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EVALUATING LIGAND ASSISTED ACTIVATION OF SMALL
MOLECULES THROUGH PROTON REDUCTION AND ALCOHOL
OXIDATION

By

Rahul Jain

M.S., Panjab University 2011

M.S., University of Louisville 2016

A Dissertation

Submitted to the Faculty of the

College of Arts and Sciences of the University of Louisville

in Partial Fulfillment of the Requirements

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Doctor of Philosophy

in Chemistry

Department of Chemistry

University of Louisville

Louisville, Kentucky

December 2017

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A Dissertation Approved on

November 29, 2017

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DEDICATION

This dissertation is dedicated to the blessings of

my late grandfather

Sh. Shibu Mal Jain

and

my late mother

Smt. Asha Jain

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ABSTRACT

EVALUATING LIGAND ASSISTED ACTIVATION OF SMALL MOLECULES THROUGH PROTON REDUCTION AND ALCOHOL OXIDATION

Rahul Jain

November 29, 2017

Hydrogen is a potential alternate to the carbon fuels to meet the future demands for energy in an eco-friendly manner. Hydrogen produced by the electrolysis of water is stored in fuel cells which on demand can be converted into electrical energy upon the reaction with oxygen. In the quest for economically viable electrocatalysts for hydrogen evolution, the work in this dissertation describes evaluation of nickel based catalysts coordinated to redox active ligands, dialkyl/diarylphosphine benzenethiol and bis(thiosemicarbazone) for their ability to generate hydrogen with external acids as a proton source. A nickel complex with the benzenethiol ligand framework follows a traditional metal-hydride route and affords a maximum turnover frequency of 51 s^{-1} with an overpotential of 1.1 V. A Ni(II) complex with the bis(thiosemicarbazone) ligand framework displayed a turnover frequency of 4161 s^{-1} operating at an overpotential of 0.52 V. Hydrogen evolution proceeds through metal-hydride intermediate distinct from the typical hydride pathway. DFT studies have been performed in gas phase and in solvent phase using polarizable continuum model (PCM) calculations to probe the mechanism of the hydrogen evolution reactions.

To further evaluate the cooperativity between the redox active ligands and metals in catalysis, complexes that facilitate alcohol oxidation to mimic the activity of galactose oxidase were explored. Copper(II) complexes with an N₄-ligand framework have been synthesized and evaluated as catalysts for oxidation of benzylic alcohols to benzylic aldehydes under aerobic conditions. Proton transfer from the protonated NMI to the imidazole arm in the ligand framework helps to open the site for the binding of TEMPO, thus driving the reaction forward. The reaction studied over the period of 4 hours resulted in yields of up to 99%. Optimum conditions are 5 mmol alcohol with 5 mol% of catalyst, NMI and TEMPO with respect to substrate in acetonitrile under aerobic conditions. To gain mechanistic insights, the components of the reaction mixture such as benzyl alcohol, catalyst concentration, NMI, oxygen flow rate, TEMPO and solvent have been varied.

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CHAPTER I

INTRODUCTION

1.1 Scope of dissertation

This dissertation describes the importance of ligand architecture in the activation of small molecules through (a) proton reduction with nickel (II) complexes having redox-active PS and N₂S₂ ligand frameworks, and (b) aerobic alcohol oxidation with copper (II) complexes containing N₄-ligand backbone. For studies involving hydrogen evolution reaction (HER) and hydrogen oxidation reactions (HOR), a series of techniques were employed including: anaerobic synthesis and techniques like nuclear magnetic resonance (NMR), Fourier-transform infrared (FT-IR), mass spectrometry (ESI-MS), single crystal X-ray crystallography, and elemental analysis. Additional techniques include electrochemical studies like cyclic voltammetry and controlled potential coulometry, product analysis using gas chromatography (GC), kinetics including kinetic isotope effect (KIE) determination, and density functional theory (DFT) studies. DFT studies were found to be crucial for gaining a mechanistic insight of hydrogen evolution reactions with N₂S₂ complex. For studies, involving oxidation of benzylic alcohols to benzylic aldehydes, similar synthesis and spectroscopic techniques were employed as described above and the product formation was analyzed using gas chromatography-mass spectrometry (GC-MS), which is a useful technique for quantitative and qualitative analysis.

Chapter 1 of this dissertation highlights the importance and need for hydrogen. It includes an introduction to hydrogenase and a review of previously reported electrocatalysts for the hydrogen evolution reaction. In Chapter 2, experimental details including the synthesis and spectroscopic characterization of the metal complexes and calculations of turnover frequencies, turnover number, and overpotential for hydrogen evolution and hydrogen oxidation reactions are presented. Computational studies employed for DFT optimizations have also been described. The chapter describes a procedure to calculate percentage yield and turnover number for analyzing the product for aerobic benzylic alcohol oxidation.

In Chapter 3, results of electrocatalytic screening of Ni(PS)_2 and Zn(PS)_2 complexes for hydrogen evolution and hydrogen oxidation reactions in dichloromethane solutions are discussed. The chapter highlights the importance of the orientation of the redox non-innocence PS chelates on the metal center. Chapter 4 of the dissertation discusses the hydrogen evolution ability of a $\text{Ni(N}_2\text{S}_2\text{)}$ complex in acetonitrile and dimethylformamide solutions. DFT studies were conducted to optimize possible intermediates involved in the reaction mechanism. Chapter 5 describes $\text{N}_4\text{-Cu}$ catalytic systems employed for aerobic oxidation of benzylic alcohols to benzylic aldehydes at room temperature. It provides a description of various substrates tested, the optimum conditions required to achieve higher yields and the mechanistic details for the catalytic reaction. Chapter 6 of the dissertation summarizes all three projects described in Chapter 3 – 5, and discusses future directions in terms of exploitation of the redox non-innocence of the ligands for catalytic reactions involving hydrogen evolution and alcohol oxidation.

1.2 Hydrogen as a fuel

From the past century, demand for energy has been gratified by the exploitation of fossil fuels like coal, petroleum, and natural gas. The energy generated by burning fossils fuels is used for transportation, electricity, and other industries. These are the non-renewable sources of energy and cannot be replenish once exhausted from the planet. For the year 2016, total consumption of energy in USA was reported to be 97.4 quadrillion BTUs. About 81% of this energy was generated using fossil fuels, while energy generated by employing renewable sources such as biomass, wind, and hydroelectric sources constituted only 10%. Figure 1.1 gives the percent distribution of the energy consumption in the U.S. in 2016.¹ The extensive use of fossil fuels is leading to increased levels of CO₂ and N₂O_x gases in the atmosphere, which is responsible for global warming and acid rain and affects life forms in all spheres whether it is on land, air, or water.² Also, the mining of fossil fuels is very expensive and the hazardous waste generated after their use is usually dumped in landfills leading to long lasting negative effects on the environment.

Figure 1.1 Percentage distribution of energy consumption in U.S. in 2016.

The adverse and irreversible effects of the use of fossil fuels on the environment has increased the search for clean alternate sources of energy. Hydrogen, a simple molecule, that can serve as a carbon-free fuel as the combustion of hydrogen in the presence of oxygen generates water as the only by-product.³ Hydrogen production from renewable sources of energy such as light, water, or biomass would be an excellent pathway to generate energy as it is environment friendly with negligible impact on the natural environment.⁴ Microorganisms like algae and cyanobacteria, in nature, generate hydrogen by splitting water through the process called biophotolysis.⁵ Also, hydrogen generation from dark fermentation and photo-fermentation of organic substrates by fermentative and photosynthetic bacteria is renewable and an environmental friendly, as it recycles the by-products from food and agricultural industries.⁶⁻⁷

1.3 Hydrogenase: Nature's catalyst for hydrogen production

Hydrogenase is a metalloenzyme that is responsible for hydrogen production and hydrogen oxidation in microorganisms by catalyzing the reactions involving protons and electrons. Hydrogenase with iron and/or nickel in the active site was discovered in 1931 in the bacterium *Escherichia Coli* and found to catalyze the reversible reduction of dye with hydrogen.⁸ Based upon the metal ion in the active center, hydrogenases, are known to occur in three different classes known as [NiFe], [FeFe] and [Fe]- hydrogenases, Figure 1.2.⁹⁻¹¹ The hydrogen molecule is heterolytically cleaved at the metal center, due to the presence of base in the proximity of the active center. The activity of hydrogenase was found to be reversibly inhibited by carbon monoxide. Generation of hydrogen occurs due to the coupling of a hydride and an exogenous proton during the enzymatic catalytic cycle.

Figure 1.2 Active sites for [NiFe] (A), [FeFe] (B) and [Fe]- only (C) hydrogenases.

The first structural characterization of [NiFe] hydrogenase was reported in 1995 by Volbeda.¹²⁻¹³ The [NiFe] hydrogenase is composed of heterodimer having a Ni ion in the larger subunit and a smaller subunit consisting of an [FeS] cluster that plays a key role as a transfer relay system for electrons. The smaller [FeS] subunit allows electron hopping across the protein matrix. Hydrogen travels between the active site and the exterior of the protein through gas channels and proton transfer occurs because of accessible deprotonated/protonated residues. [NiFe] hydrogenase has number of spectroscopically discrete states that under electron deficiency reacts with oxygen, to generate less reactivating state, best described as the *unready* state. Under reductive conditions, a peroxide ligand coordinates between the Ni and Fe ions. A more accessible state known as the *ready* state of hydrogenase enzymes is achieved under oxidizing potentials consisted of hydroxide ligand bridged between the metal centers. Carbon monoxide and sulphide inhibit the activity of the enzyme. [Fe-Fe] hydrogenases are analogous to [NiFe] hydrogenase in the manner of having one or more [FeS] clusters. Two active sites of the enzyme known as H_{ox} and H_{red} are generated. An inactive state, H_{ox}^{inact} is incapable of reacting with carbon dioxide or oxygen is obtained upon the oxidation of H_{ox} , while the active form of the enzyme is known to be naïve towards the small molecules like CO_2 and/

or O_2 . The active site of [FeFe] hydrogenase is comprised of cubane [4Fe-4S] cluster connected to a diiron [2Fe] sub cluster through a thiolate of cysteine. Both proximal and distal Fe ions are coordinated by one CO and one CN ligands. The two metal centers are bridged by a CO ligand. The postulated mechanism for hydrogen evolution with [FeFe] hydrogenase has been shown in Figure 1.3.¹⁴⁻¹⁵

Figure 1.3 Proposed hydrogen evolution mechanism for [FeFe]-hydrogenase.

The bidirectional nature of Hydrogenases to efficiently catalyze hydrogen evolution and hydrogen oxidation reactions, make them ideal candidates for energy storage

devices. The energy obtained from renewable sources like wind, solar and/ or hydrothermal can be stored in hydrogen molecule which can be used on demand.¹⁶ For instance, in fuel cells the chemical energy stored in the hydrogen can be converted into electrical energy upon the electrochemical reaction between hydrogen and oxygen, Figure 1.4.¹⁷

Figure 1.4 Representation of PEM fuel cell.¹⁷

Platinum metal, works efficiently to carry out hydrogen evolution and hydrogen oxidation electrocatalytically. But its utilization on the global scale is limited by its cost and availability.¹⁸ Pt can be easily poisoned by H_2S and CO . Hydrogenases with low cost first-row transition metals Ni and Fe in their active site, can serve as an excellent alternate to Pt due to comparable activity and reversible inhibition to H_2S and CO .¹⁹⁻²²

1.4 Hydrogenase mimics and molecular catalysts for hydrogen evolution

In the pursuit to develop efficient and economically affordable catalysts for hydrogen evolution and/or hydrogen oxidation reactions, several chemists have attempted to mimic the active sites of hydrogenases in laboratory. Few examples have been shown in Figure 1.5. Darensbourg reported first non-catalytic mimic of the enzyme with bridging thiolate and Fe-CO ligands (Figure 1.5 D, E).²³ In 2009, Rauchfuss proposed the first active

[NiFe] hydrogenase model having hydride bridge and shown to evolve hydrogen with strong acids at acceptable overpotentials (Figure 1.5 F).²⁴ Weber showed hydrogen evolution by reversible protonation of the terminal thiolate ligand attached to nickel.²⁵ Bidirectional behavior of the native enzyme, catalyzing both hydrogen production and oxidation was mimicked by Ogo.²⁶ Several mononuclear complexes have also been reported as an active functional hydrogenase mimics with the emphasis on the role of first and second coordination spheres. DuBois's nickel catalyst (Figure, 1.5 G) is one of the best reported electrocatalyst for hydrogen evolution so far.⁴

Figure 1.5 Nickel complexes reported in literature for catalyzing hydrogen evolution.

DuBois's mononuclear nickel complexes with bis(1,5-*R'*-diphospha-3,7-*R''*-diazacyclooctane) ligands has been reported to show the TON of 105 s⁻¹ at an overpotential of 0.5-0.6 V for hydrogen production and TON of 50 s⁻¹ for hydrogen oxidation at 1.0 atm. of hydrogen atmosphere at an overpotential of 0.4 V using triethylamine as an external base.⁴ The [Ni(P₂^RN₂^{R'})₂]²⁺ complexes were inspired from the active site of hydrogenase

enzyme in terms of (a) having an open coordination site for the binding of proton at the metal center, (b) close coordination of basic nitrogen site to the metal and (c) energetic similarity between the metal hydride and capability of basic ligand to accept protons, which avoids the high energy route of intermediate formation and provides reversibility in the catalytic cycle.²⁷

The HER with $[\text{Ni}(\text{P}_2^{\text{R}}\text{N}_2^{\text{R}'})_2]^{2+}$ complex was proposed to occur through ECEC type of mechanism, Figure 1.6.²⁸ In the first step, the Ni(II) species was reduced to Ni(I) species followed by protonation at the pendant amine nitrogen in the second step to yield $[\text{Ni}(\text{P}_2^{\text{R}}\text{N}_2^{\text{R}'}\text{H})(\text{P}_2^{\text{R}}\text{N}_2^{\text{R}'})]^{2+}$. In the next step, second electron addition reduced the Ni(I) species to Ni(0) species $[\text{Ni}(\text{P}_2^{\text{R}}\text{N}_2^{\text{R}'}\text{H})(\text{P}_2^{\text{R}}\text{N}_2^{\text{R}'})]^+$. After the second electron addition, an intramolecular proton transfer occurs that generates Ni(II) hydride, $[\text{HNi}(\text{P}_2^{\text{R}}\text{N}_2^{\text{R}'})_2]^+$. With the formation of Ni(II) hydride, the second proton addition takes place on the pendant amine base. In the final step of the mechanism, hydrogen is eliminated, and the original catalyst was regenerated for the next cycle. The mechanism for HER with $[\text{Ni}(\text{P}_2^{\text{R}}\text{N}_2^{\text{R}'})_2]^{2+}$ is ligand assisted metal-centered reaction as initially the substrate addition occurs on the pendant amine which directs it on the reactive metal center, which in the later steps interacts with the added proton on the ligand to form hydrogen.

Figure 1.6 Postulated mechanism for hydrogen evolution reaction by $\text{Ni}(\text{P}_2^{\text{R}}\text{N}_2^{\text{R}'})_2$.²⁸

In the hydrogen evolution reactions, the generation of metal hydride as an intermediate species has been identified to be crucial and higher activities can be achieved by the clever tuning and optimization of its reactivity. The catalysis for HER, can occur through reduction steps followed by protonation or it can be initiated by the initial protonation steps leading to the reduction in the later steps, described in Figure 1.7. Features like catalyst's structure, electrochemical potential of protons, determines the sequence of electron addition and the chemical steps.

Figure 1.7 Possible pathways for hydrogen evolution reaction in catalysis.²⁹

1.5 An introduction of redox active ligands in catalysis

The term *redox-active* ligand implies to the non-innocent ligand framework which has an ability to undergo oxidation and reduction reactions in the transition metal complexes. The redox assignments in the complexes possessing redox active ligands like dithiolenes, dioxalenes, carbenes, porphyrins, semithiocarbazones are different from the typical metal centered redox events.³⁰⁻³⁴

Gray reported the dithiolene Ni(II) complexes as a model of square planar transition metal complexes with redox-active ligands.³⁵ Chirik reported the square pyramidal Fe(0)

complex with redox active ligand bis(imino) pyridine as active catalysts for hydrogenation and hydrosilylation of unsaturated hydrocarbons.³⁶⁻³⁷ Mononuclear square planar Co(III) complexes with aminodiphenolate ligands reported by Soper showed their affinity for organozinc systems to yield C-C coupling of alkyl halides.³⁸ The redox-active ligand framework participates in the two-electron reductive elimination while cobalt ion behaves as a spectator without undergoing any change in oxidation state. Heyduk demonstrated the Zr(IV) and Ta(V) complexes with tridentate [NON] and [NNN] pincer ligands for their ability to perform reactions like imide reduction and nitrene coupling.³⁹⁻⁴⁰ In Grapperhaus lab, current research attempts focus on the complexation of the redox active ligands to cheap earth abundant first-row transition metals and analysis of the systems for their electrocatalytic ability in the field of catalysis of sustainable fuel production.

1.6 An introduction to metal-stabilized thiyl radicals

Metal-stabilized thiyl radicals are generated by the ligand-centered oxidations of the metal thiolate complexes.⁴¹ Repulsions between metal- sulfur $d\pi-p\pi$ orbitals results in the increase in the nucleophilic character of the metal thiolates, resulting in the excess of electron distribution on the 3p orbital of sulfur. Highest occupied molecular orbital (HOMO) is generated with metal-sulfur π^* -anti-bonding character. Metal-centered oxidation is observed when the HOMO is localized on the metal, while the thiyl radical species is obtained with the heavy localization of HOMO towards the sulfur. The metal stabilized thiyl radical is generated by the equal distribution of HOMO between the metal center and the sulfur atom and thus, it is difficult to exclusively assign the oxidation to be metal-centered or sulfur-centered. The significantly strong $d\pi-p\pi$ interactions between metal and sulfur imparts distribution of spin density on metal and sulfur center.⁴²⁻⁴⁴ The

highly reactive thiyl radical is stabilized by the metal center in a controlled fashion leading to their exploitation as selective catalysts for the functionalization of unsaturated hydrocarbons.

The Grapperhaus group has studied metal stabilized thiyl radicals for their ability bind simple alkene molecules like ethylene, 1-hexene, 2-ethyl-1-butene, cyclohexene etc.⁴⁵⁻⁴⁶ Ruthenium and rhenium complexes with the ligand L^1 ($L^1 =$ bis(diphenylphosphinebenzenethiolate)) has been synthesized using procedure reported by Dilworth.⁴⁷⁻⁴⁸ $Ru[(L^1)_3]^-$ generated metal stabilized thiyl radical species $Ru[(L^1)_3]^+$, upon the consecutive two electron oxidation. The cationic species thus generated $Ru[(L^1)_3]^+$, binds the alkene across the cis-sulfur giving metal-dithioether complexes, $Ru[(L^1)_3-alkene]^+$.⁴⁹ $Re(L^1)_3$ complex upon single oxidation yields $[Re(L^1)_3]^+$, which was found to bind ethylene in the reversible fashion.⁵⁰ Upon increasing the charge of the complex, an increase in the equilibrium binding constant was observed.

1.7 Ligand centered hydrogen evolution with $Re(L^1)_3$ complex

Due to the similarity in the HOMO/LUMO molecular frontier orbital arrangements in hydrogen and ethylene, recently, our group has reported the exploitation of ligand centered reactivity of $Re(L^1)_3$ complex, ($L^1 =$ diphenylphosphinebenzenethiolate) for hydrogen evolution and hydrogen oxidation.⁵¹⁻⁵² The metal center was acting as an electron pool and helped in the proper orientation the ligands to facilitate the coordination of the substrate to the sulfur atoms on the ligands. $Re(L^1)_3$ was found to electrocatalytic active for hydrogen evolution in dichloromethane solution with the turnover frequency (TOF) of $32 \pm 3 \text{ s}^{-1}$ with an overpotential of 708 mV. For hydrogen oxidation in the presence of external

base triethylamine under 1 atm. H₂ the TOF of $4 \pm 1 \text{ s}^{-1}$ with an overpotential of 670 mV has been recorded.

Mechanistic studies on the HER activity of $\text{Re}(\text{L}^1)_3$ reveal a second order dependence on the acid concentration while first order dependence on the catalyst concentration. Thus, overall the reaction was third order with the overall rate constant $k = 184 \text{ M}^{-2} \text{ s}^{-1}$. The kinetic isotope effect studies reveal the KIE ($k_{\text{H}}/k_{\text{D}}$) to be 9 ± 1 with $\text{CH}_3\text{COOH}/\text{CD}_3\text{COOD}$ and $\text{CF}_3\text{SO}_3\text{H}/\text{CF}_3\text{SO}_3\text{D}$. The higher values of KIE supports the reaction to proceeds through ligand centered route as has been reported by Gray and Fukuzumi.⁵³⁻⁵⁴ With $\text{Re}(\text{L}^1)_3$, a maximum turnover number (TON) of 54 has been recorded by performing controlled potential coulometry at a fixed potential of -1.8 V vs ferrocenium/ferrocene for 6 hours. A minimum faradaic efficiency for hydrogen evolution with $\text{Re}(\text{L}^1)_3$ has been found to be 73 %. The ligand centered hydrogen evolution reaction with $\text{Re}(\text{L}^1)_3$ was credited to the meridional arrangement of the L^1 ligands around the metal center. This leads to the coplanar orientation of lone pairs on the two sulfur atoms in the PS chelated framework.

The hydrogen evolution with $\text{Re}(\text{L}^1)_3$ was proposed to follow the ligand centered mechanism, Figure 1.8. In the initial steps, transfer of a proton and an electron to $\text{Re}(\text{L}^1)_3$ generates a neutral intermediate species, $[\text{Re}(\text{L}^1\text{H})(\text{L}^1)_2]$ with a H-atom on one of the cis-sulphur. The next step is the chemical step where with the second proton addition takes place generating protonated species $[\text{Re}(\text{L}^1)_3\cdot\text{H}_2]^+$. In the following step electrochemical reduction of $[\text{Re}(\text{L}^1)_3\cdot\text{H}_2]^+$, generates the neutral hydrogen evolving complex $[\text{Re}(\text{L}^1)_3\cdot\text{H}_2]$. The neutral complex thus generated has H-atoms coordinated to the two cis sulfurs which

through homolytic cleavage in the final step, leads to the evolution of dihydrogen as a product and regeneration of the original catalyst, $\text{Re}(\text{L}^1)_3$.⁵¹⁻⁵²

Figure 1.8 Postulated homogeneous hydrogen evolution reaction mechanism with $\text{Re}(\text{L}^1)_3$.⁵¹⁻⁵²

For hydrogen oxidation with $\text{Re}(\text{L}^1)_3$, the mechanism was proposed to occur through two-electron oxidation of $\text{Re}(\text{L}^1)_3$ in the initial stage giving dicationic $[\text{Re}(\text{L}^1)_3]^{2+}$ species. This was followed by the addition of the dihydrogen molecule giving rise to hydrogen addition complex, $[\text{Re}(\text{L}^1)_3 \cdot \text{H}_2]^{2+}$. In the final steps, cleavage of S-H bonds in the presence of external base, leads to the formation of protonated base and regeneration of the catalyst, $\text{Re}(\text{L}^1)_3$.

This dissertation describes the synthesis of tetracoordinated Ni(II) and Zn(II) analogues of diaryl/dialkylphosphinebenzenethiolate and their electrocatalytic behavior for hydrogen evolution and hydrogen oxidation in Chapter 3. In another study, Ni(II) complex with redox active ligand bis(thiosemicarbazonato) has also been evaluated for hydrogen evolution reaction and the results has been discussed in Chapter 4.

CHAPTER II

EXPERIMENTAL

2.1 Materials and reagents

All chemicals were purchased from commercial sources and used without purification unless reported otherwise. Solvents like ethanol, diethylether, dichloromethane, dimethylformamide, acetonitrile were dried and purified using an MBraun solvent purification system unless otherwise noted. Solvents like tetrahydrofuran and methanol were freshly distilled using standard distillation procedures.⁵⁵ Reactions were conducted using standard Schlenk line techniques under an inert (nitrogen or argon) atmosphere or in an argon-filled glove-box unless otherwise noted.

2.2 Physical methods

¹H NMR (400 MHz) and ³¹P NMR (161 MHz) spectra were recorded on solutions in deuterated solvents using a Varian 400 MHz spectrometer at room temperature. Elemental analyses were obtained from Midwest Microlab (Indianapolis, IN). Infrared spectra were recorded on a Thermo Nicolet Avatar 360 spectrometer with ATR attachment (4 cm⁻¹ resolution) on solid powders. Mass spectrometry (+ESI-MS) was performed by the Laboratory for Biological Mass Spectrometry at Texas A&M University. X-band electronic paramagnetic resonance (EPR) spectra were collected as powder samples at 77 K temperature using a Bruker EMX spectrometer and simulated using EasySpin.⁵⁶

Electronic absorption spectra were recorded with an Agilent 8453 diode array spectrometer with a 1 cm path length quartz cell. The sample solutions were degassed before the collecting the spectrum. The GC-MS instrument was obtained from Agilent Technologies augmented with 7820A GC system and 5975 series MSD using Helium as a carrier gas at a flow rate of 1mL/min. The oven temperature was set to 100°C. The column used was poly (5% diphenyl, 95% dimethylsiloxane) with length 30 m, 250 µm inner diameter and 0.25 µm thickness. X-ray crystallographic studies were performed by Dr. M.S. Mashuta at the Department of Chemistry, University of Louisville on an Agilent Technologies/Oxford Diffraction Gemini CCD diffractometer.

2.3 Synthesis of ligands

The ligands 2-(diphenylphosphanyl)benzenethiol (HL^1) and 2-(diisopropylphosphanyl)benzenethiol (HL^2) were prepared by slight modifications of previously reported methods.⁵⁷⁻⁵⁹ The ligand diacetyl-bis(N4-methyl-3-thiosemicarbazone) (H_2L^3) was prepared by previously reported methods.⁶⁰ The ligands 1,2-bis[(1-methyl-2-imidazolyl)methyleneamino]ethane (L^4) and [(1-methyl-4,5-dihydro-1H-imidazol-2-yl)methyl](2-ethyl)amine] (L^5) was prepared by slight modifications of previously reported methods.⁶¹

2.4 Synthesis of metal complexes

bis[2-(diphenylphosphanyl)benzenethiolato]nickel(II), $\text{Ni}(\text{L}^1)_2$. A sodium ethoxide solution (0.11 g, 1.60 mmol) was prepared in degassed ethanol (10 mL) under a nitrogen atmosphere to which solid HL^1 (0.40 g, 1.50 mmol) was added under a nitrogen and the mixture was stirred until all ligand dissolved. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.15 g, 0.75 mmol) dissolved

in degassed ethanol (10 mL) was added to the ligand solution via cannula under nitrogen atmosphere. After stirring the mixture for 10 min, color change from light green to dark green was observed. A dark green solid product $\text{Ni}(\text{L}^1)_2$ was filtered from the reaction mixture which was then washed with ethanol (20 mL) and diethyl ether (20 mL) and dried under vacuum. Yield: 0.31 g, 81 %. +ESI-MS: m/z calcd. for $\text{C}_{36}\text{H}_{28}\text{P}_2\text{S}_2\text{Ni}$ 645.39, found 645.04. $\text{C}_{36}\text{H}_{28}\text{NiP}_2\text{S}_2$ (645.39): calcd. C 66.99, H 4.37; found C 64.33, H 4.16. ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.66 (dd, J = 12.7, 5.9 Hz, 8 H), 7.49 (t, J = 7.4 Hz, 4 H), 7.40 (m, 10 H), 7.18 (t, J = 7.8 Hz, 3 H), 7.07 (m, 2 H), 6.92 (t, J = 7.5 Hz, 2 H) ppm. $^{31}\text{P}\{^1\text{H}\}$ (161 MHz, CD_2Cl_2): δ = 55.69 ppm.

bis[2-(diphenylphosphanyl)benzenethiolato]zinc(II), $\text{Zn}(\text{L}^1)_2$. To prepare $\text{Zn}(\text{L}^1)_2$, the same procedure was followed as described above for $\text{Ni}(\text{L}^1)_2$ but now the metal precursor used was zinc acetate dihydrate. The zinc acetate dihydrate solution (0.16 g, 0.75 mmol) in degassed ethanol (10 mL) was added to the ethanol solution of HL^1 containing sodium ethoxide. A white solid product $\text{Zn}(\text{L}^1)_2$ was filtered from the solution which was then washed with ethanol (20 mL) and diethyl ether (20 mL) and dried under vacuum. Yield 0.42 g, 86 %. +ESI-MS: m/z calcd. for $\text{C}_{36}\text{H}_{28}\text{P}_2\text{S}_2\text{Zn}$ 652.09, found 652.06. $\text{C}_{36}\text{H}_{28}\text{P}_2\text{S}_2\text{Zn}$ (652.06): calcd. C 66.30, H 4.32; found C 64.32, H 5.44. ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.65 (m, 4 H), 7.44 (m, 6 H), 7.33 (m, 10 H), 7.20 (m, 4 H), 7.02 (m, 2 H), 6.93 (t, J = 7.5 Hz, 2 H) ppm. $^{31}\text{P}\{^1\text{H}\}$ (161 MHz, CD_2Cl_2): δ = -9.77 ppm.

bis[2-(diisopropylphosphanyl)benzenethiolato]nickel(II), $\text{Ni}(\text{L}^2)_2$. To prepare $\text{Ni}(\text{L}^2)_2$, the same procedure was followed as described above for $\text{Ni}(\text{L}^1)_2$ but now the ligand HL^2 was used as a ligand source. HL^2 (0.30 g, 1.50 mmol) was dissolved in degassed ethanol (10 mL) and the mixture yields brown-red product $\text{Ni}(\text{L}^2)_2$ which then was washed with

ethanol (20 mL) and diethyl ether (20 mL) and dried under vacuum. Yield: 0.28 g, 88 %. Liquid diffusion of a dichloromethane/diethyl ether mixture yields orange crystals for X-ray studies (CCDC 1549464). +ESI-MS: m/z calcd. for $C_{24}H_{36}P_2S_2Ni$ 509.30, found 509.09. $C_{24}H_{36}NiP_2S_2$ (509.33): calcd. C 56.59, H 7.12; found C 53.51, H 7.67. 1H NMR (400 MHz, CD_2Cl_2): δ = 7.45 (m, 2 H), 7.30 (m, 2 H), 7.20 (m, 2 H), 6.96 (m, 2 H), 2.50 (m, 4 H), 1.24 (d, J = 7.2 Hz, 24 H) ppm. $^{31}P\{^1H\}$ (161 MHz, CD_2Cl_2): δ = 75.62 ppm.

bis[2-(diisopropylphosphanyl)benzenethiolato]zinc(II), $Zn(L^2)_2$. To prepare $Zn(L^2)_2$, the same procedure was followed as described above for $Ni(L^2)_2$ but now the metal precursor used was zinc acetate dihydrate. The zinc acetate dihydrate solution (0.16 g, 0.75 mmol) in degassed ethanol (10 mL) was added to the ethanol solution of HL^2 containing sodium ethoxide. A white solid product $Zn(L^1)_2$ was filtered from the solution which was then washed with ethanol (20 mL) and diethyl ether (20 mL) and dried under vacuum. Yield: 0.34 g, 88 %. +ESI-MS: m/z calcd. for $C_{24}H_{36}P_2S_2Zn$ 515.96, found 515.11. $C_{24}H_{36}P_2S_2Zn$ (516.00): calcd. C 55.86, H 7.03; found C 55.96, H 7.33. 1H NMR (400 MHz, CD_2Cl_2): δ = 7.89 (m, 2 H), 7.47 (m, 2 H), 7.31 (m, 2 H), 7.24 (m, 2 H), 2.26 (m, 4 H), 1.26 (d, J = 83.1 Hz, 24 H) ppm. $^{31}P\{^1H\}$ (161 MHz, CD_2Cl_2): δ = 11.5 ppm.

diacetyl-bis(N4-methyl-3-thiosemicarbazonato) Ni(II), NiL^3 . To synthesize NiL^3 complex, the ligand ATSMH₂ (1.50 g, 5.8 mmol) was dissolved in methanol and $Ni(OAc)_2 \cdot 4H_2O$ was added (1.57 g, 6.3 mmol). The reaction mixture was refluxed for 4 hours. The dark green precipitates were filtered and washed with methanol and diethyl ether and dried under vacuum. Yield: 1.56 g, 85.3%. 1H NMR (400 MHz, $DMSO-d_6$): 7.66 (2H, br. s), 2.75 (6H), 1.91 (6H, s).

Caution! Although we have experienced no problems in handling the Cu complexes of L⁴ and L⁵, metal–organic perchlorates are potentially explosive and should be handled with due care in small quantities.

[(1-methyl-4,5-dihydro-1H-imidazol-2-yl)methyl](2-ethyl)amine]copper(II), [CuL⁵][ClO₄]₂. The reduced Schiff base ligand L⁵ (0.50 g, 2.0 mmol) was dissolved in 50 ml of methanol and a slow dropwise addition of a slight excess of Cu(ClO₄)₂·6H₂O (1.0 g, 2.6 mmol) solution in 25 ml of methanol resulted in blue colored solution. The reaction mixture was stirred for 4 hours. A blue solid precipitate formation was observed after the addition of 50 ml of diethyl ether to the solution. The precipitated solid was filtered and washed with diethyl ether and then dried under vacuum. Yield 0.76 g (1.5 mmol, 75%). A royal blue prisms crystals of [CuL⁵][ClO₄]₂ (CCDC 1501547) were obtained by the liquid diffusion of methanol/ether mixture. Electronic absorption (CH₃CN (22 °C)): λ_{max} (ε) 212 nm (10350 M⁻¹ cm⁻¹), 302 nm (9150 M⁻¹ cm⁻¹), 630 nm (940 M⁻¹ cm⁻¹). FT-IR (ATR), cm⁻¹: 3509 (s, sh), 3248 (w), 2962 (w), 2839 (w), 2357 (w, b), 2242 (w), 1262 (w, sh), 1102 (s, sh), 808 (w, b), 759 (w,b). (+)ESI-MS, *m/z* calcd for [M]²⁺, [C₁₂N₆H₂₀Cu]²⁺; 155.94, Found, 155.55. Anal. Calcd. for C₁₂N₆H₂₀CuCl₂O₈: C, 28.22; H, 3.95; N, 16.45. Found: C, 28.44; H, 3.91; N, 16.13.

[Cu(HL⁵)(CH₃CN)₂][ClO₄]₃. X-ray quality crystals for [Cu(HL⁵)(CH₃CN)₂][ClO₄]₃ (CCDC 1501548) were obtained by the liquid diffusion of acetonitrile/ether solution. The crystals obtained were sapphire blue in colour with the monoclinic space group *P*2₁/*c*.

2.5 Electrochemical methods

2.5.1 Cyclic voltammetry

Cyclic Voltammetry is a technique that ramps the electrode potential with respect to time in cyclic phases. The rate of change of potential over time is known as scan rate measured in volts per unit time. In a three-electrode electrochemical cell, the potential is applied between the working electrode (glassy carbon) and reference electrode (Ag/AgCl) and the current is measured between the working electrode and counter electrode (platinum). For analysis, the graph is plotted between the current and the applied potential.⁶²⁻⁶³

A Gamry Interface potentiostat was used to perform the cyclic voltammetry (CV) and controlled potential coulometry (CPC) measurements, using glassy carbon working electrode (diameter = 6.5 mm, surface area = 0.07 cm²), a platinum wire counter electrode, and Ag/AgCl reference electrode. Before the data collection, glassy carbon electrode was polished using aqueous alumina slurry. Also, both working and counter electrodes were washed thoroughly with solvents like water, ethanol, acetone, acetonitrile, methanol, dichloromethane and then sonicated in working solvent. To conduct CV measurements, a three-neck electrochemical cell was used which was washed and dried in oven over night before recording the data. All electrochemical experiments were conducted under a N₂ atmosphere.

To conduct the CV measurements 25 ml of the working solvent was taken initially in three-neck electrochemical cell to which the working electrode, reference electrode and the counter electrode were attached. To this cell, 0.1 M electrolyte Bu₄NPF₆ was added.

Then the solvent was purged with N₂ for 15 minutes to remove any oxygen from it. A blank CV of the solvent was recorded. Then the required quantity of the compound was added to the cell and then the solvent was again purged with N₂ for 15 minutes. A CV of the compound was recorded. For evaluation of catalytic HER, external acid was added to the solution in regular intervals and data collected after each addition. An increase in the cathodic current during the potential sweep indicates the catalytic current attributed to HER. Identification of the evolved gas and quantification was done by CPC and GC analysis.

2.5.2 Controlled potential coulometry

A two-chambered electrolysis cell with a volume of 20 mL was used to perform the CPC measurements. The working compartment was fitted with a platinum working electrode (surface area = 0.07 cm²) and an Ag/AgCl reference electrode. The auxiliary compartment was fitted with a Pt wire counter electrode. The working compartment contained the acid, added to a 0.1 M Bu₄NPF₆ in the desired solvent solution, while the auxiliary compartment was filled with 0.1 M Bu₄NPF₆ in the desired solvent. Before performing experiments both the compartments were purged for 15 min with nitrogen gas and during the measurements kept under a constant nitrogen flow. A blank CPC measurement was taken and then subtracted from experimental results as a control study. Electrolysis was then measured with the addition of the catalyst.

For Ni(L¹)₂, the working compartment was filled with 0.1 M Bu₄NPF₆ dichloromethane solution. To this solution 0.50 mM Ni(L¹)₂ and 3.5 mM acetic acid and the auxiliary compartment contained 0.1 M Bu₄NPF₆ dichloromethane solution. Both working and auxiliary compartment was purged with nitrogen gas for 15 minutes.

Electrolysis measurements were performed for 24 hours. For NiL^3 , the electrolysis was done with both CH_3COOH and CF_3COOH in acetonitrile and dimethylformamide solutions. With acetic acid in acetonitrile solutions electrolysis was performed for 18 hours with 0.30 mM NiL^3 and 12.6 mM acetic acid in the working compartment with 0.1 M Bu_4NPF_6 and the auxiliary compartment contained 0.1 M Bu_4NPF_6 acetonitrile solution. In another set of experiment, with the similar concentration of supporting electrolyte in working and auxiliary compartment, electrolysis with 18 mM trifluoroacetic acid and 0.30 mM NiL^3 was performed for 18 hours. Controlled potential coulometry measurements in dimethylformamide solutions employing the similar concentrations of catalyst with 9.8 mM acetic acid and 32 mM trifluoroacetic acid in separate experiments were performed for 18 hours.

2.6 Determination of overpotential

The overpotential is the difference between the thermodynamic reduction potential for a given reaction and the potential at which the reaction occurs under a set of specific conditions.⁶⁴

$\text{E}_{\text{cat}/2}$ is defined as the potential at one-half of the i_{cat} , the maximum of catalytic current, recorded for hydrogen evolution and hydrogen oxidation reactions. The equilibrium potential E_{H^+} is calculated from the standard acid potential $\text{E}^0_{\text{H}^+}$ and the pK_a of the acid. If the standard acid potential and the pK_a of the acid are unavailable, then it can be calculated directly using open circuit potential measurements as described by Bullock *et al.*⁶⁵

2.6.1 Overpotential measurements

The overpotential (η) for proton reduction by $\text{Ni}(\text{L}^1)_2$ and NiL^3 under specific experimental conditions can be estimated as:

$$\eta = |(E_{\text{OCP}} - E_{\text{cat}/2})|$$

E_{OCP} = measured OCP under catalytic conditions specific for each reaction,

$E_{\text{cat}/2}$ = the potential at one-half of the maximum catalytic current measured for proton reduction or hydrogen oxidation by the catalyst.

To determine the overpotential for electrocatalysts $\text{Ni}(\text{L}^1)_2$ and $\text{Ni}(\text{L}^2)_2$ described in Chapter 3, Bullock's open circuit potential measurements were employed for which four electrodes set up was used. Glassy carbon electrode was used as a working electrode, annealed Pt wire as a working sense, annealed Pt wire as a counter electrode and Ag/Ag^+ as a reference electrode. A dichloromethane solution containing 0.1 M Bu_4NPF_6 was used to which the desired acid or base was added. The acid or base concentration used to calculate the OCP measurements is the concentration at which acid or base independence is observed while performing the cyclic voltammetry experiments in the dichloromethane.

To determine the overpotential for electrocatalyst NiL^3 described in Chapter 4, Artero's method was employed.⁶⁶ The acids with higher pK_a , incapable of protonating the solvents acetonitrile and dimethylformamide were reported at three different concentrations of 1 mM, 10 mM and 100 mM. For our purposes, reported E_{ref} vs Fc^+/Fc values were used to calculate the overpotential for electrocatalyst NiL^3 .

Overpotential determination with Ni(L¹)₂ using CH₃COOH in dichloromethane (HER)

$$\eta = |(E_{\text{BH}^+(\text{OCP})}) - (E_{\text{cat}/2})|$$

$$\eta = |(-0.789 - (-1.934))|$$

$$\eta = 1.14 \text{ V vs Fc}^+/\text{Fc}^0$$

Overpotential determination with Ni(L¹)₂ using HCl in dichloromethane (HER)

$$\eta = |(E_{\text{BH}^+(\text{OCP})}) - (E_{\text{cat}/2})|$$

$$\eta = |(-0.847 - (-1.934))|$$

$$\eta = 1.09 \text{ V vs Fc}^+/\text{Fc}^0$$

Overpotential determination with Ni(L¹)₂ using Et₃N in dichloromethane (HOR)

$$\eta = |(E_{\text{BH}^+(\text{OCP})}) - (E_{\text{cat}/2})|$$

$$\eta = |(0.178 - (0.510))|$$

$$\eta = 0.33 \text{ V vs Fc}^+/\text{Fc}^0$$

Overpotential determination with Ni(L²)₂ using Et₃N in dichloromethane (HOR)

$$\eta = |(E_{\text{BH}^+(\text{OCP})}) - (E_{\text{cat}/2})|$$

$$\eta = |(0.164 - (0.657))|$$

$$\eta = 0.49 \text{ V vs Fc}^+/\text{Fc}^0$$

Overpotential determination with NiL³ using CH₃COOH in acetonitrile (HER)

$$\eta = |(E_{\text{ref}}) - (E_{\text{cat}/2})|$$

$$\eta = |(-1.23) - (-1.75)|$$

$$\eta = 0.52 \text{ V vs Fc}^+/\text{Fc}^0$$

Overpotential determination with NiL³ using CF₃COOH in acetonitrile (HER)

$$\eta = |(E_{\text{ref}}) - (E_{\text{cat}/2})|$$

$$\eta = |(-0.65) - (-1.32)|$$

$$\eta = 0.67 \text{ V vs Fc}^+/\text{Fc}^0$$

Overpotential determination with NiL³ using CH₃COOH in dimethylformamide (HER)

$$\eta = |(E_{\text{ref}}) - (E_{\text{cat}/2})|$$

$$\eta = |(-1.40) - (-1.95)|$$

$$\eta = 0.55 \text{ V vs Fc}^+/\text{Fc}^0$$

2.7 Procedure for calculation of turnover frequency (TOF) for HER

The procedure to calculate the TOF has been mentioned below according to the reported literature.⁶⁷⁻⁶⁸ The current obtained with the catalyst by itself prior to the addition of acid is known as peak current, *i_p* and is given by

$$i_p = 0.4463[\text{cat}] \sqrt{\frac{FvD}{RT}} \quad 2-1$$

Equation 2-1 known as Randles-Sevcik equation that describes the relation between peak current and the catalyst concentration [cat], Faraday's constant (F), diffusion constant (D), scan rate (*v*), universal gas constant (R) and Temperature (T).⁶²

For catalytic HER reactions that are first-order in acid and first-order catalyst, the catalytic current in the presence of $\text{Ni}(\text{L}^1)_2$ with acetic acid and hydrochloric acid in dichloromethane solutions is calculated using

$$i_{\text{cat}} = nFA[\text{cat}][DkH^+]^{1/2} \quad 2-2$$

Equation 2-2 that explains the dependency of catalytic current, i_{cat} , on the first order acid concentration $[\text{H}^+]$, catalyst concentration $[\text{cat}]$, diffusion constant (D), and the electrochemical parameters like number of electrons (n), Faraday's constant (F) and the electrode area (A).

Dividing equation 2-2 by equation 2-1 yields equation 2-3

$$\frac{i_{\text{cat}}}{i_p} = \frac{n}{0.4463} \left(\frac{RTk[\text{H}^+]}{Fv} \right)^{\frac{1}{2}} \quad 2-3$$

Under pseudo first order acid concentrations, $k_{\text{obs}} = k[\text{H}^+]$, giving equation 2-4

$$\frac{i_{\text{cat}}}{i_p} = \frac{n}{0.4463} \left(\frac{RTk_{\text{obs}}}{Fv} \right)^{\frac{1}{2}} \quad 2-4$$

To obtain TOF (k_{obs}), under scan rate independent conditions at 298 K, the equation 2-4 gets deduced to equation 2-5

$$k_{\text{obs}} = v \left(\frac{\frac{i_{\text{cat}}}{i_p}}{0.35} \right)^2 \quad 2-5$$

Equation 2-5 is used under ideal conditions, when a perfect S- shaped curved is observed. But in most of the cases due to substrate depletion, catalyst degradation the perfect S- shaped cyclic voltammograms are hard to obtain.⁶⁹⁻⁷⁰ These phenomenon leads to under reported values for TOF. These drawbacks can be overcome by using Foot-of-the-wave

analysis (FOWA) where the calculation of TOF is done at the foot or initiation point of the non-ideal catalytic wave which resembles the ideal theoretical value.⁷¹⁻⁷² Foot-of-the-wave analysis (FOWA) to calculate the TOF developed by Saveant et.al.⁷³⁻⁷⁵ The prerequisite condition for the FOWA is the first step in the mechanism has to be electron reduction. Thus FOWA, is limited to ECEC, ECCE, EECC type of mechanism.⁷⁶ For Ni(L¹)₂, even though perfect S-shaped waves were not obtained in the catalysis, FOWA was not applied for TOF calculation because of the possibility of protonation in the first step with HCl as a proton source. To calculate TOF for NiL³, FOWA was employed as the catalytic mechanism for HER with NiL³ was proposed to initiate by the electron reduction in the first step. It is proposed that foot of the non-ideal wave is similar to the theoretical ideal.

Under non-ideal conditions the catalytic current i_{cat} can be given as

$$i_{cat} = \left(\frac{2FA[cat]\sqrt{Dkobs}}{1 + \exp \left[\left(\frac{F}{RT} \right) \left(E - \frac{E_{cat}}{2} \right) \right]} \right) \quad 2-6$$

Dividing 2-6 by 2-1 gives

$$i_{cat}/i_p = \frac{2\sqrt{(RT/Fv)}\sqrt{kobs}}{0.4463} \times \left(\frac{1}{1 + \exp \left[(F/RT) \left(E - \frac{E_{cat}}{2} \right) \right]} \right) \quad 2-7$$

On plotting i_{cat}/i_p vs $\left(\frac{1}{1 + \exp \left[(F/RT) \left(E - \frac{E_{cat}}{2} \right) \right]} \right)$

$$\text{slope, } m = \frac{2\sqrt{(RT/Fv)}\sqrt{kobs}}{0.4463}$$

$$i_{cat}/i_p = \frac{n}{0.4463} \sqrt{\frac{RTkcat[H^+]}{Fv}}$$

$$TOF = \frac{TOF_{max}}{1 + \exp \left[\frac{F}{RT} \left[E - \frac{E_{cat}}{2} \right] \right]}$$

$$\eta = E^0(H^+/H_2) - E$$

$$TOF = \frac{TOF_{max}}{1 + \exp\left[\frac{F}{RT}\right]\left[E^0(H^+/H_2) - \eta - \frac{E_{cat}}{2}\right]}$$

For HER/ HOR catalysts, TOF and η are the crucial parameters related to the efficacy of the catalyst. Tafel plot is generally used that relates these two parameters together. Tafel plot establishes the relation between $\log(TOF)$ and η . Thus, a direct comparison between the different catalyst can be made using these plots. In general, $TOF_{max}(s^{-1})$ can be defined as the theoretical ideal turnover frequency from FOWA, at 1M acid concentrations.⁷⁷

2.8 Procedure for calculation of kinetic isotope effect (KIE)

The kinetic isotope effect results from the change in the reaction rate of a chemical reaction when some of the atoms in the reactant are replaced by their heavy isotope.⁷⁸ Mathematically, it is the ratio of the rate constant of the reaction with the light isotope and the rate constant of the reaction with the heavy isotope.

$$KIE = k_L/k_H$$

To calculate KIE, the TOF with the normal acid is calculated using the methods above. This value is assigned as k_L . Then, in a separate experiment the TOF is calculated using *D*-acid to obtain k_H . Then, their ratio is taken to calculate KIE.

2.9 Procedure for calculation of diffusion coefficient (D)

Using the Randles-Sevcik equation,

$$i_p = 0.4463FA [cat] \sqrt{\frac{FvD}{RT}}$$

and plotting peak current vs the square root of the scan rate allows for accurate calculation of the diffusion coefficient, D.

2.10 Procedure for calculation of turnover number (TON)

TON = Moles of H₂ produced / Moles of catalyst used

2.11 Calculations for HER with Ni(L¹)₂

TOF calculations:

Using equation 2-5

$$k_{obs} = v \left(\frac{\frac{i_{cat}}{i_p}}{0.35} \right)^2$$

Calculations of TOF/*k_{obs}*.

For HER using Ni(L¹)₂ with acetic acid:

At 5V/s, *i_p* = 59.87 μA; *i_{cat}* = 66.90 μA, **TOF/*k_{obs}* = 51 s⁻¹**

For HER using Ni(L¹)₂ with hydrochloric acid:

At 5V/s, *i_p* = 59.87 μA; *i_{cat}* = 111.40 μA, **TOF/*k_{obs}* = 140 s⁻¹**

KIE calculations using Ni(L¹)₂:

$$KIE = k_{CH_3COOH} / k_{CD_3COOH} = 0.82$$

Diffusion Coefficient (D) calculations:

For Ni(L¹)₂: Using the Randles-Sevcik equation,

$$i_p = 0.4463FA [\text{cat}] \sqrt{\frac{FvD}{RT}}$$

and plotting peak current vs the square root of the scan rate allows for accurate calculation of the diffusion coefficient, D.

$$\text{Slope} \equiv 2\text{E-}5 = 0.4463FA [\text{cat}] [(FD/RT)]^{0.5}$$

$$A = 0.071 \text{ cm}^2$$

$$[\text{cat}] = 5\text{E-}7 \text{ moles/cm}^3$$

$$F = 96485 \text{ C/mole e}^-$$

R = ideal gas constant

$$T = 298 \text{ K}$$

$$D = 4.3\text{E-}6 \text{ cm}^2/\text{s in } \text{CH}_2\text{Cl}_2$$

TON Calculations:

$$\text{TON} = \text{Moles of H}_2 \text{ produced} / \text{Moles of Ni(L}^1\text{)}_2 \text{ used}$$

$$\text{TON} = (0.000043 \text{ moles H}_2 \text{ produced}) / (0.0000125 \text{ moles Ni(L}^1\text{)}_2 \text{ used})$$

$$\text{TON} = 3.4$$

2.12 Calculations for HER with NiL³

TOF calculations for NiL³ using FOWA:

To calculate TOF for HER with NiL³, FOWA was used as described above

$$\text{On plotting, } i_{\text{cat}}/i_p \text{ vs } \left(\frac{1}{1 + \exp \left[(F/RT) \left(E - \frac{E_{\text{cat}}}{2} \right) \right]} \right) \text{ using NiL}^3 \text{ with acetic acid in acetonitrile,}$$

$$\text{Slope} = m = 1.9651 = \frac{2\sqrt{(RT/Fv)}\sqrt{k_{obs}}}{0.4463}$$

$$k_{obs} = (0.4463)^2 m^2 Fv / 4RT$$

$$k_{obs} = 52.43 \text{ s}^{-1}$$

$$k_{cat} = k_{obs} / [H^+] = 52.43 / 0.0126 = 4161 \text{ s}^{-1}$$

On plotting i_{cat}/i_p vs $\left(\frac{1}{1 + \exp [(F/RT)(E - \frac{E_{cat}}{2})]} \right)$ using NiL^3 with trifluoroacetic acid in acetonitrile,

$$\text{Slope} = m = 1.3249 = \frac{2\sqrt{(RT/Fv)}\sqrt{k_{obs}}}{0.4463}$$

$$k_{obs} = (0.4463)^2 m^2 Fv / 4RT$$

$$k_{obs} = 23.83 \text{ s}^{-1}$$

$$k_{cat} = k_{obs} / [H^+] = 23.83 / 0.018 = 1324 \text{ s}^{-1}$$

On plotting i_{cat}/i_p vs $\left(\frac{1}{1 + \exp [(F/RT)(E - \frac{E_{cat}}{2})]} \right)$ using NiL^3 with acetic acid in dimethylformamide,

$$\text{Slope} = m = 1.0993 = \frac{2\sqrt{(RT/Fv)}\sqrt{k_{obs}}}{0.4463}$$

$$k_{obs} = (0.4463)^2 m^2 Fv / 4RT$$

$$k_{obs} = 11.72 \text{ s}^{-1}$$

$$k_{cat} = k_{obs} / [H^+] = 11.72 / 0.098 = 1196 \text{ s}^{-1}$$

On plotting i_{cat}/i_p vs $\left(\frac{1}{1+\exp[(F/RT)(E-\frac{E_{cat}}{2})]}\right)$ using NiL^3 with trifluoroacetic acid in dimethylformamide,

$$\text{Slope} = m = 0.6165 = \frac{2\sqrt{(RT/Fv)}\sqrt{k_{obs}}}{0.4463}$$

$$k_{obs} = (0.4463)^2 m^2 F v / 4RT$$

$$k_{obs} = 3.685 \text{ s}^{-1}$$

$$k_{cat} = k_{obs}/[H^+] = 3.685/0.032 = 115 \text{ s}^{-1}$$

Diffusion coefficient (D) with NiL^3

For 0.30 mM NiL^3 in DMF: Using the Randles-Sevcik equation,

$$i_p = 0.4463FA [cat] \sqrt{\frac{FvD}{RT}}$$

and plotting peak current vs the square root of the scan rate allows for accurate calculation of the diffusion coefficient, D.

$$\text{Slope} \equiv 3E-5 = 0.4463FA [cat] [(FD/RT)]^{0.5}$$

$$A = 0.071 \text{ cm}^2$$

$$[cat] = 3E-7 \text{ moles/cm}^3$$

$$F = 96485 \text{ C/mole e}^-$$

R = ideal gas constant

$$T = 298 \text{ K}$$

$$D = 2.74E-5 \text{ cm}^2/\text{s in DMF}$$

TON calculations:

a) NiL^3 with acetic acid in acetonitrile, Theoretical Moles of H_2 via Total Charge:

$$92 \text{ C} \times (1 \text{ mol e}^- / 96485 \text{ C}) \times (1 \text{ mol H}_2 / 2 \text{ mol e}^-) = \text{moles H}_2 \text{ theoretical}$$

$$\text{Moles H}_2 \text{ theoretical} = 0.000476 \text{ moles H}_2 \text{ based on charge from electrolysis}$$

$$\text{TON} = \text{Moles H}_2 \text{ theoretical} / \text{Moles of catalyst used}$$

$$\text{TON} = 0.000476 / 0.0000075 = 63$$

b) NiL^3 with acetic acid in dimethylformamide, Theoretical Moles of H_2 via Total Charge:

$$37 \text{ C} \times (1 \text{ mol e}^- / 96485 \text{ C}) \times (1 \text{ mol H}_2 / 2 \text{ mol e}^-) = \text{moles H}_2 \text{ theoretical}$$

$$\text{Moles H}_2 \text{ theoretical} = 0.000192 \text{ moles H}_2 \text{ based on charge from electrolysis}$$

$$\text{TON} = \text{Moles H}_2 \text{ theoretical} / \text{Moles of catalyst used}$$

$$\text{TON} = 0.000192 / 0.0000075 = 26$$

c) NiL^3 with trifluoroacetic acid in acetonitrile, Theoretical Moles of H_2 via Total Charge:

$$36 \text{ C} \times (1 \text{ mol e}^- / 96485 \text{ C}) \times (1 \text{ mol H}_2 / 2 \text{ mol e}^-) = \text{moles H}_2 \text{ theoretical}$$

$$\text{Moles H}_2 \text{ theoretical} = 0.000187 \text{ moles H}_2 \text{ based on charge from electrolysis}$$

$$\text{TON} = \text{Moles H}_2 \text{ theoretical} / \text{Moles of catalyst used}$$

$$\text{TON} = 0.000187 / 0.0000075 = 25$$

d) NiL^3 with trifluoroacetic acid in dimethylformamide, Theoretical Moles of H_2 via Total Charge:

$$23 \text{ C} \times (1 \text{ mol e}^- / 96485 \text{ C}) \times (1 \text{ mol H}_2 / 2 \text{ mol e}^-) = \text{moles H}_2 \text{ theoretical}$$

$$\text{Moles H}_2 \text{ theoretical} = 0.000119 \text{ moles H}_2 \text{ based on charge from electrolysis}$$

$$\text{TON} = \text{Moles H}_2 \text{ theoretical} / \text{Moles of catalyst used}$$

$$\text{TON} = 0.000119 / 0.0000075 = 16$$

2.13 X-ray crystallographic studies

A royal blue colored crystal of $[\text{CuL}^5][\text{ClO}_4]_2$ measured $0.40 \times 0.21 \times 0.16 \text{ mm}^3$ was obtained from the liquid diffusion of methanol/ether solution and was mounted on an Agilent Technologies/Oxford Diffraction Gemini CCD diffractometer for X-ray data collection. In order to acquire a total of 397 twenty second frame ω -scan exposures of data at 100 K to a $2\theta_{\text{max}} = 56.4^\circ$, The CrysAlisPro⁷⁹ CCD software package (v 1.171.36.32) was employed. For determining final unit cell parameters, CrysAlisPro⁷⁹ RED was used for processing the frame data giving the values of $a = 17.244(2) \text{ \AA}$, $b = 8.1023(10) \text{ \AA}$, $c = 13.7251(15) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 96.258(12)^\circ$, $\gamma = 90^\circ$, $V = 1906.2(4) \text{ \AA}^3$, $Z = 4$ and $D_{\text{calc}} = 1.780 \text{ Mg m}^{-3}$ to produce raw hkl data. The values were then corrected for absorption (transmission min./max. = 0.830/1.000; $\mu = 1.482 \text{ mm}^{-1}$) using SCALE3 ABSPACK.⁸⁰ The structure of was then solved by Direct methods using SHELX.⁸¹

Sapphire blue crystals of $[\text{Cu}(\text{HL}^5)(\text{CH}_3\text{CN})_2][\text{ClO}_4]_3$ measuring $0.26 \times 0.12 \times 0.09 \text{ mm}^3$ were obtained from the liquid diffusion of acetonitrile/ether solution and for X-ray data collection were mounted on CryoLoop on an Agilent Technologies/Oxford Diffraction Gemini CCD diffractometer. The analysis was performed using a 439, sixty-second frame ω -scan data collection strategy at 103 K to a $2\theta_{\text{max}} = 53.20^\circ$. The crystals obtained in monoclinic space group P21/c with unit cell parameters: $a = 23.0000(5) \text{ \AA}$, $b = 8.71951(15)$

$\text{\AA}$, $c = 30.2613(6) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 92.295(2)^\circ$, $\gamma = 90^\circ$, $V = 6064.0(2) \text{ \AA}^3$, $D_{\text{calc}} = 1.609 \text{ Mg m}^{-3}$, $Z = 8.12$ 678 independent data were corrected for absorption (transmission min./max. = 0.958/1.000; $\mu = 1.056 \text{ mm}^{-1}$) using SCALE3 ABSPACK.⁸⁰ The structure was solved by Direct methods using SHELXS.⁸¹

An orange colored crystal of $\text{Ni}(\text{L}^2)_2$ with a size $0.38 \times 0.30 \times 0.10 \text{ mm}^3$ was obtained by the liquid diffusion of dichloromethane/ether solution and mounted on a glass fiber on an Agilent Technologies/Oxford Diffraction Gemini CCD diffractometer for data collection. A total of 401 ten second frame ω -scan exposures of data at 100 K to a $2\theta_{\text{max}} = 56.30^\circ$ using monochromated Mo- $K\alpha$ radiation ($0.71073 \text{ \AA}$) from a sealed tube was acquired by employing the CrysAlisPro⁷⁹ CCD software package (v 1.171.36.32). Using CrysAlisPro⁷⁹ RED frame data were processed to obtain the final unit cell parameters: $a = 8.23199(17) \text{ \AA}$, $b = 20.1632(3) \text{ \AA}$, $c = 15.2322(4) \text{ \AA}$, $\beta = 99.355(3)^\circ$, $V = 2494.67(9) \text{ \AA}^3$, $D_{\text{calc}} = 1.356 \text{ Mg m}^{-3}$, $Z = 4$ to produce raw hkl data that were then corrected for absorption (transmission min./max. = 0.916/1.000; $\mu = 1.083 \text{ mm}^{-1}$) using SCALE3 ABSPACK.⁸⁰ The structure was solved by Direct methods in the space group $P2_1/n$ using SHELXS⁸¹ and refined by least-squares methods on F^2 using SHELXL.⁸¹

2.14 Computational methods

The use of computational methods tends to be helpful in the search for the solutions for chemical problems. These allows us to calculate various properties associated with the molecule such as absolute and relative energies, geometry optimization, electronic charge distribution, dipole and higher multipole moments, vibrational frequencies, electronic transitions and various other spectroscopic data. Also, to have a better insight of the structure stability and reaction mechanisms, the computational modelling done using

various available functional and basis sets gives us better understanding of the reaction pathway of the system. The theoretical methods used to perform the computational modelling can be divided into following categories.⁸² 1) *ab-initio* method: This method as the name suggests, is indicative of the beginning. To obtain the solution of the Schrodinger equation, only the physical constants are used to develop and solve the Hamiltonian for the system with no fitting of any experimental data.⁸³ Hartree-Fock (HF) method used for solving time-independent Schrödinger equation, is the simplest *ab-initio* method. HF method involves approximations such as: *a*) Born-Oppenheimer approximation (*b*) Exclusion of any relativistic effects (*c*) Consideration of the mean field of the electrons but excluding the specific interaction of the electrons with each other. 2) Semi-empirical methods: In these calculations, experimental data or the *ab-initio* calculations are fitted using simple Hamiltonian solutions. Larger systems can be studied using these methods as these are much faster than the *ab-initio* method. 3) Molecular mechanics (MM): In this method instead of using Hamiltonian, wave function or electron density, the molecule is considered as the set of atoms joined together by chemical bonds and the parameters like force constants, bond stretching, bending, and torsion are used to describe the molecular energy. Compared to *ab-initio* and semi-empirical methods, this method can be employed to very large systems involving several atoms. 4) Density functional methods (DFT): Density functional method is a methodology used for calculation of the electron density (ρ) of ground-state of the molecules. The benefit of using DFT is that it reduces the complexity of the calculations as only the energy in terms of electron density is considered and the calculation of wave-function (Φ) is not considered. So, in case of system with N electrons, it is feasible to account three variables rather than $3N$ degrees of freedom. DFT

is helpful in providing the ample understanding of the chemical properties of the molecules. The key theorems for understanding DFT are: *a) First Hohenberg-Kohn (H-K) Theorem:* The ground state properties of the system are determined by its electron density, $E = E[\rho]$, where ρ is the ground state electron density of the system. *b) Second Hohenberg-Kohn (H-K) Theorem:* The energy density functional, $E[\rho']$, where ρ' is different from the exact electron density of the system, determines the variability in the energy density functional, $E[\rho]$, giving $E[\rho'] > E[\rho]$.

According to the Kohn-Sham⁸⁴, the energy functional of the system can be equated as, $E[\rho] = T[\rho] + E_{\text{ext}}[\rho] + E_{\text{coul}}[\rho] + E_{\text{xc}}[\rho]$ 2-8

In equation 2-8, the term $E_{\text{xc}}[\rho]$ is calculated using various approximations by various methods like *a) Local Density Approximation (LDA)*, which assumes that the electron density is not much affected in non-homogeneous environment and it can be calculated using a homogeneous electron gas functional. *b) Generalized Gradient Approach* considered the actual non-homogeneous nature of electron density thus accounting for the electron density gradient.⁸⁵ *c) Hybrid Methods* employs both exchange and correlation functionals. B3LYP is the most common hybrid functional employed by inorganic and organometallic chemists to perform computational investigations.⁸⁶⁻⁸⁹

Methodology: The structural optimizations were performed using B3LYP functional and using 6-31G(d) basis set for NiL^3 complex. The results were also investigated using BP86 functional in combination with TZV/P basis set. The initial coordinates for NiL^3 complex were obtained from the reported crystal structure.⁹⁰ The calculations were carried out in gas phase and in the solution phase, using acetonitrile solvent. Using the conductor-like polarized continuum model (CPCM), the effect of polarity of the bulk solvent was taken

into consideration. In the studies described in Chapter 4, for structures with even number of electrons with spin state ($s = 0, 1$), the spin multiplicity ($M_s = 1, 3$) was considered. The calculations were performed as restricted singlet, restricted triplet and unrestricted singlet. To optimize the structures with odd number of electrons ($s = \frac{1}{2}$), the spin multiplicity ($M_s = 2$) was considered and the calculations were performed as restricted doublet. The transition states were taken as the one with single negative frequency. *Gaussian09* program was used to conduct the quantum- chemical calculations and for visualization Chemcraft software was used.

2.15 Procedure used for setting up the benzyl alcohol oxidation reaction and quantification of aldehydic products using GC-MS

The experimental procedure to obtain the data from the GC-MS has been described. To a vial containing a small stir bar, 0.5 ml (5 mmol) benzyl alcohol was dissolved in 10 ml of acetonitrile. To this solution was added; 127 mg (5 mol% of alcohol) of $[\text{CuL}^5]^{2+}$, 0.039 g TEMPO (5 mol % of alcohol) and 20 μL NMI (5mol% of alcohol). An internal standard of 0.08 M toluene solution was added. The blue colored solution was stirred for 4 hours open to air. The color of the reaction mixture was changed to dark green solution indicating the formation of the aldehyde product. 10 μL of analyte was abstracted from the solution which was diluted with acetonitrile to 1.5 ml and was analyzed by GC-MS to determine the yield and TON.

Calculation of Molarity of an internal standard (toluene)

Density of toluene = 0.87 g/mL

0.1ml weighs 0.087 g

$$\text{No. of moles} = 0.087/92.14 = 0.0009$$

$$M = (0.0009/10.63) \times 1000 = 0.08 \text{ M}$$

Total volume = 10.63 (10 mL CH₃CN + 0.51 mL C₆H₅CH₂OH + 0.02 mL NMI + 0.1 mL toluene)

$$M_1 V_1 = M_2 V_2$$

$$0.08 \times 10 \times 10^{-3} \text{ ml} = M_t \times 1.5 \text{ ml} \quad V_1 = 10 \text{ uL (volume of analyte for GC-MS)}$$

$$M_t = 0.08 \times 10 \times 10^{-3} / 1.5 = 5.3 \times 10^{-4}$$

Calculation of Molarity of Benzaldehyde (product)

$$R_F = (A_b/M_b) \times (M_t/A_t)$$

$$M_b = (A_b/R_F) \times (M_t/A_t) \quad 2-9$$

$$M_b \times 1.5 \text{ ml} = M_{b1} \times 10 \times 10^{-3} \text{ ml}$$

$$M_{b1} = (M_b \times 1.5) / 10 \times 10^{-3} \text{ put the value of } M_b \text{ from 2-9}$$

$$M_{b1} = \{(A_b/A_t) \times (M_t/0.998)\} \times (1.5/10 \times 10^{-3}) \text{ put the value of } M_t \text{ from above (} R_F = 0.998)$$

$$M_{b1} = \{(A_b/A_t) \times (0.56 \times 10^{-3} / 0.998)\} \times (1.5/10 \times 10^{-3})$$

$$M_{b1} = (A_b/A_t) \times 0.084$$

Calculations of number of moles of product (benzaldehyde)

$$N_1 = (M_{b1} \times 10.63) / 1000$$

$$\% \text{ Yield} = (N_1 / \text{number of moles of alcohol}) \times 100$$

$$\text{Standard deviation in \% yield} = (\text{dev in average } M \times 10.63) / 5 \times 100$$

Turnover number = Moles of product/ moles of catalyst used = (Average M x 10.63)/ 0.25

Standard deviation in turnover number = standard deviation in (Av M x 10.63)/ 0.25

or (standard deviation in % yield/ % yield) = (standard deviation in TON / TON)

standard deviation in TON = (standard deviation in % yield/% yield) x TON

CHAPTER III

ELECTROCATALYTIC HYDROGEN EVOLUTION AND HYDROGEN OXIDATION
WITH A Ni(PS)₂ COMPLEX

3.1 Background

As described in Chapter 1, there is a need for small molecular electrocatalysts for the hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR). While numerous HER electrocatalysts have been reported, the number of reported catalysts that perform both HER and HOR is much more limited. These include Ogo's and Rauchfuss's [Ni-Fe] complexes, DuBois's Ni(P^R₂N^R₂) complex and Re(L¹)₃.^{26, 51-52, 91} The latter complex has been extensively studied in the Grapperhaus group and was proposed to follow a ligand centered mechanism (Figure 1.8). Density functional theory calculations including functional M06 exchange correlation functional and the LANL2DZ basis set are consistent with the proposed mechanism.⁵²

Previous work done in Grapperhaus group described ability of [Re(L¹)₃]ⁿ⁺ (n = 0, 1, 2) to bind ethylene in the reversible fashion.⁴⁵ The ethylene binding was found to be in dynamic equilibrium as the cleavage of C-S bond was observed under inert conditions while ethylene purging in the dichloromethane solutions of the charged complex induces C-S bond formation. The redox controlled ethylene binding was found to show an increase in the equilibrium binding constant with the increase in the charge on Re(L¹)₃. The proposed mechanism for ethylene binding was found to follow ECE pathway. In the first

step, one electron oxidation of $\text{Re}(\text{L}^1)_3$ makes it susceptible to the ethylene binding, and the addition of ethylene molecule in the second step takes place with an equilibrium binding constant of $K_1 = 4.0 \text{ M}^{-1}$. The second electron oxidation of the di-thioether complex imparts stability to the C-S bonds and thus huge increment in the equilibrium binding constant from 4.0 M^{-1} in the single oxidized species to $K_2 = 2.5 \times 10^9$ was observed. Upon reduction of $[\text{Re}(\text{L}^1)_3]^+$ to $\text{Re}(\text{L}^1)_3$ decreases the ethylene binding and significantly lower binding constant $K_3 = 1.9 \times 10^{-11} \text{ M}^{-1}$ was recorded. The thermodynamic squares based on the ethylene affinity of $[\text{Re}(\text{L}^1)_3]^{n+}$ ($n = 0, 1, 2$) has been shown in Figure 3.1.

Figure 3.1 Schematic representation of thermodynamic squares for ethylene addition to $\text{Re}(\text{L}^1)_3]^{n+}$ ($n = 0, 1, 2$).^{45, 50}

$\text{Re}(\text{L}^1)_3$ possess a meridional arrangement of the three PS chelates, each with a p-type sulfur lone-pair that is potentially reactive. An enhancement of nucleophilic character of the metal thiolate is observed when the metal character in the highest occupied molecular orbital (HOMO) was equal to the sulfur p-type character. In these cases, oxidation of the

complex leads to a metal stabilized thiyl radical which has a radical shared between the metal and the sulfur. The thiyl radical character of cis sulfur donors supports reversible binding of simple alkenes such as ethylene to yield dithioether-metal complexes.^{45, 50} The coplanarity of the p-type lone pairs on sulfur atoms allows an out-of-phase combination of molecular orbitals that interacts with the π^* -orbital of ethylene. Also, the π -orbital of ethylene interacts with the vacant in-phase combination of sulfur p-orbitals, which are anti-bonding to the metal d-orbital, Figure 3.2. Hydrogen and ethylene share the same arrangement of HOMO/LUMO molecular frontier orbital arrangement, thus when analyzed for its ability to generate hydrogen or oxidize hydrogen, $\text{Re}(\text{L}^1)_3$ was found to be electrocatalytically active.

Figure 3.2 Frontier molecular orbitals of $\text{Re}(\text{L}^1)_3$, C_2H_4 and H_2 . (A) Meridional PS-chelates in $\text{Re}(\text{L}^1)_3$ displaying "p-type" lone-pair orientation. (B) (top) Interactions of $\text{Re}(\text{L}^1)_3$ frontier orbitals with LUMO of ethylene (B) (bottom) Interactions of $\text{Re}(\text{L}^1)_3$ frontier orbitals with HOMO of ethylene (C) HOMO/LUMO orbital symmetry of hydrogen.⁵¹

The addition of ethylene to the $\text{Re}(\text{L}^1)_3$ through the metal stabilized thiyl radical route has been shown in Figure 3.3 [path (a)]. Path (b) shows a traditional route of addition of ethylene through the dehalogenation of 1,2-dihaloalkanes. Following path (b) ethylene

can be generated back after one electron reduction of dicationic dithioether. Due to similarity in the frontier orbitals of ethylene and hydrogen, addition of hydrogen halides instead of dihaloalkanes can lead to the generation of hydrogen as a product.

Figure 3.3 Catalytic dehalogenation of dihaloalkanes.

$\text{Re}[(\text{L}^1)_3]$ was found to evolve hydrogen through the ligand centered mechanism with the maximum TOF of $32 \pm 3 \text{ s}^{-1}$. The overpotential recorded for HER with $\text{Re}[(\text{L}^1)_3]$ was 0.708 V. The Re-complex was also found to cleave dihydrogen in basic solutions with maximum TOF of $4 \pm 1 \text{ s}^{-1}$ at an overpotential of 0.970 V. This was the first ligand centered HER/HOR catalyst reported but has its limitations due to the high cost of Re-complex.⁵¹

The benzenethiol ligands serve as excellent donor atoms in the phosphanyl complexes due to the rapid deprotonation at the S-H functionality.⁹² Numerous complexes employing metals like Mo, Tc, Rh, Ir, Pd and Ni etc. has been reported in literature.⁹³ A mixture of $\text{Mo}_2\text{Cl}_3(\text{L}^1)_3$ and $\text{MoCl}_2(\text{L}^1)_2$ is generated upon the reaction of HL^1 ligand with MoCl_5 .⁹⁴ Thiolate ligand acting as a ligand and reducing agent as the +5 oxidation state of

Mo in MoCl_5 was reduced to +3 in $\text{Mo}_2\text{Cl}_3(\text{L}^1)_3$ and to +4 in $\text{MoCl}_2(\text{L}^1)_2$. Technetium (III) complex, $\text{Tc}(\text{L}^1)_3$ with HL^1 has been synthesized using $\text{TcCl}_4(\text{PPh}_3)_2$ and TcO_4^- .^{47, 95} Rhenium (III) complex, $[\text{Re}(\text{L}^1)_2(\text{S}_2\text{CNEt}_2)] \cdot (\text{CH}_3)_2\text{CO}$ in a distorted octahedral geometry has been reported by the reaction of $[\text{ReCl}_3(\text{N}_2\text{C}_5\text{H}_4\text{NH})(\text{HN}_2\text{C}_5\text{H}_4\text{N})]$, HL^1 and Et_3N in methanolic solutions.⁹⁶ A sulfur-bridged dimeric rhodium complex, $[\text{Rh}(\text{L}^1)(\text{CO})]_2$, which is found to catalyze the carbonylation of methanol to acetic acid is generated using $[\text{RhCl}(\text{CO})_2]_2$ as a metal precursor.⁹⁷ In another report, Rh(I) complex with HL^1 , $\text{Rh}(\text{L}^1)(\text{CO})(\text{PPh}_3)$ was found to reversibly bind sulfur dioxide while Ir(I) complex $\text{Ir}(\text{L}^1)(\text{CO})(\text{PPh}_3)$ showed an affinity for hydrogen.⁹⁸ $\text{Pd}(\text{L}^1)_2$ is reported to obtain by the Menshutkin-type reaction by the S-dealkylation of the corresponding thioether complex.⁹⁹ The reaction of $[\text{Ni}(\text{PMe}_3)_4]$ with HL^1 in the pentane solutions generated unstable complex, $\text{NiH}(\text{L}^1)(\text{PMe}_3)_2$, which dissociates into $\text{Ni}(\text{L}^1)(\text{PMe}_3)_2$ and $\text{Ni}(\text{L}^1)_2$ with the evolution of hydrogen.¹⁰⁰⁻¹⁰³

The synthesis of HL^2 employed the reaction of chlorodiisopropylphosphine with lithium 2-lithiobenzenethiolate in the THF solutions instead of chlorodiphenylphosphine which was used to prepare HL^1 .⁵⁹ The Iridium complex with HL^2 has been reported by Morales-Morales in 2002, by the reaction of IrCl_3 with HL^2 in the presence of triethylamine in the methanolic solutions.⁵⁹ Yellow prism crystals were obtained from dichloromethane/methanol mixture and structural determination demonstrated a distorted octahedral arrangement around the Ir. The Zn(II) complex with HL^2 was synthesized by Barry in an endeavor to isolate the CO_2 adducts upon the reaction with gaseous carbon dioxide.¹⁰⁴

In the pursuit to develop the economically viable catalysts for energy production, we employed first-row transition elements nickel and zinc metal precursors with redox non-innocent dialkyl/diarylbenzenethiol ligands. In this chapter, the syntheses, characterization and electrocatalytic behavior of nickel and zinc complexes with diphenylphosphine benzenethiol (HL^1) and diisopropylphosphine benzenethiol (HL^2) ligands have been reported.¹⁰⁵

3.2 Synthesis and spectroscopic characterization

The ligands HL^1 and HL^2 were synthesized by previously reported methods.⁵⁷⁻⁵⁹ Metal complexation was done by employing simple salts like $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{O}_2\text{CCH}_3)_2 \cdot 2\text{H}_2\text{O}$ to the deprotonated ethanolic solutions of the ligands to afford high yields up to 88%, Figure 3.4. $\text{Ni}(\text{L}^1)_2$ has been previously reported by Darensbourg by photolytic demethylation of the the bis(phosphinothioether) derivative.¹⁰¹ $\text{Zn}(\text{L}^2)_2$ has been synthesized by Kemp in the alcoholic solutions using triethylamine as an external base.¹⁰⁴ All the four complexes were characterized by employing various spectroscopic techniques including NMR, FT-IR, UV-Vis, and ESI-MS. ^1H -NMR and ^1P -NMR have been collected at room temperature in deuterated dichloromethane solutions. The results for complexes $\text{Ni}(\text{L}^1)_2$ and $\text{Zn}(\text{L}^2)_2$ were found to be consistent with prior reports. (See appendix for NMR and FT-IR data.) The electronic spectra of all the complexes have been compared below.

Figure 3.4 Synthesis of metal complexes $\text{Ni}(\text{L}^1)_2$, $\text{Ni}(\text{L}^2)_2$, $\text{Zn}(\text{L}^1)_2$ and $\text{Zn}(\text{L}^2)_2$.¹⁰⁵

The electronic spectra of all the four complexes were recorded in dichloromethane solutions, Figure 3.5. The UV-Vis spectrum of $\text{Ni}(\text{L}^1)_2$ in dichloromethane shows an intense charge transfer band at 301 nm ($18,500 \text{ M}^{-1} \text{ cm}^{-1}$) with a shoulder at 412 nm ($1860 \text{ M}^{-1} \text{ cm}^{-1}$). Also seen at 615 nm ($150 \text{ M}^{-1} \text{ cm}^{-1}$) was a weak *d-d* transition band. The comparable data for $\text{Ni}(\text{L}^1)_2$ with charge transfer bands at 298 nm ($25,560 \text{ M}^{-1} \text{ cm}^{-1}$) and 424 nm ($2850 \text{ M}^{-1} \text{ cm}^{-1}$) in chloroform has been reported by Darensbourg.¹⁰¹ The electronic spectra of $\text{Ni}(\text{L}^2)_2$ shows two high intensity bands at 303 ($14,580 \text{ M}^{-1} \text{ cm}^{-1}$) and 284 nm ($15,190 \text{ M}^{-1} \text{ cm}^{-1}$). As compared to $\text{Ni}(\text{L}^1)_2$, the charge transfer band at 412 nm was found to show a blue shift to lower wavelength at 408 nm ($2,605 \text{ M}^{-1} \text{ cm}^{-1}$). A similar blue-shift for the weak *d-d* transition from 615 nm in $\text{Ni}(\text{L}^1)_2$ to 610 nm in $\text{Ni}(\text{L}^2)_2$ ($1,185 \text{ M}^{-1} \text{ cm}^{-1}$) was observed. For $\text{Zn}(\text{L}^1)_2$, the charge transfer bands were recorded at higher energies of 272 ($23,600 \text{ M}^{-1} \text{ cm}^{-1}$) and 347 nm ($3,900 \text{ M}^{-1} \text{ cm}^{-1}$) as compared to the intense charge transfer bands of $\text{Ni}(\text{L}^1)_2$ at 301 and 412 nm. On substituting isopropyl groups in $\text{Zn}(\text{L}^2)_2$, a more intense band was observed at 279 nm ($21,352 \text{ M}^{-1} \text{ cm}^{-1}$) and a less intense band at 326 nm ($7,170 \text{ M}^{-1} \text{ cm}^{-1}$) as compared to the electronic bands of $\text{Ni}(\text{L}^2)_2$ at 303 and 284 nm.

Figure 3.5 Overlay of the electronic spectra of the metal complexes recorded in dichloromethane

3.3 Crystallographic studies

Single crystal x-ray diffraction was used to determine the solid state structure of $\text{Ni}(\text{L}^2)_2$ (CCDC 1549464). The crystal structures of $\text{Ni}(\text{L}^1)_2$ and $\text{Zn}(\text{L}^2)_2$ have been previously reported by Darensbourg and Kemp, respectively.^{101, 104} An ORTEP representation of $\text{Ni}(\text{L}^2)_2$ and $\text{Zn}(\text{L}^2)_2$ has been shown in Figure 3.6. Orange colored crystals of $\text{Ni}(\text{L}^2)_2$ in the monoclinic space group $P2_1/n$ were obtained upon liquid diffusion of a dichloromethane/ether mixture. The asymmetric unit contains a Ni(II) ion in a pseudo-square planar geometry coordinated to two phosphorus and two sulfur donors. Similar to $\text{Ni}(\text{L}^1)_2$, the bidentate chelates in $\text{Ni}(\text{L}^2)_2$ were found to be in *trans* arrangement. When compared to $\text{Ni}(\text{L}^1)_2$, $\text{Ni}(\text{L}^2)_2$ has statistically equivalent Ni-S bond distances, Table 3.1. The Ni-S distance reported for $\text{Ni}(\text{L}^1)_2$ was 2.166(3) Å whereas for $\text{Ni}(\text{L}^2)_2$, the Ni-S distances found to be 2.1591(3) and 2.1641(3) Å. The Ni-P distances for $\text{Ni}(\text{L}^2)_2$ and $\text{Ni}(\text{L}^1)_2$ were also found to be similar. The Ni-P distance of 2.173(3) Å was found in $\text{Ni}(\text{L}^1)_2$, while $\text{Ni}(\text{L}^2)_2$ has Ni-P distances of 2.1897(3) and 2.1798(3) Å. The Zn-S bonds in $\text{Zn}(\text{L}^2)_2$ were found to be longer than the $\text{Ni}(\text{L}^1)_2$ and $\text{Ni}(\text{L}^2)_2$. Zn-S1 was found to be

2.3034(4) while Zn-S2 was 2.3130(4) Å. Also, the Zn-P distances were found to be little longer. For $\text{Zn}(\text{L}^2)_2$, Zn-P1 and Zn-P2 distances were found to be 2.3966(4) and 2.3760(4) Å. The P-M-S bond angles in $\text{Ni}(\text{L}^1)_2$ and $\text{Ni}(\text{L}^2)_2$ are have values between 88.7(1) and 91.791(13)°. For $\text{Zn}(\text{L}^2)_2$, the geometry was distorted tetrahedral with S2-Zn-P2 bond angle of 89.178(12)° which was statistically equivalent to S1-Zn-P1 bond angle of 88.782(11)°. The values of S1-Zn-P2 and S2-Zn-P1 for $\text{Zn}(\text{L}^2)_2$ were 116.169(12) and 118.303(12)°, which were larger than the corresponding S-Ni-P angles in $\text{Ni}(\text{L}^1)_2$.

Figure 3.6 ORTEP¹⁰⁶ representation of $\text{Ni}(\text{L}^2)_2$ and $\text{Zn}(\text{L}^2)_2$ with thermal ellipsoids at 50% probability level.

Table 3.1 Comparison of Bond Distances (Å) and Bond Angles (°) for $\text{Ni}(\text{L}^1)_2$, $\text{Ni}(\text{L}^2)_2$ and $\text{Zn}(\text{L}^2)_2$.

	$\text{Ni}(\text{L}^1)_2$	$\text{Ni}(\text{L}^2)_2$	$\text{Zn}(\text{L}^2)_2$
M1-S1	2.166(3)	2.1591(3)	2.3066(3)
M1-S2	2.166(3)	2.1641(3)	2.3170(3)
M1-P1	2.173(3)	2.1897(3)	2.3864(3)
M1-P2	2.173(3)	2.1798(3)	2.3711(3)
S1-M1-S2	180.0(1)	177.689(15)	115.866(13)
S1-M1-P1	88.7(1)	89.503(13)	88.782(11)
S1-M1-P2	91.3(1)	89.211(13)	116.169(12)
S2-M1-P1	91.3(1)	91.791(13)	118.303(12)
S2-M1-P2	88.7(1)	89.573(13)	89.178(12)
P1-M1-P2	180.0(1)	177.325(15)	131.031(12)

3.4 Electrochemical studies

Cyclic voltammograms were obtained using 0.10 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte in 25 mL dichloromethane solutions using 0.50 mM concentrations of the complex at room temperature, Figure 3.7. The cyclic voltammogram of $\text{Ni}(\text{L}^1)_2$ when recorded at 200 mV/s in dichloromethane showed metal centered quasi-reversible oxidation $\text{Ni}^{\text{III/II}}$ at +0.25 V versus ferrocenium/ferrocene (Fc^+/Fc^0). A ligand centered irreversible oxidation at +1.22 V was attributed to the sulphur oxidation present in the ligand framework. $\text{Ni}(\text{L}^2)_2$ showed at metal centered quasi-reversible oxidation $\text{Ni}^{\text{III/II}}$ at +0.13 V versus ferrocenium/ferrocene (Fc^+/Fc^0). The shift in the oxidation event can be explained by the increased electron density by isopropyl groups at phosphorus in L^2 ligand framework. An anodic shift in the ligand-centered oxidation was observed from +1.22 V to +1.28 V. In Zinc (II) analogues, the irreversible oxidations consistent with the ligand- centered oxidations was observed at +0.71 and +0.76 V, respectively. When analyzed in the cathodic region, a quasi-reversible reduction assigned to $\text{Ni}^{\text{III/I}}$ was observed at -2.15 V vs Fc^+/Fc^0 and $\text{Ni}^{\text{I/0}}$ reduction was observed at -2.71 V. Though prior reports by Darensbourg did not mention any reduction events after -2.5 V vs Fc^+/Fc^0 . However, on the sweeping the potential to the negative potential up to -3.0V vs Fc^+/Fc^0 and then subtraction of the background current associated with the reduction of the solvent, dichloromethane reveals $\text{Ni}^{\text{I/0}}$ event which was hidden in the solvent reduction before. The reduction events recorded for $\text{Ni}(\text{L}^1)_2$ were found to be shifted by 1.61 and 1.48 V when compared with $[\text{Ni}(\text{PS-CH}_3)_2]^{2+}$ previously reported. This shift in reduction potentials was in accordance with the dissociation of the two CH_3^+ groups. Cyclic voltammogram of $\text{Ni}(\text{L}^2)_2$ shows reduction of $\text{Ni}^{\text{III/I}}$ at -2.48 V vs. Fc^+/Fc^0 . Substitution of

electron releasing isopropyl groups in $\text{Ni}(\text{L}^2)_2$ shifts the reduction potential of $\text{Ni}^{\text{I/0}}$ out of solvent window as expected, Table 3.2.

Figure 3.7 Cyclic voltammograms recorded in dichloromethane on 0.50 mM solutions of each complex with 0.1 M Bu_4NPF_6 as supporting electrolyte at a scan rate of 200 mV/s.

Table 3.2 Electrochemical data for complexes.

Compound	$\text{ML}^\bullet/\text{ML}$ (V)	Ni(III/II) (V)	Ni(II/I) (V)	Ni(I/0) (V)
$\text{Ni}(\text{L}^1)_2$	+1.22 (i)	+0.25 (q)	-2.15 (q)	-2.71 (i)
$\text{Zn}(\text{L}^1)_2$	+0.71 (i)	-	-	-
$\text{Ni}(\text{L}^2)_2$	+1.28 (i)	+0.12 (q)	-2.48 (q)	-
$\text{Zn}(\text{L}^2)_2$	+0.76 (i)	-	-	-
$[\text{Ni}(\text{PS-CH}_3)_2]^{2+}$		-	-0.54 (q)	-1.23 (i)

Data collected with 0.1 M Bu_4NPF_6 in dichloromethane solution with potentials versus Fc^+/Fc^0 . (i) denotes irreversible process and (q) denotes quasi-reversible process. For quasi-reversible events, the $E_{1/2}$ value is reported. Data for $[\text{Ni}(\text{PS-CH}_3)_2]^{2+}$ is taken from report by Darensbourg.¹⁰¹

3.5 Electrocatalytic hydrogen evolution reactions

All the four complexes $M(L^a)_2$ ($M = \text{Ni, Zn}$) ($a = 1$ or 2) have been screened for their ability to evolve hydrogen in dichloromethane solutions upon the addition of external acids CH_3COOH and HCl . Also, the complexes were studied for their ability to cleave dihydrogen molecule in the presence of external base Et_3N under 1 atm. H_2 . Only $\text{Ni}(L^1)_2$ was found to be active for both hydrogen evolution as well for the cleaving dihydrogen molecule. $\text{Ni}(L^2)_2$ was found to be active for hydrogen oxidation but was ineffective towards hydrogen evolution reactions. $\text{Zn}(L^1)_2$ and $\text{Zn}(L^2)_2$ was insufficient towards performing both HER and HOR.

3.5.1 HER with $\text{Ni}(L^1)_2$ using CH_3COOH . An increase in the cathodic currents at -2.15 V vs. Fc^+/Fc^0 was observed upon the successive additions of CH_3COOH to the solutions of $\text{Ni}(L^1)_2$, indicating electrocatalytic reduction. The cyclic voltammograms of 0.50 mM $\text{Ni}(L^1)_2$ in the presence of 0.1 M Bu_4NPF_6 in dichloromethane solutions were collected with the gradual increase in the acid concentrations and shown to display an increment in the peak intensity at -2.15 V. The data were collected at three different scan rates 0.2 V/s, 0.5 V/s and 1 V/s. At lower acid concentrations, the linear increase in the catalytic current was observed with the increase in CH_3COOH concentration, suggesting first order rate dependence with respect to acid concentration. The catalytic current becomes acid independent above 3.5 mM acid concentrations indicating that current was not diffusion controlled now and an acid saturated condition has been achieved, Figure 3.8. To evaluate turnover frequency, the data were collected at higher scan rates until the scan rate independence was achieved. For $\text{Ni}(L^1)_2$, at 5 V/s, the maximum TOF was found to be 51

s^{-1} . The overpotential of 1.1 V vs. Fc^+/Fc^0 was recorded using open circuit potential experiment.

Figure 3.8 Cyclic voltammograms (CVs) of 0.50 mM $\text{Ni}(\text{L}^1)_2$ in the presence of 0.1 M $[\text{Bu}_4\text{NPF}_6]$ in dichloromethane solution with subsequent addition of acetic acid at scan rate of 200 mV/s. CVs showing no acid (red), 1.4 mM (green), 2.8 mM (blue), 3.5 mM (black). (Inset) Plot of i_{cat}/i_p vs $[\text{CH}_3\text{COOH}]^{1/2}$

3.5.2 HER with $\text{Ni}(\text{L}^1)_2$ using HCl. When titrated with strong acid HCl, an additional cathodic event was observed at -1.9 vs. Fc^+/Fc^0 was observed which was attributed to the reduction of protonated species $\text{NiL}^1(\text{L}^1\text{H})$. Also, the cathodic increase at -2.15 vs. Fc^+/Fc^0 was observed indicating electrolytic reduction. With HCl, catalytic current becomes acid independent above 6.5 mM acid concentrations Figure 3.9. At lower acid concentrations, the linear increase in the catalytic current was observed with the increase in HCl concentration, suggesting first order rate dependence with respect to acid concentration, Figure 3.10. At higher scan rates, the maximum TOF with HCl using $\text{Ni}(\text{L}^1)_2$ was found to be 140 s^{-1} at an overpotential of 1.1 V.

Figure 3.9 Electrocatalytic hydrogen evolution reaction. Cyclic voltammograms (CVs) of 0.50 mM $\text{Ni}(\text{L}^1)_2$ in the presence of 0.1 M $[\text{Bu}_4\text{NPF}_6]$ in dichloromethane solution with subsequent addition of hydrochloric acid at scan rate of 200 mV/s. CVs showing no acid (red), 2.6 mM (blue), 3.9 mM (green), 5.2 mM (violet), 6.5 mM (yellow).

Figure 3.10 Plot of i_{cat}/i_p vs $[\text{HCl}]^{1/2}$.

Titration of $\text{Ni}(\text{L}^1)_2$ in dichloromethane solutions with HCl showed a shift in charge transfer band from 412 to 420 nm. This indicates towards the protonation of the $\text{Ni}(\text{L}^1)_2$ with HCl, Figure 3.11. Such charge transfer bands were found to be absent on titrations of $\text{Ni}(\text{L}^1)_2$ in dichloromethane solutions with CH_3COOH .

Figure 3.11 UV-Vis spectra showing titrations of $\text{Ni}(\text{L}^1)_2$ with hydrochloric acid in dichloromethane.

3.6 Mechanistic studies for hydrogen evolution reaction

When evaluated for the catalyst dependence at a fixed acetic acid concentration of 3.5 mM, the catalytic current was found to be first order dependence on the catalyst, Figure 3.12. To get more insights into the mechanism, the solutions of $\text{Ni}(\text{L}^1)_2$ was titrated with deuterated acid (CD_3COOD) and analyzed for HER. The KIE ($\text{CH}_3\text{COOH}/\text{CD}_3\text{COOD}$) observed for HER in dichloromethane solutions was 0.82 indicating inverse isotope effect which is consistent with the formation of metal hydride as suggested by reports from Gray and Fukuzumi.⁵³⁻⁵⁴

The robustness of the $\text{Ni}(\text{L}^1)_2$ was evaluated using controlled potential coulometry (CPC) experiments for 24 hours. During CPC experiments, the potential was hold to -1.9 V vs Fc^+/Fc^0 and the hydrogen was collected in dichloromethane solutions with the turnover number (TON) of 3.4 based on the total charge of 15 C.

Figure 3.12 Catalyst dependence studies. A plot showing variation catalytic current vs catalyst concentration at constant acetic acid concentration of 3.5 mM in dichloromethane solution.

Control experiments performed in the absence of $\text{Ni}(\text{L}^1)_2$ with CH_3COOH and HCl shows no catalytic current. This excludes the possibility of increase in current by the reduction of acid by itself. To analyze for any adsorbed species on the electrode surface, the working electrode (glassy carbon electrode) was taken out of the solution after performing the CV experiments and then washed with the working solvent dichloromethane and put back in the fresh dichloromethane solution containing acid and electrolyte and then CV experiments were performed. The absence of any catalytic current indicates that there was no adsorbed species or any degraded product on the electrode surface was deposited that might be responsible for catalytic current.^{51-52, 107} This indicates that the catalytic increment observed was entirely obtained from homogenous solutions.

3.6.1 Proposed mechanism for HER with $\text{Ni}(\text{L}^1)_2$. The hydrogen evolution with $\text{Ni}(\text{L}^1)_2$ was proposed to follow ECEC or CEEC mechanism, Figure 3.13. ECEC type of mechanism, with weak acid (CH_3COOH), involves the reduction (E) of $\text{Ni}(\text{L}^1)_2$ in the first step, followed by metal centered protonation (C) in the second step. This leads to the formation of $\text{Ni}(\text{III})\text{-H}$. The formed $\text{Ni}(\text{III})\text{-H}$ species was reduced (E) to $\text{Ni}(\text{II})\text{-H}$ after the addition of second electron and in the final step, the proton (C) from the solution reacts with anionic $\text{Ni}(\text{II})\text{-H}$ to release H_2 . This is in accordance with previous postulated mechanisms for HER with $\text{Ni}(\text{II})$ systems.¹⁰⁸⁻¹⁰⁹ With strong acid (HCl), the protonation event (C) occurs before the reduction leads to the formation of $[\text{NiL}^1(\text{HL}^1)]^+$. This species then gets reduced (E) to form $\text{Ni}(\text{III})\text{-H}$ after the second step. In the following step, $\text{Ni}(\text{III})\text{-H}$ species gets reduced (E) to $\text{Ni}(\text{II})\text{-H}$ which reacts with external proton (C) from the solution to evolve hydrogen,

Figure 3.13 Proposed HER mechanism with $\text{Ni}(\text{L}^1)_2$. Path (a) shows ECEC type of mechanism while Path (b) shows CEEC type of mechanism.

3.7 Electrocatalytic hydrogen oxidation reactions

3.7.1 HOR with $\text{Ni}(\text{L}^1)_2$ using Et_3N under 1 atm. H_2 . When screened for cleaving dihydrogen molecule, $\text{Ni}(\text{L}^1)_2$ was found to be active electrocatalysts in the presence of external redox active base triethylamine (Et_3N) under 1 atmosphere of hydrogen. The cyclic voltammograms of 0.50 mM $\text{Ni}(\text{L}^1)_2$ in the presence of 0.1 M Bu_4NPF_6 in dichloromethane solutions were collected with the gradual increase in the base concentrations and shown to displays an increment in the peak intensity at + 0.9V. The catalytic current becomes base independent above 1.68 mM Et_3N concentrations indicating base saturated conditions, Figure 3.14. The maximum TOF recorded for hydrogen oxidation with $\text{Ni}(\text{L}^1)_2$ using Et_3N was 23 s^{-1} with an overpotential of 0.33 V.

Figure 3.14 Electrocatalytic hydrogen oxidation reaction. Cyclic voltammograms (CVs) of 0.50 mM $\text{Ni}(\text{L}^1)_2$ in the presence of 0.1 M $[\text{Bu}_4\text{NPF}_6]$ in dichloromethane solution with subsequent addition of redox active base triethylamine under 1 atm. H_2 at scan rate of 200 mV/s.

3.7.2 HOR with $\text{Ni}(\text{L}^2)_2$ using Et_3N under 1 atm. H_2 . $\text{Ni}(\text{L}^2)_2$ was also found to catalyze hydrogen oxidation with the maximum TOF of 19 s^{-1} at an overpotential of 0.49V. The catalytic current becomes base independent above 0.84 mM Et_3N concentrations indicating

that current was not diffusion controlled now and a base saturated condition has been achieved, Figure 3.15.

Figure 3.15 Electrocatalytic hydrogen oxidation reaction. Cyclic voltammograms (CVs) of 0.50 mM $\text{Ni}(\text{L}^2)_2$ in the presence of 0.1 M $[\text{Bu}_4\text{NPF}_6]$ in dichloromethane solution with subsequent addition of redox active base triethylamine under 1 atm. H_2 at scan rate of 200 mV/s.

Control experiments were performed in the presence of $\text{Ni}(\text{L}^1)_2$ or $\text{Ni}(\text{L}^2)_2$ with Et_3N under N_2 atmosphere shows no catalytic current. This excludes the possibility of increase in the current due to oxidation of the redox active base Et_3N . Also, to be noted that, $\text{Ni}(\text{L}^1)_2$ and $\text{Ni}(\text{L}^2)_2$ were found to be inadequate for hydrogen oxidation using redox non-active bases like 2,6 lutidine $[(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N}]$.¹¹⁰ This indicates that Et_3N serves the dual role as base and redox mediator in initiating the hydrogen cleavage. Initial oxidation of Et_3N yields $[\text{NEt}_3]^+$, which on reaction with second molecule of Et_3N leads to H- atom abstraction forming protonated species $[\text{HNEt}_3]^+$ and radical species $[\text{Et}_2\text{N}^\bullet=\text{CHMe}]$.^{24, 111-113} This

radical species was the probable active radical species for H₂ oxidation, but still the exact nature of the species and exact mechanism for dihydrogen oxidation remains unresolved at this point.

3.8 Conclusions

The Ni (II) and Zn (II) complexes with dialkyl/diaryl-phosphine benzenethiolate ligands have been synthesized and characterized by spectroscopic techniques and screened for their ability to electrocatalytically evolve hydrogen and oxidize hydrogen. Ni(L¹)₂ has been found to be active electrocatalyst to evolve hydrogen with the maximum turnover frequency of 140 s⁻¹ at an overpotential of 1.1 V and oxidize dihydrogen with maximum turnover frequency of 23 s⁻¹ at an overpotential of 0.49 V. The maximum TON of 3.4 was recorded for hydrogen evolution. Ni(L²)₂ was found to be an active electrocatalyst for dihydrogen oxidation with maximum turnover frequency of 19 s⁻¹ at an overpotential of 0.33 V. The mechanism for HER with Ni(L¹)₂ was proposed to be ECEC or CEEC type. The mechanism for HOR still remains unresolved but believed to proceed through a radical species formed after the oxidation of Et₃N.

CHAPTER IV

ELECTROCATALYTIC HYDROGEN EVOLUTION REACTION WITH
BIS(THIOSEMICARBAZONATO)NI (II) COMPLEX

4.1 Background

Recently, our lab reported electrocatalytic hydrogen evolution with Zn(II) and Cu(II) by employing redox active bis(thiosemicarbazone) ligands. This chapter details the study of the evolution of hydrogen with a bis(thiosemicarbazonato) Ni(II) complex. The synthesis of these systems is comparatively convenient as compared to one described in Chapter 3 as the ligand synthesis can be done under aerobic conditions using cheap and easily available starting materials.

Bis(thiosemicarbazone) complexes, which have been known for more than 50 years, are a class of Schiff base systems generated from the elimination reaction between thiosemicarbazides and diones in the presence of catalytic amounts of acid at room temperature, Figure 4.1.⁶⁰ Bis(thiosemicarbazones) and their metal complexes have been extensively studied for their biological activities including ant-viral, anti-cancer, and anti-malarial.¹¹⁴⁻¹¹⁵ The radiolabeled Cu(II) complex, CuL³, has been explored as an imaging agent to locate the hypoxic tissues for PET studies.¹¹⁶ This has been attributed to the easy transport of Cu(II) complex through the cells while the reduced Cu(I) species gets trapped inside the cell under low oxygen amounts. CuL³ has also been evaluated for its therapeutic use for Parkinson's disease in various animal studies.¹¹⁷ Cu(II) complexes with modified

ligand glyoxalbis[N4-methylthiosemicarbazonato] has been found to increase cellular metabolism is observed in the mice cells.¹¹⁷ Additionally, the Zn(II) complex, ZnL^3 , ($\text{L}^3 =$ diacetyl-bis(N-4-methyl-3-thiosemicarbazonato)) has been found to have fluorescent properties.¹¹⁸

Figure 4.1 Schematic representation of synthesis of ligand diacetyl-bis(N-4-methyl-3-thiosemicarbazonato), H_2L^3 .

Bis(thiosemicarbazone) are redox active ligands that provide a tetradentate, square planar N_2S_2 coordination sphere. The soft donors impart stability to the lower oxidation states of the metals like zinc, copper and nickel.¹¹⁹⁻¹²³ The redox non-innocence of the ligand is attributed to the reduction of the terminal α -diimine unit into a π -radical anion.¹²³⁻

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4.1.1 Hydrogen evolution reaction with ZnL^3 and CuL^3

Present work in our group focuses on the exploitation of the redox non-innocence of the bis(thiosemicarbazone) ligands for their electrocatalytic ability to generate hydrogen using external acid source in organic solvents. ZnL^3 and CuL^3 has been found to be active electrocatalysts for hydrogen evolution reactions, Figure 4.2.¹²⁵⁻¹²⁶ ZnL^3 represents the example of the transition metal free active catalyst for hydrogen evolution reaction under homogenous conditions.

Figure 4.2 Structural representation of diacetyl-bis(N-4-methyl-3-thiosemicarbazonato) zinc(II), ZnL^3 and diacetyl-bis(N-4-methyl-3-thiosemicarbazonato) copper(II), CuL^3 complexes.

The HER activity of ZnL^3 is attributed to a ligand centered mechanism.¹²⁵ With acetic acid as a proton source in methanol solutions, ZnL is found to evolve hydrogen with the maximum TOF of 1170 s^{-1} at an overpotential of 756 mV. In acetonitrile solutions, ZnL^3 operates to evolve hydrogen with the TOF of 1170 s^{-1} at a higher overpotential of 1.07 V with an acid independent regime is observed above 23 mM of acetic acid concentrations. The lower value of overpotential recorded in methanol solutions is attributed to easier ligand protonation before the reduction step which due to the proton shuttling on the outer coordination sphere in ZnL^3 .¹²⁷ The HER catalysis is second-order in catalyst and second order with respect to acetic acid concentration. Kinetic isotope effect studies performed using deuterated acetic acid CD_3COOD gave a value of 1.2 which is inconsistent with values reported for metal hydrides. The catalyst displayed 37 turnovers over 2.5 hours at a constant potential of -1.7 V with a minimum faradaic efficiency of 85 %.

The HER mechanism for ZnL^3 is evaluated using density functional theory calculations by employing the B97D functional with the 6311 g (d) basis set. The proposed mechanism involves protonation and reduction at the ligand center giving rise to radical species ($\text{ZnHL}^{3\cdot}$), Figure 4.3. Homocoupling of two molecules of ($\text{ZnHL}^{3\cdot}$) in the later step, generates hydrogen evolving complex $[\text{Zn}_2(\text{HL}^{3\cdot})_2]$. Homolytic cleavage of the N-H bonds

leads to the evolution of hydrogen, giving back two molecules of ZnL^3 catalyst. A parallel route of the mechanism is proposed to be heterocoupling of $(\text{ZnHL}^3\cdot)$ and $[\text{Zn}(\text{H}_2\text{L}^3\cdot)]^+$ yielding $[\text{Zn}_2(\text{H}_3\text{L}^3\cdot)_2]^+$ which then evolves hydrogen in the next step and gives back ZnL^3 .

ZnL^3 is also screened for its ability to cleave dihydrogen molecule in the presence of external base triethylamine in methanolic solutions and is found to catalyze hydrogen oxidation reaction with a TOF of 72 s^{-1} under 1 atm. of H_2 on the addition of triethylamine. The overpotential recorded for HOR with ZnL^3 is 310 mV.

The metal free bis(thiosemicarbone) ligand H_2L^3 is also investigated for HER and HOR. When analyzed under acidic conditions in methanolic solutions, H_2L^3 is found to evolve hydrogen with TOF of 1320 s^{-1} at an overpotential of 1430 mV. For HOR, H_2L^3 displays a TOF of 32 s^{-1} with an overpotential of 330 mV under 1 atm. of hydrogen.¹²⁸

Figure 4.3 Postulated ligand centered mechanism for hydrogen evolution reaction with ZnL^3 .¹²⁵

In addition to ZnL^3 , the neutral, monomeric Cu(II) complex, CuL^3 , is also screened for HER activity in acetonitrile and dimethylformamide solutions.¹²⁶ In acetonitrile solutions, a maximum TOF of $9,900 \text{ s}^{-1}$ is reported at an overpotential of 0.80 V. In dimethylformamide solutions, CuL^3 is found to evolve hydrogen electrocatalytically with TOF of 5140 s^{-1} with an overpotential of 0.76 V. The maximum TON of 73 is recorded by performing by the controlled potential electrolysis at a potential of -1.65 V vs ferrocenium/ferrocene in acetonitrile solutions for 3.6 hours. While the same TON of 73 is determined in dimethylformamide solutions when the electrolysis is performed for 23.4 hours. To gain further insights into the HER mechanism, the H/D kinetic isotope effect (KIE) is evaluated and KIE of 7.54 is recorded which is consistent with ligand centered activity.⁵¹ The catalyst displays first-order dependence on the catalyst concentration and second-order dependence on the acid concentration.

To elucidate the HER mechanism for CuL^3 , density functional theory calculations using B3LYP functional and the 6-311g(d,p) basis set were performed. The mechanism for HER with CuL^3 is proposed to be CECE type, Figure 4.4. The first step involves the ligand centered protonation at hydrazine nitrogen generating cationic species $[\text{CuL}^3\text{H}]^+$. In the second step, metal centered reduction takes place that yields the neutral Cu(I) species $[\text{CuL}^3\text{H}]$. This is followed by the protonation on the second hydrazino nitrogen generating $[\text{CuL}^3\text{H}_2]^+$. In the next step, electron reduction at the ligand center gives neutral species, $[\text{CuL}^3\text{H}_2]$. The radical on the nitrogen induces the tautomeric arrangement of the proton leading to the coordination of the protons on the adjacent nitrogens in the hydrogen evolving complex. In the final step of the mechanism, the evolution of hydrogen takes place and generation of CuL^3 complex takes place. CuL^3 system demonstrates the metal-assisted

ligand-centered reactivity for hydrogen evolution where metal center is acting as an electron reservoir to facilitate the catalysis at the redox active ligand framework.¹²⁸

Figure 4.4 Proposed metal assisted ligand centered mechanism for hydrogen evolution reaction with CuL^3 .¹²⁶

4.1.2 Hydrogen evolution reaction with NiL: Straistari's catalyst

In addition to the Zn(II) and Cu(II) complexes of diacetyl-bis(N-4-methyl-3-thiosemicarbazonato) studied by our group, Straistari reported HER activity on the neutral, monomeric Ni(II) bis(thiosemicarbazonato) complex, NiL [$\text{L} = 4\text{-}\{\text{bis}(4\text{-}(p\text{-methoxyphenyl})\text{-thiosemicarbazonato})\}\text{-2,3-butane}\}$], Figure 4.5¹²⁹ The reported ligand, H_2L has been synthesized differently than diacetyl-bis(N-4-methyl-3-thiosemicarbazonato), H_2L^3 described above. H_2L has been obtained by the refluxing 2,3-dihydrazide-butane with two equivalents of 1-isothiocyanato-4-methoxy-benzene in ethanolic solutions.

Figure 4.5 Structural representation of [4-{bis(4-(p-methoxyphenyl)-thiosemicarbazonato)}-2,3-butane] Ni(II) complex NiL.¹²⁹

NiL is found to evolve hydrogen in the dimethylformamide solution with trifluoroacetic acid as an external acid. The turnover frequency of 3080 s^{-1} is recorded at an overpotential of 0.4 V. At a constant potential of -1.2 V controlled potential coulometry is performed for 16 hours and a faradaic efficiency of 80 % is determined with a TON of 21. Mechanistic details were elucidated using density functional theory calculations using BP86 functional and TZV/P basis set. The mechanism for HER is proposed to be ECEC type in which the first step is the ligand-centered reduction followed by the protonation at the coordinated nitrogen. In the next step, reduction at the metal center takes place thus, generating $d^9 \text{ Ni(I)}$. In the later step after reduction, the protonation occurs at the Ni(I) center thus yielding Ni(III)-H species. This species is considered as the catalytically active moiety to evolve hydrogen. NiL is believed to follow the ligand assisted metal centered catalysis in which the redox active ligand is facilitating the chemistry to takes place at the active metal center, Figure 4.6.

Figure 4.6 Proposed hydrogen evolution reaction mechanism with NiL.¹²⁹

4.2 Synthesis and characterization of NiL³

Analogous to the ZnL³ and CuL³ complexes described above, the neutral, monomeric Ni(II) complex, NiL³, Figure 4.7 is evaluated for its ability to evolve hydrogen. The dark green NiL³ complex is synthesized in the methanolic solutions of nickel acetate and H₂L³ as described in Chapter 2 of this dissertation. The identity is confirmed by ¹H NMR in d₆-DMSO and FT-IR spectrum collected on the solid powdered sample using ATR attachment. The single crystal x-ray structure of NiL³ is previously reported by Dilworth.⁹⁰

Figure 4.7 Structural representation of diacetyl-bis(N-4-methyl-3-thiosemicarbazonato) Ni(II), NiL³.

4.3 Electrochemical studies

Cyclic voltammograms (CVs) of 0.30 mM NiL^3 in dimethylformamide solutions, Figure 4.8 containing 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte were collected. On sweeping the potential in the cathodic region two quasi-reversible peaks and one irreversible peak were observed in the region from 0 to -2.5 vs Fc^+/Fc^0 . The first reduction event observed at -1.55 V vs Fc^+/Fc^0 is assigned to the ligand centered reduction, the second reduction event is assigned to the $\text{Ni}^{\text{II/I}}$ reduction at -2.18 V vs Fc^+/Fc^0 . CVs were collected at scan rates from 100 to 500 mV/s and an increase in the current is reported. The diffusion limited regime of the ligand-centered and $\text{Ni}^{\text{II/I}}$ reduction is established and increase in the peak current respect with respect to the potential is plotted. The resulting Cottrell plots gave the diffusion coefficient of $2.74 \times 10^{-5} \text{ cm}^2/\text{s}$ in dimethylformamide solutions using Randles- Sevcik equation.⁶²

Figure 4.8 Cyclic voltammograms of 0.30 mM NiL^3 in 25 ml dimethylformamide solution collected at scan rates from 100-500 mV/s (top). Plot of the peak current vs square root of scan rate collected from scan rates from 100-500 mV/s (bottom).

4.4 Hydrogen evolution reactions with NiL^3

Hydrogen evolution reactions with NiL^3 has been studied using acetic acid and trifluoroacetic acid as an external proton source in acetonitrile and dimethylformamide solutions. In acetonitrile, NiL^3 is found to have higher catalytic activity as compared to dimethylformamide solutions. The recorded results are explained below.

4.4.1 Electrocatalytic hydrogen evolution reaction with NiL^3 with acetic acid in acetonitrile solutions

To evaluate the HER, acetic acid is added as a proton source to 0.30 mM acetonitrile solutions of NiL^3 and CVs were at three different scan rates of 200, 500 and 1000 mV/s for acid dependent studies. An increase in the cathodic current is observed at a potential of 2.20 V vs Fc^+/Fc^0 at a scan rate of 500 mV/s. The catalytic current is found to be acid-independent at an acetic acid concentration above 12.60 mM, Figure 4.9. Upon establishing the acid independent region at these scan rates, CVs were recorded at higher scan rates in

order to establish the scan rate independent region. At a scan rate of 7000 mV/s, the cathodic current is found to be independent of the scan rate where catalytic current (i_c) of 2.32 mA is recorded. The TOF of 4161 s⁻¹ is recorded at a scan rate of 7000 mV/s using foot-of-the-wave analysis described in Chapter 2. The overpotential of 0.52 V is determined.⁶⁶

Figure 4.9 Cyclic voltammograms of 0.30 mM NiL³ in 25 ml acetonitrile solution collected at scan rate of 500mV/s with the increasing acetic acid concentrations of 0, 1.4, 2.8, 4.2, 5.6, 7.0, 8.4, 9.8, 11.2, 12.6 mM (top).

4.4.2 Electrocatalytic hydrogen evolution reaction with NiL³ with acetic acid in dimethylformamide solutions

The catalytic activity of NiL³ using acetic acid is also accessed in dimethylformamide solutions. An increase in the cathodic current at a potential of -2.32 V

vs Fc^+/Fc^0 is recorded with the successive additions of acetic acid at scan rates of 200, 500 and 1000 mV/s. The catalytic current becomes dependent of the acid concentration at an acid concentration of 9.80 mM, Figure 4.10. Using FOWA, at higher scan rate of 5000 mV/s, where the current demonstrates scan rate independence, a TOF of 1196 s^{-1} is calculated at an overpotential of 0.55 V. The increase in the catalytic current shows the second-order dependence with respect to the acid concentration.

Figure 4.10 Cyclic voltammograms of 0.30 mM NiL^3 in 25 ml dimethylformamide solution collected at scan rate of 200 mV/s with the increasing acetic acid concentrations of 0, 4.2, 5.6, 7, 8.4, 9.8 mM (top).

4.4.3 Electrocatalytic hydrogen evolution reaction with NiL^3 with trifluoroacetic acid in acetonitrile solutions

The catalytic activity of NiL^3 is also accessed using stronger acid trifluoroacetic acid in acetonitrile. In acetonitrile solutions, an increase in the cathodic current at -2.11 V vs Fc^+/Fc^0 is attributed to the catalytic reduction and the current becomes independent of

the acid concentration at an acid concentration of 18.0 mM, Figure 4.11. The TOF of 1324 s^{-1} is recorded at a scan rate of 7000 mV/s . The second order dependence on acid concentration is found when i_c/i_p is plotted with respect to the acid concentration. The overpotential of 0.67 V is recorded using trifluoroacetic acid in acetonitrile solutions.

Figure 4.11 Cyclic voltammograms of 0.30 mM NiL^3 in 25 ml acetonitrile solution collected at scan rate of 200 mV/s with the increasing trifluoroacetic acid concentrations of $0, 6, 8, 10, 12, 14, 16, 18 \text{ mM}$ (top).

4.4.4 Electrocatalytic hydrogen evolution reaction with NiL^3 with trifluoroacetic acid in dimethylformamide solutions

When analyzed in dimethylformamide solutions, catalytic current is observed at $-1.80 \text{ vs Fc}^+/\text{Fc}^0$, upon the addition of trifluoroacetic acid. The acid-independent region is

observed at an acid concentration of 32.0 mM, Figure 4.12. The TOF of 115 s^{-1} is recorded at scan rate of 5000 mV/s. The second-order acid dependence is established.

Figure 4.12 Cyclic voltammograms of 0.30 mM NiL^3 in 25 ml dimethylformamide solution collected at scan rate of 200mV/s with the increasing trifluoroacetic acid concentrations of 0, 4, 8, 12, 16, 20, 24, 32 mM (top).

Control experiments performed in the absence of NiL^3 with acetic acid and trifluoroacetic acid in acetonitrile and dimethylformamide solutions showed no significant current at corresponding catalytic potentials mentioned above. CVs were also collected by taking the working electrode (glassy carbon electrode) out of the solution after performing the acid dependent studies. Glassy carbon electrode is then polished with the working solvent and is used again with the fresh solutions containing acid and electrolyte. The

absence of any catalytic current indicates that there is no adsorbed species or any degraded product on the electrode surface is deposited that might be responsible for catalytic current. This indicates that the catalytic increment observed is entirely obtained from homogenous solutions (see appendix for CVs of control experiments).

The robustness of the catalyst NiL^3 is evaluated using controlled potential coulometry (CPC) experiments for 18 hours. The experiments were conducted in acetonitrile and dimethylformamide solutions using acetic acid and trifluoroacetic acid. In acetonitrile solutions containing 0.1 M Bu_4NPF_6 , CPC experiment is performed 0.30 mM NiL^3 and 12.60 mM acetic acid. The potential is hold at -1.75 vs Fc^+/Fc^0 . The TON of 159 is calculated based on the total charge of 92 C., Figure 4.13. Similar studies using 18.0 mM trifluoroacetic acid with 0.30 mM NiL^3 in acetonitrile solutions at an applied potential of -1.32 vs Fc^+/Fc^0 for 18 hours yielded a TON of 63 based on the total charge of 36 C.

Figure 4.13 Controlled potential coulometry of 0.30 mM NiL^3 in 0.1 M Bu_4NPF_6 with 12.6 mM acetic acid added in acetonitrile solutions.

In dimethylformamide solution containing 0.1 M Bu₄NPF₆, the CPC experiment is performed at a constant potential of -1.95 vs Fc⁺/Fc⁰ using 0.30 mM NiL³ and 9.80 mM acetic acid. The total charge of 37C is obtained over the period of 18 hours which accounted for the TON of 64. Similar results were obtained using 0.30 mM NiL³ at a constant potential of -1.48 vs Fc⁺/Fc⁰ using 32 mM trifluoroacetic acid in dimethylformamide solution, the charge of 23 C is obtained which accounted for the total TON of 40.

4.5 Mechanistic studies

To evaluate the mechanism of HER with NiL³ catalyst dependence, acid dependence, kinetic isotope effect and DFT studies were carried out, that has been described below.

4.5.1 Catalyst dependent studies at a fixed acid concentration in acetonitrile solutions

The order of the reaction is determined with respect to the concentration of the catalyst. At fixed acetic acid concentration of 12.6 mM in acetonitrile solutions, the concentration of NiL³ is varied, and the catalytic current is recorded at different catalyst concentrations of 0.125 mM, 0.25 mM, 0.50 mM and 1.00 mM. When the cathodic current obtained is plotted against the catalyst concentration, a linear relationship is established. This corresponds to the first-order dependence on the concentration of the catalyst, Figure 4.14.

Figure 4.14 Catalyst dependence studies. Plot of catalytic current catalyst concentration at a constant acid concentration of 12.6 mM in acetonitrile solutions.

4.5.2 Acid dependent studies in acetonitrile solutions

The order of the reaction with respect to acid is obtained by plotting the i_{cat}/i_p with respect to the acid concentrations. The values of i_{cat} is obtained by the cyclic voltammograms recorded under different acid concentrations. Herein, we report the acid dependent studies with acetic acid and trifluoroacetic acid in acetonitrile and dimethylformamide solutions. In all the cases, the second-order dependence with respect to acid is recorded. Figure 4.15 shows the plot of acid dependent studies with acetic acid in acetonitrile solutions at 500 mV/s. Figure 4.16 shows the plot of acid dependent studies with acetic acid in dimethylformamide solutions at 200 mV/s. Figure 4.17 shows the plot of acid dependent studies with trifluoroacetic acid in acetonitrile solutions at 200 mV/s.

Figure 4.18 shows the plot of acid dependent studies with trifluoroacetic acid in dimethylformamide solutions at 500 mV/s.

Figure 4.15 Acid dependence studies. Plot of i_{cat}/i_p vs $[CH_3COOH]$ in acetonitrile solutions at 500 mV/s.

Figure 4.16 Acid dependence studies. Plot of i_{cat}/i_p vs $[CH_3COOH]$ in dimethylformamide solutions.

Figure 4.17 Acid dependence studies. Plot of i_{cat}/i_p vs $[CF_3COOH]$ in acetonitrile solutions.

Figure 4.18 Acid dependence studies. Plot of i_{cat}/i_p vs $[CF_3COOH]$ in dimethylformamide solutions.

4.5.3 Kinetic isotope effect (KIE) studies

To get more insights into the mechanism, the acetonitrile and dimethylformamide solutions of NiL^3 were titrated with deuterated acids CD_3COOD and CF_3COOD and analyzed for HER. The KIE ($\text{CH}_3\text{COOH}/\text{CD}_3\text{COOD}$) observed for HER in acetonitrile solutions is 0.75 indicating inverse isotope effect which is consistent with the formation of metal hydride as suggested by reports from Gray and Fukuzumi.⁵³⁻⁵⁴ In dimethylformamide solutions, KIE ($\text{CH}_3\text{COOH}/\text{CD}_3\text{COOD}$) of 0.64 is observed for HER. On screening CF_3COOD , KIE of 0.54 and 0.57 is recorded in acetonitrile and dimethylformamide solutions respectively.

4.5.4 Computational studies

To have better insights into the mechanism for HER with NiL^3 , density functional theory (DFT) calculations were carried out using the B3LYP functional and the 6-311g (d,p) basis set and BP86 functional and TZV/P basis set. The geometry optimization is performed in both gas phase as well as in solvent phase using polarizable continuum model (PCM) calculations. All the input coordinates used for optimizing the geometries have been provided in appendix. Gas phase calculations carried out using B3LYP functional and the 6-311g (d,p) basis set and BP86 functional and TZV/P basis set showed similar results as discussed by Straistari.

The hydrogen evolution reaction with NiL^3 is found to follow different route with the input of solvent effects. Herein, the description of geometry optimization in acetonitrile using polarizable continuum model (PCM) calculations is given.

The input coordinates were taken from the previously reported crystal structure of NiL^3 . In the first step, the neutral NiL^3 complex is optimized as shown in Figure 4.19.

The ground state of NiL³ is best described as a restricted singlet Ni(II) (d⁸, $M_s=1$) coordinated to two nitrogens and two sulfur centers.

Figure 4.19 Optimized structure of NiL^3 with B3LYP/6311g (d, p), ($M_s = 1$, $q = 0$).

Table 4.1 shows the comparison of the bond distances obtained from the optimized structure and experimentally determined from X-ray crystallography.⁹⁰ In the optimized structure metal sulfur bond lengths are 0.05 Å longer than the experimental values. The S-Ni-N bond angles in the optimized geometry are found to be approximately 0.10- 0.48 degrees smaller than the experimentally reported values.

Table 4.1 Comparison of optimized and experimental bond distances (Å) and Bond Angles (°) for NiL^3 .

	NiL ³ (optimized)	NiL ³ (Experimental)
Ni-S1	2.208	2.155
Ni-S2	2.207	2.159
Ni-N1	1.868	1.861
Ni-N4	1.868	1.855
N1-N2	1.360	1.378
N4-N5	1.360	1.375
N1-Ni-N4	84.15	83.59
S2-Ni-N4	87.08	86.55
S1-Ni-N1	87.06	87.07
S2-Ni-S1	101.71	101.81

Next, the optimized structure of NiL^3 with B3LYP/6311g (d, p) is taken and electron is added to NiL^3 species giving one electron reduced $[\text{NiL}^3]^-$ species ($M_s = 2$, $q = -1$). Most of the spin density is found to be on the ligand backbone, Figure 4.20. This is accordance with the assignment of the first cathodic event observed in the CVs of NiL^3 to be a ligand centered reduction. Similar spin density is observed when the one electron reduced species $[\text{NiL}^3]^-$ is optimized in gas phase and solvent phase with B3LYP/6311g (d, p) and BP86/TZV/P. (see appendix)

Figure 4.20 Spin density plot of $[\text{NiL}^3]^-$ ($M_s = 2$, $q = -1$). Spin density on the H-atoms has not been included in the figure.

In the optimized $[\text{NiL}^3]^-$, the Ni-S distances are found to be 0.021 Å longer than in NiL^3 . The bond lengths of Ni-N are found to be decreased by 0.014 Å in the one electron reduced species, $[\text{NiL}^3]^-$. S-Ni-S bond angle is increased by 1.72° from 101.71° to 103.43°. The S-Ni-N bond angle is increased from 87.08° to 87.56°. The results have been summarized in Table 4.2.

Table 4.2 Comparison of optimized bond distances (Å) and Bond Angles (°) for NiL^3 and $[\text{NiL}^3]^-$

	NiL^3 (optimized)	$[\text{NiL}^3]^-$ (optimized)
Ni-S1	2.208	2.229
Ni-S2	2.207	2.229
Ni-N1	1.868	1.854
Ni-N4	1.868	1.854
N1-N2	1.360	1.372
N4-N5	1.360	1.372
N1-Ni-N4	84.15	83.59
S2-Ni-N4	87.08	87.56
S1-Ni-N1	87.06	86.54
S2-Ni-S1	101.71	103.43

Using the optimized structure of $[\text{NiL}^3]^-$, a proton is added at various positions including Ni, S and each N to evaluate the most likely site of protonation in the neutral complex $[\text{NiL}^3\text{H}]$ ($M_s = 2$, $q = 0$). For $[\text{NiL}^3\text{H}]$, the hydrazino protonated moiety is found to be energetically favored species in the PCM calculations using acetonitrile as a solvent. The energetic stability of the reduced/ protonated species $[\text{NiL}^3\text{H}]$ ($M_s = 2$, $q = 0$) has been shown in Figure 4.21. Species with protonation at the coordinated nitrogen N1 is found to be energetically similar to the hydrazino protonated moiety with the energy difference of only 2.85 kcal/mol. The species protonated at the amine nitrogen is found to be 12.56 kcal/mol higher in energy than the protonated hydrazine species. The sulfur protonation is disfavored by 13.62 kcal/mol. The formation of metal hydride is found to be least likely at this stage with the energy difference of 15.72 kcal/ mol from the most stable hydrazino protonated moiety.

Figure 4.21 Energetic stability of the reduced/ protonated species $[\text{NiL}^3\text{H}]$ using B3LYP/6311g (d, p) ($M_s = 2, q = 0$), using PCM calculations in acetonitrile solvent.

After optimizing all the possible sites for the first protonation, the electron is added in the next step to all the optimized structures obtained from Step 3. Energy minimizations of the doubly reduced and singly protonated species were performed in both the triplet ($M_s = 3, q = -1$) and singlet ($M_s = 1, q = -1$) states. Figure 4.22 shows the energetic stability of the reduced/protonated/reduced species in the triplet state. The doubly reduced, singly

protonated species with the protonation at the nickel is found to be the energetically most favorable species in the triplet state. When compared to the species protonated at the coordinated and hydrazine nitrogen, nickel protonated species is found to be lower in energy by 4.43 and 14.93 kcal/mol respectively. Triplet electronic state with the protonated amine N, is found to be energetically disfavored by 30.61 kcal/mol.

Figure 4.23 shows the energetic stability of the reduced/protonated/reduced species in the singlet state. In the singlet state, the doubly reduced, singly protonated species with the protonation at the coordinated nitrogen is found to be the energetically most favorable species. Species protonated at the hydrazine nitrogen is found to be higher in energy by 12.41 kcal/mol. Attempts to optimize the species protonated at the nickel center in the singlet state, leads to the break of the structure which is indicative of the fact that in singlet state when both the electrons are on the nickel, it will prefer square planar geometry. The species with the protonation on the amine nitrogen is found to be the highest in energy in the singlet state. Open shell singlet calculations were also carried out using unrestricted B3LYP functional to obtain the broken symmetry solutions where the electron density is on the ligand as well as on the metal. Out of all the geometries optimized for reduced/protonated/reduced species, $[\text{NiL}^3]^-$. These studies are in progress.

Figure 4.22 Energetic stability of the reduced/ protonated species/ reduced $[\text{NiL}^3\text{H}]^-$ B3LYP/6311g (d, p) ($M_s = 3$, $q = -1$), using PCM calculations in acetonitrile solvent.

Figure 4.23 Energetic stability of the reduced/ protonated species/ reduced $[\text{NiL}^3\text{H}]^-$ B3LYP/6311g (d, p) ($M_s = 1$, $q = -1$), using PCM calculations in acetonitrile solvent.

4.5.5 Proposed mechanism for HER with NiL³

The DFT studies are still in progress. Based on the experimental and theoretical studies so far, hydrogen evolution with NiL³ is proposed to occur through ECEC type. In the first step, electron addition takes place, which is a ligand centered reduction. Second step is the chemical step involving the addition of proton on the ligand framework at the hydrazino nitrogen, N² leading to the formation of protonated species Ni-N²H. Third step is the reduction step and involves the addition of electron to the protonated species which leads to the migration of the proton from the hydrazino nitrogen, N² of the ligand to the metal center making Ni(III) hydride. In the Step 4 is the chemical step which involves the addition of the proton to the coordinated nitrogen. In the final step, homolytic cleavage of the Ni(III)-H and the N-H bonds evolves hydrogen and the NiL³ is regenerated to be used for the next cycle, Figure 4.24.

Figure 4.24 Proposed mechanism for hydrogen evolution reaction with NiL³.

4.6 Conclusions

In the search of the low-cost catalysts to generate hydrogen electrocatalytically, redox non-innocence ligand bis(thiosemicarbazone) has been complexed with Ni(II) and the NiL^3 complex thus synthesized has been evaluated for its ability to evolve hydrogen in the acetonitrile and dimethylformamide solutions using acetic acid and trifluoroacetic acid as the external proton source. The maximum TOF frequency reported for NiL^3 is 4161 s^{-1} at an overpotential of 0.52V in acetonitrile solutions. Kinetic isotope effect studies revealed the inverse KIE indicating towards the possibility of formation of the metal hydride in the reaction pathway. Mechanistic dependent studies revealed the second-order dependence on the acid concentration. The order of the reaction is also found to be first-order with respect to the catalyst concentration by varying the catalyst concentrations at fixed acid concentration. With the support of DFT calculations, an ECEC type of mechanism for HER has been proposed.

CHAPTER V

COPPER CATALYSED AEROBIC OXIDATION OF BENZYLIC ALCOHOLS IN AN IMIDAZOLE CONTAINING N₄ LIGAND FRAMEWORK

5.1 Background

In organic synthesis, alcohol oxidation to aldehydes has traditionally employed various stoichiometric oxidants like chromium,¹³⁰⁻¹³¹ manganese,¹³²⁻¹³³ hypervalent iodine,¹³⁴⁻¹³⁵ and activated DMSO.¹³⁵⁻¹³⁷ Molecular oxygen can serve as an alternative oxidant, but this requires activation via a catalyst.¹³⁸⁻¹⁴³ Galactose oxidase is a naturally occurring fungal enzyme that uses oxygen to oxidizes D-galactose. The active site contains a copper (II) ion in a distorted square pyramidal geometry coordinated with two tyrosines, two histidines and a solvent molecule (i.e. water).¹⁴⁴⁻¹⁴⁷

The research described in Chapters 3 and 4 of this dissertation focused on catalytic hydrogen evolution and hydrogen oxidation, which mimics the activity of the hydrogenase enzymes. In contrast, the work in this chapter centers on catalytic alcohol oxidation, which mimics galactose oxidase. On comparison, the active sites of iron-only hydrogenase and galactose oxidase are similar as both contain redox active ligands and/or cofactors and perform multielectron reactions under physiological conditions near thermodynamic potentials.¹⁴⁸⁻¹⁵⁵ The active metal site performs these multielectron transformations synergistically with a redox active moiety positioned in its vicinity to promote the redox reactions with ease.¹⁴⁸⁻¹⁵⁵ The iron-only hydrogenase enzyme is capable of cleaving

hydrogen and has a non-innocent, redox active pyridyl unit and pterin cofactor in the proximity of Fe center.¹⁵³ In galactose oxidase, the phenoxyl radical on Tyr 272 is coordinated to the copper center in the axial or equatorial arrangement. The resonance stabilization of the radical occurs due to the antiferromagnetic coupling with copper center,¹⁵⁶⁻¹⁵⁷ Figure 5.1.

Figure 5.1 Active site of galactose oxidase (left) and iron-only hydrogenase (right).¹⁵²⁻¹⁵³

5.1.1 Mechanism of alcohol oxidation by galactose oxidase

The proposed mechanism for galactose oxidase is shown in Figure 5.2. The first step consists of the proton transfer between a metal coordinated alcohol and metal-bound Try495. After the acceptance of the proton, Try495 dissociates from the metal making the alcohol more susceptible to oxidation. In the next step, Tyr 272 abstracts the H[•] from the α - carbon bound to the alkoxide which is followed by the rearrangement of electrons. The Cu(II) center gets reduced to Cu(I) and the alcohol gets oxidized to aldehyde. Release of aldehyde takes place which is then followed by the coordination of the oxygen molecule to Cu(II) center as a superoxide radical in the third step. Superoxide radical abstracts the H[•] from the Tyr272, generating back Tyr272 radical. In the final step, hydroperoxide abstracts the proton from the Tyr495 and leaves as H₂O₂ molecule. In the later step,

coordination of the Tyr495 in the axial position generates back the catalytic center to be used in the next cycle.^{93, 158-161}

Figure 5.2 Mechanism of alcohol oxidation by galactose oxidase.¹⁶⁰

5.1.2 Copper complexes for oxidation of alcohols to aldehydes

The first use of simple copper complexes in the oxidation of alcohols to aldehydes was reported by Brackman and Gaasbeek in 1966.¹⁶² In that report, di-tert-butyl nitroxide

was used as a nitroxyl co-catalyst with phenanthroline/Cu^{II} complex to oxidize methanol to formaldehyde. This approach was further developed and refined by Semmelhack and Sheldon, who are considered pioneers in the field of Cu/nitroxyl-catalyzed aerobic alcohol oxidation.¹⁶³⁻¹⁶⁶ Semmelhack reported the oxidation of primary allylic and benzylic alcohols with CuCl and TEMPO in the presence of air in dimethylformamide solutions.¹⁶³ Sheldon, in his studies showed that use of external base KO^tBu in the presence of nitroxyl radical initiator TEMPO enhances the aerobic oxidation of allylic and benzylic alcohols at room temperature.¹⁶⁴ Potential use of 1,8-diazabicycloundec-7-ene (DBU) and *N*-methyl imidazole (NMI) as external bases in combination with Cu(II) salts and TEMPO to enhance the product yields have been explored vastly in recent years.¹⁶⁷ In the past decade, Stahl has perfected these studies with the use of Cu^IOTf/TEMPO, bipyridine, and NMI for the oxidation of wide variety of alcohols in the various solvents.¹⁶⁸⁻¹⁷¹

Figure 5.3 shows a mechanism for alcohol oxidation with Cu(I)OTf/TEMPO, bipyridine, and NMI as proposed by Stahl.¹⁶⁹ In the first step, aerobic oxidation of Cu(I) generates a peroxo-bridged, dinuclear Cu(II) complex. This is followed by H-atom transfer from TEMPOH to the Cu₂O₂ species to afford LCu(II)-OH. The Cu(II)-OH species thus formed reacts with the alcohol substrate producing alkoxide bound Cu(II) complex and releasing H₂O as the by-product. In the final step, the alkoxide species reacts with the TEMPO radical previously formed to abstracts the H-atom from the alkoxide species along with the concomitant reduction of Cu(II) to Cu(I), thus releasing aldehyde product and TEMPOH to complete the catalytic cycle.

Figure 5.3 Proposed mechanism of alcohol oxidation by $\text{Cu}^{\text{I}}\text{OTf}/\text{TEMPO}/\text{bpy}$ system.¹⁶⁹

The $\text{Cu}^{\text{I}}\text{OTf}/\text{TEMPO}/\text{bpy}$ system works best in the presence of two equivalents of NMI, thus making N_4 ligand framework if both NMI and bpy are coordinated to copper center. Several reports in the literature showed that N_4 and/or N_2O_2 chelated $\text{Cu}(\text{II})$ complexes in conjunction with nitroxyl radicals like TEMPO are active aerobic oxidation catalysts for alcohol oxidation.^{165, 172-174} Gamba studied $\text{Cu}(\text{II})$ coordinated with the neutral tetra-pyridyl ligand for the benzyl alcohol oxidation in the presence of TEMPO.¹⁷⁵ Punniyamurthy reported N_2O_2 chelated $\text{Cu}(\text{II})$ complex for the aerobic oxidation of variety of alcohols in toluene as a solvent at elevated temperatures.¹⁷⁶

In this chapter, two copper (II) complexes with N_4 ligand frameworks are evaluated for their ability to catalyse the aerobic oxidation of benzylic alcohols. The copper Schiff base complex $[\text{CuL}^4]^{2+}$ was found to reversibly bind the methanol across the metal as well as across ligand through the azomethine $\text{C}=\text{N}$ bond.¹⁷⁷ This complex was found to be inactive for the oxidation of benzylic alcohols. The reduced Schiff base complex $[\text{CuL}^5]^{2+}$ was found to be an active catalyst in the presence of TEMPO and NMI for the aerobic oxidation of benzylic alcohols to benzylic aldehydes with the maximum yields up to 99%

in 4 hours.¹⁷⁸ The comparison of the reactivity of the complexes $[\text{CuL}^4]^{2+}$ and $[\text{CuL}^5]^{2+}$ is shown in Figure 5.4.

Figure 5.4 Comparison of alcohol reactivity of $[\text{CuL}^4]^{2+}$ and $[\text{CuL}^5]^{2+}$.¹⁷⁸

5.2 Synthesis and characterization of $[\text{CuL}^5]^{2+}$

The Schiff base ligand 1,2-bis[(1-methyl-2-imidazolyl)methyleneamino]ethane (L^4) and reduced Schiff base ligand [(1-methyl-4,5-dihydro-1*H*-imidazol-2-yl)methyl](2-ethyl)amine (L^5) were prepared as previously reported by Moreno-Esparza.⁶¹ Addition of Cu(II) perchlorate to methanol solutions of L^5 yields a blue coloured precipitate of $[\text{CuL}^5]^{2+}$ upon the addition of ice cold diethyl ether. The reaction mixture was filtered, and the solid product was washed with methanol. The (+) ESI-MS showed a parent peak at $m/z = 155.54$ as expected for the dicationic reduced Schiff base complex. The low temperature (77 K) EPR spectrum in frozen acetonitrile displayed an axial signal with $g_{\perp} = 2.24$ ($A_{\perp} =$

0.000285 cm^{-1}) and $g_{\parallel} = 2.07$ ($A_{\parallel} = 0.0163 \text{ cm}^{-1}$) consistent with square planar/pyramidal Cu(II).

The electronic spectrum of $[\text{CuL}^5]^{2+}$ in acetonitrile showed charge transfer bands at 212 and 302 nm and a d-d transition at 630 nm. The bands were similar to those reported at 208, 292, 640 nm for $[\text{CuL}^4(\text{ClO}_4)][\text{ClO}_4]$ and 212, 288, and 620 nm for $[\text{Cu}(\text{L})(\text{HOCH}_3)][\text{ClO}_4]_2$ indicating highly similar electronic environments. On the addition of perchloric acid to acetonitrile solutions of $[\text{CuL}^5]^{2+}$, two concurrent protonation events are observed, Figure 5.5. The first protonation event results in the blue shift of the charge transfer bands to 216 and 308 nm and the appearance of a shoulder at 236 nm. This has been assigned to the protonation of the pendent NMI donors yielding $[(\text{Cu}(\text{HL}^5)(\text{CH}_3\text{CN})_2)]^{3+}$. This species has been isolated and characterized by x-ray crystallography. The second protonation resulted in the appearance of new bands at 216, 270 and 304 nm. This event has been assigned to the protonation of the second ligated pendent NMI to the copper metal resulting in the formation of $[\text{Cu}(\text{H}_2\text{L}^5)(\text{ClO}_4)_2]^+$, which is proposed to demetallize in solution.

Figure 5.5 UV-Vis spectra collected with the titrations of $[\text{CuL}^5]^{2+}$ with perchloric acid in acetonitrile.¹⁷⁸

5.3 Structural determinations of $[\text{CuL}^5]^{2+}$ and $[\text{Cu}(\text{HL}^5)(\text{CH}_3\text{CN})_2]^{3+}$

Using single crystal x-ray diffraction technique, the solid state structure of $[\text{CuL}^5][\text{ClO}_4]_2$ and its mono-protonated derivative $[\text{Cu}(\text{HL}^5)(\text{CH}_3\text{CN})_2][\text{ClO}_4]_3$ were determined. X-ray quality royal blue prism shaped crystals of $[\text{CuL}^5][\text{ClO}_4]_2$ in the monoclinic space group $P2_1/c$ were obtained by the liquid diffusion of methanol/ether solution. The asymmetric unit contains a single Cu(II) ion coordinated by four N-atoms ($\text{N}_1, \text{N}_3, \text{N}_4, \text{N}_5$) in a pseudo-square planar environment, Figure 5.6. X-ray quality sapphire blue crystals of $[\text{Cu}(\text{HL}^5)(\text{CH}_3\text{CN})_2][\text{ClO}_4]_3$ in the monoclinic space group $P2_1/c$ were obtained by the liquid diffusion of acetonitrile/ether solution. The asymmetric unit contains a Cu(II) coordinated in a distorted-square pyramidal environment by three N-atoms from the L^5H^+ ($\text{N}_1, \text{N}_3, \text{N}_4$) and two acetonitrile donors (N_7, N_8), Figure 5.6. One of the

imidazole nitrogen, N₅ is protonated in L⁵H⁺ and is found to be not coordinated to the metal centre.

Figure 5.6 ORTEP¹⁰⁶ representation of [CuL⁵][ClO₄]₂ (left) and [Cu(HL⁵)(CH₃CN)₂][ClO₄]₃ (right).¹⁷⁸

Selected metric parameters of [CuL⁵]²⁺ and [Cu(HL⁵)(CH₃CN)₂][ClO₄]₃ are compared in Table 5.1. The parameters for N₄-Cu complex [CuL⁶][ClO₄]₂ (L⁶ = 1,6-bis(2-pyridyl)-2,5-diazahexane) which has similar ligand framework as L⁵ previously reported by Robinson.¹⁷⁹ has also been included for comparison. The Cu-N_{amine} distances Cu1-N3 and Cu1-N4 of 2.019(2) and 2.024(2) Å for [CuL⁵]²⁺ and 2.030(2) and 2.0419(19) Å for [Cu(HL⁵)(CH₃CN)₂]³⁺ are slightly longer than the corresponding distances of 1.980(4) and 1.992(4) Å in [CuL⁶]²⁺. The Cu-N_{imidazole} distances Cu1-N1 and Cu1-N5 of 1.957(2) and 1.955(2) Å for [CuL⁵]²⁺ and the Cu1-N1 distance of 1.9565(19) for [Cu(HL⁵)(CH₃CN)₂]³⁺ are shorter than the corresponding Cu-N_{pyridyl} distances of 1.992(4) and 1.992(3) Å in [CuL⁴]²⁺. The Cu-N_{nitrile} distances to the equatorial (N7) and axial (N8) acetonitrile donors of [Cu(HL⁵)(CH₃CN)₂]³⁺ are 2.0047(19) and 2.209(2) Å, respectively. Due to the difference in ligand backbones in [CuL⁵]²⁺ and [CuL⁶]²⁺ as [CuL⁵]²⁺ contains ethylene diamine whereas [CuL⁶]²⁺ has diaminoheptane, a variation in N-Cu-N bond angles is

observed. Notably, for $[\text{CuL}^5]^{2+}$ and $[\text{CuL}^6]^{2+}$ the N1-Cu1-N5 angles are statistically equivalent, these angles are associated with the open end of the chelate with values of 110.3(9) and 110.34(14)°, respectively.

TABLE 5.1 BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[\text{CuL}^5][\text{ClO}_4]_2$, $[\text{Cu}(\text{HL}^5)(\text{CH}_3\text{CN})_2][\text{ClO}_4]_3$ AND $[\text{CuL}^6][\text{ClO}_4]_2$

DISTANCE	$[\text{CuL}^5][\text{ClO}_4]_2$	$[\text{Cu}(\text{HL}^5)(\text{CH}_3\text{CN})_2][\text{ClO}_4]_3$	$[\text{CuL}^6][\text{ClO}_4]_2^{\text{A}}$
Cu1-N1	1.957(2)	1.9565(19)	1.992(4)
Cu1-N3	2.019(2)	2.030(2)	1.980(4)
Cu1-N4	2.024(2)	2.0419(19)	1.992(4)
Cu1-N5	1.955(2)	-	1.992(3)
Cu1-N7	-	2.0047(19)	-
Cu1-N8	-	2.209(2)	-
Cu1... OClO ₃	2.589(2) ^B 2.707(2) ^C	3.0573(1) ^D	2.610 ^E 2.610 ^F
ANGLE			
N1-Cu1-N3	84.02(9)	82.11(8)	82.52(15)
N1-Cu1-N4	162.84(9)	162.14(8)	167.85(15)
N3-Cu1-N4	85.12(9)	83.96(8)	85.43(15)
N5-Cu1-N1	110.33(9)	-	110.34(14)
N5-Cu1-N3	161.36(9)	-	166.53(15)
N5-Cu1-N4	83.30(2)	-	81.79(14)
N3-Cu1-N7	-	162.21(8)	-
N3-Cu1-N8	-	98.61(8)	-

^A $[\text{CuL}^6][\text{ClO}_4]_2$ atoms are renumbered according to $[\text{CuL}^5][\text{ClO}_4]_2$.^{B-F} respective distances to perchlorate oxygens O1,O5,O21,and O11.

5.4 Catalytic oxidations: Identification of system components

All reported values are an average of at least three trials. In a typical trial, 5 mmol (0.5 mL) of benzyl alcohol was dissolved in 10 mL of acetonitrile in a vial. To this solution was added 5 mol% (with respect to substrate = w.r.t. substrate) TEMPO, 5 mol % (w.r.t. substrate) copper catalyst, and 5 mol% (w.r.t. substrate) NMI. Toluene (0.10 M) was added as an internal standard. The reaction was stirred at room temperature open to air for 4 hours during which time the color of the stock solution changed from blue to green. After 4 hrs.,

a 10 μ L aliquot was taken from the solution, diluted with acetonitrile, and analyzed by GC-MS.

To probe the dependence of the individual components on turnover number (TON) and yield, the composition of the catalyst mixture was systematically varied. For substrate concentration studies, the moles of benzyl alcohol were varied from 1 mmol to 20 mmol while keeping the quantities of $[\text{CuL}^5]^{2+}$, TEMPO, and NMI at 250 μ mol, i.e. 5 mol% with respect to 5 mmol substrate solution in 10 mL CH_3CN . Similarly, for catalyst concentration studies, the moles of catalyst were varied from 0.1 to 10 mol% w.r.t. substrate with TEMPO and NMI held constant at 5 mol% w.r.t. substrate. For TEMPO and NMI concentration studies, the equivalents of the TEMPO and NMI were varied from 0.05 to 2 and 0.5 to 10 equivalents w.r.t. $[\text{CuL}^5]^{2+}$, respectively, with all other components held at 5 mol% w.r.t. substrate. To investigate the effect of O_2 flowrate the typical reaction conditions were employed at flowrates ranging from 0.05 to 1 ml/ sec.

To evaluate the catalytic activity of $[\text{CuL}^5]^{2+}$ for its ability to oxidize benzylic alcohols under aerobic conditions we employed a series of reaction conditions. The formation of the product was analyzed using toluene as an internal standard by GC-MS. TEMPO, a co-catalyst used in the reaction mixture prevents the formation of any carboxylic acid product due to its internal ability to scavenge free radicals and avoids autoxidation.¹⁶⁶

The reaction trials were conducted using 10 ml acetonitrile as a solvent for 4 hours using 5mmol of substrate and 250 μ mol (5 mol% with respect to substrate) of $[\text{CuL}^5]^{2+}$, base, and/or radical initiator. All the reactions were monitored at room temperature i.e. 298 K. Addition of NMI as an external base to the mixture of $[\text{CuL}^5]^{2+}$, substrate and TEMPO

enhances the reaction yields. The highest activity with 76 ± 3.6 % yield is observed for the benzyl alcohol to benzaldehyde. The oxidation of selected benzylic alcohols has been summarized below in Table 5.2.

A series of control experiments have been performed to understand the catalytic efficiency of the system better. Absence of metal complex do not yield any product formation, in the presence of radical initiator TEMPO or in the presence of NMI and TEMPO (Entry 1-2). The presence of metal precursor $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ is active with lower yields of 1.5 ± 2.6 % in the presence of radical initiator and base. (Entry 6). Absence of base or initiator resulted in no product yield. Also, the presence of air is necessary to achieve the good turnover numbers. The catalytic trial run in the presence of nitrogen atmosphere resulted in no conversion of substrate to the product (Entry 8).

TABLE 5.2 OXIDATION OF THE SELECTED BENZYLIC ALCOHOLS TO THE CORRESPONDING CARBONYL COMPOUNDS AT 298 K.							
ENTRY	COMPLEX	SUBSTRATE	BASE	INITIATOR	PRODUCT	YIELD (%)	TON
1	-	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	-	TEMPO	$\text{C}_6\text{H}_5\text{CHO}$	0	0
2	-	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	NMI	TEMPO	$\text{C}_6\text{H}_5\text{CHO}$	0	0
3	$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	-	-	$\text{C}_6\text{H}_5\text{CHO}$	0	0
4	$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	-	TEMPO	$\text{C}_6\text{H}_5\text{CHO}$	0	0
5	$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	NMI	-	$\text{C}_6\text{H}_5\text{CHO}$	0	0
6	$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	NMI	TEMPO	$\text{C}_6\text{H}_5\text{CHO}$	1.5 ± 2.6	0.30
7	$[\text{CuL}^4]^{2+}$	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	NMI	TEMPO	$\text{C}_6\text{H}_5\text{CHO}$	0	0
8	$[\text{CuL}^5]^{2+}$	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	NMI	TEMPO	$\text{C}_6\text{H}_5\text{CHO}$	0	0
9	$[\text{CuL}^5]^{2+}$	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	-	TEMPO	$\text{C}_6\text{H}_5\text{CHO}$	18 ± 1.4	3.70
10	$[\text{CuL}^5]^{2+}$	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	NMI	TEMPO	$\text{C}_6\text{H}_5\text{CHO}$	76 ± 3.6	15.2
11	$[\text{CuL}^5]^{2+}$	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	DIPEA	TEMPO	$\text{C}_6\text{H}_5\text{CHO}$	32 ± 1.4	6.44
12	$[\text{CuL}^5]^{2+}$	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	DBU	TEMPO	$\text{C}_6\text{H}_5\text{CHO}$	56 ± 5.5	11.2
13	$[\text{CuL}^5]^{2+}$	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	Et_3N	TEMPO	$\text{C}_6\text{H}_5\text{CHO}$	33 ± 1.2	6.66
14	$[\text{CuL}^5]^{2+}$	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	NMI	H_2O_2	$\text{C}_6\text{H}_5\text{CHO}$	0	0
15	$[\text{CuL}^5]^{2+}$	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	NMI	TBHP	$\text{C}_6\text{H}_5\text{CHO}$	0	0
16	$[\text{CuL}^5]^{2+}$	$\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	NMI	TEMPO	$\text{NO}_2\text{C}_6\text{H}_4\text{CHO}$	99	20.0
17	$[\text{CuL}^5]^{2+}$	$\text{BrC}_6\text{H}_4\text{CH}_2\text{OH}$	NMI	TEMPO	$\text{BrC}_6\text{H}_4\text{CHO}$	85 ± 10	17.1
18	$[\text{CuL}^5]^{2+}$	$\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{OH}$	NMI	TEMPO	$\text{CH}_3\text{OC}_6\text{H}_4\text{CHO}$	52 ± 10	10.4
19	$[\text{CuL}^5]^{2+}$	$\text{C}_6\text{H}_{11}\text{OH}$	NMI	TEMPO	$\text{C}_6\text{H}_{10}\text{O}$	0	0
20	$[\text{CuL}^5]^{2+}$	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$	NMI	TEMPO	$\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{O})\text{CH}_3$	0	0

Entries 1-20 were recorded under air, except entry 8. The reaction in entry 8 was performed under nitrogen atmosphere.

The Schiff base complex $[\text{CuL}^4]^{2+}$ and the reduced Schiff base complex $[\text{CuL}^5]^{2+}$ have been evaluated for their catalytic ability to oxidize benzyl alcohol in aerobic conditions in the presence of NMI and TEMPO., $[\text{CuL}^4]^{2+}$ was found to be inadequate to catalyze benzyl alcohol to benzaldehyde whereas, $[\text{CuL}^5]^{2+}$ was found to be the active catalyst for the conversion of benzylic alcohols to benzylic aldehyde (Entry 7-8).

The entries 10- 13 shows the effect of external base to the reaction mixture. The bases differing in nucleophilicity and basicity in acetonitrile was examined and the highest catalytic activity was recorded for weakest base, NMI which has a pK_a value of 17.1. The non-coordinating base DBU which is 1, 8-diazabicycloundec-7-ene, ($pK_a = 24.13$) was found to be active for catalytic activity resulting in the product yield of 56 ± 5.5 , less than the yield recorded with NMI. This is in contrast to previous results by Stahl.¹⁷³ Bases like Et_3N ($pK_a = 18.5$) and *N,N*-diisopropylethylamine (DIPEA), pK_a 18.6, which has lower nucleophilicity than NMI have been found to yield less product formation (Entry 10-13). These results indicate that during the catalytic turnover coordination of an external base is not necessary to the active metal centre of the catalyst, $[\text{CuL}^5]^{2+}$. However, the better catalytic yields in the presence of NMI as an external base indicates the complementation of the basicity between NMI and imidazole donors of L_5 ligand framework, thus permitting fast proton exchange during catalytic cycle.

TEMPO, a nitroxyl radical initiator is vastly employed to study the oxidation of benzylic alcohols. In this study, hydroxyl radical sources like H_2O_2 and tert-butyl hydroperoxide (TBHP) have been employed.^{172, 180-181} The results have been summarised in entries 14 and 15. The hydroxyl radicals H_2O_2 and TBHP found to be inactive towards the initiation of the catalysis. This can be attributed to the non-coordinating behaviour of

the hydroxyl radicals to the metal atom, in contrast to the nitroxyl radical like TEMPO. Attempts were made to increase the temperature up to 323 K in the presence to hydroxyl radicals but still no detectable formation of product is observed.

The variety of substrates has been screened to evaluate the catalytic efficiency of $[\text{CuL}^5]^{2+}$. Entries 16-18 lists the different benzylic alcohols. The % yield of the aldehyde product was found to improve with the substitution of the electron withdrawing group like $-\text{NO}_2$ and $-\text{Br}$, in contrast to the electron releasing group like $-\text{OCH}_3$. No product yield was recorded for the acyclic alcohols like cyclohexanol (entry 19). Also, the catalytic system was found to be inactive towards the aerobic oxidation of secondary benzylic alcohols, 1-phenyl-2-propanol (entry 20).

5.5 Catalytic oxidations: Mechanistic studies

The relative concentrations of each of the components in the reaction mixture were varied to have the better understanding of the mechanism. The impact on percent yield (100 x moles product per moles of substrate) and turnover number, TON (moles product per moles of catalyst) was studied.

Variation in Substrate Concentration. In the reaction mixture volume of the substrate, benzyl alcohol was varied from 1 mmol to 20 mmol while keeping the constant molar quantities of $[\text{CuL}^5]^{2+}$, TEMPO, and NMI at 250 μmol each under an aerobic atmosphere. Figure 5.7 shows a plot of TON (left axis) and % Yield (right axis) versus alcohol concentrations. At concentrations equal to or less than 2.5 mmol of benzyl alcohol, the percent yield of $92.7 \pm 6.5\%$ is obtained. At higher concentrations of substrate, the TON shows a decrease with the maximum value recorded between 11.8 ± 1.1 and 15.3 ± 0.7 .

The equimolar ratios of $[\text{CuL}^5]^{2+}$, TEMPO, and NMI are required to obtain the high yields and TON of the product. The maximum % yield of $76 \pm 3.7\%$ is recorded for 5 mmol of the substrate. The % yield drops down to $33 \pm 1.4\%$ on using 10 mmol of the substrate. Quantitative conversion with the maximum TON are obtained when 3-4 mmol of alcohol which ranges between (0.5 mol% to 5.0 mol% catalysts) is used.

Figure 5.7 Plot of TON (red squares, left axis) and % yield (green diamonds, right axis) versus substrate quantity. $[\text{CuL}^5]^{2+} = \text{NMI} = \text{TEMPO} = 250 \mu\text{mol}$, 10 mL CH_3CN , aerobic conditions.

Variation in $[\text{CuL}^5]^{2+}$ Concentration. In the reaction mixture $[\text{CuL}^5]^{2+}$ concentrations were varied from 0.1 to 10 mol% with respect to substrate. The percent yield and TON were plotted as a function of catalyst mole percent, Figure 5.8. The concentrations of base, NMI, and radical initiator TEMPO were kept constant at 5 mol% with respect to benzyl alcohol. At 5 mol% of the catalyst loading the maximum percent yield of $76 \pm 3.7\%$ is obtained. Catalyst loading lower or higher than 5 mol% with respect to substrate results in decrease in the product yield. At higher catalyst loading of 10 mol% lowest TON of 1.1 ± 0.1 is

obtained indicating that both TEMPO and NMI is inadequate in the reaction mixture to achieve high TON. At lower catalyst loadings, limited by concentrations of $[\text{CuL}^5]^{2+}$ yields lower TON although the relative quantities of TEMPO, NMI, and/or O_2 are sufficient. The most efficient conversion occurs at 5 mol% $[\text{CuL}^5]^{2+}$ with respect to substrate.

Figure 5.8 Plot of TON (red squares, left axis) and % yield (green diamonds, right axis) versus catalyst quantity. $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ = 5 mmol, NMI = TEMPO = 250 μmol , 10 mL CH_3CN , aerobic conditions.

Variations in TEMPO Concentrations. In the further studies, loadings of the co-catalyst TEMPO were varied keeping the concentrations of $[\text{CuL}^5]^{2+}$ and NMI at 5 mol% with respect to substrate. On adding one equivalent i.e. 5 mol% of TEMPO with respect to substrate maximum turnover is obtained. At lower concentrations of TEMPO, insufficient amounts of co-catalyst with respect to other components suggests lowering in TON whereas while increasing the relative TEMPO concentrations indicates the blocking of substrate binding site, Figure 5.9.

Figure 5.9 Plot of TON versus TEMPO equivalents relative to $[\text{CuL}^5]^{2+}$. $\text{C}_6\text{H}_5\text{CH}_2\text{OH} = 5 \text{ mmol}$, $[\text{CuL}^5]^{2+} = \text{NMI} = 250 \text{ } \mu\text{mol}$, $10 \text{ mL CH}_3\text{CN}$, aerobic conditions.

Variations in NMI Concentrations. To get more insights, the concentration of external base NMI was varied keeping the $[\text{CuL}^5]^{2+}$ and TEMPO loadings of 5 mol% with respect to substrate. On increasing the NMI loading from 1 equivalent to 2 TON increases. Further increases in the concentration of NMI causes the TON to drop down, which is a trend similar to that observed with increases in the concentration of TEMPO. This suggests binding of excess base to the active site hinders the binding of the TEMPO moiety required to initiate the catalysis, Figure 5.10.

Figure 5.10 Plot of TON versus NMI equivalents relative to $[\text{CuL}^5]^{2+}$. $\text{C}_6\text{H}_5\text{CH}_2\text{OH} = 5 \text{ mmol}$, $[\text{CuL}^5]^{2+} = \text{TEMPO} = 250 \mu\text{mol}$, $10 \text{ mL CH}_3\text{CN}$, aerobic conditions.

Solvent screening. The catalytic trials were also conducted in common solvents like tetrahydrofuran (THF) and water.¹⁸²⁻¹⁸⁴ However, the yields found to drop dramatically when going from acetonitrile to these solvents. In THF, % yields of 24.04 ± 1.22 were recorded whereas using water as a solvent yield $18.93 \pm 2.32 \%$ of the product. This might be attributed to possible coordination of the oxygen containing solvent to the metal centre of the catalyst as described in the mechanism. There is a chance of competitive binding between the solvent and substrate molecule.

Variation in oxygen flow rate. To evaluate the effect of flow of oxygen on the product yield, the reaction mixture was stirred under the continuous flow of oxygen at one atmospheric pressure at different flowrates for two hours. With the increase in the flowrate of the oxygen, a linear increase in the TON is observed with the maximum TON of 17.3 at

an oxygen flowrate of 1 mL/sec for 2 hours. This is indicative of the fact that reoxidation of the catalyst by oxygen is a kinetically important step, Figure 5.11.

Figure 5.11 Plot of TON versus O₂ flowrate. C₆H₅CH₂OH = 5 mmol, [CuL⁵]²⁺ = NMI = TEMPO = 250 μmol, 10 mL CH₃CN.

5.6 Proposed mechanism for aerobic oxidation of benzylic alcohols with [CuL⁵]²⁺

Based on above results, Figure 5.12 shows a proposed mechanism for [CuL⁵]²⁺ catalysed aerobic oxidation of benzyl alcohol. In the first step, binding of the benzyl alcohol to the Cu²⁺ centre takes place. This makes the alcohol more acidic by lowering its pK_a, thus enables the external base NMI to abstract the acidic proton from the alcohol. The protonated H(NMI)⁺ is in equilibrium with one of the imidazole arms in the N4- ligand framework. In the next stage, one of the imidazole arms gets protonated and opens the site for the TEMPO to coordinate with the metal centre. This results in the formation of five-coordinate intermediate that resembles [Cu(HL⁵) (NCCH₃)₂]³⁺. H-atom transfer from the substrate to η¹-nitroxyl leads to the formation of TEMPOH.¹⁷⁴ In the next stage, aldehyde

product dissociation yields Cu(I) complex $[\text{Cu}(\text{HL}^5)]^{2+}$. In the presence of TEMPOH and O_2 , deprotonation of $[\text{Cu}(\text{HL}^5)]^{2+}$ takes place. In the final step, Cu(I) is aerobically gets oxidized to regenerate Cu(II) catalyst.

Figure 5.12 A proposed mechanism for alcohol oxidation with $[\text{CuL}^5]^{2+}$.¹⁷⁸

5.7 Conclusions

The tetradentate copper(II) complexes with N₄ ligand framework having an imidazole in the ligand framework has been synthesized, characterized and evaluated for its catalytic ability to oxidize benzylic alcohols to corresponding aldehydes. The optimum conditions to achieve quantitative yields require the combination of 5 mmol of substrate, 5 mol% catalyst with respect to substrate, 5 mol% radical initiator TEMPO with respect to substrate, 5 mol % external base NMI with respect to substrate in 10 ml of acetonitrile. Additional NMI enhances the turnover with yields up to 99% within 4 hours. The key role of the base is shown in the proposed mechanism where the base helps in the deprotonation of the coordinated substrate with subsequent proton transfer to the pendent NMI of the ligand framework. This eventually helps in the opening of the ligand framework and thus helping in the radical initiator TEMPO in binding to the copper centre.

CHAPTER VI

CONCLUSIONS AND FUTURE DIRECTIONS

This dissertation detailed the evaluation of the ligand assisted activation of small molecules through proton reduction and alcohol oxidation. First-row earth abundant transition metals Ni, Cu and Zn have been employed to develop the economically viable molecular catalysts. The ligand backbone and orientation of the ligand framework around the metal center found to play a crucial role in the reactivity and mechanistic studies of the complexes.

In the efforts to develop economical electrocatalysts for hydrogen evolution reactions, earth abundant cheap transition metal nickel has been complexed with the redox non-innocent ligands, benzenethiols and bis(thiosemicarbazones). The dialkyl/diaryl benzenethiols in Chapter 3 are the redox active ligands that undergo ligand centered oxidation at the sulfur. The orientation of the benzenethiolate ligands on the metal atom directs the coordination of the incoming proton on to the molecule. In contrast to benzenethiol ligands which undergo a one electron oxidation, the bis(thiosemicarbazone) ligand framework described in Chapter 4 undergo reduction due to presence of terminal α diimine unit. The redox non-innocence nature of the bis(thiosemicarbazone) ligand has been exploited for the proton reduction studies. In Chapter 5, the N₄-ligand framework with imidazole integrated as the part of the ligand framework was established that has been used

to oxidize benzylic alcohols to benzaldehydes under aerobic conditions. The three projects described in this dissertation has been summarized below.

Electrocatalytic hydrogen evolution and hydrogen oxidation with Ni(PS)₂ complex

Chapter 3 described the syntheses, characterization, and electrocatalytic studies of four complexes Ni(L¹)₂, Ni(L²)₂, Zn(L¹)₂ and Zn(L²)₂. Ni(L¹)₂ was found to be electrocatalytically active for hydrogen evolution and hydrogen oxidation, whereas Ni(L²)₂ was found to be electrocatalytically active for hydrogen oxidation. Zn(L¹)₂ and Zn(L²)₂ were found to be inadequate for both HER and HOR. The Re(L¹)₃ complex previously reported by our group was found to evolve hydrogen in the presence of external acids as well as cleave dihydrogen in the presence of external base under 1 atm. H₂. The drawback of Re(L¹)₃ was the high cost of the Re metal to develop catalytic systems for HER and HOR. This lead us to exploit cheap first row transition metals like nickel and zinc and complexing them with the ligand L¹. The ligand L² was also synthesized which has electron releasing isopropyl groups on phosphorus instead of electron withdrawing phenyl groups.

Out of the four complexes investigated in Chapter 3, only Ni(L¹)₂ was found to evolve hydrogen in the dichloromethane solutions with the maximum TOF of 140 s⁻¹ using HCl as an external acid source at an overpotential of 1.1 V. Ni(L¹)₂ also found to be electrocatalytically active for HER with weak acid CH₃COOH with TOF of 51s⁻¹. Mechanistic studies revealed the first-order dependence on acid and first-order dependence on the catalyst concentration. The KIE studies shows the inverse isotope effect indicating towards the formation of metal hydride during the catalysis. The mechanism for HER with weak acid is postulated to be ECEC type. In the initial step, the electron addition takes place that reduces Ni(II) species to Ni(I) species. This is followed by protonation in the

second step making Ni(III) hydride species. In the next step, the second electron addition takes place thus, reducing the Ni(III)-hydride to Ni(II)-hydride species. In this final step, the external proton from the solution interacts with the Ni(II)- hydride species to evolve hydrogen and regenerating original Ni(L¹)₂ catalyst. In electrocatalytic studies with strong acid HCl, an additional protonation event is observed in the HER studies prior to reduction of Ni(II) species to Ni(I) species. This suggests that the other route for HER mechanism can be CEEC type in which first step is the chemical step leading to the formation of [Ni(II)-H]⁺ species. In the next step, addition of electron takes place to form Ni(III) hydride species which in the final step interacts with external proton to form hydrogen. Ni(L¹)₂ is found to cleave dihydrogen in the presence of external base Et₃N under 1 atm. H₂ with the TOF of 23 s⁻¹ at an overpotential of 0.33 V. Ni(L²)₂ showed no activity for hydrogen evolution due to inaccessible Ni(II/I) reduction but cleaves dihydrogen with the TOF of 19 s⁻¹ at an overpotential of 0.49 V.

Future studies with these systems include the complexation of the benzenethiol ligands with different metals like Cu and Fe for the ability to catalyze HER and HOR. Also, modification of the ligand framework by changing the R-groups on the Phosphorus atom and substitution on the benzene ring can be taken into consideration. The future studies can include the choice of different solvent like dimethylformamide and use of other acids like HBF₄, CF₃COOH, Et₃NH⁺, DMFH⁺ etc.

Electrocatalytic hydrogen evolution with bis(thiosemicarbazonato) Ni(II) complex

The synthesis of PS-ligands requires lot of effort as the organic ligands are air, moisture and light sensitive. In the search of simple and cost-effective systems for energy production, we have explored bis(thiosemicarbazones) as potential ligand frameworks for

hydrogen evolution complexes. These N_2S_2 ligand moieties employed in Chapter 4 are easy to synthesize and are stable under atmospheric conditions. Our group has previously reported Zn(II) and Cu(II) complexes with bis(thiosemicarbazones) as active electrocatalysts for HER. In chapter 4, the electrocatalytic hydrogen evolution with bis(thiosemicarbazonato) Ni(II) (NiL^3) has been described. NiL^3 was found to evolve hydrogen in the acetonitrile solutions with the maximum TOF of 4100 s^{-1} using CH_3COOH as an external acid source at an overpotential of 0.52 V. The catalytic studies were also conducted using strong acid CF_3COOH in acetonitrile and dimethylformamide solutions. Mechanistic investigations first order dependence on the catalyst and second order dependence on the acid concentration. An inverse KIE values has been recorded which was indicative of the formation of metal hydride. DFT studies were conducted using functionals, B3LYP/6311 g and BP-86/TZV/P. The calculations were performed in gas phase and by applying Polarizable Continuum Model (PCM) calculations of solvent effects. The mechanism for HER with NiL^3 based on experimental and theoretical calculations was proposed to be ECEC type.

Future studies involve the modification of the ligand framework with substituting the R-groups on the amine nitrogen with electron withdrawing groups like $-\text{CF}_3$ to modulate the overpotential. Ligand backbone can be altered by the condensation of the different dione group other than butanedione with the modified thiosemicarbazide. Replacement of the alkyl groups in the butanedione with the aryl groups can affect the electron density observed on the ligand framework. The modified ligands complexed with first row transition metals like Ni, Zn, Cu, Mn can be screened for the ability to generate hydrogen with the external acids.

Copper catalyzed aerobic oxidation of benzylic alcohols in an imidazole containing N₄ ligand framework

This project describes the syntheses, characterization and catalytic behavior of N₄-Cu(II) complexes for oxidation of the benzylic alcohols to benzaldehydes under aerobic conditions. The galactose oxidase, is a copper containing fungal enzyme that catalyzes alcohol oxidation in nature. Various reports in literature describes the synthesis of copper coordinated systems that has been used for this purpose. Stahl group reported a simple Cu(I)/bpy/NMI system for oxidation of variety of alcohols. In this one pot reaction, NMI was added as an external base to enhance the product yield. Taking an inspiration from this work, we synthesized two Cu(II) complexes containing NMI as an integral part of the ligand framework. The thought process behind the design of this ligand framework was to evaluate the effect on the oxidation reaction if NMI was present as a part of ligand. The N₄-Cu(II) Schiff base complex is found to be inactive towards the oxidation of the benzylic alcohols whereas the N₄-Cu(II) reduced Schiff base complex found to be active for the reaction. The optimum conditions to achieve the best results under aerobic conditions were found to be: 5 mmol substrate, 5 mol% catalyst w.r.t. substrate, 5 mol% TEMPO w.r.t. substrate, 10 mol% base w.r.t. substrate. Control experiments suggests that presence of Cu(II) source, TEMPO, NMI and air are required to initiate the oxidation. Absence of any of these results in no conversion. The electron withdrawing substituted benzylic alcohols like nitrobenzylic alcohols were found to works best with [CuL⁵]²⁺ catalyst. The aliphatic alcohols and secondary benzylic alcohols found to be inactive towards their oxidation. The external base NMI founds to works best as compared to other bases like DBU and DIPEA. This can be attributed to the equilibrium established between protonated NMI and the

coordinated NMI in the ligand framework, as described in the mechanism. The hydroxyl radical initiators H_2O_2 and TBHP found to be insufficient to initiate the reactions as compared to nitroxyl radical, TEMPO.

Mechanistic studies detail the study of the variation in the one of the components of the reaction mixture at a time keeping the mass of the other substituents constant. The excess or deficiency of any of the components decrease the percentage yield suggesting that all the components must be present in the specific quantities with respect to each other to achieve high conversions. For example, excess of catalyst with respect to substrate suggests that there was not enough TEMPO and NMI to come and interact with it to get better yields and deficiency of the catalyst indicates that now although TEMPO and NMI are present but no catalyst for binding to them to get better yields. The proposed mechanism involves the binding of alcohol in the first step, thus lowering its pK_a , thus facilitating the external base NMI to abstracts the proton in the first step. In the second step, the protonated NMI establishes an equilibrium with the coordinated NMI and transfer of proton takes place, thus opening the site for the TEMPO to come and bind to the copper center. Transfer of electrons in the following step takes place and thus Cu(II) alkoxide is formed. The next step, yields TEMPOH and the aldehyde product and leaving behind Cu(I) complex. Final step, involves the formation of H_2O_2 by the abstraction of proton from the protonated coordinated NMI and TEMPOH and the regeneration of the catalyst by aerobic oxidation of Cu(I) to Cu(II) , for use in the next cycle.

Future studies involve the use of Cu(I) source in place of Cu(II) to synthesize the complex. The modification of the ligand framework with various substitutions on the imidazole framework and its effect on the alcohol oxidation. To expand the horizon of

oxidation studies with these systems, variety of other alcohol substrates can be tested for oxidation.

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Figure A17. Cyclic voltammograms (CVs) of 0.30 mM NiL^3 in dimethylformamide solution with subsequent addition of trifluoroacetic acid. CVs showing no acid, 4, 8, 12, 16, 20, 24, 32 mM (top) Voltammograms were recorded in dimethylformamide solvent with 0.10 M Bu_4NPF_6 as supporting electrolyte using a glassy carbon working electrode, platinum counter electrode, and Ag/Ag^+ reference electrode at a scan rate 500 mV/s. Potentials referenced versus ferrocenium/ferrocene (Fc^+/Fc^0) using an internal standard

Figure A18. Cyclic voltammograms (CVs) of 0.30 mM NiL^3 in dimethylformamide solution with subsequent addition of trifluoroacetic acid. CVs showing no acid, 4, 8, 12, 16, 20, 24, 32 mM (top). Voltammograms were recorded in dimethylformamide solvent with 0.10 M Bu_4NPF_6 as supporting electrolyte using a glassy carbon working electrode, platinum counter electrode, and Ag/Ag^+ reference electrode at a scan rate 1000 mV/s. Potentials referenced versus ferrocenium/ferrocene (Fc^+/Fc^0) using an internal standard.

Figure A19. Cyclic voltammograms (CVs) of 0.30 mM NiL^3 in acetonitrile solution with subsequent addition of trifluoroacetic acid. CVs showing no acid, 6, 8, 10, 12, 14, 16, 18 mM (top). Voltammograms were recorded in acetonitrile solvent with 0.10 M Bu_4NPF_6 as supporting electrolyte using a glassy carbon working electrode, platinum counter electrode, and Ag/Ag^+ reference electrode at a scan rate 500 mV/s. Potentials referenced versus ferrocenium/ferrocene (Fc^+/Fc^0) using an internal standard.

Figure A20. Cyclic voltammograms (CVs) of 0.30 mM NiL^3 in acetonitrile solution with subsequent addition of trifluoroacetic acid. CVs showing no acid, 6, 8, 10, 12, 14, 16, 18 mM (top). Voltammograms were recorded in acetonitrile solvent with 0.10 M Bu_4NPF_6 as supporting electrolyte using a glassy carbon working electrode, platinum counter electrode, and Ag/Ag^+ reference electrode at a scan rate 1000 mV/s. Potentials referenced versus ferrocenium/ferrocene (Fc^+/Fc^0) using an internal standard.

Figure A21. Foot of wave analysis for NiL^3 with acetic acid in acetonitrile solution. Plot of i_c/i_p vs $1/(1 + \exp[(F/RT)(E - E_{cat}/2)])$. (Inset) Plot of Linear fit.

Figure A22. Foot of wave analysis for NiL^3 with acetic acid in dimethylformamide solution. Plot of i_c/i_p vs $1/(1+\exp[(F/RT)(E-E_{cat}/2)])$. (Inset) Plot of Linear fit.

Figure A23. Foot of wave analysis for NiL^3 with trifluoroacetic acid in acetonitrile solution. Plot of i_c/i_p vs $1/1+\exp[(F/RT)(E-E_{cat}/2)]$. (Inset) Plot of Linear fit.

Figure A24. Foot of wave analysis for NiL^3 with trifluoroacetic acid in dimethylformamide solution. Plot of i_c/i_p vs $1/(1+\exp[(F/RT)(E-E_{cat}/2)])$. (Inset) Plot of Linear fit.

Figure A25. Control experiment for the catalysis of NiL^3 . Cyclic voltammogram of 0.30 mM NiL^3 with 20 mM trifluoroacetic acid (red) and blank acetonitrile with 20 mM acetic acid in the absence of NiL^3 (black). Voltammograms were recorded in acetonitrile solvent with 0.10 M Bu_4NPF_6 as supporting electrolyte using a glassy carbon working electrode, platinum counter electrode, and Ag/Ag^+ reference electrode at a scan rate 500 mV/s. Potentials referenced versus ferrocenium/ferrocene (Fc^+/Fc^0) using an internal standard.

Figure A26. Control experiment for the catalysis of NiL^3 . Cyclic voltammogram of 0.30 mM NiL^3 with 32 mM trifluoroacetic acid (red) and blank dimethylformamide with 32 mM trifluoroacetic acid in the absence of NiL^3 (black). Voltammograms were recorded in dimethylformamide solvent with 0.10 M Bu_4NPF_6 as supporting electrolyte using a glassy carbon working electrode, platinum counter electrode, and Ag/Ag^+ reference electrode at a scan rate 500 mV/s. Potentials referenced versus ferrocenium/ferrocene (Fc^+/Fc^0) using an internal standard.

Figure A27. Control experiment for the catalysis of NiL^3 . Cyclic voltammogram of 0.30 mM NiL^3 with 12.6 mM acetic acid (red) and blank acetonitrile with 12.6 mM acetic acid in the absence of NiL^3 (black). Voltammograms were recorded in acetonitrile solvent with 0.10 M Bu_4NPF_6 as supporting electrolyte using a glassy carbon working electrode, platinum counter electrode, and Ag/Ag^+ reference electrode at a scan rate 500 mV/s. Potentials referenced versus ferrocenium/ferrocene (Fc^+/Fc^0) using an internal standard.

Figure A28. Control experiment for the catalysis of NiL^3 . Cyclic voltammogram of 0.30 mM NiL^3 with 9.8 mM acetic acid (red) and blank dimethylformamide with 9.8 mM acetic acid in the absence of NiL^3 (black). Voltammograms were recorded in dimethylformamide solvent with 0.10 M Bu_4NPF_6 as supporting electrolyte using a glassy carbon working electrode, platinum counter electrode, and Ag/Ag^+ reference electrode at a scan rate 500 mV/s. Potentials referenced versus ferrocenium/ferrocene (Fc^+/Fc^0) using an internal standard.

Figure A29. Representation of gas chromatogram for the copper catalyzed benzyl alcohol oxidation, peaks shown are toluene (internal standard), benzaldehyde (product) and benzyl alcohol (substrate).

Figure A30. FT-IR spectrum of reduced Schiff base complex $[\text{CuL}^5](\text{ClO}_4)_2$ collected on solid sample using ATR attachment.

Figure A31. EPR spectrum of reduced Schiff base complex $[\text{CuL}^5](\text{ClO}_4)_2$ collected on frozen acetonitrile solution at 77K.

Table T1. List of selected H-bonding interactions in $[\text{CuL}^5](\text{ClO}_4)_2$ and $[\text{Cu}(\text{HL}^5)][(\text{ClO}_4)_3]$.

D-H...A	D-H (Å)	H...A (Å)	D-H...A (°)	D...A (Å)
$[\text{CuL}^5](\text{ClO}_4)_2$				
N3-H3N...O6	1.00	2.30	159	3.248(4)
N4-H4N...O1	0.99	2.20	118	2.811(3)
$[\text{Cu}(\text{HL}^5)][(\text{ClO}_4)_3]$				
N3-H3N...O1	0.82(3)	2.26(3)	156(2)	3.018(3)
N4-H4N...O22	0.87(3)	2.12(3)	173(2)	2.976(3)

A.1 Computational input coordinates for NiL³ and related compounds using B3LYP/ 6-311g(d,p) in acetonitrile

NiL³

q Ms

0 1

Ni	1.298967264	1.716422563	0.713071468
C	2.077098110	-0.852510960	0.491389295
N	1.773134330	0.186402198	-0.234431064
N	1.826356920	0.101489400	-1.609083332
C	1.456628243	1.248488769	-2.136738890
S	0.958096047	2.658176535	-1.194682486
C	2.480675590	-2.168490180	-0.075503141
N	1.431975930	1.370106900	-3.469802543
C	1.739697353	0.264210738	-4.353189292
C	1.129474089	2.336962584	3.526368011
N	1.640189805	0.652745991	2.194418338
N	1.506619816	1.073419554	3.496785633
C	1.986729953	-0.577643835	1.932880409
S	0.855462745	3.324454446	2.085124447
C	2.253656241	-1.605054861	2.980517434
N	0.938903338	2.936088342	4.704959664
C	1.056751568	2.255094468	5.980838971
H	1.250598320	2.048394390	-3.812289741
H	0.626368925	3.653618400	4.691096792
H	2.447779305	-2.126202930	-1.073134807
H	3.411691239	-2.386692390	0.219082884
H	1.854987829	-2.877224490	0.248789038
H	1.663671094	0.566649150	-5.303786215
H	2.671825422	-0.052436190	-4.177427882
H	1.096246434	-0.483766140	-4.188567690
H	2.133652700	-1.197574920	3.885317370
H	3.191349969	-1.940139030	2.886447947

H	1.615000739	-2.366394510	2.870357114
H	0.871759587	2.900905350	6.721017304
H	1.982384841	1.891085820	6.079859484
H	0.396574022	1.505426100	6.020447176

[NiL³]⁻

q Ms

-1 2

Ni	1.279394000	1.728473000	0.701506000
C	2.054425000	-0.838838000	0.494547000
N	1.754628000	0.192567000	-0.250844000
N	1.795289000	0.115240000	-1.608595000
C	1.453569000	1.257076000	-2.172022000
S	0.998444000	2.716850000	-1.252697000
C	2.460583000	-2.173227000	-0.039963000
N	1.443267000	1.344663000	-3.510105000
C	1.792845000	0.245938000	-4.400600000
C	1.064851000	2.346827000	3.544968000
N	1.589132000	0.661021000	2.203871000
N	1.446009000	1.085951000	3.488398000
C	1.962019000	-0.562709000	1.934162000
S	0.767238000	3.355634000	2.104132000
C	2.259842000	-1.598676000	2.968450000
N	0.883634000	2.917817000	4.744696000
C	1.087161000	2.228673000	6.012017000
H	1.180220000	2.229010000	-3.913481000
H	0.591456000	3.881368000	4.759247000
H	2.327023000	-2.200741000	-1.118171000
H	3.512293000	-2.375264000	0.188488000
H	1.870446000	-2.969775000	0.420415000
H	1.697229000	0.595567000	-5.427056000

H	2.820187000	-0.084378000	-4.229123000
H	1.126826000	-0.606854000	-4.249030000
H	2.302021000	-1.142731000	3.954145000
H	3.209269000	-2.096291000	2.756135000
H	1.482482000	-2.370157000	2.973738000
H	0.866880000	2.925648000	6.818578000
H	2.119722000	1.884340000	6.108203000
H	0.425926000	1.362987000	6.096122000

[NiL³H] (proton addition to the coordinated nitrogen)

q Ms

0 2

Ni	1.274391000	1.754349000	0.696257000
C	2.046816000	-0.847910000	0.522642000
N	1.660128000	0.200025000	-0.239151000
N	1.742460000	0.121429000	-1.606773000
C	1.414471000	1.232551000	-2.196058000
S	0.987525000	2.720107000	-1.292284000
C	2.487637000	-2.135446000	-0.106163000
N	1.333640000	1.298412000	-3.566953000
C	1.858696000	0.225338000	-4.398568000
C	1.109058000	2.357109000	3.571768000
N	1.670593000	0.713384000	2.179153000
N	1.488965000	1.117574000	3.478088000
C	1.983666000	-0.574006000	1.909854000
S	0.777794000	3.380374000	2.138286000
C	2.218309000	-1.556085000	3.017760000
N	0.990182000	2.959964000	4.801604000
C	1.031164000	2.174171000	6.026139000
H	1.427615000	2.229886000	-3.941893000
H	0.373894000	3.758172000	4.813096000

H	1.697392000	-2.560511000	-0.733978000
H	3.349217000	-1.972853000	-0.761944000
H	2.765438000	-2.876677000	0.641942000
H	1.684502000	0.480589000	-5.444290000
H	2.932673000	0.056972000	-4.245559000
H	1.339257000	-0.707873000	-4.174414000
H	3.024116000	-1.220831000	3.678944000
H	2.476436000	-2.542827000	2.635890000
H	1.325801000	-1.655291000	3.644299000
H	0.921340000	2.849888000	6.874826000
H	1.991121000	1.661689000	6.108526000
H	0.240015000	1.414338000	6.069086000
H	2.296359806	0.157583132	2.726420119

[NiL³H] (proton addition to the hydrazino nitrogen)

q Ms

0 2

Ni	1.274391000	1.754349000	0.696257000
C	2.046816000	-0.847910000	0.522642000
N	1.660128000	0.200025000	-0.239151000
N	1.742460000	0.121429000	-1.606773000
C	1.414471000	1.232551000	-2.196058000
S	0.987525000	2.720107000	-1.292284000
C	2.487637000	-2.135446000	-0.106163000
N	1.333640000	1.298412000	-3.566953000
C	1.858696000	0.225338000	-4.398568000
C	1.109058000	2.357109000	3.571768000
N	1.670593000	0.713384000	2.179153000
N	1.488965000	1.117574000	3.478088000
C	1.983666000	-0.574006000	1.909854000
S	0.777794000	3.380374000	2.138286000

C	2.218309000	-1.556085000	3.017760000
N	0.990182000	2.959964000	4.801604000
C	1.031164000	2.174171000	6.026139000
H	1.427615000	2.229886000	-3.941893000
H	0.373894000	3.758172000	4.813096000
H	1.697392000	-2.560511000	-0.733978000
H	3.349217000	-1.972853000	-0.761944000
H	2.765438000	-2.876677000	0.641942000
H	1.684502000	0.480589000	-5.444290000
H	2.932673000	0.056972000	-4.245559000
H	1.339257000	-0.707873000	-4.174414000
H	3.024116000	-1.220831000	3.678944000
H	2.476436000	-2.542827000	2.635890000
H	1.325801000	-1.655291000	3.644299000
H	0.921340000	2.849888000	6.874826000
H	1.991121000	1.661689000	6.108526000
H	0.240015000	1.414338000	6.069086000
H	1.633495550	0.521948739	4.268240813

[NiL³H] (proton addition to the amine nitrogen)

q Ms

0 2

Ni	1.274391000	1.754349000	0.696257000
C	2.046816000	-0.847910000	0.522642000
N	1.660128000	0.200025000	-0.239151000
N	1.742460000	0.121429000	-1.606773000
C	1.414471000	1.232551000	-2.196058000
S	0.987525000	2.720107000	-1.292284000
C	2.487637000	-2.135446000	-0.106163000
N	1.333640000	1.298412000	-3.566953000
C	1.858696000	0.225338000	-4.398568000

C	1.109058000	2.357109000	3.571768000
N	1.670593000	0.713384000	2.179153000
N	1.488965000	1.117574000	3.478088000
C	1.983666000	-0.574006000	1.909854000
S	0.777794000	3.380374000	2.138286000
C	2.218309000	-1.556085000	3.017760000
N	0.990182000	2.959964000	4.801604000
C	1.031164000	2.174171000	6.026139000
H	1.427615000	2.229886000	-3.941893000
H	0.373894000	3.758172000	4.813096000
H	1.697392000	-2.560511000	-0.733978000
H	3.349217000	-1.972853000	-0.761944000
H	2.765438000	-2.876677000	0.641942000
H	1.684502000	0.480589000	-5.444290000
H	2.932673000	0.056972000	-4.245559000
H	1.339257000	-0.707873000	-4.174414000
H	3.024116000	-1.220831000	3.678944000
H	2.476436000	-2.542827000	2.635890000
H	1.325801000	-1.655291000	3.644299000
H	0.921340000	2.849888000	6.874826000
H	1.991121000	1.661689000	6.108526000
H	0.240015000	1.414338000	6.069086000
H	1.552625912	3.328221341	4.061304481

[NiL³H] (proton addition to the sulfur)

q Ms

0 2

Ni	1.175499000	1.895996000	0.609192000
C	2.070137000	-0.739954000	0.456966000
N	1.703619000	0.249405000	-0.314778000
N	1.852986000	0.151497000	-1.662789000

C	1.598331000	1.290518000	-2.285052000
S	1.232462000	2.848594000	-1.503433000
C	2.638771000	-2.034943000	-0.041687000
N	1.629756000	1.285129000	-3.632820000
C	1.886112000	0.104392000	-4.442909000
C	0.806415000	2.290711000	3.647524000
N	1.516099000	0.746144000	2.165179000
N	1.304132000	1.096167000	3.477724000
C	1.855526000	-0.486512000	1.885032000
S	0.178679000	3.273573000	2.232031000
C	2.040125000	-1.570202000	2.902941000
N	0.706563000	2.883474000	4.863130000
C	1.164980000	2.230792000	6.084685000
H	1.487788000	2.169057000	-4.092589000
H	0.049167000	3.641922000	4.957107000
H	1.871098000	-2.817200000	-0.067652000
H	3.015932000	-1.904536000	-1.054136000
H	3.445529000	-2.392962000	0.601173000
H	1.756158000	0.374098000	-5.490316000
H	2.903933000	-0.269667000	-4.296591000
H	1.190147000	-0.699301000	-4.192257000
H	3.091424000	-1.871465000	2.959953000
H	1.466757000	-2.460946000	2.631489000
H	1.726009000	-1.226371000	3.885064000
H	1.111317000	2.952990000	6.897796000
H	2.197708000	1.903224000	5.963638000
H	0.551310000	1.359322000	6.333666000
H	0.782315000	4.424624000	2.612703000

[NiL³H] (proton addition to the nickel)

q Ms

O 2

Ni	1.274391000	1.754349000	0.696257000
C	2.046816000	-0.847910000	0.522642000
N	1.660128000	0.200025000	-0.239151000
N	1.742460000	0.121429000	-1.606773000
C	1.414471000	1.232551000	-2.196058000
S	0.987525000	2.720107000	-1.292284000
C	2.487637000	-2.135446000	-0.106163000
N	1.333640000	1.298412000	-3.566953000
C	1.858696000	0.225338000	-4.398568000
C	1.109058000	2.357109000	3.571768000
N	1.670593000	0.713384000	2.179153000
N	1.488965000	1.117574000	3.478088000
C	1.983666000	-0.574006000	1.909854000
S	0.777794000	3.380374000	2.138286000
C	2.218309000	-1.556085000	3.017760000
N	0.990182000	2.959964000	4.801604000
C	1.031164000	2.174171000	6.026139000
H	1.427615000	2.229886000	-3.941893000
H	0.373894000	3.758172000	4.813096000
H	1.697392000	-2.560511000	-0.733978000
H	3.349217000	-1.972853000	-0.761944000
H	2.765438000	-2.876677000	0.641942000
H	1.684502000	0.480589000	-5.444290000
H	2.932673000	0.056972000	-4.245559000
H	1.339257000	-0.707873000	-4.174414000
H	3.024116000	-1.220831000	3.678944000
H	2.476436000	-2.542827000	2.635890000
H	1.325801000	-1.655291000	3.644299000
H	0.921340000	2.849888000	6.874826000
H	1.991121000	1.661689000	6.108526000

H	0.240015000	1.414338000	6.069086000
H	0.764676207	3.473992151	0.333051461

[NiL³H]⁻ (electron addition after the proton is added to coordinated nitrogen)

q Ms

-1 1

Ni	1.774495000	1.844401000	0.743777000
C	2.172904000	-0.846145000	0.570352000
N	1.964194000	0.277064000	-0.193545000
N	1.871080000	0.149821000	-1.522944000
C	1.587899000	1.304781000	-2.115186000
S	1.371049000	2.808423000	-1.206049000
C	2.267129000	-2.185724000	-0.094881000
N	1.451409000	1.328842000	-3.450005000
C	1.577714000	0.155288000	-4.304385000
C	1.223245000	2.339414000	3.553909000
N	2.307757000	0.817350000	2.266661000
N	1.643077000	1.109307000	3.523736000
C	2.269703000	-0.608095000	1.918038000
S	1.301734000	3.467807000	2.165597000
C	2.451260000	-1.593843000	3.020334000
N	0.724789000	2.849085000	4.707265000
C	0.543869000	2.041852000	5.905150000
H	1.239492000	2.216035000	-3.877059000
H	0.171247000	3.686168000	4.618260000
H	1.355160000	-2.393117000	-0.659694000
H	3.092856000	-2.192382000	-0.810470000
H	2.424784000	-2.983753000	0.626917000
H	1.410216000	0.465259000	-5.334352000
H	2.574463000	-0.284003000	-4.220327000
H	0.841455000	-0.605385000	-4.034232000

H	3.415088000	-1.444784000	3.522607000
H	2.412157000	-2.617950000	2.654234000
H	1.676979000	-1.462782000	3.779319000
H	0.235265000	2.697043000	6.719113000
H	1.485074000	1.560050000	6.173854000
H	-0.212484000	1.260773000	5.768349000
H	3.295616000	1.052795000	2.412209000

[NiL³H]⁻ (electron addition after the proton is added to coordinated nitrogen)

q Ms

-1 3

Ni	1.774495000	1.844401000	0.743777000
C	2.172904000	-0.846145000	0.570352000
N	1.964194000	0.277064000	-0.193545000
N	1.871080000	0.149821000	-1.522944000
C	1.587899000	1.304781000	-2.115186000
S	1.371049000	2.808423000	-1.206049000
C	2.267129000	-2.185724000	-0.094881000
N	1.451409000	1.328842000	-3.450005000
C	1.577714000	0.155288000	-4.304385000
C	1.223245000	2.339414000	3.553909000
N	2.307757000	0.817350000	2.266661000
N	1.643077000	1.109307000	3.523736000
C	2.269703000	-0.608095000	1.918038000
S	1.301734000	3.467807000	2.165597000
C	2.451260000	-1.593843000	3.020334000
N	0.724789000	2.849085000	4.707265000
C	0.543869000	2.041852000	5.905150000
H	1.239492000	2.216035000	-3.877059000
H	0.171247000	3.686168000	4.618260000
H	1.355160000	-2.393117000	-0.659694000

H	3.092856000	-2.192382000	-0.810470000
H	2.424784000	-2.983753000	0.626917000
H	1.410216000	0.465259000	-5.334352000
H	2.574463000	-0.284003000	-4.220327000
H	0.841455000	-0.605385000	-4.034232000
H	3.415088000	-1.444784000	3.522607000
H	2.412157000	-2.617950000	2.654234000
H	1.676979000	-1.462782000	3.779319000
H	0.235265000	2.697043000	6.719113000
H	1.485074000	1.560050000	6.173854000
H	-0.212484000	1.260773000	5.768349000
H	3.295616000	1.052795000	2.412209000

[NiL³H]⁻ (electron addition after the proton is added to hydrazino nitrogen)

q Ms

-1 1

Ni	1.324576000	1.758166000	0.697860000
C	2.085008000	-0.853373000	0.514416000
N	1.712306000	0.200236000	-0.239308000
N	1.800562000	0.124394000	-1.600544000
C	1.460526000	1.242405000	-2.186785000
S	1.032778000	2.726294000	-1.284395000
C	2.538772000	-2.133948000	-0.117427000
N	1.393269000	1.304482000	-3.542641000
C	1.830343000	0.213497000	-4.399513000
C	1.010703000	2.397806000	3.581376000
N	1.801163000	0.722048000	2.164883000
N	1.451790000	1.144887000	3.437671000
C	2.005373000	-0.594789000	1.903595000
S	0.698652000	3.350869000	2.156813000
C	2.142201000	-1.601827000	3.003499000

N	0.827103000	2.908861000	4.805375000
C	1.037907000	2.187713000	6.054344000
H	1.356138000	2.227443000	-3.943560000
H	0.430865000	3.834498000	4.844494000
H	1.761966000	-2.547496000	-0.767401000
H	3.415316000	-1.959799000	-0.748803000
H	2.800550000	-2.882639000	0.628542000
H	1.619939000	0.482225000	-5.434360000
H	2.902095000	0.008367000	-4.294187000
H	1.285961000	-0.699995000	-4.153685000
H	2.976764000	-1.363951000	3.674103000
H	2.314807000	-2.601112000	2.610148000
H	1.231622000	-1.646357000	3.612875000
H	0.813562000	2.861239000	6.877811000
H	2.078212000	1.863488000	6.151535000
H	0.379455000	1.316576000	6.128162000
H	1.737523000	0.587750000	4.233479000

[NiL³H]⁻ (electron addition after the proton is added to hydrazino nitrogen)

q Ms

-1 3

Ni	1.324576000	1.758166000	0.697860000
C	2.085008000	-0.853373000	0.514416000
N	1.712306000	0.200236000	-0.239308000
N	1.800562000	0.124394000	-1.600544000
C	1.460526000	1.242405000	-2.186785000
S	1.032778000	2.726294000	-1.284395000
C	2.538772000	-2.133948000	-0.117427000
N	1.393269000	1.304482000	-3.542641000
C	1.830343000	0.213497000	-4.399513000
C	1.010703000	2.397806000	3.581376000

N	1.801163000	0.722048000	2.164883000
N	1.451790000	1.144887000	3.437671000
C	2.005373000	-0.594789000	1.903595000
S	0.698652000	3.350869000	2.156813000
C	2.142201000	-1.601827000	3.003499000
N	0.827103000	2.908861000	4.805375000
C	1.037907000	2.187713000	6.054344000
H	1.356138000	2.227443000	-3.943560000
H	0.430865000	3.834498000	4.844494000
H	1.761966000	-2.547496000	-0.767401000
H	3.415316000	-1.959799000	-0.748803000
H	2.800550000	-2.882639000	0.628542000
H	1.619939000	0.482225000	-5.434360000
H	2.902095000	0.008367000	-4.294187000
H	1.285961000	-0.699995000	-4.153685000
H	2.976764000	-1.363951000	3.674103000
H	2.314807000	-2.601112000	2.610148000
H	1.231622000	-1.646357000	3.612875000
H	0.813562000	2.861239000	6.877811000
H	2.078212000	1.863488000	6.151535000
H	0.379455000	1.316576000	6.128162000
H	1.737523000	0.587750000	4.233479000

[NiL³H]⁻ (electron addition after the proton is added to amine nitrogen)

q Ms

-1 1

Ni	1.302513000	1.775453000	0.654754000
C	2.054121000	-0.837723000	0.517614000
N	1.740877000	0.223585000	-0.254319000
N	1.785025000	0.112548000	-1.612271000
C	1.455662000	1.225595000	-2.217123000

S	1.023138000	2.718086000	-1.335065000
C	2.438072000	-2.146979000	-0.101743000
N	1.409340000	1.270026000	-3.573196000
C	1.867053000	0.175850000	-4.414433000
C	1.123341000	2.410674000	3.454781000
N	1.617207000	0.728439000	2.151668000
N	1.485629000	1.175819000	3.415935000
C	1.974920000	-0.561031000	1.900392000
S	0.817798000	3.449347000	2.074183000
C	2.234429000	-1.516679000	3.021059000
N	0.971679000	3.020721000	4.799427000
C	1.075019000	2.095381000	5.979522000
H	1.327507000	2.183255000	-3.988865000
H	0.066586000	3.500045000	4.827859000
H	1.620766000	-2.544401000	-0.711489000
H	3.293640000	-2.019661000	-0.771234000
H	2.697340000	-2.889381000	0.651069000
H	1.684528000	0.441582000	-5.455191000
H	2.935492000	-0.027857000	-4.279685000
H	1.316700000	-0.737822000	-4.181352000
H	3.053341000	-1.161853000	3.655414000
H	2.489896000	-2.509304000	2.655313000
H	1.354232000	-1.604024000	3.665997000
H	0.945373000	2.697343000	6.876148000
H	2.052331000	1.625230000	5.961667000
H	0.294233000	1.346109000	5.895814000
H	1.669150000	3.765860000	4.898788000

[NiL³H]⁻ (electron addition after the proton is added to amine nitrogen)

q Ms

-1 3

Ni	1.302513000	1.775453000	0.654754000
C	2.054121000	-0.837723000	0.517614000
N	1.740877000	0.223585000	-0.254319000
N	1.785025000	0.112548000	-1.612271000
C	1.455662000	1.225595000	-2.217123000
S	1.023138000	2.718086000	-1.335065000
C	2.438072000	-2.146979000	-0.101743000
N	1.409340000	1.270026000	-3.573196000
C	1.867053000	0.175850000	-4.414433000
C	1.123341000	2.410674000	3.454781000
N	1.617207000	0.728439000	2.151668000
N	1.485629000	1.175819000	3.415935000
C	1.974920000	-0.561031000	1.900392000
S	0.817798000	3.449347000	2.074183000
C	2.234429000	-1.516679000	3.021059000
N	0.971679000	3.020721000	4.799427000
C	1.075019000	2.095381000	5.979522000
H	1.327507000	2.183255000	-3.988865000
H	0.066586000	3.500045000	4.827859000
H	1.620766000	-2.544401000	-0.711489000
H	3.293640000	-2.019661000	-0.771234000
H	2.697340000	-2.889381000	0.651069000
H	1.684528000	0.441582000	-5.455191000
H	2.935492000	-0.027857000	-4.279685000
H	1.316700000	-0.737822000	-4.181352000
H	3.053341000	-1.161853000	3.655414000
H	2.489896000	-2.509304000	2.655313000
H	1.354232000	-1.604024000	3.665997000
H	0.945373000	2.697343000	6.876148000
H	2.052331000	1.625230000	5.961667000
H	0.294233000	1.346109000	5.895814000

H	1.669150000	3.765860000	4.898788000
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[NiL³H]⁻ (electron addition after the proton is added to sulfur)

q Ms

-1 1

Ni	1.161620000	1.900323000	0.606730000
C	2.060863000	-0.736436000	0.466771000
N	1.691085000	0.252092000	-0.313248000
N	1.845989000	0.153901000	-1.662101000
C	1.586439000	1.291198000	-2.287022000
S	1.205583000	2.847043000	-1.507819000
C	2.635663000	-2.032691000	-0.022522000
N	1.623078000	1.285840000	-3.635395000
C	1.900305000	0.108931000	-4.444150000
C	0.809580000	2.288168000	3.639179000
N	1.506984000	0.761399000	2.168574000
N	1.297697000	1.117014000	3.477920000
C	1.844103000	-0.475840000	1.894488000
S	0.171162000	3.275454000	2.233219000
C	2.026989000	-1.554768000	2.918085000
N	0.722981000	2.867735000	4.843662000
C	1.186933000	2.202937000	6.056669000
H	1.483903000	2.170063000	-4.095525000
H	0.059797000	3.619376000	4.947024000
H	1.873350000	-2.820415000	-0.035934000
H	3.006253000	-1.909673000	-1.038065000
H	3.448510000	-2.378753000	0.619385000
H	1.780399000	0.379251000	-5.492607000
H	2.919683000	-0.255959000	-4.286038000
H	1.208774000	-0.701577000	-4.203426000
H	3.079815000	-1.848834000	2.985010000

H	1.461807000	-2.450182000	2.645149000
H	1.702935000	-1.209401000	3.896435000
H	1.135570000	2.916832000	6.877177000
H	2.219839000	1.878139000	5.928306000
H	0.575581000	1.328013000	6.299323000
H	0.773511000	4.428390000	2.610730000

[NiL³H]⁻ (electron addition after the proton is added to sulfur)

q Ms

-1 3

Ni	1.161620000	1.900323000	0.606730000
C	2.060863000	-0.736436000	0.466771000
N	1.691085000	0.252092000	-0.313248000
N	1.845989000	0.153901000	-1.662101000
C	1.586439000	1.291198000	-2.287022000
S	1.205583000	2.847043000	-1.507819000
C	2.635663000	-2.032691000	-0.022522000
N	1.623078000	1.285840000	-3.635395000
C	1.900305000	0.108931000	-4.444150000
C	0.809580000	2.288168000	3.639179000
N	1.506984000	0.761399000	2.168574000
N	1.297697000	1.117014000	3.477920000
C	1.844103000	-0.475840000	1.894488000
S	0.171162000	3.275454000	2.233219000
C	2.026989000	-1.554768000	2.918085000
N	0.722981000	2.867735000	4.843662000
C	1.186933000	2.202937000	6.056669000
H	1.483903000	2.170063000	-4.095525000
H	0.059797000	3.619376000	4.947024000
H	1.873350000	-2.820415000	-0.035934000
H	3.006253000	-1.909673000	-1.038065000

H	3.448510000	-2.378753000	0.619385000
H	1.780399000	0.379251000	-5.492607000
H	2.919683000	-0.255959000	-4.286038000
H	1.208774000	-0.701577000	-4.203426000
H	3.079815000	-1.848834000	2.985010000
H	1.461807000	-2.450182000	2.645149000
H	1.702935000	-1.209401000	3.896435000
H	1.135570000	2.916832000	6.877177000
H	2.219839000	1.878139000	5.928306000
H	0.575581000	1.328013000	6.299323000
H	0.773511000	4.428390000	2.610730000

[NiL³H]⁻ (electron addition after the proton is added to nickel)

q Ms

-1 1

Ni	1.117862000	1.880134000	0.645834000
C	2.038253000	-0.754321000	0.466918000
N	1.619196000	0.197616000	-0.316321000
N	1.743459000	0.131661000	-1.665345000
C	1.473687000	1.281954000	-2.249336000
S	1.085187000	2.807536000	-1.393876000
C	2.641403000	-2.036165000	-0.017205000
N	1.491236000	1.350964000	-3.591149000
C	1.766626000	0.213547000	-4.458434000
C	0.792509000	2.343552000	3.587498000
N	1.553394000	0.779113000	2.181245000
N	1.371074000	1.159691000	3.467069000
C	1.879930000	-0.456142000	1.902292000
S	0.184765000	3.329103000	2.239934000
C	2.089736000	-1.480829000	2.972550000
N	0.635887000	2.839834000	4.827854000

C	1.075247000	2.161648000	6.038981000
H	1.369084000	2.258755000	-4.009205000
H	0.143243000	3.713755000	4.911446000
H	1.964234000	-2.877148000	0.164676000
H	2.830160000	-1.972182000	-1.086302000
H	3.577137000	-2.252150000	0.504165000
H	1.646376000	0.537112000	-5.491023000
H	2.785387000	-0.157257000	-4.315220000
H	1.071792000	-0.603869000	-4.255695000
H	2.974973000	-1.235123000	3.567988000
H	2.213738000	-2.479525000	2.558858000
H	1.239922000	-1.478906000	3.658648000
H	0.843528000	2.800049000	6.890021000
H	2.151417000	1.975837000	6.014051000
H	0.565232000	1.202173000	6.162070000
H	2.453316000	2.349586000	0.520196000

[NiL³H]⁻ (electron addition after the proton is added to nickel)

q Ms

-1 3

Ni	1.117862000	1.880134000	0.645834000
C	2.038253000	-0.754321000	0.466918000
N	1.619196000	0.197616000	-0.316321000
N	1.743459000	0.131661000	-1.665345000
C	1.473687000	1.281954000	-2.249336000
S	1.085187000	2.807536000	-1.393876000
C	2.641403000	-2.036165000	-0.017205000
N	1.491236000	1.350964000	-3.591149000
C	1.766626000	0.213547000	-4.458434000
C	0.792509000	2.343552000	3.587498000
N	1.553394000	0.779113000	2.181245000

N	1.371074000	1.159691000	3.467069000
C	1.879930000	-0.456142000	1.902292000
S	0.184765000	3.329103000	2.239934000
C	2.089736000	-1.480829000	2.972550000
N	0.635887000	2.839834000	4.827854000
C	1.075247000	2.161648000	6.038981000
H	1.369084000	2.258755000	-4.009205000
H	0.143243000	3.713755000	4.911446000
H	1.964234000	-2.877148000	0.164676000
H	2.830160000	-1.972182000	-1.086302000
H	3.577137000	-2.252150000	0.504165000
H	1.646376000	0.537112000	-5.491023000
H	2.785387000	-0.157257000	-4.315220000
H	1.071792000	-0.603869000	-4.255695000
H	2.974973000	-1.235123000	3.567988000
H	2.213738000	-2.479525000	2.558858000
H	1.239922000	-1.478906000	3.658648000
H	0.843528000	2.800049000	6.890021000
H	2.151417000	1.975837000	6.014051000
H	0.565232000	1.202173000	6.162070000
H	2.453316000	2.349586000	0.520196000

A.2 Computational input coordinates for NiL³ and related compounds using B3LYP/ 6-311g(d,p) in gas phase

NiL³

q Ms

0 1

Ni	1.298967264	1.716422563	0.713071468
C	2.077098110	-0.852510960	0.491389295
N	1.773134330	0.186402198	-0.234431064
N	1.826356920	0.101489400	-1.609083332
C	1.456628243	1.248488769	-2.136738890

S	0.958096047	2.658176535	-1.194682486
C	2.480675590	-2.168490180	-0.075503141
N	1.431975930	1.370106900	-3.469802543
C	1.739697353	0.264210738	-4.353189292
C	1.129474089	2.336962584	3.526368011
N	1.640189805	0.652745991	2.194418338
N	1.506619816	1.073419554	3.496785633
C	1.986729953	-0.577643835	1.932880409
S	0.855462745	3.324454446	2.085124447
C	2.253656241	-1.605054861	2.980517434
N	0.938903338	2.936088342	4.704959664
C	1.056751568	2.255094468	5.980838971
H	1.250598320	2.048394390	-3.812289741
H	0.626368925	3.653618400	4.691096792
H	2.447779305	-2.126202930	-1.073134807
H	3.411691239	-2.386692390	0.219082884
H	1.854987829	-2.877224490	0.248789038
H	1.663671094	0.566649150	-5.303786215
H	2.671825422	-0.052436190	-4.177427882
H	1.096246434	-0.483766140	-4.188567690
H	2.133652700	-1.197574920	3.885317370
H	3.191349969	-1.940139030	2.886447947
H	1.615000739	-2.366394510	2.870357114
H	0.871759587	2.900905350	6.721017304
H	1.982384841	1.891085820	6.079859484
H	0.396574022	1.505426100	6.020447176

[NiL³]⁻

q Ms

-1 2

Ni	1.288373000	1.729320000	0.702379000
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C	2.058206000	-0.839305000	0.496014000
N	1.757519000	0.190999000	-0.250996000
N	1.792502000	0.113566000	-1.605526000
C	1.451161000	1.264846000	-2.155209000
S	1.008754000	2.718796000	-1.247548000
C	2.461495000	-2.172613000	-0.048134000
N	1.435834000	1.347184000	-3.498688000
C	1.774208000	0.243113000	-4.381906000
C	1.075329000	2.350450000	3.526893000
N	1.593877000	0.659829000	2.205504000
N	1.453601000	1.085744000	3.486476000
C	1.963092000	-0.564778000	1.933515000
S	0.788673000	3.358742000	2.100452000
C	2.259873000	-1.596297000	2.974975000
N	0.892338000	2.920195000	4.732633000
C	1.089275000	2.225906000	5.994684000
H	1.174322000	2.234633000	-3.893909000
H	0.604572000	3.884190000	4.737759000
H	2.441302000	-2.144538000	-1.134733000
H	3.470136000	-2.440684000	0.282606000
H	1.785649000	-2.958645000	0.303169000
H	1.668477000	0.580777000	-5.412866000
H	2.802486000	-0.089606000	-4.217951000
H	1.110582000	-0.608997000	-4.214494000
H	2.149497000	-1.159166000	3.964222000
H	3.278242000	-1.981717000	2.864134000
H	1.579071000	-2.448923000	2.884364000
H	0.866283000	2.917047000	6.807494000
H	2.120655000	1.877609000	6.093791000
H	0.428922000	1.358336000	6.071025000

[NiL³H] (proton addition to the coordinated nitrogen)

q Ms

0 2

Ni	1.129334000	1.714428000	0.693898000
C	1.956995000	-0.862091000	0.521920000
N	1.635719000	0.196692000	-0.250047000
N	1.677846000	0.113264000	-1.614312000
C	1.309854000	1.215261000	-2.181263000
S	0.825106000	2.676425000	-1.294551000
C	2.379520000	-2.183360000	-0.051889000
N	1.256392000	1.281522000	-3.566399000
C	1.958121000	0.284862000	-4.354697000
C	0.944135000	2.317933000	3.548759000
N	1.439312000	0.652539000	2.186616000
N	1.337338000	1.088374000	3.479027000
C	1.863486000	-0.597227000	1.906315000
S	0.625050000	3.341664000	2.132291000
C	2.200486000	-1.596561000	2.974564000
N	0.723552000	2.891140000	4.793277000
C	1.271197000	2.254268000	5.977111000
H	1.337483000	2.230155000	-3.900159000
H	0.812946000	3.895671000	4.765145000
H	2.322145000	-2.135029000	-1.138285000
H	3.409380000	-2.440791000	0.228309000
H	1.739463000	-3.003140000	0.297464000
H	1.805282000	0.502736000	-5.415494000
H	3.038219000	0.244486000	-4.146185000
H	1.550569000	-0.704042000	-4.137845000
H	1.961166000	-1.173021000	3.948879000
H	3.266149000	-1.861506000	2.968104000
H	1.638891000	-2.530160000	2.847590000

H	0.996191000	2.845842000	6.854932000
H	2.365765000	2.141591000	5.945643000
H	0.847215000	1.254091000	6.081410000
H	1.238764613	-0.030347806	2.889073369

[NiL³H] (proton addition to the hydrazino nitrogen)

q Ms

0 2

Ni	1.129334000	1.714428000	0.693898000
C	1.956995000	-0.862091000	0.521920000
N	1.635719000	0.196692000	-0.250047000
N	1.677846000	0.113264000	-1.614312000
C	1.309854000	1.215261000	-2.181263000
S	0.825106000	2.676425000	-1.294551000
C	2.379520000	-2.183360000	-0.051889000
N	1.256392000	1.281522000	-3.566399000
C	1.958121000	0.284862000	-4.354697000
C	0.944135000	2.317933000	3.548759000
N	1.439312000	0.652539000	2.186616000
N	1.337338000	1.088374000	3.479027000
C	1.863486000	-0.597227000	1.906315000
S	0.625050000	3.341664000	2.132291000
C	2.200486000	-1.596561000	2.974564000
N	0.723552000	2.891140000	4.793277000
C	1.271197000	2.254268000	5.977111000
H	1.337483000	2.230155000	-3.900159000
H	0.812946000	3.895671000	4.765145000
H	2.322145000	-2.135029000	-1.138285000
H	3.409380000	-2.440791000	0.228309000
H	1.739463000	-3.003140000	0.297464000
H	1.805282000	0.502736000	-5.415494000

H	3.038219000	0.244486000	-4.146185000
H	1.550569000	-0.704042000	-4.137845000
H	1.961166000	-1.173021000	3.948879000
H	3.266149000	-1.861506000	2.968104000
H	1.638891000	-2.530160000	2.847590000
H	0.996191000	2.845842000	6.854932000
H	2.365765000	2.141591000	5.945643000
H	0.847215000	1.254091000	6.081410000
H	1.542977113	0.521924391	4.277054190

[NiL³H] (proton addition to the amine nitrogen)

q Ms

0 2

Ni	1.129334000	1.714428000	0.693898000
C	1.956995000	-0.862091000	0.521920000
N	1.635719000	0.196692000	-0.250047000
N	1.677846000	0.113264000	-1.614312000
C	1.309854000	1.215261000	-2.181263000
S	0.825106000	2.676425000	-1.294551000
C	2.379520000	-2.183360000	-0.051889000
N	1.256392000	1.281522000	-3.566399000
C	1.958121000	0.284862000	-4.354697000
C	0.944135000	2.317933000	3.548759000
N	1.439312000	0.652539000	2.186616000
N	1.337338000	1.088374000	3.479027000
C	1.863486000	-0.597227000	1.906315000
S	0.625050000	3.341664000	2.132291000
C	2.200486000	-1.596561000	2.974564000
N	0.723552000	2.891140000	4.793277000
C	1.271197000	2.254268000	5.977111000
H	1.337483000	2.230155000	-3.900159000

H	0.812946000	3.895671000	4.765145000
H	2.322145000	-2.135029000	-1.138285000
H	3.409380000	-2.440791000	0.228309000
H	1.739463000	-3.003140000	0.297464000
H	1.805282000	0.502736000	-5.415494000
H	3.038219000	0.244486000	-4.146185000
H	1.550569000	-0.704042000	-4.137845000
H	1.961166000	-1.173021000	3.948879000
H	3.266149000	-1.861506000	2.968104000
H	1.638891000	-2.530160000	2.847590000
H	0.996191000	2.845842000	6.854932000
H	2.365765000	2.141591000	5.945643000
H	0.847215000	1.254091000	6.081410000
H	0.240021952	2.095640736	5.158488738

[NiL³H] (proton addition to the sulfur)

q Ms

0 2

Ni	1.129334000	1.714428000	0.693898000
C	1.956995000	-0.862091000	0.521920000
N	1.635719000	0.196692000	-0.250047000
N	1.677846000	0.113264000	-1.614312000
C	1.309854000	1.215261000	-2.181263000
S	0.825106000	2.676425000	-1.294551000
C	2.379520000	-2.183360000	-0.051889000
N	1.256392000	1.281522000	-3.566399000
C	1.958121000	0.284862000	-4.354697000
C	0.944135000	2.317933000	3.548759000
N	1.439312000	0.652539000	2.186616000
N	1.337338000	1.088374000	3.479027000
C	1.863486000	-0.597227000	1.906315000

S	0.625050000	3.341664000	2.132291000
C	2.200486000	-1.596561000	2.974564000
N	0.723552000	2.891140000	4.793277000
C	1.271197000	2.254268000	5.977111000
H	1.337483000	2.230155000	-3.900159000
H	0.812946000	3.895671000	4.765145000
H	2.322145000	-2.135029000	-1.138285000
H	3.409380000	-2.440791000	0.228309000
H	1.739463000	-3.003140000	0.297464000
H	1.805282000	0.502736000	-5.415494000
H	3.038219000	0.244486000	-4.146185000
H	1.550569000	-0.704042000	-4.137845000
H	1.961166000	-1.173021000	3.948879000
H	3.266149000	-1.861506000	2.968104000
H	1.638891000	-2.530160000	2.847590000
H	0.996191000	2.845842000	6.854932000
H	2.365765000	2.141591000	5.945643000
H	0.847215000	1.254091000	6.081410000
H	0.232859051	4.603985455	1.985216852

[NiL³H] (proton addition to the nickel)

q Ms

0 2

Ni	1.129334000	1.714428000	0.693898000
C	1.956995000	-0.862091000	0.521920000
N	1.635719000	0.196692000	-0.250047000
N	1.677846000	0.113264000	-1.614312000
C	1.309854000	1.215261000	-2.181263000
S	0.825106000	2.676425000	-1.294551000
C	2.379520000	-2.183360000	-0.051889000
N	1.256392000	1.281522000	-3.566399000

C	1.958121000	0.284862000	-4.354697000
C	0.944135000	2.317933000	3.548759000
N	1.439312000	0.652539000	2.186616000
N	1.337338000	1.088374000	3.479027000
C	1.863486000	-0.597227000	1.906315000
S	0.625050000	3.341664000	2.132291000
C	2.200486000	-1.596561000	2.974564000
N	0.723552000	2.891140000	4.793277000
C	1.271197000	2.254268000	5.977111000
H	1.337483000	2.230155000	-3.900159000
H	0.812946000	3.895671000	4.765145000
H	2.322145000	-2.135029000	-1.138285000
H	3.409380000	-2.440791000	0.228309000
H	1.739463000	-3.003140000	0.297464000
H	1.805282000	0.502736000	-5.415494000
H	3.038219000	0.244486000	-4.146185000
H	1.550569000	-0.704042000	-4.137845000
H	1.961166000	-1.173021000	3.948879000
H	3.266149000	-1.861506000	2.968104000
H	1.638891000	-2.530160000	2.847590000
H	0.996191000	2.845842000	6.854932000
H	2.365765000	2.141591000	5.945643000
H	0.847215000	1.254091000	6.081410000
H	0.555106194	3.413496452	0.330127711

[NiL³H]⁻ (electron addition after the proton is added to coordinated nitrogen)

q Ms

-1 1

Ni	0.834982000	1.574848000	0.738947000
C	1.912962000	-0.919928000	0.573027000
N	1.522196000	0.152198000	-0.192910000

N	1.723517000	0.112375000	-1.514241000
C	1.369195000	1.256613000	-2.092694000
S	0.734813000	2.627858000	-1.196026000
C	2.565484000	-2.096327000	-0.087961000
N	1.512378000	1.362567000	-3.429177000
C	2.088220000	0.322847000	-4.266826000
C	0.956940000	2.258143000	3.540436000
N	0.870145000	0.403817000	2.250981000
N	1.254644000	0.991533000	3.523212000
C	1.657972000	-0.787310000	1.913009000
S	0.315587000	3.175078000	2.154006000
C	1.988805000	-1.728630000	3.020423000
N	1.094531000	2.952296000	4.700540000
C	1.664562000	2.359795000	5.898398000
H	1.278048000	2.251348000	-3.838741000
H	1.115163000	3.954425000	4.605875000
H	1.898280000	-2.518994000	-0.842967000
H	3.470467000	-1.780495000	-0.612199000
H	2.821054000	-2.872487000	0.630821000
H	2.011231000	0.636344000	-5.307925000
H	3.140367000	0.148895000	-4.021853000
H	1.549417000	-0.617635000	-4.135855000
H	1.080807000	-2.173869000	3.448688000
H	2.483592000	-1.188684000	3.829958000
H	2.635785000	-2.536776000	2.682406000
H	1.545879000	3.061021000	6.725402000
H	2.727996000	2.119623000	5.780336000
H	1.136687000	1.435512000	6.137290000
H	-0.098634000	0.089670000	2.374821000

[NiL³H][−] (electron addition after the proton is added to coordinated nitrogen)

q Ms

-1 3

Ni	0.834982000	1.574848000	0.738947000
C	1.912962000	-0.919928000	0.573027000
N	1.522196000	0.152198000	-0.192910000
N	1.723517000	0.112375000	-1.514241000
C	1.369195000	1.256613000	-2.092694000
S	0.734813000	2.627858000	-1.196026000
C	2.565484000	-2.096327000	-0.087961000
N	1.512378000	1.362567000	-3.429177000
C	2.088220000	0.322847000	-4.266826000
C	0.956940000	2.258143000	3.540436000
N	0.870145000	0.403817000	2.250981000
N	1.254644000	0.991533000	3.523212000
C	1.657972000	-0.787310000	1.913009000
S	0.315587000	3.175078000	2.154006000
C	1.988805000	-1.728630000	3.020423000
N	1.094531000	2.952296000	4.700540000
C	1.664562000	2.359795000	5.898398000
H	1.278048000	2.251348000	-3.838741000
H	1.115163000	3.954425000	4.605875000
H	1.898280000	-2.518994000	-0.842967000
H	3.470467000	-1.780495000	-0.612199000
H	2.821054000	-2.872487000	0.630821000
H	2.011231000	0.636344000	-5.307925000
H	3.140367000	0.148895000	-4.021853000
H	1.549417000	-0.617635000	-4.135855000
H	1.080807000	-2.173869000	3.448688000
H	2.483592000	-1.188684000	3.829958000
H	2.635785000	-2.536776000	2.682406000
H	1.545879000	3.061021000	6.725402000

H	2.727996000	2.119623000	5.780336000
H	1.136687000	1.435512000	6.137290000
H	-0.098634000	0.089670000	2.374821000

[NiL³H]⁻ (electron addition after the proton is added to hydrazino nitrogen)

q Ms

-1 1

Ni	1.150798000	1.695109000	0.696974000
C	1.988392000	-0.889697000	0.514561000
N	1.680225000	0.184449000	-0.238195000
N	1.694529000	0.085652000	-1.591200000
C	1.352214000	1.215514000	-2.165223000
S	0.888329000	2.675352000	-1.270944000
C	2.361872000	-2.188852000	-0.131311000
N	1.333378000	1.284418000	-3.520613000
C	1.830511000	0.219904000	-4.372691000
C	1.079796000	2.417361000	3.559499000
N	1.302842000	0.563268000	2.165842000
N	1.391249000	1.122094000	3.434881000
C	1.897366000	-0.635472000	1.898880000
S	0.844127000	3.381802000	2.150036000
C	2.340488000	-1.546167000	3.001094000
N	0.927403000	2.947306000	4.797099000
C	1.233509000	2.258096000	6.036729000
H	1.183422000	2.197016000	-3.916120000
H	0.794885000	3.945055000	4.816320000
H	3.214649000	-2.054100000	-0.802233000
H	2.609919000	-2.954354000	0.603923000
H	1.537654000	-2.557585000	-0.749321000
H	1.613730000	0.474118000	-5.411094000
H	2.910505000	0.070011000	-4.257544000

H	1.334392000	-0.720456000	-4.125819000
H	1.508912000	-1.833139000	3.660023000
H	3.108124000	-1.070332000	3.625426000
H	2.771560000	-2.465438000	2.609796000
H	1.062786000	2.941774000	6.866693000
H	2.277352000	1.922456000	6.075088000
H	0.577110000	1.392498000	6.183868000
H	1.365257000	0.500279000	4.232757000

[NiL³H]⁻ (electron addition after the proton is added to hydrazino nitrogen)

q Ms

-1 3

Ni	1.150798000	1.695109000	0.696974000
C	1.988392000	-0.889697000	0.514561000
N	1.680225000	0.184449000	-0.238195000
N	1.694529000	0.085652000	-1.591200000
C	1.352214000	1.215514000	-2.165223000
S	0.888329000	2.675352000	-1.270944000
C	2.361872000	-2.188852000	-0.131311000
N	1.333378000	1.284418000	-3.520613000
C	1.830511000	0.219904000	-4.372691000
C	1.079796000	2.417361000	3.559499000
N	1.302842000	0.563268000	2.165842000
N	1.391249000	1.122094000	3.434881000
C	1.897366000	-0.635472000	1.898880000
S	0.844127000	3.381802000	2.150036000
C	2.340488000	-1.546167000	3.001094000
N	0.927403000	2.947306000	4.797099000
C	1.233509000	2.258096000	6.036729000
H	1.183422000	2.197016000	-3.916120000
H	0.794885000	3.945055000	4.816320000

H	3.214649000	-2.054100000	-0.802233000
H	2.609919000	-2.954354000	0.603923000
H	1.537654000	-2.557585000	-0.749321000
H	1.613730000	0.474118000	-5.411094000
H	2.910505000	0.070011000	-4.257544000
H	1.334392000	-0.720456000	-4.125819000
H	1.508912000	-1.833139000	3.660023000
H	3.108124000	-1.070332000	3.625426000
H	2.771560000	-2.465438000	2.609796000
H	1.062786000	2.941774000	6.866693000
H	2.277352000	1.922456000	6.075088000
H	0.577110000	1.392498000	6.183868000
H	1.365257000	0.500279000	4.232757000

[NiL³H]⁻ (electron addition after the proton is added to amine nitrogen)

q Ms

-1 1

Ni	1.250264000	1.576326000	0.856916000
C	1.817225000	-1.062032000	0.501575000
N	1.663949000	0.095517000	-0.170297000
N	1.808747000	0.114552000	-1.518416000
C	1.609602000	1.313664000	-2.014707000
S	1.215617000	2.732484000	-1.029795000
C	2.141219000	-2.324946000	-0.235775000
N	1.691695000	1.488915000	-3.359427000
C	2.146004000	0.448078000	-4.262853000
C	0.896946000	1.957895000	3.654878000
N	1.344704000	0.352258000	2.256634000
N	1.149258000	0.689840000	3.537417000
C	1.641254000	-0.926826000	1.894897000
S	0.773663000	3.158892000	2.404677000

C	1.747461000	-2.004358000	2.925392000
N	0.654412000	2.359378000	5.059850000
C	1.698732000	3.269650000	5.645252000
H	1.683628000	2.441982000	-3.681204000
H	-0.262130000	2.815655000	5.125288000
H	1.363747000	-2.548393000	-0.972109000
H	3.073566000	-2.212383000	-0.796500000
H	2.237954000	-3.174593000	0.439168000
H	2.012003000	0.792962000	-5.289192000
H	3.200825000	0.193028000	-4.104339000
H	1.557413000	-0.458407000	-4.112382000
H	0.805437000	-2.111111000	3.474503000
H	2.514177000	-1.756928000	3.667560000
H	1.997001000	-2.966731000	2.481486000
H	1.417120000	3.532250000	6.665449000
H	1.755844000	4.151600000	5.011911000
H	2.646211000	2.736240000	5.623403000
H	0.610778000	1.477198000	5.579357000

[NiL³H]⁻ (electron addition after the proton is added to amine nitrogen)

q Ms

-1 3

Ni	1.250264000	1.576326000	0.856916000
C	1.817225000	-1.062032000	0.501575000
N	1.663949000	0.095517000	-0.170297000
N	1.808747000	0.114552000	-1.518416000
C	1.609602000	1.313664000	-2.014707000
S	1.215617000	2.732484000	-1.029795000
C	2.141219000	-2.324946000	-0.235775000
N	1.691695000	1.488915000	-3.359427000
C	2.146004000	0.448078000	-4.262853000

C	0.896946000	1.957895000	3.654878000
N	1.344704000	0.352258000	2.256634000
N	1.149258000	0.689840000	3.537417000
C	1.641254000	-0.926826000	1.894897000
S	0.773663000	3.158892000	2.404677000
C	1.747461000	-2.004358000	2.925392000
N	0.654412000	2.359378000	5.059850000
C	1.698732000	3.269650000	5.645252000
H	1.683628000	2.441982000	-3.681204000
H	-0.262130000	2.815655000	5.125288000
H	1.363747000	-2.548393000	-0.972109000
H	3.073566000	-2.212383000	-0.796500000
H	2.237954000	-3.174593000	0.439168000
H	2.012003000	0.792962000	-5.289192000
H	3.200825000	0.193028000	-4.104339000
H	1.557413000	-0.458407000	-4.112382000
H	0.805437000	-2.111111000	3.474503000
H	2.514177000	-1.756928000	3.667560000
H	1.997001000	-2.966731000	2.481486000
H	1.417120000	3.532250000	6.665449000
H	1.755844000	4.151600000	5.011911000
H	2.646211000	2.736240000	5.623403000
H	0.610778000	1.477198000	5.579357000

[NiL³H]⁻ (electron addition after the proton is added to sulfur)

q Ms

-1 1

Ni	1.234494000	1.900497000	0.602129000
C	2.017142000	-0.766649000	0.465988000
N	1.794166000	0.270524000	-0.311546000
N	1.753191000	0.124459000	-1.650274000

C	1.343664000	1.231045000	-2.262844000
S	0.726891000	2.690736000	-1.489177000
C	2.285579000	-2.152157000	-0.043130000
N	1.380275000	1.226103000	-3.612327000
C	1.866458000	0.115068000	-4.411447000
C	1.233515000	2.416761000	3.625578000
N	1.517264000	0.752095000	2.158505000
N	1.468829000	1.164661000	3.467742000
C	1.983636000	-0.446253000	1.886210000
S	1.257569000	3.582513000	2.213047000
C	2.434010000	-1.428810000	2.924532000
N	0.932720000	2.969485000	4.836121000
C	0.909353000	2.141655000	6.037820000
H	1.002408000	2.039501000	-4.067834000
H	1.235894000	3.923970000	4.957665000
H	2.387518000	-2.120458000	-1.125868000
H	3.201436000	-2.566144000	0.389726000
H	1.468079000	-2.838122000	0.206448000
H	1.827799000	0.403544000	-5.462540000
H	2.896995000	-0.134637000	-4.147677000
H	1.255359000	-0.780287000	-4.263295000
H	2.197787000	-1.063314000	3.921019000
H	3.514945000	-1.595146000	2.859797000
H	1.951705000	-2.398272000	2.771659000
H	0.541559000	2.747628000	6.866378000
H	1.898365000	1.741566000	6.287524000
H	0.232771000	1.301364000	5.883823000
H	0.105790000	4.207074000	2.571591000

[NiL³H]⁻ (electron addition after the proton is added to sulfur)

q Ms

-1 3

Ni	1.234494000	1.900497000	0.602129000
C	2.017142000	-0.766649000	0.465988000
N	1.794166000	0.270524000	-0.311546000
N	1.753191000	0.124459000	-1.650274000
C	1.343664000	1.231045000	-2.262844000
S	0.726891000	2.690736000	-1.489177000
C	2.285579000	-2.152157000	-0.043130000
N	1.380275000	1.226103000	-3.612327000
C	1.866458000	0.115068000	-4.411447000
C	1.233515000	2.416761000	3.625578000
N	1.517264000	0.752095000	2.158505000
N	1.468829000	1.164661000	3.467742000
C	1.983636000	-0.446253000	1.886210000
S	1.257569000	3.582513000	2.213047000
C	2.434010000	-1.428810000	2.924532000
N	0.932720000	2.969485000	4.836121000
C	0.909353000	2.141655000	6.037820000
H	1.002408000	2.039501000	-4.067834000
H	1.235894000	3.923970000	4.957665000
H	2.387518000	-2.120458000	-1.125868000
H	3.201436000	-2.566144000	0.389726000
H	1.468079000	-2.838122000	0.206448000
H	1.827799000	0.403544000	-5.462540000
H	2.896995000	-0.134637000	-4.147677000
H	1.255359000	-0.780287000	-4.263295000
H	2.197787000	-1.063314000	3.921019000
H	3.514945000	-1.595146000	2.859797000
H	1.951705000	-2.398272000	2.771659000
H	0.541559000	2.747628000	6.866378000
H	1.898365000	1.741566000	6.287524000

H	0.232771000	1.301364000	5.883823000
H	0.105790000	4.207074000	2.571591000

[NiL³H]⁻ (electron addition after the proton is added to nickel)

q Ms

-1 1

Ni	1.007394000	1.810096000	0.617830000
C	2.003694000	-0.780807000	0.466033000
N	1.838103000	0.263185000	-0.301017000
N	1.886663000	0.157216000	-1.654437000
C	1.332820000	1.194968000	-2.244087000
S	0.455943000	2.507227000	-1.412710000
C	2.337701000	-2.146598000	-0.049592000
N	1.382480000	1.272723000	-3.590088000
C	2.016089000	0.270035000	-4.429603000
C	1.297090000	2.425941000	3.545998000
N	1.365534000	0.678283000	2.175187000
N	1.289763000	1.110869000	3.454226000
C	1.855093000	-0.501800000	1.901486000
S	1.520928000	3.528755000	2.185141000
C	2.287806000	-1.479945000	2.950491000
N	1.170962000	2.977604000	4.773255000
C	1.047824000	2.200742000	5.994909000
H	0.873847000	2.027426000	-4.018436000
H	1.209709000	3.981234000	4.822127000
H	2.464736000	-2.107610000	-1.128808000
H	3.257261000	-2.522652000	0.408714000
H	1.541187000	-2.859242000	0.188711000
H	1.981962000	0.612956000	-5.463838000
H	3.057746000	0.125330000	-4.135521000
H	1.505339000	-0.695123000	-4.354264000

H	1.885248000	-1.186022000	3.917272000
H	3.380760000	-1.506745000	3.028938000
H	1.953406000	-2.490789000	2.705434000
H	0.947585000	2.890278000	6.833178000
H	1.927662000	1.570068000	6.153182000
H	0.169197000	1.551904000	5.959275000
H	-0.072118000	2.590004000	1.131268000

[NiL³H]⁻ (electron addition after the proton is added to nickel)

q Ms

-1 3

Ni	1.007394000	1.810096000	0.617830000
C	2.003694000	-0.780807000	0.466033000
N	1.838103000	0.263185000	-0.301017000
N	1.886663000	0.157216000	-1.654437000
C	1.332820000	1.194968000	-2.244087000
S	0.455943000	2.507227000	-1.412710000
C	2.337701000	-2.146598000	-0.049592000
N	1.382480000	1.272723000	-3.590088000
C	2.016089000	0.270035000	-4.429603000
C	1.297090000	2.425941000	3.545998000
N	1.365534000	0.678283000	2.175187000
N	1.289763000	1.110869000	3.454226000
C	1.855093000	-0.501800000	1.901486000
S	1.520928000	3.528755000	2.185141000
C	2.287806000	-1.479945000	2.950491000
N	1.170962000	2.977604000	4.773255000
C	1.047824000	2.200742000	5.994909000
H	0.873847000	2.027426000	-4.018436000
H	1.209709000	3.981234000	4.822127000
H	2.464736000	-2.107610000	-1.128808000

H	3.257261000	-2.522652000	0.408714000
H	1.541187000	-2.859242000	0.188711000
H	1.981962000	0.612956000	-5.463838000
H	3.057746000	0.125330000	-4.135521000
H	1.505339000	-0.695123000	-4.354264000
H	1.885248000	-1.186022000	3.917272000
H	3.380760000	-1.506745000	3.028938000
H	1.953406000	-2.490789000	2.705434000
H	0.947585000	2.890278000	6.833178000
H	1.927662000	1.570068000	6.153182000
H	0.169197000	1.551904000	5.959275000
H	-0.199147253	2.549958837	0.433215775

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Candidacy Fee Award, U of L, KY, Fall 2016.

PUBLICATIONS:

1) R. Jain, T. J. Gibson, M. S. Mashuta, R. M. Buchanan, C. A. Grapperhaus, "Copper catalysed aerobic oxidation of benzylic alcohols in an imidazole containing N₄ ligand framework" *Dalton Trans.*, 2016,45, 18356-18364
(*From themed collection: Reactions Facilitated by Ligand Design.*)

2) R. Jain, M. S. Mashuta, R. M. Buchanan, C. A. Grapperhaus, "Electrocatalytic Hydrogen Evolution and Hydrogen Oxidation with a Ni(PS)₂ Complex", *Eur. J. Inorg. Chem.*, 2017, 31, 3714-3719

3) R. Jain, R. M. Buchanan, C. A. Grapperhaus, "Electrocatalytic Hydrogen Evolution with Ni(N₂S₂) complex" (*manuscript in prepn.*)

PRESENTATIONS:

1) R. Jain, R. M. Buchanan, C. A. Grapperhaus, "*Electrocatalytic hydrogen evolution reaction with bis(thiosemicarbazonato) Ni(II) complex*" The Southeastern Regional Meeting of ACS (SERMACS), Charlotte, North Carolina - Nov. 2017 (poster)

2) R. Jain, A. Z. Haddad, M. S. Mashuta, C. A. Grapperhaus "*Synthesis, characterization and electrochemical properties of new tetracoordinated Ni(II) and Zn(II) complexes with P₂S₂ type ligand framework*" Pacificchem- The International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, USA- Dec. 2015 (poster)

3) R. Jain, "*Evaluating ligand assisted activation of small molecules through alcohol oxidation and proton reduction*" Invited talk for Inorganic Chemistry Seminar Series, Department of Chemistry, Louisiana State University, Baton Rouge, LA- Sept. 2017. (invited talk)

4) R. Jain, A. Z. Haddad, M. S. Mashuta, R. M. Buchanan, C. A. Grapperhaus, "*Electrocatalytic hydrogen production and hydrogen oxidation using tetradentate Nickel (II) and Zinc (II) complexes with P₂S₂ ligand framework: Synthesis, Characterization and Mechanistic Insights*" 254th ACS National Meeting and Exposition, Washington, DC - Aug. 2017. (talk)

5) R. Jain, T. J. Gibson, M. S. Mashuta, R. M. Buchanan, C. A. Grapperhaus, "*Copper catalysed aerobic oxidation of benzylic alcohols in an imidazole containing N₄ ligand framework*" GSC Graduate Research Conference, University of Louisville, KY- Mar. 2017. (talk)

6) R. Jain, T. J. Gibson, M. S. Mashuta, R. M. Buchanan, C. A. Grapperhaus, "*Copper catalysed aerobic oxidation of benzylic alcohols in an imidazole containing N₄ ligand framework*" 102nd meeting of the Kentucky Academy of Sciences (KAS), University of Louisville, KY- Nov. 2016. (talk)