Isolation of a Phenyl Substituted Imidazolinium Ligand and its Transformation into a Transition metal N-Heterocyclic Carbene Complex

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Abstract

In this study we describe a class of compounds known as N-heterocyclic carbenes. These compounds are well known for their strong σ-donating character. A reliable synthetic route for the synthesis of a phenyl substituted N-heterocyclic carbene on a tridentate pincer ligand framework is presented. The hope is that the stability of the phenyl substituted tridentate framework would make for a suitable ligand system when incorporated into high spin transition metal complexes. The phenyl substituted N-heterocyclic carbene has been synthesized and coordinated to Cu, Co and Fe starting materials. Crystallographic and electrochemical studies have been carried out for a N-heterocyclic carbene Cu(I) complex. Preliminary reactivity studies on the Cu(I) complex have been started. Characterization of Co(II) and Fe(II) NHC complexes are underway.
Introduction

History of N-heterocyclic Carbenes

With carbenes being significant actors as transient intermediates, carbene chemistry has been an area of growing interests over the past five decades.\textsuperscript{1-4} After Doering introduced carbenes to organic chemistry in the 1950s and Fischer introduced them to organometallic chemistry in 1964, carbenes have developed a repertoire of interesting synthetic and catalytic applications.\textsuperscript{5,6} Over the past two decades, we have developed a keen understanding of carbene chemistry such as the effects of carbene substituents have on ground-state spin multiplicity. Using various synthetic techniques, characterizations and analysis of reactivity, our understanding of carbene chemistry has advanced significantly.

Understanding the stability of singlet carbenes was one of the key interests of chemists during the early developments of carbene chemistry. It was know that the electronic and steric features of carbene substituents had an effect on the ground-state multiplicity and therefore the stability of carbenes. The electronic and steric effects that carbene substituents have on carbene spin multiplicity allows for specific tailoring of carbene substituents that cater to the desired chemistry of a carbene. For example the singlet state of a carbene is favored by a relatively large $\sigma$-$P_x$ separation. This was experimentally confirmed when Hoffman observed that a potential of 2 eV is needed to achieve a singlet ground state while a potential below 1.5 eV gives a triplet ground state.\textsuperscript{7} Moreover, the steric and electronic effects that carbene substituents have on spin multiplicity bare resemblance to crystal-field theory relationships where strong-fields have low spin configurations and weak field have high spin configurations.

Though a wide range of carbenes were synthetically prepared and characterized in the 1950s\textsuperscript{8}, many of these novel carbenes were unstable and stability was not a concern until the
In general, bulkier substituents can be used to stabilize both singlet and triplet carbenes. When dealing with triplet carbenes, which are typically highly reactive, stabilization can only be achieved with sterically bulky substituents. In fact, designing stabilizing substituents for singlet carbenes has proven to be much easier than designing substituents for triplet carbenes. This arises from the fact that all that is needed to stabilize a singlet carbene is a substituent that preserves the electroneutrality of the carbene center.

Of particular interest are the stabilized singlet carbenes, diaminocarbenes, due to their practical use as ligands in transition metal catalysts. More specifically, N-heterocyclic carbenes are target molecules being good σ-donating nucleophiles of great practicality in organic and organometallic chemistry. Arduengo reported the synthesis, structure, and characterization of the first crystalline N-heterocyclic Carbenes (NHCs). Since then, NHCs have gained considerable attention over the past few decades in the field of coordination chemistry. In fact NHCs have notable properties that have allowed for the synthesis of Fischer-type carbene complexes of most transition metals.

**Stability of Carbenes (sterics)**

Being that carbenes, especially during earlier period of development, were known to be unstable developing methods of tuning stability was a primary concern. It was well established that a simple way to stabilize carbenes is through adding sterically bulky substituents to carbenes. This method can help stabilize both singlet and triplet carbenes. Moreover, bulky substituents that lead to a linear geometry are favored for triplet carbenes. This is due to the fact that increasing the size of bulky substituents as well as the number of bulky substituents broadens the carbene bond angle. For example dimethylcarbene is bent with a bond angle of 111° which leads to a singlet state. Conversely, di(tert-butyl) carbenes and
diadamantylcarbenes have carbene bond angles of 143° and 152° respectively which favor triplet states.\textsuperscript{12a,b}

**Stability of N-heterocyclic Carbenes (Electronics)**

The effects of carbene substituents’ electronegativity on multiplicity are currently well understood. It is known that $\sigma$-electron-withdrawing groups favor the singlet configuration over the triplet state. This is attributed to the fact that the $\sigma$-electron withdrawing substituents inductively stabilize the $\sigma$-nonbonding orbital by increasing its s character and leaving the $P_\pi$ orbital unperturbed\textsuperscript{3}. The stabilization of the $\sigma$-nonbonding orbital cause an increase the in the $\sigma$-$P_\pi$ gap which leads to the singlet configuration. Conversely a smaller $\sigma$-$P_\pi$ gap, which would result from electropositive substituents, would lead to a triplet configuration. This was demonstrated by Harrison et al\textsuperscript{9a,b} who showed that carbene multiplicity changes from triplet to singlet when electropositive Li substituents are replaced with hydrogen then fluorine atoms.
**Figure 1.** Influence of electronegativity of carbene substituents on ground state spin multiplicity.

The shift from triplet to singlet is due to a significant increase in the $\sigma$- $P_z$ gap due to the increase in electronegativity of the carbene substituents. This shift is illustrated in Figure 1. The carbene with electropositive lithium has the singlet configuration being the state with a higher energy and the triplet configuration being the state with the lower energy implying that the triplet state is preferred. A similar description can be made for a carbene with two hydrogens. The hydrogen case is rationalized through the fact that the hydrogens are not $\sigma$-electron withdrawing enough to stabilize the $\sigma$ nonbonding orbital. This results in the triplet state being favored. In the carbene with two fluorine substituents, the fluorine act as good $\sigma$-electron withdrawing groups which inductively stabilizes the $\sigma$-nonbonding orbital which results in the singlet state being favored. Generally carbene are relatively reactive and electronic tuning serve as a better tool for stabilization that steric tuning. Moreover it is relatively more facile to stabilize a singlet carbene than a triplet carbene whether it is through steric or electronic tuning. With this in mind it is no surprise that electronically tuning carbenes of the singlet state has been a particular interest in the field of carbene ligand synthesis.
Figure 2. (a) Molecular orbital diagram for carbenes with $\sigma$-electron withdrawing substituents. (b) Molecular orbital diagram for carbenes with $\sigma$-electron donating substituents.

As shown in figure 2a, the non-bonding $\sigma$ orbital ($a_1$) is stabilized by $\sigma$ electron withdrawing groups, which lead to a decrease in the energy of the $\sigma$ orbital ($a_1$). While the non-bonding $\sigma$ orbital decreased in energy the $P_\pi$ orbital remained unchanged which led to a significant increase in the $\sigma$-$P_\pi$ gap. This leads to the $\sigma$ ($a_1$) orbital being filled and the $P_\pi$ orbital being left unoccupied. Since there are no unoccupied electrons the multiplicity is 1, which indicates a singlet. In figure 2b, the energy of the non-bonding $\sigma$ orbital goes up due to which significantly decreased the $\sigma$-$P_\pi$ gap. This lead to both the $\sigma$ ($a_1$) orbital and the $P_\pi$ orbital being occupied by one electron, which is indicative of a triplet.

Though inductive electronic effects have a large influence on carbene spin multiplicity, such as in a carbon with electropositive Li substituents, mesomeric effects can have a much larger influence on multiplicity. There are two classes of carbene substituents: X-type ($\pi$-electron donating substituents) and Z-type ($\pi$-electron withdrawing substituents). Examples of X-type substituents include fluorine, chlorine and iodine. Examples of Z-type substituents include carbonyl, boryl and silyl substituents. Z-type substituents lead to linear or quasilinear carbenes in the triplet state. X-type substituents lead to bent or quasilinear carbenes in the singlet state. The interactions responsible for each spin configuration involve the carbon orbitals ($s$, $P_x$, $P_y$, $P_z$) and the orbitals of the $\sigma$ and $P_\pi$ orbitals of the carbene substituents.
Figure 3. X type π-electron donating substituents, σ- electron withdrawing substituents on carbene.

X-X carbenes are predicted to be bent with a singlet spin configuration. The symmetric combination of lone pairs on the π-electron donating carbene substituents (also σ- electron withdrawing substituents as noted in Figure 1) increases the energy of P_π the orbital. This causes an increase in the σ- P_π gap that leads to a singlet configuration as shown in Figure 4. Moreover carbene-X type substituent bonds acquire multiple bond character, which suggests that there is a superposition of two zwitterionic structures with a negatively charged central carbene. Carbenes that are representative of this structure include dimethoxycarbenes, dihalocarbenes and diaminocarbenes.

The groups of XX carbenes that are of primary focus in this thesis are diaminocarbenes. Again, these carbenes contain two nitrogen atoms, which are good π- donating and σ- attracting substituents. Diaminocarbenes are relatively stable since the lone pairs on the nitrogen atoms significantly reduce the electron deficiency of the carbene. Additionally, the nitrogen atoms inductively stabilize the electron pair on the central carbene. This is illustrated in Figure 4. The first person to note the increase in stability of carbenes by addition of two amino groups was Wanzlick.\textsuperscript{13} Upon this realization, in 1960, Wanzlick attempted to synthesize 1,3-diphenylimidazolidin-2-ylidene.\textsuperscript{13} This reaction proceeded through thermal elimination of chloroform as shown in Scheme 1. In another example, Wanzlick and co-workers showed that an imidazolium salt can be deprotonated by potassium tert-butoxide.\textsuperscript{13} The synthesis of these
carbenes salts led to Arduengo\textsuperscript{1,2} preparing the first stable crystalline carbenes as shown in Scheme 2.

**Figure 4.** The nitrogen lone pairs in the diaminocarbene stabilize the empty p-orbital of the carbene.

**Scheme 1**

\[
\begin{align*}
\text{Scheme 2} \\
\text{a: } R=\text{Ph}, R'=\text{H} \\
\text{b: } R=R'=\text{Ph} \\
\text{c: } R=\text{Ad}, R'=\text{H}
\end{align*}
\]
Carbenes a and b, in Scheme 2, were trapped but not isolated. Carbene c is a thermally stable colorless crystalline compound with a melting point between 240-241°C without decomposition. The imidazolium salts and carbenes in Scheme 2 lay the framework for the ligand that will be studied extensively throughout this thesis.

**[NCN] N-heterocyclic Carbenes**

Arduengo’s previous work influenced the development of a variety of NHC donors in polydentate arrays in combination with donors such as pyridine, oxazolines, and phosphines to give tripodal and pincer ligands. An example of this development comes from Fryzuk and co-workers who successfully described the coordination chemistry of a tridentate diamidocarbene ligand (Figure 5). The motive behind developing robust novel catalysts is to improve catalyst shelf life. A major issue in designing selective, homogeneous catalysts with fast turnovers is that the ancillary ligands incorporated into the metal complexes often dissociate or undergo side reactions that significantly alter binding modes. Through structural and electronic modifications, the goal is to develop efficient catalysts with robust multidentate NHC ligands that increase the catalyst stability.

Fryzuk and co-workers developed a diamido NHC ligand system and extensively studied the coordination chemistry with tantalum starting materials. Fryzuk worked with two tridentate diamido NHC ligands as shown in Figure 5. These ligands are NHC ligands flanked by two
amine arms with different substituents as shown below. Fryzuk and co-workers previously reported the synthesis of $^{\rho}_{-}\text{Tol}[\text{NCN}]-\text{H}_2$ and $^{\text{Mes}}[\text{NCN}]-\text{H}_2$ in the literature.\textsuperscript{19}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{NHC flanked by two amino groups with \textit{para}-tolyl substituents (left). NHC flanked by two amino groups with mesityl substituents (right).}
\end{figure}

**Tridentate Coordination Mode for NCN Ligand Systems**

A tridentate coordination system is a favorable as it is less likely to dissociate from the metal center, compared to bidentate and monodentate ligands, which translates to a longer shelf life and greater catalytic efficiency. Fryzuk and co-workers sought study tridentate coordination mode for the NCN ligand system. Many groups have incorporated tridentate coordination binding ligand systems into lithium metal centers using lithium amide precursors.\textsuperscript{22-24} Building on this work, the Fryzuk group sought to promote the tridentate binding mode of the diamido NHC ligand, through the synthesis of dilithium diamido NHC derivatives. 2 equivalents of butyl lithium were added to both the $^{\rho}_{-}\text{Tol}[\text{NCN}]-\text{H}_2$ and $^{\text{Mes}}[\text{NCN}]-\text{H}_2$ ligand systems in hexanes as shown in Scheme 3.

**Scheme 3**
Due to the low solubility of the dilithium diamido NHC derivative a solid state crystal structure was not obtained. The structure shown in Scheme 3 was presumed on the basis of a similar dilithium diamido N-heterocyclic phosphine derivative Li₂[NPN]²⁵⁻²⁶. The dilithium diamido NHC derivative were both characterized spectroscopically.

**Tridentate Isopropyl Substituted NHC [PCP]**

This was one of the first developments of tridentate coordination mode for an NCN system. This inspired the development of new classes of tridentate ligands such as diphosphino carbenes ([PCP] ligands).²⁷ The initial goal of the Fryzuk group was to synthesize an unsaturated NHC-based PCP ligand system. The proposed restrosynthetic pathway is shown in Scheme 6. The rationale was that this ligand system could be assembled through glyoxal condensation of the appropriate aryl amine to form the corresponding diimine.³¹ The diimine would then be condensed using formaldehyde and HCl to give the imidazolinium salt NHC precursor.

**Scheme 4**

![Scheme 4 Diagram]

Efforts to condense the diimine has been met with failure when use of glyoxal and 2,3-butadiene were both attempted in condensation reactions. This caused the Fryzuk group to turn to the saturated version of the NHC shown in Scheme 4. The assembly requires chemospecific alkylation at the amine site while the phosphines are protected as phosphine sulfides using S₈ in the presence of 1,2-dibromoethane as shown in scheme 5. The resulting product is further reacted
with triethylorthoformate in the presence of NH$_4$PF$_6$ to give the imidazolinium salt.

**Scheme 5**

The imidazolinium salt is soluble in THF and CH$_2$Cl$_2$ but insoluble in nonpolar solvents such as toluene and hexanes. The ligand precursor was fully characterized by NMR, X-ray crystallography and elemental analysis. The deprotonation of the imidazolium salt with KHMDS gives the free PCP carbene as shown in Scheme 6, while the use of the base KO'Bu gives a neutral protected carbene (also shown in Scheme 6).
Scheme 6

Cationic Group 10 Metal hydrides

It is common to deprotonate the imidazolinium salt with bases like KH and KHMDS prior to generating the metal NHC complex.\textsuperscript{38-39} Interestingly it is also possible to add the NHC precursor, which is acidic, to metal starting materials with basic ligands. The basic ligand in the metal starting material may serve as an internal base. One may also form metal NHC complex through transmetallation using silver NHC complexes. Finally, oxidative addition of the iminium C-H bond is another useful way to introduce an NHC into a metal complex. Upon preparing the isopropyl substituted [{PCP}H]PF\textsubscript{6} salt, the Fryzuk group completed series of oxidative addition reactions with group 10 metals. Specifically, C-H oxidative addition was observed in the isopropyl substituted [{PCP}H]PF\textsubscript{6} upon adding Ni(COD)\textsubscript{2}, Pd(PPh\textsubscript{3})\textsubscript{4} and Pt(PPh\textsubscript{3})\textsubscript{4} which contain Ni(0), Pd(0) and Pt(0) respectively (Scheme 7)

Scheme 7
NHC Rhodium Complex

Rhodium transition metal complexes are also of interest due to their applications to alkyne dimerization\textsuperscript{28}, C-H bond activation\textsuperscript{29}, and carbon dioxide reduction\textsuperscript{30}. The Fryzuk group sought to study the coordination of an isopropyl substituted [PCP] ligand to a Rh starting material. The study began with the deprotonation of the ([PCP]H)PF$_6$ ligand precursor using KHMDS in THF. Next the carbene product was to a half equivalent of [Rh(COD)Cl]$_2$ to give [PCP]RhCl shown in Scheme 8.

Scheme 8

X-ray diffraction analysis was done on [PCP]RhCl after obtaining crystals through slow evaporation of THF. The structure assumes a slightly distorted square planar geometry. This distorted geometry is similar to that of the cationic [PCP] platinum and palladium complexes.\textsuperscript{31} The central NHC ring is twisted above and below the plane defined by the carbene and the phosphine donors with torsion angles 46.23 and 37.38°. This is similar to the torsion angles of 41.5 and 35.5 in the complex.\textsuperscript{32} The Rh1-C1 bond distance is...
1.929(5) Å, which is relatively short, compared to typical Rh-C carbene bond distances.\textsuperscript{32} This is likely due to the trans influence of the chloride adduct.

\textbf{Figure 6.} The solid state crystal structure of [PCP]RhCl assuming a tridentate configuration and distorted square planar geometry.

\section*{Results and Discussions}

\section*{Synthetic Route}

The plan for the synthesis of the tridentate NHC began with condensing an aniline derivative with glyoxal. A diimine would be produced from this reaction, which would have to be reduced to give the desired diamine (Scheme 9). The reduction would be done using LiAH_4 at -120 °C in the glovebox to give the diamine species. The condensation reaction gave a low yield, which led us to turn to using dibromoethane instead of glyoxal.

\textbf{Scheme 9}
The new plan was to react \( o \)-fluoroaniline with dibromoethane at 130 °C in the presence of NEt'Pr\(_2\). The reaction mixture was extracted using KOH solution and dichloromethane (DCM). The product is contained in the DCM phase while the aqueous phase contained protonated NEt'Pr\(_2\). The combined organic layers were dried using MgSO\(_4\) and filtered through celite. Upon concentrating organic layer via rotary evaporation, the contents were recrystallized in EtOH. Crystals crashed out of the EtOH solution and starting materials and reaction byproducts were contained in the EtOH. Upon removing residual solvent from the white crystalline solid we proceeded to the next reaction. In the next reaction we converted the fluorine substituted phenyl rings to phosphine side-arms using KPPh\(_2\) at 100 °C in dioxane under N\(_2\) as shown in (Scheme 10). Upon cooling the reaction is worked up using H\(_2\)O and DCM. The DCM layer is concentrated and the reaction mixture is recrystallized in toluene. Finally, in a glovebox atmosphere, we add the diphenylphosphine NHC precursor to CH(OEt)\(_3\) in excess, in the presence of 1 equivalent of NH\(_4\)PF\(_6\) and heated at 100 °C. The reaction was cooled to room temperature and pentane was added. A white power crashed out of solution and was filtered out and to give the desired imidazolinium salt: (\( \text{Ph}^\text{P} [\text{PCP}] \text{H} \))PF\(_6\).

**Scheme 10**

![Scheme 10](attachment:image.png)
Scheme for the synthetic route to $(\text{Ph}[\text{PCP}]\text{H})\text{PF}_6$.

The diamine ligand was characterized by $^1\text{H}$ NMR. The phenyl protons show up as a multiplet between 6.6-7.0 ppm, backbone protons as a singlet at 3.45 ppm and the amine protons show up as a singlet at 4.15 ppm (Figure 7).

![Figure 7](image)

$^1\text{H}$ NMR of the diamine NHC precursor in CD$_2$Cl$_2$

The diphenylphosphine compound was characterized by $^1\text{H}$ NMR and $^{31}\text{P}$ NMR. The aryl region is found as a multiplet between 6.6-7.3 ppm. This indicates a downfield shift of the aryl protons. The backbone protons show up as a singlet at 3.28 ppm. The amine group is found as a broad singlet at 5 ppm. The amine protons in the diphenylphosphine are shifted downfield relative to the amine protons in the diamine. The phosphine groups show up as a singlet at -25.967 ppm in $^{31}\text{P}$ NMR.
Figure 10

$^1$H NMR and $^{31}$P NMR of the diphenylphosphine ($^{Ph}$[PCP]H)PF$_6$ precursor in CD$_2$Cl$_2$

We characterized ($^{Ph}$[PCP]H)PF$_6$ by $^1$H NMR and $^{31}$P NMR. The aryl protons show up around 7.3-6.6 ppm. The backbone protons show up as a singlet at 3.32 ppm. The carbene proton shows up as a singlet a 9.28 ppm. Various solvent peaks are present as well, such as THF at 3.56 and 1.72 ppm, diethyl ether at 3.31 and 1.05 ppm, and DCM at 5.7 ppm. The phosphorus signal in the $^{31}$P NMR shows up as a singlet at 15.6 ppm. The phosphorus signal shifts drastically when going from the diphenylphosphine to ($^{Ph}$[PCP]H)PF$_6$ from -25.967 ppm to 15.6 ppm. This is expected since PF$_6$ counteranion changes the phosphorus environment resulting in a shift downfield (Figure 8).

Figure 8

$^1$H NMR and $^{31}$P NMR of ($^{Ph}$[PCP]H)PF$_6$ in DMSO-$d^6$

Synthetic Route to ($^{Ph}$[PCP]H)Cl

The synthesis of the phenyl substituted imidazolinium salt, with a chloride counteranion, was complete by Pan and co-workers.$^{40}$ Two equivalents of o-fluoroaniline was combined with 1,2-dibromoethane in the presence of NEt$_2$Pr$_2$ at 130 °C, just as in scheme 14, to give the corresponding diamine. The diamine was then reacted with KPPH$_2$ in refluxing dioxane to obtain the diphenylphosphine imidazolinium precursor. Next triethylorthoformate was added in the presence of HCl to the diphenylphosphine at 120 °C (Scheme 11). The imidazolinium salt was
analyzed by $^1$H NMR and $^{31}$P NMR. The carbene proton signal, taken in CD$_2$Cl$_2$, showed up as a singlet at 8.14 ppm.

**Scheme 11**

The chloride counteranion in the imidazolinium salt in Scheme 11 can be abstracted using TlPF$_6$ to give the corresponding PF$_6$- salt (Scheme 12). In the $^{31}$P NMR the PF$_6$ signal shows up as a septet at -143.3 ppm confirming the transformation from the chloride salt to the PF$_6$ salt. This gives an alternate route for synthesized the imidazolinium PF$_6$ salt.

**Scheme 12**

**Metallation with Pt(0) and Pd(0)**

The chloride imidazolinium salt was reacted with Pt(PPh$_3$)$_4$ to give the complex shown in scheme 16. The structure formed is a NHC-Pt(II)-chloride species which contrast with the C-H bond oxidative addition isopropyl substituted PF$_6$ salt reported by Fryzuk and coworkers$^{31}$. The Thomas group also reported the coordination of this NHC ligand to Pd(PPh$_3$)$_4$ and now we are focusing on its coordination to other metals. These metal starting materials are high low spin and form 4-coordinate square planar M(II) complexes with the NHC ligand$^{40}$. 
Scheme 13

Metallation with Cu(I)

While the Thomas Group previously reported coordination low spin Pt(II) and Pd(II) complexes, we now focus on the coordination of a high spin Cu(I) starting material to our imidazolinium PF$_6$ salt (scheme 14). The reaction begins with dissolving $^{Ph}[PCP]H$PF$_6$ in THF and deprotonating with KHMDS at -120 °C in the glovebox. After 30 minutes of stirring at room temperature, the reaction is filtered through celite in order to remove KPF$_6$. Next CuI(PPh$_3$)$_3$ was added while stirring at room temperature. After letting the reaction run overnight a yellow solid crashed out of solution. The yellow solid is filtered through celite and dissolved in DCM. The THF layer contains unreacted ligand, KHMDS and HMDS. The DCM layer contained our $^{Ph}[PCP]$CuI complex.

Scheme 14

The $^{Ph}[PCP]$CuI complex was characterized by $^1$H NMR and $^{31}$P NMR in CD$_2$Cl$_2$. The CuI(PPh$_3$)$_3$ compound was a favorable starting material since it coordinated to make a stabilized
d^{10} diamagnetic NHC complex. This complex can easily be analyzed by $^1$H NMR without having to assign paramagnetic shifts. Additionally, the complex’s diamagnetic nature allows for analysis by $^{31}$P NMR.

In the $^1$H NMR for $^{Ph}[\text{PCP}]\text{CuI}$, 11 distinct proton signals are observed while the expected number of proton shifts is 7 (Figure 9). The additional four peaks may be solvent peaks. The aryl protons show up between 7.56-7.0 ppm. The backbone protons show up as a multiplet at 3.88 ppm and 5.4 ppm. There is a drastic phosphorus shift from 15.6 ppm to -14.216 going from the PF$_6$ salt to the $^{Ph}[\text{PCP}]\text{CuI}$ complex.

**Figure 9**

$^1$H NMR and $^{31}$P NMR of the $^{Ph}[\text{PCP}]\text{CuI}$ complex in CD$_2$Cl$_2$.

**Crystallographic Studies of $^{Ph}[\text{PCP}]\text{CuI}$**

Crystals of the $^{Ph}[\text{PCP}]\text{CuI}$ complex were grown in CD$_2$Cl$_2$. The X-ray crystal structure of the $^{Ph}[\text{PCP}]\text{CuI}$ complex is shown in Figure 10. The geometry between the N-C-N plane and the C(NHC)-Cu bond vector is trigonal planar. The N1-C(NHC)-N2 bond angle is 106.9°. The N1-C(NHC)-Cu angle is 128.15° and the N2-C(NHC)-Cu plane has an angle of 122.89°. The central Cu is distorted tetrahedral.
Figure 10. Displacement ellipsoid (50%) representation of the $^{Ph}[\text{PCP}]\text{CuI}$ complex. For clarity, all hydrogen atoms are omitted. Relevant interatomic distances (Å) and angles (deg):

$\text{Cu1- I1, 2.6247(3); Cu1-P1, 2.2176(7); Cu1-P2, 2.2768(7); Cu1-C39, 1.982(2); N1-C39-N2, 106.9(2); N1-C39-Cu1, 128.15(17); N2-C39-Cu1, 122.89(17); I1-Cu1-P1, 115.28(2); I1-Cu1-P2, 104.900(19); P1-Cu1-P2, 126.00(3); I1-Cu1-C39, 120.54(7); P1-Cu1-C39, 97.97(7); P2-Cu1-C39, 90.67(7).}$

**Electrochemical Studies of $^{Ph}[\text{PCP}]\text{CuI}$ Complex**

Cyclic voltammetry of the $^{Ph}[\text{PCP}]\text{CuI}$ complex reveals two-electron oxidation (Figure 11). The first oxidation occurs at a potential of -0.153 V and is fully reversible. The second oxidation is quasi-reversible and occurs at a voltage of +0.239 V. The first oxidation is going from Cu(I) to Cu(II). The second oxidation may either be going from Cu(II) to Cu(III) or it may be the oxidation of the ligand. We proceed to try oxidizing our $^{Ph}[\text{PCP}]\text{CuI}$ species with AgPF$_6$ as described below.
Figure 11. CV for $^{Ph}[PCP]CuI$. (2 mM in 0.4 M [$^4Bu_4N$][PF$_6$] in THF, scan rate = 100 mV/s, potentials are referenced to Fc, starting potential: 0.50 V, lowest potential: -0.80 V).

**Oxidation With AgPF$_6$**

We tried oxidizing the $^{Ph}[PCP]CuI$ complex with AgPF$_6$ to go from Cu(I) to Cu(II) (scheme 18). The Cu(I) species was dissolved in DCM and AgPF$_6$ was added under light sensitive conditions and in a glovebox atmosphere. The reaction was filtered after 24 hours to remove Ag(0). The DCM was pumped off to give a pink solid. A speculative product for this oxidation is shown in Scheme 15.

**Scheme 15**
The reaction contents were analyzed by $^1$H NMR and $^{31}$P NMR (Figure 12). The product(s) obtained from this oxidation are unknown. It is notable that the proposed oxidation from Cu(I) to Cu(II) did not occur since a paramagnetic $^1$H NMR would be observed. The presence of phosphorus signal in the $^{31}$P NMR spectrum also confirms that Cu(II) wasn’t formed. A possibility is that a transmetallation may have occurred between Cu and Ag. Another possibility is that the oxidant may have abstracted the iodide. It is also possible that the addition of AgPF$_6$ may have led to the decomposition of our complex.

Figure 12. $^1$H NMR and $^{31}$P NMR of the Ph[PCP]CuI complex in CD$_2$Cl$_2$.

In the future we plan on oxidizing our Ph[PCP]CuI with [Cp$_2$Fe](PF$_6$) (Scheme 16). Since this is a milder oxidant we propose that we may transform out Cu(I) species to Cu(II) without decomposing our ligand.

Scheme 16
Metallation with Co(II) Starting Material

We attempted to metallate the (Ph[PCP]H)PF$_6$ salt with CoCl$_2$(PPh$_3$)$_2$. The PF$_6$ salt was dissolved in THF and deprotonated with KHMDS at -120 °C. The reaction mixture was warmed to room temperature and filtered, after 30 minutes of stirring, through celite for the removal of KPF$_6$. Next CoCl$_2$(PPh$_3$)$_2$ was added to the reaction mixture and stirred over 24 hours (Scheme 17). A red solid crashed out after 24 hours and was filtered through celite. The solid was dissolved in DCM, pumped and analyzed by $^1$H NMR. The structure proposed in scheme 19 is speculative since we’ve only been able to obtain a paramagnetic $^1$H NMR. Additionally, due to the paramagnetic nature of the complex, the reaction contents could not be analyzed by $^{31}$P NMR.

**Scheme 17**

In the $^1$H NMR for the Ph[PCP]CoCl$_2$ complex, 12 distinct proton signals are observed while the expected number of proton shifts is 7 (figure 13). The additional five peaks may be solvent peaks. We tried recrystallizing in CD$_2$Cl$_2$, but the solubility was too low for an ideal recrystallization system. Additionally, more solid slowly crashed out of the CD$_2$Cl$_2$ solution over
24 hours meaning the solubility of our reaction contents went down over time. We posit that CD$_2$Cl$_2$ may be decomposing our ligand. Dimerization of our ligand may also cause the shift in solubility.

![Figure 13. $^1$H NMR of the NHC $^{Ph}[PCP]CoCl_2$ complex in CD$_2$Cl$_2$](image)

**Metallation with Fe(II) Starting Material**

Finally, we tried coordinating ($^{Ph}[PCP]H$)PF$_6$ to FeCl$_2$(PPh$_3$)$_2$. ($^{Ph}[PCP]H$)PF$_6$ was dissolved in THF and deprotonated with KHMDS at -120 °C (Scheme 18). After 30 minutes, KPF$_6$ was filtered out through celite. Next FeCl$_2$(PPh$_3$)$_2$ was added at room temperature and the reaction was stirred for 24 hours. The next day red solid crashed out and was filtered and dissolved in DCM. The DCM was pumped off and the residual solid was analyzed by $^1$H NMR in CD$_2$Cl$_2$.

**Scheme 18**

$^{Ph}[PCP]FeCl_2$, 11 distinct proton signals are observed while the expected number of proton shifts is 7 (figure 16). The additional four peaks may be solvent peaks. Just as in the Co(II) case, solubility of the $^{Ph}[PCP]FeCl_2$ in CD$_2$Cl$_2$ decreased overtime. We think the CD$_2$Cl$_2$ may be decomposing our $^{Ph}[PCP]FeCl_2$ species as well.
The $d^{10}$ configuration of the $\text{Ph}[\text{PCP}]\text{CuI}$ complex makes the species diamagnetic and relatively simple to analyze by $^1\text{H}$ NMR. Also, this electronic configuration causes the complex to be quite stable since all of the $d$ orbital electrons are filled. Thus this stable complex is easy to recrystallize in polar solvents such as DCM without decomposition. In contrast, both the $\text{Ph}[\text{PCP}]\text{FeCl}_2$ and $\text{Ph}[\text{PCP}]\text{CoCl}_2$ complexes are paramagnetic complexes that seem to decompose in polar solvents such as DCM. The identity of the Fe and Co species has not been confirmed, since crystals suitable for X-ray crystallography have not been grown. Work on the Fe(II) and Co(II) is still ongoing.
Conclusions

Thus far, we have reported the synthesis of the first tridentate pincer ligand containing an N-heterocyclic carbene. The initial synthetic route using glyoxal to condense o-fluoroaniline was unsuccessful. Using dibromoethane, in the presence of NEt\text{Pr}_2 and o-fluoroaniline, to synthesize the diamine ligand served as a successful first step. The synthetic route discussed culminated a procedure that reliably yields the desired imidazolinium salt. We’ve reported clean $^1$H NMR and $^{31}$P NMR spectra of the $^{(Ph)}$[PCP]H)PF$_6$ and the $^{Ph}$[PCP]CuI complex. We have also obtained a crystal structure for $^{Ph}$[PCP]CuI. We have characterized the geometry about the central Cu(I) as distorted tetrahedral. We have also reported CV data for our $^{Ph}$[PCP]CuI complex and found that this Cu(I) species can undergo a 2-electron oxidation. We propose that the first oxidation, which is fully reversible, goes from Cu(I) to Cu(II). The second oxidation which is quasi-reversesible, may either go from Cu(II) to Cu(III) or may be the oxidation of the
ligand. We then tried oxidizing $^{Ph}[PCP]Cu$ with AgPF$_6$ to go from Cu(I) to Cu(II) but this does not give a clean product. Finally we tried coordinating $(^{Ph}[PCP]H)$PF$_6$ to Fe(II) and Co(II) starting materials. While clean paramagnetic $^1$H NMR spectra for the $^{Ph}[PCP]FeCl$_2 and $^{Ph}[PCP]CoCl$_2 complexes were obtained their identities are yet to be confirmed. We plan on solving a crystal structure for both Fe(II) and Co(II) and studying the electrochemical properties of each complex. We plan to continue our focus on coordinating $(^{Ph}[PCP]H)$PF$_6$ to different high spin transition metal starting materials and studying the redox activity of these complexes.

**Experimental**

**General Considerations**

Reactions sensitive to air or moisture were performed in an MBraun LABmaster sp glove box under nitrogen atmosphere. Solvents used for such reactions were degassed and dried by sparging with Argon gas, passing through an activated alumina column, and storing under 3 Å molecular sieves in the glovebox. NMR data was collected using a Varian Inova 400MHz spectrometer. $^1$H NMR shifts were referenced to residual solvent peaks, and all $^{31}$P NMR shifts were referenced to a standard of 85% H$_3$PO$_4$. Deuterated benzene and chloroform were purchased from Cambridge Isotope Laboratories, Inc. Deuterated solvents for air sensitive materials were degassed and dried via repeated freeze-pump-thaw cycles and dried over 3 Å molecular sieves. Reactants and bench solvents were purchased from Aldrich, Strem, or Alfa
Aesar and used without further purification. Elemental microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA.

**Synthesis of N,N-bis(2-fluorophenyl)ethane-1,2-diamine**

In a 100 mL pressure flask equipped with a reflux condenser, o-fluoroaniline (11.5 mL, 120 mmol), 1,2-dibromoethane (5.1 mL, 60 mmol) and diisopropylethylamine (22 mL, 126 mmol) were heated to 130 °C for 24 hours. Upon cooling to room temperature the reaction mixture was extracted using with H₂O (50 mL) and dichloromethane (50 mL). A 0.5 KOH solution (50 mL) was added to the aqueous layer followed by another extraction with 50 mL of dichloromethane. The combined organic layer was dried with MgSO₄ and then filtered through a filter frit. The volatiles were then removed via rotary evaporation. The residual white solid was then recrystallized in EtOH to give a pure powdery white solid (11.9 g, 85 %). ¹H NMR (CD₂Cl₂): δ 7.00 (m, 4H, Ar-H), 6.80 (m, 2H, Ar-H), 6.60 (m, 2H, Ar-H), 4.15 (s, br, 2H, NH₂), 3.45 (s, 4H, CH₂).

**Synthesis of N,N-bis(2-(diphenylphosphino)phenyl)ethane-1,2-diamine**

In a 100 mL round bottom flask N,N-bis(2-fluorophenyl)ethane-1,2-diamine (1.09 g, 4.4 mmol) was dissolved in degassed, dry dioxane (40 mL) and transferred to a pressure flask containing KPPh₂ (2.47 g, 11.03 mmol). The reaction was refluxed for 24 hours. Upon cooling the solvent was removed *in vacuo* and the residual solid was extracted with H₂O (50 mL) and dichloromethane (50 mL). The combined organic layers were dried with MgSO₄ and filtered through a filter frit. The volatiles were then removed via rotary evaporation. The remaining solids were recrystallized in toluene, yielding an analytically pure powdery white solid (2.04 g, 80%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.3 (m, 8H, Ar-H), 7.10 (m, 4H, Ar-H), 6.96 (m, 12H, Ar-H), 6.74 (m, 2H, Ar-H), 6.6 (m, 2H, Ar-H), 5.00 (s, br, 2H, NH₂), 3.28 (s, 4H, CH₂). ³¹P NMR
Synthesis of 3-Bis(o-diphenylphosphino)phenyl-1H-imidazolinium Hexafluorophosphate, (Ph[PCP]H)PF₆

N,N-bis(2-(diphenylphosphino)phenyl)ethane-1,2-diamine (200 mg, 0.344 mmol) was added to CH(OEt)₃ (10 mL) in the presence of NH₄PF₆ (56 mg, 0.344 mmol) in a 20 mL vial. The reaction was allowed to reflux for 24 hours to ensure completion. The reaction was quenched with 20 mL of pentane and pale white solid crashed out of solution. The precipitate was filtered through a filter frit and washed with pentane. Volatiles were removed from the collected precipitate in vacuo to afford a white analytically pure product (210 mg, 83%). ¹H NMR (400 MHz, d⁶-DMSO): δ 9.28 (s, 1H, C-H), 7.3 (m, 8H, Ar-H), 7.10 (m, 4H, Ar-H), 6.96 (m, 12H, Ar-H), 6.74 (m, 2H, Ar-H), 6.6 (m, 2H, Ar-H), 3.32 (s, 4H, CH₂). ³¹P NMR (161.8 MHz, C₆D₆): δ -15.606.

Synthesis of Ph[PCP]CuI

A solution of KHMDS (5.0 mg, 0.027 mmol) in THF (3 mL) was added to a solution of (Ph[PCP]H)PF₆ (20 mg, 0.027 mmol) in THF (10 mL) at -120 °C. Next the reaction mixture was filtered through celite and added to a 20 mL vial with CuI(PPh₃)₃ (26.38 mg, 0.027 mmol). The reaction was allowed to stir at room temperature for 24 hours, resulting in the formation of a yellow precipitate. The yellow precipitate was collected via filtration and dissolved in DCM. The volatiles were removed in vacuo to afford analytically pure product (20.58 mg, 90%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.57 (m, 8H, Ar-H), 7.40 (m, 4H, Ar-H), 7.20 (m, 12H, Ar-H), 7.10 (m, 2H, Ar-H), 7.05 (m, 2H, Ar-H), 3.80 (s, 2H, CH₂), 3.60 (s, 2H, CH₂). ³¹P NMR (161.8 MHz, C₆D₆): δ -14.216.

Synthesis of Ph[PCP]CoCl₂
A solution of KHMDS (5.0 mg, 0.027 mmol) in THF (3 mL) was added to a solution of 
\((^\text{Ph}[\text{PCP}]\text{H})\text{PF}_6\) (20 mg, 0.027 mmol) in THF (10 mL) at -120 °C. Next the reaction mixture was 
filtered through celite and added to a 20 mL vial with CoCl\(_2\)(PPh\(_3\))\(_2\) (17.7 mg, 0.027 mmol). The 
reaction was allowed to stir at room temperature for 24 hours, resulting in the formation of a red-
orange precipitate. The precipitate was collected via filtration and dissolved in DCM. The 
volatile were removed in vacuo to afford analytically pure product (15 mg, 77.3%).\(^1\)H NMR 
(400 MHz, CD\(_2\)Cl\(_2\)): δ 9.633 (m, 8H, Ar-H), 8.169 (m, 4H, Ar-H), 6.705 (m, 12H, Ar-H), 6.204 
(m, 2H, Ar-H), 5.875 (m, 2H, Ar-H), 3.528 (s, 2H, CH\(_2\)), 1.605 (s, 2H, CH\(_2\)).

**Synthesis of ^\text{Ph}[\text{PCP}]\text{FeCl}_2**

A solution of KHMDS (5.0 mg, 0.027 mmol) in THF (3 mL) was added to a solution of 
\((^\text{Ph}[\text{PCP}]\text{H})\text{PF}_6\) (20 mg, 0.027 mmol) in THF (10 mL) at -120 °C. Next the reaction mixture was 
filtered through celite and added to a 20 mL vial with FeCl\(_2\)(PPh\(_3\))\(_2\) (17.7 mg, 0.027 mmol). The 
reaction was allowed to stir at room temperature for 24 hours, resulting in the formation of a red-
orange precipitate. The precipitate was collected via filtration and dissolved in DCM. The 
volatile were removed in vacuo to afford analytically pure product (16 mg, 82.5%).\(^1\)H NMR 
(400 MHz, CD\(_2\)Cl\(_2\)): δ 12.024 (m, 8H, Ar-H), 11.042 (m, 4H, Ar-H), 6.991(m, 12H, Ar-H), 
5.216 (m, 2H, Ar-H), 5.100 (m, 2H, Ar-H), 3.916 (s, 2H, CH\(_2\)), 1.697 (s, 2H, CH\(_2\)).
References


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