dinitrogen reduction.
Figure 3-1. The proposed iron-sulfur active site of FeMoco for dinitrogen reduction.

Figure 3-2. Proposed mechanism of E₄ intermediate in dinitrogen fixation with the Fe2, 3, 6, and 7 face of FeMoco.¹⁴
Figure 3-3. X-ray structure of tri-iron tri-sulfide complex (Fe$_3$S$_3$L).
Figure 3-4. Infrared spectra of Fe₃S₃L crystal (top) and (A) in Scheme 3-1 (bottom).
Figure 3-5. The high resolution mass spectra of Fe$_3$S$_3$L crystal (left) and the low resolution mass spectra of toluene extraction from Fe$_3$S$_2$BrL reaction (right).

Figure 3-6. The crystal structures of Fe$_3$(NH$_2$)$_3$L (left) and Fe$_3$(OMe)$_3$L (right).
Scheme 3-1. The proposed reaction scheme to synthesize [3Fe-2S] and [3Fe-1S] species using Fe₃Br₃L.

Scheme 3-2. The proposed reaction schemes to synthesize [3Fe-2S] and [3Fe-1S] species using Fe₃(OMe)₃L or Fe₃(NH₂)₃L.
CHAPTER 4
CONCLUSION

In this work, the synthesis of two trinuclear (β-diketiminate) cobalt complexes, 2 (Co$_3$Cl$_3$L) and 3 (Co$_3$Br$_3$L), were carried out with improved recrystallization conditions resulting in higher yields. Additionally, these complexes were characterized using FT-IR, UV-vis, Evans method, and X-ray crystallography. Reduction reactions were attempted using 2 and 3 with various molar equivalents of reducing reagents in presence of dinitrogen. However, the yields on protonated N-products (ammonia and hydrazine) from the indophenol test of the tricobalt reduction products were markedly low. To examine the potential of releasing of N$_2$ derived ligands from trinuclear cobalt(II) clusters, tri(amido)tricobalt(II) complex, 4, was synthesized. According to the results from the indophenol assay of 4, we validate the low yields of ammonia (or hydrazine) were not attributed to incomplete release of N$_2$ derived ligands in the complex 2 reduction products. Further experiments including testing different reducing agents and $^{15}$N labeling studies are needed. These steps are required to improve the reactivity of complexes 2 and 3 towards N$_2$ and probe the initial N$_2$ reduction products. Moreover, synthesis of trinuclear cobalt sulfide complex will be accomplished to have similar purpose to model a four-rion belt, a fragment of FeMoco.

In order to model a fragment of the iron-molybdenum cofactor, [4Fe-4S], sulfide-bridged triiron clusters of the type Fe$_3$S$_{3-x}$Br$_x$L (where 1≤x≤3) were synthesized and preliminary characterization is included in this thesis. However, in-depth characterization including X-ray crystal structure is required to elucidate the structure of the resulting clusters. One future goal is to evaluate the electronic coupling within such sulfide-bridged triiron clusters, and if this coupling has an effect on N$_2$ reduction. These reduction reactions will be attempted using milder reducing agents, alkali graphites, alkali metals, or alkali metal/naphthalene
mixtures. Moreover, attempting to protonate the bound sulfide ligands can show, if any, how strong an effect protonated sulfide ligands have on the potential of cleavage $\text{N}_2$ and releasing $\text{N}_2$ derived ligands.
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BIOGRAPHICAL SKETCH

Jeong-Ah Lee earned her Bachelor of Science degree in fine chemistry from Seoul National University of Science and Technology in 2009 at South Korea as scholarship student because of perfect grades.

She received my Master of Science degree in fine chemistry in 2012 from Seoul National University of Science and Technology at South Korea. While pursuing her degree, She worked as a research and teaching assistant instructor for the department of chemistry. She has presented her research at international conference meetings and workshops including American Chemical Society.

With a fellowship granted from the National Research Foundation of Korea, She has worked in Prof. Jan Rohde’s lab at the department of chemistry at the University of Iowa as a visiting scholar for a year.

In 2012 Jeong-Ah Lee joined the graduate school in Chemistry at University of Florida in United State. She has been the recipient of awards including a University of Florida Outstanding Achievement. While pursuing her degree, she worked as a teaching assistant instructor for the department of chemistry.