SYNTHESIS OF NOVEL COPPER(I) *N*-HETEROCYCLIC CARBENE COMPLEXES BEARING NITROGEN DONOR LIGANDS

By

MATTHEW CURTIS BARDEAUX

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University of Tulsa

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Thesis Approved:

Dr. Laleh Tahsini

Thesis Adviser

Dr. Allen Apblett

Dr. Jimmie Weaver

Dr. Jeff White

Name: Matthew Bardeaux

Date of Degree: JULY, 2017

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Abstract: *N*-Heterocyclic carbenes are becoming a widely used class of metal complexes due to their physical and chemical properties. These applications include catalysis, materials, medicine, and photoluminescence. Rational design of transition metal complexes bearing NHC ligands can be achieved using certain synthetic methods. Herein, we report the synthesis of series of Cu(I)-*N*-heterocyclic carbenes bearing either dipyridylamine ligands or diimine ligands as potential candidates for future photoluminescent studies.

TABLE OF CONTENTS

Chapter Page

LIST OF FIGURES

Figure Page

Chapter 1

Chapter 2

Figure Page

Chapter 3

CHAPTER I

INTRODUCTION

N-heterocyclic carbenes (NHCs) have been uses in catalysis, medicine, and photoluminescence. As such, an influx of research on the synthesis and applications of these species has been initiated. We report herein current studies into these applications as well as new Cu(I)-NHC complexes with potential applications in photoluminescence.

1.1 Introduction to NHCs

The modern era of *N*-heterocyclic carbenes (hereafter referred to as NHCs) began with a report in 1991 from Arduengo's group[1]. In this report, a crystalline NHC consisting of an imidazole ring with adamantyl substituents (IAd) was synthesized. This crystalline NHC was prepared by deprotonation of the corresponding imidazolium salt in the presence of a strong base such as NaH and was surprisingly thermally stable and storable for long periods of time. This is due to the kinetic stabilization by disfavoring sterically the dimerization into the olefin form, also known as the Wanzlick equilibrium.

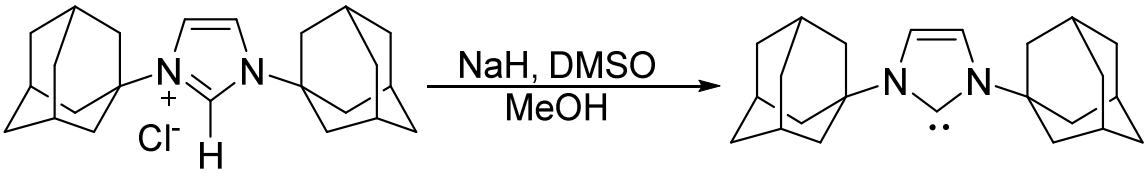


Figure 1. Reaction conditions for the formation of IAd.

As these compounds began being studied more extensively, many feature came to light, including being electron rich (due to resonance), neutral σ-donor ligands. This is due to the fact that NHCs were initially considered to be mimics of phospine ligands[2].

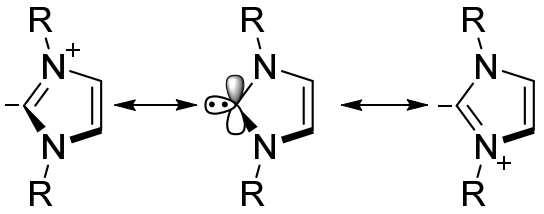


Figure 2. Resonance structures of NHCs

As a result, many comparisons between the two ligand series have been made. The first of these comparisons lies in their Tolman electronic parameters. The Tolman electronic parameter was originally developed for phosphine ligands and is a measure of the electron-donating ability of a ligand by measuring the IR-stretching frequencies of carbonyl ligands in model transition metal carbonyl complexes[3]. The more electron-donating the ligand of interest, the more electron-rich the metal center becomes, increasing the degree of π-backbonding into the carbonyl ligands and thus reducing their bond order and infrared stretching frequency. NHCs have lower Tolman electronic parameters, thus making them, in general, more electron-donating than phosphines. As such, this lends towards thermodynamically stronger metal-ligand bonds than in phosphine ligands. This is shown in greater bond dissociation energies as well as shorter metal-ligand bond lengths in NHCs over phosphine ligands.[4]

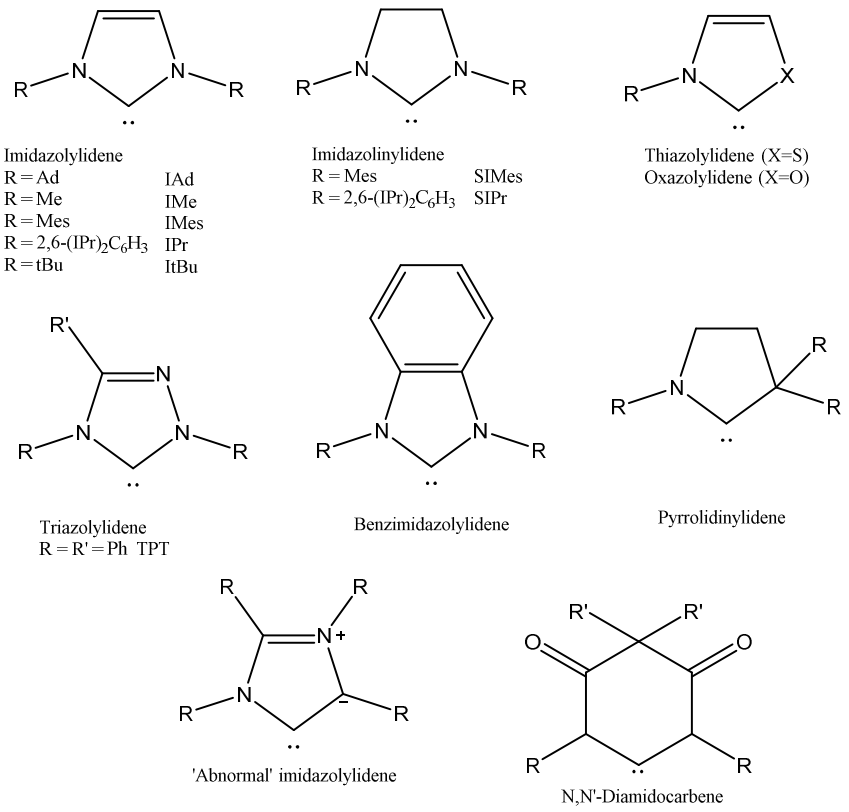


Figure 3. Structures of commonly employed classes of NHCs[5-10]

The other main feature in NHCs is the ease in controlling steric and electronic properties of the compounds. In general, the more electron rich a NHC is, the better electron donor it is[7,11]. One such common example of this is the imidazole series, with imidazoline being the strongest electron donor and benzimidazole the weakest.

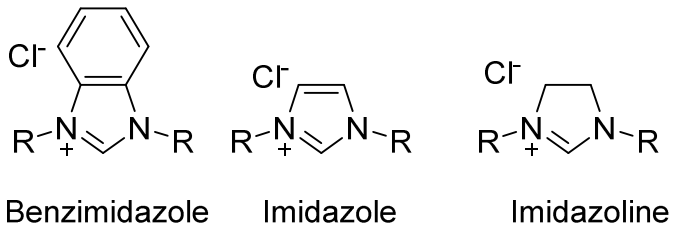


Figure 4. Common NHC azole rings

1.1.1 NHCs in metal catalysis

The first report of NHCs in catalysis was by Herrmann and coworkers, using a imidazole-2-ylidene-palladium catalyst in the Mizoroki-Heck reaction[12]. As more NHCs have been synthesized, many more metals have been employed for catalysis of various reactions.[19-21]

1.1.1.1 Pd-NHC catalysis

One of the classes of reactions that palladium NHCs can oxidize are oxidation reactions. The first of these reactions to be discussed was performed by Sigman and coworkers.[13] In this study, they were able to oxidize secondary alcohols into ketones, with the Pd-NHC complex withstanding the aerobic oxidation conditions, suggesting there is no ligand dissociation from the palladium center even with the cycling of oxidation states of the palladium between Pd^{II} and Pd^{0}.

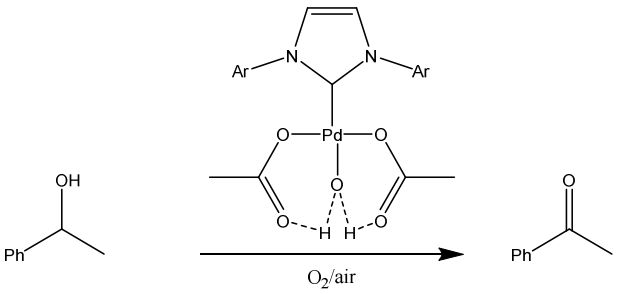


Figure 5. Sigman alcohol oxidation

Another important reaction is Herrmann's oxidation of methane utilizing a bidentate NHC bound to a palladium center.[14] The reaction is an oxidation of methane with trifluoroacetic acid and potassium persulfate. It is noteworthy that this reaction does work with palladium(II) acetate with no ligand present, but the yields are two to three times lower. Interestingly, chelating nitrogen-donor ligands were found to fail under examined conditions, making this transformation unique to NHC ligands.

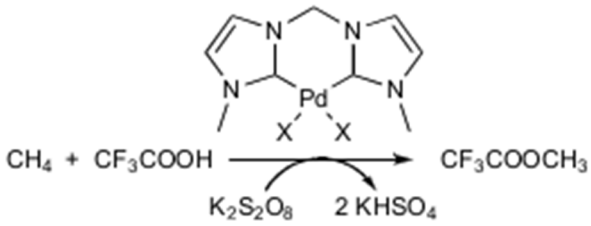


Figure 6. Hermann methane oxidation

Nolan and coworkers were able to perform α-arylation of carbonyls under relatively mild conditions (60 °C) with short reaction times (1 to 3 hours).[15] This reaction which was performed using a IPr ligand bound to a palladium (II) center was initially applied to ketones, but was extended to both esters and amides.

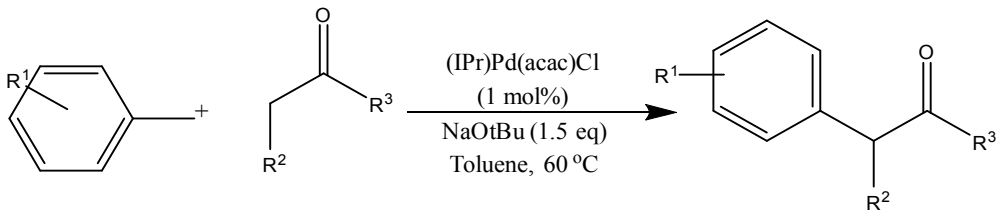


Figure 7. Nolan α-arylation of carbonyls

Nolan also employed Pd-NHCs on the Kumada cross-coupling, which involves the coupling of either an alkyl, vinyl, or aryl halide to a Grignard reagent[16]. The noteworthy experimental point, however, is that this was the first reported successful coupling between an unactivated aryl chloride with an aryl-Grigard reagent. Later, the same studies were performed using primary alkyl halides and it was found that NHCs are efficient ligands for primary alkyl couplings with aryl-Grignard reagents as well.

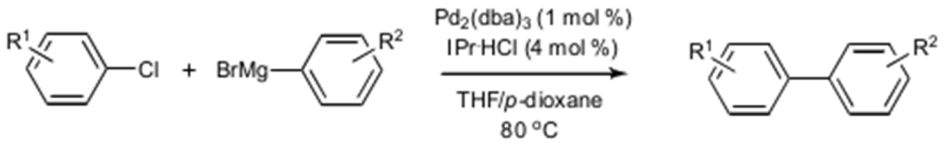


Figure 8. Kumada coupling utilizing Pd-NHC complex catalyst

Another reaction studied by Nolan was the Buchwald-Hartwig coupling.[17] In this reaction, coupling occurs between an amine and an aryl halide. The reaction requires the use of a palladium catalyst and a strong base to deprotonate the amine. Again, he was able to employ a Pd-NHC at 1 mol% loading to catalyze the reaction between aryl chloride and secondary amines in two hours at room temperature.

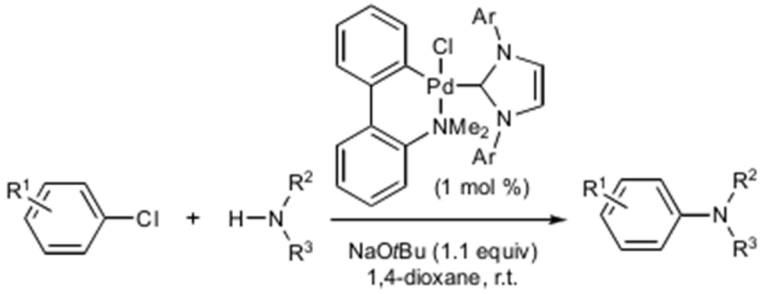


Figure 9. Buchwald-Hartwig coupling utilizing Pd-NHC complex catalyst

1.1.1.2 Other metal-NHC catalysis

Hartwig and coworkers utilized a Ru-NHC to improve ring closing metathesis reactions on highly substituted and electron-poor olefinic reactions giving rise to tetrasubstituted products.[18] This was due to the ability of the NHC ligands to stabilize the active metal species in solution. Prior to this, only Schrock alkylidene catalysts could provide high yields in this metathesis.[19,20] The new Ru-NHCs were much more efficient as well as more stable in storage than their Schrock counterparts.

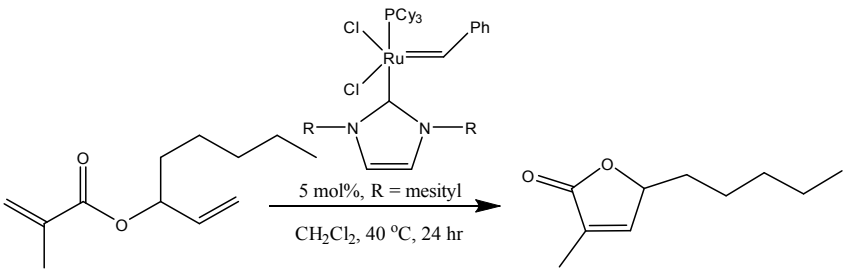


Figure 10. Ring closing metathesis using Ru-NHC

Cetinkaya and coworkers applied rhodium and ruthenium NHC complexes to cyclopropanation reactions. Their initial logic in broaching this structure of catalyst was due to the fact that "...heterofunctional ligands...have been found to confer interesting properties to their metal complexes, such as dynamic behavior via reversible dissociation of the weaker metal-ligand bond resulting in unique catalytic properties." Seven catalysts were synthesized with this concept in mind, and all were tested for efficiency in cyclopropanation reactions, as shown in the scheme below. The catalyst shown below was able to catalyze the reaction in four hours with 71% yield at 80 °C.[21]

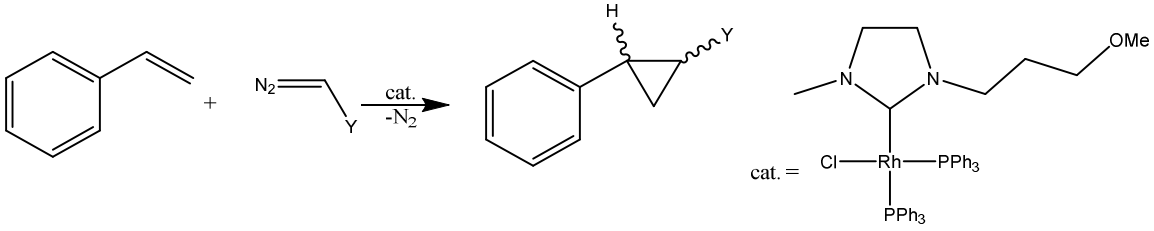


Figure 11. Cyclopropanation via Rh-NHCs

1.1.2 NHCs in medicine and materials

Bielawski and coworkers were able to develop a series of palladium(II) and platinum(II)-NHC based polymers using benzene linked bis(NHC) units.[22] These polymers exhibit self-healing properties due to the reversibility of the metal-ligand coordination.

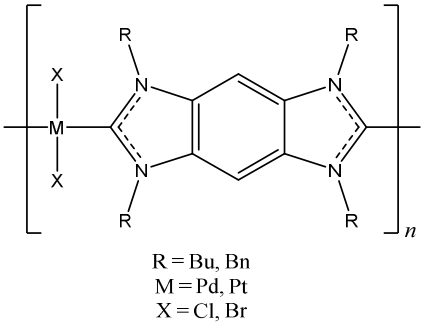
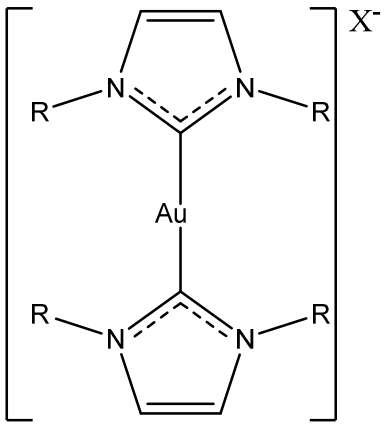


Figure 12, Self-healing polymers containing NHCs

Other polymers with NHC architecture have shown electronic coupling between metal centers and others acting as phosphors.[23]

Publications showcasing the medicinal capabilities of silver- and gold-NHCs, respectively as antibacterial and anticancer agents, have become increasingly popular as of late.[24] One particular complex architecture, imidazol-2-ylidene– and imidazolin-2-ylidene–Ag complexes, have low minimum inhibitory concentrations (<10μg/mL) for both Gram-positive and Gram-negative bacteria. A potential anticancer reagent, shown below, developed by Berners-Price and coworkers induces apoptosis by selective inhibition of the selenoenzyme thioredoxin reductase, an enzyme known to overexpress in human cancers.[25]



R - iPr, nPr, Et
X = Cl, Br

Figure 13, Potential Au-NHC anticancer agent

1.2 Introduction to photoluminescence

When a compound absorbs a photon, its energy increases, causing electrons to go into an excited state, known as S_2. After this initial excitation, some energy is let off as heat or vibrational energy to lower the electron into another excited state, S_1. After entering the S_1 state, the electron can relax back to the ground state by emitting a photon. This process is known as fluorescence and typically has a lifetime on the scale of nanoseconds. The energy of the emitted photon is limited by the energy of the photon required to initially excite the electron initially, thus affecting the wavelength of light let off by a molecule. The electron can also drop in energy by entering into a triplet state via a process known as intersystem crossing. The fate of the electron is still the same; however, this process, known as phosphorescence, is spin forbidden and thus the lifetime of this process is on the scale of milliseconds. Pictured below is a Jablonski diagram, which is a common way to illustrate these processes.[27]

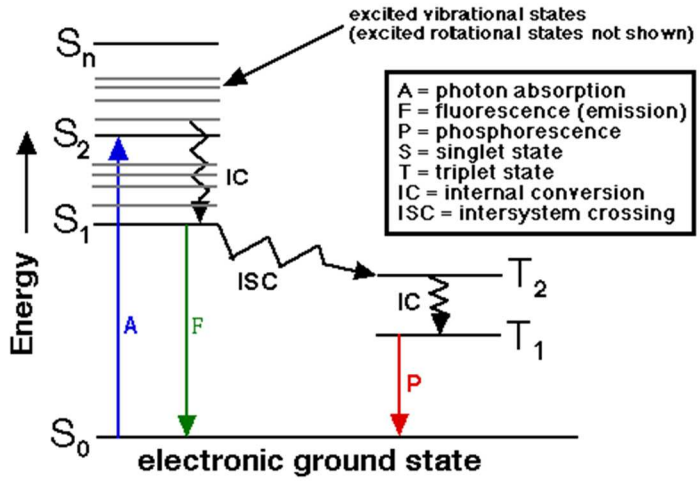


Figure 14, Jablonski diagram illustrating common emission pathways

1.2.1 Photoluminescent compounds

Traditionally, organic molecules are most commonly associated with fluorescence. Some of the more common organic compounds that fluoresce are quinine[27] (compound found in tonic water; exc: 250 and 350 nm, em: 450 nm), pyranine[28] (also a pH indicator; exc: 454 nm, em: 511-520 nm dependent on pH), fluorescein[29] (a common dye, exc: 472 nm, em: 520 nm).

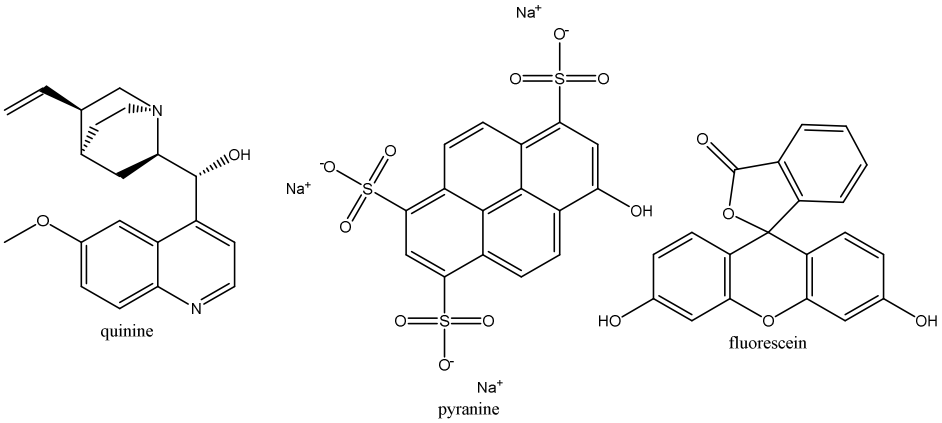


Figure 15, Photoluminescent organic compounds

When considering design of LEDs, one major problem with traditional fluorescent organic molecules is that their highest quantum yield is achieved when they are in solution. When designing products such as Light Emitting Diodes (LEDs), compounds in solution are typically not viable. For an LED, a compound that will fluoresce in the solid state is generally needed. Typical compounds found in semiconductors, which control the color of the LED, are aluminum gallium arsenide (red), gallium(III) phosphide (orange to yellow), gallium(III) nitride (pure green), and zinc selenide (blue). [30]

Recently, many fluorescent Cu(I)-containing complexes have been synthesized.[31,32] As these complexes continue to be synthesized and characterized, structural features that can be considered necessary for fluorescence are beginning to be discovered. Some key features found in the literature are aromatic nitrogen or phosphorus chelating agents.[31,32]

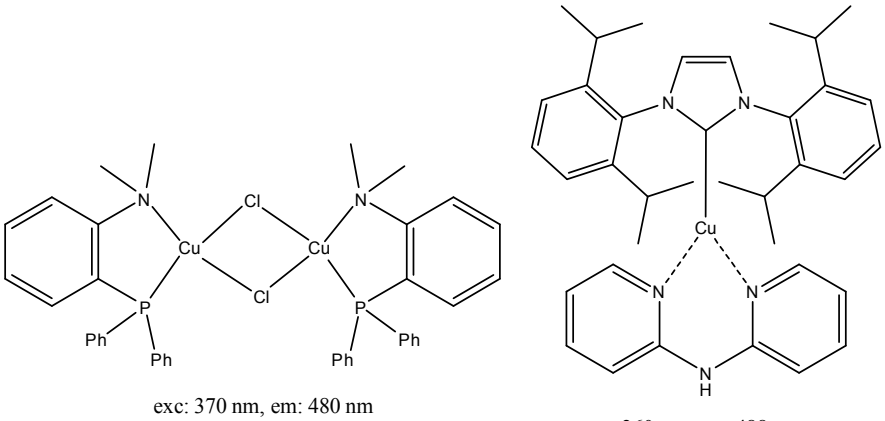


Figure 16, Photoluminescent Cu(I) complexes

Within the last year, Gaillard and coworkers constructed a light-emitting electrochemical cell utilizing a Cu(I)-NHC and a dipyridylamine derivative ligand.[33] This cell worked under low applied currents, while at higher currents, the complex began to be susceptible to redox mediated decomposition. While not entirely successful, this study is an important proof-of-concept for further development of light-emitting electrochemical cells.

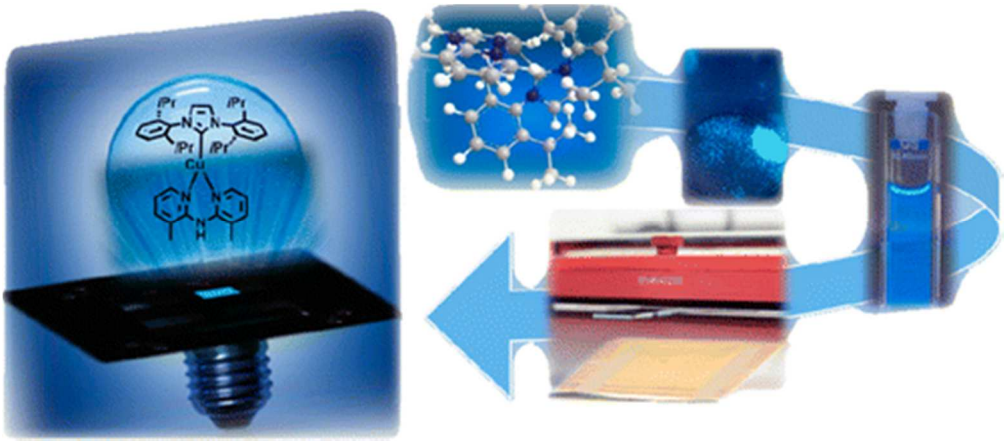


Figure 17, Schematic of a light-emitting electrochemical cell utilizing Cu(I)-NHC complex

1.3 Goals of this study

The purpose of this study was to synthesize new Cu(I)-NHC complexes that are potentially photoluminescent. Based on the above examples and the literature, a few points were evident. The ligands chosen would need to be aromatic in nature and contain either nitrogen- or phosphine-donors. In fact, many of the known photoluminescent complexes in the literature, for both tetracoordinate and tricoordinate copper(I) species bear ligands such as phenanthroline, pyridyl azolate, or diphosphine ligands.[34-40] Due to the success of the dipyridylamines used as co-ligands with a NHC, with regards to applications into a light-emitting electrochemical cell[33], we chose to continue to expand on this library, as everything that had been reported were symmetrically substituted. Our other choices came from a class of ligands known as diazodienes, or diimines, given that they are nitrogen chelating agents and aromatic.

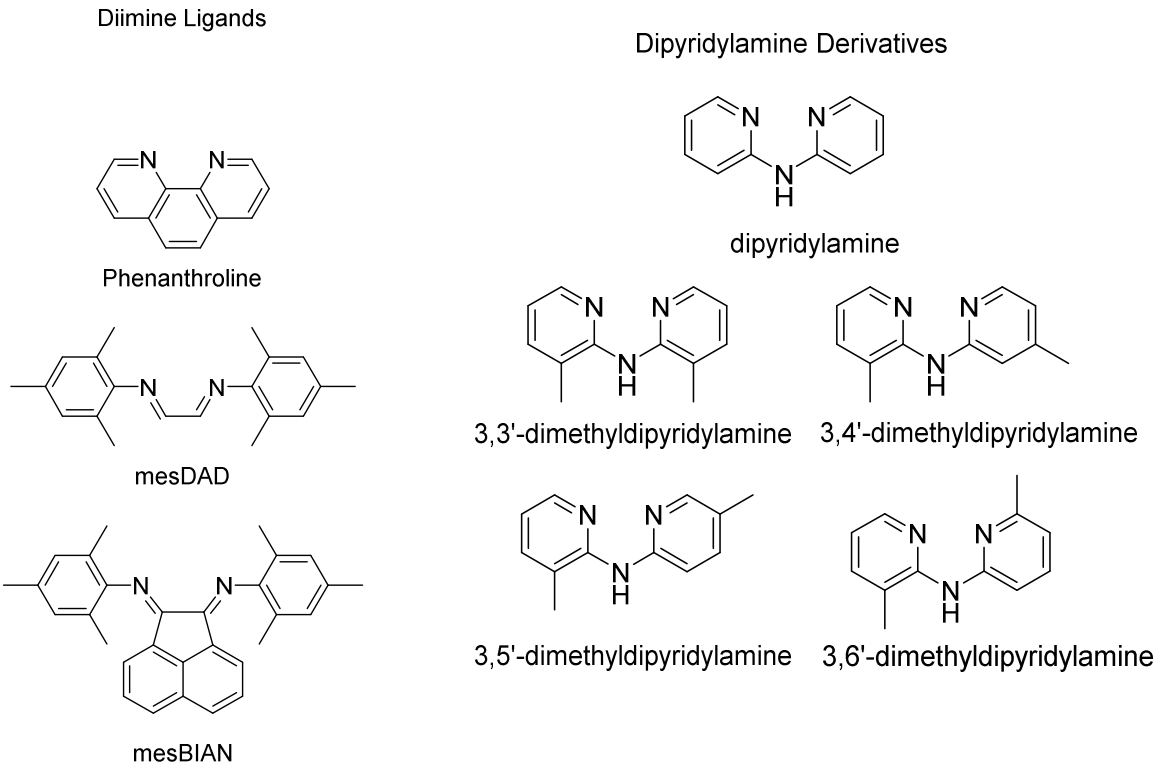


Figure 18, Ligands chosen to be synthesized

Next came the choice of carbene; based on the previous success of the IPr carbene in other examples, such as the light-emitting electrochemical cell, we chose to proceed with this carbene. Following reaction with a copper(I) source and ligand, we expect the following complexes.

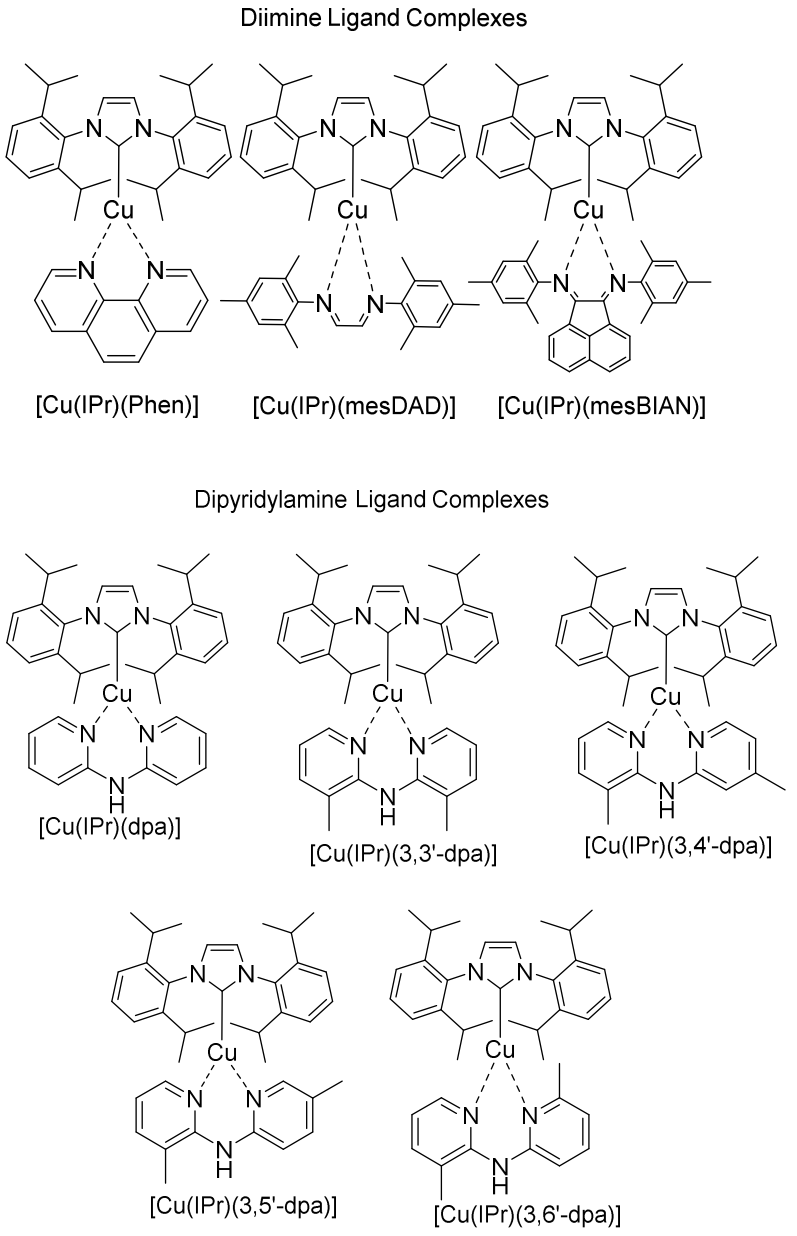


Figure 19, Complexes chosen to be synthesized

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CHAPTER II

SYNTHESIS OF LIGANDS

2.1 Introduction

2.1.1 Diimines

Diimines are a class of compounds containing two imine groups, the most common of which are 1,2- and 1,3- substituted. These architectures can then be integrated as ligands into transition metal complexes or as precursors to heterocyclic systems, such as NHCs.[1,2]

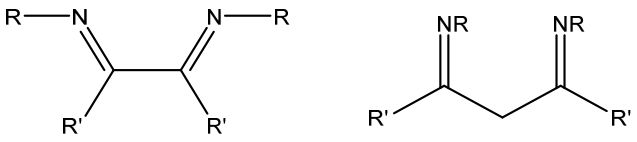

Figure 20, General structures of 1,2- and 1,3-diimines

2.1.1.1 Diimine synthesis

The synthesis of diimines is a relatively simple process that involves a condensation reaction between a dialdehyde or a diketone and an amine source, producing the final product and water.[3,4]

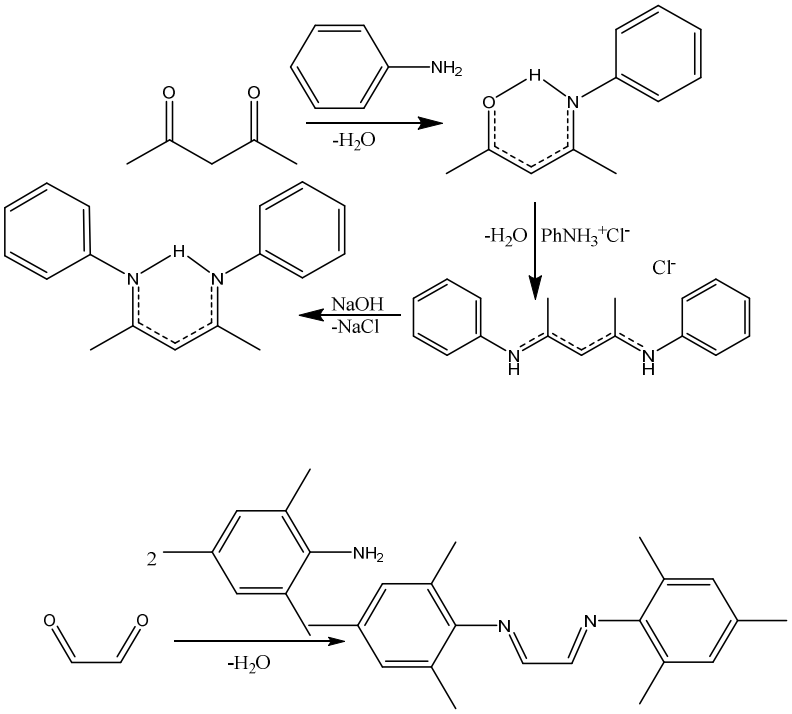

Figure 21, Syntheses of 1,2- and 1,3-diimines

In the reaction utilizing acetylacetone above, aniline condenses with the acetylacetone once, instead of twice, to release water. Due to the tautomerization of the system, only one nitrogen atom can react at this stage. Adding in aniline hydrochloride further allows the intermediate to react, allowing for the formation of the 1,3-diimine hydrochloride. Further treatment with sodium hydroxide frees the ligand and generates sodium chloride.[3]

In the reaction utilizing glyoxal, a straightforward condensation reaction takes place. That is, glyoxal reacts with two molecules of 2,4,6-trimethylaniline to release water and the 1,2-diimine.[4]

2.1.1.2 Diimines as ligands

In most cases, when coordinating to a metal center, the diimine ligands act as a chelating agent where both nitrogen atoms bind to the metal center. Numerous transition metal complexes

containing diamine ligands have been synthesized and examined for their catalytic activity in processes such as the polymerization of ethylene.[5,6,7]

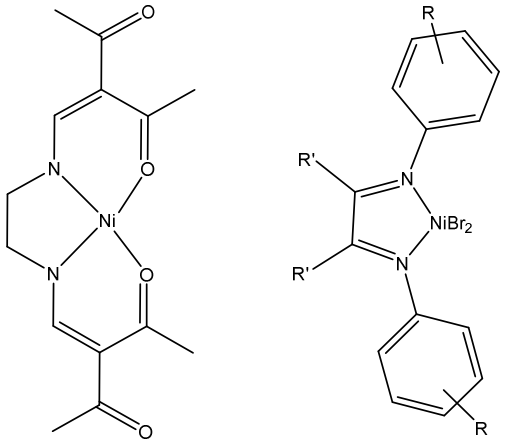

Figure 22. Diimines as ligands in transition metal complexes

2.1.1.3 Diimines as precursors for heterocyclic ring systems

Diimines can also be used to synthesize heterocyclic ring systems, typically in the form of imidazolium salts. In this process, the diimine undergoes a condensation reaction with formaldehyde to form the imidazolium moiety. A halide source is needed to provide a counter-ion for the positively charged nitrogen.[8]

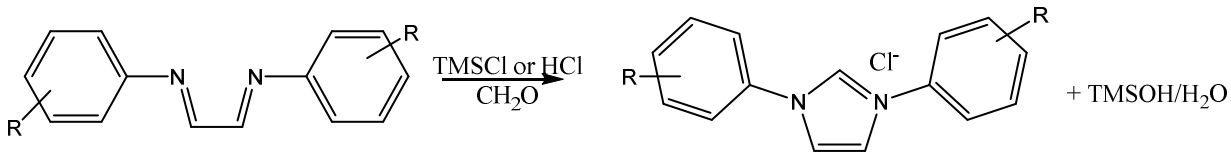

Figure 23, Diimines as precursors of heterocycles

2.1.2 Dipyridylamines

The other main class of ligands utilized in this study are dimethyl-substituted derivatives of 2,2'-dipyridylamine. The major structural change in the architecture is the addition of one methyl group to each pyridyl ring system to adopt a general structure of dimethyl-2,2'-dipyridylamine.

As with the diimines, dipyridylamines will coordinate to a metal center through both nitrogen atoms. This has resulted in various complexes used for biological applications.[9,10,11]

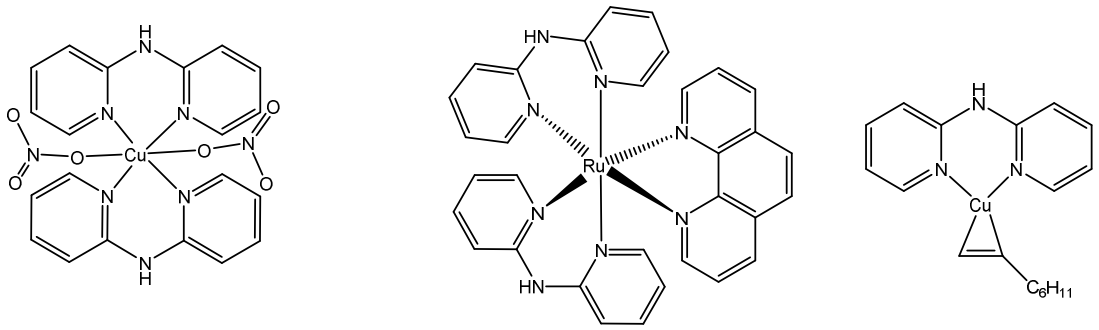

Figure 24, Transition metal complexes bearing dipyridylamine

2.1.2.1 Synthesis of dipyridylamines

The synthesis of these compounds is most commonly performed using the Buchwald-Hartwig coupling reaction. In this reaction, coupling occurs between an amine and an aryl halide. The reaction requires the use of a palladium catalyst and a strong base to deprotonate the amine.[12]

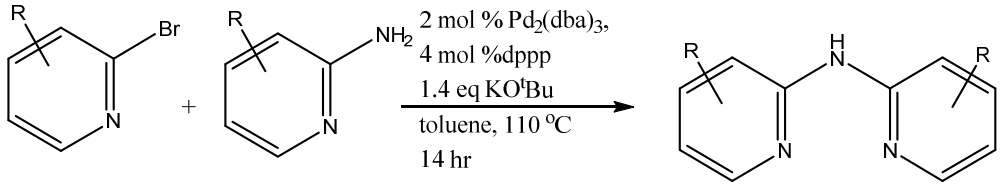

Figure 25, Buchwald-Hartwig coupling conditions

2.2 Experimental Section

General

All reactions were carried out in air unless otherwise stated. Solvents were distilled under nitrogen flow and should be considered dry unless otherwise stated. ^{1}H-NMR and ^{13}C-NMR Spectra were acquired in $CDCl_3$ using a Bruker 400 MHz spectrometer. ^{1}H-NMR solvent references were set at 7.26 ppm and ^{13}C-NMR set at 77.16 ppm.

2.2.1 Synthesis of DippDAD

A 100 mL pear shaped flask equipped with a stir bar was charged with 2,6-diisopropylaniline (1.88g, 10.6 mmol) and 20 mL methanol. Glyoxal (40% aqueous solution, 0.77g, 5.3 mmol) was diluted with methanol (20 mL) and added to the colorless diisopropylaniline solution. The resulting yellow-orange solution was stirred for 24 hr at room temperature. A bright yellow precipitate formed within ten minutes. After 24 hr, the yellow-orange solution was filtered through a fritted funnel and the solid rinsed with methanol (2 x 20 mL) and water (1 x 20 mL). The solid was then dried in vacuo to give a bright yellow powder of mass 1.5g (75%).

Spectral Data: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.18 (q, *J* = 5.5 Hz, 3H), 2.95 (hept, *J* = 6.9 Hz, 2H), 1.22 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ = 163.6, 147.4, 134.4, 129.0, 126.6, 20.9, 18.4.

Elemental Analysis: Theoretical: C:82.93, H:9.64, N:7.44; Found: C:82.63, H:9.76, N:7.39

2.2.2 Synthesis of mesDAD

A 100 mL pear shaped flask equipped with a stir bar was charged with 2,4,6-trimethylaniline (1.84g, 13.6 mmol) and 20 mL methanol. Glyoxal (40% aqueous solution, 0.99g, 6.8 mmol) was

diluted with methanol (20 mL). The colorless solution of glyoxal was added to the colorless mesitylamine solution. The resulting yellow-orange solution was stirred for 24 hrs at room temperature. A bright yellow precipitate formed within ten minutes. After 24 hr, the yellow-orange solution was filtered through a fritted funnel and the solid rinsed with methanol (2 x 20 mL) and water (1 x 20 mL). The solid was then dried *in vacuo* to give a bright yellow powder of mass 1.5g (75%).

Spectral Data: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (s, 2H), 6.91 (s, 4H), 2.29 (s, 6H), 2.16 (s, 12H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.5, 146.4, 133.2, 127.9, 127.9, 127.6, 125.5, 76.2 19.7, 17.2, 17.1, 17.1.

Elemental Analysis: C:82.15, H:8.27, N:9.58; Found: C:81.87, H:8.42, N:9.58

2.2.3 Synthesis of mesBIAN

A 100 mL pear shaped flask equipped with a stir bar was charged with 2,4,6-trimethylamine (1.5g, 11.2 mmol) and 20 mL methanol. A suspension of acenaphthenequinone (1g, 5.5 mmol) in methanol (20 mL). The suspension was added to the colorless mesitylamine solution. The resulting red solution was stirred for 5 days at room temperature. After 5 days, the red suspension was filtered through a fritted funnel and the solid rinsed with methanol (2 x 20 mL). The solid was then dried *in vacuo* to give a bright orange powder of mass 2.13g (93%).

Spectral Data: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, J = 8.2 Hz, 2H), 7.40 (dd, J = 8.4, 7.1 Hz, 2H), 6.97 (s, 4H), 6.77 (d, J = 7.1 Hz, 2H), 2.38 (s, 6H), 2.09 (s, 12H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.1, 146.8, 132.8, 129.7, 128.9, 128.8, 128.2, 124.6, 122.5, 77.5, 77.5, 76.9, 76.7, 76.5, 20.9, 17.7.

Elemental Analysis: Theoretical: C:86.50, H:6.78, N:6.72; Found: C:86.42, H:6.70, N:6.70

2.2.4 Synthesis of IPr·HCl

A 100mL pear shaped flask was equipped with a magnetic stir bar. To the flask DippDAD, paraformaldehyde, and 20 mL ethyl acetate were added. The flask was then lowered into a 70 ^{o}C oil bath. A solution of chlorotrimethylsilane in 10 mL ethyl acetate was then added to the warm solution. The resulting orange-red solution was stirred for three hours at 70 ^{o}C. The color changed to a back-brown and the mixture was cooled to room temperature. The suspension was then filtered through a fritted funnel and the resulting purple solid was washed twice with ethyl acetate (2 x 20 mL) and once with *t*-butylmethylether (20 mL). The pink solid was then dried *in vacuo* to give a pink solid of mass.

Spectral Data: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.03 (d, *J* = 1.6 Hz, 1H), 8.08 (d, *J* = 1.5 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 4H), 2.38 (hept, *J* = 6.8 Hz, 4H), 1.20 (dd, *J* = 17.1, 6.8 Hz, 25H).

2.2.5 Synthesis of 3,3'-dmdpa

To a 20 mL vial, tris(dibenzylideneacetone)dipalladium(0) (75% purity, 40 mg, 0.035 mmol) in 1 mL toluene was added. To this, 1,3-bis(diphenylphosphino)propane (29 mg, 0.07 mmol)in 1 mL toluene was added, followed by the addition of 2-bromo-3-methylpyridine (300 mg, 1.7 mmol) in 1 mL toluene and 2-amino-3-methylpyridine (227 mg, 2.1 mmol) in 1 mL toluene. To the resulting orange suspension, 1 mL toluene and potassium-*tert*-butoxide (270 mg, 2.4 mmol) were added. The vial was removed from the glove box and lowered into a 110 ^{o}C oil bath, stirring for 14 hours. After stirring, the reaction was filtered over Celite and the Celite was washed with approximately 50 mL ethyl acetate. The solvent in the orange-brown filtrate was removed *in vacuo*. The orange-brown oil was passed through a silica gel column (60:40; ethyl acetate:hexane). The product was

collected as a yellow solution. Solvent was removed through rotary evaporation, yielding an orange solid of mass 326 mg (94%).

Spectral Data: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 8.04 (m, 4H), 7.39 (dd, *J* = 7.3, 1.7 Hz, 4H), 6.81 (dd, *J* = 7.3, 4.9 Hz, 4H), 6.36 (s, 1H), 2.16 (s, 12H).

2.2.6 Synthesis of 3,4'-dmdpa

To a 20 mL vial, Tris(dibenzylideneacetone)dipalladium(0) (75% purity, 40 mg, 0.035 mmol) in 1 mL toluene was added. To this, 1,3-Bis(diphenylphosphino)propane (29 mg, 0.07 mmol)in 1 mL toluene was added, followed by the addition of 2-bromo-4-methylpyridine (300 mg, 1.7 mmol) in 1 mL toluene and 2-amino-3-methylpyridine (227 mg, 2.1 mmol) in 1 mL toluene. To the resulting orange suspension, 1 mL toluene and potassium-*tert*-butoxide (270 mg, 2.4 mmol) were added. The vial was removed from the glove box and lowered into a 110^{o}C oil bath, stirring for 14 hours. After stirring, the reaction was filtered over Celite and the Celite was washed with approximately 50 mL ethyl acetate. The solvent in the orange-brown filtrate was removed *in vacuo*. The orange-brown oil was passed through a silica gel column (60:40; ethyl acetate:hexane). The product was collected as a yellow solution. Solvent was removed through rotary evaporation, yielding a thick orange oil of mass 330 mg (95%).

Spectral Data: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 – 8.21 (m, 1H), 8.18 (dd, *J* = 5.0, 1.8 Hz, 1H), 8.09 (d, *J* = 5.1 Hz, 1H), 7.40 (ddd, *J* = 7.3, 1.9, 0.9 Hz, 1H), 7.01 (s, 1H), 6.79 (dd, *J* = 7.3, 5.0 Hz, 1H), 6.72 (dd, *J* = 5.2, 1.4 Hz, 1H), 2.33 (d, *J* = 34.1 Hz, 6H).

2.2.7 Synthesis of 3,5'-dmdpa

To a 20 mL vial, Tris(dibenzylideneacetone)dipalladium(0) (75% purity, 40 mg, 0.035 mmol) in 1 mL toluene was added. To this, 1,3-Bis(diphenylphosphino)propane (29 mg, 0.07 mmol)in 1 mL toluene was added, followed by the addition of 2-bromo-5-methylpyridine (300 mg, 1.7 mmol) in

1 mL toluene and 2-amino-3-methylpyridine (227 mg, 2.1 mmol) in 1 mL toluene. To the resulting orange suspension, 1 mL toluene and potassium-*tert*-butoxide (270 mg, 2.4 mmol) were added. The vial was removed from the glove box and lowered into a 110°C oil bath, stirring for 14 hours. After stirring, the reaction was filtered over Celite and the Celite was washed with approximately 50 mL ethyl acetate. The solvent in the orange-brown filtrate was removed *in vacuo*. The orange-brown oil was passed through a silica gel column (60:40; ethyl acetate:hexane). The product was collected as a yellow solution. Solvent was removed through rotary evaporation, yielding a thick orange oil of mass 312 mg (90%).

Spectral Data: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 8.6 Hz, 1H), 8.14 (dd, *J* = 5.1, 1.8 Hz, 1H), 8.05 (d, *J* = 2.4 Hz, 1H), 7.48 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.39 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.02 (s, 1H), 6.76 (dd, *J* = 7.3, 5.0 Hz, 1H), 2.28 (d, *J* = 5.9 Hz, 6H).

2.2.8 Synthesis of 3,6'-dmdpa

To a 20 mL vial, Tris(dibenzylideneacetone)dipalladium(0) (75% purity, 40 mg, 0.035 mmol) in 1 mL toluene was added. To this, 1,3-Bis(diphenylphosphino)propane (29 mg, 0.07 mmol)in 1 mL toluene was added, followed by the addition of 2-bromo-6-methylpyridine (300 mg, 1.7 mmol) in 1 mL toluene and 2-amino-3-methylpyridine (227 mg, 2.1 mmol) in 1 mL toluene. To the resulting orange suspension, 1 mL toluene and potassium-*tert*-butoxide (270 mg, 2.4 mmol) were added. The vial was removed from the glove box and lowered into a 110°C oil bath, stirring for 14 hours. After stirring, the reaction was filtered over Celite and the Celite was washed with approximately 50 mL ethyl acetate. The solvent in the orange-brown filtrate was removed *in vacuo*. The orange-brown oil was passed through a silica gel column (60:40; ethyl acetate:hexane). The product was collected as a yellow solution. Solvent was removed through rotary evaporation, yielding a thick orange oil of mass 312 mg.

Spectral Data: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.4 Hz, 2H), 8.08 (dd, *J* = 5.0, 1.7 Hz, 2H), 7.48 (dd, *J* = 8.4, 7.4 Hz, 2H), 7.35 – 7.28 (m, 2H), 6.95 (s, 1H), 6.74 – 6.63 (m, 4H), 2.38 (s, 6H), 2.23 (s, 6H).

2.3 Results and Discussion

2.3.1 Synthesis of DippDAD

Following the synthetic route from the Delaude group[4], the condensation reaction to form this diimine was successful; the identity of the compound was confirmed by ^{1}H-NMR, ^{13}C-NMR, and elemental analysis. The final yield for this product was approximately 75%.

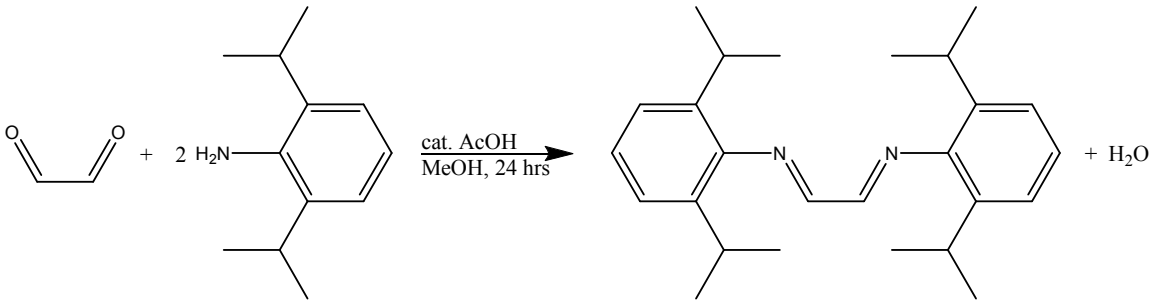

Figure 26. Synthesis of DippDAD

2.3.2 Synthesis of mesDAD

Following the success of the synthesis of DippDAD, the same conditions were applied to the mesityl derivative of the diazodiene. This yielded similar results, with yields approximately 70%, confirmed by ^{1}H-NMR, ^{13}C-NMR, and elemental analysis.

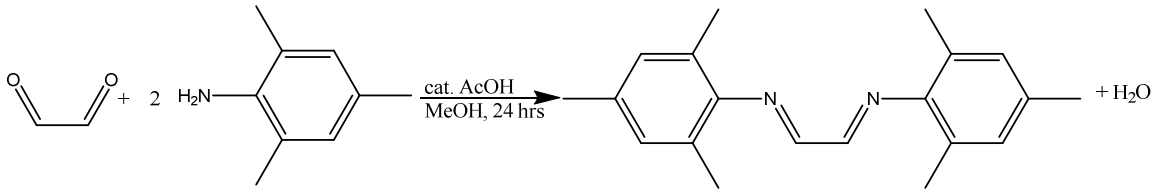

Figure 27. Synthesis of mesDAD

2.3.3 Synthesis of mesBIAN

As with the diazodienes, the synthesis of this acenaphthenequinone derivative was straightforward. The same procedure was followed, with the only modification in reaction time (1 day extended to 5 days). Again, the compound was confirmed by ^{1}H-NMR, ^{13}C-NMR, and elemental analysis. The yield was approximately 93%.

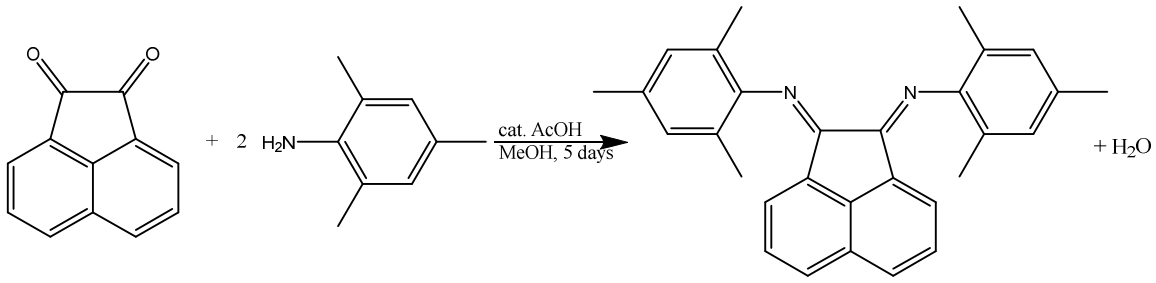

Figure 28. Synthesis of mesBIAN

2.3.4 Synthesis of IPr·HCl

As with the diazodienes, the procedure employed was adapted from the Delaude group. the condensation reaction to form this imidazolium salt was successful; the identity of the compound was confirmed by ^{1}H-NMR. The final yield for this product was approximately 75%.

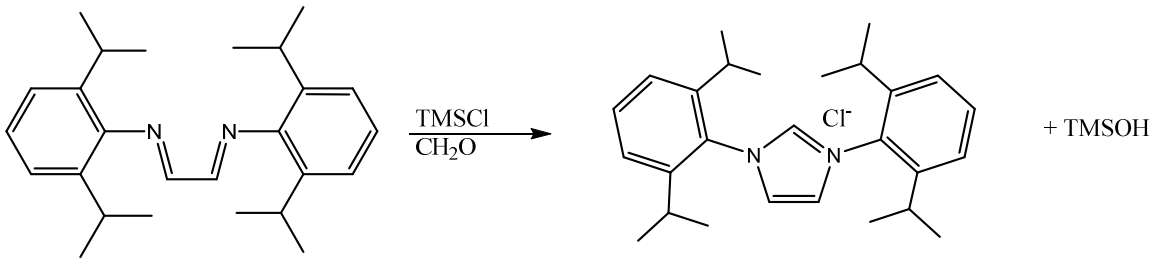

Figure 29. Synthesis of IPr·HCl

2.3.5 Synthesis of 3,3'-dmdpa

Synthesis of the dipyridylamine derivatives all followed the procedure set by Gaillard and coworkers. This involves the use of tris(dibenzylideneacetone)dipalladium(0) and 1,3-bis(diphenylphosphino)propane as the active catalytic species for the Buchwald-Hartwig coupling reaction between the requisite aryl halide and methylpyridine. The major problem faced in this synthesis was the removal of trace solvent (ethyl acetate and hexane). Multiple techniques (heating under vacuum, ether trituration) were employed, but were not successful. The product was confirmed by ^{1}H-NMR. The yield was approximately 94%.

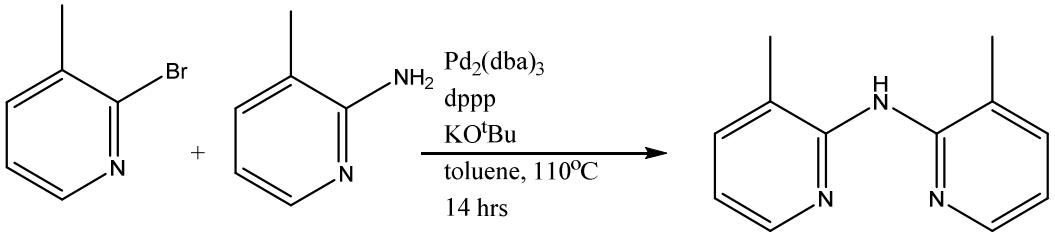

Figure 30. Synthesis of 3,3'-dmdpa

2.3.6 Synthesis of 3,4'-dmdpa

As a compound not yet synthesized, the same procedure was employed for this compound as for 3,3'-dmdpa. Again, the synthesis was successful, as confirmed by ^{1}H-NMR, but solvent was still trapped in the oil after multiple attempts of removal. The yield was approximately 95%.

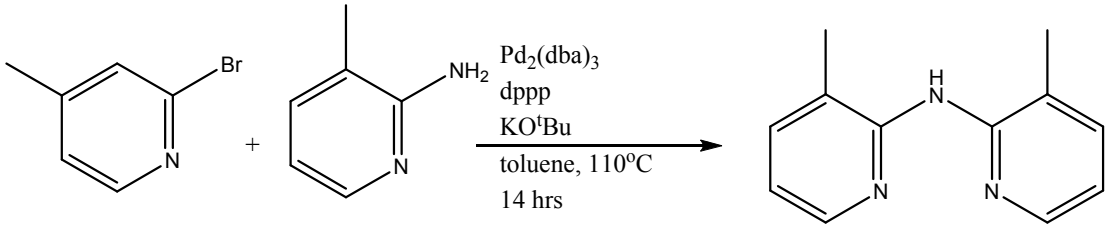

Figure 31. Synthesis of 3,4'-dmdpa

2.3.7 Synthesis of 3,5'-dmdpa

As another compound not yet synthesized, the same procedure was employed for this compound as for 3,3'- and 3,4'-dmdpa. Again, the synthesis was successful, as confirmed by ^{1}H-NMR, but solvent was still trapped in the oil after multiple attempts of removal. The yield was approximately 90%.

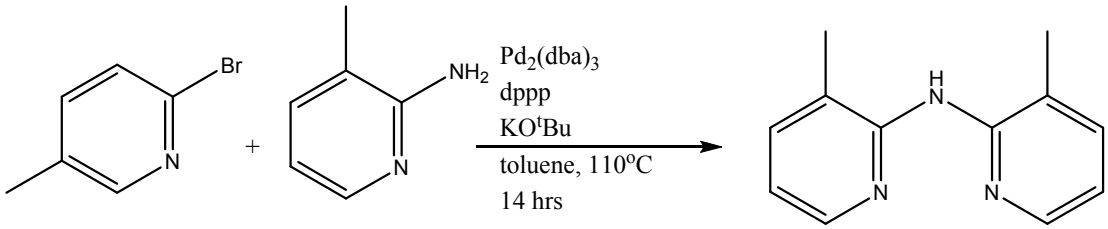

Figure 32. Synthesis of 3,5'-dmdpa

2.3.8 Synthesis of 3,6'-dmdpa

As another compound not yet synthesized, the same procedure was employed for this compound as for 3,3'- and 3,4'-dmdpa. Again, the synthesis was successful, as confirmed by ^{1}H-NMR, but

solvent was still trapped in the oil after multiple attempts of removal. The yield was approximately 90%.

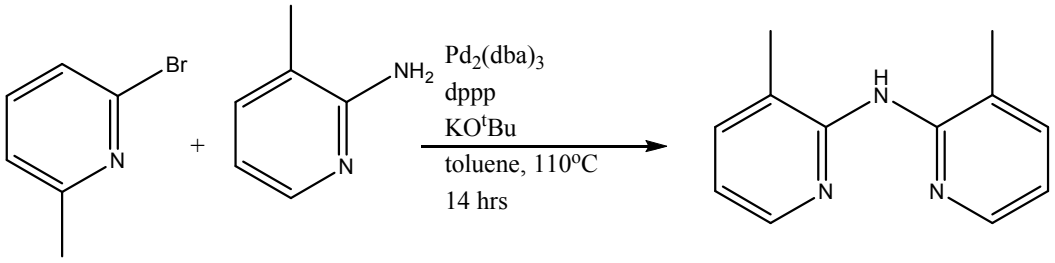

Figure 33. Synthesis of 3,6'-dmdpa

2.4 References

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CHAPTER III

SYNTHESIS OF COMPLEXES

3.1 Introduction

As previously discussed, NHCs are becoming more widely used for a variety of purposes, namely as catalysts and photoluminescent compounds. As such, understanding various syntheses of these complexes are extremely important. One of the common frameworks for the basis of many more complex structures is the neutral, mononuclear Cu(I)-NHC, [1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I) chloride, or [Cu(IPr)Cl].[1] This initial framework allows for the formation of mainly mono-NHC metal complexes through ligand exchange reactions. Bis-carbenes chelating to metal centers can undergo various synthetic pathways to arrive at the final metal NHC.

3.1.1 Initial Syntheses of Metal-NHC complexes

As previously mentioned, one of the initial reports of NHCs was by Wanzlick and Schonherr; however, in the same year, there was another synthesis found by Ofele. Ofele was attempting to synthesize dihydro-complexes from various heterocyclic salts.[2]

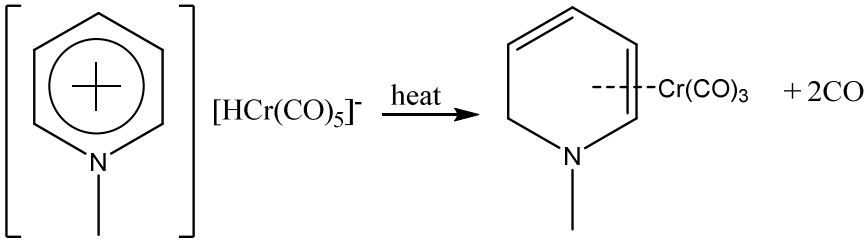

Figure 34. Ofele's synthesis of pyridyl chromium salts

However, the figure above illustrates the reaction which actually takes place; a hydrogen atom from the anion acting as a hydride source, resulting in the reduction of pyridinium and oxidized chromium. The chromium adopts η-2 chromium coordination, resulting in the release of two molecules of carbon monoxide. However, when heat was applied to the relevant imidazolium salts, the reaction did not occur as with the pyridinium salt.

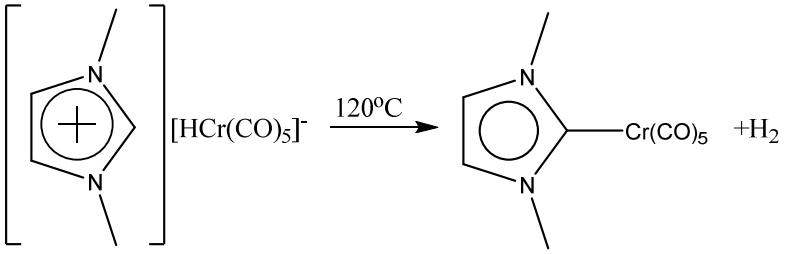

Figure 35. Ofele's observed reaction with imidazolium salts

Instead, hydrogen gas evolution was observed, which proves a different mechanism. In this process, the acidic proton and the proton on the chromium anion couple, resulting in the production of the hydrogen gas. This leaves a free carbene that is able to coordinate to the chromium center and form the metal-NHC complex.

Wanzlick's carbene was directly synthesized from a nucleophilic carbene. In this reaction, the acetate ion acts as a base to deprotonate the imidazolium salt to free the carbene and allow the mercury atom to then coordinate to two carbenes to form a bis-NHC complex[3].

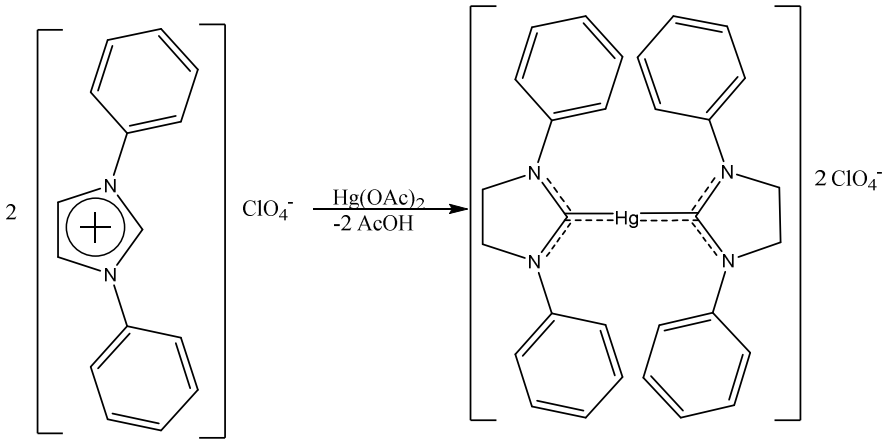

Figure 36. Wanlick's NHC synthesis

3.1.2 Bis-carbene metal complexes

Wanzlick's reaction is just one of the syntheses for formation of bis-carbene metal complexes. Another example of these complexes utilizing methylene linkers, which involves a step of transmetallation followed by an intramolecular deprotonation and generation of an acid. One case is in the formation of a nickel complex, where we observe a transmetallation of a carbene ligand onto a Ni(II) center, forming a [Ni(NHC)(OAc)] complex. This complex then forms the bos-carbene species. With the presence of acetate ions, the complex then undergoes an intramolecular deprotonation, resulting in the tetracoordinate complex along with 2 molecules of hydroiodic acid[4].

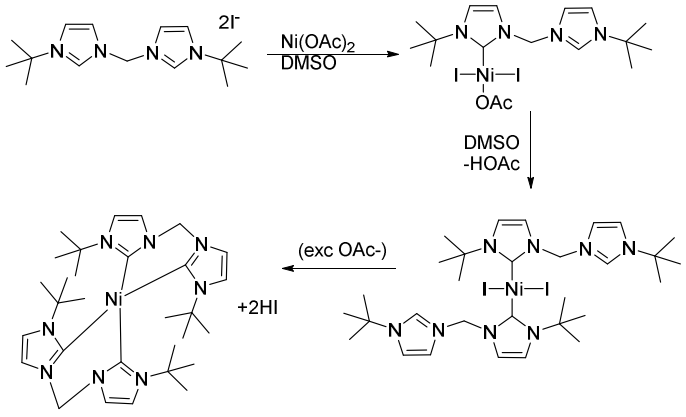

Figure 37. Synthesis of a Ni-NHC

3.1.3 Synthetic methods for [Cu(IPr)Cl]

Two major synthetic routes exist for the synthesis of [Cu(IPr)Cl]: a route through copper(I) oxide[5,6] and a route through copper(I) chloride[6].

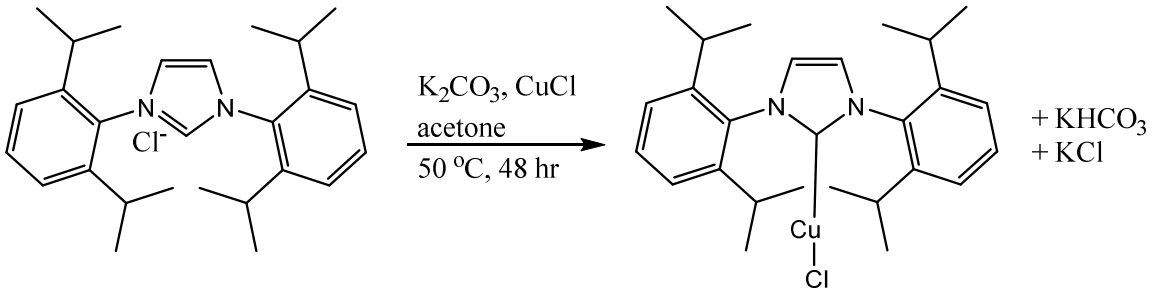

Figure 38. Synthesis of [Cu(IPr)Cl] via copper(I) chloride

The synthesis of [Cu(IPr)Cl] is a fairly straightforward reaction. Potassium carbonate is needed as a base to deprotonate the imidazolium salt to form *in situ* the free carbene that is then free to coordinate to the copper(I) chloride. The acetone in this reaction, as found experimentally, cannot be dry, as the residual water found in wet acetone is needed to help dissolve the potassium carbonate to allow the reaction to take place.

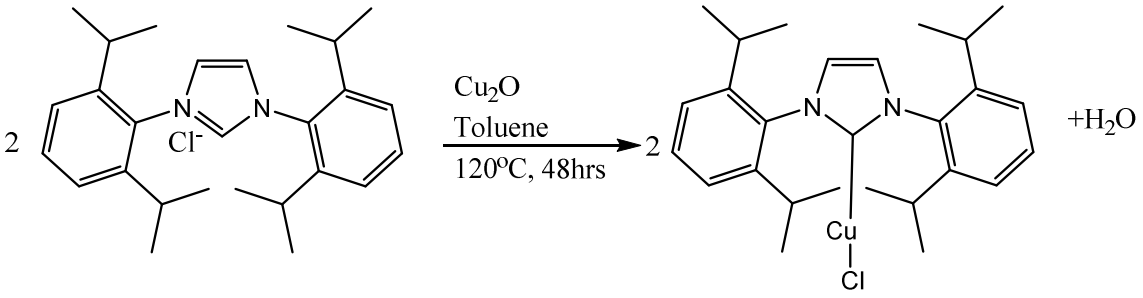

Figure 39. Synthesis of [Cu(IPr)Cl] via copper(I) oxide

The copper(I) oxide route proceeds in a similar manner. The copper(I) oxide abstracts the acidic protons on the imidazolium salts to release one molecule of water, which then allows the copper atom to coordinate to the carbene. This then allows the chlorine atom to coordinate and then form the neutral complex.

3.1.4 Ligand Exchange reactions utilizing NHC complexes

Ligand exchange is a type of reaction where ligands on molecules are exchanged with another. The figure below showcases this; Christian Jandl was attempting to study ligand exchange properties of palladium(II)-NHC complexes[7]. He found when treating the complex with two different types of counterions, different forms of the complex formed: a cationic form and a neutral form. This is due to the coordinating ability of the individual ligands. In the case of the acetate ion, the oxygens have an affinity to bind to metal centers, thereby causing a direct inner-sphere ligand exchange reaction and forming a neutral complex. When the same complex was treated with a tetrafluoroborate source, a cationic complex formed. This is due to the inability of the anion to directly bind to the metal center.

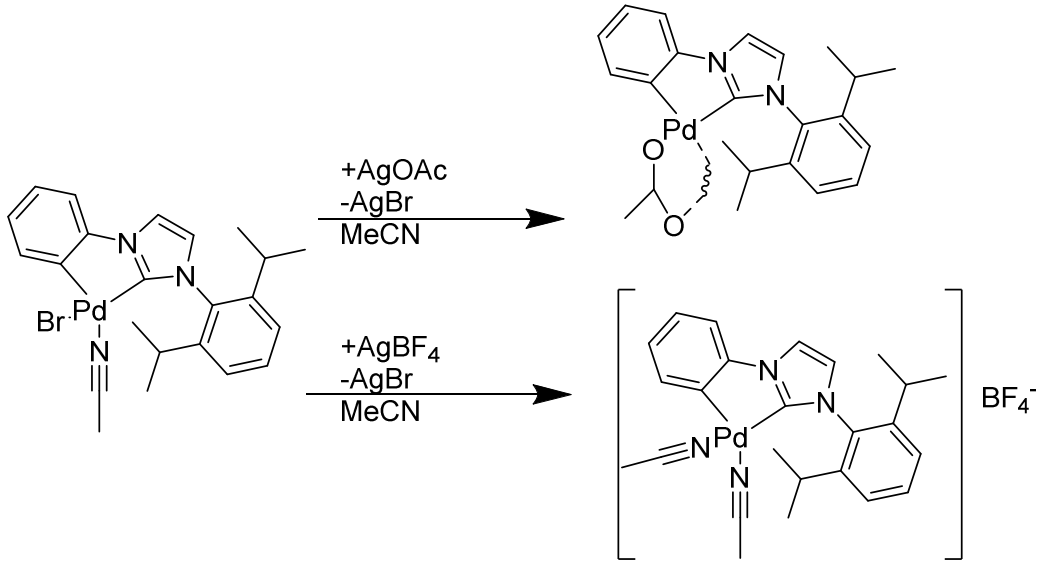

Figure 40. Jandl's ligand exchange experiments with Pd(II)-NHC complexes

Another case of ligand exchange is found in interactions with the same molecules. In this case, Bergbreiter and coworkers were attempting to study the ligand exchange properties of Ag(I)-NHC complexes[8]. What they found after initially synthesizing their initial neutral complex is that it existed in equilibrium with another ionic species, shown below. Here we see a chlorine atom being exchanged by a NHC to form a bis-NHC with a dichlorosilver(I) anion.

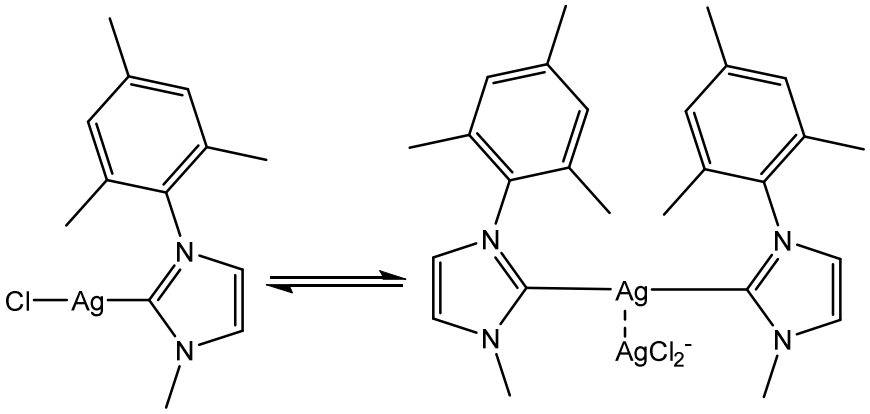

Figure 41. Bergbreiter's studies on Ag(I)-NHC complex ligand exchange ability

3.2 Experimental Section

General

All reactions were carried out in inert atmosphere were used unless otherwise stated. Solvents were distilled under nitrogen flow and should be considered dry unless otherwise stated. Phenanthroline was further purified before use. ^{1}H-NMR Spectra were acquired in $CDCl_3$ or CD_3CN using a Bruker 400 MHz spectrometer. Solvent references were set at 7.26 ppm for chloroform and 1.94ppm for acetonitrile.

3.2.1 Synthesis of [Cu(IPr)Cl] (1)

A 20 mL screw-top vial was equipped with a stir bar followed by addition of 300 mg (0.706 mmol) IPr·HCl, 296 mg (2.14 mmol) potassium carbonate, and 104 (1.05 mmol) mg copper(I)

chloride. The vial was then removed from the glove box and 7 mL of acetone was added. The vial was then lowered into a 50˚C oil bath and stirred at 500 rpm for approximately 48 hours. The resulting green suspension was cooled to room temperature and filtered over Celite. The Celite was washed with dichloromethane and the filtrate was then concentrated to approximately 2 mL. 30 mL Hexane was then added to the filtrate, resulting in the formation of white solid. The supernatant was decanted off and the product dried and brought back into the glove box. The white solid was then recrystallized via slow diffusion of hexane into tetrahydrofuran. The white microcrystals were dried, yielding a mass of 260 mg (75%) of [Cu(IPr)Cl].

Spectral Data: ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.56 (t, J = 7.8 Hz, 2H), 7.45 – 7.36 (m, 6H), 2.56 (hept, J = 6.9 Hz, 4H), 1.24 (dd, J = 9.7, 6.9 Hz, 24H).

3.2.2 Synthesis of [Cu(IPr)(Phen)]PF_6 (2)

A 20 mL screw-top vial was equipped with a stir bar followed by addition of 78 mg (0.1599 mmol) [Cu(IPr)Cl] and 2.5 mL tetrahydrofuran was added. Another solution of 29 mg (0.1599 mmol) phenanthroline in 2 mL of THF was then added to the former solution. This resulted in a dark red solution that stirred for 2 hours. 260 mg (1.599 mmol) ammonium hexafluorophosphate and approximately 1 mL THF was then added to the dark red solution, immediately resulting in a yellow suspension. The suspension was stirred for 7 hours, after which it was stopped and then filtered over Celite. The resulting clear, yellow filtrate then had solvent removed *in vacuo*, resulting in a yellow solid. The solid was removed from the glove box and recrystallized from a slow diffusion of ether into dichloromethane. The yellow crystals were dried and collected at 100 mg (81%).

Spectral Data: ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.47 (dd, J = 8.2, 1.5 Hz, 2H), 7.95 (s, 2H), 7.76 (t, J = 7.8 Hz, 2H), 7.61 – 7.49 (m, 8H), 6.87 (s, 2H), 2.72 (hept, J = 6.9 Hz, 4H), 1.23 (d, J = 6.9 Hz, 12H), 0.97 (d, J = 6.9 Hz, 12H).

3.2.3 Synthesis of [Cu(IPr)(mesBIAN)]PF_6 (3)

A 20 mL screw-top vial was equipped with a stir bar followed by addition of 78 mg (0.1599 mmol) [Cu(IPr)Cl] and 2.5 mL tetrahydrofuran was added. Another solution of 67 mg (0.1599 mmol) mesBIAN in 2 mL of THF was then added to the former solution. This resulted in a dark brown solution that stirred for 2 hours. 260 mg (1.599 mmol) ammonium hexafluorophosphate and approximately 1 mL THF was then added to the dark brown solution. The suspension was stirred for 7 hours, after which it was stopped and then filtered over Celite. The resulting clear, brown filtrate then had solvent removed *in vacuo*, resulting in a brown solid. The solid was removed from the glove box and recrystallized from a slow diffusion of hexane into tetrahydrofuran. The brown crystals were dried and collected at 138 mg (85%).

Spectral Data: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 7.9 Hz, 1H), 7.56 – 7.39 (m, 4H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.18 – 7.07 (m, 6H), 6.89 (s, 2H), 6.41 (d, *J* = 7.3 Hz, 1H), 2.59 (hept, *J* = 13.7, 6.9 Hz, 4H), 2.42 (s, 5H), 2.21 (s, 3H), 1.95 (s, 4H), 1.59 (s, 6H), 1.30 (d, *J* = 6.9 Hz, 3H), 1.23 (d, *J* = 6.9 Hz, 4H), 1.09 (d, *J* = 6.8 Hz, 7H), 0.90 (d, *J* = 6.9 Hz, 7H).

3.2.4 Synthesis of [Cu(IPr)(dpa)]PF_6 (4)

A 20 mL screw-top vial was equipped with a stir bar followed by addition of 78 mg (0.1599 mmol) [Cu(IPr)Cl] and 2.5 mL acetone was added. Another solution of 27 mg (0.1599 mmol) dpa in 2 mL of acetone was then added to the former solution. This resulted in a clear, colorless solution that stirred for 2 hours. 294 mg (1.599 mmol) potassium hexafluorophosphate and approximately 1 mL acetone was then added to the colorless solution. The suspension was stirred for 7 hours, after which it was stopped and then filtered over Celite. The resulting clear, colorless filtrate then had solvent removed *in vacuo*, resulting in a white solid. The solid was recrystallized from a slow diffusion of hexane into dichloromethane. The white crystals were dried and collected at 105 mg (85%).

Spectral Data: ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.08−8.13 (s, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 4H), 7.22 (s, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.31 (t, *J* = 6.4 Hz, 2H),), 6.17 (d, *J* = 5.4 Hz, 2H), 2.65 (hept, *J* = 6.9 Hz, 4H) 1.23 (d, *J* = 6.9 Hz, 12H), 1.08 (d, *J* = 6.9 Hz, 12H).

3.2.5 Synthesis of [Cu(IPr)(3,3'-dmdpa)]PF_6 (5)

A 20 mL screw-top vial was equipped with a stir bar followed by addition of 78 mg (0.1599 mmol) [Cu(IPr)Cl] and 2.5 mL acetone was added. Another solution of 32 mg (0.1599 mmol) 3,3'-dmdpa in 2 mL of acetone was then added to the former solution. This resulted in a clear, colorless solution that stirred for 2 hours. 294 mg (1.599 mmol) potassium hexafluorophosphate and approximately 1 mL acetone was then added to the colorless solution. The suspension was stirred for 7 hours, after which it was stopped and then filtered over Celite. The resulting clear, pale yellow filtrate then had solvent removed *in vacuo*, resulting in a pale yellow solid. The solid was recrystallized from a slow diffusion of hexane into dichloromethane. The yellow crystals were dried and collected at 127 mg (85%).

Spectral Data: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (t, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 6.9 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 4H), 7.28 (s, 2H), 6.74 (s, 1H), 6.43 (dd, *J* = 7.4, 5.5 Hz, 2H), 6.22 (dd, *J* = 5.5, 1.8 Hz, 2H), 2.67 (hept, *J* = 6.9 Hz, 4H), 2.36 (s, 6H), 1.25 (d, *J* = 6.9 Hz, 13H), 1.10 (d, *J* = 6.9 Hz, 13H).

3.2.6 Synthesis of [Cu(IPr)(3,4'-dmdpa)]PF_6 (6)

A 20 mL screw-top vial was equipped with a stir bar followed by addition of 78 mg (0.1599 mmol) [Cu(IPr)Cl] and 2.5 mL acetone was added. Another solution of 32 mg (0.1599 mmol) 3,4'-dmdpa in 2 mL of acetone was then added to the former solution. This resulted in a clear, colorless solution that stirred for 2 hours. 294 mg (1.599 mmol) potassium hexafluorophosphate and approximately 1 mL acetone was then added to the colorless solution. The suspension was stirred

for 7 hours, after which it was stopped and then filtered over Celite. The resulting clear, pale yellow filtrate then had solvent removed *in vacuo*, resulting in a pale yellow solid. The solid was recrystallized from a slow diffusion of hexane into dichloromethane. The yellow crystals were dried and collected at 127 mg (85%).

Spectral Data: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.06 (m, 6H), 6.23 – 6.06 (m, 2H), 2.58 (hept, *J* = 6.9 Hz, 4H), 2.27 (s, 2H), 2.18 (s, 2H), 1.16 (d, *J* = 6.9 Hz, 12H), 1.02 (d, *J* = 6.9 Hz, 12H).

3.2.7 Synthesis of [Cu(IPr)(3,5'-dmdpa)]PF_6 (7)

A 20 mL screw-top vial was equipped with a stir bar followed by addition of 78 mg (0.1599 mmol) [Cu(IPr)Cl] and 2.5 mL acetone was added. Another solution of 32 mg (0.1599 mmol) 3,5'-dmdpa in 2 mL of acetone was then added to the former solution. This resulted in a clear, colorless solution that stirred for 2 hours. 294 mg (1.599 mmol) potassium hexafluorophosphate and approximately 1 mL acetone was then added to the colorless solution. The suspension was stirred for 7 hours, after which it was stopped and then filtered over Celite. The resulting clear, pale yellow filtrate then had solvent removed *in vacuo*, resulting in a pale yellow solid. The solid was recrystallized from a slow diffusion of hexane into dichloromethane. The yellow crystals were dried and collected at 127 mg (85%).

Spectral Data: ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.58 (t, *J* = 7.8 Hz, 2H), 7.45 (s, 4H), 7.37 (d, *J* = 7.8 Hz, 4H), 7.21 (s, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.65 (s, 1H), 6.59 (s, 1H), 6.47 (s, 1H), 2.73 (hept, *J* = 6.9 Hz, 4H), 2.26 (s, 3H), 2.05 (s, 3H), 1.21 (d, *J* = 6.9 Hz, 12H), 1.11 (d, *J* = 6.9 Hz, 12H).

3.3 Results and Discussion

3.3.1 Synthesis of [Cu(IPr)Cl] (1)

As another well-studied complex, multiple synthetic routes were available. We opted for a modified Nolan (CuCl) synthetic route, utilizing copper(I) chloride and potassium carbonate, with slight changes to time (24 to 48 hours). This synthesis gave us consistently clean product with yields around 75%, confirmed by ^{1}H-NMR.

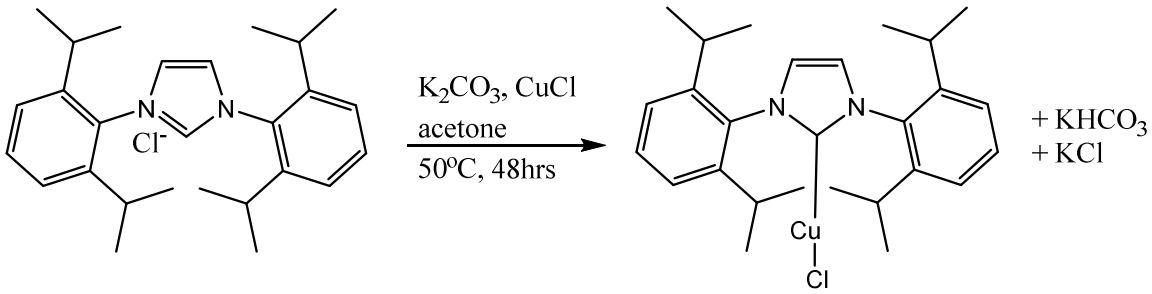

Figure 42. Modified synthesis of [Cu(IPr)Cl] via CuCl

3.3.2 Synthesis of [Cu(IPr)(Phen)]PF_6 (2)

Complex **2** has been previously synthesized by Gaillard and coworkers following a procedure utilizing the copper(I) oxide route for synthesis of the initial carbene[9]. After the carbene was isolated, it was dissolved with phenanthroline in ethanol and refluxed for 1 hour, all under a Schlenk line. This results in an inner sphere ligand exchange, where the chlorine atom is replaced by the phenanthroline ligand. After cooling, an aqueous solution of potassium hexafluorophosphate was then added for an outer sphere ligand exchange, resulting in the formation of two compounds: the desired [Cu(IPr)(Phen)]PF_6 and potassium chloride.

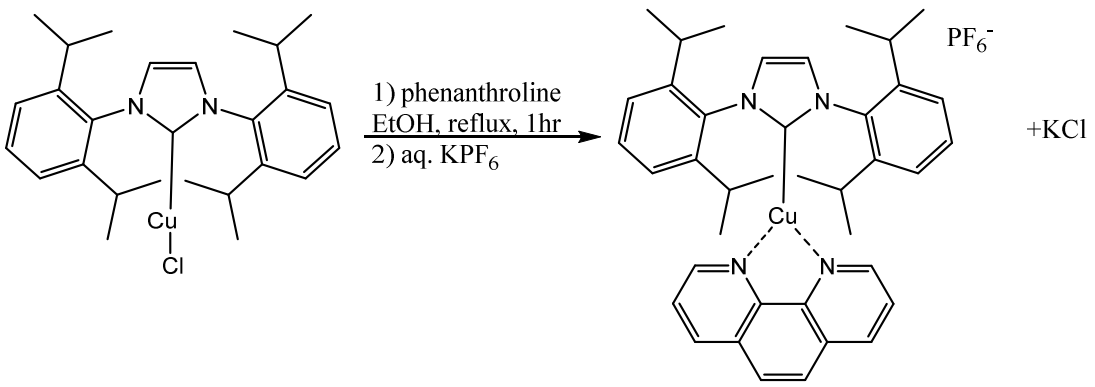

Figure 43. Synthesis of [Cu(IPr)(Phen)]PF_6

For our purposes, we decided to perform the reaction without heat to simplify the procedure, as [Cu(IPr)Cl] is air sensitive itself. The essential steps are the same: the inner sphere ligand exchange, where phenanthroline is exchanged with chlorine atoms and the outer sphere ligand exchange, where the counterions exchange, in this case resulting in [Cu(IPr)(Phen)]PF_6 and ammonium chloride. The complex was confirmed by ^{1}H-NMR.

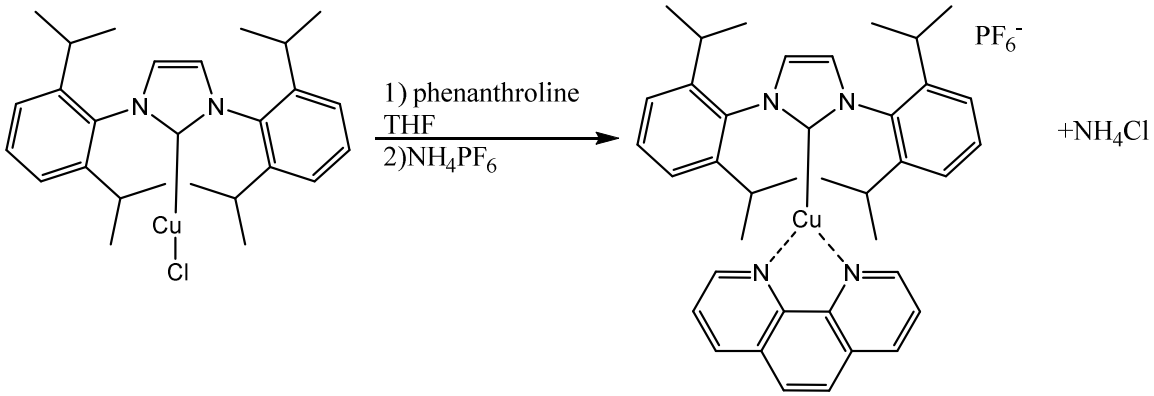

Figure 44. Modified Synthesis of [Cu(IPr)(Phen)]PF_6

This procedure gave good yields (81%) and did not require setup with a Schlenk line; instead, the reaction was performed in the glove box until purification, where the sample was removed from the glove box and handled in air. However, reaction time was longer than in the case of refluxing.

3.3.3 Synthesis of [Cu(IPr)(mesBIAN)]PF_6 (3)

Following the success with the synthesis of complex **2**, the same procedure was utilized for the formation of complex **3**. This complex was isolated in good yields (85%) and its structure was confirmed by X-ray crystallography.

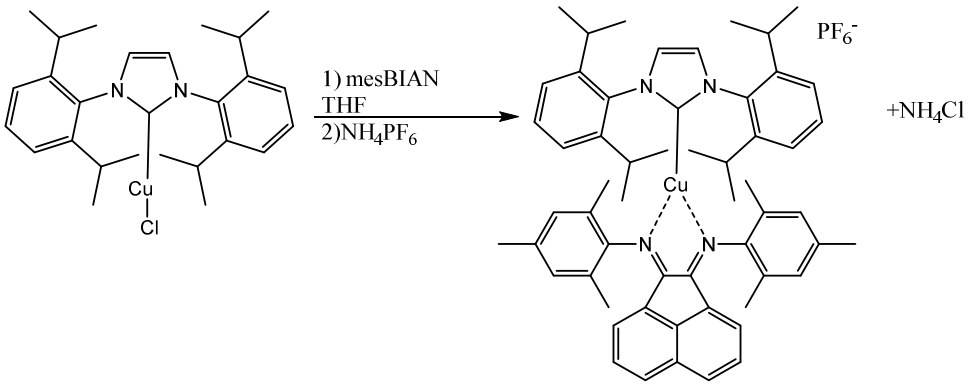

Figure 45. Synthesis of [Cu(IPr)(mesBIAN)]PF_6

The ^{1}H-NMR and ^{13}C-NMR were much less informative, giving different responses in different solvents. The reason for the difference in response is unknown; however elemental analysis does support the purity of the bulk material of which NMR is incapable. It is however interesting to note that in deuterated acetonitrile, there are three sharp features found; these most likely correspond to the signals found from the aromatic protons on the carbene as well as the methine proton on the isopropyl groups.

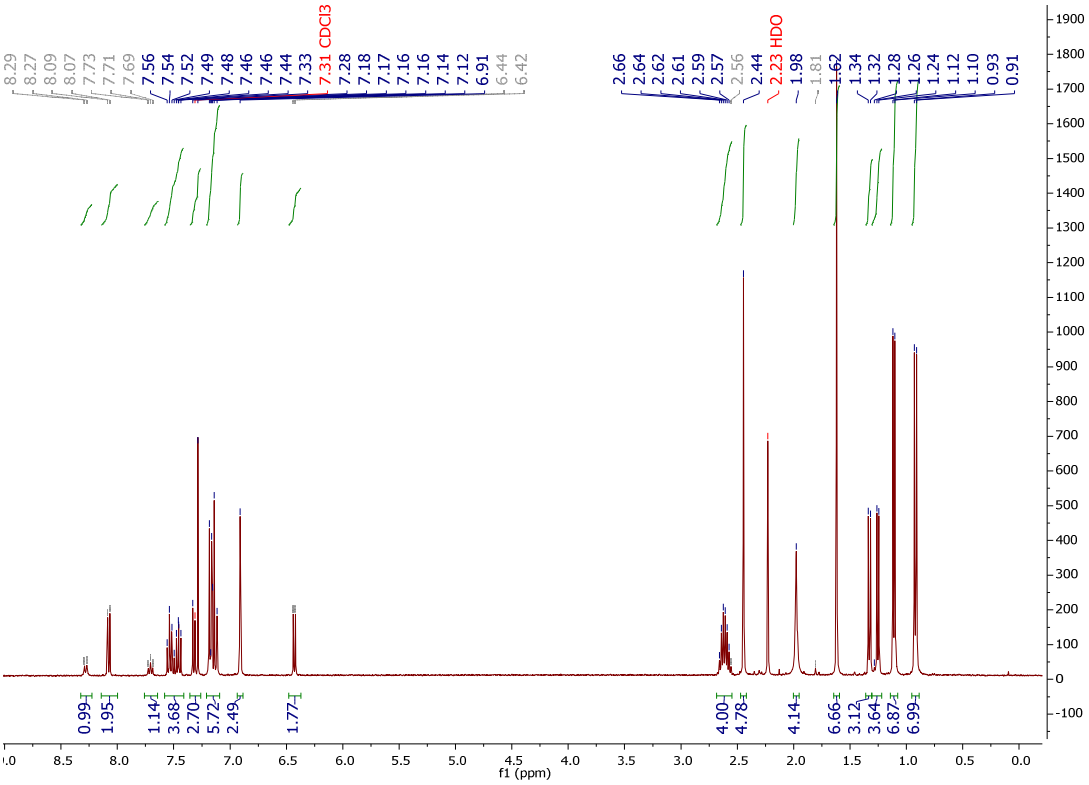

Figure 46. ^{1}H-NMR of [Cu(IPr)(mesBIAN)]PF_6 in $CDCl_3$

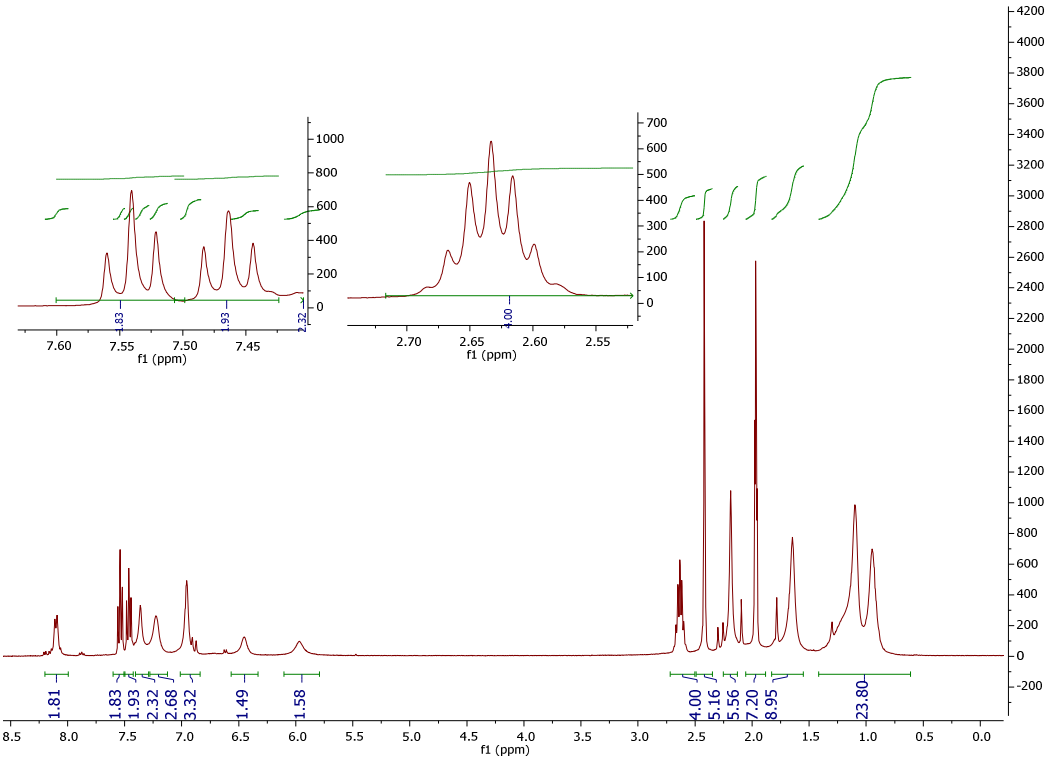

Figure 47. ^{1}H-NMR of [Cu(IPr)(mesBIAN)]PF_6 in CD_3CN

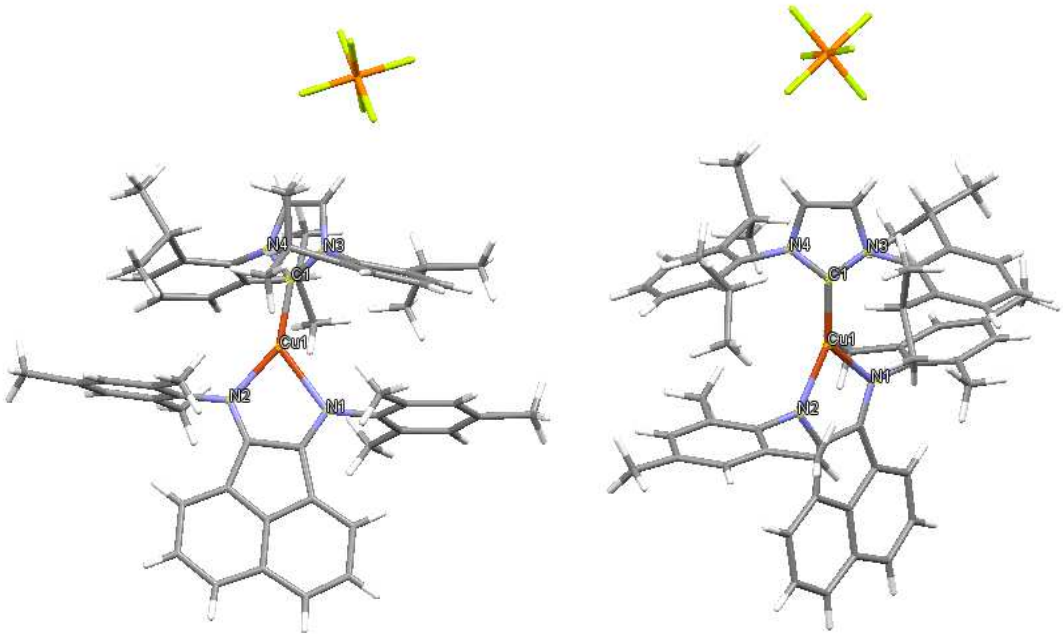

Figure 48. Crystal structure of [Cu(IPr)(mesBIAN)]PF_6

As previously mentioned, the crystal structure shown above (above figure shows two different snapshots of the molecule at different orientations) does confirm the complex was successfully synthesized. Both nitrogen atoms on the ligand coordinate to the copper center and the carbene is still present. The copper-carbene bond length is 1.922(3) Å and is comparable to average bond lengths with an NHC and sterically bulky diimine ligand.[10-15] However, unique to this class of compounds is the different bond lengths of the copper-nitrogen bonds. For this compound, the bond lengths are 2.231(3) and 2.062(2) Angstroms. This does compare to the literature[16-19] with other sterically bulky ligands, ranging on average from 1.940 to 2.211Angstroms, with different bond lengths for both copper-nitrogen bond lengths.

3.3.4 Synthesis of [Cu(IPr)(dpa)]PF_6 (4)

We employed our new synthetic methods for complexes **2** and **3** to another complex (**4**) which was synthesized by Gaillard and coworkers[9] and obtained good yields (85%) were obtained. The structure was confirmed by ^{1}H-NMR.

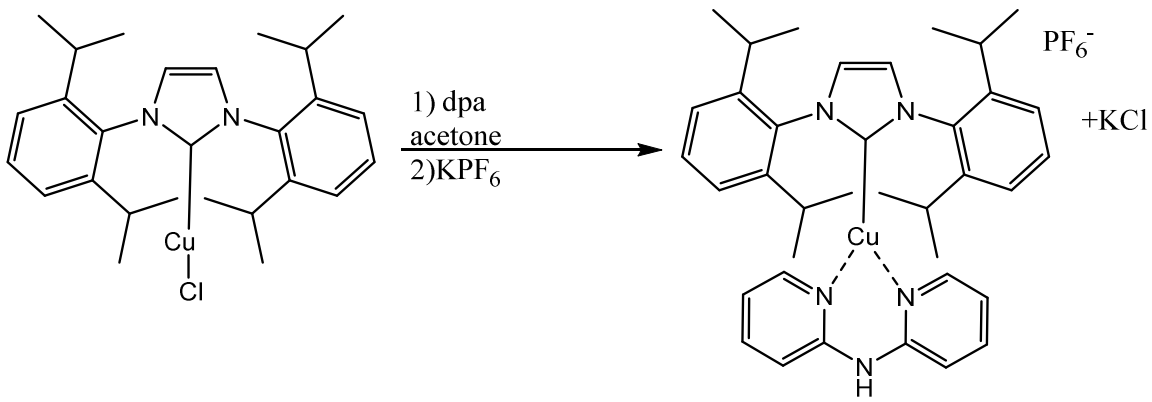

Figure 49. Synthesis of [Cu(IPr)(dpa)]PF_6

3.3.5 Synthesis of [Cu(IPr)(3,n'-dmdpa)]PF_6 (5-7)

As our synthetic procedure proved to be viable for all of the complexes thus far, we employed it for all of the dimethylpyridyl chelated complexes (3,3'-, 3,4'-, and 3,5'-dmdpa). For all complexes, the yields were good (approximately 85%) and confirmed by ^{1}H-NMR.

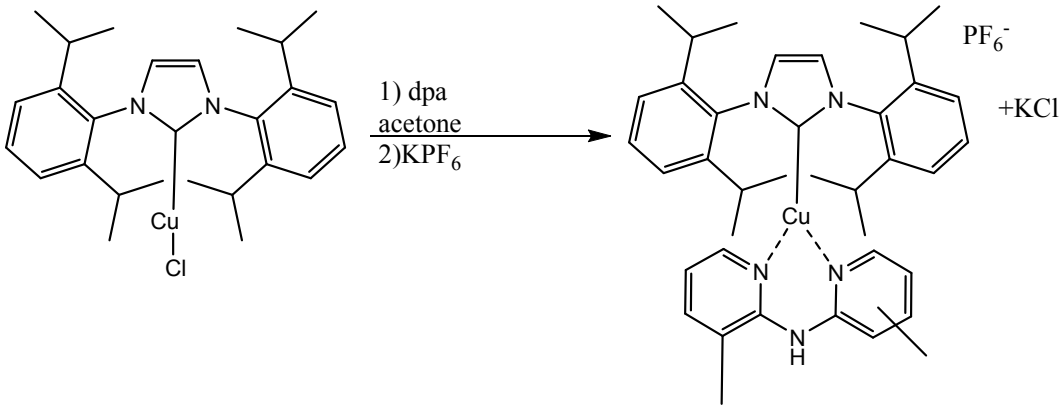

Figure 50. Synthesis of [Cu(IPr)(3,n'-dmdpa)]PF_6

3.4 Conclusions

A series of Cu(I)-NHC complexes were synthesized, characterized by ^{1}H-NMR. Further analysis needs to be performed to fully confirm their structure. These complexes used two classes of nitrogen chelating agents, dipyridylamines and diimines. Further studies on these complexes to identify their applications need to be performed, such as cyclic voltammetry, UV-Vis, X-Ray crystallography, and ^{13}C-NMR.

3.5 References

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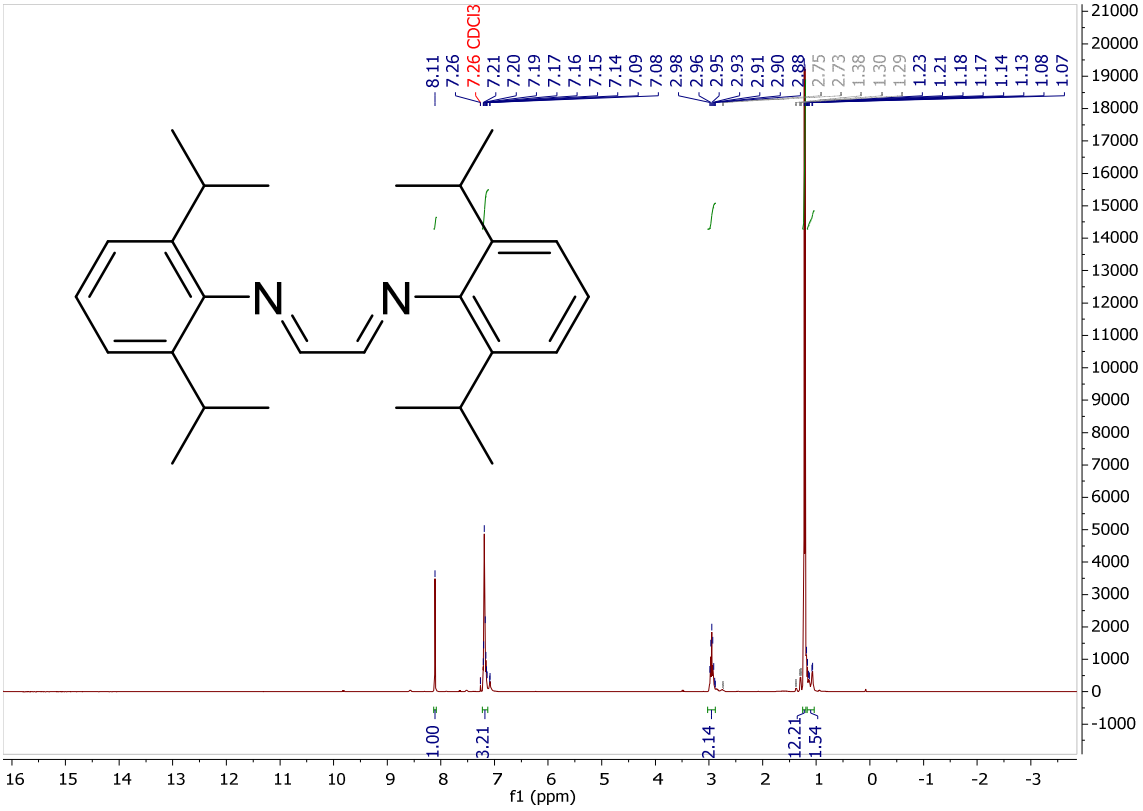
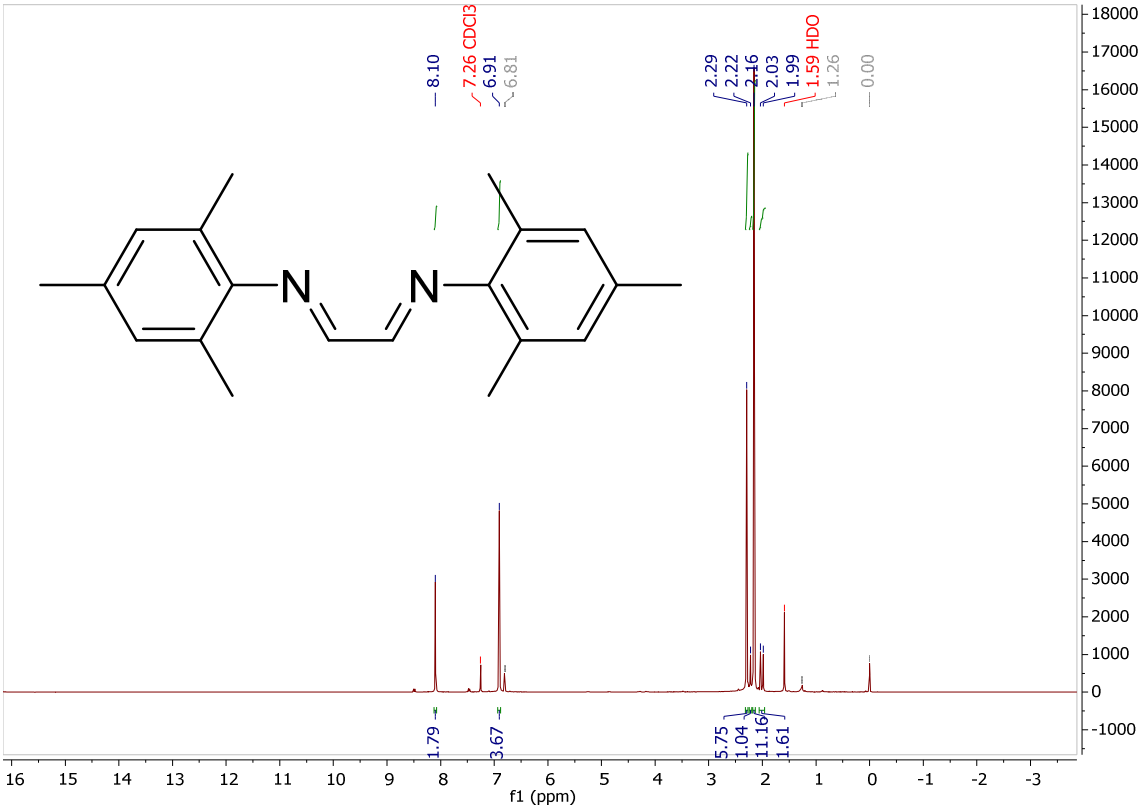
APPENDICES

Appendix 1: ^{1}H-NMR Spectra

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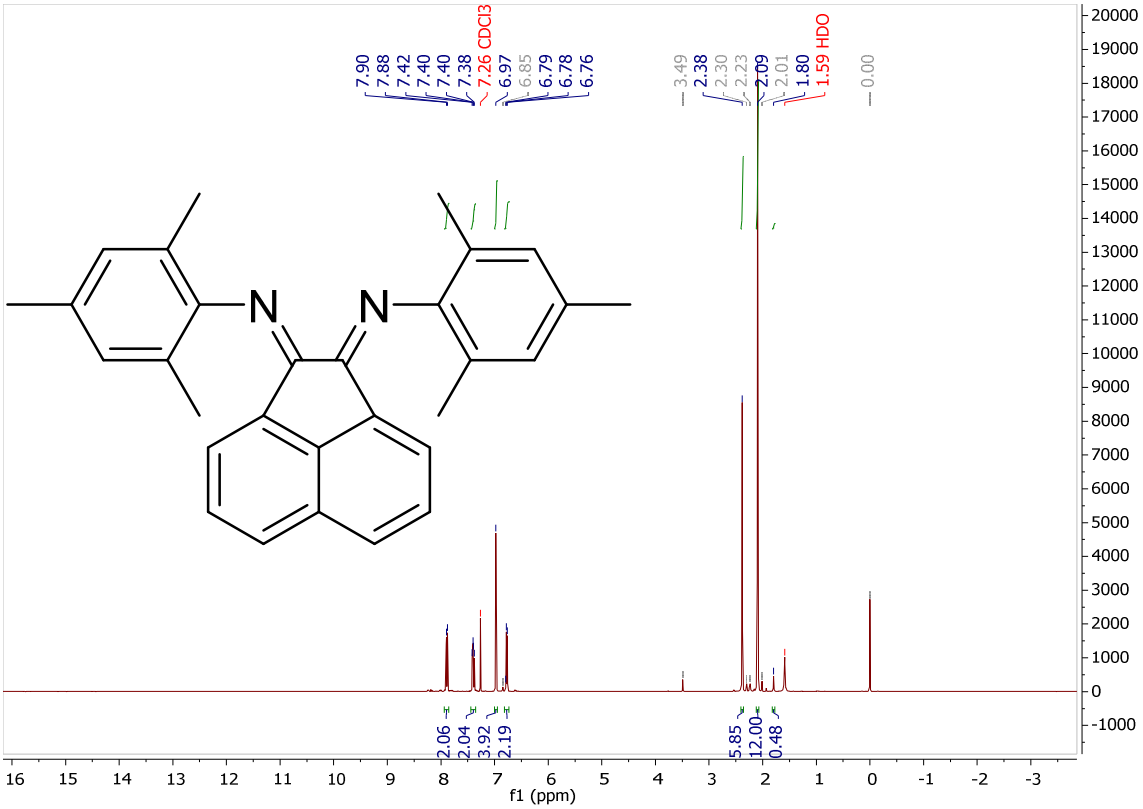
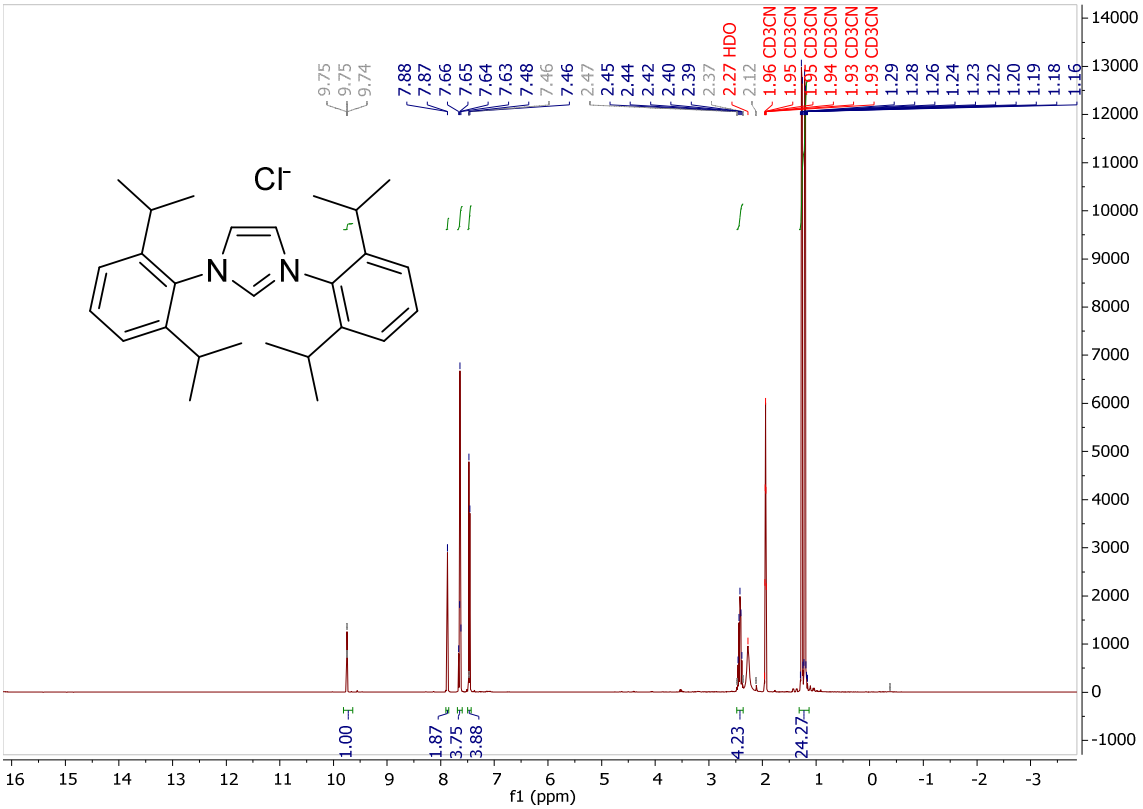
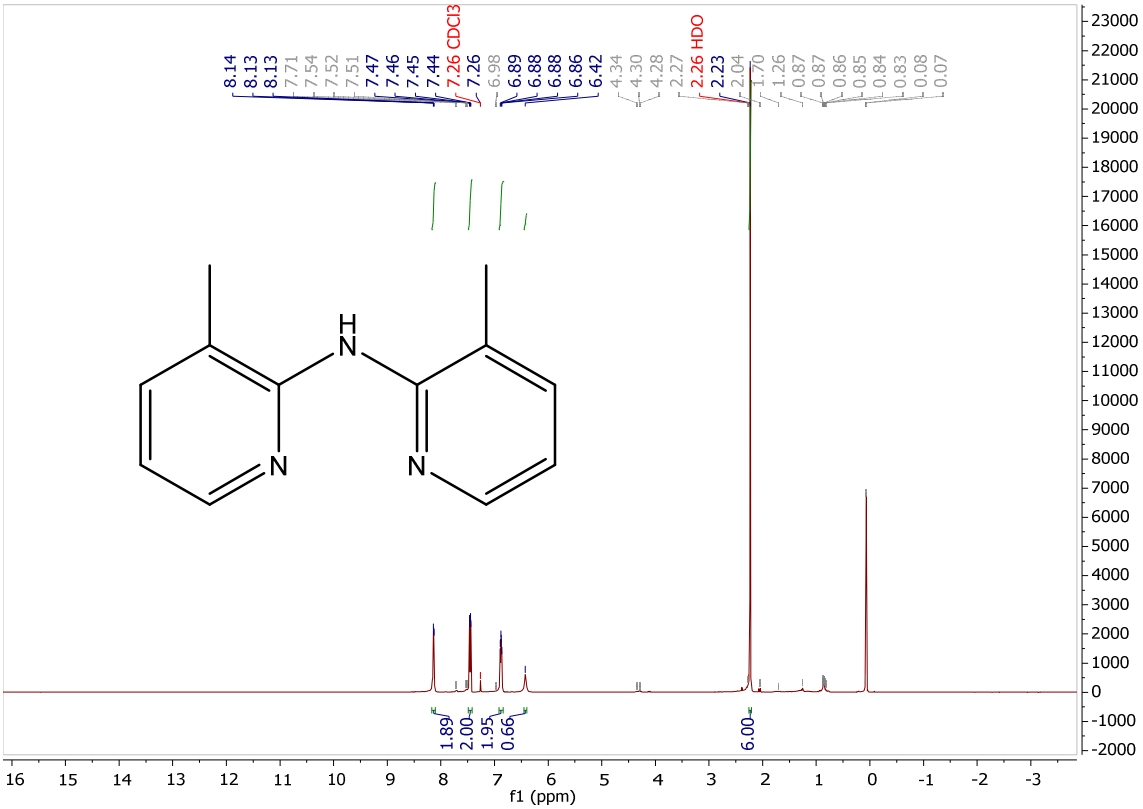
7.26 CDCl3
6.91
6.81
2.29
2.22
2.16
2.03
1.99
1.59 HDO
1.26
0.00
1.79
3.67
5.75
1.04
11.16
1.61
f1 (ppm)


7.90
7.88
7.42
7.40
7.40
7.38
7.26 CDCl3
6.97
6.85
6.79
6.78
6.76
3.49
2.38
2.30
2.23
2.09
2.01
1.80
1.59 HDO
0.00
2.06
2.04
3.92
2.19
5.85
12.00
0.48
f1 (ppm)


Cl-
N
N
9.75
9.75
9.74
7.88
7.87
7.66
7.65
7.64
7.63
7.48
7.46
7.46
2.47
2.45
2.44
2.42
2.40
2.39
2.37
2.27 HDO
2.12
1.96 CD3CN
1.95 CD3CN
1.95 CD3CN
1.94 CD3CN
1.93 CD3CN
1.93 CD3CN
1.29
1.28
1.26
1.24
1.23
1.22
1.20
1.19
1.18
1.16
1.00
1.87
3.75
3.88
4.23
24.27
f1 (ppm)


H
N
N
N
8.14
8.13
8.13
7.71
7.54
7.52
7.51
7.47
7.46
7.45
7.44
7.26 CDCl3
7.26
6.98
6.89
6.88
6.88
6.86
6.42
4.34
4.30
4.28
2.27
2.26 HDO
2.23
2.04
1.70
1.26
0.87
0.87
0.86
0.85
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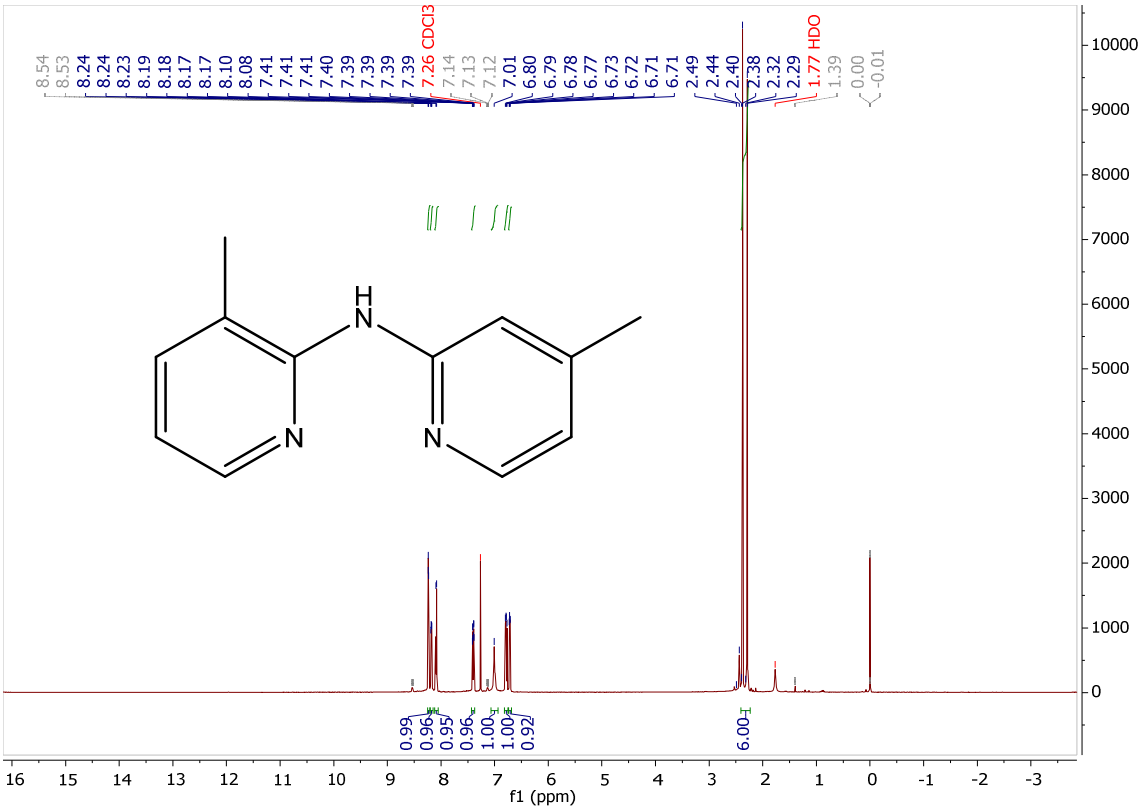
0.83
0.08
0.07
1.89
2.00
1.95
0.66
6.00
f1 (ppm)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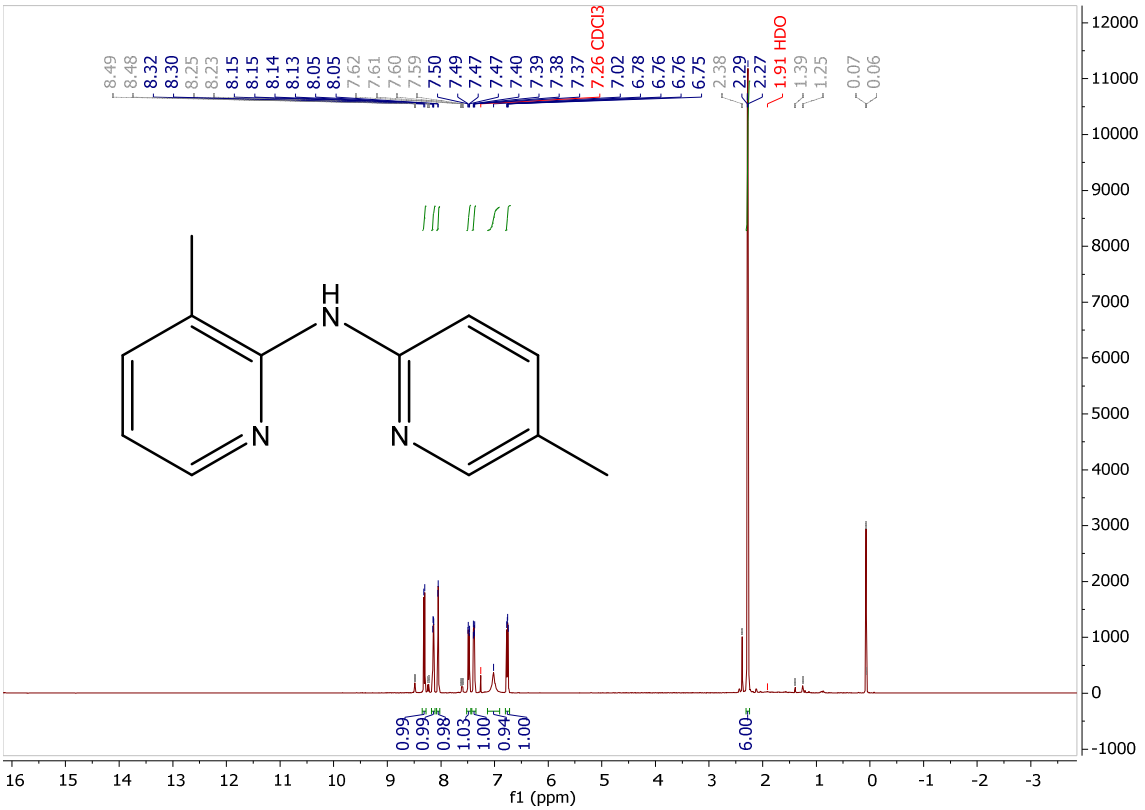
H
N
N
N
0.99 0.96 0.95 0.96 1.00 1.00 0.92 6.00
f1 (ppm)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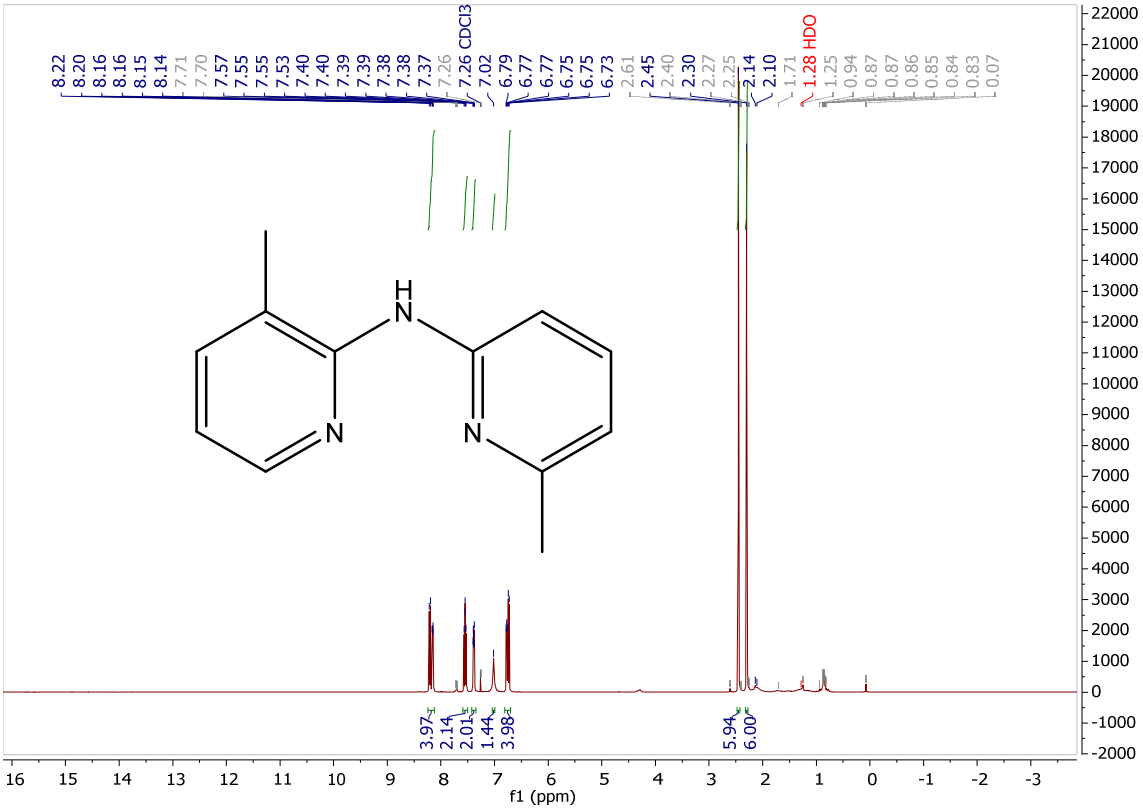
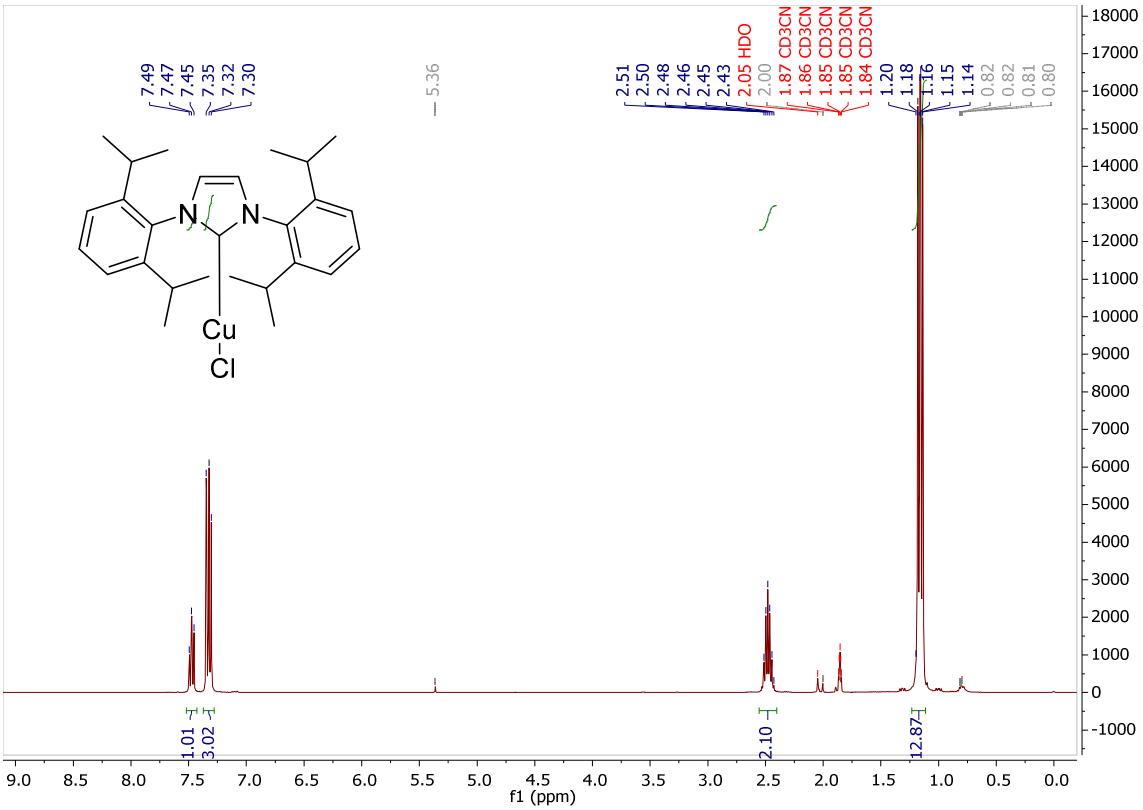
H
N
N
N
0.99 0.99 0.98 1.03 1.00 0.94 1.00 6.00
f1 (ppm)


8.22
8.20
8.16
8.16
8.15
8.14
7.71
7.70
7.57
7.55
7.55
7.53
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.26
7.26 CDCl3
7.02
6.79
6.77
6.77
6.75
6.75
6.73
2.61
2.45
2.40
2.30
2.27
2.25
2.14
2.10
1.71
1.28 HDO
1.25
0.94
0.87
0.87
0.86
0.85
0.84
0.83
0.07
H
N
N
N
3.97
2.14
2.01
1.44
3.98
5.94
6.00
f1 (ppm)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7.47
7.45
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5.36
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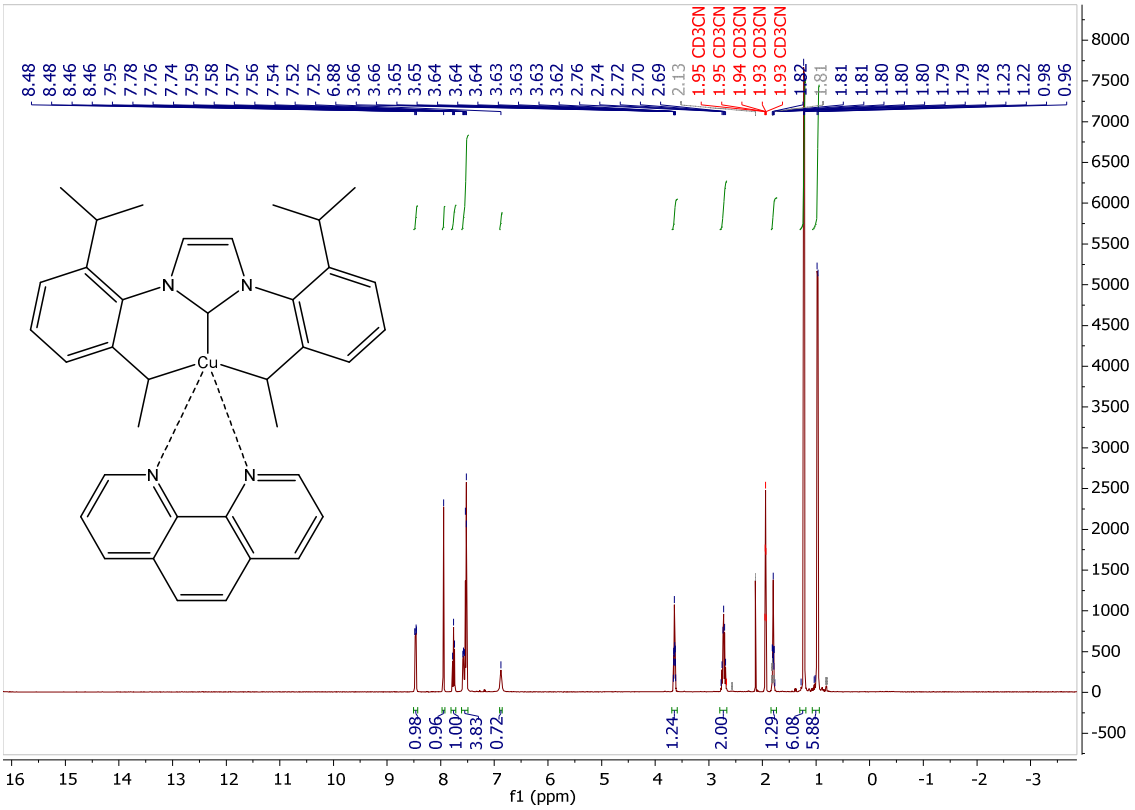
2.50
2.48
2.46
2.45
2.43
2.05 HDO
2.00
1.87 CD3CN
1.86 CD3CN
1.85 CD3CN
1.85 CD3CN
1.84 CD3CN
1.20
1.18
1.16
1.15
1.14
0.82
0.82
0.81
0.80
N
N
Cu
Cl
1.01
3.02
2.10
12.87
f1 (ppm)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Cu
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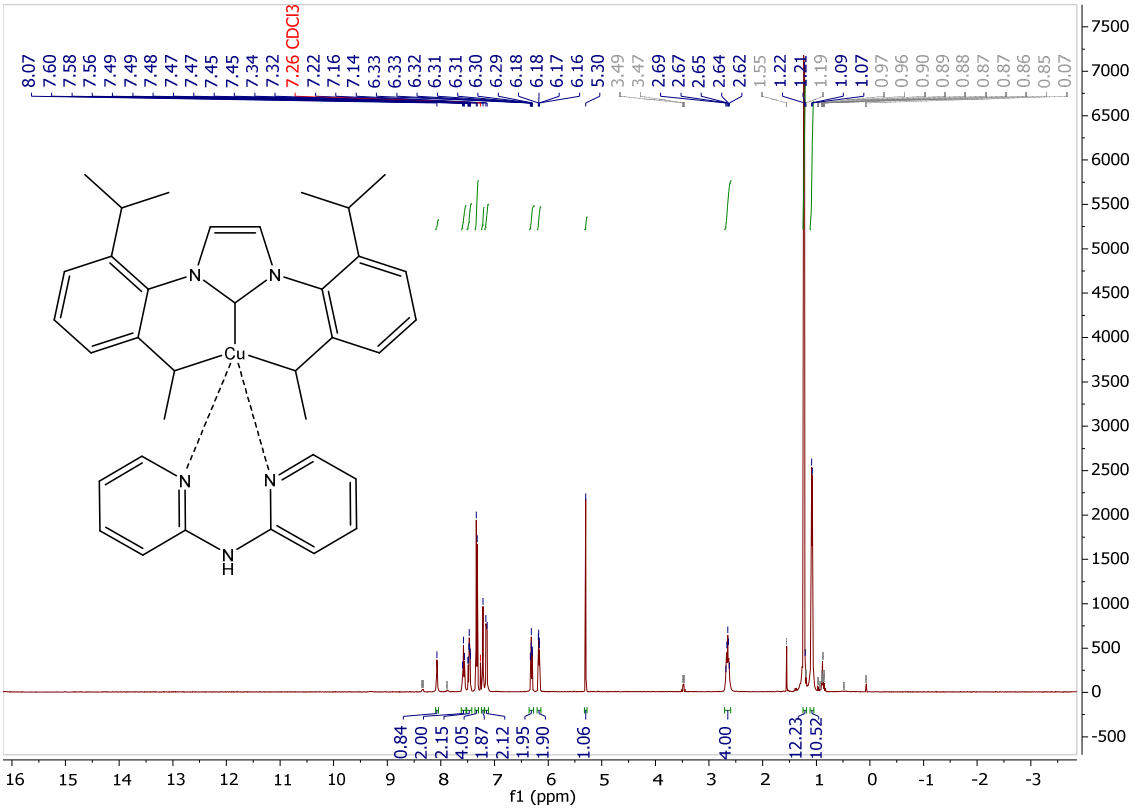
f1 (ppm)


8.07 7.60 7.58 7.56 7.49 7.49 7.48 7.47 7.47 7.45 7.45 7.34 7.32 7.26 CDCl3 7.22 7.16 7.14 6.33 6.33 6.32 6.31 6.31 6.30 6.29 6.18 6.18 6.17 6.16 5.30 3.49 3.47 2.69 2.67 2.65 2.64 2.62 1.55 1.22 1.21 1.19 1.09 1.07 0.97 0.96 0.90 0.89 0.88 0.87 0.87 0.86 0.85 0.07
Cu
H
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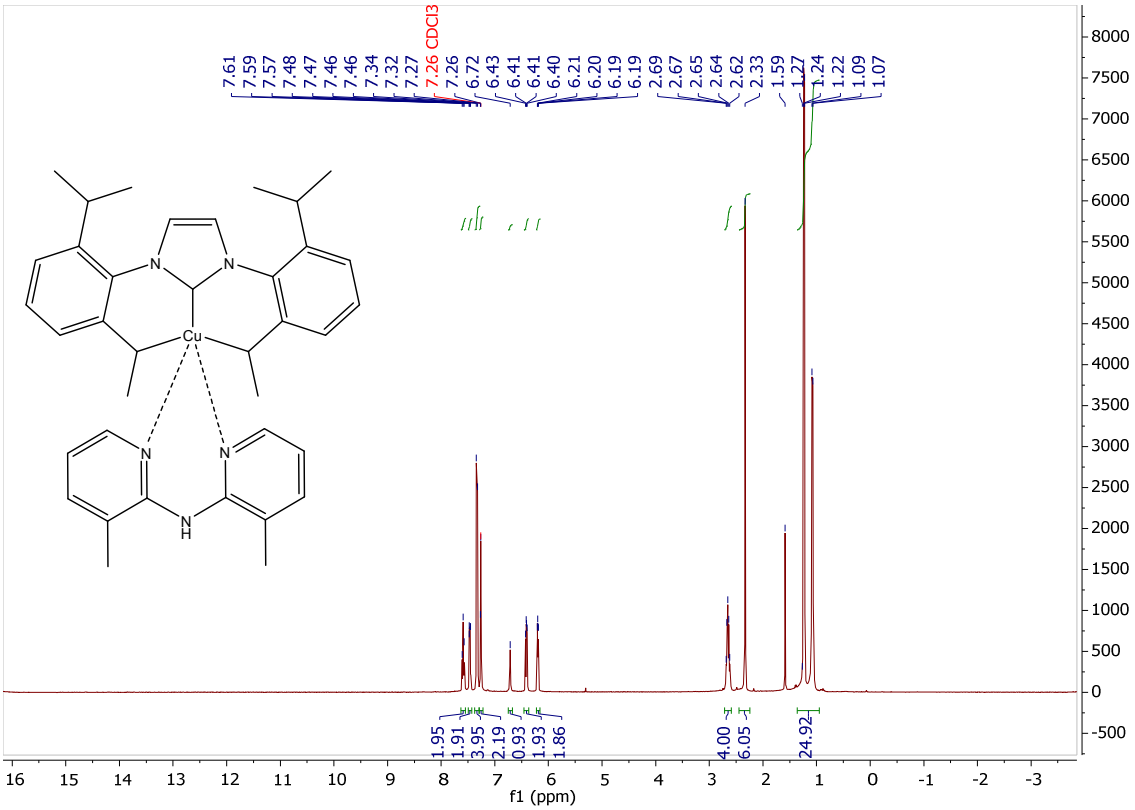
f1 (ppm)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7.34
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7.27
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6.72
6.43
6.41
6.41
6.40
6.21
6.20
6.19
6.19
2.69
2.67
2.65
2.64
2.62
2.33
1.59
1.27
1.24
1.22
1.09
1.07
Cu
N
N
N
N
H
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3.95
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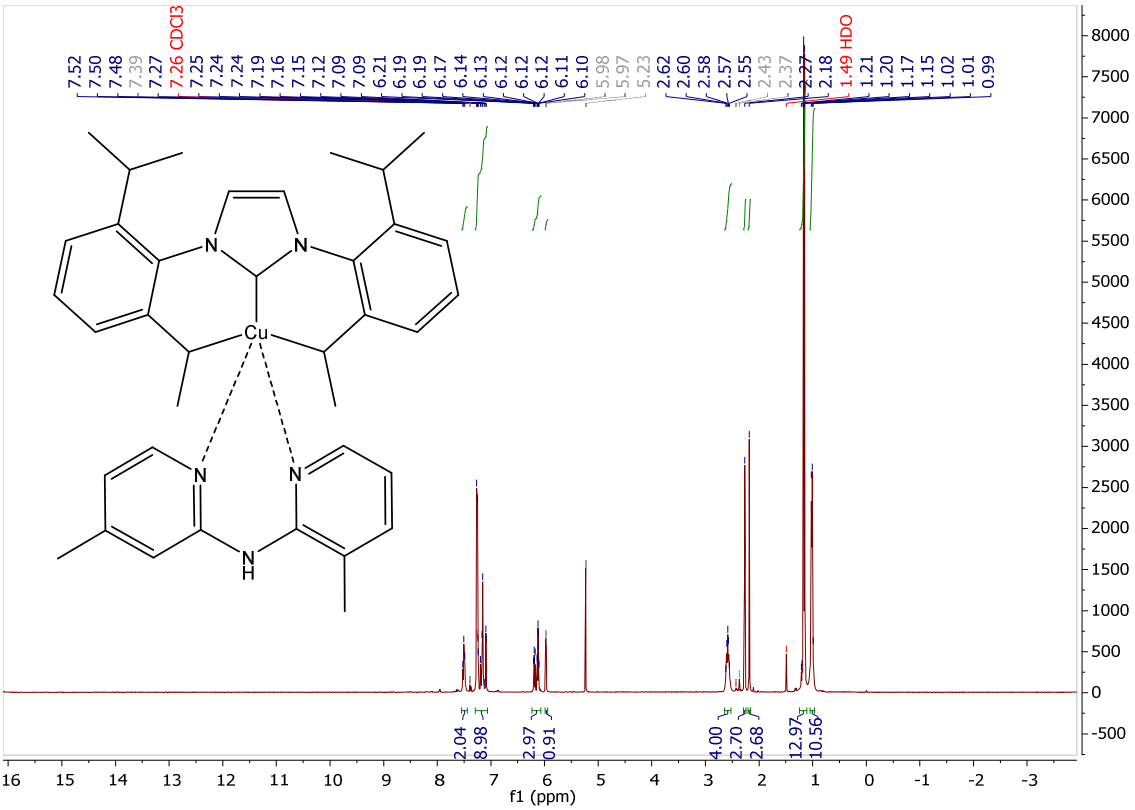
4.00
6.05
24.92
f1 (ppm)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7.12
7.09
7.09
6.21
6.19
6.19
6.17
6.14
6.13
6.12
6.12
6.12
6.11
6.10
5.98
5.97
5.23
2.62
2.60
2.58
2.57
2.55
2.43
2.37
2.27
2.18
1.49 HDO
1.21
1.20
1.17
1.15
1.02
1.01
0.99
Cu
N
N
N
N
H
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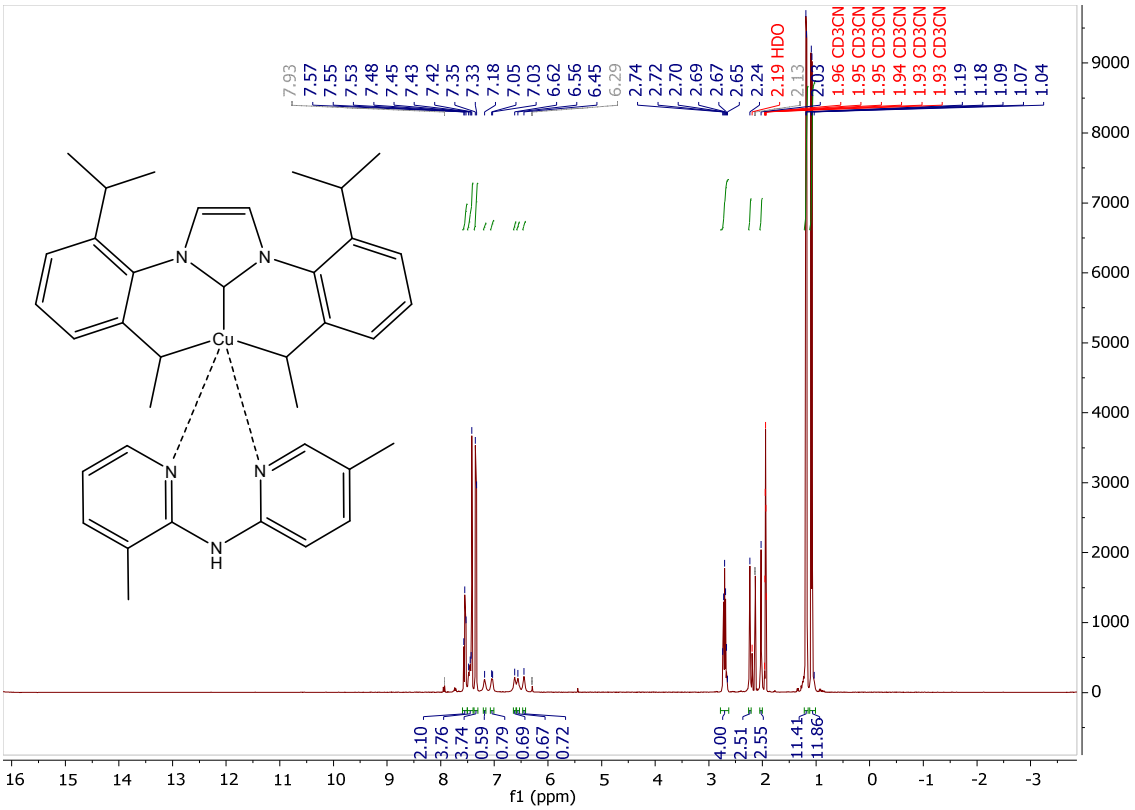
f1 (ppm)


7.93
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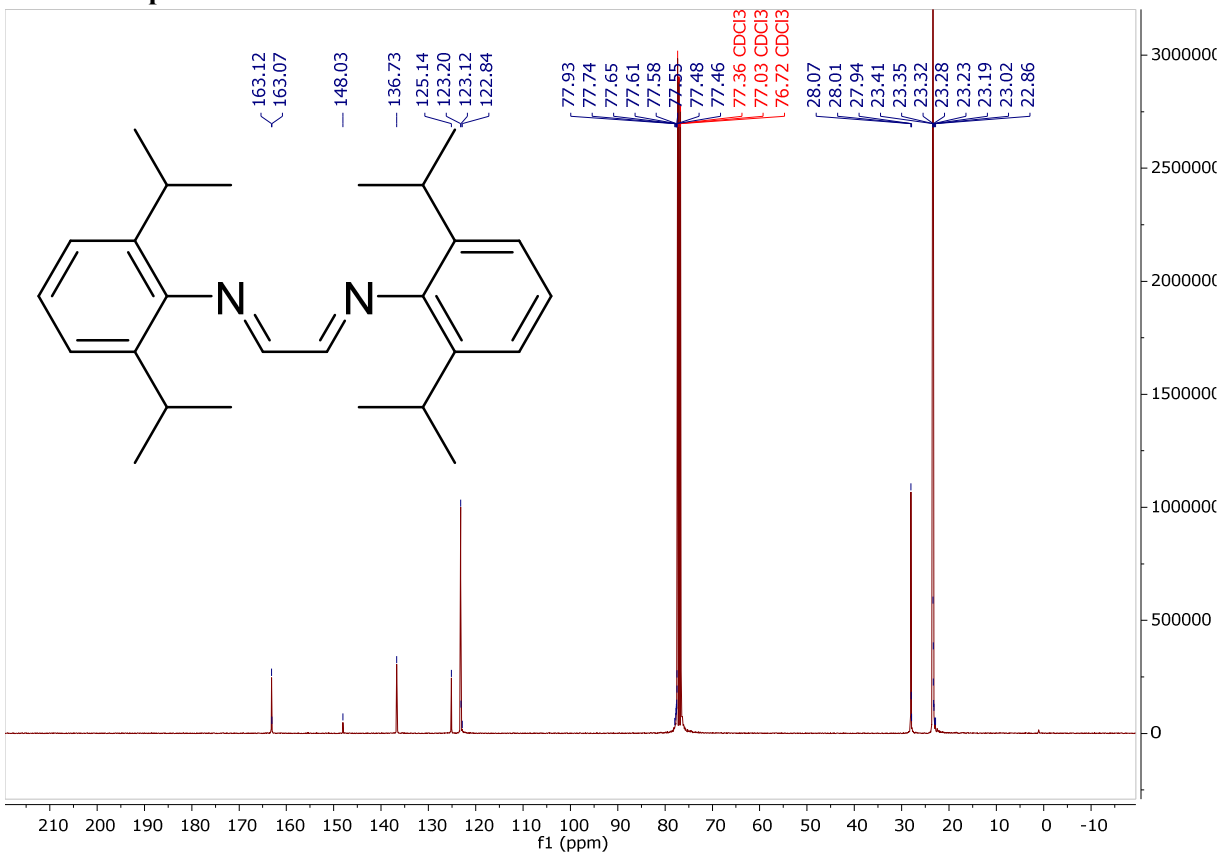
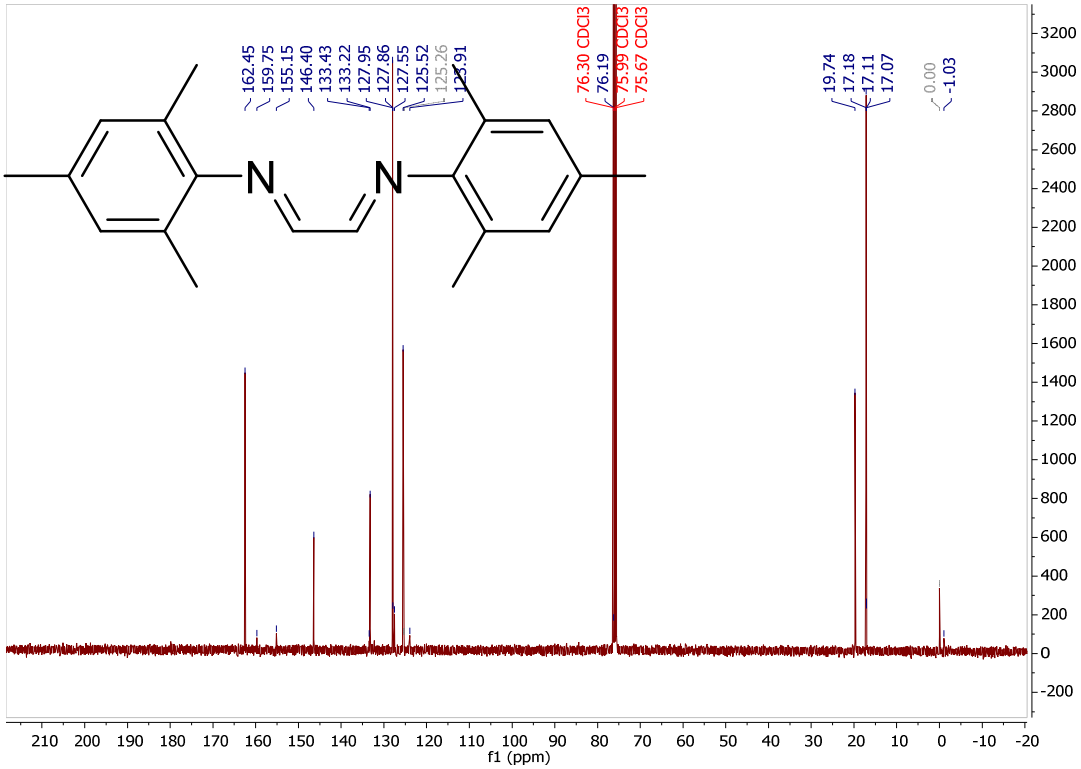
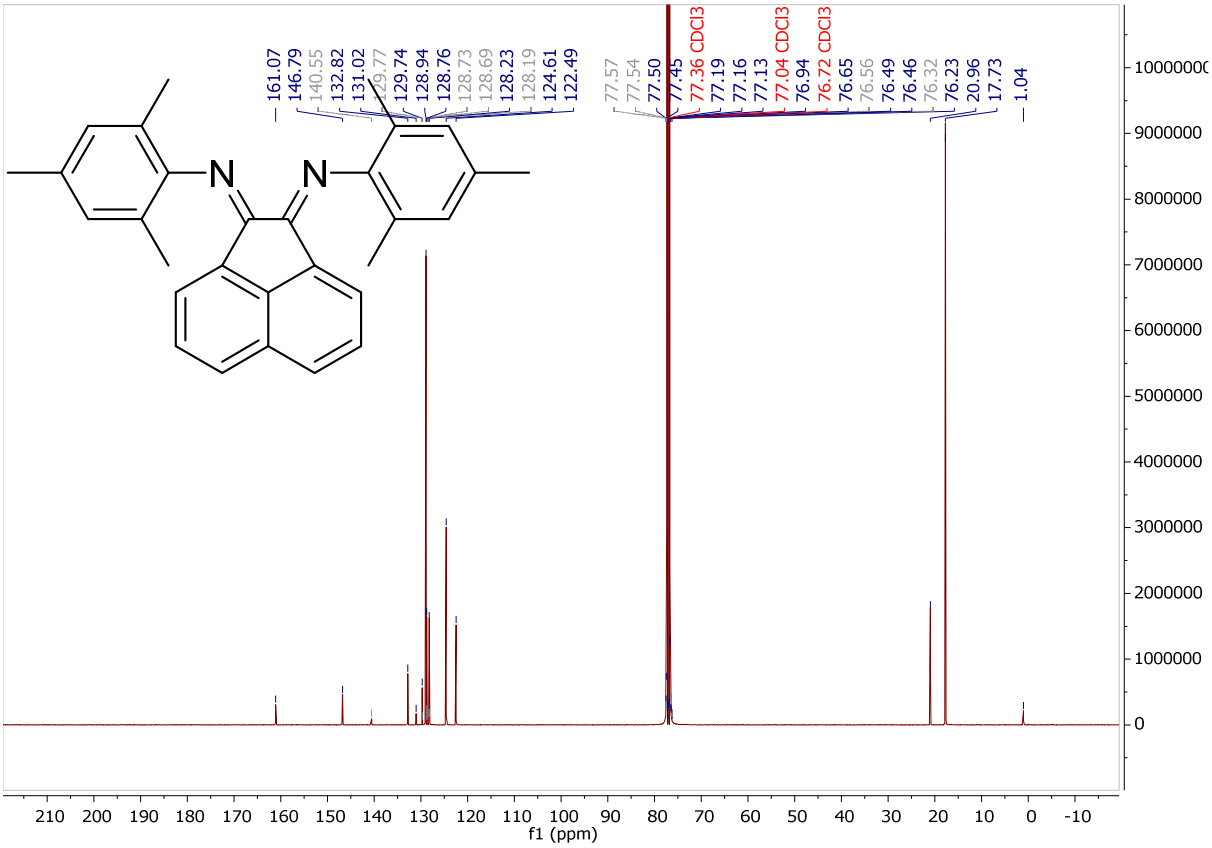
7.18
7.05
7.03
6.62
6.56
6.45
6.29
2.74
2.72
2.70
2.69
2.67
2.65
2.24
2.19 HDO
2.13
2.03
1.96 CD3CN
1.95 CD3CN
1.95 CD3CN
1.94 CD3CN
1.93 CD3CN
1.93 CD3CN
1.19
1.18
1.09
1.07
1.04
Cu
N
N
N
N
H
2.10
3.76
3.74
0.59
0.79
0.69
0.67
0.72
4.00
2.51
2.55
11.41
11.86
f1 (ppm)

^{13}C-NMR Spectra






161.07
146.79
140.55
132.82
131.02
129.77
129.74
128.94
128.76
128.73
128.69
128.23
128.19
124.61
122.49
77.57
77.54
77.50
77.45
77.36 CDCl3
77.19
77.16
77.13
77.04 CDCl3
76.94
76.72 CDCl3
76.65
76.56
76.49
76.46
76.32
76.23
20.96
17.73
1.04
N
N
1000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Appendix 3: EA Data

Atlantic Microlab, Inc.

Sample No. MB-I-211

6180 Atlantic Blvd. Suite M
Norcross, GA 30071
www.atlanticmicrolab.com

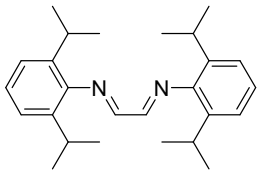
Company/School Oklahoma State University
Dept. Chemistry
Address 107 Physical Science, Room 342
City, State, Zip Stillwater, OK 74078
Name Matt Bardeaux Date 10/14/2016
Phone (918) 899-6158

Professor/Supervisor: Laleh Tahsini
PO# / CC# 170319

Element	Theory	Found	
C	82.93	82.63	
H	9.64	9.76	
N	7.44	7.39	

Single ☒ Duplicate ☐
Elements Present:
Analyze for: C, H and N
Hygroscopic ☐ Explosive ☐
M.P. _____ B.P. _____
To be dried: Yes ☐ No ☒
Temp. _____ Vac. _____ Time _____
Rush Service ☐ Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.
Include Email Address or FAX # Below
tahsini@okstate.edu

Date Received OCT 19 P.M. Date Completed OCT 20 2016
Remarks:



Atlantic Microlab, Inc.

Sample No. MB-I-211

6180 Atlantic Blvd. Suite M
Norcross, GA 30071
www.atlanticmicrolab.com

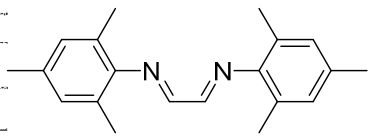
Company/School Oklahoma State University
Dept. Chemistry
Address 107 Physical Science, Room 342
City, State, Zip Stillwater, OK 74078
Name Matt Bardeaux Date 10/14/2016
Phone (918) 899-6158

Professor/Supervisor: Laleh Tahsini
PO# / CC# 170319

Element	Theory	Found	
C	82.93	82.63	
H	9.64	9.76	
N	7.44	7.39	

Single ☒ Duplicate ☐
Elements Present:
Analyze for: C, H and N
Hygroscopic ☐ Explosive ☐
M.P. _____ B.P. _____
To be dried: Yes ☐ No ☒
Temp. _____ Vac. _____ Time _____
Rush Service ☐ Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.
Include Email Address or FAX # Below
tahsini@okstate.edu

Date Received OCT 19 P.M. Date Completed OCT 20 2016
Remarks:



Atlantic Microlab, Inc.

Sample No. MB-I-49B

6180 Atlantic Blvd. Suite M
Norcross, GA 30071
www.atlanticmicrolab.com

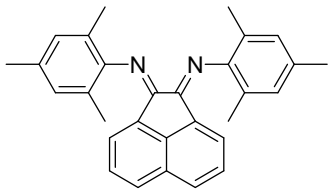
Company/School Oklahoma State University
Dept. Chemistry
Address 107 Physical Science, Room 342
City, State, Zip Stillwater, OK 74078
Name Matt Bardeaux Date 08/12/2016
Phone (918) 899-6158

Professor/Supervisor: Laleh Tahsini
PO# / CC# 161244

Element	Theory	Found	
C	86.50	86.42	
H	6.78	6.70	
N	6.72	6.70	

Single ☒ Duplicate ☐
Elements Present:
Analyze for: C, H and N
Hygroscopic ☐ Explosive ☐
M.P. _____ B.P. _____
To be dried: Yes ☐ No ☒
Temp. _____ Vac. _____ Time _____
Rush Service ☐ Rush service guarantees analyses will be completed and results available by 5 PM EST on the day the sample is received by 11 AM.
Include Email Address or FAX # Below
tahsini@okstate.edu

Date Received AUG 17 P.M. Date Completed AUG 18 2016
Remarks:



VITA

Matthew Bardeaux

Candidate for the Degree of

Master of Science

Thesis: SYNTHESIS OF NOVEL COPPER(I) *N*-HETEROCYCLIC CARBENE COMPLEXES BEARING NITROGEN DONOR LIGANDS

Major Field: Chemistry

Biographical:

Education:

Completed the requirements for the Master of Science in Chemistry at Oklahoma State University, Stillwater, Oklahoma in July, 2017.

Completed the requirements for the Bachelor of Science in Chemistry at University of Tulsa, Tulsa, Oklahoma in 2015.

Professional Memberships: American Chemical Society