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SYNTHESIS AND HETEROALLENE REACTIVITY OF BIS(ALDIMINO)PYRIDINE NICKEL COMPLEXES IN FOUR DIFFERENT OXIDATION STATES

by

BLAKE R. REED

DISSERTATION

Submitted to the Graduate School of Wayne State University Detroit, Michigan in partial fulfillment of the requirements for the degree of

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Approved By:

_________________________________________
Advisor                  Date
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CHAPTER 1: INTRODUCTION

1.1. Discussion on Carbon Dioxide and Its Role in Affecting the Environment

This dissertation focuses on the design of molecular complexes for the activation of small molecules, with a particular focus on CO\(_2\) and related heteroallenes. Carbon dioxide has many detrimental effects on the environment, including global warming and a possible role in the depletion of the ozone layer in the atmosphere.\(^1\) The increase in carbon dioxide levels in our atmosphere is facilitated by increased use of fossil fuels over the course of the past 100 years.\(^2\) From a chemist’s perspective, this provides an opportunity, as the carbon dioxide is virtually a ubiquitous and free source of carbon to use as a precursor for organic transformations.

1.2. The Use of Carbon Dioxide in Organic Transformations

Carbon dioxide has many uses in organic chemistry (Figure 1.1).\(^3\)\(^-\)\(^6\) One particular subfield in which CO\(_2\) has found an important application is polymer chemistry.\(^6\) Incorporation of CO\(_2\) as a copolymer with “high-energy” co-reactants such as oxirane, alkynes, and ideally olefins, can open doors to new useful industrial products. CO\(_2\) can also be incorporated into organic molecules by being converted to valuable functional groups such as lactones or carboxylic acids. Carbon dioxide can also be used towards building C\(_2\) and C\(_4\) products to be used in organic synthesis.\(^3\)\(^-\)\(^6\) Finally, CO\(_2\) has uses as precursor for fuels. It can be reductively split to form “energy storage” molecules, such as carbon monoxide, methanol, and methane.\(^5\)
1.3. Activation of Carbon Dioxide in the Absence/Presence of Transition Metal Catalysis

In the absence of a catalytic pathway, CO$_2$ activation has to proceed first via a one-electron reduced intermediate, CO$_2$ radical anion ($\text{CO}_2^-$). The formation of $\text{CO}_2^-$ is highly unfavorable, requiring a thermodynamic potential of -1.97 V vs. the normal hydrogen electrode (NHE). From this intermediate, several transformations are possible (Figure 1.2). As the radical is located on the “C” atom in $\text{CO}_2^-$, the simplest transformation is the C-C coupling of two $\text{CO}_2^-$ to form oxalate. This reaction is also the quickest method to make a C$_2$ building block towards other organic molecules. Other possible pathways include a nucleophilic attack of an oxygen atom in CO$_2$ on the radical carbon, and subsequent reductive splitting to produce CO and CO$_3^{2-}$. A third possible transformation is an H atom abstraction by $\text{CO}_2^-$ to make formate.
Figure 1.2. Activation of CO$_2$ without the use of transition metal catalysis.

Transition metal catalysis in CO$_2$ reduction helps to overcome the otherwise obligatory high barrier required for CO$_2^-$ formation (Figure 1.3). For instance, a thermodynamic potential for oxalate formation from CO$_2$ is only -0.90 V vs. NHE, compared with -1.97 V for CO$_2^-$.

Formation of formate and carbon monoxide have even lower thermodynamic potentials than that, at -0.61 and -0.53 V vs. NHE, respectively.$^3$ Another benefit of using transition metals to catalyze reductive transformations of CO$_2$ is the ability to perform multi-electron transformations. For example, conversion of CO$_2$ to formate is a two-electron process. Using a transition metal catalyst, the two-electron transformation can be carried out in one step, as opposed to two single-electron processes.
This project specifically focuses on the design of inexpensive and earth-abundant catalysts, featuring a base metal in redox-active ancillary ligand environments. Our metal of choice is nickel, as nickel is an earth-abundant 3d metal that has been shown previously to activate and reduce CO$_2$ and a related heteroallene, CS$_2$. While the major benefit of such study, if successful, would come from developing a useful CO$_2$ reduction catalyst, the use of CS$_2$ can help to find such a catalyst and to understand the fundamental chemistry of heteroallenes with transition metals. CS$_2$ often demonstrates similar chemistry to that of CO$_2$, while also being a liquid (CO$_2$ is a gas) and somewhat more reactive.

Several groups have shown that “metalloradical”, or one-electron metal reagents can enable C-C bond formation from CO$_2$ or CS$_2$. For example, Dahl and coworkers showed that a nickel(I) reagent, Ni(Cp*)(CO) dimer, could reductively couple CS$_2$ to tetrathiooxalate.
Similarly, Evans and coworkers (Figure 1.4, top left) have shown that a samarium(II) complex reductively couples CO$_2$ to form oxalate.$^8$ Although these complexes show promise as catalysts for reductive coupling of heteroallenes, unfortunately they were unable to remove the respective “oxalate” from the system, thereby rendering the complex dead from the perspective of catalysis. Other relatively common route of heteroallene activation include reductive splitting to form “CX” (CO, CS) and “X” (O, S); such a transformation usually requires a two-electron metal reagent. Sadighi and coworkers used a copper-boryl complex to reductively split CO$_2$ to give CO and “O” in the form of boryloxide (Figure 1.4, top right).$^9$ Thomas and coworkers used a heterobimetallic zirconium/cobalt complex to reductively split CO$_2$ into carbon monoxide and a bridging oxo; both products were directly observed as ligands (Figure 1.4, bottom right).$^{10}$

Bouwman and coworkers designed a di-copper system that is able to couple CO$_2$ into oxalate (Figure 1.5).$^{11}$ It is also the only well-defined homogeneous system that is able to
electrocatalytically generate oxalate from CO₂. By adding Li⁺ ions (to remove oxalate as Li₂C₂O₄) and electrons (to reduce copper(II) to copper(I)), the catalyst can be regenerated.

![Catalytic conversion of CO₂ to oxalate by a well-defined di-copper(I) complex.](image)

**Figure 1.5.** Catalytic conversion of CO₂ to oxalate by a well-defined di-copper(I) complex.¹¹

Binding of CO₂ and CS₂ to the transition metals prior to their activation is of interest as it may affect the reduction routes. Heteroallenes exhibit several binding modes, the most prominent in mononuclear chemistry being the “η¹” mode and the “η²” mode (Figure 1.6).⁴ The η² mode (or side-on mode), akin to the η² mode of ethylene, is somewhat more common, as it allows both σ donation and π back-donation. As with ethylene, this coordination mode is somewhat less productive in terms of ensuing chemistry. If productive, it generally leads to a reaction at both carbon and oxygen/sulfur, as both atoms are affected by this binding mode.⁷ An example for the η² mode of CO₂ and CS₂, reported by Hillhouse and coworkers, is shown in **Figure 1.6, left.¹²** Another possible binding mode, η¹ (or end-on), involves only the interaction with the central carbon.⁴ This binding mode relies primarily on the donation from an electron—
rich metal to the electron-deficient carbon atom of CO$_2$/CS$_2$; it is more common for coordinative saturated electron-rich complexes. An example of $\eta^1$-bound CO$_2$ to the hexacoordinate electron-rich iridium(I), reported by Herskovitz and coworkers, is shown in Figure 1.6, right.$^{13}$

Figure 1.6. Examples of $\eta^2$- (left) and $\eta^1$- (right) bound heteroallenes.$^{12,13}$

1.4. Discussion of Redox Non-Innocent Ligands

Traditionally, most organometallic catalytic processes, including electrochemical reduction of CO$_2$, relied on noble metal catalysts.$^{14}$ Noble metal catalysts are generally less sensitive to air and moisture, less poisoned by common by-products of catalysis (e.g. CO), and therefore enable better and longer-term productivity. In recent years, there has been a significant interest in developing base-metal catalysts.$^{15,16}$ Base metals are significantly more abundant and less expensive than noble metals. Thus, base-metal catalysis is more sustainable in the long run, and is more cost-effective. A common problem with base metals, however, is that while noble metals generally enable one-step multi-electron transformations (i.e. Rh(I)/Rh(III) couple), base metals generally show one-electron chemistry (i.e. Fe(II)/Fe(III) couple). One possible solution to remedy this problem is to utilize redox active ligands.$^{15,16}$ Redox-active ligands enable multi-electron transformations at base metal centers at accessible redox potentials.$^{15,16}$
In this project, we use bis(imino)pyridines as ancillary ligands to facilitate redox transformations. Bis(imino)pyridine ligands are among the most commonly used ligands in transition metal catalysis due, in large part, to the ease of their synthesis and to their ability to accept up to three electrons into the π system. This redox “non-innocence” allows for base metals to achieve multi-electron redox transformations, whereas only one electron transformations would be possible without the use of redox non-innocent ligands. It has been recently shown that bis(imino)pyridines allow even multi-electron catalysis of CO₂ reduction at completely inactive redox metals such as Al(III).

A specific example of redox activity of bis(imino)pyridine, [NNN], ligands is given below. Chirik and coworkers demonstrated that Co[NNN]Cl₂ can be reduced by two electrons to give Co[NNN](N₂) with charged species of Co(II) and [NNN]²⁻ (Figure 1.7). In spite of being relatively oxidized, the cobalt acts as a reduced metal center, as the [NNN]²⁻ can shuttle electrons through the metal to a substrate. The redox activity of bis(imino)pyridine ligands has been verified using different experimental techniques, among them Electron Paramagnetic Resonance and UV-visible spectroscopy. X-ray crystallography provides one of the easiest ways to detect electron delocalization into the ligand, as certain bond distances in the ligand are highly sensitive to ligand reduction. These bonds specifically include the C=N imino bond and the C(imine)-C(pyridine) bonds, as ligand reduction leads to the development of the C-N single bond character and the C-C double bond character. In the fully oxidized state, imine C=N double bonds have lengths of around 1.27-1.28 Å, C-C single bonds show a bond length of 1.48 Å, and pyridine C=N double bonds have bond lengths of 1.34 Å. In the one-electron reduced state, imine C=N double bonds lengthen to 1.31-1.32 Å, C-C single bonds shorten to 1.43-1.44 Å, and
pyridine C=N double bonds lengthen to 1.37 Å. Further reduction by one more electron leads to further lengthening of C=N double bonds and shortening of C-C single bonds. Imine C=N bonds lengthen to 1.33 Å, C-C single bonds shorten to 1.42 Å, and pyridine C=N double bonds lengthen to 1.38 Å.

Figure 1.7. Example of a redox-active bis(imino)pyridine system with Co(II)

1.5. Previous Work in Our Research Lab

Previous studies conducted by our lab with bidentate, redox-active, iminopyridine ligated complexes, both mononuclear and homodinuclear, have shown promise towards the activation of heteroallenes (Figure 1.8 and Figure 1.9).\textsuperscript{20, 21} As noted earlier, CS\textsubscript{2} has been explored as an isoelectronic analogue of CO\textsubscript{2} because it is easier to handle, due to it being a liquid, as well as being more reactive, due to the longer and weaker C=S double bonds. Because the iminopyridine ligand is bidentate, the CS\textsubscript{2} coordinates in an η\textsuperscript{2} (or side-on) orientation, similarly to the coordination mode found in the nickel diphosphine complex reported by Hillhouse and coworkers (Figure 1.6).\textsuperscript{12} Our attempts to induce C-C coupling (of two bound CS\textsubscript{2} molecules) or C-S splitting were not successful, as all our manipulations led to CS\textsubscript{2} liberation instead.\textsuperscript{20, 21} DFT calculations showed there is insufficient radical character located on the carbon atom to allow for coupling to occur.\textsuperscript{20} Furthermore, as described above, the η\textsuperscript{2} coordination mode rarely leads to productive reactivity, especially for carbon disulfide. Following these studies, my work has focused on the related, tridentate bis(imino)pyridine
ligands, with the goal of forcing different coordination modes of bound CO$_2$/CS$_2$ in the reduced nickel complexes, and thereby achieving their reduction.

1.6. Summary and Outlook

Reactivity of transition metal complexes with CO$_2$ is an important field of research due to the applications in energy storage and incorporation of CO$_2$ into organic compounds. Recently, first-row (or “base”) transition metals have been targeted for catalysis due to their low cost and high abundance. There have been many examples of complexes that reduce heteroallenes using transition metals. Unfortunately, most of these reactions are not reversible, and require high reduction potentials. We are looking towards making systems that not only facilitate reduction of heteroallenes, but also can be reduced to remove the product and regenerate the catalyst.
Redox non-innocent ligands provide a useful scaffold to allow multi-electron transformations using first-row (base) transition metals. Our lab has previously demonstrated that bidentate redox-active ligands can be used to stabilize nickel(0) and allow the nickel center to coordinate CS$_2$. However, the obtained CS$_2$ complexes did not lead to productive chemistry, likely due to the unfavorable side-on coordination that is enabled by the bidentate iminopyridine. This led us to explore tridentate bis(imino)pyridine, [NNN], pincer-type ligands as a possible nickel ligand environment for activation of heteroallenes.

1.7. Goals and Objectives

Our overall goal in this research is to develop catalysts for reductive transformations of CO$_2$ and CS$_2$, and explore fundamental chemistry of heteroallene activation at transition metal complexes with redox-active ligands. Following previous research conducted in our lab using bidentate aldiminopyridine ligands [NN], we have designed a tridentate bis(aldimino)pyridine system, henceforth abbreviated as [NNN] (Figure 1.10). We postulated that the tridentate nature of the [NNN] ligand would force $\eta^1$ binding of CO$_2$ through the carbon atom (only) in square planar geometry. Such binding would enable a more “activated” form of CO$_2$ which may then lead to its successful reduction to oxalate, CO, or formic acid. We also chose to use nickel as our base transition metal to be used in our catalyst. Nickel is a late, electron-rich metal which has been previously shown to react with CO$_2$. 
Figure 1.10. Design of the bis(imino)pyridine system.

An additional important goal of my research was to understand the electronic structure of [NNN]-nickel complexes and its impact on the reactivity of nickel-bis(imino)pyridine complexes in various oxidation states. The question of the distribution of charge in metal-redox active ligand complexes has attracted the attention of many researchers in the last 10 years or so. Bis(imino)pyridine complexes of nearly every transition metal and many group elements were studied. However, only very few of these complexes contained aldimines, as most of the work focused on ketimino complexes. As detailed below in Figure 1.11, we postulated that less electron-rich aldimines may present a different electronic effect and thus lead to a different electronic structure and reactivity. This postulate was based on the previous work of our lab. As the precise assignment of the metal/ligand charge may be somewhat ambiguous, throughout this work we will assign oxidation states to the combination of metal and ligand: (Ni[NNN])\textsuperscript{2+}, (Ni[NNN])\textsuperscript{1+}, (Ni[NNN])\textsuperscript{0}, (Ni[NNN])\textsuperscript{1-}. The reactivity will be investigated as a function of the overall oxidation state of the system.
Figure 1.11. Comparison of bis(aldimino)pyridines and bis(ketimino)pyridines

Aldimine:
- Less electron rich
- Less radical delocalization into the ligand
- Less significant steric effect

Ketimine:
- More electron rich
- More radical delocalization into the ligand
- More significant steric effect
Toward the realization of these goals, we have defined four objectives:

1. **Synthesis of Bis(imino)pyridine Ligands and Their Corresponding Nickel(II) Complexes** \((\text{Ni}[\text{NNN}])^{2+}\). Synthesis and characterization of the ligands and complexes is addressed in Chapter 2.

2. **Synthesis and Characterization of One-electron Reduced \((\text{Ni}[\text{NNN}])^{1+}\) Complexes and Their Reactivity.** Objective 2 involves synthesis of \((\text{Ni}[\text{NNN}])^{1+}\) complexes and their characterization. Structural and electronic relationships will be discussed. Reactivity with heteroallenes and other small molecules is conducted. This objective is addressed in Chapter 3.

3. **Synthesis and Characterization of two-Electron Reduced Complexes and Their Reactivity.** Synthesis of \((\text{Ni}[\text{NNN}])^{0}\) complexes using two different methods were conducted. The complexes were characterized and reactivity with heteroallenes is evaluated. This objective is addressed in Chapter 4.

4. **Investigation of the Electrocatalytic Reactivity of the \((\text{Ni}[\text{NNN}])^{1-}\) state.** Electrochemical reduction of the \((\text{Ni}[\text{NNN}])^{2+}\) shows that a \((\text{Ni}[\text{NNN}])^{1-}\) state is accessible. Thus, we conducted electrocatalytic studies targeting reactivity of \((\text{Ni}[\text{NNN}])^{1-}\) state in the presence/absence of \(\text{CO}_2\). These results will be discussed in Chapter 5.

This chemistry was conducted over the course of the last four years and will comprise the body of the dissertation.
2.1. Introduction

As suggested in the introduction, we are interested in using a redox non-innocent [NNN] ligand as an intramolecular electron storage “capacitor” for the activation of heteroallenes. Many groups have previously synthesized [NNN] ligands with varying R and R’ groups, and investigated the reactivity of their transition metal complexes in the activation of small molecules.\textsuperscript{17} However, most of the previously investigated bis(imino)pyridine complexes involved bis(ketimino)pyridine ligands; only few reports have dealt with the reactivity of bis(aldimino)pyridines. Bis(aldimino)pyridines are less electron-rich than bis(ketimino)pyridines and also feature somewhat different electronic effects. Recently, Chirik and coworkers have shown that bis(ketimino)pyridine ligands may lead to different chemistry than bis(aldimino)pyridine type ligands.\textsuperscript{30} The authors have shown that for Fe[NNN](CO)\textsubscript{2}, the ketimine variant contained a more electron rich iron center. For the bidentate iminopyridine systems, our group has previously demonstrated a stark difference in the reactivity of aldiminopyridine versus ketiminopyridines with nickel(0), likely due to the different electronic effects. Hoping to delineate the electronic differences between bis(ketimino)pyridines and bis(aldimino)pyridines, and discover new reactivity, our research focused on the bis(aldimino)pyridine complexes. As described below, we synthesized a variety of bis(aldimino)pyridine, [NNN], ligands with various groups on the imine arms to explore steric and electronic effects on the electronic structure and reactivity of our complexes.
2.2. Synthesis of [NNN] Ligands

The electron-rich, [NNN]a-c ligands are made through a condensation reaction of 2,6-pyridinedicarboxaldehyde and a primary amine to form the bis(aldimino)pyridine (Figure 2.1). By using different substituted primary anilines, 2,6-diisopropylphenyl, 2,4,6-trimethylphenyl, and 4-methoxyphenyl respectively, we are able to make different ligands with varying steric bulk and/or electronic properties. For the electron-deficient N-aryl substituents, [NNN]d,e, 4-trifluoromethylphenyl and 3,5-bis(trifluoromethyl)phenyl respectively, we were not able to isolate the free ligand in a good yield, due to the more difficult condensation of the electron-poor anilines. The complexes of these ligands were synthesized directly in one-pot reaction as described below.

![Figure 2.1. Synthesis of [NNN]a-c ligands](image)

2.3. Synthesis and Structural Characterization of Ni[NNN]X₂ Complexes

Next, we turned to the synthesis of nickel(II) complexes, 1a-Br₂, 1a-Cl₂, 1b-Br₂, 1c-Br₂, 1d-Br₂, and 1e-Br₂. Synthesis of 1a-Br₂, 1a-Cl₂, 1b-Br₂, and 1c-Br₂ were conducted at room temperature in THF by addition of the ligand to NiBr₂(DME) or NiCl₂(DME), followed by stirring for 1 h (Figure 2.2).
Synthesis of $1a$-$c$. Synthesis of $1d$-$Br_2$ and $1e$-$Br_2$ were conducted at room temperature in THF by addition of the corresponding aniline to 2,6-pyridinedicarboxaldehyde, and then subsequent addition of NiBr$_2$(DME). The reaction was stirred overnight. The complexes were isolated as crystalline solids in yields described in Figure 2.3. The complexes were characterized by $^1$H NMR, IR, mass spectrometry, elemental analysis, and single-crystal X-ray diffraction.

Figure 2.3. Synthesis of $1d$-$Br_2$ and $1e$-$Br_2$. Selected solid-state structures are shown below. When the complexes are crystallized from coordinating solvents (i.e. acetonitrile), we observe an equivalent of the solvent complexed to the metal resulting in hexa-coordinate, distorted octahedral geometry. The use of a non-coordinating solvent, such as dichloromethane, leads to the formation of penta-coordinate nickel(II) centers, whose geometry is an intermediate between square pyramidal...
and trigonal bipyramidal. The distortion of the nickel(II) center can be quantified using the term $\tau_5$ (tau).\textsuperscript{31} $\tau_5$ values range from 0 to 1 and are calculated with a formula of $\tau_5 = (\beta - \alpha)/60$ where $\beta$ is the most obtuse angle and $\alpha$ is the largest angle opposite $\beta$. A perfect square pyramidal geometry features $\tau_5 = 0$ and perfect trigonal bipyramidal geometry demonstrates $\tau_5 = 1$. For 1a-Br$_2$, $\tau_5 = 0.0995$ and for 1a-Cl$_2$, $\tau_5 = 0.0075$, indicating a slightly distorted square pyramidal geometry.

**Figure 2.4.** Crystal structure of 1a-Br$_2$. H-atoms omitted for clarity.

**Figure 2.5.** Crystal structure of 1a-Cl$_2$. H-atoms omitted for clarity.
Figure 2.6. Crystal structure of 1d-Br$_2$. H-atoms omitted for clarity.
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*Table 2.1. Experimental crystallographic parameters for 1a-Br₂, 1a-Cl₂, and 1d-Br₂.*
2.4. Discussion of Paramagnetic NMR Spectra of Ni[NNN]X₂ Complexes

Compounds 1a-1d all demonstrate well-resolved paramagnetically shifted \(^1\)H NMR spectra that span approximately a 70-80 ppm range (from -10 ppm to +70 ppm). Compound 1e-Br₂ is only sparingly soluble in CD₂Cl₂ and therefore its spectrum will not be discussed. As an example, the \(^1\)H NMR spectrum of compound 1b-Br₂ is shown in Figure 2.7. We assign the lowest-field peak at 69.1 ppm to the meta-H of the pyridine (H\(^f\)). We note that Bryliakov and coworkers have reported \(^1\)H NMR spectra of the related bis(ketimino)pyridine nickel(II) dichloride complexes, in which the peak around 70 ppm was also assigned to a pyridine meta-H.\(^{32}\) Pyridine meta protons of other complexes all appear in the similar region (69.1 ppm for 1a-Br₂, 66.4 ppm for 1a-Cl₂, 61.9 ppm for 1c-Br₂, 60.7 ppm for 1d-Br₂). Pyridine para-H resonance is observed at 11.4 ppm for 1b-Br₂; similar chemical-shift values are observed for other complexes (12.9 ppm for 1a-Br₂, 14.2 ppm for 1a-Cl₂, 10.8 ppm for 1c-Br₂ and 11.0 ppm for 1d-Br₂). Resonances associated with the \(^{1}\)Pr groups are observed at -1.6 (CH₃) and 3.6 (CH) ppm, and N-Ar protons appear at 13.9 (meta-H, H\(^f\)) and at -4.9 (para-H, H\(^a\)) ppm. We were not able to observe imino protons in the spectrum of 1b-Br₂, or in the spectra of other complexes.

The NMR spectra of compounds 1a-1d clearly demonstrate their paramagnetic nature. We have previously reported solution magnetic moments for compounds 1a-Br₂ and 1a-Cl₂ that were measured in a coordinating solvent, CD₃CN. These magnetic moments were consistent with two unpaired electrons (\(\mu_{\text{eff}} = 3.0 \mu_B\)). In our present investigation, we have also measured solution magnetic moments of selected compounds (1a-Br₂ and 1c-Br₂) in a non-coordinating solvent CD₂Cl₂. The observed nearly identical values, 2.48 \(\mu_B\) (1a-Br₂) and 2.50 \(\mu_B\) (1c-Br₂) were
also consistent with two unpaired electrons (2.83 μB for spin-only moments), as expected for the high-spin nickel(II) complexes.

![Image of NMR spectrum](image)

**Figure 2.7.** $^1$H NMR spectrum of 1a-Br$_2$ in CD$_2$Cl$_2$.

### 2.5. Cyclic Voltammetry of Ni[NNN]X$_2$ Complexes

The cyclic voltammograms (CV) of complexes 1a-Br$_2$ - 1e-Br$_2$ are given in Figure 2.8 and Figure 2.9. Complex 1a-Br$_2$ demonstrates five reduction events (at -0.73 V, -1.26 V, -2.33 V, -2.57 V, and -2.73 V vs. FeCp$_2$/FeCp$_2$, respectively) of which the first three appear to be quasi-reversible. Complexes 1a-Cl$_2$ and 1b-Br$_2$ demonstrate similar behavior, each exhibiting five reduction events. In contrast, four reductions are observed for complex 1c-Br$_2$ and 1e-Br$_2$ and only three for 1d-Br$_2$ in the solvent-accessible range. For all complexes, the first two events take place at similar potentials, implying that the reductions are not strongly dependent on the steric or electronic nature of the N-aryl substituents. The accessibility of the first two reduction
potentials implies that bis(aldimino)pyridine nickel systems can be isolated in at least three different oxidation states. It is likely that the first two (quasi-reversible) events are bis(imino)pyridine ligand-based, at least on a CV timescale. We note that in a related study on bis(imino)pyridine complexes with main group elements (Zn and Mg), Berben and coworkers found that the first reductions took place at similar potentials, but were irreversible due to the chloride loss.\textsuperscript{18c} Intriguingly, in the present case, the first electrochemical reduction is quasi-reversible; however, chemical reduction of complexes 1a-Br\textsubscript{2} (or 1a-Cl\textsubscript{2}) and 1b-Br\textsubscript{2} leads to the isolation of mono-halide complexes (2a-X and 2b-Br, see Chapter 3). Scan rate dependent studies for 1a-Cl\textsubscript{2} and 1a-Br\textsubscript{2} show evidence of an electrochemical-chemical (EC) mechanism at slow scan rates consistent with the assignment of a ligand based reduction followed by halide dissociation. In fact, the second reduction potential follows a similar EC reactivity with ligand based reduction of 1a-Cl\textsubscript{2} and 1a-Br\textsubscript{2} ultimately resulting in halide loss and formation of the identical neutral tetra-coordinate species 2a-X (or 2b-Br) in each case.
Figure 2.8. Cyclic voltammograms of 1a-Br$_2$ – 1d-Br$_2$ recorded under 1 atm Ar at 100 mV/s at a glassy carbon electrode in a 0.1 M Bu$_4$NPF$_6$ acetonitrile supporting electrolyte.
Figure 2.9. Cyclic voltammograms of 1e-Br$_2$ recorded under 1 atm Ar at 100 mV/s at a glassy carbon electrode in a 0.1 M Bu$_4$NPF$_6$ acetonitrile supporting electrolyte.

Given the electrochemical reversibility, facile first reduction, and the mono-halide structures of the mono-reduced products (*vide infra*), we were curious to find out whether complexes 1a-Br₂ – 1e-Br₂ exist as mono-cations in solution. To test for that, we decided to abstract Cl⁻ from 1a-Cl₂ and then to analyze the products using ¹H NMR spectroscopy. Treatment of compound 1a-Cl₂ with TIPF₆ results in the precipitation of TICl and formation of a red solution, from which the cationic compound [1a-Cl](PF₆) was isolated (Figure 2.10.).

![Figure 2.10. Synthesis of [1a-Cl](PF₆).]
$^1$H NMR spectrum of compound [1a-Cl](PF$_6$) is drastically different from the spectrum of compound 1a-Cl$_2$. The spectrum of compound 1a-Cl$_2$ (Figure 2.11, top) demonstrates six resonances spread over ~70 ppm spectral window, consistent with the paramagnetic compound in solution. In contrast, $^1$H NMR spectrum of compound [1a-Cl]$^+$ contains all of the expected resonances within a 1-9 ppm spectral window, consistent with a diamagnetic compound in solution (Figure 2.11, bottom). It is likely that the diamagnetic nature of [1a-Cl](PF$_6$) results from the square-planar geometry at the Ni(II) d$^8$ center. Similar behavior was observed for the bromide complex 1a-Br$_2$: bromide abstraction with TIPF$_6$ produced a diamagnetic product [1a-Br](PF$_6$), that was characterized by $^1$H NMR spectroscopy. These experiments indicate that square-pyramidal complexes 1a-e retain their structure in solution. We note that bis(ketimino)pyridine nickel(II) methyl cations were also reported to demonstrate a diamagnetic NMR spectrum due to its square-planar geometry.$^{19}$
Figure 2.1. Top: $^1$H NMR spectrum of $1a$-$Cl_2$ in CD$_2$Cl$_2$. Bottom: $^1$H NMR spectrum of $1a$-$Cl$(PF$_6$)$_2$ in CD$_2$Cl$_2$.

2.7. Summary and Conclusions

Nickel(II) complexes, $1a$-$Br_2$ – $1e$-$Br_2$, were prepared either by the reaction of NiX$_2$•DME with the [NNN] ligand, or by addition of NiX$_2$•DME in situ to the condensation reaction of 2,6-pyridinedicarboxaldehyde with various anilines. Single-crystal X-ray structures show that $1a$-$Br_2$ – $1e$-$Br_2$ crystallize as penta- or hexa-coordinate complexes depending on the solvent used. By using coordinating solvents, such as acetonitrile, an equivalent of the solvent is shown to bind to the metal center. By using non-coordinating solvents, we observe 5-coordinate complexes with no solvent bound. $\tau_5$ for these complexes are <0.100, demonstrating a distorted square pyramidal geometry. Compounds $1a$-$Br_2$ – $1d$-$Br_2$ exhibit well resolved paramagnetic NMR
spectra with resonances spanning ~ -10 to 70 ppm. Cyclic voltammograms of 1a-Br2 - 1e-Br2 were obtained under argon. For 1a-Br2, 1a-Cl2, and 1b-Br2, we observe the presence of five reduction events, with three being quasi reversible. For 1a-Br2 – 1d-Br2, the first two reduction events appear to occur at similar potentials, implying that the reductions are not dependent on the steric and electronic nature of the ligands. Also, this allows us to conclude that at least two reduced states can be isolated. Halide abstraction forces the complex into a diamagnetic, square-planar geometry. By comparing the 1H NMR spectra of 1a-Cl2 and [1a-Cl](PF6), we were able to conclude that compounds 1a-Br2 - 1e-Br2 remain penta-coordinate in solution.

2.8. Experimental Details

**General Methods and Procedures.** All air-sensitive compounds were made in a nitrogen-filled glovebox. [NNN]a,b were synthesized as previously described.33 NiBr2-(DME), NiCl2-(DME), TIPF6, all anilines were purchased from Aldrich and used as received. 2,6-Pyridinedicarboxaldehyde was purchased from TCI Chemicals and used as received. All solvents were purchased from Fisher and were of HPLC grade. Solvents were purified using an MBRAUN purification system and stored over 3 Å molecular sieves. Compounds were characterized by 1H NMR spectroscopy, x-ray crystallography, elemental analysis, and Evans method for magnetic susceptibility. NMRs and magnetic susceptibility measurements were recorded at the Lumigen Instrument Center (Wayne State University) on a Varian 400 MHz NMR spectrometer at room temperature in C6D6 or CD2Cl2. Elemental analysis was conducted by Midwest Microlab, LLC.
**X-ray Crystallographic Details.** The structures of 1a-Br$_2$, 1a-Cl$_2$, and 1d-Br$_2$ were determined by x-ray crystallography. A Bruker APEXII/Kappa three circle goniometer platform diffractometer with an APEX-2 detector was used to mount the crystals. A graphic monochromator was employed for wavelength selection of the Mo Kα radiation (λ = 0.71073 Å). The data were processed and the structure was solved using the APEX-2 software supplied by Bruker-AXS. The structure was refined by standard difference Fourier techniques with SHELXL (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms were placed in calculated positions using a standard riding model and refined isotropically; all other atoms were refined anisotropically.

[NNN]$^3$. To a solution of 2,6-pyridinedicarboxaldehyde (500 mg, 3.70 mmol) in 5 mL of toluene, 2 drops of glacial acetic acid was added, followed by p-anisidine (911 mg, 7.40 mmol) in 3 mL of toluene. The solution immediately turned cloudy yellow. After 24 hours, the solution is filtered and washed with toluene. The solid is collected and dried, giving the product as a yellow solid (1.00 g, 2.4 mmol, 66%). $^1$H NMR (400 MHz, C$_6$D$_6$): δ 8.86 (s, 2H), 8.31 (d, $J$ = 8 Hz, 2H), 7.30 (d, $J$ = 9 Hz, 4H), 7.17 (t, $J$ = 16 Hz, 1H), 6.75 (d, 4H), 3.27 (s, 6H) ppm. Anal. Calcd for C$_{21}$H$_{19}$N$_3$O$_2$: C, 73.03; H, 5.54; N, 12.17. Found: C, 73.04; H, 5.56; N, 12.18.

1a-Cl$_2$. To a solution of nickel(II) chloride dimethoxyethane complex (48 mg, 0.22 mmol) in 3 mL THF was added a solution of [NNN]$^3$ (100 mg, 0.22 mmol) in THF (2 mL). The reaction was stirred at ambient temperature for 1.5 h. Volatiles were removed in vacuo, and the resulting brown solid was washed with ether (10 mL). The solid was dissolved in CH$_2$Cl$_2$ (2 mL), covered with ether (20 mL), and allowed to stand for 24 h at -30 °C. The solid was collected, washed with ether, and dried, giving the product as orange crystalline solid (119 mg, 0.20
mmol, 93%). $^1$H NMR (CD$_2$Cl$_2$): δ 66.4 ($\Delta \nu_{1/2} = 62$ Hz), 15.2 ($\Delta \nu_{1/2} = 18$ Hz), 14.2 ($\Delta \nu_{1/2} = 33$ Hz), 5.2 ($\Delta \nu_{1/2} = 194$ Hz), 1.7 ($\Delta \nu_{1/2} = 95$ Hz), -4.2 ($\Delta \nu_{1/2} = 24$ Hz) ppm. Anal. Calcd for C$_{31}$H$_{39}$N$_3$Cl$_2$Ni: C, 63.84; H, 6.74; N, 7.20. Found: C, 63.46; H, 6.52; N, 7.09. $\mu_{\text{eff}}$ (Evans method, CD$_3$CN, 298 K): 3.12 $\mu_B$. X-ray quality crystals were obtained by vapor diffusion of ether into a saturated THF solution of purified 1a-Cl$_2$.

1a-Br$_2$. To a solution of nickel(II) bromide dimethoxyethane complex (68 mg, 0.22 mmol) in THF (3 mL) was added a solution of [NNN]$^a$ (100 mg, 0.22 mmol) in THF (2 mL). The reaction was stirred at ambient temperature for 1.5 h. Volatiles were removed in vacuo, and the resulting brown solid was washed with ether (10 mL). The solid was dissolved in CH$_2$Cl$_2$ (2 mL), covered with ether (20 mL), and allowed to stand for 24 h at -30 °C. The solid was collected, washed with ether, and dried, giving the product as brown crystalline solid (127 mg 0.19 mmol, 86%). $^1$H NMR (CD$_2$Cl$_2$): δ 68.9 ($\Delta \nu_{1/2} = 105$ Hz), 13.9 ($\Delta \nu_{1/2} = 27$ Hz), 11.4 ($\Delta \nu_{1/2} = 43$ Hz), 3.8 ($\Delta \nu_{1/2} = 16$ Hz), 1.6 ($\Delta \nu_{1/2} = 39$ Hz), -4.9 ($\Delta \nu_{1/2} = 34$ Hz) ppm. Anal. Calcd for C$_{31}$H$_{39}$N$_3$Br$_2$Ni: C, 55.39; H, 5.85; N, 6.25. Found: C, 55.30; H, 6.16; N, 5.99. $\mu_{\text{eff}}$ (Evans method, CD$_3$CN, 298 K): 3.10 $\mu_B$. X-ray quality crystals were obtained by slow diffusion of ether into a saturated CH$_2$Cl$_2$ solution of 1a-Br$_2$.

1b-Br$_2$. To a solution of nickel(II) bromide dimethoxyethane complex (42 mg, 0.135 mmol) in 2 mL THF was added a solution of [NNN]$^b$ (50 mg, 0.135 mmol) in 1 mL THF. After 1 hour, volatiles were removed in vacuo, and the resulting brown solid was washed with 5 mL ether. The solid was dissolved in minimal amounts of THF, covered with 15 mL of ether, and allowed to stand for 24 h at -30 °C. The solid was collected, washed with ether, and dried, giving the product as a reddish-brown crystalline solid (75 mg, 0.128 mmol, 95%). $^3$H NMR (400 MHz,
CD$_2$Cl$_2$): δ 69.10 (2H, ∆ν$_{1/2}$ = 92 Hz), 16.04 (6H, ∆ν$_{1/2}$ = 12 Hz), 14.13 (4H, ∆ν$_{1/2}$ = 16 Hz), 12.52 (1H, ∆ν$_{1/2}$ = 40 Hz), 12.09 (12H, ∆ν$_{1/2}$ = 88 Hz), 1.59 (2H, ∆ν$_{1/2}$ = 20 Hz) ppm. $\mu_{\text{eff}}$ (Evans method, 400 MHz, CD$_2$Cl$_2$, 298 K): 2.48 $\mu_B$. Anal Calcd for C$_{25}$H$_{27}$Br$_2$N$_3$Ni: C, 51.07; H, 4.63; N, 7.15. Found: C, 50.69; H, 4.63; N, 6.85. ESI-MS Calcd for [C$_{25}$H$_{27}$Br$_2$N$_3$Ni]$^+$: 506.0742. Found: 506.0714.

1c-Br$_2$. To a solution of nickel(II) bromide dimethoxyethane complex (89 mg, 0.290 mmol) in 2 mL THF was added a solution of [NNN]$^-$ (100 mg, 0.290 mmol) in 1 mL THF. After 1 hour, volatiles were removed in vacuo, and the resulting brown solid was washed with 5 mL ether. The solid was dissolved in minimal amounts of THF, covered with 15 mL of ether, and allowed to stand for 24 h at -30 °C. The solid was collected, washed with ether, and dried, giving the product as a reddish-brown crystalline solid (149 mg, 0.264 mmol, 91%). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 61.93 (2H, ∆ν$_{1/2}$ = 140 Hz), 10.77 (1H, ∆ν$_{1/2}$ = 36 Hz), -6.75 6H, ∆ν$_{1/2}$ = 8 Hz), -7.00 (4H, ∆ν$_{1/2}$ = 16 Hz), -10.13 (2H, ∆ν$_{1/2}$ = 8 Hz), -10.50 (4H, ∆ν$_{1/2}$ = 24 Hz) ppm. $\mu_{\text{eff}}$ (Evans method, 400 MHz, CD$_2$Cl$_2$, 298 K): 2.50 $\mu_B$. Anal Calcd for C$_{21}$H$_{19}$Br$_2$N$_3$NiO$_2$•CH$_3$CN: C, 45.66; H, 3.67; N, 9.26; Found: C, 45.19; H, 3.52; N, 9.10. ESI-MS Calcd for [C$_{27}$H$_{19}$N$_3$NiO$_2$•3CH$_3$CN]$^{2+}$: 263.0814. Found: 263.0454.

1d-Br$_2$. To a solution of 2,6-pyridinedicarboxaldehyde (50 mg, 0.370 mmol) in 5 mL of THF, 2 drops of glacial acetic acid was added, followed by 4-trifluoromethylaniline (0.093 mL, 0.740 mmol). After the reaction was stirred for 1 h, nickel(II) bromide dimethoxyethane complex (114 mg, 0.370 mmol) in 2 mL THF was added. The reaction was stirred at room temperature. After 24 h, volatiles were removed in vacuo, and the resulting reddish brown solid was washed with 5 mL ether. The solid was dissolved in minimal amounts of CH$_3$CN, covered with 15 mL of ether, and allowed to stand for 24 h at -10 °C. The solid was collected, washed
with ether, and dried, giving the product as a reddish-brown crystalline solid (227 mg, 0.355 mmol, 96%). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 60.67 (2H, $\Delta v_{1/2} = 136$ Hz), 10.96 (1H, $\Delta v_{1/2} = 40$ Hz), -6.76 (2H, $\Delta v_{1/2} = 20$ Hz), -10.20 (4H, $\Delta v_{1/2} = 92$ Hz) ppm. $^{19}$F NMR (400 MHz, CD$_2$Cl$_2$): δ -50.53 ppm. Anal Calcd for C$_{21}$H$_{13}$Br$_2$F$_6$N$_3$Ni•3H$_2$O: C, 36.35; H, 2.76; N, 6.06. Found: C, 35.95; H, 2.27; N, 5.90. ESI-MS Calcd for [C$_{21}$H$_{13}$F$_6$N$_3$Ni•3CH$_3$CN]$^{2+}$: 301.0582. Found: 301.0779. X-ray quality crystals were obtained by vapor diffusion of ether into a saturated ACN solution of purified 1d.

1e-Br$_2$. To a solution of 2,6-pyrindinedicarboxaldehyde (50 mg, 0.370 mmol) in 5 mL of THF, 2 drops of glacial acetic acid was added, followed by 3,5-bis(trifluoromethyl)aniline (0.066 mL, 0.740 mmol). After the reaction was stirred for 1 h, nickel(II) bromide dimethoxyethane complex (114 mg, 0.370 mmol) in 2 mL THF was added. The reaction was stirred at room temperature. After 24 h, volatiles were removed in vacuo, and the resulting reddish brown solid was washed with 5 mL ether. The solid was dissolved in minimal amounts of CH$_3$CN, covered with 15 mL of ether, and allowed to stand for 24 h at -10 °C. The solid was collected, washed with ether, and dried, giving the product as a reddish-brown crystalline solid (215 mg, 0.277 mmol, 75%). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 71.80 (2H, $\Delta v_{1/2} = 132$ Hz), 23.07 (1H, $\Delta v_{1/2} = 52$ Hz), 7.02 (2H, $\Delta v_{1/2} = 36$ Hz), 3.69 (2H, $\Delta v_{1/2} = 80$ Hz), 1.94 (4H, $\Delta v_{1/2} = 104$ Hz) ppm. $^{19}$F NMR (400 MHz, CD$_2$Cl$_2$): δ -63.64, -65.19 ppm. Anal Calcd for C$_{23}$H$_{11}$Br$_2$F$_{12}$N$_3$Ni: C, 35.61; H, 1.43; N, 5.42. Found: C, 34.91; H, 1.64; N, 5.16. ESI-MS Calcd for [C$_{23}$H$_{11}$F$_{12}$N$_3$Ni•3CH$_3$CN]$^{2+}$: 369.0456. Found: 369.0189.

[1a-Cl](PF$_6$). To a suspension of thallium hexafluorophosphate, TlPF$_6$, (18 mg, 0.051 mmol) in DCM (1 mL), an orange solution of Ni[NNN]Cl$_2$ (30 mg, 0.051 mmol) in DCM (2 mL) is added. The reaction color turned red. The reaction mixture was stirred at ambient temperature
for 1 h, filtered, and the solvent was evaporated. The resulting orange solid was dissolved in DCM (ca. 2 mL) covered in hexanes (ca. 10 mL). The solvent was decanted and the solid was dried to give the product in 74% yield (26 mg, 0.038 mmol). Anal. Calcd for C31H39ClF6N3NiP: C, 53.75; H, 5.67; N, 6.07. Found: C, 53.13; H, 5.40; N, 5.95. 1H NMR (400 MHz, DCM-d2): δ 8.56 (1H), 8.37 (2H), 8.01 (1H), 7.34 (2H), 3.44 (m, 4H), 1.43 (d, J = 5 Hz 12H), 1.25 (d, J = 5 Hz 12H). 19F NMR (400 MHz, DCM-d2): δ -71.27, -73.17.
CHAPTER 3: SYNTHESIS AND CHARACTERIZATION OF ONE-ELECTRON REDUCED (Ni[NNN])$^{1+}$ COMPLEXES AND THEIR REACTIVITY

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3.1. Introduction

Previous studies have shown the ability of nickel(I) to activate and reduce heteroallenes. Specifically, Dahl and coworkers used a nickel(I) complex to reductively couple CS$_2$ to give tetrathiooxalate (Figure 1.4). However, the reduction of nickel(II) to nickel(I) generally requires relatively negative potentials making it thus a less viable candidate for a catalytic metal in heteroallene reduction. We postulated that the reduction of the overall redox-active ligand/metal ensemble (Ni[NNN])$^{2+}$ to the (Ni[NNN])$^{1+}$ state may require significantly less negative potential while providing a sufficient nickel(I) character on the metal.

Survey of the existing bis(imino)pyridine literature reveals that the large majority of the previously investigated bis(imino)pyridine nickel complexes encompass ketimine sidearms. Several groups have recently reported that reduction of bis(ketimino)pyridine-ligated nickel(II) dihalides invariably forms square-planar nickel(II) products and a ligand based radical anion. Figure 3.1 shows three such complexes: bis(ketimino)pyridine nickel chloride, reported by Rohde and coworkers, and bis(ketimino)pyridine nickel methyl and dinitrogen complexes, reported by Gambarotta and coworkers. This assignment for the Ni[NNN]$_{\text{iPr}}$Cl system reported by Rohde and coworkers was made based on (1) EPR spectrometry (g value of 2.016, consistent with a ligand-based radical anion); and (2) square planar geometry consistent with nickel(II). According to Gambarotta and coworkers, Ni[NNN]$_{\text{iPr}}$Me displays ligand bond lengths consistent with a singly reduced ligand with nickel(II). Similarly, Ni[NNN]$_{\text{iPr}}$ (N$_2$) was assigned as nickel(II)
with a doubly reduced ligand based on bond lengths and the square planar geometry. In contrast, the chemistry of bis(aldimino)pyridines has received considerably less attention. In light of the recent report indicating that bis(aldimino)pyridines may demonstrate a significantly different chemistry from bis(ketimino)pyridines, we decided to interrogate the one-electron reduction of our Ni([NNN])\textsuperscript{2+} complexes, hoping that the use of bis(aldimino)pyridine ligands may lead to a different electronic structure and different reactivity at the metal center.

![Figure 3.1. Previously reported square planar nickel complexes of the related bis(ketimino)pyridine ligand. Ar = 2,6-diisopropylphenyl.](image)

### 3.2. Design and Synthesis of Ni[NNN]X Complexes

Our CV studies (Figure 2.8) on (Ni[NNN])\textsuperscript{2+} complexes demonstrated that the first, quasi-reversible, electrochemical reduction takes place around -0.7 – -0.8 V. To achieve chemical reduction, we treated complexes (Ni[NNN])\textsuperscript{2+} with a strong and soluble one-electron reductant CoCp\textsuperscript{*2} (reduction potential of -2.0 V). Addition of one equivalent of CoCp\textsuperscript{*2} to 1a-Br\textsubscript{2} and 1a-Cl\textsubscript{2} at room temperature resulted in an immediate color change from deep orange to a dark purple solution. Purple crystals of 2a-Br and 2a-Cl were obtained from THF/ether in yields described in Figure 3.2. The complexes were characterized by single-crystal X-ray diffractometry, UV-visible spectroscopy, solution magnetometry, elemental analysis, and EPR spectroscopy (only 2a-Br).
Figure 3.2. Synthesis of 2a-b.

The structures of complexes 2a-Br and 2a-Cl are given in Figures 3.3 and 3.4, respectively. Most significantly, and in a sharp contrast to the previously reported nickel chloride and methyl complexes of bis(ketimino)pyridine ligands (Figure 3.1), 2a-Br and 2a-Cl manifest non-planar structures. Interestingly, 2a-Br crystallizes as two different solvates from the same solvent mixture (THF/ether), named 2a-Br-I and 2a-Br-II, with both having P-1 symmetry but featuring different unit cell parameters and different solvent content of the unit cell (Ni[NNN]Br₂THF and Ni[NNN]Br·THF·OEt₂) (Figure 3.3). Overall, these two polymorphs demonstrate similar structural parameters with the major difference being the N<sub>py</sub>-Ni-Br angle (Figure 3.5). For both, the geometry of the Ni site is non-planar. Nickel centers are removed 0.29 and 0.32 Å from the [NNN] plane, and the N<sub>py</sub>-Ni-Br angles are 161.4(1) and 156.5(1)°. 2a-Cl co-crystallizes with two THF molecules in the unit cell and has P-1 symmetry. The nickel center is removed 0.37 Å from the [NNN] plane and the N<sub>py</sub>-Ni-Cl angle is 162.3(1)° (Figure 3.4). In comparison, the structure of bis(ketimino)pyridine variant Ni[NNN]Cl demonstrated N<sub>py</sub>-Ni-Cl angle of 179°. Another interesting structural difference is the torsion C<sup>α</sup>-N-C<sup>β</sup>-C<sup>γ</sup> angle (Figure 3.5). For the bis(ketiminopyridine), Ni[NNN]Cl, we observe torsion angles of 88.26° and 84.25°, indicating almost perpendicular phenyl rings relative to the ligand backbone. For the
bis(aldimino)pyridine complexes, $2a$-$Br$ and $2a$-$Cl$, we observe more torsion of the nitrogen R-groups. The torsion angles found are 81.93° and 59.31°, 82.61° and 59.96°, and 81.92° and 60.39° for $2a$-$Br$-$I$, $2a$-$Br$-$II$, and $2a$-$Cl$ respectively. We observe a correlation that the $C^\alpha$-$N$-$C^\beta$-$C^\gamma$ torsion angle decreases as the $N_{py}$-$Ni$-$X$ angle decreases.

**Figure 3.3.** Crystal structures of the two polymorphs of $2a$-$Br$. 50% probability ellipsoids. H atoms and solvent molecules are omitted for clarity.

**Figure 3.4.** Crystal structure of $2a$-$Cl$. 50% probability ellipsoids. H atoms and solvent molecules are omitted for clarity.
We were curious to determine whether this effect was limited to a relatively bulky N-aryl group, 2,6-diisopropylphenyl. Thus, we investigated the one-electron reduction of other (Ni[NNN])$^{2+}$ complexes, 1b-Br$_2$, 1c-Br$_2$, and 1e-Br$_2$. The one-electron reduction of 1b-Br$_2$ formed a purple solution. Recrystallization of the crude product from cold ether led to the isolation of brown 2b-Br in 60% yield (Figure 3.2). Reduction of 1c-Br$_2$ and 1e-Br$_2$ led to a paramagnetic brown solid that did not produce X-ray quality crystals, thus, these products were not characterized further.

Complex 2b-Br was characterized by solution magnetometry, elemental analysis and X-ray crystallography. Measured magnetic moment of 2b-Br was 1.71 $\mu_B$, consistent with one unpaired electron. The crystal structure of 2b-Br (obtained from cold ether) demonstrates three different isomers differing primarily by the N$_{py}$-Ni-Br angle. These findings agree with our previous observation of two different structural isomers (differing by N$_{py}$-Ni-Br angle) in the crystal structure of 2b-Br. In the structure of 2b-Br, the N$_{py}$-Ni-Br angles range from the nearly linear 178.2(1) to the distorted 170.4(1)° and 165.4(1)° (Figure 3.5). Significantly, these values correlate well with the deviation of the N-aryl substituent from its perpendicular (to the NNN plane) arrangement (measured by the C$^\alpha$-N-C$^\beta$-C$^\gamma$ torsion angle, Figure 3.6). Thus, for the nearly

![Figure 3.5. Depiction of the N$_{py}$-Ni-Br and torsion C$^\alpha$-N-C$^\beta$-C$^\gamma$ angles](image)
linear $N_{py}$-Ni-Br angle of 178.2(1)$^\circ$, nearly perpendicular torsion angles of 87.1$^\circ$ and 87.7$^\circ$ are observed (isomer 2b·Br-I); for the slightly distorted angle of 170.4(1), the N-mesityl group slightly bends from the perfectly perpendicular arrangement (72.4$^\circ$ and 73.8$^\circ$, isomer 2b·Br-II); and finally for the $N_{py}$-Ni3-Br3 angle of 165.4(1)$^\circ$, further distortion from the perpendicular values found, as manifested by the values of 64.1$^\circ$ and 70.5$^\circ$ (2b·Br-III). This further strengthens our argument of the torsion angle decreasing as the $N_{py}$-Ni-X angle decreases.
Figure 3.6. Crystal structures of the three isomers observed in the asymmetric unit of 2b-Br. 40% probability ellipsoids. H-atoms and solvent molecules are omitted for clarity.
Table 3.1. Experimental Crystallographic parameters for 2a-Br-I, 2a-Br-II, 2a-Cl, and 2b.

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<th>2a-Cl</th>
<th>2b-Br</th>
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3.3. Electron Paramagnetic Resonance Data for Ni[NNN]X Complexes

X-ray structures of complexes 2a-X and 2b-Br demonstrated non-planar geometry at nickel. These findings may indicate that the complexes demonstrate significant “metalloradical”, or nickel(I) character, in contrast to the square-planar nickel(II) in bis(ketimino)pyridines. To gain further evidence for the presence of the spin density on the metal, we pursued EPR spectroscopy on a representative complex 2a-Br, in collaboration with Dr. Sebastian Stoian at the National High Magnetic Field Laboratory. An obtained high-frequency (406.4 GHz) EPR spectrum for 2a-Br is shown in Figure 3.7. This spectrum of complex 2a-Br shows two nearly identical S = 1/2 species which we attribute to the two different isomers observed in the crystal structure. The dominant species demonstrate g values of 2.236, 2.144, and 2.048, which are considerably larger than the g value of 2.00 generally expected for an organic radical. In comparison, Rohde’s square planar bis(ketimino)pyridine complex demonstrates a single g value of 2.016. The g values for the minor isomer are even further away from the organic radical values (Figure 3.7). Thus, our EPR data demonstrates that a sizeable amount of unpaired spin is localized on the metal ion. Two situations can describe this experimental data. One possibility is a nickel(I) center with a d⁹ configuration. The other possibility is a high-spin nickel(II) center that is anti-ferromagnetically coupled to a ligand radical. Although EPR alone cannot distinguish between these two possibilities, the g values fall within the range detected for other genuine nickel(I) complexes.
Figure 3.7. High-frequency EPR spectrum recorded for a ground solid sample of 2a-Br at 10 K and 406.4 GHz. The spectrum exhibits two nearly identical $S = 1/2$ species. The resonances of the major component are found at $g = 2.236(5), 2.144(4), \text{ and } 2.048(6)$. The minor component resonances are labeled by (*) and are found at $g = 2.263(3), 2.140(3), \text{ and } 2.071(2)$. The inset shows the field vs. frequency dependence of the resonances of the major component.

3.4. DFT Calculations of Ni[NNN]X Complexes

To further interpret the electronic structure of our complex, we turned to DFT studies.\textsuperscript{36} In collaboration with Professor Richard Lord at Grand Valley State University, we were able to determine that the $S = 1/2$ state is favored by 11.4 kcal/mol over the $S = 3/2$ state. Geometry optimization measurements show a convergence to a slightly non-planar structure with a $N_{py}$-Ni-X angle of ~177°. These optimized structures show a geometry that is quite different from what is observed in the crystal structures. Also, these optimized structures can be best described as low-spin, nickel(II) with a radical located on the ligand, consistent with the Rohde’s
structure, but inconsistent with our observed structures. To elucidate the discrepancies between our EPR/XRD data and DFT data, we performed constrained optimizations where, starting from the optimized geometry, we varied the N_{py}-Ni-X angle in increments down to a minimum angle of 140° (Tables 3.2 and 3.3). The first significant discovery with this experiment is that the energy requirement for this transformation is a mere 7 kcal/mol. Important structural changes that are observed include lengthening of the C_{py}-C_{im} bonds and shortening of the C_{im}-N_{im} bonds, as anticipated in the reduction of bis(imino)pyridine. Also, the dihedral angle corresponding to the deviation of the aryl groups from perpendicular decreases to ~65°. Spin densities of the nickel and ligand change dramatically, with an increase on nickel from 0.06 to 0.36 and a decrease on the ligand from 0.96 to 0.79. These results suggest that relatively weak (i.e. crystal lattice) interactions may influence the non-planarity of our complexes.

We believe that the structural differences in bis(ketimino)pyridine nickel(I) complexes versus bis(aldimino)pyridine nickel(I) complexes are due to the existence of a less bulky, imino-substituent, proton. Because of less significant steric bulk, it allows the phenyl ring attached to the imino-nitrogen to rotate away from the perpendicular position (Figure 3.5). This, in turn, pushes the halide out of the NNN plane which puts spin density on the nickel, due to the changes in overall electronic structure. Our DFT calculations demonstrate that the energy requirement for this to happen is not significant.
Table 3.2 Results of constrained optimizations of 2a-Br

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<th>160°</th>
<th>150°</th>
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<tr>
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Table 3.3 Results of constrained optimizations of 2a-Cl

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3.5. Reactivity of Ni[NNN]X Complexes

We have also investigated the reactivity of the (Ni[NNN])<sup>1+</sup> complexes as exemplified by 2a-Br. The reactivity of the bis(imino)pyridine nickel complexes with O<sub>2</sub> lends further credence to the different electronic structures of bis(ketimino)pyridine nickel complex vs. the bis(aldimino)pyridine nickel complex (Figure 3.8). Rohde and coworkers reported that the reaction with O<sub>2</sub> led to ligand modification (oxidation, Figure 3.8 top). This was expected as their complex displays a ligand-based radical; the reaction therefore is initiated via coupling of the ligand-based radical with dioxygen. In contrast, upon reaction of the bis(aldimino)pyridine nickel complex with O<sub>2</sub>, no ligand modification was observed. Instead, we see presence of 1a-
Br$_2$ as well as the free ligand, [NNN]$^\circ$ (by proton NMR spectroscopy), with is consistent with metal oxidation and further disproportionation. Thus, in our case, metal-based reactivity is observed. We also obtained an insoluble white material, possibly nickel oxide. No oxidized ligand was detected by NMR or mass spectrometry.

![Reaction diagram]

Figure 3.8. Reaction of the bis(ketimino)pyridine and bis(aldimino)pyridine Ni[NNN]X complexes with O$_2$.

Next, we investigated the reactivity of 2a-Br with heteroallenes. When treated with CS$_2$, a purple solution of complex 2a-Br undergoes color change to brown. Crystallization of the reaction products from hexanes affords bright-yellow crystals of [NNN]$^\circ$. Our repeated attempts to determine the nature of the metallated products were not successful. Based on the related iminopyridine chemistry, we propose that we form some sort of nickel-CS$_2$ complexes, that lose bis(imino)pyridine ligand. No reaction with CO$_2$ was observed, both with 1 equiv. of CO$_2$ or under 1 atm of CO$_2$.

To further probe the “metalloradical” character of the nickel center in 2a-Br, we have also studied its reactivity with phenyl disulfide, PhSSPh. Phenyl disulfide serves as a precursor to a PhS$^\bullet$ species, that are expected to couple with the metalloradical. The reaction of 2a-Br
with PhSSPh leads to the formation of \((\text{Ni(SPh)}_2)_\text{11}\), along with [NNN]³ (Figure 3.9). \((\text{Ni(SPh)}_2)_\text{11}\) is a ring compound featuring eleven nickel(II) centers bridged by thiophenolates; each nickel center is square-planar. While the formation and structure of \((\text{Ni(SPh)}_2)_\text{11}\) was previously reported,³⁷ it was synthesized via a salt metathesis reaction of \(\text{NiCl}_2\) with \(\text{NaSPh}\), while in the present case it is obtained via a one-electron oxidation with “PhS•”. In summary, we clearly demonstrate expected metal-based metalloradical reactivity. However, most of the observed reactions of 2a-Br eventually result in demetallation of Ni[NNN]Br to afford a free ligand along with various Ni(II) salts.

![Figure 3.9](image)

**Figure 3.9.** Reaction of 2a-Br with phenyldisulfide yields the formation of a metallocycle containing 11 nickel atoms, each bridged by two phenylsulfides.
3.6. Summary and Conclusions

(Ni[NNN])\(^{1+}\) complexes 2a-b were synthesized by the reduction of 1a-b using either CoCp\(^{+}\)_2 or KC\(_8\). Single crystal x-ray structures of 2a-Br and 2b-Br show that multiple polymorphs of the complexes are present in solid state, with varying N\(_{py}\)-Ni-X bond angles. EPR of 2a-Br confirms this, showing two sets of EPR resonances, as well as showing that spin density is located on the nickel center, as evidenced by g-values significantly higher than 2.00. DFT calculations were utilized to determine constrained optimizations of 2a-Br and 2a-Cl. This data shows that although the minimized structure has a N\(_{py}\)-Ni-X angle of close to 180\(^\circ\), the energy penalty for decreasing this angle is very small. This finding agrees with the “shallow potential”
proposed by the existence of multiple N\textsubscript{py}-Ni-X isomers existing in the solid state. Thus, our conclusion is that the differences in electronic structures of the bis(aldimino)pyridine and bis(ketimino)pyridine complexes are due to the steric effect of the hydrogen vs. methyl substituents on the imine. The imino-methyl constrains the dihedral angle of the aryl group, whereas the imino hydrogens enable rotation of the N-aryl group thus causing the halide to distort out of the N-N-N plane. 2a-Br reacts with O\textsubscript{2}, showing oxidation at the metal, and formation of 1a-Br\textsubscript{2} and [NNN]\textsuperscript{a}. Similarly, attempts at reacting 2a-Br with phenyldisulfide and CS\textsubscript{2} leads to the formation of nickel(II) as well as demetallation to form [NNN]\textsuperscript{a}. Overall, our reactivity studies agree with a significant metalloradical, or nickel(I), character. However, the lability of the [NNN] ligand at (Ni[NNN])\textsuperscript{1+}, while also consistent with the metal-based reactivity (the ligand is fully oxidized and therefore binds weaker), nevertheless constitutes an “Achilles heel” of our system. We observe no reactivity with CO\textsubscript{2}. Because of the lack of reactivity with CO\textsubscript{2}, and the [NNN] ligand lability in CS\textsubscript{2} chemistry, we moved next toward more reduced (Ni[NNN])\textsuperscript{0} complexes.

3.7. Experimental Details

General Methods and Procedures. All air sensitive compounds were made in a nitrogen-filled glovebox. CoCp\textsuperscript{*2} and KC\textsubscript{8} were purchased from Aldrich and used as received. All solvents were purchased from Fisher Scientific and are of HPLC grade. Solvents were purified using an MBRAUN purification system and stored over 3 Å molecular sieves. Compounds were characterized by x-ray crystallography, elemental analysis, UV-visible spectroscopy, and Evans method for magnetic susceptibility. Elemental analysis was conducted by Midwest Microlab, LLC. UV-visible spectra were recorded on a Shimadzu UV-1800 spectrometer. Magnetic
susceptibility measurements were recorded at the Lumigen Instrument Center (Wayne State University) on a Varian 400 MHz NMR spectrometer at room temperature in C₆D₆.

**X-ray Crystallographic Details.** The structures of 2a-Br, 2a-Cl, and 2b-Br were determined by x-ray crystallography. A Bruker APEXII/Kappa three circle goniometer platform diffractometer with an APEX-2 detector was used to mount the crystals. A graphic monochromator was employed for wavelength selection of the Mo Kα radiation (λ = 0.71073 Å). The data were processed and the structure was solved using the APEX-2 software supplied by Bruker-AXS. The structure was refined by standard difference Fourier techniques with SHELXL (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms were placed in calculated positions using a standard riding model and refined isotropically; all other atoms were refined anisotropically.

**2a-Br.** To the orange solution of compound 1a-Br₂ (100 mg, 0.15 mmol) in THF (3 mL) was added a solution of CoCp*₂ (49 mg, 0.15 mmol) in THF (3 mL). The reaction color turned dark purple. The reaction mixture was stirred at ambient temperature for 2 h, filtered, and evaporated. The resulting purple-black solid was washed with hexanes and ether, and dissolved in THF (ca. 1 mL). Vapor diffusion of ether into the THF solution at −30 °C led to the formation of dark purple crystals. The crystals were dried under vacuum for several hours to give compound 2a-Br in 47% yield (42 mg, 0.07 mmol). Compound 2a-Br is air- and moisture-sensitive. Anal. Calcd for C₃₁H₃₉N₃BrNi: C, 62.87; H, 6.64; N, 7.09. Found: C, 63.21; H, 6.61; N, 7.30. \( \mu_{\text{eff}} \) (Evans method, C₆D₆, 298 K): 1.35 \( \mu_B \). Absorption Spectrum (toluene): \( \lambda_{\text{max}} \) (\( \epsilon_M \)) 331 (7979) 534 (1369) 699 (759) 933 (835) nm. X-ray quality crystals for the x-ray data collection were obtained by vapor diffusion of ether into a saturated THF solution of purified 2a-Br.
2a-Cl. To the orange solution of compound 1a-Cl₂ (100 mg, 0.17 mmol) in THF (3 mL) was added a solution of CoCp*₂ (56 mg, 0.17 mmol) in THF (3 mL). The reaction color turned dark purple. The reaction mixture was stirred at ambient temperature for 2 h, filtered, and evaporated. The resulting black solid was washed with hexanes and ether, and dissolved in THF (ca. 1 mL). Diffusion of ether into the THF solution at −30 °C led to the formation of black crystals. The crystals were dried under vacuum for several hours to give compound 2a-Cl in 37% yield (35 mg, 0.06 mmol). Compound 2a-Cl is air- and moisture-sensitive. Anal. Calcd for C₃₁H₃₉N₃ClNi: C, 67.97; H, 7.18; N, 7.67. Found: C, 67.68; H, 7.05; N, 7.20. \( \mu_{\text{eff}} \) (Evans method, C₆D₆, 298 K): 1.09 \( \mu_B \). Absorption Spectrum (toluene): \( \lambda_{\text{max}} \ (\varepsilon_M) \) 331 (13429) 465 (2413) 532 (1750) 694 (940) 910 (1028) nm. X-ray quality crystals for the X-ray data collection were obtained by vapor diffusion of ether into a saturated THF solution of purified 2a-Cl.

2b-Br. To an orange solution of 1b-Br₂ (142 mg, 0.241 mmol) in THF (3 mL) a suspension of KC₈ was added (33 mg, 0.241 mmol) in THF (1 mL). The reaction color turned dark purple. The reaction mixture was stirred at ambient temperature for 1 h, filtered, and evaporated. The resulting brown solid was washed with hexanes and ether, and dissolved in THF (ca. 1 mL). The solution was covered with 15 mL of hexanes, and allowed to stand for 24 h at -30°C. The solid was collected, washed with hexanes, and dried, giving the product as a brown crystalline solid (73 mg, 0.143 mmol, 60%). 2b-Br is air- and moisture-sensitive. \( \mu_{\text{eff}} \) (Evans, 400 MHz, C₆D₆, 298K): 1.71 \( \mu_B \). Absorption Spectrum (THF): \( \lambda_{\text{max}} \ (\varepsilon_M) \) 335 (9434) 531 (1935) 703 (1013) 939 (1059) nm. X-ray quality crystals for the X-ray data collection were obtained by vapor diffusion of ether into a saturated THF solution.
CHAPTER 4: SYNTHESIS AND CHARACTERIZATION OF TWO-ELECTRON REDUCED COMPLEXES AND THEIR REACTIVITY

4.1. Introduction

As described in the previous chapter, albeit our “nickel(I)” complexes \((\text{Ni[NNN]})^{1+}\) demonstrated the desired metalloradical character, no reactivity with \(\text{CO}_2\) was observed. Furthermore, the tridentate ligand demonstrated unexpected lability at the \((\text{Ni[NNN]})^{1+}\) state. Thus, we turned to investigate the two-electron reduced state of the \(\text{Ni[NNN]}_2\) precursors. This chapter focuses on our research involving synthesis and reactivity of \((\text{Ni[NNN]})^0\) complexes, featuring formally nickel(0) centers. We anticipated that these complexes will engage in reactivity with heteroallenes, as numerous examples of the reactions between formally nickel(0) precursors and \(\text{CO}_2/\text{CS}_2\) have been previously reported, including by our own group.\(^{20,21}\) Selected examples of the reactivity are presented in Figure 1.6, Figure 1.8, and Figure 1.9. Hillhouse and coworkers demonstrate that nickel(0) of a chelating diphosphine ligand binds \(\text{CS}_2\) or \(\text{CO}_2\) “side-on”, \(\eta^2\).\(^{12}\) Similarly, our group demonstrated that an iminopyridine-nickel(0) complex binds \(\text{CS}_2\) in a similar fashion (Figure 1.9). In both cases, the \(\eta^2\)-bound heteroallene is rendered somewhat unreactive toward further reduction. In contrast, Sadighi and coworkers demonstrates that the reaction of a Ni(0)-carbene precursor with \(\text{CO}_2\) leads to its reductive splitting to form a bridging carbon monoxide between two nickel centers.\(^9\)

To access the desired \((\text{Ni[NNN]})^0\) complexes, two different synthetic routes were undertaken. The first route involved the direct reaction of a ligand precursor [NNN] with a nickel(0) precursor. In the second route, formally nickel(0) complexes were accessed via a one-electron reduction of \((\text{Ni[NNN]})^{1+}\) complexes. Intriguingly, in selected cases, the two routes led
to different products. Synthesis, structures, and spectroscopic features of (Ni[NNN])\(^0\) will be described, followed by the discussion of their reactivity with heteroallenes.

### 4.2. Synthesis of (Ni[NNN])\(^0\) Complexes Using Ni(COD)\(_2\)

We and others have previously shown that commercially available bis(1,5-cyclooctadiene)nickel(0), Ni(COD)\(_2\), provides the precursor of choice to the entry into the chemistry of formally nickel(0).\(^{20,21}\) Therefore, our initial attempts to access these species relied on the use of Ni(COD)\(_2\). Treatment of Ni(COD)\(_2\) with one equivalent of [NNN]\(^a\) at room temperature results in the formation of the mixture of Ni[NNN]\(^a\) (COD) (3a-COD) and Ni([NNN]\(^a\))\(_2\) (3a), according to \(^1\)H NMR spectroscopy (Figure 4.1). Running the reaction at -30 °C led to the similar mixture of products. Extraction and recrystallization of this mixture from hexane leads reproducibly to a mixture of crystals of 3a-COD and 3a. Both types of crystals are black and feature similar morphology, making their separation challenging. \(^1\)H NMR spectrum of the mixture demonstrates approximately 60% of 3a-COD to 40% of 3a. Treatment of Ni(COD)\(_2\) with two equivalents of [NNN]\(^a\) leads to the formation of Ni([NNN]\(^a\))\(_2\) (3a) isolated in 30% yield by recrystallization from hexanes. EA of Ni([NNN]\(^a\))\(_2\) indicates pure 3a, however, the NMR spectrum of crystallized 3a contains peaks consistent with a small amount of the free ligand, [NNN]\(^a\) (<10%). We postulate that 3a undergoes partial decomposition in solution to give free ligand and 4a (see below).
Figure 4.1. Reaction of [NNN]$^a$ with Ni(COD)$_2$

X-ray crystal structures for 3a-COD and 3a (Figures 4.2 and 4.3) demonstrate tetra-coordinate nickel centers. In both complexes, the potentially tridentate [NNN]$^a$ ligand is bound to Ni via only one iminopyridine unit; the second imine is unbound. The bidentate coordination mode of [NNN]$^a$ is reminiscent of the coordination mode of the bidentate iminopyridine ligands in the reduced Ni[NN] complexes.

Figure 4.2. Crystal structure of complex 3a-COD. 50% probability ellipsoids. H-atoms and co-crystallized solvent molecules omitted for clarity.
Figure 4.3. Crystal structure of 3a. 50% probability ellipsoids. H-atoms and co-crystallized solvent omitted for clarity.

The experimental data above indicates that the tridentate coordination of [NNN]$^a$ is not observed at the Ni(0) state. To determine whether it is the steric effect (of bulky 2,6-diisopropylphenyl groups) that is responsible for the bidentate ligation of [NNN]$^b$, we evaluated the reactivity of [NNN]$^b$ with Ni(COD)$_2$. Treatment of Ni(COD)$_2$ with [NNN]$^b$ (1 equiv.) leads to the formation of 0.5 equiv. of Ni([NNN]$^b$)$_2$ (3b) along with unreacted Ni(COD)$_2$, observed by $^1$H NMR spectroscopy (Figure 4.4). Pure 3b can be obtained by treating Ni(COD)$_2$ with two equivalents of [NNN]$^b$, followed by recrystallization from hexane (95% yield). Both the solid-state (Figure 4.5) and the solution structure of 3b are consistent with the bidentate coordination of bis(imino)pyridine. We conclude that the bidentate coordination of [NNN] to the reduced nickel does not depend on the sterics of the ligand, but is likely determined by the
favorable electronic structure of \((\text{Ni}[\text{NN}]_2)\) fragment, that allows for the delocalization of the reducing equivalents into both iminopyridines.

\[
\begin{array}{cccc}
\text{Mes} & \text{N} & \text{N} & \text{Mes} \\
\text{N} & \text{N} & \text{Mes} \\
\end{array} + \text{Ni(COD)}_2 \rightarrow \frac{1}{2} \begin{array}{c}
\text{Mes} \\
\text{N} \\
\text{N} \\
\text{Mes} \\
\end{array} + \frac{1}{2} \text{Ni(COD)}_2
\]

Mes = 2,4,6-trimethylphenyl
COD = 1,5-cyclooctadiene

**Figure 4.4.** Reactivity of \([\text{NNN}]^b\) with Ni(COD)$_2$

**Figure 4.5.** Crystal structure of 3b, 50% percent probability ellipsoids. H-atoms omitted for clarity.
**Table 4.1.** Experimental crystallographic parameters for 3a, 3a-COD, and 3b.

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Close examination of the structures of 3a, 3a-COD, and 3b demonstrates that there is a significant difference in the corresponding C-C and C=N bond distances between bound and unbound iminopyridines, signifying a mono-reduced state of nickel-bound iminopyridines, vs. neutral unbound iminopyridines. Table 4.2 lists the respective bond lengths of nickel(0) complexes, 3a, 3a-COD, and 3b, compared to the nickel(II) complex, 1a-Br₂. 1a-Br₂ shows typical C=N and C-C bond lengths corresponding to a neutral ligand:¹⁹ C=N imino bonds are 1.274(3) and 1.271(3) Å, and the C_{imino}-C_{pyridine} bonds are 1.475(3) and 1.473(3) Å. The unbound imine arm of the (Ni[NNN])⁰ complexes shows bond lengths comparable to bond lengths of a neutral ligand. For instance, C=N_{imino} distances of 1.270(4) and 1.279(4) Å and C_{imino}-C_{pyridine} distances of 1.468(5) and 1.460(4) Å (C-C) are observed for the free imino arms of 3b and 3a-COD, respectively. In contrast, the bound imine shows significantly lengthened C=N bonds and shortened C-C bonds. Thus, C=N_{imino} bond distances of 1.332(4) and 1.316(4) Å and C_{imino}-C_{pyridine} bond distances of 1.415(5) and 1.415(4) Å (C-C) are observed for the coordinated imino-arms of 3b and 3a-COD, respectively. This finding is consistent with the partial reduction of the iminopyridine as explained in Figure 1.7 in the Introduction.
Table 4.2. Selected bond lengths for 1a-Br₂, 3a, 3a-COD, and 3b.

<table>
<thead>
<tr>
<th></th>
<th>C=N \text{im}^a</th>
<th>C-C\text{a}</th>
<th>C=N_p\text{y}^a</th>
<th>C=N_p\text{y}^b</th>
<th>C-C^b</th>
<th>C=N_{im}^b</th>
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</thead>
<tbody>
<tr>
<td>1a-Br₂</td>
<td>1.274(3)\text{c}</td>
<td>1.475(3)\text{c}</td>
<td>1.335(3)\text{c}</td>
<td>1.335(3)\text{c}</td>
<td>1.473(3)\text{c}</td>
<td>1.271(3)\text{c}</td>
</tr>
<tr>
<td>3a(1)</td>
<td>1.326(8)</td>
<td>1.412(9)</td>
<td>1.365(8)</td>
<td>1.390(8)</td>
<td>1.476(9)</td>
<td>1.278(8)</td>
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<tr>
<td>3a(2)</td>
<td>1.320(7)</td>
<td>1.413(8)</td>
<td>1.377(7)</td>
<td>1.387(8)</td>
<td>1.482(9)</td>
<td>1.282(8)</td>
</tr>
<tr>
<td>3a-COD</td>
<td>1.316(4)</td>
<td>1.415(4)</td>
<td>1.379(4)</td>
<td>1.381(4)</td>
<td>1.460(4)</td>
<td>1.279(4)</td>
</tr>
<tr>
<td>3b(1)</td>
<td>1.332(4)</td>
<td>1.415(5)</td>
<td>1.381(4)</td>
<td>1.370(4)</td>
<td>1.468(5)</td>
<td>1.270(4)</td>
</tr>
<tr>
<td>3b(2)</td>
<td>1.324(4)</td>
<td>1.422(5)</td>
<td>1.379(4)</td>
<td>1.377(4)</td>
<td>1.472(5)</td>
<td>1.254(4)</td>
</tr>
<tr>
<td>3a-DPA</td>
<td>1.294(3)</td>
<td>1.442(3)</td>
<td>1.367(3)</td>
<td>1.361(3)</td>
<td>1.465(3)</td>
<td>1.273(3)</td>
</tr>
</tbody>
</table>

\text{a} Bound iminopyridine. \text{b} Unbound iminopyridine. \text{c} In 1a-Br₂, both iminopyridines are bound.

4.3. VT-NMR Studies of Ni[NNN]\text{b}

The $^1$H NMR spectrum of 3a demonstrates two sharp sets of signals at room temperature, one attributable to the coordinated iminopyridine, another to the “dangling” side. In contrast, the room-temperature proton spectrum of 3b shows broad peaks, which may indicate a dynamic process which exchanges bound site for the unbound one via a presumed tridentate intermediate. To shed light on this transformation, we conducted a VT-NMR study of compound 3b in deuterated toluene ($C_7D_8$). Figure 4.6 shows the aromatic regions of the proton spectra taken at different temperatures. The room-temperature spectrum (295 K) shows two sharp resonances, a triplet at 7.74 ppm (attributed to the protons in the 4’ position of the pyridine, $H^i$), and a singlet around 6.62 ppm, attributed to the four protons of the mesityl groups. Cooling the sample to 233 K slows the dynamic process, allowing the peaks of the bound and unbound imine arms to resolve. Specifically, the imino proton of the bound arm ($H^3$) appears as a sharp singlet at 9.43 ppm, and the imino proton of the unbound arm ($H^3$) resonates at 8.93 ppm. Pyridine meta protons (3’ and 5’ positions, $H^e$ and $H^d$) are observed as
two sharp doublets, at 9.10 ppm and 6.40 ppm. Finally, the protons of the bound N-Mes appear as two singlets, while the protons of the unbound N-Mes appear as a single sharp singlet. The overall number of the peaks is consistent with the C₂ symmetry observed in the solid state. Heating the sample to higher temperatures (i.e. 348 K) equilibrates the imino and N-Mes protons that appear as a sharp singlet each (relative intensities 2 and 4). H_c remains a sharp triplet around 7.75 ppm throughout all temperatures because there is single H_c proton (for each bis(imino)pyridine) which therefore cannot undergo a dynamic process. The equilibration of the sidearms likely proceeds through a coordination of the “unbound” arm to the metal, followed by the detachment of the “bound” arm. A ΔG‡ value of approximately 14 kcal mol⁻¹ was obtained from the coalescence temperature of the imine peaks.³⁸
Figure 4.6 VT-NMR performed on compound 3b (in toluene-d$_8$) ranging from 233K to 348K. Signals marked with * belong to the toluene-d$_8$.

4.4. Formation of a Ni[NNN](DPA) Complex

We postulated that “bidentate” binding mode of COD prevents tridentate coordination of bis(imino)pyridine in 3a-COD, and therefore decided to replace COD with diphenylacetylene (DPA). Addition of DPA to a mixture of Ni(COD)$_2$ and [NNN]$^9$ results in the clean formation of 3a-DPA (33% isolated yield, Figure 4.7). However, X-ray crystallography and NMR spectroscopy again indicate that 3a-DPA contains an $\kappa^2$-bound bis(imino)pyridine with one coordinated and one free iminopyridine chelates (Figure 4.8). Proton NMR spectrum of 3a-DPA features broad peaks, consistent with the dynamic process in solution, as observed for 3a. As for the structures
of 3a, 3a-COD, and 3b, the C=N and C-C bonds in the structure of 3a-DPA shows significant differences between bound and unbound iminopyridines (see Figure 4.8 for details, and Table 4.2 for the bond metrics). The structure also demonstrates significant elongation of the triple CC bond of acetylene to 1.91 Å, consistent with its significant activation.

![Chemical Reaction Diagram](image)

**Figure 4.7.** Reaction of [NNN]³ with Ni(COD)₂ and diphenylacetylene.
Figure 4.8. X-ray structure of complex 3a-DPA, 50% probability ellipsoids. Two independent molecules are observed in the asymmetric unit displaying similar structures.
Table 4.3. Experimental crystallographic parameters for 3a-DPA.

<table>
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<th>Parameter</th>
<th>Value</th>
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<td>formula</td>
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</tr>
<tr>
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<td>space group</td>
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<td>$wR_2^b$ (all data)</td>
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4.5. Synthesis of (Ni[NNN])^0 Complexes by Reduction of (Ni[NNN])^{1+}

As the direct reaction of [NNN] ligands with Ni(COD)\_2 did not allow clean isolation of the non-homoleptic complexes, we turned to investigate the reduction of (Ni[NNN])^{1+} precursors. Treatment of 2a-Br with one equivalent of KC\_8 produced compound 4a (Figure 4.9), which was isolated as black crystals by recrystallization from hexane. Thus, chemical reduction of (Ni[NNN])^{1+} leads to a different product than the direct reaction of Ni(0) with the ligand precursor. In contrast, one-electron reduction of 2b-Br produced again bis(homoleptic) 3b. Treatment of complexes 1c-Br\_2 and 1d-Br\_2 with two equivalents of KC\_8 led to the formation of dark solutions from which no isolable products could be obtained.

![Figure 4.9. Reaction of 2a-Br with KC\_8.](image)

The structure of 4a is given in Figure 4.10. Compound 4a is a dimer of “Ni[NNN]” units, in which each bis(imino)pyridine ligand binds via an iminopyridine chelate on one side to one nickel, and via an η\(^2\) imino bond on the other side to another nickel. The structure is not crystallographically centrosymmetric, demonstrating slightly different bond distances on two sides. A similar dimeric structure with a bis(ketimino)pyridine ligand was reported by Budzelaar, Gambarotta and coworkers.\(^{22}\) The chief difference between the previously reported structure and the present structure is that the bis(ketimino)pyridine ligand undergoes chemical modification via dimerization of deprotonated imino CH\_2 groups, whereas bis(aldimino)pyridine
[NNN]$^3$ appears unmodified in the structure of 4a. The overall coordination around nickel centers in 4a is similar to the Budzelaar/Gambarotta’s structure, featuring distorted square-pyramidal metal geometry: the dihedral angles between Ni1N3C1/Ni2C2N6 and Ni1N1N2/N2N4N5 planes are 157° and 161°. The side-on bound imino groups demonstrate significant elongation of C=N bonds, 1.37 (2) and 1.41(2) Å, consistent with previous reports of nickel-bound η$^2$ imino.$^{22}$ The $^1$H NMR spectrum of 4a demonstrates effective $C_2$ symmetry in solution, presenting one signal for the imino protons at 8.59 ppm, and the signal for the “nickelaziridine” proton at 5.41 ppm.
**Figure 4.10.** Crystal structure of 4a. 50% probability ellipsoids. Selected bond distances: N3 – C1 1.37(1), N6-C2 1.41(1), N1 – C3 1.29(1), C3 – C4 1.43(1), C1 – C5 1.47(1), C2 – C6 1.48(1), N4 – C7 1.29(1), C7 – C8 1.45(1) Å.

**Figure 4.11.** The structure of the bis(ketimino)pyridine “analogue” of 4a featuring a C-C bond between deprotonated imino-methyl groups.\(^{22}\)
Table 4.4. Experimental crystallographic parameters for 4a.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>4a</th>
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</thead>
<tbody>
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</tr>
<tr>
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</tr>
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</tr>
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<td>wR&lt;sub&gt;2&lt;/sub&gt; [(I&gt;2σ)]</td>
<td>0.2219</td>
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<tr>
<td>GOF (F²)</td>
<td>1.089</td>
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</table>
4.6. Reactivity of the (Ni[NNN])₂ Complex

Following the synthesis of compound 4a, we have investigated its reactivity with CS₂ and CO₂. The reactivity with CS₂ was conducted in toluene-d₈. The addition of one equivalent of CS₂ to the black solution of 4a produced blue solution and black precipitate. The ¹H NMR spectrum of the soluble phase demonstrated the presence of the free ligand; we were unable to determine the nature of the black precipitate. No reaction with CO₂ was observed upon treatment of the toluene solution of 4a with a stoichiometric amount of CO₂ or stirring of 4a under CO₂ atmosphere for one hour.

4.7. Summary and Conclusions

Due to the lack of reactivity of nickel(I) complexes with heteroallenes, we pursued nickel(0) complexes as precursors for CS₂ and CO₂ activation. Reactions of Ni(COD)₂, a nickel(0) precursor, with [NNN]ₐₕ produced preferentially bis(homoleptic) complexes which show no further reactivity due to the saturated coordination sphere. Using [NNN]ₐ, we also observed the formation of 3a-COD, but could not separate it from the bis(homoleptic) complex due to similar solubility and instability in solution. The reaction of Ni(COD)₂ with one equivalent of [NNN]ₐ in the presence of diphenylacetylene led to the formation of Ni[NNN]ₐ(DPA). In all cases, a potentially tridentate bis(imino)pyridine manifests bidentate coordination of the ligand to the nickel, with one arm left “dangling”. VT-NMR experiments demonstrate that the dangling and the bound arms exchange, via a likely tridentate intermediate. Reduction of 2b-Br once again leads to the presence of 3b, but the reduction of 2a-Br leads to the species, dimer (Ni₂[NNN]ₐ, 4a. As in all other “nickel(0)” complexes, 4a shows a bidentate coordination environment on nickel, with the nickel also being bound through an η² imino bond from the other equivalent of
Reactivity of 4a with CS₂ leads to an insoluble black precipitate and free [NNN]³; again, no reactivity with CO₂ was observed.

Several major conclusions can be derived. First, a potentially tridentate ligand [NNN]³ displays invariably a bidentate coordination mode at (Ni[NNN]³)⁰ state, reminiscent of the bidentate iminopyridine. Second, the ligand demonstrates lability and easily dissociates from the metal. Surprisingly, in contrast to our expectations, tridentate iminopyridines are even more labile than bidentate iminopyridine. Thus, our lab was previously able to isolate and report series of stable Ni[NN](CS₂) complexes with bidentate iminopyridines by treating Ni[NN](COD) with CS₂. Our attempts to prepare the analogous complexes with tridentate bis(imino)pyridine led instead to the liberation of bis(imino)pyridine and likely formation of some sort of insoluble nickel sulfide/carbon disulfide adducts. Finally, no reaction with CO₂ was observed. Thus, as the (Ni[NNN]⁰) state proved insufficient for CO₂ activation, and cyclic voltammetry demonstrates an additional quasi-reversible third reduction event for (1a and 1b), we decided to explore the reactivity of (Ni[NNN])¹⁻ complexes with CO₂.

4.8. Experimental Details

**General Methods and Procedures.** All air sensitive compounds were synthesized in a nitrogen-filled glove box. Compounds 2a-Br and 2b-Br were synthesized as previously described. KC₈ was purchased from Aldrich and used as received. Ni(COD)₂ was purchased from TCI Chemicals and used as received. All solvents were purchased from Fisher and are of HPLC grade. Solvents were purified using an MBRAUN purification system and stored over 3 Å molecular sieves. Compounds were characterized by x-ray crystallography, elemental analysis, and ¹H NMR spectroscopy. Elemental analysis was conducted by Midwest Microlab, LLC. ¹H
NMR spectroscopy was conducted at the Lumigen Instrument Center (Wayne State University) on a Varian 400 MHz NMR spectrometer at room temperature and Varian 500 MHz NMR spectrometer at variable temperatures.

**X-ray Crystallographic Details.** The structures of 3a, 3a-COD, 3b, 3a-DPA, and 4a were determined by x-ray crystallography. A Bruker APEXII/Kappa three circle goniometer platform diffractometer with an APEX-2 detector was used to mount the crystals. A graphic monochromator was employed for wavelength selection of the Mo Kα radiation (λ = 0.71073 Å). The data were processed and the structure was solved using the APEX-2 software supplied by Bruker-AXS. The structure was refined by standard difference Fourier techniques with SHELXL (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms were placed in calculated positions using a standard riding model and refined isotropically; all other atoms were refined anisotropically.

**3a.** To a yellow solution of [NNN]$^a$ (50 mg, 0.110 mmol) in THF (3 mL) was added a yellow solution of Ni(COD)$_2$ (15 mg, 0.055 mmol) in THF (2 mL). The reaction color slowly turned blue/green. The reaction mixture was stirred at ambient temperature for 24 h, filtered and evaporated. The resulting blue/green solid was dissolved in hexanes (ca. 2 mL) and allowed to stand for 24 h at -30°C, which led to the formation of dark green crystals. The crystals were dried to give the product in 56% yield (30 mg, 0.031 mmol). 3a is air and moisture sensitive. $^1$H NMR (400 MHz, C$_6$D$_6$): δ 10.03 (s, 2H), 9.19 (s, 2H), 9.08 (d, J = 7 Hz, 2H), 7.67 (t, J = 6 Hz, 2H), 7.03 (d, J = 7 Hz, 8H), 6.97 (t, J = 7 Hz, 4H), 5.11 (m, 2H), 3.07 (m, 4H), 2.22 (m, 2H), 1.20 (d, J = 7 Hz, 12H), 1.17 (d, J = 7 Hz, 12H), 0.98 (d, J = 7 Hz, 6H), 0.93 (d, J = 7 Hz, 6H), 0.90 (d, J = 7 Hz,
6H), 0.51 (d, J = 7 Hz, 6H). X-ray quality crystals for the X-ray data collection were obtained by crystallization from hexanes at -30°C.

**3a/3a-COD.** To a yellow solution of [NNN]³ (25 mg, 0.055 mmol) in THF (3 mL) was added a yellow solution of Ni(COD)₂ (15 mg, 0.055 mmol) in THF (2 mL). The reaction color slowly turned blue. The reaction mixture was stirred at ambient temperature for 1 h, filtered and evaporated. The resulting blue solid was dissolved in hexanes (ca. 2 mL) and allowed to stand for 24 h at -30°C, which led to the formation of dark blue crystals. Crystallization attempts led to the mixture of 3a and 3a-COD crystals. ¹H NMR (400 MHz, toluene-d⁸): δ 11.65 (2H), 10.00 (2H), 9.13 (2H), 9.03 (2H), 8.68 (1H), 8.63 (1H), 8.47 (2H), 8.25 (2H), 7.67 (2H), 7.45 (2H), 7.26 (4H), 7.09 (8H), 6.97 (2H), 6.77 (2H), 6.45 (2H), 5.53 (4H), 5.06 (2H), 3.88 (2H), 3.49 (2H), 3.26 (2H), 3.08 (4H), 2.71 (2H), 2.40 (2H), 2.20 (2H), 1.30 (8H), 1.14 (24H), 0.93 (6H), 0.44 (6H). X-ray quality crystals for the X-ray data collection were obtained by crystallization from hexanes at -30°C.

**3b.** To a purple solution of 2b (126 mg, 0.248 mmol) in THF (3 mL) was added a suspension of KC₈ (34 mg, 0.248 mmol) in THF (1 mL). The reaction color turned black. The reaction mixture was stirred at ambient temperature for 1 h, filtered, and evaporated. The resulting black solid was dissolved in hexanes (ca. 2 mL) and allowed to stand for 24 h at -30°C, which led to the formation of black crystals. The crystals were dried to give the product in 95% yield (94 mg, 0.118 mmol). 3b is air- and moisture-sensitive. Anal. Calcd for C₅₀H₅₄N₆Ni: C, 75.28; H, 6.82; N, 10.54. Found: C, 74.88; H, 7.06; N, 10.35. ¹H NMR (500 MHz, THF-d⁸, 348K): δ 9.35 (s, 2H), 7.76 (t, J = 7 Hz, 1H), 6.68 (s, 4H), 2.16 (s, 6H), 2.01 (s, 12H). ¹H NMR (500 MHz, THF-d⁸, 295K): δ 9.26 (s, 2H), 8.98 (s, 1H), 7.74 (t, J = 7 Hz 1H), 6.69 (s, 4H), 6.49 (s, 1H), 2.18 (s,
3H), 2.17 (s, 9H), 2.13 (s, 3H). \(^1\)H NMR (500 MHz, THF-\textit{d}^8, 233K): \(\delta\) 9.43 (s, 1H), 9.10 (d, \(J = 7\) Hz, 1H), 8.93 (s, 1H), 7.73 (t, \(J = 8\) Hz, 1H), 6.78 (s, 1H), 6.70 (s, 2H), 6.64 (s, 1H), 6.40 (d, \(J = 8\) Hz, 1H), 2.43 (s, 3H), 2.31 (s, 3H), 2.24 (s, 6H), 2.08 (s, 3H), 1.43 (s, 3H). X-ray quality crystals for the X-ray data collection were obtained by crystallization from hexanes at -30°C.

\textbf{3a-DPA.} To a yellow solution of nickel(0) bis(cyclooctadiene) (18 mg, 0.066 mmol) in THF (2 mL), a yellow solution of [NNN]\(^a\) (30 mg, 0.066 mmol) in THF (1 mL) was added. Over the course of 5 min, the reaction turned blue. After the reaction color changed, a colorless solution of diphenylacetylene (12 mg, 0.066 mmol) in THF (1 mL) was added. The reaction color turned blue-green. The reaction was stirred for 1 h and the solvent was evaporated. The solid was dissolved in hexanes and allowed to stand for 3 days at -30°C, which led to the formation of green-black crystals. The crystals were dried to give the product in 33% yield (15 mg, 0.022 mmol). \textbf{3a-DPA} is air- and moisture-sensitive. Anal. Calcd for C\(_{45}\)H\(_{49}\)N\(_3\)Ni: C, 78.26; H, 7.15; N, 6.08. Found: C, 78.08; H, 7.20; N, 5.50. \(^1\)H NMR (400 MHz, toluene-\textit{d}^8): \(\delta\) 9.84 (2H), 8.48 (1H), 8.26 (1H), 7.46 (3H), 6.81 (4H), 3.18 (4H), 1.05 (24H). X-ray quality crystals for the X-ray data collection were obtained by crystallization from hexanes at -30°C.

\textbf{4a.} To a purple solution of \textbf{2a-Br} (96 mg, 0.162 mmol) in THF (3 mL) was added a suspension of KC\(_8\) (22 mg, 0.162 mmol) in THF (1 mL). The reaction color turned black. The reaction mixture was stirred at ambient temperature for 1 h, filtered, and evaporated. The resulting black solid was dissolved in hexanes (ca. 2 mL) and allowed to stand for 24 h at -30 °C, which led to the formation of black crystals. The crystals were dried to give the product ((Ni[NNN])\(_2\), \textbf{4a}) in 60% yield (50 mg, 0.049 mmol). \textbf{4a} is air- and moisture-sensitive. Anal. Calcd for C\(_{31}\)H\(_{39}\)N\(_3\)Ni: C, 72.67; H, 7.67; N, 8.20. Found: C, 72.85; H, 7.98; N, 7.95. \(^1\)H NMR (400 MHz,
THF-d₈): δ 8.59 (s, 1H), 7.78 (d, J = 8 Hz, 1H), 7.54 (t, J = 7 Hz, 1H), 7.26 (m, 2H), 7.16 (d, J = 7 Hz, 1H), 7.12 (s, 1H), 6.76 (s, 4H), 4.35 (m, 2H), 3.09 (m, 2H), 1.46 (d, J = 6 Hz, 3H), 1.23 (d, J = 6 Hz, 3H), 1.00 (d, J = 7 Hz, 3H), 0.96 (d, J = 7 Hz, 3H). X-ray quality crystals for the X-ray data collection were obtained by crystallization from hexanes at -30°C.
CHAPTER 5: FORMATION AND REACTIVITY OF (Ni[NNN])$^{1+}$ STATE

5.1. Introduction

As we did not observe CO$_2$ reactivity of our bis(aldimino)pyridine nickel complexes in the (Ni[NNN])$^{1+}$ and (Ni[NNN])$^{0}$ oxidation states (Chapters 3 and 4), we have turned to explore possibilities of reduction using electrochemical means. Nickel complexes have been previously shown to catalyze reduction of CO$_2$ using electrolysis.$^{39-42}$ CV experiments presented in Chapter 2 demonstrate that Ni[NNN] complexes are capable of reaching oxidation states beyond (Ni[NNN])$^{0}$. Thus, we decided to investigate the in-situ reactivity of (Ni[NNN])$^{1+}$. This chapter focuses on our research in collaboration with Prof. Jonathan Rochford at the University of Massachusetts Boston, that focuses on the investigation of electrocatalytic reactivity of our bis(aldimino)pyridine nickel complexes.

5.2. Cyclic Voltammetry of Ni[NNN]X$_2$ Complexes in the Presence of CO$_2$

In Chapter 2, we demonstrated that complexes Ni[NNN]$^\text{Br}_2$ (1a-Br$_2$) and Ni[NNN]$^\text{Br}_2$ (1b-Br$_2$) show three quasi-reversible reduction peaks under Ar. As the first two reductions lead to the formation of (Ni[NNN])$^{+1}$ and (Ni[NNN])$^{0}$ species (which were isolated and characterized in chapters 3 and 4), the third reduction must form (Ni[NNN])$^{-1}$ species. Upon repeating cyclic voltammetry studies under 1 atm of CO$_2$ for 1a-e, a growth in Faradaic current is observed at the third reduction wave for 1a-Br$_2$, 1a-Cl$_2$, and 1b-Br$_2$; no catalytic wave was observed for the complexes 1c-Br$_2$, 1d-Br$_2$ and 1e-Br$_2$ (Figure 5.1). Figures 5.2 and 5.3 specifically show the catalytic current observed for compounds 1a-Br$_2$ and 1a-Cl$_2$ under CO$_2$ as compared with their electrochemical performance under Ar. In the absence of an excess of proton source (limiting
any Ni-H formation), the anticipated CO$_2$ reduction product here, consistent with related Ni catalysts, is CO.

Figure 5.1. Cyclic voltammograms of 1a-e under 1 atm CO$_2$ at 100 mV/s.
Figure 5.2. Cyclic voltammograms of 1a-Br$_2$ recorded under 1 atm Ar (blue) and 1 atm CO$_2$ (red) at 100 mV/s.
Figure 5.3. Cyclic voltammograms of 1a-Cl₂ recorded under 1 atm Ar (blue) and 1 atm CO₂ (red) at 100 mV/s.

Cyclic voltammetry studies show reasonable promise that CO could be a formation product of bulk electrolysis at the third reduction wave. Therefore, we looked towards bulk electrolysis to determine the products of catalysis for 1a-Br₂. However, bulk electrolysis shows <3% Faradaic efficiency for CO. Gas Chromatography determined instead an 89% Faradaic yield for H₂ (Figure 5.4). NMR shows no evidence of alternative liquid reduction products such as formic acid. This behavior is similar to that reported for a bis(ketimino)pyridine Mn monocarbonyl catalyst where it was suggested that CO₂ promotes formation of carbonic acid
generating a facile proton source in-situ promoting H₂ evolution. Likewise, catalytic current was enhanced upon addition of methanol as a sacrificial proton source as well as a stronger proton source such as acetic acid (Figure 5.5). For example, an eight-fold increase in catalytic current ($i_{\text{cat}}/i_p = 30$) is observed for 1a-Br₂ in the presence of 5 M MeOH, albeit at a more negative potential of -2.90 V vs Fc⁺/0, corresponding to a TOF of 180 s⁻¹ (Figure 5.6). Bulk electrolysis in the presence of 1 M MeOH showed a similar product selectivity favoring H₂ evolution (Faradaic yield = 89%), however with reduced turnover (Figure 5.4).

**Figure 5.4.** Plots of CO and H₂ turnover numbers (TONs) recorded by gas chromatography during bulk electrolysis in the absence and presence of methanol.
Figure 5.5. Cyclic voltammetry of 1a-Br₂ recorded under 1 atm Ar and 1 atm CO₂ with incremental acetic acid concentrations (100 mV/s; 3 mm glassy carbon disc working electrode in a 0.1 M Bu₄PF₆ acetonitrile supporting electrolyte).
5.3. Summary and Conclusions

Electrochemical studies of 1a-Br₂, 1a-Cl₂, and 1b-Br₂ display a growth of catalytic current when observed under 1 atm of CO₂ at the third reduction event. While typically symptomatic of catalytic CO₂ conversion, Faradaic yields of H₂ support a high selectivity of Ni NNN pincer electrocatalysts for H₂ evolution; only relatively small amount of CO by-product was observed. While disappointing that selective CO₂ reduction was not observed, the high selectivity for H₂ evolution is promising should the overpotential and TON be optimized to compete with established nickel pincer H₂ evolving catalysts. We also note that this study serves as an
important warning for the community: not every catalyst that demonstrates a catalytic wave in the presence of CO₂ functions as a CO₂ reduction catalyst! Unambiguous determination of the nature of the reduction products is essential in order to conclude that CO₂ reduction is in fact happening.

5.4. Experimental Details

Cyclic voltammetry was carried out on a CH Instruments 620E potentiostat. A custom three electrode cell was used for both CV and bulk electrolysis experiments, allowing airtight introduction of working, counter, and reference electrodes as well as septa for gas purging. Gas cylinders were ordered from Airgas containing known ratios of Ar:CO₂ (100:0, 80:20, 60:40, 50:50, 40:60, 20:80, 0:100). For cyclic voltammetry, glassy carbon (3 mm diameter) and Pt wire were used as working and counter electrodes, respectively, with 0.1 M Bu₄NPF₆ in spectrophotometric grade acetonitrile as the supporting electrolyte. A non-aqueous reference electrode was used to minimize ohmic potential drop at the solvent interface. This consisted of a Ag wire in 0.1 M Bu₄NPF₆ acetonitrile supporting electrolyte isolated by a vycor frit and was calibrated using the ferrocenium/ferrocene redox couple as a pseudo reference (+0.45 V vs. SCE). Redox potentials (E) were determined from cyclic voltammetry as \((E_{pa} + E_{pc})/2\), where \(E_{pa}\) and \(E_{pc}\) are the anodic and cathodic peak potentials respectively. Where \(E\) could not be calculated due to irreversible behavior, \(E_{pc}\) or \(E_{pa}\) are reported accordingly. For controlled potential electrolysis experiments a vitreous carbon working electrode was used (soldered to a copper wire), a Pt gauze counter electrode was used isolated via a fine porosity vycor tube+frit to minimize mass transfer resistance. Gas chromatography data were recorded on a custom Shimadzu GC-2014 instrument where a Ni “methanizer” catalyst was used to convert CO to CH₄.
prior to quantification by the thermally conductivity detector. H₂ was simultaneously monitored by a flame ionization detector during the same injection. The GC was precalibrated for CO and H₂ sensitivity by mimicking bulk electrolysis conditions (i.e. 5 mL supporting electrolyte in the same cell, with electrodes, under 1 atm CO₂). Standard curves for H₂ and CO were generated using this cell where known volumes of the analyte gas (H₂ or CO) were injected and the solution stirred for 15 min to allow equilibration of the analyte between the electrolyte and headspace prior to GC injection.
CHAPTER 6: CONCLUSIONS AND FUTURE DIRECTIONS

Carbon dioxide is an abundant source of carbon in the atmosphere. This molecule, while being harmful to the environment, can be utilized in organic transformations. The use of base metals to achieve these transformations has become more important recently, due to their high abundance and relatively low cost. Most reductive transformations of carbon dioxide require two electrons (e.g. formation of CO or formic acid). Usually base metals undergo one-electron redox couples. Because of this, redox non-innocent ligands have been of interest. By employing a redox non-innocent ligand, a base metal catalyst can undergo two-electron redox couples, as the redox non-innocent ligand can accept electron density and release it “on demand”. Furthermore, reduction of most base metals to the states required for CO₂ activation requires prohibitively high potentials in the absence of redox non-innocent ligands. The electron-accepting property of the ligand to stabilize highly reduced base metals can help to avoid the need for prohibitively high reduction potentials. My research has specifically focused on nickel. Nickel is a base metal that has been previously utilized for catalytic CO₂ reduction as, on one hand, it is sufficiently reducing (in nickel(I) and nickel(0) states) to activate CO₂, and on the other hand it is sufficiently non-oxophilic to be able to liberate bound products of CO₂ reduction (such as oxalate, formate, or oxo).

We chose tridentate bis(aldimino)pyridines as our redox non-innocent ligand based on prior work conducted in our lab. Our previous research showed that bidentate aldimino(pyridine) ligands allow CS₂ to coordinate in an η² fashion. DFT studies show that electron density is located on the sulfur atoms as opposed to on the carbon, which is required
for reductive coupling/splitting. Because bis(aldimino)pyridines are tridentate, we hoped that this would force an η¹ binding mode of heteroallenes through only the carbon.

A series of nickel(II) complexes were synthesized. These complexes were shown to have either penta- or hexa-coordinate nickel based on the solvent used (coordinating solvents such as CAN show an equivalent bound to the metal). These complexes have well resolved paramagnetic NMR spectra which range from -10 to 70 ppm. Cyclic voltammograms of the complexes show the existence of 5 reductions (three of which are quasi-reversible) for 1a-Br₂, 1a-Cl₂, and 1b-Br₂. This led us to look into more reduced states of the complexes.

One-electron reduction of the 1a-b led to nickel(I) complexes with surprisingly distorted square-planar geometries. We compared these structures to previously reported bis(ketimino)pyridine “nickel(I)” complexes. Previously reported bis(ketimino)pyridine “nickel(I)” complex is perfectly square planar and shows no spin density located on the metal by EPR (isotropic g value of about 2.01). Thus, in agreement with all previous bis(imino)pyridine literature, that complex was found to demonstrate full delocalization of the electron into the redox-active ligand, with nickel being in fact nickel(II). For our bis(aldimino)pyridine complexes, the EPR spectrum of 1a-Br₂ shows g values significantly higher than 2.01, indicating some spin density located on the metal. Based on DFT calculations, we attribute the difference in the electronic structures between bis(ketimino)pyridine and bis(aldimino)pyridines to the existence of a less bulky substituent on the imine carbon, proton (vs. methyl in bis(ketimino)pyridine). This proton allows the aryl substituent at lateral nitrogens to rotate away from the preferred perpendicular positions to the pyridine ring, which allows the halide to bend out of the plane, which in turn adds spin density to the metal. Thus, we were able to achieve a desired
“metalloradical”, or partly nickel(I) character, and demonstrated a significant difference in the electronic structure and reactivity between otherwise nearly identical bis(ketimino)pyridine and bis(aldimino)pyridine nickel complexes. However, despite this significant nickel(I) character, our bis(aldimino)pyridine complexes did not lead to a productive reactivity with heteroallenes. In the case of CS$_2$, a reaction was observed; however, further investigation revealed that CS$_2$ removes the [NNN] ligand from nickel. No reactivity with CO$_2$ was observed at with nickel(I) bis(aldimino)pyridine complexes.

(Ni[NNN])$^0$ complexes were made by reacting the bis(aldimino)pyridine ligands with Ni(COD)$_2$, or by the mixture of Ni(COD)$_2$ with diphenylacetylene. As an alternative method to access (Ni[NNN])$^0$, we reduced (Ni[NNN])$^{1+}$ complexes by one electron. A variety of different products containing formally “nickel(0)” were obtained. Surprisingly, in all cases bidentate coordination of potentially tridentate bis(aldimino)pyridine was observed, with one imine arm not bound to the metal. Comparison of bond metrics of bound and unbound iminopyridine “arms” reveals the existence of a reduced ligand in the bound “arm”, as evidenced by shortened C-C single bonds and lengthened C=N double bonds. In the unbound arm, the presence of a neutral ligand is confirmed by typical C-C single bonds and C=N double bonds.

The one-electron reduction of nickel(I) complex led to the formation of peculiar dimer in which each ligand binds to one nickel through the “typical” bidentate coordination mode of bis(aldimino)pyridine, and to the other nickel through an η$^2$ bound imine. Except for the elongation in the C=N bond, no chemical modification in the ligand was observed. A comparison with the parallel chemistry of bis(ketimino)pyridine is crucial for the understanding of difference between bis(aldimino)pyridine and bis(ketimino)pyridine ligands. Gambarotta and
coworkers reported a nearly identical structure of bis(ketimino)pyridine nickel dimer. However, in the ketimino case, the dimerization is accompanied by C-C (Me) bond formation that has to result from the development of the radical character at the ligand. We conclude that “nickel(0)” chemistry again demonstrates that bis(aldimino)pyridines possess significantly different electronic structure, with less electron delocalization into the ligand. Again, despite the presence of the reduced metal center, no reactivity with CO$_2$ was observed at the “nickel(0)” state, and the reaction with CS$_2$ was found to release the iminopyridine. We propose that the observed lability of bis(aldimino)pyridine is due to its bidentate coordination.

Our electrochemical studies revealed that an additional redox state, Ni[NNN]$^{1-}$, (formally nickel(1-)) could be reached electrochemically. Electrochemical reduction under CO$_2$ demonstrates a significant increase in catalytic current at the third reduction event. This finding confirms the lack of reactivity with CO$_2$ at the Ni[NNN]$^{1+}$ and Ni[NNN]$^0$ states, Bulk electrolysis of 1a-Br$_2$ at this voltage determined that the catalysis produces <3% Faradaic yield for CO and 89% for H$_2$. We believe that CO$_3^{2-}$ being produced in solution facilitates the formation of H$_2$. This process has been previously observed.

Thus, several important conclusions can be derived from my research. First, while both bis(aldimino)pyridines and bis(ketimino)pyridines are redox-active ligands, there are significant differences between them. Bis(aldimino)pyridines are less “redox-active”, undergo less reduction, enable more spin density on the metal, and are stable toward common decomposition process encountered for bis(imino)pyridine that generally result from the radical delocalization in the ligand. Unfortunately, this behavior is accompanied by the increased lability of bis(aldimino)pyridines (as compared with bis(ketimino)pyridines) in the
metal coordination. In nearly every attempted reaction with a small molecule (O\textsubscript{2}, CS\textsubscript{2}, PhSSPh), the small molecule was found to replace [NNN] ligand at the metal. The second important conclusion is that, in contrast to our expectations, only the third reduction led to a catalytic reactivity, and this reactivity involved mostly hydrogen reformation, with only very small amount of CO by-product.

In the future, we would like to synthesize Ni[NNN]\textsuperscript{1-} complexes and observe their chemical reactivity with heteroallenes. We hypothesized that formation of CO\textsubscript{3}\textsuperscript{2-} leads to formation of H\textsubscript{2} gas in a bulk electrolysis setting. It is possible that we will be able to observe different reactivity in non-electrochemistry conditions. Another area that we would like to explore is complexes of bis(aldimino)pyridine ligands using other late first-row metals such as copper or cobalt. Copper and cobalt are also electron-rich base metals which could show promise in reactivity with heteroallenes.

Bouwman and coworkers show an example of a dinuclear copper complex that is able to bind and reductively couple carbon dioxide. In the future, we will explore dinuclear [NNN] complexes. These complexes would utilize a redox non-innocent ligand, unlike with Bouwman’s complex, but place the reactive metals in close proximity to each other to hopefully induce reductive coupling. We also believe the dinuclear complexes will favor CO\textsubscript{2} reactivity over H\textsubscript{2} formation electrochemically, because of the forced close proximity of the two metal centers.

We will also investigate the chemistry bis(ketimino)pyridines in regard of CX\textsubscript{2} reduction. By using more bulky imino substituents, such as phenyl, we might be able to observe different chemistry due to steric influences of the ligand. By using larger imino groups, this may prevent the imine arms from rotating away from the metal and force a tridentate binding mode.
Finally, bis(imino)pyridines are only one form of tridentate redox non-innocent ligands. There are many examples of NCN ligands which incorporate either an anionic carbon or a carbene into the redox non-innocent ligand. Because we observed the [NNN] ligand easily dissociating from the nickel center when CS$_2$ was introduced, it is possible that by using a ligand with a stronger M-C bond, it could prevent this from happening by making ligand coordination more robust.
APPENDIX A: PERSONAL/LICENSE AGREEMENTS FOR COPYRIGHTED MATERIAL

Portions of Chapters 2 and 3 were reproduced from the following reference: Reed, B. R.; Stoian, S. A.; Lord, R. L.; Groysman, S. “The Aldimine Effect in Bis(imino)pyridine Complexes: Non-Planar Nickel(I) Complexes of a Bis(aldimino)pyridine Ligand” Chem. Commun. 2015, 51, 6496. with the permission from the Royal Society of Chemistry.
APPENDIX B: SUPPLEMENTARY MATERIAL FOR CHAPTER 2

1. NMR Spectra

Figure B.1. $^1$H NMR spectrum of [NNN]$^c$
Figure B.2. $^1$H NMR spectrum of 1a-Cl$_2$
Figure B.3. $^1$H NMR spectrum of 1b-Br$_2$
Figure B.4. $^1$H NMR spectrum of 1c-Br$_2$
Figure B.5. $^1$H NMR spectrum of 1d-Br$_2$
Figure B.6. $^{19}$F NMR spectrum of 1d-Br$_2$
Figure B.7. $^1$H NMR spectrum of 1e-Br$_2$
Figure B.8. $^{19}$F NMR spectrum of 1e-Br$_2$
Figure B.9. $^1$H NMR spectrum of 1a-Cl(PF$_6$)
Figure B.10. $^{19}$F NMR spectrum of 1a-Cl(PF$_6$)
2. Evans Method Formula and Procedure

The Evans method\textsuperscript{44} was performed on 1a-c using a Wilmad coaxial insert and a standard NMR tube. A solution with a known concentration was used, and added to the insert, with the other NMR tube containing a blank solvent. NMR spectra were taken as previously described. The molar susceptibility was calculated using Equation 1:

\[
\chi_m = \left[ \frac{3\Delta \nu}{4\pi m \nu_0} + \chi_0 \right] M \tag{1}
\]

where \(\Delta \nu\) is the peak separation in Hertz, \(m\) is the concentration of the solution (g/mL), \(\nu_0\) is the spectrometer operating frequency in Hertz, \(\chi_0\) is the molar susceptibility of the solvent (in cm\(^3\)/g), and \(M\) is the molar mass of the compound (g/mol).

The solution state effective magnetic moment (\(\mu_{\text{eff}}\)) was calculated using Equation 2:

\[
\mu_{\text{eff}} = \sqrt{(2383)(\chi_m)} \tag{2}
\]

Pascal’s constants were used to calculate diamagnetic corrections. The data is reported below in Table B.1.

**Table B.1.** Spin only magnetic moments calculated using the Evans method

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\mu_{\text{calc}} (\mu_B))</th>
<th>(\mu_{\text{obs}} (\mu_B))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a-Cl(_2)</td>
<td>2.82</td>
<td>3.12</td>
</tr>
<tr>
<td>1a-Br(_2)</td>
<td>2.82</td>
<td>3.10</td>
</tr>
<tr>
<td>1b-Br(_2)</td>
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<td>2.48</td>
</tr>
<tr>
<td>1c-Br(_2)</td>
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<td>2.50</td>
</tr>
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</table>
3. Mass Spectra

Figure B.11. Mass spectrum of $1b$-$Br_2$
Figure B.12. Mass spectrum of 1c-Br$_2$
Figure B.13. Mass spectrum of 1c-Br$_2$
Figure B.14. Mass spectrum of 1c-Br₂
APPENDIX C: SUPPLEMENTARY MATERIAL FOR CHAPTER 3

1. Evans Method Formula and Procedure

Evans method was performed according to the formula and procedure detailed in Appendix B.2.

Table C.1. Spin only magnetic moments calculated using the Evans method

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<th>$\mu_{\text{calc}} (\mu_B)$</th>
<th>$\mu_{\text{obs}} (\mu_B)$</th>
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<td>1a-Cl</td>
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</tr>
<tr>
<td>1b-Br</td>
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2. UV-Visible Spectra

Figure C.1. UV-vis spectra of 2a-Cl at three concentrations (see legend). The spectra were collected in the range of 300-1000 nm.
Figure C.2. UV-vis spectra of 2a-Br at three concentrations (see legend). The spectra were collected in the range of 300-1000 nm.
Figure C.3. UV-vis spectra of 2b-Br at three concentrations (see legend). The spectra were collected in the range of 300-1000 nm.
3. Computational Details

Electronic structure calculations were carried out using DFT\textsuperscript{45} as implemented in Gaussian09.\textsuperscript{46} Geometry optimizations were initially performed at the B3LYP\textsuperscript{47-50} level of theory using 6-31G(d,p) for main group atoms and LANL2DZ\textsuperscript{51} for nickel, but the bond lengths differed significantly from the experimental X-ray structure for 2a-Br and 2a-Cl. Thus, we reoptimized the structures with larger triple-zeta basis sets for all atoms (6-311G(d,p) and def2TZVP\textsuperscript{52}) and found similar results for both basis sets that matched the experimental metrics other than the $N_\text{py}–\text{Ni}–X$ angle. We chose to use the 6-311G(d,p) basis set for further analysis due to the difference in calculation cost. No symmetry constraints were imposed during geometry optimizations, and multiple starting geometries were found to converge to similar geometries other than trivial differences in the methyl groups of the aryl arms. All optimized structures were confirmed to have stable wavefunctions,\textsuperscript{53,54} and to be local minima by analyzing the harmonic frequencies.\textsuperscript{55,56}

We performed constrained optimizations varying that angle from its optimized value near linearity to a significant bend of 140°. This range covers all of the experimentally observed $N_\text{py}–\text{Ni}–X$ angles in the X-ray structures. A summary of the bond length metrics, the deviation of the imino aryl group torsional angle from perpendicular, and spin densities condensed to Ni, X, and the bis-iminopyridine (L) are presented. The angle deviation has a small energetic penalty of ~2-4 kcal/mol to reach the experimentally observed angles. It is interesting to note that as the angle varies, there is a strong correlation to the rotation of the bulky imino aryl groups. Is it possible that the ability (or inability) of these aryl groups to rotate due to the C$_\text{im}$ substituent is responsible for the stark difference in the aldimine and ketimine ligands? We
performed analogous constrained optimizations on the bis(ketimino)pyridine and bis(aldimino)pyridine (Ni[NNN])^1+ complexes. Qualitatively similar results are found, but the energetic penalty for the angle variation is larger (~1.5x) and the variation in the aryl rotation is much smaller (14-18° vs. 22–25°). Based on this computational evidence, we interpret the effect of the aldimine versus ketimine ligand to be largely steric in nature.
Table C.2. Comparison of primary coordination sphere metrics (Angstroms, degrees) for computationally optimized (S=½ only) and X-ray structures. Average values from the two arms are recorded for the X-ray data, and the computational data only differed in decimal places beyond those reported here.

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<th>2a-Cl_{calc} 6-311G(d,p)</th>
<th>2a-Cl_{calc} def2TZVP</th>
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<td>1.968</td>
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<td>2.181</td>
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<table>
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<td>2.215</td>
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<td>Ni-Br</td>
<td>2.309(1)</td>
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<td>2.324</td>
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<td>N_{pyr}-C_{pyr}</td>
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<td>1.355</td>
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<td>1.360</td>
</tr>
<tr>
<td>C_{pyr}-C_{imine}</td>
<td>1.445(6)</td>
<td>1.460</td>
<td>1.430</td>
<td>1.430</td>
</tr>
<tr>
<td>C_{imine}-N_{imine}</td>
<td>1.300(5)</td>
<td>1.290</td>
<td>1.319</td>
<td>1.309</td>
</tr>
<tr>
<td>N_{pyr}-Ni-Br</td>
<td>161.4(1)</td>
<td>166.4</td>
<td>176.7</td>
<td>174.1</td>
</tr>
</tbody>
</table>
Table C.3. Summary of structural parameters, spin densities, and electronic energy (relative to relaxed minimum) for optimized structures holding N_{pyr}-Ni-Cl fixed for 2a-Cl

<table>
<thead>
<tr>
<th></th>
<th>177.6°</th>
<th>170°</th>
<th>160°</th>
<th>150°</th>
<th>140°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Cl</td>
<td>2.181</td>
<td>2.187</td>
<td>2.197</td>
<td>2.208</td>
<td>2.219</td>
</tr>
<tr>
<td>Ni-N_{py}</td>
<td>1.826</td>
<td>1.833</td>
<td>1.842</td>
<td>1.854</td>
<td>1.866</td>
</tr>
<tr>
<td>Ni-N_{im}</td>
<td>1.930</td>
<td>1.943</td>
<td>1.961</td>
<td>1.981</td>
<td>2.000</td>
</tr>
<tr>
<td>N_{py}-C_{py}</td>
<td>1.366</td>
<td>1.366</td>
<td>1.365</td>
<td>1.363</td>
<td>1.360</td>
</tr>
<tr>
<td>C_{py}-C_{im}</td>
<td>1.431</td>
<td>1.432</td>
<td>1.434</td>
<td>1.437</td>
<td>1.440</td>
</tr>
<tr>
<td>C_{im}-N_{im}</td>
<td>1.320</td>
<td>1.318</td>
<td>1.315</td>
<td>1.313</td>
<td>1.311</td>
</tr>
<tr>
<td>C_{im}-N_{im}-C_{Ar}-C_{Ar,ortho}</td>
<td>86.5</td>
<td>83.4</td>
<td>76.7</td>
<td>73.6</td>
<td>68.3</td>
</tr>
<tr>
<td>Ni spin density</td>
<td>0.04</td>
<td>0.08</td>
<td>0.15</td>
<td>0.22</td>
<td>0.31</td>
</tr>
<tr>
<td>Cl spin density</td>
<td>0.0</td>
<td>0.00</td>
<td>-0.02</td>
<td>-0.04</td>
<td>-0.05</td>
</tr>
<tr>
<td>L spin density</td>
<td>0.95</td>
<td>0.92</td>
<td>0.83</td>
<td>0.82</td>
<td>0.74</td>
</tr>
<tr>
<td>Relative E(SCF)</td>
<td>0.00</td>
<td>0.50</td>
<td>2.19</td>
<td>4.66</td>
<td>7.64</td>
</tr>
</tbody>
</table>
4. EPR Spectroscopy

We have recorded a series of high-frequency EPR spectra on a sample ground polycrystalline 2a-Br. Figure C.3 and C.4 show a series of frequency-dependent spectra recorded at 10 and 150 K, respectively. Inspection of these spectra shows that they account for two very similar species that are characterized by slightly different g-values $g_{x,y,z} = 2.236(5), 2.144(4), 2.048(6)$ for the dominant component and $g_{x,y,z} = 2.263(3), 2.140(3), 2.071(2)$ for the minor fraction. The fits of the resonance field vs. frequency dependence go through zero and show a strict linear relationship. These observations demonstrate that we observe a genuine Kramers doublet that is free of weak exchange interactions.

Figure C.4. Frequency dependence of the signal observed for 2a-Br recorded at 10 K.
Figure C.5. Temperature dependence of the spectra (of 2a-Br) recorded at 406.4 GHz. The spectra are normalized and color coded from deep blue for the spectrum recorded at 5 K to deep red for 150 K.
Figure C.6. Frequency dependence of the spectra (2a-Br) recorded at 150 K.
Figure C.7. Frequency dependence of the resonance field determined from the analysis of 10 K spectra. The solid lines are linear fits. The fact that the fits go through zero demonstrate that we are observing a genuine Kramers doublet; that is, a doublet that is strictly degenerate in zero-field. The slopes of these dependencies are in fact the actual g values.
APPENDIX D: SUPPLEMENTARY MATERIAL FOR CHAPTER 4

1. NMR Spectra

Figure D.1. $^1$H NMR spectrum of 3a
Figure D.2. $^1$H NMR spectrum of 3a/ 3a-COD mixture
Figure D.3. $^1$H NMR spectrum of 3a/3a-COD showing only the aromatic region
Figure D.4. $^1$H VT-NMR of 3b from 233 K to 348 K
Figure D.5. $^1$H NMR spectrum of 3a-DPA
Figure D.6. $^1$H NMR spectrum of 4a
Figure E.1. Plot of cathodic and anodic currents versus the square root of the scan rate illustrating the irreversible nature of the anodic wave for the second redox wave of Ni(NNN)Br₂, i.e. 

\[ \text{Ni(NNN)Br} + e^- \rightarrow [\text{Ni(NNN)Br}]^- \rightarrow \text{Ni(NNN)} + \text{Br}^- \]
Figure E.2. Plot of cathodic and anodic currents versus the square root of the scan rate illustrating the irreversible nature of the anodic wave for the second redox wave of Ni(NNN)Br$_2$, i.e. Ni(NNN)Br + e$^-$ → [Ni(NNN)Br]$^-$ → Ni(NNN) + Br$^-$. 

$E = -0.86$ V vs Fe$^{4+0}$
Figure E.3. Plot of cathodic and anodic currents versus the square root of the scan rate illustrating the irreversible nature of the anodic wave for the second redox wave of Ni(NNN)Cl₂, i.e. Ni(NNN)Cl + e⁻ → [Ni(NNN)Cl]⁻ → Ni(NNN) + Cl⁻.
Figure E.4. Linear plot of catalytic current versus catalyst concentration.
**Figure E.5.** Linear plot of catalytic current versus CO$_2$ concentration.
REFERENCES


36. B3LYP/6-311G(d,p).


ABSTRACT

SYNTHESIS AND HETEROALLENE REACTIVITY OF BIS(ALDIMINO)PYRIDINE NICKEL COMPLEXES IN FOUR DIFFERENT OXIDATION STATES

by

BLAKE R. REED

August 2016

Advisor: Dr. Stanislav Groysman

Major: Chemistry

Degree: Doctor of Philosophy

A series of redox non-innocent bis(aldimino)pyridine ligands were synthesized. These were then reacted with nickel(II) salts to form Ni[NNN]X₂ complexes. Cyclic voltammograms of these nickel(II) complexes suggest that more reduced states can be achieved. Reduction of these nickel(II) complexes lead to distorted square planar complexes with the halide bent ~20° out of the plane. EPR suggests that spin density is located on the metal as g-values of >2.01 were obtained. This differs from previously reported analogous bis(ketimino)pyridine complexes, which show a ligand-based radical and nickel(II). DFT confirms that as the N_pyr-Ni-X angle decreases, spin density on the nickel increases. Because of the imino proton as opposed to the imino methyl group, the halide can distort out of the plane and put the spin density on the nickel. Reaction with PhSSPh leads to the formation of (Ni(SPh)₂)_11. This is the first example of nickel(I) reductively splitting PhSSPh to form this product. Reaction with CS₂ results in free ligand, suggesting that CS₂ replaces [NNN]. No reactivity with CO₂ was observed.

[NNN] was reacted with Ni(COD)₂. [NNN]ᵃ formed a mixture of Ni[NNN](COD) and Ni[NNN]₂. [NNN]ᵇ forms only Ni[NNN]₂. In both cases, [NNN] ligand binds in a bidentate fashion
to the nickel. Because of this, we moved to reduction of Ni[NNN]X. Reduction of Ni[NNN]X led to the formation of a dimer, (Ni[NNN])₂. Each nickel is bound in a bidentate fashion to one ligand and bound through the imine bond of the other ligand. Reactivity with CS₂ again leads to the formation of free ligand and an unknown paramagnetic nickel solid. This complex does not react with CO₂.

Based on the CV data of Ni[NNN]X₂, there are three-quasi-reversible reduction waves. In order to access the (Ni[NNN])¹⁻ state, we turned to electrochemistry. Cyclic voltammetry of Ni[NNN]X₂ in the presence of CO₂ shows an increase in catalytic current. Bulk electrolysis experiments show a low (<3%) Faradaic yield for CO and a high (89%) Faradaic yield for H₂.
AUTOBIOGRAPHICAL STATEMENT

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Select Presentations


