Investigations of Intramolecular Copper (I)-arene Interactions using a NS2-macrocyclic Ligand with Different Pendant Aryl Arms

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Investigations of Intramolecular Copper(I)-Arene Interactions using a NS$_2$-Macrocyclic Ligand with Different Pendant Aryl Arms

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Department of Chemistry
Colby College
Waterville, Maine
2002
Investigations of Intramolecular Copper(I)-Arene Interactions using a NS$_2$-Macrocyclic Ligand with Different Pendant Aryl Arms

A thesis submitted to the chemistry department at Colby College as a requirement for graduation with honors in chemistry

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# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vita</td>
<td>iv</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>v</td>
</tr>
<tr>
<td>Abstract</td>
<td>1</td>
</tr>
<tr>
<td>Introduction</td>
<td>2</td>
</tr>
<tr>
<td>Experimental</td>
<td>7</td>
</tr>
<tr>
<td>Theory</td>
<td>12</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>19</td>
</tr>
<tr>
<td>Conclusion</td>
<td>29</td>
</tr>
<tr>
<td>References</td>
<td>30</td>
</tr>
<tr>
<td>Spectrum List</td>
<td>32</td>
</tr>
</tbody>
</table>
Vita

Paul June Hyun Lee, the son of John Jung Hoon Lee and Grace Soon Woo Lee, was born on the 22th of October, 1980 in Los Angeles, California. He spent most of his life in Southern California, attending Wonderland Elementary, Sepulveda Junior High, and Van Nuys High School.

In 1998, Paul matriculated to Colby College in Waterville, ME where he spent 2 years involved in research with Professor Rebecca Conry Ph.D. He graduated in 1998 with a B.A. with Honors in Chemistry.

Paul plan to continue his studies in pursue of a Ph.D. in Chemistry at Northwestern University in Evanston, IL.
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I would like to thank Professor Stephen Dunham for teaching how to use the variable temperature NMR.

But most importantly, I would like to thank my family who without their unwavering support and love, I would not be here today. To my mother, Grace Soon Woo Lee, and my father John Jung Hoon Lee, and to my sister Esther J. Lee, for their unconditional love and guidance, I dedicate this paper to you.
Abstract

Two macrocyclic ligands with a pendant phenyl group - \( N-[2-(1\text{-phenyl})\text{ethyl}]-1\text{-aza}-4,8\text{-dithiacyclodecane} \) (L1) and \( N-[2-(1\text{-phenyl})\text{propyl}]-1\text{-aza}-4,8\text{-dithiacyclodecane} \) (L2) has been synthesized and characterized. The copper(I)-triphenylphosphine complex \([\text{L}1\text{Cu(PPh3)}]\text{OTf} \), (2) was synthesized from L1, \( \frac{1}{2}(\text{C}_6\text{H}_5)[\text{CuOTf}]_2 \), and PPh3. The complexes \([\text{L}1\text{Cu}]\text{OTf} \) and \([\text{L}2\text{Cu}]\text{OTf} \) 3 were also synthesized and characterized using \(^{13}\text{C}\) and \(^1\text{H}\) NMR, UV-vis and IR spectroscopy, and ESI-MS. In CD\(_2\text{Cl}_2\), 1 was found to have a fluxional behavior with the barrier \( \Delta G \) to the process estimated at 9-11 kcal/mol. Variable temp. NMR spectroscopy of 1 gave compelling evidence that the phenyl-appended group is bound in an intramolecular \( \eta^1 \)-fashion with the copper center. At room temperature, 1 and 3 were found to be in a fluxional process of the bound and unbound arene system. In CD\(_2\text{Cl}_2\), the barrier to the fluxional process for 2 was found to be much less than 1; \( \Delta G = 2-8 \) kcal/mol. The location of binding on the aryl linker arm for 1 and 3 is hypothesized to be at the \( \pi \)-system adjacent to the linker arm. (DFT) pBP/\( \text{DN}^* \) and RHF - 6-31g* molecular orbital calculations have been performed to better understand the complexes 1 and 3.
Introduction

Transition metal complexes have found important uses as catalysts. These catalysts were found to have a variety of applications in industrial processes, bench-top reactions, and medicinal chemistry. Some examples of such catalytic processes include olefin polymerization and hydrosulfurization. The steric bulk of *ansa*-bridged metallocene systems were found to inhibit termination reactions more strongly than insertion reactions thereby polymerizing olefins.\(^1\) In a study by Spera\(^2\), *S*-alkylthiophenium metal complexes were found to promote hydrosulfurization, which involve carbon-sulfur bond cleavage to form highly electrophilic metallasyclopropenes. The naphthalene bound copper(I) complex (Figure 1a),\(^3\) made by the Conry group, was found to aziridinate olefins (Figure 1b).\(^4\)

![Figure 1: a) The Naphthyl-appended copper(I) complex b) Aziridination reaction of olefin by Naphthyl-appended copper(I) complex.](image)

Aziridination reactions find importance as aziridines provide regioselective, synthetic routes in organic chemistry.\(^5\) Several aziridine containing natural products were also found to have potent cytotoxic properties such as anti-tumor antibiotics.\(^6\) There is still much more to understand about transition metal complexes. Much is not known about the mechanisms that drive these catalytic processes. An aspect of transition metal-ligand chemistry that still is not well understood is in the area of transition metal $\eta^2$-olefin interaction. The Conry group has been active in elucidating this chemistry, and this
paper, which springs from the Conry group, explores the factors that might be involved in transition metal \( \eta^2 \)-olefin interactions.

Transition metal \( \eta^2 \)-olefin interactions were first postulated by Dewar in 1945, when he suggested that alkenes might be able to donate \( \pi \)-electrons to form dative bonds; bonds resembling those made from lone pair electrons. Shortly after, Chatt and Duncanson published a paper which took Dewar's groundbreaking idea and experimentally used it to describe transition metal–olefin complexes. Metal ions were found to bind to \( \pi \) systems of olefins as seen in Figure 2.

Copper(I)-arene interactions are examples of Dewar-Chatt-Duncanson binding. A coordinated \( \pi \) system to a metal ion similarly consists of two components: 1) the sigma type orbital interaction where \( \pi \)-electrons from the olefin fill an empty orbital on the metal ion and 2) \( \pi \)-backbonding, where electron density from a filled metal \( d \)-orbital is donated to empty anti-bonding orbitals on the olefin. Chatt hinted at the possibility of this retro-dative bonding; "A bonding which is typified by olefins where it appears that \( d \) electrons from the metal as well as two electrons from the ligand are required." This \( \eta^2 \) transition metal-olefin binding mode was found to be generally weaker than covalent bonds.

Copper-arene binding is relatively rare. In the literature, only a handful of structurally-characterized Cu(I)-arene complexes have been reported before 1995.
However, these structures are polymeric and exist only in solid state, making it difficult to isolate and study the Dewar-Chatt-Duncanson interaction of metal-arene binding. These complexes do not bind the arene in solution, and electronic/steric manipulations of the Cu(I)arene binding are difficult to make systems seen in Figure 3. Since then, some dimeric copper(I) structures also have been synthesized (Figure 4).13

The copper centers of the dimer in Figure 4 were dimer appeared to have a preferential binding mode and were found to bind to the $\pi-$system between the *ipso* and *ortho* carbons of the arene part of the complex in solid state. Although this study was aimed at studying organometallic Cu species and not specifically copper-arene interactions, their results help us to better understand Cu(I) complexes by the isolation of the Cu(I)-arene interaction with the metal ion.
Our Cu(I) systems have the copper ion bound to a NS₄ macrocyclic base with a linked pendant aryl arm, which is free to interact with the copper ion (Figure 5). At room temperature, the phenyl-group is speculated to be involved in a fluxional process for both 1 and 3, where the phenyl-appended group is bound to the copper center in an η² fashion and where the phenyl group is unbound. Copper(I) is usually a colorless metal ion and has 10 electrons in its valence d orbital shell. The 18-electron rule of organometallic chemistry is observed for these complexes. This study set out to determine the location and strength of copper(I)-arene interaction for the η² binding geometry seen in 1 and 3. Figure 5.

![Complex 1](image1)

![Complex 2](image2)

![Complex 3](image3)

Figure 5: The Cu(I) complexes that are the subject of our investigation.

This research is a follow up study to that for the first reported solution binding Cu-arene complex with a naphthyl-appended NS₂ – macrocyclic ligand that also bound the naphthalene ligand in the solid state. (Figure 1) This complex was fully characterized; however, there were many questions that remained to be answered about the Cu-arene interaction. We wanted to study the steric and electronic effects on the observed Cu-arene binding site. For this research project, the aryl group was changed from a naphthyl group to a phenyl group to look at some electronic factors that might influence the copper-arene binding. We also wanted to probe the role of the linker arm in this system and to test whether increasing the length of linking chain from an ethylene group to a propylene group would make changes to the copper-arene binding site. These slight transformations of the aryl group and linker arm were compared with the
naphthylene bound system to better understand how the increase in flexibility and the change in electronic structure would influence the copper-arene interaction. Some DFT and Hartree-Fock computational studies have been performed to explain experimental observations.
Experimental Section

**General Procedures.** All reactions were performed open to air using the typical organic synthetic techniques or when specified, under an atmosphere of purified nitrogen gas, using standard Schlenk techniques. Solvents used for these air-free reactions were freshly distilled from CaH₂ prior to use. The Selecto Scientific silica gel, with particle sizes of 63-200 μm was used in the column separation. The IR spectrum was performed on a Mattson Instrument Galaxy Series FTIR 4020 using NaCl plates for the Nujol mull spectrum. The Hewlett-Packard 8452A diode array spectrophotometer was used to take UV-vis spectra. A Hewlett-Packard 5890 gas chromatogram and 5970 Series mass selector was used to acquire the GC-MS data. The direct-infusion technique was used on an Agilent 1100 series LC/MSD trap for the mass analysis of our complexes. $^{13}$C, $^{31}$P, and $^1$H NMR spectra were recorded at various temperatures on a Bruker Avance 400 MHz NMR spectrometer. The $^{31}$P spectrum was taken using a H$_3$PO$_4$ standard.

Calculations were performed using a SGI Indigo workstation as a front end to a SGI Origin 2000 desktop supercomputer with 4 250 MHz R1000 processors, 4 MB of 2nd level cache, and 500 MB memory. Structures were built for the Spartan DFT calculation were built on the expert builder and minimized using molecular mechanics before submitting the DFT calculation. GausView was used as a front end to build the Z matrix for the Hartree Fock calculations for Gaussian 98.

**Experimental Procedure:**

**Preparation of N,N-Bis-di-[ethyl-(toluene-4-sulfonyl)-ester]-methyl-sulfonamide, “Tritosyl”:** Diethanolamine (25.293 g, 0.2405 mol) was stirred with pyridine (232 mL, 2.87 mol) for 10 min in an ice bath. Then p-toluenesulfonyl chloride (136.4 g, 0.715 mol) was added in ~5 mL portions to the solution, waiting after each addition for the p-toluenesulfonyl chloride (TsCl) to dissolve. The solution initially turned a bright yellow, then turned to a deep purple color. The solution was allowed to stir for ~3 hours after all the TsCl was added. A premixed solution of conc. HCl (68.7 mL) and deionized H$_2$O (332 mL) was added dropwise to the solution over a course of ~2 hours. Solid yellow precipitates formed; the resulting mixture was left to stir overnight, allowing the ice to
melt and the solution to return to room temperature. The precipitate was filtered and washed with several portions of ~30 mL of water. The resulting solids were recrystallized in boiling methanol and refrigerated overnight. The resulting yellow crystals were filtered and washed with several portions of ~10 mL ether followed by two portions ~10 mL ethanol. Yield: 89.946 g (0.1584 mol, 65.7%) \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.75 (d, \(J = 8.6\) Hz, 4 H), 7.61 (d, \(J = 8.3\) Hz, 2 H), 7.36 (d, \(J = 8.3\) Hz, 4 H), 7.29 (d, \(J = 6.1\) Hz, 2 H), 4.11 (t, \(J = 6.1\) Hz, 4 H), 3.37 (t, \(J = 6.1\) Hz, 4 H), 2.44 (m, 8 H).

**Preparation of 4-(Toluene-4-sulfonyl)-[1,7,4]dithiazecane, “Tosylated Ring”** – A premixed solution, made of tritosyl (22.823 g, 0.0402 mol), 1,3 propanedithiol (4 mL, 0.0398 mol), and 600 mL of DMF was added dropwise to a mixture of dried cesium carbonate (26.698 g, 0.08194 mol) and \(N,N\)-dimethylformamide (2.2 L of DMF), which was pre-heated to ~60 °C under inert atmosphere. The resulting mixture was stirred for an additional 2 days over which time it turned an orange-brownish color. The DMF was distilled away until ~700 mL of solution was left. This solution was then added slowly to 1000 mL of ice water and stirred until the ice melted. The beige solid precipitate that formed in the flask was filtered away and was dried overnight and then was recrystallized in boiling ethanol. Yield 10.194 g (0.0307 mol, 76 %) \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.62 (d, \(J = 8.1\) Hz, 2 H), 7.26 (d, \(J = 7.9\) Hz, 2 H), 7.20 (s, 1 H), 3.13 (q, \(J = 6.1\) Hz, 8 H), 3.02 (m, 4 H), 2.36 (s, 2 H), 1.84 (m, \(J = 6.1\) Hz, 2 H)

**Preparation of [1,7,4]Dithiazecane, “Detosylated Ring”**: Tosylated ring (7.136 g, 0.0215 mol) was added to a solution of phenol (6.193 g, 0.0658 mol), acetic acid (183 mL, 3.198 mol), and 48% hydrobromic acid (9 mL, 0.166 mol). The solution was refluxed for ~43 hours in the dark. After 30 min, the solution turned a dark brown color. The solution was cooled and filtered, and the solvent was distilled away. Deionized H\(_2\)O (250 mL) was added to the resulting dark brown oil and this mixture was stirred vigorously overnight. Note: the oil and aqueous layer are not miscible. The brown oil layer was filtered to leave the yellow aqueous layer. NaOH pellets were added in ~1 g portions to the yellow filtrate while stirring until the pH of the solution reached 10-11. The solution first turned cloudy white, then quickly changed to a pink color. Chloroform
(174 mL) was added and the mixture was allowed to stirred vigorously overnight. The chloroform layer was separated from the aqueous layer and washed three times with a ~50 mL 10% NaOH solution. The chloroform was removed to leave a dark yellow oil. Yield 2.2402 g (0.0126 mol, 58.6%) \( ^1H \text{ NMR (CDCl}_3 \delta 3.06 (m, 8 H), 2.73 (m, 4 H), 1.85 (h, J = 2.0 Hz , J = 6.1 Hz, 2 H), 1.60 (t, J = 5.3 Hz, 1 H). } \) \( ^{13}C \text{ NMR (CDCl}_3 \delta 49.6, 34.4, 30.2, 29.1. } \) GC-MS \( t_{ret} = 8.2 \text{ min; 177 (M}^+\text{, 80%).} \)

\[ N-[2-(1\text{-phenyl)ethyll]-1-aza-4,8-dithiacyclodecane, (L1): \] A solution of the “detosylated ring” (1.517 g, 8.57 mmol), 2-bromoethylbenzene (1.2 mL, 8.75 mmol), triethylamine (3.6 mL, 25.61 mmol), and toluene (62 mL) was heated to reflux for 72 hours. The solution turned an orange color with clear precipitates forming along the wall of the flask. After cooling to room temperature, the solution was filtered and the solvent was distilled away to leave a yellow oil. The oil was extracted 3 times with a 10% HCl solution (a total of 100 mL). Then oil was washed with deionized H\textsubscript{2}O (40 mL). The aqueous layers were combined. NaOH pellets were added in ~3 g portions to the aqueous solution while stirring until pH reached 10-11. White precipitates formed. The aqueous layer was extracted with 4 portions of ether (30 mL each). The ether was distilled to give a yellow, brown oil, which was loaded onto a silica gel column using 50 % hexane /50 % ethyl acetate as effluent. The first fraction (\( R_f \) value = 0.911) was collected and the solvent was removed to give the product. Yield 0.1064 g (0.378 mmol, 4.4%) \( ^1H \text{ NMR (CDCl}_3 \delta 7.28 (m, 4 H), 7.19 (dd, J = 2.8 Hz, J = 6.1 Hz, 1 H), 3.06 (t, J = 6.8 Hz, 4 H), 2.83 (m, 6 H), 2.75 (m, 2 H), 2.70 (m, 4 H), 1.84 (q, J = 6.3 Hz, 2H). } \) \( ^{13}C \text{ NMR (CDCl}_3 \delta 172.5, 142.6, 130.3, 129.7, 127.2, 57.5, 33.8, 31.6, 21.0, 14.6. } \) GC-MS: \( t_{ret} = 18.7 \text{ min; } m/z 281 (M}^+\text{, 100%).} \)

\[ \text{Preparation of [L1CuOTf], (1): A solution mixture of nitromethane (8 mL) and L1 (0.279 g, 0.991 mmol) was added dropwise to Cu(OTf) (OTf = CF}_3SO}_2 \text{) (0.266 g, (0.652 mmol) in an inert atmosphere of N}_2 \text{. The solution turned a green color. The mixture was stirred for 55 min, then solvent was removed to leave a brown flaky product. The complex was recrystallized by first dissolving it in nitromethane, followed by the dropwise addition of diethyl ether. A brown oil precipitated out of the solution when the} \]
flask was cooled in an ice bath. The oil and the solution were separated via a fritted filter and dried separately in vacuo. Yield 0.213 g (0.619 mmol, 94.9 %) 1H NMR (CD3NO2) δ - 1.67 (t of q, J = 2.27 Hz, J = 7.8 Hz, 1 H), 2.11 (t of q, J = 2.4 Hz, J = 9.6 Hz, 1 H), 2.84 (m, 2 H), 2.69 (dd, J = 2.0 Hz, J = 7.8 Hz, 2 H), 2.90 (m, 4 H), 2.86 (m, 2 H), 3.14 (q, J = 6.1 Hz, 2 H), 3.10 (t, J = 6.1 Hz, 2 H), 2.99 (m, 2 H), 7.38 (m, 2 H), 7.38 (m, 2 H), 7.47 (m, 2 H). IR (NaCl), cm⁻¹ - 1262 ms u(S=O), 1156 ms u(S=O), 1029 m u(C-F), 726 m u(S-C). ESI-MS: 344.1 m/z. UV-vis (CH2Cl2): 236 (3960), 256 (3500), 292 (1050)

Preparation of [L1Cu(PPh3)OTf], (2): A solution of triphenylphosphine (0.110 g, 0.419 mmol), L1 (0.1064 g, 0.378 mmol), and nitromethane (~18 mL) was added dropwise to Cu(OTf) (0.104 g, 0.255 mmol) in an O2-free environment. The solution turned a dark green color. After stirring for ~2 hours, the solvent was removed in vacuo to leave white/gray solids. The sample was recrystallized from nitromethane by the addition of diethyl ether to precipitate fluffy white solids. The product was filtered and dried under vacuum for ~4 hr. Yield = 0.123 g (0.203 mmol, 79.6 %) 1H NMR (CD3NO2) δ 1.93 (t of q, J = 2.0 Hz, J = 8.1 Hz, 1 H, q), 2.42 (q, J = 6.1 Hz, 1 H), 2.96 (m, 2 H), 3.18 (m, 2 H), 3.09 (m, 2 H), 3.21 (m, 2 H), 3.42 (m, 2 H), 3.13 (m, 2 H), 2.81 (m, 2 H), 2.92 (6, 2H, m), 6.71 (dd, J = 1.8 Hz, J = 7.6 Hz, 2 H, q), 7.13 (m, 2 H), 7.15 (m, 1 H), 7.47 (m, 6 H), 7.47 (m, 6 H), 7.47 (m, 3 H) 31P (CD3NO2) δ 6.545. IR (NaCl) 1265 m u(S=O), 1139 m u(S=O), 1093 m, 1028 m u(C-F), 749 ms u(S-C), 696 m, 636 m. ESI-MS - 605.9 m/z, 344.0 m/z. UV-vis (CH2Cl2): 232 (1645), 256 (1160)

Preparation of N-[2-(1-phenyl)propyl]-1-aza-4,8-dithiacyclodecane, (L2): A solution of 1-bromo-3-phenyl propane (0.89 mL, 5.85 mmol), “desosylated ring” (1.047 g, 3.73 mmol), triethylamine (2.5 mL), and toluene (61 mL) was stirred and refluxed for ~72 hours. After the solution was cooled, the clear precipitates were filtered away. The solution was extracted (3x) with 10% HCl solution (total 100 mL) and aqueous layers were combined. NaOH pellets were added to the aqueous layer in portions of ~3 g (total 10 g) until the pH became 10-11 and yellow precipitates formed in solution. The solution was extracted with diethyl ether (~150 mL) and the organic layer was collected. The
solvent was distilled away to leave a yellow oil. Purification was accomplished with column chromatography, using a mixture 50% Hexane/ 50% ethyl acetate as the elution solvent. Yield 0.288 (0.976 mmol, 26.2 %) \( ^1\)H NMR \( \delta 1.84 \) (t of q, \( J = 2.3 \) Hz, \( J = 7.33 \) Hz, 4 H), 2.50 (m, \( J = 7.33 \) Hz, 2H), 2.64 (m, 4 H), 2.67 (m, 4 H), 3.13 (t, \( J = 6.4 \) Hz, 4 H), 7.16 (t of p, \( J = 2.3 \) Hz, \( J = 6.6 \) Hz, 1 H, m), 7.29 (4 H, m). \(^{13}\)C NMR \( \delta 30.0, 31.5, 31.6, 33.9, 55.5, 57.9, 127.0, 129.7, 132.5, 144.5 \) GC-MS: \( t_{ret} = 32.2 \) min; 295 (M^+)

**Preparation of [L2CuOTf], (3):** A solution of nitromethane (~8 mL) and L2 (0.1237 g, 0.418 mmol) was added dropwise to Cu(OTf) (0.115 g, 0.287 mmol) in an inert N\(_2\) environment. The solution immediately turned yellow, then turned to a greenish-yellow. After stirring for ~1 hour, the solvent was evaporated to leave a brown-green solid. The complex was recrystallized using nitromethane to dissolve the sample and diethyl ether to precipitate out a brown oil when the solution was put into a cold bath. The oil was separated and dried to leave the complex 3. Yield = 0.096 g (0.268 mmol, 93.3%). \(^1\)H NMR (CD\(_2\)Cl\(_2\)) \( \delta 1.69 \) (m, 1 H), 2.10 (q, \( J = 6.4 \) Hz, 1 H), 2.99 (m, 2 H), 2.75 (m, 2 H), 2.78 (m, 2 H), 2.97 (m, 2 H), 3.11 (m, 2 H), 2.77 (m, 2 H), 2.83 (t, 2 H), 1.90 (m, 2 H), 2.55 (t, 2 H), 7.41 (m, 2 H), 7.25 (q, 2 H), 7.10 (t, \( J = 7.5 \) Hz, 1 H). IR (NaCl) - 1262 ms \( \nu(S=O), 1172 \) ms \( \nu(S=O), 1092 \) m, 1035 m \( \nu(C-F), 800 \) w, 743 m \( \nu(S-C). \) ESI-MS: 358.1 \( m/z \). UV-vis (CH\(_2\)Cl\(_2\)): 232 (1250), 256 (1200), 296 (270)
Theory

Molecular energies can be separated into three additive energy types. 1) the translation of each atom in the molecule; 2) the rotation of the whole molecule; and 3) the motion of the electrons in the system. Vibrational spectroscopy selectively observes the translation of the atoms in relation with each other in the molecule. The rotations of the whole molecule are observed in microwaves region. The transitions of electrons are observed in the visible and ultraviolet regions of the electromagnetic spectrum.

Spectroscopic and mass spectrometry studies were carried out on complexes 1, 2 and 3 to determine if there is a Cu-arene interaction and if so, the activation energy of the fluxional process and location of the copper(I)-arene interaction in the NS₂-macrocycle with a linked aryl system was determined. By comparing the spectroscopic data of the L₁ to the data of 1, we were able to observe the chemical shifts and mark the differences that the copper ion made in the ligand system. By following these differences, we can track the binding sites of the copper-arene interaction. The same spectroscopic techniques were used to compare L₂ with 3 to understand the effect of a longer linker chain on the copper-arene binding site. Computational methods were used to better understand the system under investigation.

Infrared Spectroscopy – As in many other spectroscopic techniques, molecules are excited to a higher energy state with the absorption of infrared radiation. This absorption process is quantized meaning that the molecule can absorb at selected frequencies that correspond to the bending and stretching vibrations specific to the molecule. The energy absorbed in infrared spectroscopy ranges from 2 to 10 kcal/mol. In the absorption process, when the incident frequency matches the vibrational frequency of the molecule, the energy absorbed serves to amplify the vibration in the molecule and can be observed as an absorption peak in the spectrum.

Infrared spectroscopy can be a powerful technique to determine structure, functional groups, and symmetries of molecules. By observing vibrational bands in the IR spectrum, bond lengths and force constants can be calculated. IR bands can also be compared to correlation tables and assigned to vibrational modes. Infrared spectroscopy
is rather simple and a spectrum is easy to take. However, there are limitations to this technique. It should be noted that not all modes are infrared active. Only those modes involving a dipole moment are quantum mechanically allowed to absorb infrared radiation. Symmetrical modes are not observed because they do not have electrical dipole moment, which allows for effective energy transfer with incoming radiation.

**UV-visible Spectroscopy** -- The part of the electromagnetic spectrum between the wavelengths of 190 nm to 800 nm, is called the ultraviolet (UV) and visible (vis) region. When UV-vis radiation is passed through a sample, electronic excitation processes occur to give an absorbance spectrum. These quantized absorptions result in wavelength peaks that correspond to the energy difference between the excited and ground state.

UV-visible experiments are useful because they are simple, time efficient, and give us information about the electronic transitions of our molecule. This is a powerful technique when monitoring charge transfer bands in transition metal complexes. Photochemical reactions cause electrons to jump from their ground state to an excited state, then back down again. This shuffling of charge causes a reorganization of the inner-shell and outer-shell electronic environments. When the metal can transfer electrons directly to the ligand, an extra band will appear in the UV-vis spectrum.

Molar absorptivity can be calculated using the Beer-Lambert Law:

$$\log(I/I_0) = \varepsilon \cdot c \cdot l$$

($I_0$ = intensity of the light incident upon the sample cell, $I$ = intensity of the light leaving the sample cell, $c$ = molar concentration of the sample, $l$ = length of the sample cell (cm) $\varepsilon$ = molar absorptivity)

Using group theory calculations for a metal center with an NS$_2$ ligand, a molecular orbital diagram was constructed (Figure 6).
Figure 6: The predicted molecular orbital diagram for the complexes 1 and 3

The HOMO is predicted to be the electrons in the non-bonding d_{xy}, d_{x^2-y^2}, and d_{yz} orbitals of the copper(I) metal center. The LUMO is rationalized to be the antibonding orbitals between the copper and olefin. This makes sense because any additional electrons would destabilize the Dewar-Chatt interaction.
Nuclear Magnetic Resonance Spectroscopy (NMR) – NMR spectroscopy is a versatile tool for chemists to probe the structure and environments of the molecules. Carbon and proton NMR spectroscopy are standard NMR techniques used when characterizing a compound. In addition, various 2-D techniques, such as correlated spectroscopy (COSY) and Heteronuclear Multiple Quantum Coherence (HMQC) are available to help in deciphering more information about the compound of interest. COSY is able to show proton coupling in through-bond interactions and are useful in assigning proton peaks by following the resulting coupling chain.

NMR spectroscopy can be used to study many different nuclei, such as $^2$H, $^{13}$C, $^{14}$N, $^{17}$O, $^{31}$P, and a host of other nuclei with a spin of at least a one half. By monitoring the different nuclei, we can learn more about the part of the compound of interest that contain those nuclei.

Variable temperature NMR spectroscopy is useful in determining the activation energy barrier of a fluxional process. By lowering the temperature, in essence taking away energy from the system, we can monitor coalescence temperature of the system. With determination of the coalescence temperature, $\Delta G$ of the fluxional process can be roughly estimated using Figure 7.
Electrospray Ionization Mass Spectrometry (ESI-MS) – Mass Spectrometry has developed into a highly accurate technique. This method determines the mass to charge (m/z) ratio of an ion and can be a useful technique to identify compounds based on the m/z values. Electrospray ionization (ESI) first nebulizes with a spray needle and rapid nitrogen flow. Then a high electrical potential is used to desolvate the ion. The solvent is evaporated and sample is passed along to the ion trap. ESI is a relatively soft ionization technique, meaning it does not fragment the molecules as much as other techniques.

Isotope patterns can be observed in the mass spectrum. Isotope patterns are predictable and many programs are available to display good isotope patterns. Using the applet found in reference 19, the isotope patterns for complexes 1, 2, and 3 were calculated.
<table>
<thead>
<tr>
<th>Complex 1</th>
<th>Complex 2</th>
<th>Complex 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>monoisotopic parent mass:</td>
<td>344</td>
<td>606</td>
</tr>
<tr>
<td>smallest mass:</td>
<td>344.0568</td>
<td>606.1479</td>
</tr>
<tr>
<td>mass of tallest peak</td>
<td>344</td>
<td>606</td>
</tr>
<tr>
<td>exact parent mass</td>
<td>344.0568</td>
<td>606.1479</td>
</tr>
<tr>
<td>average molar mass</td>
<td>345.0644</td>
<td>607.3865</td>
</tr>
<tr>
<td>Formula</td>
<td>$C_{14}H_{20}NS_2Cu$</td>
<td>$C_{14}H_{20}NS_2PCu$</td>
</tr>
</tbody>
</table>

Table 1: Predicted masses for complexes 1, 2, and 3

Figure 8: Predicted isotope patterns of complex 1, 2, and 3
The isotope patterns appear pretty similar to each. The pattern can be mainly attributed to the isotope abundance of the copper ion.

**Computational Studies** – Computational calculations can be used to determine molecular orbital bonding and conformations of metal complexes. There are a variety of levels of molecular calculations ranging from low level calculations to higher, more complicated calculations. Molecular mechanics is the lowest of the levels because it only takes into account classical potential energies of the molecule. Semi-empirical calculations are the next level in calculations because they start out with approximations of integrals of the Hartree-Fock theory. Semi-empirical calculations use experimental data to find some of these integrals. *Ab initio* calculations solve the integrals directly without using experimental data. *Ab initio* methods can be computer time expensive but can yield predictions that are closer to experimental results. Density functional theory (DFT) calculations include the effect of electron-electron correlations to find molecular orbitals of molecules. The HOMO and LUMO molecular orbitals are calculated using electron density values and simulations of electron motions to approximate electron-electron correlations.20

Because some molecules are complex, it is best to use a low-level calculation before moving to more higher-level calculations. Geometry converge is difficult with complex molecules. However, if the molecule is simple, then higher level calculations would not take long and would yield more accurate molecular orbitals. A balance is made between the level of calculation needed and how much time and computer resources are available.
Results and Discussion

Synthesis and Characterization of N-[2-(1-phenyl)ethyl]-1-aza-4,8-dithiacyclodecane, (L1). The ligand L1, N-[2-(1-phenyl)ethyl]-1-aza-4,8-dithiacyclodecane was synthesized in four steps. The first three steps produced the precursor parent macrocycle $S_2N[10]$-ane. This synthesis was carried out with the same methodology as reported by Chandrasekhar and McAuley.\(^{21}\)

To complete L1, the phenyl appended linker arm was added by reacting 2-bromo-ethyl-benzene with the $S_2N[10]$-ane macrocycle from Figure 25. The resulting product was initially purified using an acid/base extraction, by first adding acid to protonate the nitrogen on L1, making the product soluble in water, then adding base to deprotonate the ligand to filter out the impurities without acid/base properties. The product was separated from the aqueous layer by dissolving L1 in an organic layer. The organic layer was removed and L1 was further purified by column chromatography, using a 1:1 hexane / ethyl-acetate as mixture elution solvents. L1 was the first compound to come off the
column with an Rf value of 0.911, and is a clear oil. The L1 was fairly stable, but must be refrigerated. After two weeks out on the bench top, L1 began to show degradation. L1 was characterized by GC-MS as well as $^{13}$C and $^1$H NMR spectroscopy.

![Figure 10: Synthesis of L1](image)

**Synthesis and Characterization of [L1Cu]OTf, 1** – Stoichiometric amounts of L1 and CuOTf were added together in nitromethane to give 1. Complex 1 was isolated by the removal of the nitromethane solvent and was recrystallized at room temperature from NO$_2$CH$_3$ by the addition of Et$_2$O. The brown oil that precipitated out was collected and dried in vacuo. $^1$H NMR spectroscopy determined that the oil contained 1. Complex 1 was found to be fairly O$_2$ sensitive, turning a bright green color after 1 hour exposure in nitromethane to the air. Complex 1 has been characterized using $^{13}$C and $^1$H NMR, UV-vis and IR spectroscopy, IR, and ESI-MS.

![Figure 11: Synthesis of complex 1](image)

**Synthesis of [L1 Cu(PPh$_3$)]OTf, 2.** – The L1 was coordinated to copper(I) in a 1:1:1 stoichiometric reaction of L1, triphenylphosphine (PPh$_3$) and CuOTf. Complex 2 was recrystallized at room temperature by adding Et$_2$O to NO$_2$CH$_3$. The crystals of complex 2 are white in color and show a remarkable stability in air. Complex 2 has been characterized using $^{13}$C, $^{31}$P, and $^1$H NMR, IR, UV-vis spectroscopy, ESI-MS, and X-ray crystallography.
Synthesis and Characterization $N$-[2-(1-phenyl)propyl]-1-aza-4,8-dithiaclodecane, (L2). - The ligand L2, $N$-[2-(1-phenyl)propyl]-1-aza-4,8-dithiaclodecane was synthesized using a similar methodology to L1. The first three steps of the synthesis are the same, but the fourth step requires 1-bromo-phenyl-propane to be added to the NS$_2$ [10]ane to get L2. The ligand L2 was characterized using GC-MS, and $^1$H, $^1$H NMR spectroscopy.

Synthesis of [L2Cu]OTf, 3 - The ligand L2 was reacted in a 1:1 stoichiometry with CuOTf in nitromethane to give the product [L2Cu]OTf 3. The product was separated by solvent extraction at room temperature using the same synthetic procedure as 1. Similarly, a brown oil precipitated out of the solvent, and the oil contained 2 as determined by $^1$H NMR spectroscopy. This complex 3 had a similar greenish color as 1. Complex 3 was also determined to be O$_2$ sensitive and turns a bright green color in nitromethane within 2 hours upon being open to air. Complex 2 was characterized using $^{13}$C and $^1$H NMR, UV-vis Spectroscopy, IR, and ESI-MS.
Infrared Spectroscopic studies on complexes 1-3 – The infrared spectra for 1-3 were taken as Nujol mulls. A sample scan of mineral oil and the NaCl plate was taken and compared to the scan taken of mineral oil and sample on the NaCl plate. The additional peaks seen were assumed to be sample peaks.

Complexes 1, 2, and 3 exhibited peaks corresponding to the anion $\text{CF}_3\text{SO}_3^-$. The peaks at 1265 cm$^{-1}$ and 1139 were attributed to the S-O bonds, the peak at 1028 cm$^{-1}$ can be assigned as a C-F stretch. These peaks appear to correspond to the vibrational modes of the triflate anion only. This is probably due the low concentration samples, since the OTf peaks should be strong, but the complex peaks are medium to weak.

The IR spectrum of complex 2 was compared to an IR spectrum of triphenylphosphine and two of the same peaks appear in both spectra at 749 cm$^{-1}$ and 696 cm$^{-1}$, which are a reflection of the aromatic C=C bends from the phenyl rings. Smaller peaks at the same wavenumber appeared on the spectra for 1 and 3, but the peaks are too small to be determined to be considered significant. The signal was dominated by mineral oil and triflate.

Mass Spectrometry Studies - Mass spectrometry studies were performed using electrospray ionization with solutions of 1, 2, and 3 at concentrations of around 3.0e-5 M in CH$_2$Cl$_2$.

An ESI-MS spectrum of 1 gave a molecular ion at $m/z=344.1$. The experimental isotope patterns matched the predicted pattern as seen in Table 1. No other peaks were observed for the solution sample of 1. Complex 2 gave two peaks, a less abundant peak at 605.9 $m/z$ and a larger peak at 344.0 $m/z$. The cluster at 606 $m/z$ did not show the predicted isotope pattern, rather gave a messy array of peaks. After further analysis, it was observed that the M$^+$ peaks appeared to be the right isotope peaks patterns but that the same isotope patterns appear to be shifted up by half a mass unit. The isotope
pattern was rationalized to be a dimer with a \( z = 2 \) and \( M^+ = 2M+1 \) which breaks apart in the ion-trap, or the identity of the peak cannot be determined at this time. The other major peak was a fragment peak at 344.0 \( m/z \). This \( m/z \) value is the equal to that of 1, and this can be attributed to 2. The isotope pattern at 344 \( m/z \) was clean and resembled that found for 1. The triphenylphosphine ligand is thought to fragment from 2 to give 1, or is partly dissociated in solution. Complex 3 gave the ESI-MS spectra with a mass peak at 358.1 \( m/z \) with no other fragmentation pattern. The isotope pattern corresponded well with the predicted isotope pattern found in Figure 17.

The ESI-MS mass spectra gave compelling evidence that the complexes 1-3 were present in the solutions, although the experimental peaks were different by 0.1 than the calculated mass unit. This suggested that the experimental data were reliable, seeing the difference of predicted and actual mass units was less than 0.08%. However, MS does not give us information about purity, because only positive charged molecules were detected. MS gave us information that the complexes 1-3 were synthesized, but it did not give us insight into the copper-arene interactions.

**UV-vis Spectroscopy** – UV-vis spectroscopy turned out to be a very powerful tool to probe for potential copper-arene interactions. The Shimazaki group reported that UV-vis spectroscopy can be used to look for Cu-arene metal to ligand charge transfer bands (MLCT). By the observation of a shoulder peak in the UV-vis spectrum at 308 nm, they were able to see an indication of a Cu(I)-arene interaction. Shoulder peaks were observed in the UV-vis spectra of complexes 1 and 3 at 292 nm and 296 nm, respectively, but were not observed for 2. The aryl group in L1 and L2 is able to interact with the copper centers for 1 and 3, but cannot in complex 2, because the bulky triphenylphosphine group blocks access to the Cu(I) ion. The charge transfer bands can be a quick indication of electronic communications between metal ions and their ligands.

Complex 2 absorbed in the UV range at the wavelengths 232 nm and 256 nm. The lack of color can be attributed to this UV-vis absorption and the lack of any absorption in the visible because 2 reflect all the visible light. Complexes 1 and 3 also absorb around the same region of the UV-vis spectrum and are expected to be white. Complexes 1 and 3 are not colorless, but rather green, indicating that there are some
impurities in the sample. If 1 and 3 were pure, during the recrystallization step, the product would of crystallized out rather than oiling out.

**NMR Spectroscopic Characterization of Complex 1** - 

$^1$H and $^{13}$C NMR spectra for 1 were compared to the spectra for L1. All the proton peaks were assigned for ligand L1 and 1. The $^1$H NMR spectrum for 1 had sharp peaks and was well resolved at room temperature around the aliphatic region in CD$_3$NO$_2$ solution. When the solution was heated to a temperature higher than room temperature, the resolution did not change for 1. However, when the solution was cooled the peaks began to coalesce. This indicated that complex 1 was undergoing a fluxional process at room temperature (Figure 16).

The solvent was changed to CD$_2$Cl$_2$ to access lower temperatures for 1. At room temperature, the data suggest that a fast exchange process is probably occurring between the two species. Similar to that reported for [L$^{Na}$Cu], one species is thought to be the complex with the phenyl group bound to the copper ion and the other species is the complex with the arene group no longer interacting with the ion as in Figure 16.

![Fluxional process of 1 at room temperature](image)

Comparing the aromatic regions of the $^{13}$C NMR of spectra of L1 and 1 at room temperature, it is observed that the ipso carbon resonance has shifted upfield by 7 ppm, and the meta carbon was found to shift upfield by 3 ppm. The ortho carbons did not shift more than 1 ppm. The $^{13}$C NMR spectrum below the coalescence temperature at -70 °C revealed the aromatic region to have six inequivalent carbons. The arene of 1 is found to bind with the copper in a $\eta^3$ fashion because the six inequivalent carbons on the aryl system indicate that the aryl symmetry of L1 was broken. These preliminary room
temperature and low temperature NMR studies for 1 suggest that the arene is most likely interacting with the copper ion at the \( \pi \) system adjacent to the carbon of the linker arm.

Using variable temperature \(^1\)H NMR spectroscopy, a coalescence temperature of \(-60\) °C was determined for 1. Using a correlation graph found in Paudler Figure 7,\(^{23}\) an estimated activation energy \( (E_a) \) of 9-11 kcal/mol was determined for the fluxional process that is occurring. In support of \( \eta^1 \) copper-arene binding, the \(^{13}\)C NMR spectrum at \(-70\) °C displays six inequivalent phenyl carbon peaks, indicating that the two-fold symmetry of the phenyl group has been lost.

**NMR Spectroscopic Characterization of Complex 3** - Complex 3 was predicted to have a lower barrier for fluxional process than that of complex 1, because the extra carbon on the linker arm allows greater flexibility. VT-NMR studies showed that the aliphatic peaks for complex 3 were found to broaden as temperature decreased. This broadening of peaks indicated that at room temperature, the complex was undergoing a fast exchange process, probably between a complex with the arene bound to the copper ion and a complex with the arene unbound, similar to that seen for the naphthyl complex (Figure 1a).

The temperature was dropped to the limits of the Bruker Avance NMR instrument until \(-85\) °C, but the coalescence temperature was not reached. Thus, the coalescence temperature for 3 was determined to be below \(-80\) °C. This is likely because the longer chain favors the arene to flop around and causes the Cu(I)-arene binding to be more entropically disfavored. From the VT-NMR data, an estimation of \( E_a \) between \(-2\)-9 kcal/mol for the barrier associated with the fluxional process was determined for 3.\(^{24}\)

When the aromatic region in the \(^{13}\)C NMR spectrum of L2 is compared with the aromatic region for 3, we see that the \textit{ipso} and \textit{para} carbon peaks show up on top of one another and the \textit{meta} position carbon has shifted upfield by 3 ppm. This suggest that the arene of 3 is interacting with the copper ion but the location of binding was not determined from the data.
Computational Studies - Calculational studies have been used to study the frontier orbitals for complexes 1 and 3. Hartree-Fock (HF) and Density Functional Theory (DFT) calculations were used to study these copper-arene systems. DFT calculations are the most frequently used for transition metals.\(^{25,26}\) Although transition metal complexes have a large number of electrons, DFT calculations were able to geometry converge. The Spartan DFT package used at the pBP/DN* was used for these systems because it has a better chance of converging and less computationally demanding. DN*, which is comparable to 6-31G* with some 6-31+G* character, was used geometry optimization to save computational time. No solvation was used in the calculations. In contrast, Hartree Fock methods were used for the Gaussian calculations for the simpler molecules without metal ions. RHF-6-31g* calculations were used for the self-consistent field density population analysis of the electronic structures for 1-methyl-naphthalene and toluene.

Complexes 1 and 3 were geometry optimized and the surfaces of the HOMO and LUMO's were calculated using Spartan DFT pBP/DN* calculations. Using frontier orbital theory, bonding occurs when the electrons of the HOMO interact in a constructive manner with an empty LUMO orbital. In Figure 23, the Spartan DFT calculation for complex 1 indicate that the HOMO orbital on the π system adjacent to the linker arm is poised to constructively interact with the LUMO on the copper ion (Figure 18). The LUMO plot for 1 has a different conformation than the HOMO plot in Figure 18. The LUMO for 1 was replaced for a LUMO from a different conformation because the LUMO on Figure 18 illustrates orbital on the copper more distinctly. It was noticed that the other LUMO had orbitals around the copper that interacted with some of the π
electrons on the arene part of 1. Similar orbital pictures for the HOMO and LUMO were observed for 3. (Figure 19) The most favorable binding position on the aryl ring for L1 and L2 for the copper center is for the π system adjacent to the linker arm for complexes 1 and 3. The electrons are available from the HOMO to interact with the empty LUMO on the copper ion. The multiple DFT calculations for 1 and 3 were carried out and some of the HOMOs’ and LUMOs’ of the copper ion were found it interact with the π systems on the arene.

Figure 18: The DFT orbital calculations for 1

Figure 19: The DFT orbital calculations for 3
Hartree-Fock (HF) calculations were performed in Gaussian 98 using the RHF-6-31g* method. The larger negative numbers for the self-consistent field (SCF) density calculations correlate to larger electron density on the atoms. This calculation isolates the aryl ligand and studies its electronic properties in depth. The two positions of 1-methyl-naphthalene that have the most electrons are on carbon adjacent to the linker arm and two positions away from the linker arm in next ring structure. Although the carbon in the next ring over is more electron rich, the secondary carbon adjacent to the linker arm is more likely to donate its electrons to the Cu(I) because it is probably more available sterically. This can explain the naphthyl-bound copper(I) complex affinity binding (Figure 1a) to that carbon site. HF studies for toluene showed that the two meta carbons were not equivalent and was found to have an asymmetric electron density calculation. It is not understood why the HF calculations gave these results seen in Figure 20. The favorable binding site for toluene was determined to be the carbon next to the linker arm. These calculational results are consistent with the observation in the $^{13}$C NMR spectrum for complex 1, which suggest that the $\pi$ position adjacent to the linker arm is the most likely place for the copper ion to bind.

Figure 20: Hartree-Focke Calculations of SCF density population calculation.
Conclusion:

The ligands L1 and L2 and three copper(I) complexes 1-3 have been synthesized and partially characterized. The arene appears to bind to the copper ion and is involved in an fluxional process with an activation energy of 9-11 kcal/mol for complex 1 which is a smaller barrier than the naphthalene complex in Figure 1, which has a ΔG of 12-13 kcal/mol. Complex 3 was found to have an even lower barrier to the fluxional process with ΔG of less than 8 kcal/mol. These spectroscopic data, coupled with computational data, have revealed some subtle interplay that steric and electronic effects have on the copper-arene binding. The evidence collected is still inconclusive as to what factors play the larger role in Cu(I)-arene binding. There is still much more to be done to gather more data points. New ligands with electron donating and withdrawing groups on the arene ring could bring new insights into the role that electronics plays in the arene-copper binding strength and location. Also, making a ligand with a methyl group on the linker arm should stabilize the entropic effects of the fluxional process. More can be discovered about this system by making facile replacements in the ligand and to continue with higher level calculational studies.
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Spectrum List:

Spectrum 1: Proton NMR of [L1Cu(OTf)] (1) in CD3NO2 at RT
Spectrum 2: Carbon NMR of [L1Cu(OTf)] (1) in CD3NO2 at RT
Spectrum 3: Carbon NMR of [L1Cu(OTf)] (1) in CD3NO2 at -70 °C
Spectrum 4: ESI-MS of [L1Cu(OTf)] (1) in CH2Cl2
Spectrum 5: Variable Temperature NMR of [L1Cu(OTf)] (1) in CD2Cl2
Spectrum 6: UV-Vis Spectrum [L1Cu(OTf)] (1) in CH2Cl2 - Conc: 3.78e-5 M
Spectrum 7: Nujol Mull Infrared Spectrum [L1Cu(OTf)] (1) using NaCl plates
Spectrum 8: Proton NMR of [L1Cu(PPPh3)OTf] (2) in CD3NO2 at RT
Spectrum 9: Phosphorus NMR of [L1Cu(PPPh3)OTf] (2) in CD3NO2 at RT
Spectrum 10: ESI-MS of [L1Cu(PPPh3)OTf] (2)
Spectrum 11: UV-Vis Spectra [L1Cu(PPPh3)OTf] (2) in CH2Cl2: 4.445e-5 M
Spectrum 12: Nujol Mull Infrared Spectrum of [L1Cu(PPPh3)OTf] (2) using NaCl plates
Spectrum 13: Proton NMR of [L2Cu(PPPh3)OTf] (3) in CD3NO2 at RT
Spectrum 15: Variable Temperature NMR of [L2Cu(OTf)] (3) in CD2Cl2
Spectrum 14: Carbon NMR of [L2Cu(PPPh3)OTf] (3) in CD3NO2 at RT
Spectrum 16: ESI-MS of [L2Cu(PPPh3)OTf] (3)
Spectrum 17: UV-Vis Spectrum of [L2Cu(PPPh3)OTf] (3) - Conc: 6.19e-5 M
Spectrum 18: Nujol Mull Infrared Spectrum of [L2Cu(PPPh3)OTf] (3) using NaCl plates
Spectrum 1: Proton NMR of [L1Cu(OTf)] (1) in CD$_3$NO$_2$ at RT
Spectrum 2: Carbon NMR of [L1Cu(OTf)] (1) in CD$_3$NO$_2$ at RT

Spectrum 3: Carbon NMR of [L1Cu(OTf)] (1) in CD$_3$NO$_2$ at -70 °C
Spectrum 4: ESI-MS of [L1Cu(OTf)] (1) in CH$_2$Cl$_2$
Spectrum 5: Variable Temperature NMR of \([\text{LICu(OIf)}] (1)\)

Spectrum 6: UV-Vis Spectrum \([\text{LICu(OTf)}] (1)\) in \(\text{CH}_2\text{Cl}_2\) - Conc: 3.78e-5 M
Spectrum 7: Nujol Mull Infrared Spectrum \([\text{L}1\text{Cu(OTf)}]\) (1) using NaCl plates
Spectrum 8: Proton NMR of [L1Cu(PPh₃)OTf] (2) in CD₃NO₂ at RT

Spectrum 9: Phosphorus NMR of [L1Cu(PPh₃)OTf] (2) in CD₃NO₂ at RT
Spectrum 10: ESI-MS of \([L1Cu(PPh)_3OTf]\) (2)
Spectrum 11: UV-Vis Spectra $[\text{LiCu(PPh}_3\text{)OTf}]$ (2) in CH$_2$Cl$_2$: 4.445e-5 M

Spectrum 12: Nujol Mulls Infrared Spectrum of $[\text{LiCu(PPh}_3\text{)OTf}]$ (2) using NaCl plates
Spectrum 13: Proton NMR of \([\text{L}_2\text{Cu(PPh}_3\text{)}\text{OTf}]\) (3) in CD\textsubscript{3}NO\textsubscript{2} at RT

Spectrum 14: Carbon NMR of \([\text{L}_2\text{Cu(PPh}_3\text{)}\text{OTf}]\) (3) in CD\textsubscript{3}NO\textsubscript{2} at RT
Spectrum 15: Variable Temperature NMR of [L2Cu(OTF)] (3)
Spectrum 16: ESI-MS of \([\text{L2Cu(PPh}_3\text{)OTf}] (3)\)
Spectrum 17: UV-Vis Spectrum of [L2Cu(PPh3)OTf] (3) - Conc: 6.19e-5 M

Spectrum 18: Nujol Mull Infrared Spectrum of [L2Cu(PPh3)OTf] (3) using NaCl plates