INVESTIGATIONS INTO RARE 3-COORDINATE PALLADIUM COMPLEXES AND NEW APPLICATIONS OF COPPER IN COUPLING REACTIONS

A Thesis Submitted to the College of Graduate Studies and Research in Partial Fulfillment of the Requirements for the Degree of Masters of Science in the Department of Chemistry University of Saskatchewan Saskatoon

By Tony Chau

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Acknowledgements

I would like to thank Professor Stephen R. Foley for taking me on as his student in the MSc. Program. His constructive criticism and support has made this program such an enjoyable experience. Throughout the past years Dr. Foley not only was a strong mentor but also an amazing friend that really provided the guidance that made me into the chemist I am today.

I would like to thank the University of Saskatchewan and the Department of Chemistry for accepting me as a MSc. Student and providing me with a welcoming environment that has made my years in this program pleasant.

I would like to thank Advisory Committee, especially Jens Mueller for his support and advice. He has been an inspiration with his input and knowledge that really expanded my interest in chemistry to new heights.

I would like to thank all the staff at the Saskatchewan Structural Sciences Centre for the facilities they have provided. Along with this a special thanks to Dr. J. Wilson Quail and Dr. Gabriele Schatte for their expertise in solving crystal structures.

I would like to thank the present and past members of the Foley group, Robin Wu, Sam Li, Curtis Ball, Amanda Oberhofer, Jackson Chitanda, Tressia Paulose, and Jeremy Olsen for their contribution and criticisms towards the projects.

Finally a special thanks to Pia Wennek for being a secondary mentor and an amazing lab manager.

All this could not be done without the help of all these people thank so much.
To Ma Familia
Abstract

In this thesis, the paper is divided into 2 parts, each corresponding to 2 individual projects. We started with looking into the synthesis of 3-coordinate palladium complexes incorporating a nacnac ligated system for academic interest. We utilized \([\{2,6-\text{iPr}_2\text{Ph}\}_2\text{nacnac}\text{PdCl}\}]_2\) as the precursor into synthesizing these 3-coordinate palladium complexes. Through many failed attempts of manipulating different substrates, we were able to synthesize a 4-coordinate \([\{2,6-\text{iPr}_2\text{Ph}\}_2\text{nacnacPdCl}\}(\text{NH}_2\text{Ph})]\).

The second project deals with the application of dibromobis(1,1'-dibenzyl-3,3'-methylenediiimidazolin-2,2'-diylidene)dicopper(I) complex to catalysis. We decided to focus our attentions specifically on carbonyl reduction of ketones being that hydrosilations with copper catalysts have only been recently looked at. The dibromobis(1,1'-dibenzyl-3,3'-methylenediiimidazolin-2,2'-diylidene)dicopper(I) complex proved to be very effective at hydrosilations of a wide variety of ketones at high temperatures. We further investigated the scope of the dibromobis(1,1'-dibenzyl-3,3'-methylenediiimidazolin-2,2'-diylidene)dicopper(I) catalyst by testing it on the arylation and alkylation of imidazole. The arylation of imidazole showed little to no conversion, whereas the alkylation proved to be quite active for both alkyl bromides and chlorides. We also looked at the attempts in synthesizing bulkier analogues of dibromobis(1,1'-dibenzyl-3,3'-methylenediiimidazolin-2,2'-diylidene)dicopper(I) by varying the benzyl groups to 2,6-diisopropylphenyl and mesityl groups. However, results show that there were difficulties in coordinating these bulkier ligands onto copper. Optimization of complexing bulkier ligands onto copper needs to be conducted before one can proceed onto further reactions.
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Ac.................................................................CH₂CO
acac..............................................................Acetylacetonato
Dipp..............................................................Dissopropylphenyl
Bz.................................................................Benzyl
Cy..............................................................Cyclohexyl
dba.............................................................Dibenzylideneacetone
DMA.............................................................Dimethylacetamide
DMF.............................................................N,N-Dimethylformamide
DMSO...........................................................Dimethyl Sulphoxide
equiv...........................................................Equivalent
Fc.................................................................Ferrocenyli
M.................................................................Has generally been used for metals
NHC...............................................................N-heterocyclic carbene
NMR.............................................................Nuclear Magnetic Resonance
py.................................................................Pyridine
R.................................................................Has generally been used for alkyls or aryls
rt.................................................................Room temperature
THF.............................................................Tetrahydrofuran
X.................................................................Has generally been used for halogens
All...............................................................Allyl
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General Information:

Chapter 1  Introduction

1.1  3-Coordinated Palladium Complexes in Literature

1.1.1  Nacnac Ligands

β-Diketiminato (nacnac) ligands are nitrogen analogues of widely used acetylacetonato ligands that have been given the nickname acac. The synthesis and study of nacnac ligands was first published in 1968 by Canadian researchers. Their research led to prominent exploration of nacnac ligands on late transitional metals especially with copper, cobalt and nickel. β-Diketimines are versatile compounds that can be easily synthesized by reacting diketone with a primary amine in a condensation reaction yielding a β-diimine (Scheme 1.1).

Scheme 1.1 The synthesis of a β-dimine and the subsequent tautomerization to the corresponding enamine.

\[
\text{Diketone} + 2\text{NH}_2\text{R} \rightarrow \text{β-Dimine} \rightarrow \text{β-Diketimine (Enamine)} \rightarrow \text{β-Diketiminato}
\]

This β-diimine readily tautomerizes into a more stable β-diketimine (enamine), which in turn can be deprotonated to form β-diketiminato ligands. These β-diketiminato ligands are bidentate, mono-anionic, 4-electron donors that possess properties that can be especially useful in the synthesis of metal complexes. Nacnac ligands are especially useful in organometallic chemistry where the ligand can be easily manipulated to increase steric protection about the metal center by altering the substituents attached to the nitrogen atoms with bulkier groups. These ligands also possess the property of being bidentate, which generally creates more stability on the metal centers than monodentate ligands through chelation. More specifically, \([2,6-\text{Pr}_2\text{Ph}]_2\text{nacnac}\) ligands recently have become increasingly popular in metal coordination chemistry, through the
ease of stabilizing unusual oxidation states and geometries for many main group elements and transition metals.  

![Figure 1.1](image)

**Figure 1.1** The structure of [(2,6-iPr<sub>2</sub>Ph)<sub>2</sub>nacnac].

Nacnac ligands have been used to isolate rare 3-coordinate Fe(II), Cu(II), Zn(II), and 5-coordinate Pt(IV) complexes. The bulky 2,6-di-isopropylphenyl groups attached to the nitrogen sterically protect the metal center allowing the synthesis of these rare geometries.

### 1.1.2 3-Coordinate Palladium Complexes

In the last three decades unsaturated metal complexes containing a vacant coordination site have been proposed as intermediates for many catalytic reactions, such as hydrogenation, hydroformylation, olefin polymerization, and various palladium catalyzed cross-coupling reactions (Buckwald-Hartwig, Sonogashira, Suzuki, etc). Evidence, shows that d<sup>8</sup> 3-coordinate metal complexes have been isolated and characterized before in literature; however palladium complexes have had very little exploration in reactivity and stability. 3-coordinate palladium complexes employing a diimine ligand have been proposed to be active catalysts in Suzuki, Heck, Sonogashira, and Hiyama cross-coupling reactions.

*Attempted Synthesis of 3-Coordinate Palladium*

Studies show the synthesis of 3-coordinate palladium complexes is rather difficult, due to the presence of a vacant coordination site, which makes the complex very susceptible to solvent interaction or dimerization, from a 14-electron 3-coordinate to a more stable 16-electron 4-coordinate species.
Hartwig was the first to make any significant progress in the synthesis of 3-coordinate palladium complexes. Hartwig being one of the leaders in the area of C-N coupling proposed many mechanisms for cross-coupling reactions going through a 3-coordinate palladium intermediate.\textsuperscript{13}

**Scheme 1.2** The proposed catalytic pathway for cross-coupling reactions going through a 3-coordinate intermediate.

Very little is known about 3-coordinate palladium intermediates, especially in terms of stability, properties, and reactivity.

In 2003, Nolan \textit{et al.} made attempts at synthesizing a cationic 3-coordinate palladium employing the widely used mondentate N-heterocyclic carbene ligands by method of chloride abstraction (Scheme 1.3).\textsuperscript{14} They found that the cationic complex were very unstable and decomposed upon work up; therefore, making it very difficult to fully characterized what was thought to be the desired complex.\textsuperscript{14} However, Nolan \textit{et al.} was able to eventually characterize one of their compounds, where crystallographic data shows a 4-coordinate palladium with a coordinating
acetonitrile occupying the fourth site.\textsuperscript{14} This suggests that his complexes are only stable in the presence of acetonitrile, and decomposes very readily upon the removal of solvent.\textsuperscript{14}

**Scheme 1.3** Nolan et al. attempted synthesis of a 3-coordinated ligated cationic NHC palladium complex.\textsuperscript{14}

\[
\begin{align*}
\text{R}^\text{All-Pd-Cl} + \text{All-Pd-N-CN} &\rightarrow [\text{R}^\text{All-Pd-N-CN}]^+ \quad \text{PF}_6^- \\
\text{R} = 2,6-iPr_2C_6H_3 \\
\text{All} = \begin{array}{c}
\text{N} \\
\end{array}
\end{align*}
\]

In 2005, Porschke et al. continued Nolan’s work by treating the similar NHC palladium precursors to that of Nolan’s with a variety of thallium salt reagents rather than silver salts (Scheme 1.4).\textsuperscript{15} The resulting product that was produced was neither the solvated 4-coordinate product nor the desired 3-coordinate complex but rather a binuclear species bridged by a chloride.\textsuperscript{15}

**Scheme 1.4** Porschke et al. attempted synthesis of a 3-coordinated ligated cationic NHC palladium complex.\textsuperscript{15}

\[
\begin{align*}
\text{R}^\text{All-Pd-Cl} + \text{TIPF}_6 &\rightarrow [\text{R}^\text{All-Pd-N-N-C-N-Pd-All}]^+ \quad \text{PF}_6^- \\
\text{R} = 2,6-iPr_2C_6H_3 \\
\text{All} = \begin{array}{c}
\text{N} \\
\end{array}
\end{align*}
\]

In that same year, Glorius et al. was able to generate what was proposed as a cationic low-coordinate palladium complex by chloride abstraction with silver salts (Scheme 1.5).\textsuperscript{16} However, the complex that was very unstable despite the intramolecular stabilization of the double bond and never was able to be fully characterize the complex, where only $^1$H NMR spectroscopy was able to be obtained for this species.\textsuperscript{16}
Scheme 1.5  Glorus et al. attempted synthesis of a 3-coordinated ligated cationic NHC palladium complex.\textsuperscript{16}

\[
\begin{align*}
\text{Scheme 1.5} & \quad \text{Glorius et al. attempted synthesis of a 3-coordinated ligated cationic NHC palladium complex.}^\text{16} \\
\end{align*}
\]

In 2010, Hartwig et al. treated several bidentate phosphine ligated palladium halide dimeric compounds with potassium aryl substituted amides (Scheme 1.6 and 1.7).\textsuperscript{17} They claimed that their species occurred in equilibrium between a 3-coordinate and dimerized product, where the 3-coordinate complex was not isolated.\textsuperscript{17} They also show that the complexes that did not undergo dimerization contained a coordinating THF, yielding a 4-coordinate species.\textsuperscript{17}

Scheme 1.6  Hartwig et al. attempted synthesis of a 3-coordinated ligated phosphine palladium complex in equilibrium with a 4-coordinate dimer.\textsuperscript{17}

\[
\begin{align*}
\text{Scheme 1.6} & \quad \text{Hartwig et al. attempted synthesis of a 3-coordinate ligated phosphine palladium complex in equilibrium with a 4-coordinate dimer.}^\text{17} \\
\end{align*}
\]

Scheme 1.7  Hartwig et al. synthesis of a 4-coordinate palladium complex with a THF solvent donor.\textsuperscript{17}

\[
\begin{align*}
\text{Scheme 1.7} & \quad \text{Hartwig et al. synthesis of a 4-coordinate palladium complex with a THF solvent donor.}^\text{17} \\
\end{align*}
\]

From the above examples, the synthesis of 3-coordinate palladium complexes appears to be very reactive, where decomposition happens readily. The instability of these intermediates makes it rather difficult to isolate, where the characterized product was never the desired product. This
shows that the synthesis of 3-coordinate palladium intermediates require fine tuning of sterics and electronics to be able to successfully isolate this species.

3-Coordinate Palladium with Agostic Interaction

Though the concept of synthesizing a 3-coordinate palladium species appears to be relatively simple, the fundamental isolation of these complexes are rather challenging. The presence of sterically hindered ligands was believed to inhibit dimerization and solvent interaction.

In 2002, Hartwig et al. synthesized several aryl palladium halide complexes that appeared to be monomeric 3-coordinate species; however after obtaining the crystallographic data it was evident that these complexes were not true 3-coordinate species (Scheme 1.8). The crystal structures show that these complexes suffer from weak agostic interaction between the C-H bond of the ligand with the vacant coordination site on palladium.

**Scheme 1.8** Hartwig et al. synthesis of aryl palladium halide complex with agostic interactions.

\[
Pd(dba)_{2} + \text{L} + \text{PhX (Excess)} \xrightarrow{\text{THF or neat, 25^\circ C}} \text{Ph-Pd} \_L^X
\]

\( \text{L} = 1-\text{AdP}^3\text{Bu}, \ X = \text{Br} \)

\( \text{L} = 2-\text{AdP}^3\text{Bu}, \ X = \text{Br} \)

\( \text{L} = \text{P}^3\text{Bu}_3, \ X = \text{I} \)

In 2004, Hartwig et al. continued their work with 3-coordinate palladium complexes using a similar approach of aryl halide palladium compounds, however, increasing the steric bulk on the phosphine position to inhibit agostic interaction (Scheme 1.9). They replaced substituents attached to the phosphine with a bulky ferrocene, where the Cp rings are substituted with phenyls. Despite the increase in steric bulk, the crystallography of the product still shows presence of agostic interaction.
In that same paper, they showed isolation of a wide variety of 3-coordinate aryl triflate palladium compounds analogous to his chloride derivatives (Scheme 1.10). Hartwig et al. was able to characterized one of these 3-coordinate palladium compounds, which also showed weak agostic interaction into the vacant site of the palladium.

In that same year, they made a second attempt at forming a 3-coordinate palladium species containing a heteroaromatic group (Scheme 1.11). They reacted 2-thienyl bromide with a bulky phosphine in presence of a bulky potassium reagent to form a 3-coordinate palladium complex.
Scheme 1.11  Hartwig et al. synthesis of aryl palladium halide Q-phos ligated complex with agostic interactions.\textsuperscript{20}

\[
\text{Pd(P\textsubscript{3}Bu\textsubscript{3})\textsubscript{2} \xrightarrow{\text{neat KNAr}_2} i\text{Bu}_3\text{P-Pd-NAr}_2}
\]

\[
\text{Ar} = 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3
\]

Once again the crystal structure shows bond distances consistent with that of agostic interactions involving the butyl hydrogens of the phosphine.\textsuperscript{20}

In 2005, after the many failed attempts at synthesizing 3-coordinate palladium employing NHC as ancillary ligands, Bertrand et al. was able to isolate and characterize low-coordinate palladium (Scheme 1.12).\textsuperscript{21} They utilized an alkylamino carbene complex as their starting precursor and were able to isolate a 2-coordinate palladium species by means of chloride abstraction that also suffered clear indication of agostic interactions in the crystallography.\textsuperscript{21}

Scheme 1.12  Bertrand et al. synthesis of a low coordinate palladium complex with agostic interactions.\textsuperscript{21}

\[
\text{Ar-}\text{N-iPr-All-Pd-Cl} \xrightarrow{\text{AgBF}_6} \begin{cases} 
\text{Ar-}\text{N-iPr-All-Pd} & \text{Ar} = 2,6-i\text{Pr}_2\text{C}_6\text{H}_3 \\
\text{BF}_4^- & \end{cases}
\]

In 2007, Hartwig et al. isolated several monomeric 3-coordinate palladium species, by treating their previously synthesized aryl palladium halide complexes with a variety of bulky sodium aryloxides (Scheme 1.13).\textsuperscript{22} They were able to isolate and characterized two monomeric palladium aryloxides, where in both the crystallography showed Pd-H bond distances that are within the region of agostic interactions.\textsuperscript{22}
Scheme 1.13 Hartwig et al. synthesis of palladium aryloxide complexes with agostic interactions.\textsuperscript{22}

\[
\begin{align*}
\text{C7H8} & \quad 25^\circ\text{C} \\
1\text{-Ad}^\prime\text{Bu}_2\text{P} & \quad \text{Pd} & \quad \text{Br} \\
\text{AgOTf} & \quad \text{NaOAr} \\
\end{align*}
\]

Ar = (2,4,6-(tBu)\textsubscript{3}C\textsubscript{6}H\textsubscript{2}), R = H
Ar = C(CH\textsubscript{3})\textsubscript{2}(CF\textsubscript{3}), R = H
Ar = C(CH\textsubscript{3})\textsubscript{2}(CF\textsubscript{3}), R = Me

Recently in 2011, Rourke et al. synthesized a 14-electron aryl palladium species employing a bidentate pyridine ligand system by reacting the ligated palladium acetate species with potassium chloride (Scheme 1.14).\textsuperscript{23} After the obtaining the crystallography, it was evident that the bond distance show trends that are resemblance of that consistent with agostic interactions.\textsuperscript{23}

Scheme 1.14 Rourke et al. synthesis of low coordinate pyridine ligated palladium complex with agostic interactions.\textsuperscript{23}

Even though, these structures remain 14 electron monomeric species, they are not considered true 3-coordinate palladium do to the agostic interaction occupying the remaining vacant site on palladium.

\textit{True 3-Coordinate Palladium Species}

3-Coordinate palladium complexes are very rare, where only a handful of true 3-coordinate palladium complexes without agostic interaction actually exist in literature with evidence of crystallography. It has been reported that complexes possessing agostic interaction typically have bond distance within the region of 2.74Å to 2.94Å.\textsuperscript{20} To truly possess a 3-coordinate species the C-H bond distance must lie outside this region, so that the spatial orientation of the ligand lies outside the fourth site of the palladium.
In 2004, Hartwig et al. was the first group to isolate a true 3-coordinate palladium species with full characterization of the compound (Scheme 1.15). They took their previously synthesized 3-coordinate aryl palladium complexes with agostic interaction and treated these precursors with a bulky potassium amide reagent to abstract the chloride. Their rational was the amide group possesses a greater amount of bulk in comparison to the single halide should be able to inhibit rotation and force the hydrogens away from the coordination site. After obtaining the crystal structure the bond distances show that the ligand’s hydrogens lay outside the square plane of the palladium. This implies that only three of the sites are occupied in the square plane sphere, suggesting a true 3-coordinate species free from agostic interaction.

Scheme 1.15 Hartwig et al. synthesis of true 3-coordinate palladium complexes without agostic interaction.

In the same year, shortly after Hartwigs discoveries, Kabuto et al. a Japanese group out of Tahoko University, synthesized the first 14-electron 3-coordinate disilene palladium complex and observed the degree of sigma donation of the disilene ligand onto palladium; however no further chemistry was conducted on these complexes (Scheme 1.16).

Scheme 1.16 Kabuto et al. synthesis of a 3-coordinate disilene palladium complex.
1.1.2 T-Shape Vs Trigonal Planar

These 3-coordinate structures tend to adopt a geometry favoring a T-shape rather than the trigonal planar orientation. The crystal structures show that the bond angles vary closer to that of an ideal T-shape (90°, 90°, 180°) rather than that of a trigonal planar (120°, 120°, 120°). This trend was evident with 3-coordinate palladium with and without agostic interaction.

1.1.3 Research Goals

There are many synthetic pathways that one can propose by which a 3-coordinate palladium can be formed; a common pathway is a simple one-step reaction to yield the desired monomeric 3-coordinate species. Many groups made attempts in forming a low-coordinate palladium by reacting palladium acetate with a protonated ligand, to yield the corresponding 3-coordinate species. However, palladium acetate transition metal species have been reported to commonly form either a monomeric species with a chelating acetate or a dimeric species with a bridging acetate.23

Our group previously attempted the synthesis of 3-coordinate palladium intermediates by utilizing a 4-coordinate monomeric palladium acetate species as the precursor (Scheme 1.17).25 The following compounds appear to be very unstable, where there was no clear characterization that suggested that the 3-coordinate species was being formed.25

Scheme 1.17 The attempted synthesis of a 3-coordinate palladium complex, by utilization of a palladium acetate complex.25

\[ \begin{align*}
\text{R} = \text{aniline, cyclohexylamine, butylamine, adamantylamine}
\end{align*} \]
Palladium acetate species tend to be very difficult to characterize, therefore are reacted with a halide salt to form the corresponding palladium halide counterparts. In most examples in literature the precursors into forming a 3-coordinate palladium generally possesses a halide. Halides are typically better leaving groups then that of acetates, where halide abstractions are more common for the synthesis of 3-coordinate palladiums.

In this thesis we attempt to synthesize a 3-coordinate palladium by chloride abstraction of a 4-coordinate palladium chloride dimer, employing a nacnac ligand as our precursor. We anticipate that the chlorine being a good leaving group will allow substitution of the substrate on palladium and, depending on the sterics of the substrate, can inhibit dimerization. We also use computational analysis to provide insight into the steric and geometry of our 3-coordinate species.

1.2 Applications of N-Heterocyclic Carbene Copper Complexes

1.2.1 N-Heterocyclic Carbene (NHC) Ligands

Ever since the discovery of the first isolable free carbene by Arduengo, NHCs have emerged as a dominant class of ligands. Their strong \( \sigma \)-donating ability and tunable steric bulk about the metal center makes them a very ideal choice for ligand systems in catalysis. Along with these properties, NHCs tend to be very thermally stable compounds and water inert in comparison to that of the widely used phosphine-based ligands. It has been known in literature that monodentate and chelating NHCs ligated systems are highly active in a wide array of coupling reactions and catalysis. The use of NHCs in metal mediated reactions has been heavily investigated for many transition metals, such as palladium and nickel; however, they still remain relatively unexplored for copper-based reactions.

Though many monodentate NHC copper complexes are known to be active in catalysis, only a few have been actually isolated, but rather used as precursor’s in \textit{situ} reactions.
1.2.2 \textit{Di}(N-heterocyclic Carbenes) (\textit{diNHC}) Ligands

Poly-NHC’s have been synthesized and studied on late transition metals in literature; however, these ancillary ligands on copper still remain scarce. Till this day there has been only a handful poly-NHC on copper that have been fully characterized in literature with crystallographic evidence.

In 2001, Arnold \textit{et al.} synthesized the first NHC-based chelating ligand incorporating an alkoxide functional group by reacting their silver complex with copper iodide, yielding a cationic dinuclear species (Scheme 1.18).\textsuperscript{29} The crystallography shows that each copper center was tetradentately bridging coordinated to two alkoxides and two carbenes.\textsuperscript{29}

\textbf{Scheme 1.18} \hspace{1cm} Arnold \textit{et al.} synthesis of \textit{diNHC} copper complex with bridging alkoxides.\textsuperscript{29}

\begin{center}
\includegraphics[width=\textwidth]{Scheme1.18.png}
\end{center}

In 2003, Meyer \textit{et al.} synthesized several tripodal triNHC copper species.\textsuperscript{30} They reacted their \textit{tert}-butyl substituted triNHC free ligand with a tetraacetonitrile copper salt, to yield an unusually coordinated copper species (Scheme 1.19).\textsuperscript{30}

\textbf{Scheme 1.19} \hspace{1cm} Meyer \textit{et al.} synthesis of tripodal bisdiaminoalkenyl triNHC copper complex.\textsuperscript{30}
With slight modification to their tripodal ligand system they were able to isolate a mononuclear species where the ligand was tetradentately coordinated to the copper metal (Scheme 1.20).\textsuperscript{31}

**Scheme 1.20** Meyer *et al.* synthesis of tripodal mononuclear tridentately coordinated triNHC copper complex.\textsuperscript{31}

They also display that by adding 2:3 ratio of ligand with respect to copper, yielded a trinuclear species (Scheme 1.21).\textsuperscript{31} The crystallography shows that the molecule contains two coppers that are bounded in T-shape geometry by two pendant carbene ligators and an anchoring nitrogen, while the third carbene was coordinated to the central copper.\textsuperscript{31}

**Scheme 1.21** Meyer *et al.* synthesis of tripodal trinuclear triNHC containing two pendant carbene ligators and an anchoring nitrogen copper complex.\textsuperscript{31}
They also found that utilizing the silver oxide route into forming their tripodal copper complex yielded a trinuclear copper species, where all three cuprous ions are bounded bidentately by two different carbenes (Scheme 1.22).\textsuperscript{31}

**Scheme 1.22** Meyer et al. synthesis of tripodal cationic bidentately coordinated triNHC copper complex.\textsuperscript{31}

In 2009, Hoffman et al. synthesized a very unusual coordinated neutral copper bound diNHC polymer by deprotonation the corresponding diNHC salt followed by a sequential reaction with copper bromide (Scheme 1.23).\textsuperscript{32} The resulting crystallography showed that the compound was indeed a polymer, where each copper was directly bounded to a ligand, while still bridging at the bromine, with a bonding motif of (-L-Cu-(μ-Br)\textsubscript{2}-Cu-L-\textsubscript{n}).\textsuperscript{32}

**Scheme 1.23** Hoffman et al. synthesis of diNHC copper polymer.\textsuperscript{32}

In attempts to synthesize an acetonitrile adduct from the polymer, they reacted their deprotonated diNHC with a tetraacetonitrile copper salt, where the resulting crystal structure showed a product consistent with presumably a nucleophillic attack of the CH\textsubscript{2} bridging unit on the bisimidazolium
salt and not a polymeric complex (Scheme 1.24). The crystallography also showed a single diNHC bound to two copper centers in different environments.³²

**Scheme 1.24**  Hoffman *et al.* synthesis of diNHC with coordinated imidazole.³²

Hoffman *et al.*, proceeded on breaking up the chain by reacting the polymeric copper species with an amine (Scheme 1.25). The crystal structure showed a similar structure to that of the scheme above, but with an amine-bound copper.³²

**Scheme 1.25**  Hoffman *et al.* synthesis of diNHC with coordinated amine.³²

In that same year, Tsubomura *et al.* synthesized a methyl-substituted diNHC copper complex by transmetallation of the silver carbene with the corresponding copper salts (Scheme 1.26).³³ The diNHC ligand that was utilized in the synthesis of these copper complexes are very similar ligands to that employed by Hoffman *et al.*, where only difference was in the steric bulk of the alkyl group attached to the nitrogen.³³ Tsubomura *et al.* found that the resulting species that was formed was not polymeric but rather dimeric compound with bridging copper centers.³³
Scheme 1.26  Tsubomura et al. synthesis of a dinuclear diNHC copper complex with bridging copper centers.\(^{33}\)

\[
\begin{align*}
\text{Scheme 1.26:} & \quad \text{Tsubomura et al. synthesis of a dinuclear diNHC copper complex with bridging copper centers.}^{33} \\
\end{align*}
\]

Roughly around the same time, Albrecht et al. showed that they were able to synthesize a wide variety of new NHC copper(I) complexes by a methodology different than the more traditional transmetallation of the silver carbene salts with copper.\(^{34}\) Among the majority of mono-NHC copper complexes, they isolated and characterized an isopropyl substituted diNHC mono-anionic copper(I) complex following a very similar prep to that of Tsbomura (Scheme 1.27). The resulting crystal structure showed conclusions consistent with Tsbomura, where the compound was rather dinuclear with bridging copper centers.\(^{34}\)

Scheme 1.27  Albrecht et al. synthesis of a dinuclear diNHC copper complex with bridging copper centers.\(^{34}\)

In 2010, Chen et al. synthesized several substituted NHC-bridged pyrazole copper complexes by reacting the ligand salt with silver oxide, followed by a transmetallation with copper powder
(Scheme 1.28). They showed that by altering the steric and electronic attached to the NHC affects the coordination environments around copper. They were able to isolate a hexadentate pyridine substituted NHC complex containing two copper ions and a hydroxide.

**Scheme 1.28** Chen *et al.* synthesis of a pyzole bridged diNHC copper complex with pendant pyridine donor arms.

They also isolated a cationic pyridine substituted NHC complex where the aromatic group was orientated in a position closer to the copper (Scheme 1.29). They found that the complex contained two tetradeionate coppers and two pentadentate coppers with a coordinating pyridine.

**Scheme 1.29** Chen *et al.* synthesis of a cationic diNHC copper complex with bridging hydroxals.

Then Chen *et al.*, preceded to synthesizing a thienyl analogue of the NHC ligated copper complex (Scheme 1.30). After obtaining the crystal structure, they found the complex
possesses only two coppers each bound 4-coordinately by 2 pyrolates and 2 carbenes. The crystal structure showed that the thienyl sulfur was not coordinated to copper.\textsuperscript{35}

**Scheme 1.30** Chen et al. synthesis of a thienyl diNHC copper complex.\textsuperscript{35}

In that same year, Lin et al. published a paper on the synthesis of a dinuclear diNHC copper complex (Scheme 1.31).\textsuperscript{36} They utilized a substituted methyl and tert-butyl dimeric bis-NHC copper complex as their precursor. They showed that in presence of O\textsubscript{2} there was coupling of the imidazoles by a C-C bond.\textsuperscript{36} The resulting crystal structure showed that the coppers were bounded bidentately by the nitrogen of two different carbenes.\textsuperscript{36}

**Scheme 1.31** Lin et al. synthesis of a dimidazole ligated diNHC copper complex.\textsuperscript{36}

Though it is clear that there have been several examples of poly-NHC copper systems that are fully characterized in literature; however, very few have been tested for catalysis, where the focus of these papers are the synthesis aspect of making these complexes itself.
1.2.3 Hydrosilations

Carbonyl reduction of aldehyde and ketones have been studied for decades especially with transition metals, Ti,\textsuperscript{37} Rh,\textsuperscript{38} Ru,\textsuperscript{39} and Ir;\textsuperscript{40} however, are not very active towards sterically hindered substrates and require a large amount loading catalyst.\textsuperscript{37-40}

Hydrosilations of a copper-based catalyst have only been recently investigated. Having copper as a catalyst provides a cheaper alternative to previous catalyst sources (ie Ti, Rh, Ru, and Ir), which was first discovered in 1988 by the Stryker et al., where they showed that their hexameric copper hydride complex, known as the Stryker’s reagent, was effective in hydrosilation.\textsuperscript{41} The Stryker’s reagent was able to reduce simple aldehydes and ketones however, was never tested for sterically demanding substrates.\textsuperscript{41} Since then, copper-catalyzed hydrosilations only started taking off in the early 2000’s. Several groups showed very strong advancement in copper catalyzed in situ reactions that were very active in hydrosilation of asymmetric aldehydes and ketones.\textsuperscript{42} Many of the ligand systems employed in these in situ reactions were phosphine ligated systems.\textsuperscript{42} Among these groups, Lipshutz et al. was really the largest players in copper-catalyzed asymmetric hydrosilation of ketones, showing results with not only high yield and short reaction time, but also extremely high enantioselectivity’s.\textsuperscript{42} However, despite the remarkable achievement in copper catalyzed asymmetric hydrosilations, the reduction of sterically hindered carbyons was yet to be tested.\textsuperscript{42} It wasn’t until 2005, Nolan et al. published a paper on copper catalyzed NHC systems for hydrosilations of ketones, specifically focusing on varying the sterics surrounding the carbonyl.\textsuperscript{43} They showed that his NHC systems catalyzed a wide array of very sterically demanding ketones that has not yet been tested in literature at high yields and minimal reaction times.\textsuperscript{43} From all the examples in literature for copper catalyzed hydrosilation of aldehydes and ketones, the majority have been in situ reactions and there are only several examples of well-defined systems present.
Figure 1.2  The effective well defined copper systems for hydrosilations of ketones in literature.

To this date, Lipshutz’s bi-aryl phosphine copper hydride complex and Nolan’s NHC copper chloride systems are the most effective catalyst for asymmetric and sterically hindered hydrosilations of ketones, respectively.

1.2.4  C-N Coupling of Imidazole (N-Arylation and N-Alkylation)

Arylation of imidazoles has been discovered for over a century; however arylation employing copper has only been recently studied. Copper catalyzed arylation of imidazoles first started in the early 2006, where Taillefer et al. utilized copper oxide in situ reactions with a series of oxime ligands for the arylation of aryl bromide and iodides with imidazoles. He showed moderate yields for the bromides in mild reaction conditions. Since then, yields have not improved drastically for the arylation of imidazoles, where the majority of the aryl reagents tested were bromides and iodides. Very little progress or investigation has been done with the coupling of aryl chlorides with imidazoles, and effectively yields are relatively low. Therefore, N-arylation of imidazoles has shown high yields for that of aryl iodides and rather moderate yields for
bromides, which also generally requires more punishing reaction conditions.\textsuperscript{44-45} Once again, most copper systems developed for the arylation of imidazoles are in \textit{situ} reactions, and only a few examples of well-defined systems are known.

![Chemical structures](image)

**Figure 1.3** The effective copper systems for arylation of imidazole in literature.\textsuperscript{44-45}

Although transitional metal catalyzed arylation of imidazoles has been known for decades, metal mediated alkylation coupling of imidazoles remains virtually non-existent. There was only one example of copper catalyzed alkylation of imidazoles known in literature. In 2003, Almanza \textit{et al.} showed coupling of aryl azoles with imidazole catalyzed by copper carbenoid.\textsuperscript{46} They showed very efficient yields for a variety of coupled alkyl imidazoles; however the drawback of these reactions are the aryl azole precursors are not commercially available and need to be synthesized.

The attraction to utilizing substituted chlorides over bromides and iodides was the fact that chlorides are more commercially available and cheaper. Chlorides are fundamentally more
challenging to couple, due to the nature of the bond strength of the C-Cl bond being less readily to break and undergo oxidative addition, then that of bromides and iodides. As one can see, the need for a copper system that can couple substituted chlorides with imidazoles at high yields and less rigorous conditions is essential.

Alkylation and arylation of imidazoles has not always proceeded by metal mediated reactions, but rather more commonly made by synthetic routes. Substituted imidazoles are generally synthesized by activating imidazole with a strong base and followed by addition of the substituted halide.\textsuperscript{47} This method has been shown to produce moderate yields, and mainly substituted bromides and iodides are employed.\textsuperscript{47} However, this methodology only works on primary and secondary substituted halides. The SN2 attack of the activated imidazole onto the alpha carbon will not undergo for tertiary substituted halides. The synthesis of more complicated substituted imidazoles, requires a more rigorous synthesis of reacting glyoxyl with the corresponding amine followed several sequential addition at specific time intervals of reagents (formaldehyde, phosphoric acid, ammonium chloride, and sodium hydroxide) over several days, while only achieving moderate yields.\textsuperscript{48} Thus, a more simplified and efficient synthesis for more complex substituted imidazoles needs to be developed.

\subsection*{1.2.5 Research Goals}

The objective of this project was to synthesize a Cu(I) precatalyst incorporating a diNHC ligand. Literature precedence shows that group 11 complexes containing diNHC are likely to show the ligand bridging the copper centers, whereas group 10 complexes show the diNHC coordinating in a chelating fashion. A synergetic effect of two copper centers within proximity possibly could open doors for a new reaction pathway incorporating two copper centers in the catalysis. By varying the substituents on the diNHC, a variety of complexes with different steric protection about the metal center can be synthesized and allow further understanding of the relationship between steric bulk in the system with coordination environment of the metal center. We also want to investigate the catalytic activity of these diNHC Cu(I) systems in hydrosilation of sterically hindered ketones. Secondly, we want to study if Cu(I) complexes are active in C-N
coupling of imidazoles. Metal mediated alkylation of imidazole utilizing 2° and 3° alkyl halides does not exist in the literature.
Chapter 2  Results and Discussion

2.1  Attempts to Synthesize 3-Coordinate Palladium

2.1.1  Synthesis of $\{(2,6^{1}\text{Pr}_2\text{Ph})_2\text{nacnac}\}\text{PdCl}_2$

The $\{(2,6^{1}\text{Pr}_2\text{Ph})_2\text{nacnacH}\}$ β-diketime complex was prepared by reacting 2,4 pentadione with 2 equivalence of 2,6-diisopropylaniline in a condensation reaction.\(^3\)

**Scheme 2.1** The synthesis of $\{(2,6^{1}\text{Pr}_2\text{Ph})_2\text{nacnacH}\}$.\(^3\)

![Scheme 2.1](image)

The \(^1\)H NMR spectra of the $\{(2,6^{1}\text{Pr}_2\text{Ph})_2\text{nacnacH}\}$ compound was consistent to that of literature.\(^3\)

$\{(2,6^{1}\text{Pr}_2\text{Ph})_2\text{nacnacH}\}$ was then reacted with one equivalent of palladium acetate yielding red $\{(2,6^{1}\text{Pr}_2\text{Ph})_2\text{nacnac}\}\text{Pd(OAc)}$ compound.\(^25\)

**Scheme 2.2** The synthesis of $\{(2,6^{1}\text{Pr}_2\text{Ph})_2\text{nacnac}\}\text{Pd(OAc)}$.\(^25\)

![Scheme 2.2](image)

The presence of the acetate in this 4-coordinate species, should give rise in another new 3-proton singlet, corresponding to its methyl group. Certainly, the \(^1\)H NMR shows that the signal at \(~1.06\) ppm fits this criterion. The other key element to observe is the N-H at \(~12\) ppm from the $\{(2,6^{1}\text{Pr}_2\text{Ph})_2\text{nacnacH}\}$ ligand spectra should no longer be present in this product. The \(^1\)H NMR
clearly shows absence of this signal, signifying that the \( [(2,6-^tPr_2Ph)_2nacnac]Pd(OAc) \) was isolated because the \(^1\text{H} \) NMR accurately matches literature.\(^{25} \)

The \( [(2,6-^tPr_2Ph)_2nacnac]Pd(OAc) \) was then reacted with excess lithium chloride (LiCl), to precipitate off lithium acetate (LiOAc) producing the green \( [(2,6-^tPr_2Ph)_2nacnac]PdCl\)\(_2\) dimer.\(^{25} \)

**Scheme 2.3** The synthesis of \( [(2,6-^tPr_2Ph)_2nacnac]PdCl\)\(_2\).\(^{25} \)

This compound has been synthesized by a previous PhD student in the Foley group; however has not yet been published.\(^{25} \) The \(^1\text{H} \) NMR of the isolated \( [(2,6-^tPr_2Ph)_2nacnac]PdCl\)\(_2\) dimer, shows that all the signals do indeed shift slightly up field from the proton signals of the \( [(2,6-^tPr_2Ph)_2nacnac]Pd(OAc) \) compound. This was notable for all signals even in the phenyl region, where the 2 proton triplet and 4 proton doublet are no longer overlapping. The key determining factor that indicates the reaction has come to completion is the disappearance of the acetate peak. \( [(2,6-^tPr_2Ph)_2nacnac]PdCl\)\(_2\) \(^1\text{H} \) NMR clearly shows no signal that represents the acetate appearing around the 1ppm region. The \( [(2,6-^tPr_2Ph)_2nacnac]PdCl\)\(_2\) was used as the reactant in the following experiments in attempts to form our desired 3-coodinate palladium species.
2.1.2 Attempted Synthesis of \[\{(2,6-^iPr_2Ph)_2nacnac\}Pd[N(TMS)_2]\] (TMS = trimethylsilyl)

**Scheme 2.4** The attempted synthesis of \[\{(2,6-^iPr_2Ph)_2nacnac\}Pd[N(TMS)_2]\].

The first attempts at the synthesis of a 3-coordinate species was by reaction of the dinuclear \[\{(2,6-^iPr_2Ph)_2nacnac\}PdCl_2\] in stoichiometric amounts with potassium bis-trimethylsilylamide (KN(TMS)_2) in toluene for 24 hours at ambient temperatures. Potassium bis-trimethylsilylamide was the first reactant choice because nitrogen being a good electron donor can bind on the metal center eliminating potassium chloride; with hope the bulky trimethylsilylamide group can inhibit dimerization. The reaction appears to have no immediate colour change and remained a dark green solution. After reacting for 24 hours, the observations still remained the same. An \(^1\)H NMR was taken from an aliquot of the reaction mixture and shows no presence of new signals, where the signals correspond to the reactants \[\{(2,6-^iPr_2Ph)_2nacnac\}PdCl_2\] and potassium bis-trimethylsilylamide. This reaction was reproduced, using excess amounts of potassium bis-trimethylsilylamide in attempts to strongly drive reaction towards the formation of \[\{(2,6-^iPr_2Ph)_2nacnac\}Pd[N(TMS)_2]\]. Once again, the \(^1\)H NMR shows no reaction and the signals directly match that of the \[\{(2,6-^iPr_2Ph)_2nacnac\}PdCl_2\] dimer and potassium bis-trimethylsilylamide starting materials. This reaction was then heated at ~80°C for 24 hours. After the 24 hour duration, the mixture stayed green and the \(^1\)H NMR continued to show no reaction between the two reactants. The temperature of the reaction was increased to ~110°C for 24 hours, hoping to force the reaction past its activation energy resulting in the formation of the product. The reaction showed a colour change from green to brown overnight. The \(^1\)H NMR spectra of this reaction showed the absence of \[\{(2,6-^iPr_2Ph)_2nacnac\}PdCl_2\], however rather than the expected product, the free ligand (nacnacH) was observed along with several TMS signals. This result suggested that there was possibility of a reaction when heated at ~110°C but the
product that was formed was very unstable and heat sensitive; therefore decomposing the product to the resulting free ligand.

2.1.3 Attempted Synthesis of $\left[\{2,6-^iPr_2Ph\}_2\text{nacnac}\right]Pd(O^tBu)$.

**Scheme 2.5** The attempted synthesis of $\left[\{2,6-^iPr_2Ph\}_2\text{nacnac}\right]Pd(O^tBu)$.

Based on the assumption that the potassium bis-trimethylsilylamide substrate was too bulky, potassium $^t$-butoxide being a smaller reactant was used to synthesize a 3-coordinate palladium complex. Similarly to potassium bis-trimethylsilylamide, potassium was used to eliminate potassium chloride, with the exception of replacing the nitrogen with oxygen to coordinate onto the palladium center. The reaction was prepared with $\left[\{2,6-^iPr_2Ph\}_2\text{nacnac}\right]PdCl_2$ and potassium $^t$-butoxide in stoichiometric amounts. Toluene was the solvent used to ensure that both components are in solution and stirred for 24 hours at room temperature. Similarly to the potassium bis-trimethylsilylamide reaction, the $^1$H NMR shows no sign of new product peaks, where only the reactant signals are present. The reaction was heated to 60$^\circ$C, expecting to use temperature to drive the reaction to the product side of the equilibrium. The reaction mixture showed no colour change from the initial green and the $^1$H NMR showed no reaction occurring. The final attempt using potassium $^t$-butoxide was increasing the reaction temperature to 80$^\circ$C. The $^1$H NMR shows strong presence of the reactant signals, with also the emergence to a new set of signals that correspond to the free ligand. This result suggests that the product was slowly decomposing as the temperature was increasing. With this hypothesis no further reactions were conducted using heat.
2.1.4 Attempted Synthesis of \[((2,6-^{i}Pr_{2}Ph)_{2}nacnac)Pd\{NH(2,4,6Me_{3})Ph}\]\]

**Scheme 2.6** The attempted synthesis of \[((2,6-^{i}Pr_{2}Ph)_{2}nacnac)Pd\{NH(2,4,6Me_{3})Ph}\].

The next reactant that was used in the synthesis of a 3-coordinate palladium complex begins with the lithiation of 2,4,6-trimethylaniline with butyl lithium under the conditions of stirring the mixture at ~-78°C for 2 hours. The reaction mixture was brought to room temperature and \[((2,6-^{i}Pr_{2}Ph)_{2}nacnac)PdCl\]_{2} was added in stoichiometric amounts to the reaction vessel and stirred at room temperature for 24 hours. An \textsuperscript{1}H NMR was taken from a sample aliquot of the reaction, which shows that the reaction did not proceed and only reactant was active in the spectra. This result implies that the substrate again being too bulky to bind onto the metal center.
2.1.5 Attempted Synthesis of \([[2,6-^{i}\text{Pr}_2\text{Ph}]_2\text{nacnac}]\text{Pd(NHPh)}\)]

**Scheme 2.7** The attempted synthesis of \([[2,6-^{i}\text{Pr}_2\text{Ph}]_2\text{nacnac}]\text{Pd(NHPh)}\)]

Based on the same notion that phenyl rings are oriented in a fashion that allows easier access to the Pd center, a similar approach was taken but simplifying the aryl group of the substrate. Aniline was used in this experiment in attempts to form a 3-coordinate \([[2,6-^{i}\text{Pr}_2\text{Ph}]_2\text{nacnac}]\text{Pd(NHPh)}\)]. Two equivalents of aniline (\(\text{NH}_2\text{C}_6\text{H}_5\)) were added to the \([[2,6-^{i}\text{Pr}_2\text{Ph}]_2\text{nacnac}]\text{PdCl}_2\)] and reacted at room temperature overnight. There appear to be no colour change from its original compound. A \(^1\text{H} \text{NMR}\) was taken from an aliquot of the solution, which shows weak emergence of new signals in the presence of stronger reactant signals. This result concludes that the reaction did not proceed to completion. The mixture was allowed to react for another 24 hours. The \(^1\text{H} \text{NMR}\) spectra showed little change from the last spectra and the reactant peaks are still stronger than the product signal. The solution was then heated to 60\(^\circ\text{C}\) for 24 hours to speed up the reaction. The \(^1\text{H} \text{NMR}\) spectra of this solution, after being heating to 60\(^\circ\text{C}\) showed very minimal change. The mixture was further heated to \(\sim 110\text{\(^{\circ}\text{C}\)}\) overnight to induce an interaction between the reactants. The \(^1\text{H} \text{NMR}\) spectrum of this solution shows absence of the product and formation of the free ligand. The experiment was replicated in the same conditions at room temperature except in large excess of aniline (5 equivalence). After the 24 hour duration, the reaction was no longer a green colour and changed to a red solution. The \(^1\text{H} \text{NMR}\) of this experiment shows that the product signals have increased significantly and the present of the \([[2,6-^{i}\text{Pr}_2\text{Ph}]_2\text{nacnac}]\text{PdCl}_2\) reactant have decreased. More aniline (20 equivalence) was added to the point where the presence of the \([[2,6-^{i}\text{Pr}_2\text{Ph}]_2\text{nacnac}]\text{PdCl}_2\) dimer was no longer dominant in comparison to that of the new product peaks.
The spectra shows that the methyl of the 2,6-diisopropylphenyl for the \([(2,6-iPr_2Ph)_2\text{nacnac} \text{PdCl(NH}_2\text{Ph})]\] exhibited 4 doublets, each integrating to 6 protons (Scheme 2.7). This indicates that the synthesized product exhibits reduced symmetry (ie. $C_s$ symmetric). This indicates that the hydrogen signals associated with both the diisopropylphenyl and the methyl groups in the backbone are no longer in the same environment. The $^1H$ NMR also shows that there are two 2 septets representative of the methines of the diisopropyl now having different shifts. The methyls in the backbone of the ligand are also very different and produce two singlets each integrating for 3H, instead of one singlet due to the loss in symmetry. The broad 2 proton peak appearing close to the pentet at $\sim 4.00$ ppm was representative of the 2 hydrogen atoms attached to the nitrogen on the aniline coordinated on the metal center. The signals of the phenyl on the aniline should also be present in the spectra; however the excess aniline makes it very difficult to extract any information in this region. Since, a large excess of aniline was required to drive the reaction to form the product \([(2,6-iPr_2Ph)_2\text{nacnac} \text{PdCl(NH}_2\text{Ph})]\], the removal of aniline was very difficult to pump off without heating being that it attains a boiling point of $\sim 194^\circ$C. The product was proven in the previous experiment to be fairly heat sensitive and will decompose the product to the free ligand if heated. Isolation of the product from the excess aniline was done by crystallization in toluene over several days. A crystal structure of the product was obtained and it was evident that the product formed was the proposed \([(2,6-iPr_2Ph)_2\text{nacnac} \text{PdCl(NH}_2\text{Ph})]\) 4-coordinate species.

The crystal structure shows that the complex has a square planar environment about the palladium center. Table 3 shows that the bond angles are consistent with that of an ideal square planar geometry.
Figure 2.1  Crystal structure of \[\{(2,6-iPr_2Ph)_{2}nacnac\}PdCl(NH_2Ph)\].

Table 2.1  Crystal data and refinement parameter for \[\{(2,6-iPr_2Ph)_{2}nacnac\}PdCl(NH_2Ph)\].

<table>
<thead>
<tr>
<th>Properties</th>
<th>[{(2,6-iPr_2Ph)_{2}nacnac}PdCl(NH_2Ph)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{41}H_{55}Cl_{1}N_{4}Pd_{1}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>745.74</td>
</tr>
<tr>
<td>Crystal Color, Habit</td>
<td>pink, irregular plate-like</td>
</tr>
<tr>
<td>Crystal dimensions (mm)</td>
<td>0.16 × 0.12 × 0.05</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>(P2_1/n) [non-standard setting of (P2_1/c); No. 14]</td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>16.9112(4)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>11.7648(3)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>19.8746(5)</td>
</tr>
<tr>
<td>(\alpha) (°)</td>
<td>90</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>100.0690(10)</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
<td>90</td>
</tr>
<tr>
<td>(V) (Å(^3))</td>
<td>3893.29(17)</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>(F(000))</td>
<td>1568</td>
</tr>
<tr>
<td>Density ((\rho_{calcd}))</td>
<td>1.272 Mg/m(^3)</td>
</tr>
</tbody>
</table>
Absorption coefficient (μ) | 4.711 mm⁻¹  
--- | ---  
Wavelength (Mo Kα) | 1.54184 Å  
Temperature | -100(2) °C [173(2) K]  
Theta range for data collection | 3.77 to 69.93°  
Final R \[ F_o^2 > 2\sigma(F_o^2) \] | R1=0.0578, R2=0.1495

Table 2.2  The bond distances for \([((2,6^{−}Pr_2Ph)_2nacnac]PdCl(NH_2Ph))\].

<table>
<thead>
<tr>
<th>Bond Distances</th>
<th>(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(1)-N(2)</td>
<td>2.019(3)</td>
</tr>
<tr>
<td>Pd(1)-N(1)</td>
<td>2.024(3)</td>
</tr>
<tr>
<td>Pd(1)-N(31)</td>
<td>2.092(3)</td>
</tr>
<tr>
<td>Pd(1)-Cl(1)</td>
<td>2.3375(7)</td>
</tr>
<tr>
<td>N(1)-C(13)</td>
<td>1.329(4)</td>
</tr>
<tr>
<td>N(1)-C(1)</td>
<td>1.434(5)</td>
</tr>
<tr>
<td>N(1)-C(15)</td>
<td>1.328(5)</td>
</tr>
<tr>
<td>N(2)-C(18)</td>
<td>1.435(5)</td>
</tr>
<tr>
<td>N(31)-C(31)</td>
<td>1.461(5)</td>
</tr>
<tr>
<td>N(31)-H(31A)</td>
<td>0.89(5)</td>
</tr>
<tr>
<td>N(31)-H(31B)</td>
<td>0.83(6)</td>
</tr>
</tbody>
</table>

Table 2.3  The bond angles for \([((2,6^{−}Pr_2Ph)_2nacnac]PdCl(NH_2Ph))\].

<table>
<thead>
<tr>
<th>Interatomic Angles</th>
<th>(º)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(2)-Pd(1)-N(1)</td>
<td>91.83(12)</td>
</tr>
<tr>
<td>N(2)-Pd(1)-N(31)</td>
<td>91.64(13)</td>
</tr>
<tr>
<td>N(1)-Pd(1)-N(31)</td>
<td>176.46(11)</td>
</tr>
<tr>
<td>N(2)-Pd(1)-Cl(1)</td>
<td>174.15(10)</td>
</tr>
<tr>
<td>N(1)-Pd(1)-Cl(1)</td>
<td>92.61(8)</td>
</tr>
<tr>
<td>N(31)-Pd(1)-Cl(1)</td>
<td>83.97(9)</td>
</tr>
<tr>
<td>C(13)-N(1)-C(1)</td>
<td>116.7(3)</td>
</tr>
<tr>
<td>C(13)-N(1)-Pd(1)</td>
<td>124.3(3)</td>
</tr>
</tbody>
</table>
C(1)-N(1)-Pd(1)  118.7(2)
C(15)-N(2)-C(18)  117.6(3)
C(15)-N(2)-Pd(1)  124.9(3)
C(18)-N(2)-Pd(1)  117.5(2)
C(2)-C(1)-C(6)  120.8(4)
C(2)-C(1)-N(1)  121.0(3)
C(6)-C(1)-N(1)  118.2(4)

However, when obtaining a $^1$H NMR of the crystals, the spectra shows predominantly the $\{(2,6$i$Pr_2Ph)_2\text{nacnac}\text{PdCl}\}_2$ dimer. This suggests that excess aniline was required to produce the $\{(2,6$i$Pr_2Ph)_2\text{nacnac}\text{PdCl(NH}_2\text{Ph)}\}$. This proposes that aniline was only weakly coordinated onto the palladium center and requires a heavy excess of aniline to drive the reaction towards the 4-coordinated $\{(2,6$i$Pr_2Ph)_2\text{nacnac}\text{PdCl(NH}_2\text{Ph)}\}$ species.

This trend was also observed from the crystals of the $\{(2,6$i$Pr_2Ph)_2\text{nacnac}\text{PdCl(NH}_2\text{Ph)}\}$. As mentioned above, when excess aniline was added the reaction mixture turns from a green colour to a red solution, which was consistent to the crystal colour of the $\{(2,6$i$Pr_2Ph)_2\text{nacnac}\text{PdCl}\}_2$. When the red $\{(2,6$i$Pr_2Ph)_2\text{nacnac}\text{PdCl(NH}_2\text{Ph)}\}$ crystal was removed from the solution of aniline and submerged into oil, overtime an observation of a green crystalline product began to form around the red crystals. Periodically over several minutes, the red crystals gradually disappear to a point where only this new green product was formed. The green product that was formed had a $^1$H NMR spectra that was consistent to that of the $\{(2,6$i$Pr_2Ph)_2\text{nacnac}\text{PdCl}\}_2$. This result was very consistent with the observation from above because when the crystal was taken out of solution, $\{(2,6$i$Pr_2Ph)_2\text{nacnac}\text{PdCl(NH}_2\text{Ph)}\}$ was no longer in an environment saturated with aniline the compound reverts to the more stable $\{(2,6$i$Pr_2Ph)_2\text{nacnac}\text{PdCl}\}_2$. 

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Figure 2.2 The transformation of \([[(2,6-^{t}\text{iPr}_2\text{Ph})_2\text{nacnac}]\text{PdCl}(\text{NH}_2\text{Ph})]\) crystals to \([(2,6-^{t}\text{iPr}_2\text{Ph})_2\text{nacnac}]\text{PdCl}2\) crystals.

Taking this into consideration a few conditions must be manipulated before using \([(2,6-^{t}\text{iPr}_2\text{Ph})_2\text{nacnac}]\text{PdCl}(\text{NH}_2\text{Ph})\) as a precursor to forming a 3-coordinate palladium species.

In order to synthesized a 3-coordinate species using \([(2,6-^{t}\text{iPr}_2\text{Ph})_2\text{nacnac}]\text{PdCl}(\text{NH}_2\text{Ph})\], the chlorine and proton must be removed. We rationalized by adding BuLi, the reaction can drive off butane by producing lithium chloride and forming the desired 3-coordinate \([(2,6-^{t}\text{iPr}_2\text{Ph})_2\text{nacnac}]\text{Pd}(\text{NHPh})\).

Scheme 2.8 The synthesis of \([(2,6-^{t}\text{iPr}_2\text{Ph})_2\text{nacnac}]\text{Pd}(\text{NHPh})\).

The amount of butyl lithium that was added has to not only be equivalent to that of the amount of \([(2,6-^{t}\text{iPr}_2\text{Ph})_2\text{nacnac}]\text{Pd}(\text{NH}_2\text{Ph})\) added but also take into the account the excess aniline that was left in solution, in order to achieve proper reaction conditions. By adding this amount of BuLi ensures that there was not competing lithiation between the \([(2,6-^{t}\text{iPr}_2\text{Ph})_2\text{nacnac}]\text{Pd}(\text{NH}_2\text{Ph})\) and the aniline. The reaction was allowed to stir for 24 hrs and a \(^1\text{H}\) NMR was taken from the resulting mixture. The spectra show no visible product signals and
only peaks from the starting materials. A second method was conducted for the removal of the proton and chlorine from the \( \{[2,6-^{i}{Pr}_{2}Ph]_{2}nacnac\}PdCl(NH_{2}Ph) \), by using heat. It has been shown in literature that by using enough heat for specific reactions, one can drive off HCl. A solution mixture of \( \{[2,6-^{i}{Pr}_{2}Ph]_{2}nacnac\}PdCl(NH_{2}Ph) \) and excess aniline in toluene was heated to 110°C for 24 hrs and a \(^{1}H\) NMR was obtained. The obtained spectrum showed signals corresponding to the free ligand suggesting that heat led to decomposition, which matches the observation from the previous experiments using heat in this chapter.

A secondary route was developed into forming the \( \{[2,6-^{i}{Pr}_{2}Ph]_{2}nacnac\}Pd(NHPh) \) by the use of adding \( \{[2,6-^{i}{Pr}_{2}Ph]_{2}nacnac\}PdCl \)\textsubscript{2} directly to a controlled amount of lithiated aniline. This route allows us to form the 3-coordinate species by adding a stoichiometric amount of aniline rather than in excess. This would eliminate any possibilities for competing lithiation from having several reactants in solution \( \{[2,6-^{i}{Pr}_{2}Ph]_{2}nacnac\}PdCl(NH_{2}Ph) \) and excess aniline from the previous route.

**Scheme 2.9** The synthesis of \( \{[2,6-^{i}{Pr}_{2}Ph]_{2}nacnac\}Pd(NHPh) \).

![Scheme 2.9](image)

After conducting the reaction, the mixture was allowed to stir for 24 hours. Based on the observation from the colour of the solution being green suggests that the reaction did not undergo. After a \(^{1}H\) NMR was taken from the mixture, the spectrum shows only visible peaks from the starting material.
2.1.6 Computational Analysis (Geometry)

A DFT calculation at the B3LYP level using a 6-31G* basis set was used to calculate the energy minimum for a simplified representation of Hartwig’s 3-coordinate palladium complex.

![Diagram of Hartwig’s 3-coordinate palladium complex]

**Figure 2.3** Hartwig’s 3-coordinate structures.

It was critical to ensure that pseudo-potentials are incorporated into the results to reduce the complexity of the calculation and its computational time. When calculating energy minimums for a compound, we are interested in the valence electrons because they contribute to a large part of the chemical bonding and most of the molecules physical properties, whereas the core electrons are very little affected by their atomic environments. In a valence electron wave function near the atomic nuclei there should be the presence of rapid oscillations. These oscillations give rise in a kinetic energy that requires plane waves to accurately represent the behavior of the molecule. The numbers of oscillations are directly proportional to the number of core electrons that are present in the compound. Heavier atoms that have a large number of core electrons, in turn would produce a large number of oscillations, which requires a large number of plane waves. Clearly, this would propose as a problem for heavy transition metals such as palladium, where the calculation might be too difficult for the program to produce representative results. The solution to this problem is replacing the true potential of the core region with much weaker pseudo potentials. The pseudo potential function sets the core electrons to an average value to simplify the calculation because the effect of core electrons does not vary drastically across the periodic table. This reduces the number of terms required for the plane wave expansion and significantly reduces the computational time. The Hartwig ligand was reduced to a phenyl, bisphenylamide and a phosphine around the palladium center.
Figure 2.4  The depiction of Hartwig’s reduced structure using DFT calculation.

Figure 2.4 shows that from the results of the calculations the geometry of Hartwig’s reduced structure indeed does adopt a distorted T-shape conformation.

Table 2.4  The bond angles of Hartwig’s reduced 3-coordinate structure.

<table>
<thead>
<tr>
<th>Angle</th>
<th>Ideal T-shape (°)</th>
<th>Hartwig’s 3-Coordinate Complex (A) (°) (Literature)</th>
<th>Hartwig’s reduced structure (Computational) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angle A</td>
<td>180</td>
<td>168.23</td>
<td>156.37</td>
</tr>
<tr>
<td>Angle B</td>
<td>90</td>
<td>89.09</td>
<td>91.38</td>
</tr>
<tr>
<td>Angle C</td>
<td>90</td>
<td>102.68</td>
<td>112.26</td>
</tr>
</tbody>
</table>

Table 2.4 shows that Hartwig’s compound has bond angles closer to a true T-shape geometry in comparison to the calculated reduce structure. One can drive a molecule to a T-shape structure by heavily shifting the steric bulk all to one ligand, while keeping the size of the other ligands constant. This theory explains the inductive reasoning for Hartwig’s compound being a closer to the ideal T-shape because Hartwig’s bis-phenylamide has two trifluoromethyl groups attached to the phenyl ring highly favouring the steric bulk to one ligand in comparison to others. This theory further explains Hartwigs B structure in figure 2.3 having bond angles straying more away from the ideal T-shape then his A structure. In his A structure the steric bulk was heavily favoring his amido ligand. In compound B the phosphine ligand has ferrocene with phenyls on
every carbon, which significantly increases in size distributing the steric bulk more evenly. With this rational Hartwig’s compound most resembling a true T-shape should be in the following order A>B>C. The same calculation was conducted on a simplified version of our hypothesized 3-coordinate compound. The methyl and diisopropylphenyl groups were removed from the compound to simplify the calculation. In first run, the compound adopted a trigonal planar geometry with an energy of -1075009.55 KJ/mol.

![Figure 2.5](image) The depiction of our trigonal planar reduced structure using DFT calculation.

Even though, this trigonal planar was the concluding geometry for this calculation, it is incorrect to assume that this conformation is its local minimum. The IR of this trigonal planar structure displays the presence of an imaginary frequency. This suggests that the trigonal planar geometry was a transition state and not a local minimum. A minimum or maximum was determined by applying a second order differentiation to a function. A positive value corresponds to a minimum, whereas negative to a maximum. The frequency was the square root of the second derivative of the energy, therefore cannot be a negative value under the root. A negative value under the root suggests that the function was complex and this directly correlates to the imaginary vibrations in IR. A second run of the calculation was conducted using the same conditions and basis except the molecule was built in a different fashion. This time the structure adopted a T-shape conformation with an energy of -1075191.03 KJ/mol.
Figure 2.6  The depiction of our T-shape reduced structure using DFT calculation.

The energy values obtained from the DFT calculations are relative terms used for comparative purposes and not used as an absolute value. The T-shape conformation was calculated to have a lower energy than that of the trigonal planar, therefore being more stable. The IR spectrum of this compound obtained from Spartan does not contain any imaginary vibration states, which indicates that this energy is a minimum. This suggests that more than likely palladium complexes that are 3-coordinate will tend to favor a T-shape geometry then that of a trigonal planar orientation.

Table 2.5  The bond angles and energies of a trigonal and T-shape geometry for our hypothesized reduced 3-coordinate species.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Energy (KJ/mol)</th>
<th>IR Spectra</th>
<th>Bond A (°)</th>
<th>Bond B (°)</th>
<th>Bond C (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trigonal Planar</td>
<td>-1075009.55</td>
<td>Imaginary</td>
<td>86.21°</td>
<td>136.89°</td>
<td>136.89°</td>
</tr>
<tr>
<td>T-Shape</td>
<td>-1075191.03</td>
<td>Real</td>
<td>104.37°</td>
<td>166.14°</td>
<td>89.49°</td>
</tr>
</tbody>
</table>
2.1.7 Computational Analysis (Steric Bulk)

The structure of \( [(2,6-\text{iPr}_2\text{Ph})_2\text{nacnac}]\text{PdCl(NH}_2\text{Ph}) \) and \( [(2,6-\text{iPr}_2\text{Ph})_2\text{nacnac}]\text{PdCl}_2 \) was built in Spartan and the space-filling orientation was observed. The dark green molecule represents the palladium center that should not be confused for the lighter green molecule of chlorine.

**Figure 2.7** The space-filling diagram of \( [(2,6-\text{iPr}_2\text{Ph})_2\text{nacnac}]\text{PdCl}_2 \).

**Figure 2.8** The space-filling diagram of \( [(2,6-\text{iPr}_2\text{Ph})_2\text{nacnac}]\text{PdCl(NH}_2\text{Ph}) \).
The $\left\{ (2,6-^i\text{Pr}_2\text{Ph})_2\text{nacnac} \right\} \text{PdCl}_2$ space filling diagram was observed at the side view of the molecule because the reactive site at the palladium center was only present between the phenyl rings attached to the metal. The figure suggest that the reactive site for $\left\{ (2,6-^i\text{Pr}_2\text{Ph})_2\text{nacnac} \right\} \text{PdCl}_2$ was very limited because there was only two areas of the molecule that the substrate can react with and these sites appear to be fairly small. As for the $\left\{ (2,6-^i\text{Pr}_2\text{Ph})_2\text{nacnac} \right\} \text{PdCl(NH}_2\text{Ph)}$, the molecule was viewed from the bottom to observe its reactive site on the palladium center. The space-filling diagram shows that there was only one reactive site on this molecule; however its reactive site is bigger than that of the $\left\{ (2,6-^i\text{Pr}_2\text{Ph})_2\text{nacnac} \right\} \text{PdCl}_2$. $\left\{ (2,6-^i\text{Pr}_2\text{Ph})_2\text{nacnac} \right\} \text{PdCl(NH}_2\text{Ph)}$ potentially could be the easier route to synthesizing the 3-coordinate compound because it has a larger reactive site, allowing the substrate to come in a coordinate and eliminate chlorine more readily.

With the same ideology as the $\left\{ (2,6-^i\text{Pr}_2\text{Ph})_2\text{nacnac} \right\} \text{PdCl(NH}_2\text{Ph)}$ we rationalized a similar steric bulk with $\left\{ (2,6-^i\text{Pr}_2\text{Ph})_2\text{nacnac} \right\} \text{Pd(OAc)}$.

![Figure 2.9](image)

**Figure 2.9** The space fill diagram for $\left\{ (2,6-^i\text{Pr}_2\text{Ph})_2\text{nacnac} \right\} \text{Pd(OAc)}$.

The space-filling diagram of the $\left\{ (2,6-^i\text{Pr}_2\text{Ph})_2\text{nacnac} \right\} \text{Pd(OAc)}$ compound indeed does show similar steric bulk about the palladium metal center. The diagram shows that the reactive site was substantially larger than of the $\left\{ (2,6-^i\text{Pr}_2\text{Ph})_2\text{nacnac} \right\} \text{PdCl}_2$. Since $\left\{ (2,6-^i\text{Pr}_2\text{Ph})_2\text{nacnac} \right\} \text{Pd(OAc)}$ was a monomeric species the steric bulk was substantially less because it only contains steric protection from 2 bulky 2,6-diisopropylphenyl, whereas the $\left\{ (2,6-$
\[ (\text{Pr}_2\text{Ph})_2\text{nacnac}\text{PdCl}_2 \] contains 4. The main difference in steric bulk lies in the acetate substituent coordinating on the palladium. The acetate substituent visually is quite bulky; however only contains 2 dimensional steric bulk seeing that its structure was more flat, whereas 2,6-diisopropylphenyl was more bulky in a 3 dimensional arrangement. Taking this into consideration we suspect that \[ [(\text{2,6-Pr}_2\text{Ph})_2\text{nacnac}]\text{Pd(OAc)} \] would have a larger reactive site allowing the substrate to come in an coordinate easier.

### 2.2 N-Heterocyclic Copper Complexes and Applications in Catalysis

#### 2.2.1 Synthesis of 1, 1'-Dibenzyl-3,3'-methylenediimidazolin-2,2'-diyldenedibromide

1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diyldenedibromide was synthesized according to literature by first reacting benzyl bromide with imidazole and 4 equivalent of sodium hydride in THF.\(^47\)

**Scheme 2.10** The synthesis of 1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diyldenedibromide

![Scheme 2.10](image)

The resulting benzyl substituted imidazole was then reacted in neat dibromomethane at 80°C, resulting in the formation of 1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diyldenedibromide as a white precipitate, which was isolated and washed with ether.\(^47\)

#### 2.2.2 Synthesis of Dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diyldene)dicopper(I)

The synthesis of dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diyldene)dicopper(I) was synthesized by deprotonation of 1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-
diylidenedibromide with KN(TMS)$_2$ and subsequently reacting the resulting free carbone with bromotris(triphenylphosphine)copper(I) in THF. This yields a slightly pink precipitate, which upon isolation was the dibromobis(1,1’-dibenzyl-3,3’-methylenediimidazolin-2,2’-diylidene)dicopper(I) catalyst.

**Scheme 2.11** The synthesis of dibromobis(1,1’-dibenzyl-3,3’-methylenediimidazolin-2,2’-diylidene)dicopper(I)

![Scheme diagram](image)

**Figure 2.10** The crystal structure of dibromobis(1,1’-dibenzyl-3,3’-methylenediimidazolin-2,2’-diylidene)dicopper(I).
Table 2.6 Crystal data and refinement parameter for dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diylidene)dicopper(I).

<table>
<thead>
<tr>
<th>Properties</th>
<th>dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diylidene)dicopper(I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{42}H_{40}Br_{2}Cu_{2}N_{8}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>943.72</td>
</tr>
<tr>
<td>Crystal Color, Habit</td>
<td>Pink</td>
</tr>
<tr>
<td>Space group</td>
<td>P - 1</td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>8.1754(2)</td>
</tr>
<tr>
<td>(b) (Å)</td>
<td>10.2863(4)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>12.2036(4)</td>
</tr>
<tr>
<td>(a) (°)</td>
<td>95.069(2)</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>105.563(3)</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
<td>91.804(2)</td>
</tr>
<tr>
<td>V (Å(^3))</td>
<td>983.13(6)</td>
</tr>
<tr>
<td>(Z)</td>
<td>1</td>
</tr>
<tr>
<td>(F(000))</td>
<td>476.0</td>
</tr>
<tr>
<td>Density ((\rho_{\text{calc}}))</td>
<td>1.594Mg/m(^3)</td>
</tr>
<tr>
<td>Absorption coefficient ((\mu))</td>
<td>3.156 mm(^{-1})</td>
</tr>
<tr>
<td>Wavelength (Mo K(_{\alpha}))</td>
<td>0.71073Å</td>
</tr>
<tr>
<td>Temperature</td>
<td>173 K</td>
</tr>
<tr>
<td>Theta (Max)</td>
<td>25.030</td>
</tr>
<tr>
<td>Final R ([F_o^- &gt; 2\sigma(F_o^-)])</td>
<td>R1 = 0.0716, R2 = 0.2149</td>
</tr>
</tbody>
</table>

The crystal structure above shows that the dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diylidene)dicopper(I) complex was a dimeric species, where the copper was bridged at the NHCs. This presented us with an opportunity to explore the differences between bridging diNHC versus that of monodentate NHC systems, where we still tested our system for hydrosilation and compared our results to that of Nolan’s NHC copper complexes. This benzyl
substituted diNHC copper complex shows very limited solubility in a wide variety of polar and nonpolar solvents.

2.2.3 *Synthesis of Bulkier 1,1'-2,6-Diisopropylphenyl-3,3'-methylenediimidazolin-2,2'-diylidenedibromide and 1,1'-2,4,6-Trimethylphenyl-3,3'-methylenediimidazolin-2,2'-diylidenedibromide*

The results above show that when using a 1-benzylimidazole as the precursor for complexation with copper led to a dinuclear species, suggesting that there was not enough steric protection about the metal center to inhibit dimerization. By varying the substituent attached to the NHC with bulkier groups, we hypothesized that the increase steric protection can inhibit dimerization, forming our initially proposed bidentate mononuclear chelating species. 2,6-diisopropylphenyl and mesityl were the target analogues chosen to increase steric protection around the copper center. These two systems provide steric bulk in 3 dimensions rather than the 2 dimension present in the benzyl group. Also, it has been known in our group that by adding 2,6-diisopropylphenyl or mesityl substituents onto NHC complexes increases the solubility of the systems.

**Scheme 2.12** The reaction scheme for the synthesis of 1,1'-2,6-diisopropylphenyl-3,3'-methylenediimidazolin-2,2'-diylidenedibromide and 1,1'-2,4,6-trimethylphenyl-3,3'-methylenediimidazolin-2,2'-diylidenedibromide

![Reaction Scheme](image)

The route into synthesizing a mesityl or a 2,6-diisopropylphenyl diimidazolium dibromide salt was made differently than that of the benzyl analogue. The reaction of aryl bromide with imidazole in presence of sodium hydrde can only be conducted on primary and secondary aryl
compounds. The two desired 1-substituted imidazoles are tertiary aryl amines, where the reaction with activated imidazole will not undergo. These substituted imidazoles were synthesized by literature prep in 2003, by reacting glyoxyl with the desired aryl amine in methanol with a sequence addition of necessary reagents while refluxing.\(^4\) The order of addition was crucial in obtaining a pure and high product yield.\(^4\)

**Scheme 2.13** The reaction scheme for the synthesis of tertiary substituted imidazoles.

When the substituted imidazole was formed it was reacted in stoichiometric amounts of dibromomethane in xylene to form the diimidazolium dibromide salt. This reaction differs from the synthesis dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diylidene)dicopper(I) being that it requires more rigorous conditions to form this compound. This reaction requires superheating to 200°C in xylene for 2 days to form the desired product. The \(^1\)H NMR of both bulkier analogues was consistent with that to literature, where the crude product that was isolated remained relatively clean from impurities. The crude products were used in the following complexation without any form of purification.
Scheme 2.14 The reaction scheme for the synthesis of 1,1'-2,6-diisopropylphenyl-3,3'-methylenediimidazolin-2,2'-diylidenedibromide and 1,1'-2,4,6-trimethylphenyl-3,3'-methylenediimidazolin-2,2'-diylidenedibromide.

![Reaction scheme](image)

2.2.4 Synthesis of 1,1'-2,6-Diisopropylphenyl-3,3'-methylenediimidazolin-2,2'-diylidenedibromidecopper(I) and 1,1'-2,4,6-Trimethylphenyl-3,3'-methylenediimidazolin-2,2'-diylidenedibromidecopper(I)

The first attempts at complexation was conducted similarly to the previous reaction of deprotonation of the ligand by addition of KN(TMS)₂ followed by an immediate reaction with Cu(PPh₃)₃Br.

Scheme 2.15 The synthesis of bisNHC copper complex employing Cu(PPh₃)₃Br as copper source.

![Complexation scheme](image)
After the addition of the KN(TMS)$_2$ the solution mixture immediately turned green. When the Cu(PPh$_3$)$_3$Br was added the solution gradually turned into a brown colour. Based on observations alone this suggests there was reaction taking place; however since the addition of the 2,6-dissopropylphenyl increases the solubility of the system, the product remains in solution rather than precipitating. This poses to be a problem because the complexation results in 3 equivalence of triphenylphosphine being displaced into solution along with the desired product. A $^1$H NMR of the mixture was obtained, where the spectrum shows inconclusive results with no visible product peak. Attempts to isolate a product by precipitation out of hexanes all remained unsuccessful.

After realizing the difficulties in separating the product from the triphenylphosphine, an alternative route was taken for the complexation of the ligands onto copper. By alternating the copper source to copper(I) halides, eliminates having triphenylphosphine in solution, therefore the product can be easily isolated by working up the reaction without separation from any biproducts.

**Scheme 2.16** The reaction scheme for the synthesis of bis-NHC copper complex employing copper (I) halide as copper source.
The following reactions produced a complicated \(^1\)H NMR, where no evident of any product peaks were present. Once, again based on observations there appears to be a reaction taking place based on colour change; however no relevant information can be obtained from the spectrums.

2.2.5 *Hydrosilations*

From the above results, the only successful copper catalyst that was synthesized was the dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diylidene)dicopper(I), while the bulky 2,4,6-mesityl and 2,6-diisopropylphenyl analogues require a more optimization to work out the necessary conditions for complexation. Therefore, only the dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diylidene)dicopper(I) catalyst was tested for catalysis. The catalyst was first tested for hydrosilation of benzophenone in toluene at 80°C at 3 mol% catalyst, mimicking that of Nolan’s conditions.\(^{43}\) Since, the dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diylidene)dicopper(I) is a dinuclear species each mol of catalyst actually represents 2 copper centers. Therefore hydrosilations were conducted using both 1.5 mol % and 3 mol % of loading catalyst to obtain a similar assessment of loading catalyst to that of Nolan’s. The catalyst showed relatively mediocre results of 50% yields within 48hrs, which is significantly lower than Nolan’s systems of 99% at 15 minutes. The poor solubility of the catalyst was rationalized a major contributing factor to the low yield. By switching to more polar solvents, this should increase dissolution of the catalyst in turn increasing activity of the reaction by allowing easier contact of the catalyst with the substrate. The catalyst solubility was screened among a wide variety of solvents; however still showed poor solubility in polar reagents. Dried acetonitrile and dioxane were the two polar solvent used to test the catalyst reactivity in comparison to that of using toluene as a solvent. Table 3, shows that when switching to more polar solvent, such as acetonitrile or dioxane the results show increase in activity but still values far from that of Nolan’s yields. We rationalized that if solubility was indeed the issue, using temperature as a variable could increase the dissolution of the catalyst. Before these reactions can be conducted, the catalyst must be capable of withstanding reaction conditions at harsh temperatures. By performing thermal gravimetric analysis (TGA) on dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diylidene)dicopper(I), the temperature
at which the catalyst starts to decompose can be determined. The TGA plot shows that dibromobis(1,1’-dibenzyl-3,3’-methylenediimidazolin-2,2’-diylidene)dicopper(I) starts to decompose at 250°C, suggesting that increasing temperature should not be a problem. While trying to keep the conditions of Nolan’s systems relatively the same, xylene would be the most ideal solvent of choice. Seeing how xylene has very similar properties to that of toluene, but also having a higher boiling point, it is the perfect choice to conduct hydrosilations at higher temperatures. As shown in table 3, by increasing temperature to 140°C in xylene gave a 100% yield in 19 hrs.

Scheme 2.17  The reaction scheme for the hydrosilations of benzophenone.

Table 2.7  Optimizing conditions for hydrosilation (solvent, temperature, loading catalyst).

<table>
<thead>
<tr>
<th>Trial</th>
<th>Catalyst Type</th>
<th>Catalyst (mol%)</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (hr)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>N/A</td>
<td>Xylene</td>
<td>140</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>3</td>
<td>Toluene</td>
<td>80</td>
<td>48</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>3</td>
<td>Dioxane</td>
<td>80</td>
<td>48</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1.5</td>
<td>MeCN</td>
<td>90</td>
<td>1.25</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>3</td>
<td>Xylene</td>
<td>120</td>
<td>48</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>1.5</td>
<td>Xylene</td>
<td>140</td>
<td>19</td>
<td>100</td>
</tr>
</tbody>
</table>

Now that the loading catalyst, solvent, and temperature have been optimized for the benzophenone, the optimal reaction time needs to be determined. The hydrosilation of benzophenone was optimized by taking aliquots at specific time interval, to determine the optimal reaction time that produces greatest percentage yield. Table 2.7, shows after 1 hour the
activity reaches above 90 percent and does not increase significantly after that. This suggests that the optimal reaction time for benzophenone is approximately 1 hour duration.

**Table 2.8** Optimizing conditions for hydrosilation of benzophenone.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Catalyst Type</th>
<th>Catalyst Amount</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (hr)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1.5</td>
<td>Xylene</td>
<td>140</td>
<td>0.25</td>
<td>37</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1.5</td>
<td>Xylene</td>
<td>140</td>
<td>0.5</td>
<td>81</td>
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<td>1</td>
<td>1.5</td>
<td>Xylene</td>
<td>140</td>
<td>0.75</td>
<td>95</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1.5</td>
<td>Xylene</td>
<td>140</td>
<td>1</td>
<td>96</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>1.5</td>
<td>Xylene</td>
<td>140</td>
<td>1.25</td>
<td>97</td>
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<td>1.5</td>
<td>Xylene</td>
<td>140</td>
<td>2</td>
<td>100</td>
</tr>
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<td>7</td>
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<td>1.5</td>
<td>Xylene</td>
<td>140</td>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>1.5</td>
<td>Xylene</td>
<td>140</td>
<td>4</td>
<td>100</td>
</tr>
</tbody>
</table>

After optimizing conditions for benzophenone, this catalyst was tested against more bulky substrates. These variety of substrates shown in table 2.9, were chosen because they cover a wide range of steric bulk about the ketone. The results show that the catalyst activity produced exceptional yields for all substrates apart from 2,4,6-trimethylacetophenone. According to Nolan’s results, 2,4,6-trimethylacetophenone was the most difficult substrate to hydrosilate, requiring rigorous reaction time of 24 hours and only achieving a maximum yield of 80%. Our results show that although the conversion is only 20 percent at 24 hours, our system is still active in hydrosilating 2,4,6-trimethylacetophenone.

**Scheme 2.18** The reaction scheme for the hydrosilations of substituted ketones.
Table 2.9  Hydrosilation of hindered ketones.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>Time (hr)</th>
<th>Percent Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Substrate" /></td>
<td><img src="image2" alt="Product" /></td>
<td>1.25</td>
<td>97</td>
</tr>
<tr>
<td><img src="image3" alt="Substrate" /></td>
<td><img src="image4" alt="Product" /></td>
<td>2</td>
<td>80</td>
</tr>
<tr>
<td><img src="image5" alt="Substrate" /></td>
<td><img src="image6" alt="Product" /></td>
<td>9</td>
<td>83</td>
</tr>
<tr>
<td><img src="image7" alt="Substrate" /></td>
<td><img src="image8" alt="Product" /></td>
<td>24</td>
<td>18</td>
</tr>
</tbody>
</table>

2.2.6  Proposed Mechanism for Hydrosilation

There have been several mechanisms that have been proposed as possible reaction pathway for hydrosilation of substituted ketones utilizing copper. We propose the most plausible catalytic pathway in the schematic below, where the copper precatalyst was first activated by the base to form a copper alkoxide. This compound copper alkoxide then further reacts with one equivalent of triethylsilane to form a more active copper hydride species. This active copper hydride catalyst then reacts with the corresponding ketone, where the hydride adds across the carbonyl bond of the substrate. This intermediate further reacts with another equivalent of triethylsilane, reductively eliminating the product regenerating the copper hydride catalyst species.
Scheme 2.19  The proposed catalytic pathway for hydrosilation of ketones.

As one can see, scheme 2.19 does not show the complete structure of our active catalyst because its structure was unknown. Since our precatalyst was a dimeric species, it makes it difficult to propose an exact structure of the active species. Given the structure of our system, this suggest that our active catalyst could still remain a dimeric species, where the catalysis could happen at two copper centers simultaneously rather than one shown in the schematic above.

2.2.7  Arylation of Imidazole

From the above results, our copper system appears to be active in carbonyl reduction of various ketones. We further tested the versatility of our copper catalyst, by conducting a series of C-N coupling reaction involving the arylation of imidazoles. We first tested the effectiveness of our catalyst system on non-substituted phenyl halides. It has been known in literature arylation genuinely requires harsh heating conditions to drive the coupling reaction. Literature precedence
shows that typical high boiling solvents such as DMF and DMA were used for this type catalysis. First we tested arylation of imidazole employing non-substituted phenyl halides as our substrates, where results showed high yields for the iodide but only moderate yields for the bromides. Subsequently we tested the ruggedness of our catalyst with an array of substituted activated and deactivated aryl compounds. The results below (Table 2.10) show the catalysis was conducted on a series of bromides and chlorides containing an electron withdrawing or donating group in the \textit{para}-position of the phenyl ring. Table 2.10 displays that the catalyst was not active for catalyzing any substituted aryl halides in DMA at high temperatures for 24 hours.

\textbf{Scheme 2.20} The reaction scheme for the arylation of imidazole in DMA using dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diylidene)dicopper(I).

\[
\text{R-X} + \text{Imidazole} \xrightarrow{\text{DMA/140 °C/24 hr}} \text{Product} \quad \text{Cu(I), Cs}_2\text{CO}_3
\]

\textbf{Table 2.10} Arylation of imidazole using dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diylidene)dicopper(I) in DMA.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate (R-X)</th>
<th>Product</th>
<th>Yield (Major)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{Br} )</td>
<td>( \text{N} )</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>( \text{Cl} )</td>
<td>( \text{N} )</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>( \text{NO} )</td>
<td>( \text{N} )</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>( \text{I} )</td>
<td>( \text{N} )</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>( \text{Br} )</td>
<td>( \text{N} )</td>
<td>47</td>
</tr>
</tbody>
</table>
Therefore, a secondary approach was to optimize solvents. DMA is a high boiling solvent which causes work up of the reaction to be more difficult. In general the procedure requires an aqueous workup followed a DCM extraction, because DMA is very difficult solvent to remove. The major downfall of this procedure was DMA was partially soluble in both the aqueous and DCM phases. This suggests that some of the product still remain in the aqueous layer and resulting in poor recovery. Therefore, test reactions were done using acetonitrile, where no aqueous workup was required and heating at less rigorous temperatures. However, results show very low yields for the phenyl halides and once again no activity for the activated and non-activated aryl compounds.

**Scheme 2.21** The reaction scheme for the arylation of imidazole in MeCN using dibromobis(1,1’-dibenzyl-3,3’-methyleneimidazolin-2,2’-diylidene)dicopper(I).

\[
R-X + \text{MeCN/80 °C/24 hr} \xrightarrow{\text{Cu(Source), Cs}_2\text{CO}_3} R: \text{N} \quad \text{N}
\]
Table 2.11  Arylation of imidazole using dibromobis(1,1'-dibenzyl-3,3'-methyleneimidazolin-2,2'-diylidene)dicopper(I) in MeCN.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate (R-X)</th>
<th>Product</th>
<th>Yield (Major)</th>
</tr>
</thead>
<tbody>
<tr>
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<td><img src="image2" alt="image" /></td>
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<td><img src="image3" alt="image" /></td>
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<td><img src="image7" alt="image" /></td>
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</tr>
<tr>
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<td><img src="image10" alt="image" /></td>
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<tr>
<td>6</td>
<td><img src="image11" alt="image" /></td>
<td><img src="image12" alt="image" /></td>
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<td><img src="image21" alt="image" /></td>
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</tr>
</tbody>
</table>

This suggests that the reactions require high temperature to drive the arylation of imidazoles and more optimal conditions must be developed for the arylation of imidazoles using our catalyst. The arylation was also tested using Cu(PPh₃)₃Br as the catalyst source, and results show similar
trends to that of our copper system for activated and deactivated substituted imidazoles. The yields actually appear to be lower for the arylation of phenyl halide; therefore shows that Cu(PPh$_3$)$_3$Br isn’t our active system in the catalysis.

**Scheme 2.22** The reaction scheme for the arylation of imidazole in DMA using bromotris(triphenylphosphine)copper(I).

$$\text{R-X} + \text{imidazole} \xrightarrow{\text{DMA/140 °C/24 hr}} \text{Cu(I), Cs$_2$CO$_3$} \rightarrow \text{imidazole product}$$

**Table 2.12** Arylation of imidazole using bromotris(triphenylphosphine)copper(I) in DMA.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate (R-X)</th>
<th>Product</th>
<th>Yield (Major)</th>
</tr>
</thead>
<tbody>
<tr>
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<td><img src="image_2.png" alt="image_2" /></td>
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</tr>
<tr>
<td>2</td>
<td><img src="image_3.png" alt="image_3" /></td>
<td><img src="image_4.png" alt="image_4" /></td>
<td>0</td>
</tr>
<tr>
<td>3</td>
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<td><img src="image_6.png" alt="image_6" /></td>
<td>26</td>
</tr>
</tbody>
</table>

2.2.8 *Alkylation of Imidazole*

We further tested the ruggedness of our system by testing our copper catalyst with a variety of substituted alkyl halides. It shows that our copper system is very active for primary and secondary alkyl halides in acetonitrile for 24 hours. Our copper catalyst shows very high yields ranging from 80-100 percent for primary and secondary alkyl bromides. Additionally, our systems also show to be active in catalyzing the more difficult to couple alkyl chlorides done in moderate to high yields. Catalysis was conducted on alkyl iodides, where results show mixture of two products. The secondary product that is formed is determined to be the disubstituted imidazolium halide. This suggests that the coupling occurs at such a rapid rate allowing substitution at both nitrogens. This trend was only ever observed for primary and secondary
alkyl iodides. Therefore, the scope of alkyl halides were more investigated on bromides and chlorides because of commercial abundance and lower cost of the starting material and greater difficulty to couple. The bromides and chlorides form only one major product which was the desired single substituted imidazole. As for tertiary substituted alkyl halides, results show that our copper pre catalyst was not active in alkylation of imidazole in acetonitrile at 80°C overnight.

**Scheme 2.23** The reaction scheme for the alkylation of imidazole in MeCN using dibromobis(1,1'-dibenzyl-3,3'-methylenimidazolin-2,2'-diylidene)dicopper(I).

![Reaction Scheme](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate (R-X)</th>
<th>Product</th>
<th>Yield (Major)</th>
<th>Yield (Minor)</th>
</tr>
</thead>
<tbody>
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<td>14</td>
</tr>
<tr>
<td>2</td>
<td>R-Br</td>
<td><img src="image" alt="Imidazole" /></td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>R-Cl</td>
<td><img src="image" alt="Imidazole" /></td>
<td>27</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>R-BR</td>
<td><img src="image" alt="Imidazole" /></td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>R-Cl</td>
<td><img src="image" alt="Imidazole" /></td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>R-Br</td>
<td><img src="image" alt="Imidazole" /></td>
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<td>0</td>
</tr>
<tr>
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<td>R-Cl</td>
<td><img src="image" alt="Imidazole" /></td>
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<td>0</td>
</tr>
<tr>
<td>8</td>
<td>R-Br</td>
<td><img src="image" alt="Imidazole" /></td>
<td>62</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>R-Cl</td>
<td><img src="image" alt="Imidazole" /></td>
<td>44</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table 2.13** Alkylation of imidazole using dibromobis(1,1'-dibenzyl-3,3'-methylenimidazolin-2,2'-diylidene)dicopper(I) in MeCN.
| 10 | \( \text{C}_{10} \text{H}_{15}Br \) | \( \text{Imidazole} \) | 91 | 0 |
| 11 | \( \text{Cl} \text{C}_{10} \text{H}_{15} \) | | 57 | 0 |
| 12 | \( \text{Ph} \text{Br} \) | \( \text{Imidazole} \text{Ph} \) | 100 | 0 |
| 13 | \( \text{Ph} \text{Cl} \) | \( \text{Imidazole} \text{Ph} \) | 85 | 0 |
| 14 | \( \text{Me} \text{Br} \) | \( \text{Imidazole} \text{Me} \) | 0 | 0 |
| 15 | \( \text{Me} \text{Cl} \) | \( \text{Imidazole} \text{Me} \) | 0 | 0 |
| 16 | \( \text{Br} \text{C} \text{C} \text{H} \) | \( \text{Imidazole} \text{Br} \) | 0 | 0 |
| 17 | \( \text{I} \) | \( \text{Imidazole} \) | 43 | 11 |

### 2.2.9 Proposed Mechanism for Arylation and Alkylation of Imidazole

The mechanism for the arylation and alkylation of imidazole are similar to that of the catalytic pathways proposed for C-N coupling. Differently than hydrosilation, the base of the reaction was not used to activate the catalyst but rather the imidazole to increase its nucleophilicity. The imidazole then coordinates onto the copper, followed by an oxidative addition of the alkyl or aryl halide. The following step is reductive elimination of the alkylated or arylated imidazole, along with regeneration of the copper halide species.
Scheme 2.24  The proposed catalytic pathway for the alkylation or arylation of imidazole.
Chapter 3  Conclusions

3.1  Summary of the Attempted Synthesis of 3-Coordinate Palladium Complexes

3.1.1  \[\{(2,6-^t\text{Pr}_2\text{Ph})_2\text{nacnac}\text{PdCl}\}_2\]

We have not successfully synthesized a 3-coordinate compound using multiple potassium and lithium substrates in a one-step reaction. The $^1$H NMR spectrums showed no reaction and only signals pertaining to starting material. Using Spartan, we were able to observe that the \[\{(2,6-^t\text{Pr}_2\text{Ph})_2\text{nacnac}\text{PdCl}\}_2\] target compound to forming the 3-coordinate species was more bulky than expected. The results illustrated that the \[\{(2,6-^t\text{Pr}_2\text{Ph})_2\text{nacnac}\text{PdCl}\}_2\] dimer contains too much steric protection about the metal center limiting the accessibility for the substrate to coordinate onto the palladium. These results suggest that the lithium and potassium based reagents that were employed were too bulky and cannot enter the reactive site.

3.1.2  \[\{(2,6-^t\text{Pr}_2\text{Ph})_2\text{nacnac}\text{PdCl}(\text{NH}_2\text{Ph})\}\]

In contrast, the aniline was the only substrate that was able to break up the \[(2,6-^t\text{Pr}_2\text{Ph})_2\text{nacnacPdCl}\] dimer forming \[\{(2,6-^t\text{Pr}_2\text{Ph})_2\text{nacnac}\text{PdCl}(\text{NH}_2\text{Ph})\}\]; however the structure that was formed still remained 4-coordinate species. The $^1$H NMR spectrum of this \[\{(2,6-^t\text{Pr}_2\text{Ph})_2\text{nacnac}\text{PdCl}(\text{NH}_2\text{Ph})\}\] shows that the proton attached to the nitrogen of the aniline integrates for 2 protons indicating that the chlorine has not yet been eliminated and a 3-coordinate species was not formed. The data clearly indicates that aniline was a small enough substrate that allows just enough access to the palladium center. Many reactions were conducted using this \[\{(2,6-^t\text{Pr}_2\text{Ph})_2\text{nacnac}\text{PdCl}(\text{NH}_2\text{Ph})\}\] as the precursor for a 3-coordinate product; however, $^1$H NMR spectrum shows only starting material. The formation of \[\{(2,6-^t\text{Pr}_2\text{Ph})_2\text{nacnac}\text{PdCl}(\text{NH}_2\text{Ph})\}\] must be in presence of an excess of aniline to drive this reaction, because the aniline palladium bond was only weakly coordinated. Therefore, when removed from a saturated environment of aniline the reaction reverts back to the \[\{(2,6-^t\text{Pr}_2\text{Ph})_2\text{nacnac}\text{PdCl}\}_2\] complex and free aniline.
3.1.3  Computational Analysis

Using Spartan we were able to show that the expected geometry of our 3-coordinate species should favour a T-shape geometry instead a trigonal planar. The values obtained from the DFT calculations states that the T-shape was more stable then trigonal planar, where the trigonal planar geometry was merely transition state. However, one should take into consideration that the structure that was represented in Spartan was a reduced version of the actual molecule for simplification purposes therefore; the results will not be a perfect representation of our compounds.

3.2  Summary of the Results for the Catalysis of N-Heterocyclic Copper Complexes

3.2.1  Dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diylidene)dicopper(I)

In conclusion, our synthesized dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diylidene)dicopper(I) precatalyst was very effective in hydrosilations of bulky ketones. Although our systems produced very poor yields and long reaction times at low temperature, we have proven that by varying temperature we can increase the activity of the system. Our catalyst possesses properties that are in general very ideal and advantageous for catalytic reactions. Dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diylidene)dicopper(I) shows high thermal stability and long catalytic lifetime. Our dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diylidene)dicopper(I) precatalyst shows comparable results to the best systems for hydrosilation known to literature.

As for C-N coupling of imidazole, conclusively we can say that our pre-catalyst was poor system for arylation altogether. Literature precedence suggests that these reactions require harsh conditions and high temperatures, where our system was only able to catalyze simple aryl halides, such a phenyl halides. As for the deactivated and activated substituted halides, our system showed no activity for either even at high temperatures in DMA. Although our dibromobis(1,1'-dibenzyl-3,3'-methylenediimidazolin-2,2'-diylidene)dicopper(I) catalyst is shown to be very ineffective for the arylation, it turns out that our system was very efficient in
alkylation of imidazole. Not only, our system was effective in coupling alkyl bromides, but also very active for alkyl chlorides. This is very desirable because chlorides are generally the most difficult of the halides to couple. The C-Cl bond is a stronger bond and requires more energy to break that bond; therefore typically are more difficult to break then that of other halide carbon bonds. Our results show that our system was able to catalyze alkyl bromide and alkyl chlorides at high yields and moderate reaction conditions. As mentioned before, alkylation of imidazole utilizing copper has not been known in literature; therefore our system is the first known example. Not only is our system is the first known system but also produced results in high yields.

3.2.2 1,1'-2,6-Diisopropylphenyl-3,3'-bisimidazolium Dibromide and 1,1'-2,4,6-Mesityl-3,3'-bisimidazolium Dibromide

The synthesis of a more bulky and more soluble ligands was successful in high yield and good purity. The attempts of forming a copper catalyst by employing these systems still remained unsuccessful. While using several copper sources and methodology, there was no conclusive information that can be obtained from the $^1$H NMR of the experiments. This could suggest that maybe the system was too bulky to allow coordination of the copper center and more studies needs to be done to conducted to actively make a conclusion.
Chapter 4  Future Works

4.1 Future Experiments to Reduce the Steric of the Reaction

4.1.1 Manipulating the Substrate

Even though a 3-coordinate species was not able to be synthesized, the results open doors for different approaches that can be taken into consideration for the isolation of these unsaturated palladium complexes. Spartan illustrates \( [(2,6-^tPr_2Ph)_2nacnac]PdCl)_2 \) was too bulky, therefore the substrate must be reduced for future experiments. The results obtained from this research suggest that one should start with the smallest reactant that should likely react in theory, such as MeLi.

Scheme 4.1 The reaction of \( [(2,6-^tPr_2Ph)_2nacnac]PdCl)_2 \) with MeLi.

If this reaction shows promising results, then attempts to use bulkier reactants should be further explored.

4.1.2 Manipulating the Precursor

After many unsuccessful attempts in synthesizing a 3-coordinate species using the \( [(2,6-^tPr_2Ph)_2nacnac]PdCl)_2 \), our group rationalized \( [(2,6-^tPr_2Ph)_2nacnac]Pd(OAc) \) as the replacing precursor could be a better route to forming the 3-coordinate palladium species. \( [(2,6-^tPr_2Ph)_2nacnac]Pd(OAc) \) was a monomeric species that has different electronics and steric bulk around the metal center in comparison to that of the \( [(2,6-^tPr_2Ph)_2nacnac]PdCl)_2 \) dimer. We
theorized that the acetate group on this precursor was a better leaving group than the chlorine on the original chloride bridged dimer precursor. The Spartan space-filling diagrams results also show a larger reactive site for the substrates to coordinate from less 3 dimensional steric bulk. Using \(((2,6'-\text{Pr}_2\text{Ph})_2\text{nacnac})\text{Pd(OAc}_2\) instead of \(((2,6'-\text{Pr}_2\text{Ph})_2\text{nacnac})\text{PdCl(NH}_2\text{Ph)}}\) allows less complicated conditions of having to deal with excess aniline. Seeing that the \(((2,6'-\text{Pr}_2\text{Ph})_2\text{nacnac})\text{Pd(OAc)}}\) was an easily isolable product, whereas \(((2,6'-\text{Pr}_2\text{Ph})_2\text{nacnac})\text{PdCl(NH}_2\text{Ph)}}\) was not, routes into a 3-coordinate species should be used for this more ideal precursor.

**Scheme 4.2** The reaction of \(((2,6'-\text{Pr}_2\text{Ph})_2\text{nacnac})\text{Pd(OAc)}}\) with triphenylmethanethiol.

![Scheme 4.2](image)

The second route deals with forming a 4-coordinate \(((2,6'-\text{Pr}_2\text{Ph})_2\text{nacnac})\text{Pd(OAc)(NH}_2\text{Ph)}}\) species and driving off the acetic acid or lithium acetate to form the 3-coordinate species.

**Scheme 4.3** The formation of \(((2,6'-\text{Pr}_2\text{Ph})_2\text{nacnac})\text{Pd(NHPh)}}\) using a 4-coordinate \(((2,6'-\text{Pr}_2\text{Ph})_2\text{nacnac})\text{Pd(OAc)(NH}_2\text{Ph)}}\) as the precursor.

![Scheme 4.3](image)
4.1.3 Manipulating Nac Nac Ligand

Computational analysis shows that the \[ \{(2,6-iPr_2Ph)_2nacnac\}PdCl\}_2 \] dimer was very sterically bulky. By altering the substituents attached to the nitrogen of the nacnac ligand with something less sterically bulky, this can reduce the amount of ligand protection about the palladium, allowing the reactive site to be more accessible.

4.2 Developing Different Analogues of DiNHC Copper Complexes

4.2.1 Long-Chain Alkanes

Even though the dibromobis(1,1'-dibenzyl-3,3'-methylenedimidazolin-2,2'-diylidene)dicopper(I) precatalyst showed promising results, its limitation still remains in its solubility, requiring rigorous reaction conditions. Therefore, a more soluble catalyst system needs to be developed. It has been known to literature that having ligand systems containing long chain alkanes as substituents can increase solubility; however trading off steric bulk. The longer chain generally led to greater the solubility.

Figure 4.1 A diNHC incorporating long chain alkanes substituents.

By synthesizing a system incorporating these long chain alkanes, we can increase the solubility of the catalyst, therefore a wider range of solvents can be utilize in hydrosilations.
4.2.2 Cyclohexyl

Nolan most effective catalyst system was a mondentate NHC with cyclohexyls substituents. The cyclohexyls must contribute an electronic effect to the system that may play a role in the activity of the reaction. If we are able to synthesize a cyclohexyl analogue of our precatalyst, the electronics of the cyclohexyl may increase the activity in our system also.

![Figure 4.2](image_url)  
**Figure 4.2** A diNHC incorporating cyclohexyl substituents.

4.2.3 Crystallization

From the results obtained for the attempted synthesis of the 2,6-disspropylphenyl and 2,4,6-mesityl substituted bis-imidazolium copper reactions, the $^1$H NMR shows inconclusive results. Even though, there seems to be a reaction taking place, the compound that was being formed was still questionable. Therefore, crystallization is currently taking place to crystallize out what we hoped to be the desired product.
Chapter 5 Experimental

**General Information.** Unless otherwise stated, all reactions were performed under N2 using standard Schlenk techniques or in a N2-filled drybox. Solvents were dried using an MBraun solvent purification system and stored under nitrogen. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker 500 MHz Advance spectrometer. Chemical shifts for $^1$H and $^{13}$C NMR spectroscopy are reported in ppm in reference to the $^1$H and $^{13}$C resonances of C$_6$D$_6$ ($^1$H: $\delta$ 7.16; $^{13}$C: $\delta$ 128.39) or CDCl$_3$ ($^1$H: $\delta$ 7.24; $^{13}$C: $\delta$ 77.24). Coupling constants are given in Hz. Elemental analysis was performed on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectrum data were obtained using Applied Biosystem QSTAR®XL MS/MS System (ESI-Q-TOF) and VG70 SE (Double Focusing EI). Reagents were purchased from the Sigma-Aldrich Chemical Company and used as received.

5.1 The Synthesis of Precursor for 3-Coordinate Palladium Complexes

5.1.1 Synthesis of [(2,6-$^3$Pr$_2$Ph)$_2$napnacH]$^3$

A mixture of 2,4 pentanedione (1.51 mL, 14.7 mmol) with 2,6 diisopropylaniline (6.27 mL, 33.2 mmol) in the presence of hydrochloric acid (1.20 mL) was refluxed in ethanol (60 mL) for 3 days. After the 3 day duration the reaction mixture proceeded to a brown colour. This mixture was then concentrated. A solution of saturated sodium carbonate was added to the brown crude, followed by an extraction with dichloromethane (3x10 mL). The organic layer was concentrated and then recrystallized in methanol. Prior to the recrystallization, immediate white crystals are precipitated from the brown methanol solution. This solution was filtered and the white crystals of the [(2,6-$^3$Pr$_2$Ph)$_2$napnacH] was isolated. (Yield: 3.73g, 60.5%)

$^1$H NMR (CDCl$_3$): $\delta$ 12.09 (s, NH, 1H), 7.11 (m, CH$_{ar}$ 6H), 4.86 (s, CH$_{backbone}$, 1H), 3.10 (m, CH, 4H), 1.70 (s, CH$_3$, 6H), 1.19 (d, CH$_3$, 12H ), 1.13 (d, CH$_3$, 12H).
5.1.2 *Synthesis of \([\{(2,6-i^\text{Pr}_2\text{Ph})_2\text{nacnac}\}\text{Pd(OAc)}]^\text{25}\)*

\([(2,6-i^\text{Pr}_2\text{Ph})_2\text{nacnacH}]\) (1.023g, 2.443 mmol) was reacted with palladium acetate (0.5627g, 2.506 mmol) in toluene (30 mL) at room temperature for 24 hours. The reaction mixture was filtered to remove any palladium black build up, where the filtrate was concentrated via invacuo yielding a red solid. \((\text{Yield: } 1.358g, 95.4\%)\)

\(^1\text{H NMR (C}_6\text{D}_6\): } \delta 7.13 (t, \text{CH}_\text{ar}, 2H), 7.11 (d, \text{CH}_\text{ar}, 4H), 4.89 (s, \text{CH}_\text{backbone}, 1H), 3.71 (m, \text{CH}, 4H), 1.70 (d, \text{CH}_3, 12H), 1.53 (s, \text{CH}_3, 6H ), 1.22 (d, \text{CH}_3, 12H).

5.1.3 *Synthesis of \([\{(2,6-i^\text{Pr}_2\text{Ph})_2\text{nacnac}\}\text{PdCl}]^\text{25}\)*

A solution of \([\{(2,6-i^\text{Pr}_2\text{Ph})_2\text{nacnac}\}\text{Pd(OAc)}]\) (1.016 g, 1.742 mmol) was reacted with excess LiCl (1.454 g, 34.30 mmol) in toluene (10mL) for 2 days at 110°C. After the 2 day duration, the initial red reaction mixture turned into a dark green solution. This solution was filtered for the removal of palladium black and the filtrate was concentrated yielding a green product. The reaction mixture was filtered to remove any palladium black build up, where the filtrate was concentrated yielding a green solid. \([\{(2,6-i^\text{Pr}_2\text{Ph})_2\text{nacnac}\}\text{PdCl}_2]\) was then further dried in vacuo, where the crude was used as is for further reactions. \((\text{Yield: } 0.895g, 91.8 \%)\)

\(^1\text{H NMR (C}_6\text{D}_6\): } \delta 7.02 (t, \text{CH}_\text{ar}, 4H), 6.97 (d, \text{CH}_\text{ar}, 8H), 4.72 (s, \text{CH}_\text{backbone}, 2H), 3.38 (m, \text{CH}, 8H), 1.51 (d, \text{CH}_3, 24H), 1.45 (s, \text{CH}_3, 12H ), 1.12 (d, \text{CH}_3, 24H).

5.1.4 *Synthesis of \([\{(2,6-i^\text{Pr}_2\text{Ph})_2\text{nacnac}\}\text{PdCl(NH}_2\text{Ph)}]\)

A mixture of \([(2,6-i^\text{Pr}_2\text{Ph})_2\text{nacnacPdCl}_2]\) (0.210 g, 0.188 mmol) with aniline (0.326 mL, 3.57 mmol) in toluene was stirred for 24 hours at ambient temperature. The reaction mixture turned into a red solution from the initial green solution. The solvent was removed in vacuo; however due to the added excess aniline to drive the reaction to the 4-coordinate species, the product could not be isolated from the aniline.
Note the meta-CH and para-CH that are attached to the NH₂Ph are not extractable from the NMR spectra because of large presence of excess aniline. The excess aniline peaks are likely to be overlapping those CH signals in the phenyl ring of the product.

5.2 The Synthesis of Copper Complex and Catalytic Products

5.2.1 Synthesis of 1-Benzylimidazole

In a Schlenk flask benzyl bromide (3.49 mL, 29.4 mmol) was added to a mixture of imidazole (2.025 g, 29.74 mmol) and 4 equivalent of sodium hydride (3.061 g, 127.5 mmol) in THF, affording a bright yellow solution after approximately 10 minutes. The solution was stirred overnight yielding a green milky solution, which was then filtered isolating a brown filtrate and a green precipitate. The mother liquor was concentrated via vacuo, leaving a brown solid. The crude benzyl imidazole was used for the subsequent step without further purification and assumed 100% yield. (Yield: N/A)

\(^1\text{H NMR (CDCl}_3\): \(\delta\) 7.53 (s, CH, 1H), 7.34 (m, CH, 3H), 7.24 (d, CH, 2H), 7.06 (s, CH, 1H), 6.89 (s, CH, 1H), 5.10 (s, CH₂, 2H).

5.2.2 Synthesis of 1,1′-Dibenzyl-3,3′-methyleneimidazolin-2,2'-diylidenedibromide

To a pressure vessel a solution of 1-benzylimidazole (unpurified) was heated (80°C) in neat dibromomethane (5mL) for 24 hours. After the allotted duration a white precipitate was formed in the dibromomethane solution. The reaction was then filtered, isolating the white precipitate from the mother liquor. The precipitate was washed with 3 x 10 mL addition of THF and further
dried in vacuo. Without any further purification 1,1'-dibenzyl-3,3'-methylenedimidazolin-2,2'-diylidenedibromide was used for the complexation with bromotris(triphenylphosphine)copper(I) (Yield: 1.841g, 26%)

\(^1\text{H NMR}\) (DMSO): \(\delta\) 9.08 (s, CH, 2H), 8.13 (s, CH, 2H), 7.93 (s, CH, 2H), 7.44 (m, CH\text{ar}, 10H), 6.72 (s, CH\text{2}, 2H), 5.52 (s, CH\text{2}, 4H).

5.2.3) Synthesis of Bromotris(triphenylphosphine)copper(I)\(^{50}\)

To an Erlenmeyer triphenylphoshine (3.025 g, 11.53 mmol) was heated to a boil in methanol and stirred till complete dissolution. Dibromocopper(II) (0.654g, 2.93 mmol) was then added to the solution, where an immediate white precipitate was formed. The reaction was allowed to stir for an additional 30 minutes to ensure that the reaction has reach completion. The corresponding mixture was then filtered, where the precipitate was washed with 3 x 10mL addition of ice-cold methanol. The isolated bromotris(triphenylphosphine)copper(I) was further dried in vacuo to remove any trace solvent.

5.2.4 Synthesis of Dibromobis(1,1'-dibenzyl-3,3'-methylenedimidazolin-2,2'-diylidene)dicopper(I)

In an oven dried round-bottom 1,1'-dibenzyl-3,3'-methylenedimidazolin-2,2'-diylidenedibromide (0.491 g, 1.00 mmol) in THF (5mL) and 2.2 equivalent of potassium bistrimethylsilylamide (0.453 g, 2.27 mmol) was added in THF resulting in a green cloudy mixture after ~4 min under nitrogen. This mixture was filtered into a second vessel containing a suspension of bromotris(triphenylphosphine)copper(I) (0.941 g, 1.01 mmol) in THF (5mL) and stirred overnight. The resulting mixture turned into a milky beige solution, which was then filtered leaving a brown precipitate and a brown filtrate. The filtrate was discarded and the precipitate was washed 3x10mL of THF. This precipitate was isolated and further dried under vacuum. Without further purification, the crude product was tested for catalysis reaction. (Yield: 0.3451g, 73%)
$^1$H NMR (CDCl$_3$): δ 7.66 (s, CH, 2H), 7.20 (m, CH, 8H), 7.02 (d, CH, 4H), 6.70 (s, CH$_2$, 2H), 5.04 (s, CH$_2$, 4H).

General Procedure for Hydrosilation Reaction with Dibromobis(1,1'-dibenzyl-3,3'-methylenedimidazolin-2,2'-diylidene)dicopper(I)

In an oven-dried vial with a septum screw cap was charged inside the glove box with dibromobis(1,1'-dibenzyl-3,3'-methylenedimidazolin-2,2'-diylidene)dicopper(I) (0.030 g, 0.032 mmol) (Catalyst), sodium tert-butoxide (0.024 g, 0.250 mmol) (Base), and dodecahydrophenylene (0.051g, 0.212 mmol) (Internal Standard) in dry xylene (5mL) , then stirred at 140°C for 10 min. After the ten minute duration, triethylsilane (1.01 mL, 6.33 mmol) in xylene (1mL) was added via syringe through the septum. The mixture was stirred for another 20 min before the addition of ketone in xylene (1mL) was added to the reaction. The reaction was allowed to proceed at 140°C while sampling aliquots at different time intervals. The reaction mixture was cooled to room temperature, opened to air, and concentrated in vacuo. The reaction was monitored by $^1$H NMR where the yield was calculated by the integration ratio of the product to internal standard peak, dodecahydrophenylene. The $^1$H NMR spectra were consistent with previously reported spectra from literature.

5.2.5 (Diphenylmethoxy)triethylsilane

Using the general procedure benzophenone (0.392 g, 2.15 mmol) was added to a reaction mixture of triethylsilane, dibromobis(1,1'-dibenzyl-3,3'-methylenedimidazolin-2,2'-diylidene)dicopper(I) (catalyst), sodium tert-butoxide (base) and dodecahydrophenylene (internal standard) in xylene and heated at 140°C. (Yield: 97%)

$^1$H NMR (CDCl$_3$): δ 7.38 (d, 4H), 7.30 (t, 4H), 7.22 (t, 2H), 5.78 (s, 1H), 0.90 (t, 9H), 0.58 (q, 6H).
5.2.6 (1-Isopropyl-2-methylpropoxy)triethylsilane

Using the general procedure 2,4-dimethylpentanone (0.301 mL, 2.19 mmol) was added to a reaction mixture of triethylsilane, dibromobis(1,1’-dibenzyl-3,3’-methyleneimidazolin-2,2’-diyliidene)dicopper(I) (catalyst), sodium tert-butoxide (base) and dodecahydrophenylene (internal standard) in xylene and heated at 140°C. (Yield: 80%) 

\[ ^1H \text{ NMR (CDCl}_3\text{)}: \delta 3.32 \text{ (t, 1H,)}, 1.76 \text{ (q, 2H,)}, 1.01 \text{ (t, 9H,)}, 0.66 \text{ (q, 6H).} \]

5.2.7 (1-tert-Butyl-2,2-dimethylpropoxy)triethylsilane

Using the general procedure 2,2,4,4-tetramethylpentanone (0.364 mL, 2.19 mmol) was added to a reaction mixture of triethylsilane, dibromobis(1,1’-dibenzyl-3,3’-methyleneimidazolin-2,2’-diyliidene)dicopper(I) (catalyst), sodium tert-butoxide (base) and dodecahydrophenylene (internal standard) in xylene and heated at 140°C. (Yield: 83%) 

\[ ^1H \text{ NMR (CDCl}_3\text{)}: \delta 3.19 \text{ (s, 1H)}, 1.05 \text{ (t, 9H,)}, 1.03 \text{ (s, 18H,)}, 0.70 \text{ (q, 6H).} \]

5.2.8 Triethyl[1-(2,4,6-trimethylphenyl)ethoxy]silane

Using the general procedure 2,4,6-trimethylacetophenone (0.353 mL, 2.11 mmol) was added to a reaction mixture of triethylsilane, dibromobis(1,1’-dibenzyl-3,3’-methyleneimidazolin-2,2’-diyliidene)dicopper(I) (catalyst), sodium tert-butoxide (base) and dodecahydrophenylene (internal standard) in xylene and heated at 140°C. (Yield: 20%) 

\[ ^1H \text{ NMR (CDCl}_3\text{)}: \delta 6.72 \text{ (s, 2H,)}, 5.24 \text{ (q, 1H,)}, 2.45 \text{ (s, 6H,)}, 2.27 \text{ (s, 3H)}, 1.43 \text{ (d, 3H,)}, 0.87 \text{ (t, 9H,)}, 0.54 \text{ (q, 6H).} \]
General Procedure for C-N coupling Reactions

Procedure A

In an oven dried 30 mL reaction vial equipped with a stir bar was charged with 2 mol% catalyst (0.02 mmol), base (Cs₂CO₃) (1.4 mmol) and imidazole (1.2 mmol). Under nitrogen, dried solvent (DMA or DMF) (5 mL) and substituted halide (aryl or alkyl) (1 mmol), were added. The vial was sealed with a Teflon cap and was preheated to the appropriate temperature. After the specified time the vial was removed from the bath and water (20 mL) was added followed by extraction with dichloromethane (3 x 10 mL). The combined organic layers were washed with saturated aqueous NaCl (15 mL), dried over anhydrous MgSO₄ and filtered. Internal standard (dodecahydrotriphenylene) (0.1mmol) was added to the dried organic filtrate and concentrated in vacuo. The ¹H NMR was run in CDCl₃, where the yield was calculated by the integration ratio of the product to internal standard peak. The ¹H NMR were consistent with previously reported spectra from literature.

Procedure B

In an oven dried 30 mL reaction vial equipped with a stir bar was charged with 2 mol% catalyst (0.02 mmol), base (Cs₂CO₃) (1.4 mmol) and imidazole (1.2 mmol). Under nitrogen, dried solvent (MeCN) (5 mL) and substituted halide (aryl or alkyl) (1 mmol), were added. The vial was sealed with a Teflon cap and was preheated to the appropriate temperature. After the specified time the vial was removed from the bath and open to air. Internal standard (dodecahydrotriphenylene) (0.1mmol) was added to the reaction mixture and concentrated in vacuo. The ¹H NMR was ran in CDCl₃, where the yield was calculated by the integration ratio of the product to internal standard peak. The ¹H NMR were consistent with previously reported spectra from literature.

5.2.9 1-Phenylimidazole

Using the general procedure A phenyl halide (I or Br) (0.111 mL, 1.00 mmol or 0.105 mL, 1.00 mmol) was added to a reaction mixture of dibromobis(1,1'-dibenzyl-3,3'-methyleneimidazol-
2,2’-diylidene)dicopper(I) (catalyst), CsCO₃ (base), Imidazole and dodecahydrophenylene (Internal Standard) and heated to the appropriate temperature. (Yield: 90% (I); 47% (Br))

**¹H NMR (CDCl₃):** δ 7.83 (s, CH, 1H), 7.38-7.41 (m, CH, 2H), 7.29-7.34 (m, CH, 3H), 7.26 (s, CH, 1H) 7.11 (d, CH, 1H).

5.2.10 1-Isopropylimidazole

Using the general procedure A or B isopropyl halide (I or Br or Cl) (0.10 mL, 1.00 mmol or 0.094 mL, 1.00 mmol) was added to a reaction mixture of dibromobis(1,1’-dibenzyl-3,3’-methyleneimidazolin-2,2’-diylidene)dicopper(I) (catalyst), CsCO₃ (base), Imidazole and dodecahydrophenylene (Internal Standard) and heated to the appropriate temperature. (Yield: 72% (I); 80% (Br); 27% (Cl))

**¹H NMR (CDCl₃):** δ 7.54 (s, CH, 1H), 7.03 (s, CH, 1H), 6.93 (s, CH, 1H), 4.32 (m, CH, 1H) 1.46 (d, CH₃, 6H).

5.2.11 1-Butylimidazole

Using the general procedure B 1-butyl halide (Br or Cl) (0.11 mL, 1.0 mmol or 0.11 mL, 1.0 mmol) was added to a reaction mixture of dibromobis(1,1’-dibenzyl-3,3’-methyleneimidazolin-2,2’-diylidene)dicopper(I) (catalyst), CsCO₃ (base), Imidazole and dodecahydrophenylene (Internal Standard) and heated to the appropriate temperature. (Yield: 100% (Br); 90% (Cl))

**¹H NMR (CDCl₃):** δ 7.51 (s, CH, 1H), 7.12 (s, CH, 1H), 6.87 (s, CH, 1H), 3.89 (t, CH₂, 2H), 1.73 (m, CH₂, 2H), 1.30 (q, CH₂, 2H), 0.89 (t, CH₃, 3H).

5.2.12 1-2-Butylimidazole

Using the general procedure B 2-butyl halide (Br or Cl) (0.11 mL, 1.0 mmol or 0.11 mL, 1.0 mmol) was added to a reaction mixture of dibromobis(1,1’-dibenzyl-3,3’-methyleneimidazolin-
2,2’-diylidene)dicopper(I) (catalyst), CsCO$_3$ (base), Imidazole and dodecahydrophenylene (Internal Standard) and heated to the appropriate temperature. (Yield: 57% (Br); 22% (Cl))

$^1$H NMR (CDCl$_3$): δ 7.48 (s, CH, 1H), 7.29 (s, CH, 1H), 6.88 (s, CH, 1H), 4.02 (m, CH, 1H) 1.71 (m, CH$_2$, 2H), 1.44 (d, CH$_3$, 3H) 0.83 (t, CH$_3$, 3H).

5.2.13 1-Nonylimidazole

Using the general procedure B 1-nonyl halide (Br) (0.19 mL, 1.0 mmol) was added to a reaction mixture of dibromobis(1,1'-dibenzyl-3,3'-methylenedimidazolin-2,2'-diylidene)dicopper(I) (catalyst), CsCO$_3$ (base), Imidazole and dodecahydrophenylene (Internal Standard) and heated to the appropriate temperature. (Yield: 91% (Br))

$^1$H NMR (CDCl$_3$): δ 7.42 (s, CH, 1H), 7.01 (s, CH, 1H), 6.87 (s, CH, 1H), 3.88 (m, CH$_2$, 2H), 1.73 (m, CH$_2$, 2H), 1.21 (s, CH$_2$, 12H), 0.83 (m, CH$_3$, 3H).

5.2.14 1-Butyl-3-methylimidazole

Using the general procedure B 1-butyl-3methyl halide (Cl) (0.098 mL, 1.0 mmol) was added to a reaction mixture of dibromobis(1,1'-dibenzyl-3,3'-methylenedimidazolin-2,2'-diylidene)dicopper(I) (catalyst), CsCO$_3$ (base), Imidazole and dodecahydrophenylene (Internal Standard) and heated to the appropriate temperature. (Yield: 57% (Cl))

$^1$H NMR (CDCl$_3$): δ 7.44 (s, CH, 1H), 7.02 (s, CH, 1H), 6.89 (s, CH, 1H), 3.92 (t, CH$_2$, 2H), 1.65 (q, CH$_2$, 2H), 1.55 (s, CH, 1H), 0.92 (d, CH$_3$, 6H).

5.2.15 1-Benzylimidazole

Using the general procedure B 1-benzyl halide (Br or Cl) (0.12 mL, 1.0 mmol or 0.12 mL, 1.0 mmol) was added to a reaction mixture of dibromobis(1,1'-dibenzyl-3,3'-methylenedimidazolin-
2,2'-diylidene)dicopper(I) (catalyst), CsCO$_3$ (base), Imidazole and dodecahydrophenylene (Internal Standard) and heated to the appropriate temperature. (Yield: 85% (Br); 100% (Cl))

$^1$H NMR (CDCl$_3$): $\delta$ 7.53 (s, CH, 1H), 7.34 (m, CH, 3H), 7.24 (d, CH, 2H), 7.06 (s, CH, 1H), 6.89 (s, CH, 1H), 5.10 (s, CH$_2$, 2H).

5.2.16 1-Allylimidazole

Using the general procedure B 1-allyl halide (Br or Cl) (0.087 mL, 1.0 mmol or 0.072 mL, 1.0 mmol) was added to a reaction mixture of dibromobis(1,1'-dibenzyl-3,3'-methylenedimidazolin-2,2'-diylidene)dicopper(I) (catalyst), CsCO$_3$ (base), Imidazole and dodecahydrophenylene (Internal Standard) and heated to the appropriate temperature. (Yield: 62% (Br); 44% (Cl))

$^1$H NMR (CDCl$_3$): $\delta$ 7.47 (s, CH, 1H), 7.19 (s, CH, 1H), 6.90 (s, CH, 1H), 5.96 (m, CH, 1H), 5.24-5.26 (dd, CH, 2H.), 4.53 (d, CH$_2$, 2H).
Chapter 6 References


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