

ABSTRACT

GURKIN, JOSHUA TAYLOR. Synthesis and Characterization of Ruthenium(II) and Platinum(IV) Complexes with Anionic Heteroatomic Ligands. (Under the direction of T. Brent Gunnoe.)

Isolated and fully characterized complexes of late transition metals in low oxidation states possessing amido and alkoxo ligands are relatively rare. These ligands often exhibit nucleophilic and/or basic reactivity. This reactivity is due, at least in part, to the disruption of ligand to metal π -bonding. Reports of early transition metals with low d-electron counts with imido ligands facilitating C-H activation suggest that if later transition metals with amido or aryloxo ligands can be isolated, C-H activation reactivity may be observed.

Ruthenium(II) complexes that catalyze the H/D exchange of N-H and O-H protons at anilido and hydroxo ligands, respectively, with deuterated solvents have been reported, and studies of related systems could shed significant light on C-H activation in these types of reactions. Observing changes in the rate of C-H activation based on specific changes to transition metal complexes could give insight into the creation of highly active C-H activation catalysts.

Presented here are synthetic efforts toward late transition metal complexes with formally anionic heteroatomic ligands. The synthesis and initial characterization of $[\text{EpRu}(\text{Cl})(\text{PPh}_3)(\text{NCMe})][\text{Cl}]$, $[\text{EpRu}(\text{py})_2\text{Cl}][\text{Cl}]$, $[\text{EpRu}(\text{py})_2\text{Cl}][\text{Cl}]$, $[\text{EpRu}(\text{OHMe})(\text{PMe}_3)(\text{Cl})][\text{BAr}'_4]$ are reported {Ep = 1,1,1-tris(pyrazolyl)ethane, py = *N*-pyridine, Ar' = 3,5-(CF₃)-C₆H₃}. The lack of solubility yielded these complexes ineffective for further synthetic manipulation.

Additionally presented is the synthesis and characterization of (*t*bpy)Pt(Me)₂(I)₂ and (*t*bpy)Pt(Me)(NHPPh)(I)₂ (*t*bpy = 4,4'-*tert*-butyl-2,2'-bipyridine). Attempted syntheses of (*t*bpy)Pt(NHPPh)₂(I)₂ and (*t*bpy)Pt(Cl)(NHPPh)(I)₂ are also reported. Initial reactivity of (*t*bpy)Pt(Me)₂(I)₂ and the decomposition of (*t*bpy)Pt(Me)(NHPPh)(I)₂ are further reported.

Synthesis and Characterization of Ruthenium(II) and Platinum(IV) Complexes with Anionic
Heteroatomic Ligands

by
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DEDICATION

This work is dedicated to the Glory of God and to my loving wife Sharon Marie Gurkin for her unfailing love and constant encouragement.

BIOGRAPHY

Joshua Taylor Gurkin was born on July 29, 1984 in Washington, NC to Zack and Beth Gurkin. In 1996, his mother married Steve Mizelle who quickly became his dad. From an early age he felt a desire to teach. He grew up in church choirs and thoroughly enjoyed music; ergo, he anticipated a career teaching music following in the footsteps of his grandmother. During middle school he discovered that he had a talent for web design and computer programming. His career goals now possibly included a computer science degree. However, a funny thing happened on the way to a music or computer science major. In 10th grade Josh took his first chemistry course with Mrs. Marie Swann. He was instantly hooked. He continued to AP Chemistry and then chose to pursue a major in chemistry at Campbell University. His desire had become teaching chemistry to high school students and to impart the same love for chemistry he had developed to future generations.

While at Campbell, Josh quickly found enjoyment in tutoring chemistry and math. He continued to develop web sites and web applications for local civic groups and churches as well as for Spence Hackney Design as an independent contractor. During his chemistry courses, his professors noticed he had a knack for teaching and strongly encouraged him to start teaching labs as well as leading a group study session for chemistry, the first of its kind at Campbell. Due to his ability, his professors encouraged him to pursue a graduate degree. During his senior year he participated in senior research on alternative fuels in the area of biomass ethanol and hydrogen.

During their Campbell careers, Josh met Sharon Dove. Their relationship began as weekly chemistry tutoring sessions (Sharon was a pre-pharmacy student at the time). Following several semesters of friendship, their relationship blossomed. They were engaged on December 26, 2004. On May 15, 2006, Sharon and Josh graduated from Campbell, Sharon with a Bachelor of Science in Elementary Education and Josh with a Bachelor of Science in Chemistry, *Magna Cum Laude*. Just five days later on May 20, 2006, Josh and Sharon were married. During the summer of 2006, Josh taught chemistry labs for summer school at Campbell University.

In the fall of 2006, Josh began graduate school at NC State University where he studied organometallic chemistry with Dr. T. Brent Gunnoe. He worked on complexes with ruthenium(II) and platinum(IV) centers. After three years of working in the field, Josh decided that he would take a break from full-time chemistry work.

Following his graduation, he will begin employment as Director of Information Technology and Director of Billing for Family Legacy Mental Health Services, Inc. in Raleigh, NC while satisfying his desire to teach by tutoring area students in the fields of chemistry and mathematics.

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My dad, Steve Mizelle, deserves a great deal of thanks as well. You have been an awesome example of how to be a strong Christian husband. You have taught me more than you probably realize about life, love, and how to treat people. You impress me more than you realize with your generosity and success. You have blessed our lives since you became a part of our family, and I honestly do not know what life would be like without you.

Thank you to my sister, Mandy, for always being no more than a phone call away. You have shown me how to have great energy for life as well as perseverance when things get tough. I love you.

To my grandparents, Zack & Loreta (Granddaddy & Grandmama) Gurkin and E.H. & Amy (Papa & Mama Amy) Williams, I owe a debt of gratitude. For your faith in me and your examples of how to live, I will be forever grateful. To Granddaddy and Mama Amy, your example of how to look death in the face and be ready for it has been a lesson in faith for all of us. To Grandmama and Papa, your faith and steadfastness in the midst of your spouses' deaths have been a lesson in strength.

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Thank you to all the members of the NC State Chemistry Department. You have all been exceptionally helpful in any number of ways. Thanks to Dr. Sankar for all assistance with NMR experiments. Matt Lyndon deserves special thanks for tremendous help with GC-MS. Thanks also to Dr. Jeffrey Petersen at West Virginia University for solving my crystal structure.

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I'd also like to thank the Gunnoe Group for all the help in and out of the lab. To the senior students, Karl, Nick, John, Colleen, and Sam; for your kind and patient tutelage and to Brad and Joanna for great conversations and helping hands in the lab.

Thank you especially to Brent Gunnoe for serving as my advisor. I am grateful that I was able to work under your tutelage and learn from your experience. You have given me a great deal of time and I appreciate your patience.

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CHAPTER 1

1 Introduction

1.1 Utility of Organometallic Complexes in Homogeneous Catalysis

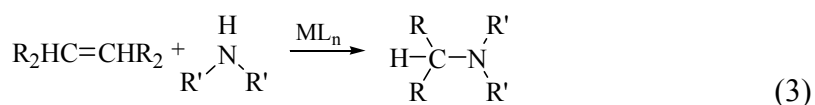
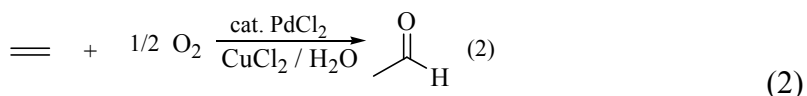
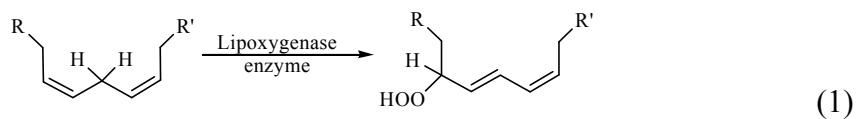
Many industrial processes are carried out utilizing heterogeneous catalysts. Though heterogeneous catalysts often exhibit excellent stability and recoverability, one major drawback is the inability to fine tune catalysts for specific reactivity. In contrast, homogeneous catalysts often function under milder reaction conditions compared with heterogeneous systems, and the single site nature of these catalysts can enhance control of reactivity.¹ By varying the metal identity, ancillary ligands, and metal oxidation state, homogeneous catalysts often can be systematically tuned to carry out reactions with high selectivity.

The importance of advances in homogeneous catalysis has been recognized by the scientific community. In 2005, Robert Grubbs shared the Nobel Prize in Chemistry for his contributions to the field.² Grubbs work includes ruthenium-carbene catalysts that have been shown to carry out ring-closing metathesis (RCM) as well as ring-opening metathesis polymerization (ROMP). These transformations have become commonplace in organic synthesis.² Further evidence of the importance of his work is the fact that his catalysts can be purchased from commercial sources as “Grubbs’ Catalyst”.

Palladium catalysts have been utilized for Stille-³ and Negishi-^{3,4} type coupling reactions. These reactions proceed through oxidative addition of a “pre-functionalized” alkyl- or aryl- halide bond across the Pd catalyst, followed by transmetallation of a metal-

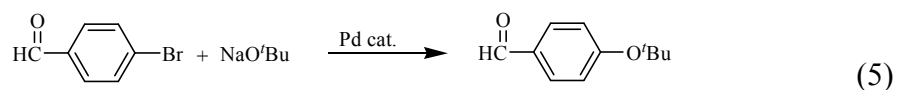
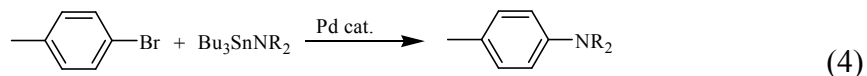
alkyl (often tin for Stille or zinc for Negishi), and completed by reductive elimination of the final organic product.

Transition metal catalysts with formally anionic or dianionic heteroatomic ligands (*e.g.*, amido, oxo, imido, alkoxide, hydroxide, etc.) play an important role in many industrial systems as well as biological processes.⁵⁻⁷ For example, iron-sulfur clusters are present in many biological systems and are known to promote electron transfer reactions.^{8,9} The lipoxygenase enzyme catalyzes the oxidation of 1,4-diene fragments (eq 1).¹⁰⁻¹² Also, nitrogenase enzymes possess iron-sulfur clusters that are central to the conversion of N₂, protons, and electrons to NH₃. Although the mechanism is still debated, it is possible that the catalytic cycle involves M=NH and M-NH₂ intermediates.^{13,14} Methane monooxygenase has been shown to catalyze the partial oxidation of methane to methanol utilizing a binuclear iron-oxide core.^{12,15-17}



The industrially important Wacker process (eq 2)¹⁸⁻²¹ implements a homogeneous catalyst to affect partial oxidation of ethylene to acetaldehyde using oxygen and has been speculated to involve Pd-OH moieties. The hydroamination (eq 3) and hydroalkoxylation of olefins is carried out using metal catalysts and, in some cases, may involve M-NHR or M-OR

systems.²²⁻²⁴ Transition metal based complexes that functionalize aryl halides have also been reported. For example, Pd catalysts that carry out aryl amination (eq 4) and etheration (eq. 5) have been reported by Buchwald and Hartwig respectively.²⁵⁻³²



1.2 Hydrocarbon C-H Activation

Activation of C-H bonds has been the subject of a great deal of study during the last several decades due to the ubiquity of C-H bonds in chemical feedstocks derived from petroleum, coal, and natural gas. The ability to selectively functionalize C-H bonds lends to the production of value-added chemicals. New catalysts for the selective transformation of hydrocarbons as well as C-H bonds or more chemically complex materials would have broad utility for bulk chemical synthesis and the fine chemical industry.

One major difficulty in the transformation of C-H bonds is selectivity. Even simple hydrocarbons can offer primary, secondary, or tertiary sp^3 hybridized groups as well as C-H bonds of sp and sp^2 hybridized moieties. Further complicating the matter is the fact that C-H bonds are typically quite strong. With common bond dissociation energies ranging from approximately 90-120 kcal/mol,³³ C-H bonds do not undergo facile homolytic bond cleavage. Additionally, the covalent nature of C-H bonds limits heterolytic nucleophilic or electrophilic reactivity. But, transition metal systems offer the possibility to facilitate C-H activation and control selectivity. For example, Flood and co workers have reported a CnRh(D)(L)(R)

complex {Cn = 1,4,7-triazacyclononane, L = P(OMe)₃, R=decyl} that selectively carries out H/D exchange between the deuteride ligand and only the stronger, terminal C-H bonds of the alkyl ligand as opposed to the weaker internal C-H bonds.³⁴

Jones and co-workers have also reported that the fragment [Tp'Rh(CNCH₂CMe₃)] {Tp' = hydrotris(3,5-dimethylpyrazolyl)borate} selectively activates terminal C-H bonds on chloroalkane fragments. The activated C-H bonds are not α to the chloride. This provides yet another example of transition metal complexes which selectively activate stronger C-H bonds versus weaker C-H bonds.³⁵

Additionally, Dr. Yucee Feng from the Gunnoe group reported TpRu(PMe₃)₂(OH) which catalyzes H/D exchange between toluene-*d*₈ solvent and the hydroxyl ligand with higher selectivity for the stronger aryl C-H bonds versus the methyl C-H bonds of the solvent at a rate greater than 2 to 1.³⁶ In fact, transition metal systems often exhibit kinetic and/or thermal selectivity for the activation of stronger C-H bonds.

1.3 Methane

An example of potential application of selective catalysts for hydrocarbon functionalization is the conversion of methane (the predominant component of natural gas) to liquid fuels (e.g., the reaction of methane and oxygen to yield methanol). Recent fluctuations in the price of crude oil have contributed to economic instability (Figure 1). As a result of the economic stresses, as well as concern over environmental and national security issues, the development of large scale domestic alternatives to foreign petroleum has become a priority.

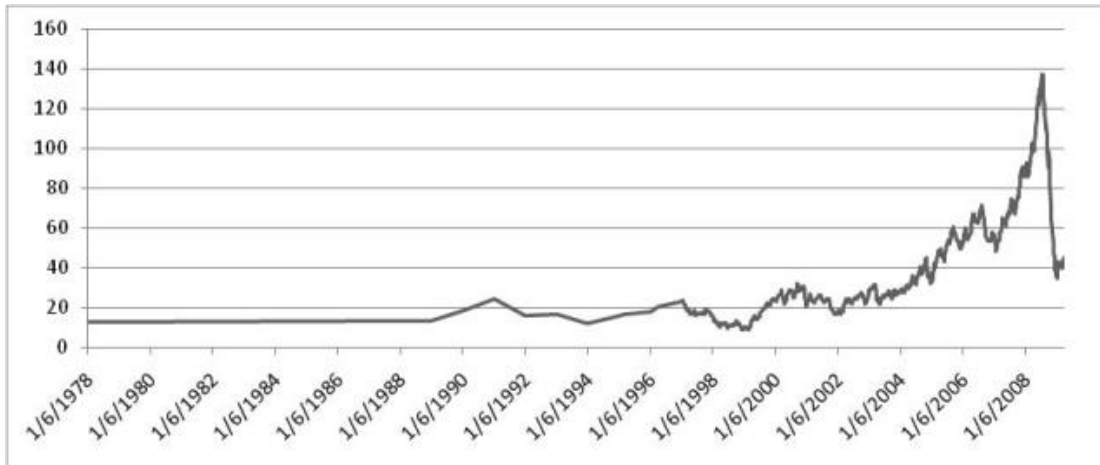


Figure 1. Weighted average (by export) of a barrel of crude oil [prices in USD(\$)].

Substantial methane reserves are available in the form of natural gas. For example, it is estimated that approximately 6.7 trillion cubic meters of reserves are present in the United States,³⁷ and unconventional reserves are of enormous magnitude. Some estimates suggest that sufficient domestic methane reserves exist to fuel transportation for half a century. However, the expense of transporting methane, which is a gas that is difficult to compress, has limited its use. In late 2008, Gov. Sarah Palin of Alaska signed a bill which authorized her state to issue a license to TransCanada Corporation. This license grants the company permission to build a 1,715 mile pipeline to transport methane from Alaska's North Slope at Prudhoe Bay to the Alberta Hub in Canada.³⁸ This pipeline will not likely be operational until late 2018. Additionally, the project will likely cost between \$30 and \$40 billion and will require \$500 million in seed money from the state of Alaska.³⁹ In order for methane to be utilized on a broader scale, including as a fuel in the transportation sector, processes for the conversion of methane to liquids must be developed. Simple compression under high

pressure is not currently economically viable on a large scale and is not compatible with current infrastructure for transportation.

As an energy carrier, methanol possesses many advantages. For example, methanol can be mixed with gasoline as a fuel additive just like ethanol. With minor adjustments to automobile engines and fuel distribution mechanisms, methanol can be utilized as a fuel in internal combustion engines similar to “flex fuel” vehicles that run on E85. In fact, China, the fastest-growing methanol market in the world, has begun to build an infrastructure based on methanol/gasoline blends including M15 fuel for private vehicles and buildup of a fleet of public transportation vehicles that run on M85. Within 1 to 2 years, it is estimated that China will have the capacity to produce methanol at a rate that is about 50% of the current global production.⁴⁰ Methanol, though lower in energy density than gasoline, has a higher octane number, and therefore, burns more completely and efficiently. Additionally, methods for conversion of methanol to gasoline are known.⁴¹ Furthermore, fuel cell technology has already developed that uses methanol for the generation of electricity. Methanol can also be converted to dimethylether (DME), which is a diesel fuel.^{42,43} Thus, new catalyst technologies, which are scalable, for the conversion of methane to methanol could open the door to more widespread use of methane.

1.4 Partial Oxidation of Hydrocarbons

1.4.1 Background and Challenges

Alcohols represent a key building block in the industrial and fine chemical markets. Many current methods for synthesis of alcohols are capital and energy intensive. The partial

oxidation of hydrocarbons to alcohols using oxygen or an oxidant that can be easily regenerated from oxygen could provide a route that is scalable and would potentially permit a more economically viable and atom economical pathway for the production of alcohols. Alkanes, however, are generally inert due, in part, to the non-polar nature of the C-H bonds as well as the relatively high C-H bond dissociation energies (~95-105 kcal/mol). Also, alkanes only weakly coordinate to transition metals, which provide an inhibition to the development of metal-mediated catalysis. Often the oxidation of alkanes to alcohols produces over oxidized products. For example, in methane oxidation in addition to methanol formaldehyde, formic acid, carbon monoxide, and carbon dioxide can be produced. Of these products, methanol has the smallest ΔH (-30.4 kcal/mol) from the starting methane. Furthermore, methanol is a more reactive substrate than methane. Methanol's C-H bonds are weaker than those of methane due to the electron withdrawing nature of the hydroxyl group. Alcohols can often coordinate to an empty coordination site on a metal center better than alkanes lending themselves to further unfavorable reactivity. As a result, the controlled *partial* oxidation of alkanes and arenes to alcohols is challenging.

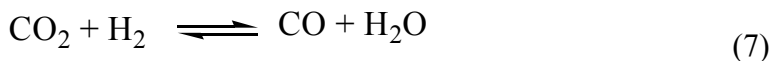
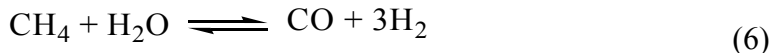
1.4.2 Current Routes for Production of Alcohols from Hydrocarbons

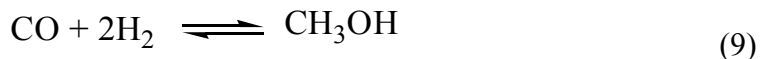
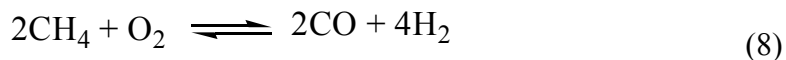
Current methods for the production of methanol (and other alcohols) are not only energy intensive processes, but also have a tendency to produce excessive and often hazardous byproducts.^{44,45} For example, one method by which phenol is industrially produced includes the use of concentrated sulfuric acid followed by sodium hydroxide. Alternatively, reacting benzene, HCl, and O₂ over a Cu/Fe co-catalyst system under forcing

(*i.e.*, high temperature and pressure) conditions produces chlorobenzene. Reacting chlorobenzene with water or NaOH under high temperature and pressure results in phenol production with byproducts of NaCl or HCl respectively.⁴⁵ The most common process for industrial synthesis of phenol is the cumene process. Placing benzene and propene under high temperature (250° C) and pressure (30 atm) in the presence of an acid (usually H₃PO₄) results in the production of cumene. Oxidation in slightly basic conditions produces a cumene radical followed by the formation of cumene hydroperoxide. Hydrolysis in acidic conditions followed by rearrangement yields phenol and acetone.^{46,47} Replacing these harsh conditions with an atom economical method would result in more environmentally benign and cheaper production of phenol.

Currently, methanol is synthesized via the formation of synthesis gas (“syngas”) Syngas, a mixture of CO and H₂, is produced from natural gas (mostly methane) and steam (eq 6). Carbon dioxide can also be used to produce carbon monoxide for syngas through the water-gas shift reaction (eq 7). Syngas can also be produced by direct oxidation of methane to carbon monoxide using oxygen (eq 8).

Syngas is then catalytically converted to methanol (eq 9) under high pressure (250-350 atm) and high temperature (300-400 °C).⁴² While this process is industrially useful, it is capital and energy intensive. The conversion of methane to methanol via syngas is only economically competitive when crude oil prices are high.





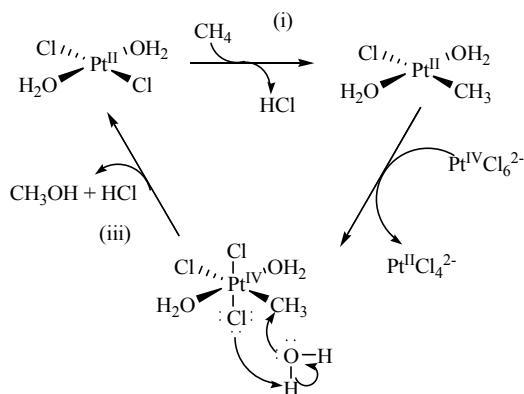
In general the problem of methanol production can be summarized by stating the fact that all products are easily oxidized into the thermodynamically stable and chemically inert products H_2O and CO . The majority of the synthesis methods for producing methanol require forcing conditions such as high pressure and temperature; however, under these conditions further oxidation to undesirable decomposition products is extremely facile (see Table 1).⁴⁸

Table 1. Relative Stabilities of partial oxidation products.⁴⁸

Compound	Products of Decomposition	log K			
		400 K	600 K	800 K	1000 K
CH₃OH	$\text{CO} + 2\text{H}_2$	-0.21	4.00	6.21	7.57
CH₂O	$\text{CO} + \text{H}_2$	5.08	5.46	5.72	5.88
CO	$\text{C} + \frac{1}{2} \text{O}_2$	-19.13	-14.34	-11.93	-10.48

To negate the unfavorable side reactions (*i.e.*, decomposition of oxy-functionalized products), Sokolovskii and coworkers have utilized two trapping methods, condensation and adsorption. While providing better conversion to methanol, this method still only results in ~50% isolated yield.⁴⁸ What is needed is a new, atom economical method to directly convert methane to methanol with minimal side reactions and no environmentally detrimental byproducts.

There have been many forays into the oxidation of methane to methanol.⁴⁸⁻⁵⁵ Although some catalysts are known to carry out oxidation from methane to methanol, none are viable to be scaled up.



Scheme 1. Catalytic cycle of the Shilov system.

One notable example in this area is the Shilov system which utilizes a platinum(II) center of the type $[\text{PtX}_4]^{2-}$ ($\text{X} = \text{Cl}^-$, OH^- , or OH_2). This system electrophilically adds to methane to produce $[\text{X}_3\text{Pt}(\text{CH}_3)]^{2-}$ (Scheme 1, i). Following the addition of the methyl group, platinum(IV)hexachloride oxidizes the active complex to a Pt(IV) center (Scheme 1, ii). Upon oxidation, the Pt-Me bond is rendered susceptible to a nucleophilic attack by water which leads to the reductive elimination of MeOH and HCl returning the system to its starting state (Scheme 1, iii).^{53,54,56} One major limitation of this system is the requirement for a stoichiometric quantity of $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$ relative to methanol produced to carry out the oxidation of the catalyst complex. This cost greatly limits the system's ability to be utilized on a large scale.^{54,57,58}

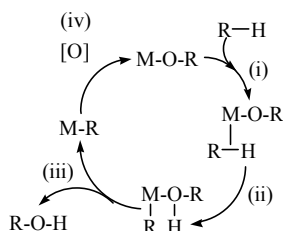
Also, Sen and co-workers have utilized a Pd(II) catalyst which catalyzes the production of methyltrifluoroacetate from methane using and peroxytrifluoroacetic acid (generated upon addition of H_2O_2 and trifluoroacetic anhydride). During the reaction, excess trifluoroacetic anhydride is utilized to remove all trace water. The methyltrifluoroacetate can

be hydrolyzed to produce methanol. Inhibiting the production of methanol *in situ* prevents further oxidation to CO₂ and H₂O.⁵⁹

More recently, a mercury(II) catalyst has been utilized by Periana *et al.* to generate CH₃OSO₃H. Mercury(II) bisulfate reacts with methane in sulfuric acid to produce methyl mercury(II) bisulfate. Further reaction with sulfuric acid produces the methylbisulfate and mercury(I)bisulfate. Re-oxidation to mercury(II) bisulfate is achieved through reaction with sulfuric acid.⁶⁰ Additionally, Periana and co-workers have carried out selective oxidation of methane to a “protected” methyl ester (methyl bisulfate) using (bpym)Pt(Cl)₂ in sulfuric acid (bpym = 2,2’-bipyrimidyl). The methyl bisulfate could lead to the selective production of methanol without further oxidation to undesired products.⁶¹

1.4.3 Catalytic Cycle

Our group has been approaching hydrocarbon oxidation utilizing a new strategy. The two linchpins are C-H activation using late transition metal alkoxy (or aryloxy) systems, which we demonstrated for the first time using Ru(II) (see below),^{36,62} and oxy-insertion reactions. Thus, the catalyst system would carry out the partial oxidation cycle (Scheme 2) using an oxygen atom source to convert a metal-hydrocarbyl bond (M-R) to a metal alkoxy (or aryloxy, M-OR). A key concept here is that metal-oxo complexes are avoided (see below).

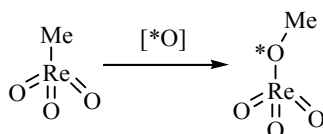


Scheme 2. Proposed catalytic cycle for the partial oxidation of hydrocarbon to alcohol.

The proposed cycle possesses two key steps: 1) **oxy-functionalization** (Scheme 2, iv) wherein an oxygen atom is inserted in the M-R bond to produce a M-O-R moiety and 2) **C-H activation** (Scheme 2, ii) where a new R-H molecule is coordinated and the R-H bond and the M-OR bond undergo metathesis to regenerate M-R and produce R-O-H.

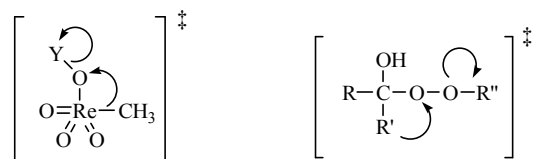
2 Oxy-Functionalization of Metal-Carbon Bonds

One key step in the partial oxidation of hydrocarbons is C-O bond formation (oxy-functionalization). Substantial effort has been directed toward the design of metal-oxo systems that can insert the oxo ligand into a metal-carbon bond. Mayer and coworkers have synthesized a $[\text{TpRe}(\text{O})(\text{OSMe}_2)(\text{Ph})][\text{OTf}]$ complex that undergoes phenyl-to-oxo migration through a $[\text{TpRe}(\text{O})_2(\text{Ph})]^+$ intermediate to produce a Re-OPh bond.⁶³ This study is a *rare* example of the well defined insertion of an oxo ligand into a metal-carbon bond. This transformation is surprising due to the thermodynamics typically observed in M-oxo complexes. The metal oxo complex typically has a lower ΔG° than does the resultant M-OR complex. In addition to a general thermodynamic inhibition, oxo insertion into M-R bonds likely suffers kinetically from the need to combine two generally nucleophilic moieties, a hydrocarbyl and an oxo ligand.



Scheme 3. Periana's (Me)Re(O)₃ system. {^{*}O = ¹⁷O}.

Recently, (Me)Re(O)₃ (MTO) (Scheme 3) was shown to stoichiometrically transfer an oxygen atom from external oxidants (*e.g.*, H₂O₂, PhIO, IO₄[−]) into a Re-Me bond resulting in the Re-OMe complex.⁶⁴ Through isotopically labeled oxidants, the fact that the oxygen was directly transferred from the oxidant and not a result of a migration to one of the oxo ligands was substantiated.⁶⁴ The proposed mechanism, which has been supported by calculations, resembles a Baeyer-Villiger type reaction (Scheme 4) where the oxidant coordinates to the metal center and is then attacked by the methyl group yielding a net methoxy ligand. In this analogy, the metal is the equivalent of the carbonyl group of the organic variant. Based on these results, we believe that creating a complex which can insert an oxygen atom into a M-Me bond is a matter of achieving the proper tuning.

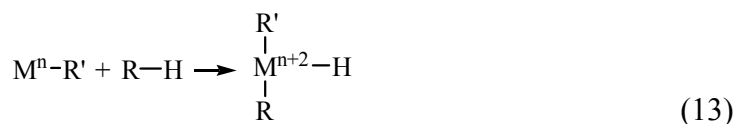
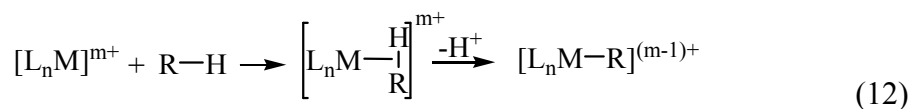
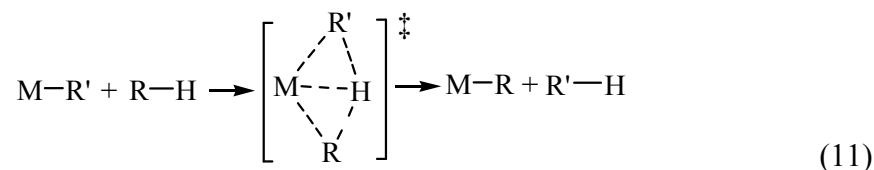
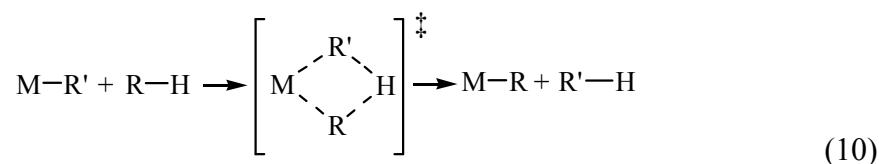


Scheme 4. The proposed transition state for MTO (left) resembles a Baeyer-Villiger reaction (right).

3 C-H Activation

There are several mechanisms through which metal-mediated C-H activation occurs including σ -bond metathesis (SBM), oxidative addition (OA), and electrophilic substitution (ES). The σ -bond metathesis mechanism (eq 10) is characterized by a concerted process via a four-center, four-electron transition state. The transfer of σ -bonds is not stepwise and is

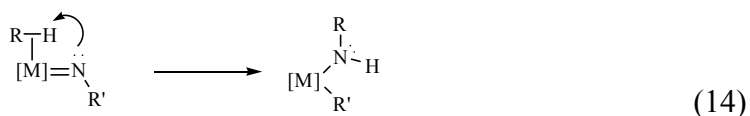
characterized by an almost square transition state.⁶⁵ C-H activation via SBM is typically invoked for d^0 metal centers which cannot activate C-H bonds via oxidative addition due to the lack of redox flexibility.⁵⁰ Oxidative Hydrogen Migration (eq 11) is a variant of SBM in which there exists a M-H interaction in the transition state. This transformation has been recently suggested for middle to late transition metals with d-electron counts > 0 .⁶⁶ This interaction gives a close M \cdots H bond distance and suggests oxidative character in the transition state. According to calculations, the M \cdots H bond results in a kite shaped geometry in the transition state.⁶⁶



In the electrophilic substitution mechanism (eq 12), the coordination of the C-H bond activates it toward the release of a proton to a halide or other base in solution.⁵⁰ Oxidative addition (eq 13) involves the insertion of the metal into the C-H bond resulting in a formal two electron loss by the metal.

As discussed below, our current hypothesis is that transition metal complexes possessing an anionic heteroatomic ligand coordinate a C-H bond in an open coordination site, polarize the bond rendering the proton acidic, and then the lone pair on the heteroatomic ligand deprotonates the C-H bond. Examples of transition metals with a M-X moiety which carry out C-H activation are known. For example, highly electrophilic, d^0 , early transition metals with metal nitrene ligands have been shown to activate C-H bonds (eq 14).⁶⁷⁻⁷²

The electrophilic metal center promotes coordination and activation of a C-H bond. The polarity of the M=N bond combined with the acidity imparted by C-H coordination to the metal center drives reactivity. The net 1,2-addition of the C-H bond across the metal-nitrene yields a metal-alkyl bond and a metal amido ligand. Because of the d^0 early transition metal center and its lack of redox flexibility, reductive elimination of the alkyl amido is unlikely.



The Gunnoe Group has been studying the nature of metal-heteroatom bonding using *late(r)* transition metals (*e.g.*, Ru, Cu, and Pt) including use for C-H activation.^{36,62,73-87} Relatively few complexes have been reported that activate C-H bonds across a M-X bond.^{36,62,88} Most germane here, we have reported evidence that complexes of the type $\text{TpRu}(\text{PMe}_3)_2\text{X}$ ($\text{X} = \text{OH}, \text{NHPh}$) activate aromatic C-H bonds.^{62,89} Though no X-H products are directly observed, H/D exchange between the deuterated solvent and the proton at the heteroatom was observed. Mechanistic studies suggest that initial ligand dissociation is followed by arene coordination. The C-H bond of the arene is activated and the proton is

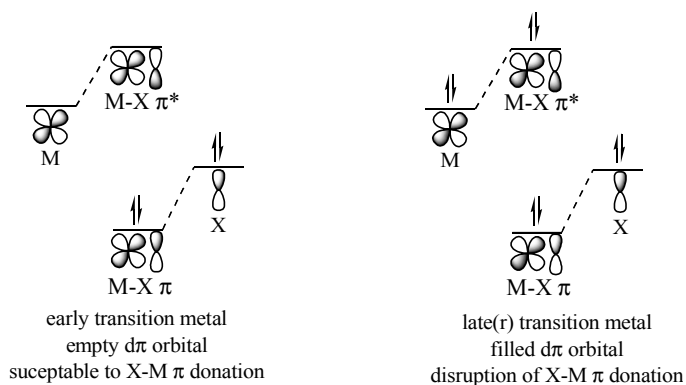


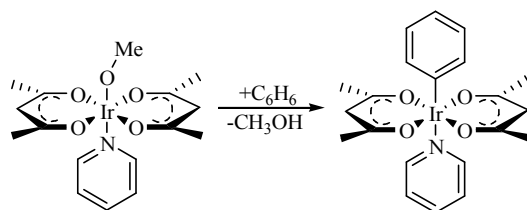
Figure 2. Comparison of early transition metal with low d-electron count to late transition metal with high d-electron count with regard to M-X bonding.

If late metal complexes possessing an anionic heteroatomic ligand can be synthesized and isolated, the π -disruption can be utilized to achieve greater reactivity. Caulton has indicated that if a filled/filled interaction (Figure 2 – right side) is present, a higher energy π -orbital is present compared to a complex with the ability to engage in M-X π -bonding (Figure 2 – left side). The result of this interaction is a lone pair that is fairly reactive and typically undergo basic or nucleophilic reactivity.⁹²

Utilizing the reactivity anticipated by the filled/filled interaction, we believe that C-H activation across M-X can be promoted by increasing the basicity of the lone pair (see below for further discussion). Similar to the reactivity observed with early transition metal complexes possessing imido ligands that produce amido ligands by the net 1,2-addition of C-H bonds across the M-X bond (see above), we believe that utilizing later transition metals and amido ligands, C-H activation yielding coordinated amine could be achieved.

To that end the Gunnoe Group began by targeting Ru(II) complexes which possess metal-heteroatom bonds with the premise that “...by accessing Ru(II) complexes that possess an open coordination site and a nondative nitrogen-based ligand, it might be feasible to

transiently bind nonpolar X-H (e.g., H-H or C-H) bonds to the metal center, thereby activating the substrate toward *intramolecular* deprotonation."⁷³ The complex (PCP)Ru(CO)(NH₂) {PCP = 2,6-(CH₂P^tBu₂)₂C₆H₃} has been shown to activate dihydrogen stoichiometrically to produce ammonia and (PCP)Ru(CO)(H). Activation of C-H bonds can be closely compared to the activation of H-H bonds. The bonds have similar dissociation enthalpies (105 kcal/mol for H-H; 104 kcal/mol for H-CH₃). This complex also was shown to activate the C-H bonds on the *tert*-butyl groups on the PCP ligand *intramolecularly* to yield ammonia and a cyclometalated species.



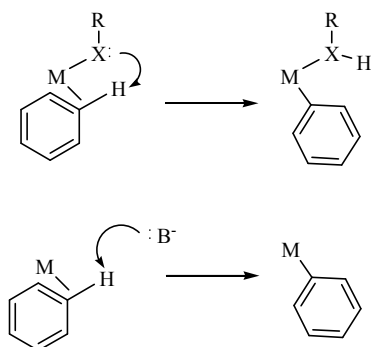
Scheme 6. Periana's Ir complex that activates C-H bonds across M-O bonds

Also, Periana and coworkers have synthesized the Ir(III) complexes (acac)₂Ir(OMe)(L) (acac = acetylacetonate; L = pyridine or MeOH) which stoichiometrically activate benzene C-H bonds across the Ir-OMe bond to produce methanol and a Ir-Ph bond (Scheme 6).⁸⁸ Calculations presented by Periana and Goddard suggest that the mechanism resembles that of an electrophilic substitution mechanism wherein the “base” that removes the proton is the lone pair on the non dative ligand which is coordinated to the metal center.⁹³

Macgregor and Davies have performed calculations on the complex [Pd(DBMA-H)(OAc)₂]⁺ (DBMA-H = dimethylbenzylamine) to shed light on the mechanism of intramolecular C-H activation. The system in question undergoes coordination and

activation of an *ortho*-C-H bond of the benzylamine to produce a cyclometalated species and coordinated HOAc. The calculations suggested an electrophilic activation of the C-H bond with an *intramolecular* base for deprotonation.^{94,95}

Recently, Goldberg *et al.* have reported a (PNP)Rh^I(OR) {PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine; R = Ph, Ac, CH₂CF₃, or H} system that carries out C-H activation.^{96,97} The complexes where R = CH₂CF₃ or H were shown to undergo stoichiometric benzene activation to produce the phenyl complex, (PNP)Rh(Ph) and free ROH. When R = Ph or Ac, the complex carries out catalytic H/D exchange between water and arenes. The mechanistic studies of this system revealed a mechanism that is distinct from that proposed for our Ru(II) system and Periana's Ir(III) system. The mechanism described involves initial dissociation of the OR⁻ group followed by coordination and activation of arene with subsequent deprotonation of the activated C-H bond by the previously dissociated OR⁻. The transformation resembles traditional electrophilic substitution (Scheme 7).



Scheme 7. The IPT mechanism resembles (top) an electrophilic substitution mechanism (bottom) with the “base” being the lone pair of the heteroatomic ligand as opposed to external.

The amalgam of studies suggest that one mode of C-H activation for by late transition metal systems with alkoxo or amido ligands is an intramolecular proton transfer (IPT).⁸⁷ This process occurs by initial coordination of the C-H bond. This coordination imparts polarization to the C-H bond rendering it more acidic. The heteroatomic ligand lone pair then acts as a base and plucks the proton from the C-H bond. Hence, similar to electrophilic substitution, the metal activates the C-H bond to transfer a proton to a base; however, in the IPT system, the proton transfer is *intramolecular* and the metal is proposed to be involved in a 4-center/6-electron transition state. Periana and Goddard have termed this an internal electrophilic substitution.⁹³

The intramolecular proton transfer model suggests that increasing the basicity of the heteroatomic ligand should facilitate the reaction; however, the magnitude of this impact has not been experimentally probed. Interestingly, Goddard and Periana have calculated that the basicity of the heteroatomic ligand of their Ir(III) systems will have little impact on the activation energy of C-H activation,⁹³ while calculations by Gunnoe and Cundari for other systems indicate the potential for substantial influence.⁸⁷

Compared to more traditional modes of metal-mediated C-H activation (*e.g.*, oxidative addition, electrophilic substitution, σ -bond metathesis), little is known about C-H activation via intramolecular proton transfer. Our group has been seeking to delineate such reactions by preparing a range of late transition metal complexes with high *d* electron counts and anionic heteroatomic ligands and studying C-H activation reactions. Our goals are to

explore the influence of metal identity, oxidation state, identity of auxiliary ligands, and the nature of the heteroatomic ligands on C-H activation reactions.

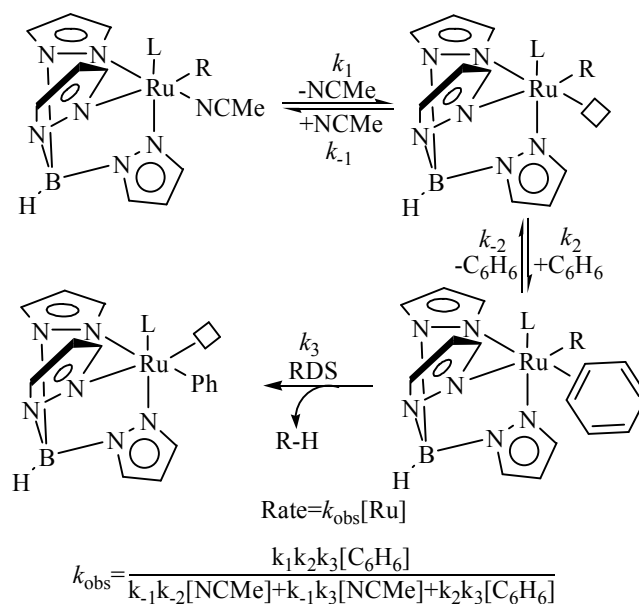
4 Considerations for Design of Targeted Complexes

Based on our current thinking of the C-H activation and oxy-insertion mechanisms for complexes possessing heteroatomic ligands, we propose that the following considerations are necessary for a catalyst to function as shown in Scheme 2. An electrophilic metal center will facilitate coordination of the hydrocarbon as well as activation of the C-H bond toward IPT. Due to the nature of the IPT mechanism, the lone pair on the heteroatom must be free to remove the proton and, hence, not be engaged in π -bonding with the metal. This is achieved by metal centers with filled $d\pi$ orbitals. Despite substantial effort to observe insertion of an oxo ligand into M-R bonds, to our knowledge, only a single example of a well-defined reaction (under thermal conditions) has been reported.⁶³ Thus, we anticipate the need to avoid the formation of metal-oxo (*i.e.*, $M\equiv O$) systems. An electrophilic metal center should facilitate activation of the oxidant and therefore insertion of the oxygen into the M-R bond.

5 Research Goals

Previous studies of C-H activation by $TpRu(L)(L')R$ systems by the Gunnoe group have utilized coordinatively saturated species with the open coordination site generated by dissociation of L' ($L' = NCMe$ or PMe_3). Kinetic studies of these complexes are complicated by dissociation of L' , which is reversible and competes with hydrocarbon coordination. The combination of dissociation and coordinative competition renders the observed rate constant

an amalgam of terms which is difficult to deconvolute and garner data specific to the single C-H activation step (Scheme 8).



Scheme 8. C-H activation with convoluted k_{obs} .⁸²

In order to improve understanding of factors impacting C-H activation, the research presented herein centers on studying the general nature of C-H activation by 1,2-addition across M-X (X = NHPH, OH) bonds. In order to more precisely study the C-H activation step, a series of complexes containing heteroatomic ligands which possess either an open coordination site or an easily accessed coordination site are targeted.

In one pursuit I have attempted the synthesis of d^6 Ru(II) complexes possessing amido and alkoxo ligands. Compounds analogous to the $\text{TpRu}(\text{PMe})_2(\text{X})$ systems (see above) were sought {Tp = hydridotris(pyrazolyl)borate}. However, in place of the monoanionic Tp ligand framework, complexes with the neutral analogue Ep were desired {Ep = 1,1,1-tris(pyrazolyl)ethane}. Utilizing Ep could allow easier access to an open

coordination site as well as providing a more electrophilic metal center (see Chapter 3). Both of these characteristics should yield a more active complex.

In a second line of study I have carried out the oxidation of Pt(II) complexes to Pt(IV) utilizing elemental iodine. These complexes allow continued study in the octahedral d^6 paradigm. The higher oxidation state could also provide a more electron-deficient complex. The complexes may also provide easy access to an open coordination site by removing an iodide ligand and utilizing a non-coordinating, anionic counterion (see Chapter 2).

CHAPTER 2

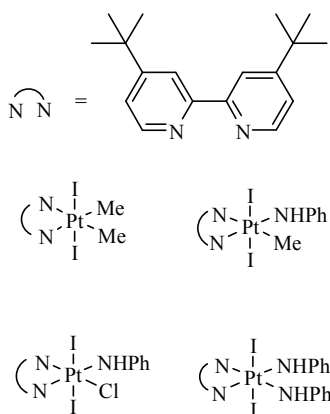
1 Rationale for Pt(IV) Chemistry

As a part of the Gunnoe Group's broader effort to develop catalysts for C-H functionalization based on the cycle shown in Scheme 2, (Chapter 1), the feasibility for C-H activation by Pt(IV) complexes that possess NR_2 and OR ligands is a focus of study. Here, we wish to study the 1,2-addition of C-H bonds across Pt-NR₂ and Pt-OR bonds and to understand the mechanistic features of the reaction. Many investigators, including Puddephatt, Bercaw and Labinger, Tilset, Periana, Goldberg and Templeton, have carried out studies of C-H activation by Pt(II) complexes.⁹⁸⁻¹⁰⁶ Likewise, we anticipate that Pt(IV) systems can be utilized for the C-H activation of arenes and alkanes. While C-H activation by Pt in lower oxidation states is routinely accepted, only a few complexes with the Pt(IV) oxidation states have been reported to exhibit C-H activation,¹⁰⁷⁻¹¹⁰ and the data do not clearly demonstrate that the C-H activation step occurs via a Pt(IV) metal center. Thus, one might expect that C-H activation by Pt(IV) is inherently challenging. We anticipate, however, that C-H activation at a Pt(IV) center with amido or alkoxo ligands is feasible. The $(\text{acac})_2\text{Ir}(\text{OMe})(\text{py})$ (py = pyridine) complex possesses an Ir(III) metal center and has been shown to initiate C-H activation at the metal center. Other Ir(III) complexes have also been shown to activate C-H bonds.^{88,111} We propose that it is plausible that a carefully tuned ligand set coordinated to a metal that is one group to the right on the periodic table should be able to carry out C-H activation. Furthermore, until our recent report,¹¹² no examples of

Pt(IV)-X (X = OR, NR₂) complexes have been reported. Therefore, C-H activation with Pt(IV) systems of this type has not been attempted to our knowledge.

The Gunnoe group has reported octahedral d⁶ Pt^{IV} systems of the type (NCN)PtX₃ {NCN = 2,6-(pyrazolyl-CH₂)₂C₆H₃}; X = alkyl, halide, or anilido ligand}.^{112,113} The complex (NCN)Pt(Me)₂(NHPh) has been shown to react with dihydrogen to produce aniline and uncharacterized Pt products. Furthermore, (NCN)Pt(Me)₂(NHPh) reacts with phenylacetylene to produce aniline and (NCN)Pt(Me)₂(C≡CPh).

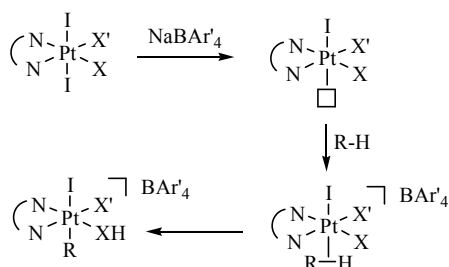
Recently the Gunnoe group reported a Pt^{II} d⁸ system that catalyzes ethylene hydroarylation.¹¹⁴ Heating (100°C) a catalytic amount of (t₄bpy)Pt(Ph)₂ (t₄bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) in benzene with 1 equivalent of HBAr^F₄ under ethylene pressure results in ~12 turnovers of ethylbenzene after 16 hours. Additionally, heating [(t₄bpy)Pt(Ph)(THF)][BAr^F₄] at 100°C for 16 hours under 17 psi of ethylene pressure results in ~66 turnovers of ethylbenzene, which is nearly 100% yield based on the limiting reagent, ethylene.



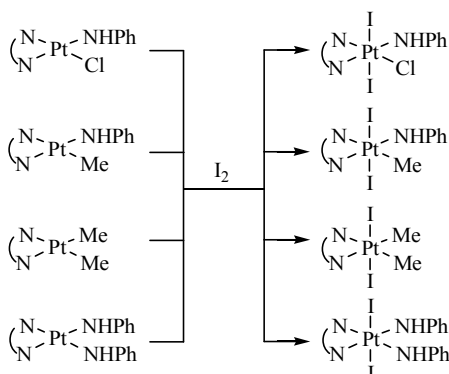
Scheme 9. Target Pt(IV) complexes.

In unpublished work, the Gunnoe group has observed methanol production using a Pt(IV) complex. Hence, we are initiating a broad study of related systems to establish fundamental considerations. For example, the Gunnoe group is exploring the (*t*-bpy)PtX₂ framework as a starting point toward furthering understanding both the oxy-insertion step and the C-H activation step of the methane to methanol partial oxidation cycle. In addition to our unpublished results, Bercaw and Labinger have reported related Pt(II) hydroxy systems that activate C-H bonds.^{115,116} Therefore the study C-H activation using a series of Pt(IV) complexes containing NR₂ and OR ligands (Scheme 9) is targeted. The four-coordinate Pt(II) complexes (*t*-bpy)Pt(Me)₂, (*t*-bpy)Pt(Me)(NHPH), (*t*-bpy)Pt(NHPH)₂, and (*t*-bpy)Pt(NHPH)(Cl) will serve as entry points for this work.¹¹⁷⁻¹¹⁹ The latter three complexes have been prepared by the Gunnoe Group, but are unpublished.

Oxidation of these *d*⁸ square planar complexes will be used to provide octahedral Pt(IV) complexes, from which cationic five-coordinate systems that can coordinate and activate C-H bonds of hydrocarbons will be generated (Scheme 10). The primary goals of our research in this area are to: 1) determine feasibility of C-H activation via 1,2-addition across Pt(IV)-X (X = OR or NR₂) bonds, 2) determine relative propensity for C-H activation by Pt-R versus Pt-X ligands, 3) determine the relative propensity for C-H activation by Pt(IV) and Pt(II) systems, and 4) extend systems that activate C-H bonds toward catalyst development.



Scheme 10. *In situ* generation of a 5-coordinate Pt(IV) complex with subsequent C-H activation (X = Me, Cl, or NHPH; Ar^F₄ = 3,5-CF₃-phenyl).



Scheme 11. Conversion of Pt(II) complexes to Pt(IV) bisiodide complexes.

Often implicated as active species in metal-mediated transformations, coordinatively unsaturated complexes can be extremely reactive and must often be produced *in situ*. The active species for the complexes presented herein will most probably need to be generated utilizing this method. Goldberg and co-workers, however, have shown that 5-coordinate Pt(IV) complexes possessing multiple alkyl ligands have a penchant for C-C reductive elimination to give Pt(II) products. For example, the 5-coordinate d⁶ complex (DtBPP)Pt(Me)₃ {DtBPP = 3,5-di-*tert*-butyl-2-(2-pyridyl)pyrrolidine} was shown to thermally decompose to produce methane (CH₄ and CH₃D) in addition to ethane and a dinuclear Pt complex.¹²⁰ The mechanism posited by the authors' proceeds with initial C-C

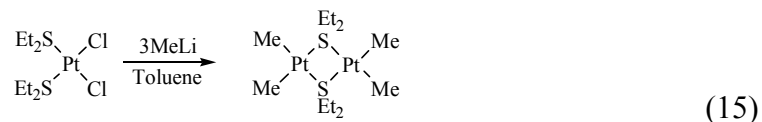
reductive elimination to produce ethane followed by C-H activation through two pathways which both ultimately yield a stable dinuclear complex.

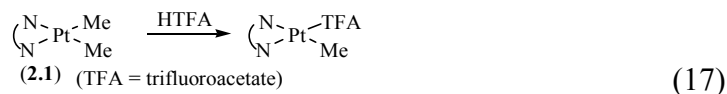
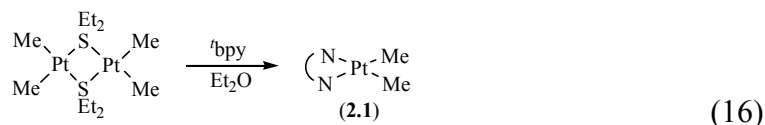
Furthermore, Goldberg and co-workers have carried out studies which indicate that reductive elimination from 6-coordinate platinum complexes proceeds through a five coordinate pathway rather than direct reductive elimination from the six coordinate species, an intermolecular mechanism, or a radical pathway.^{106,120-128}

One goal of this study is to generate five-coordinate Pt(IV) systems with alkyl and amido ligands to study and compare C-H activation. But, the conversion of six-coordinate Pt(IV) precursors to five-coordinate cations might result in rapid C-C and or C-N reductive elimination.¹²⁴ As a result, I planned to prepare systems with Pt-R, Pt(R)(NHR), Pt(NHR)₂, and Pt(NHR) (no Pt-R or other Pt-NHPh units in the latter system, see Scheme 9).

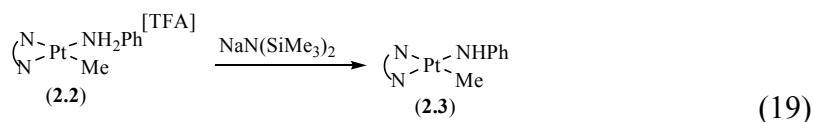
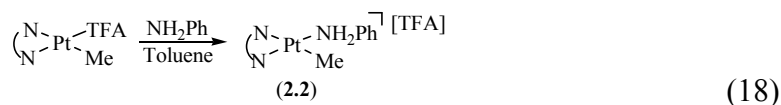
2 Results

Synthesis of (^tbpy)Pt(Me)₂ and Derivatives. Systems developed by Puddephatt have proved to be ideal entry points for this chemistry. The dimer [Me₂Pt(μ -SMe₂)]₂ was prepared according to published procedure (eq 15).¹²⁹ When stirred with ^tbpy in diethyl ether, the dimer was broken up to yield (^tbpy)Pt(Me)₂ (**2.1**)(eq 16).¹¹⁸ Treatment of (^tbpy)Pt(Me)₂ with HTFA (TFA = trifluoroacetate) results in conversion to (^tbpy)Pt(Me)(TFA) (eq 17).^{118,119}

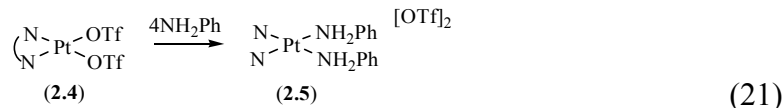
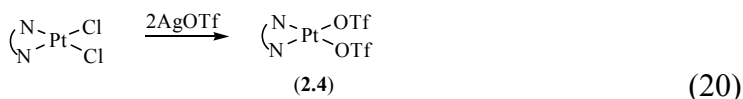


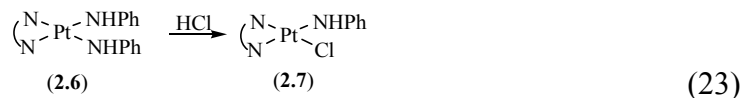
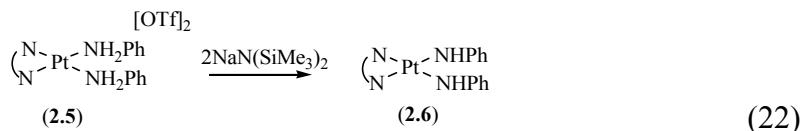


As developed by Dr. Colleen Munro-Leighton,¹³⁰ heating (^tbpy)Pt(Me)(TFA) in toluene with aniline produces [(^tbpy)Pt(Me)(NH₂Ph)][TFA] (**2.2**) (eq 18). Deprotonation of **2.2** with one equivalent of [Na][N(SiMe₃)₂] yields (^tbpy)Pt(Me)(NHPH) (**2.3**) (eq 19).



Synthesis of (^tbpy)Pt(NHPH)₂ and derivatives. Stirring (^tbpy)Pt(Cl)₂ in methylene chloride with 2 equivalents of AgOTf produces (^tbpy)Pt(OTf)₂ (**2.4**) (eq 20).¹¹⁹ Utilizing further chemistry originally developed by Dr. Colleen Munro-Leighton,¹³⁰ addition of excess aniline to a CH₂Cl₂ solution of (^tbpy)Pt(OTf)₂ yields [(^tbpy)Pt(NH₂Ph)₂][OTf]₂ (**2.5**) (eq 21) in 15 minutes. Deprotonation with 2 equivalents of [Na][N(SiMe₃)₂] produces (^tbpy)Pt(NHPH)₂ (**2.6**) (eq 22).¹³⁰ Slow addition of 1 equivalent of HCl in diethylether gives (^tbpy)Pt(NHPH)(Cl) (**2.7**) (eq 23).¹³⁰





Oxidation of (*t*bpy)Pt(Me)₂ with elemental iodine. I found that stirring complex **2.1** in benzene with iodine results in conversion to the bisiodide Pt(IV) complex (*t*bpy)Pt(Me)₂(I)₂ (**2.8**) (eq 24). The product is isolated by removal of solvent. In an attempt to facilitate the removal of solvent (due to the fact that benzene easily freezes while under vacuum), utilizing THF as an alternative solvent was attempted. Tetrahydrofuran, however, proved not to be a viable solvent for this oxidation reaction. Utilizing THF results in incomplete conversion.

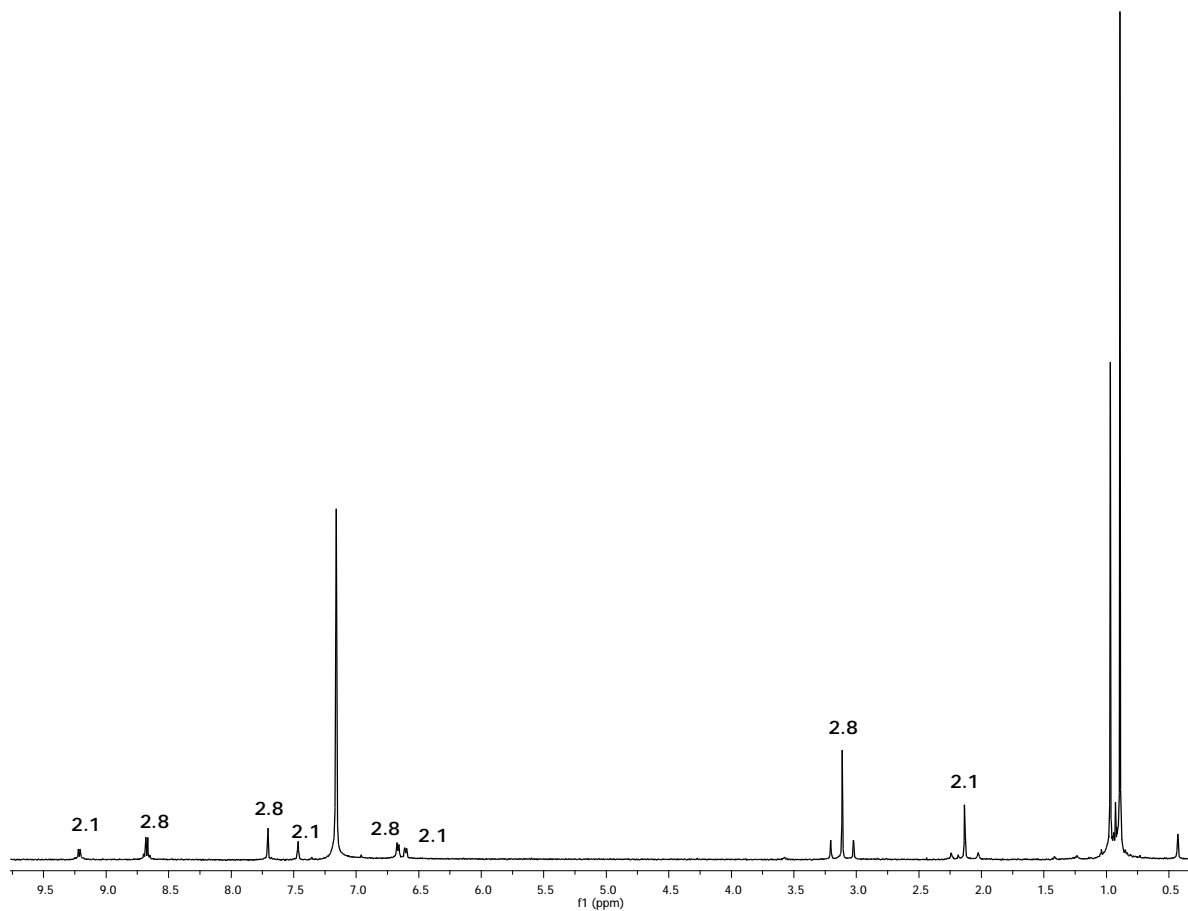
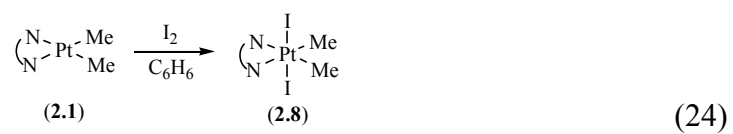
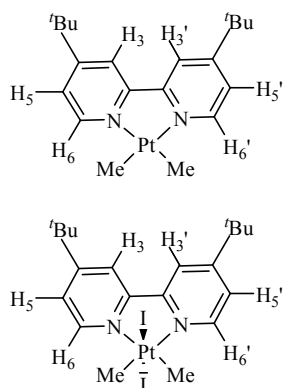


Figure 3. THF does not appear to be a viable solvent for synthesis of **2.8** and appears to lead to incomplete conversion (in benzene- d_6).





Scheme 12. Numbering scheme for ^1H NMR spectra of $(t\text{-bpy})\text{Pt}(\text{Me})_2$ (**2.1**) and $(t\text{-bpy})\text{Pt}(\text{Me})_2(\text{I})_2$ (**2.8**).

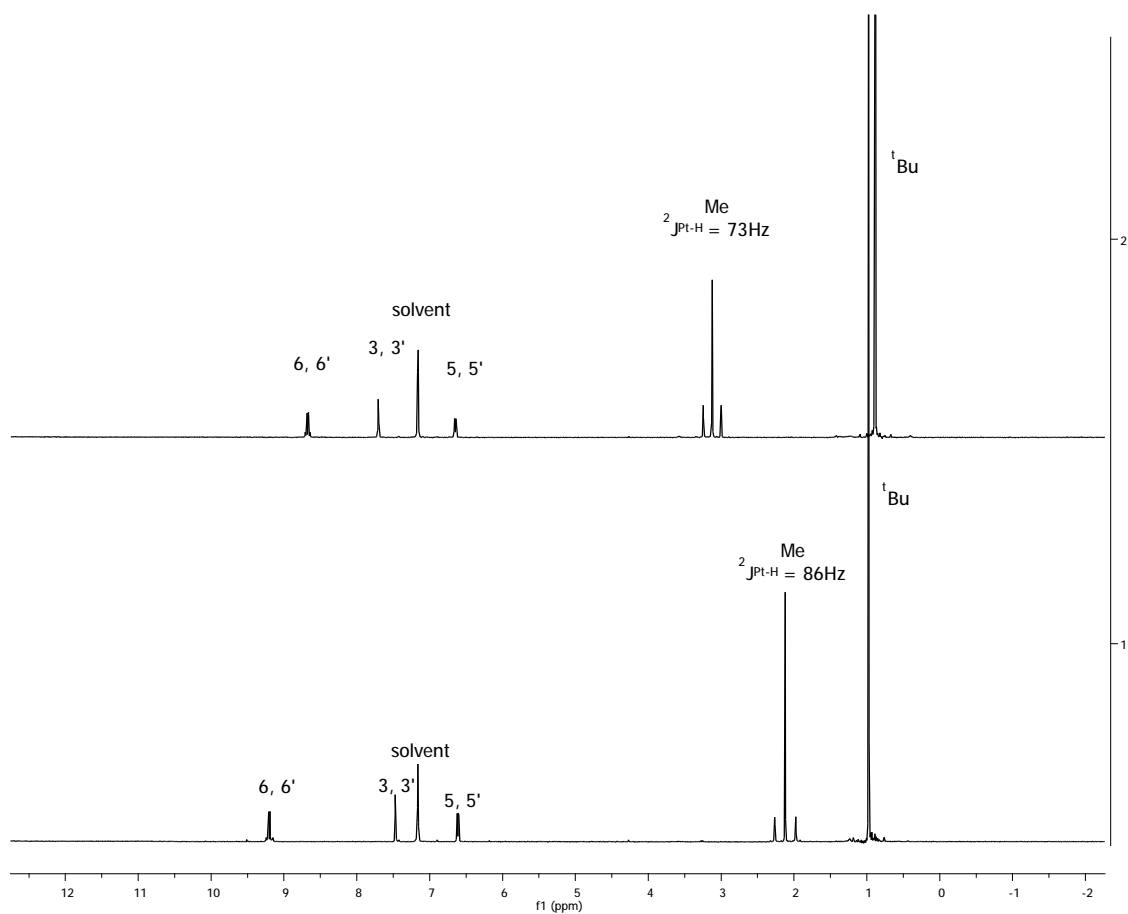
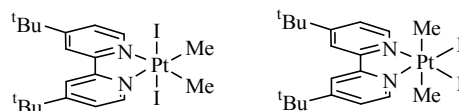


Figure 4. ^1H NMR spectra of $(t\text{-bpy})\text{Pt}(\text{Me})_2$ (**2.1** - bottom) and $(t\text{-bpy})\text{Pt}(\text{Me})_2(\text{I})_2$ (**2.8** - top) in benzene- d_6 .



Scheme 13. There are two possible configurations for the Pt(IV) product (**2.8**) based on the ^1H NMR spectrum.

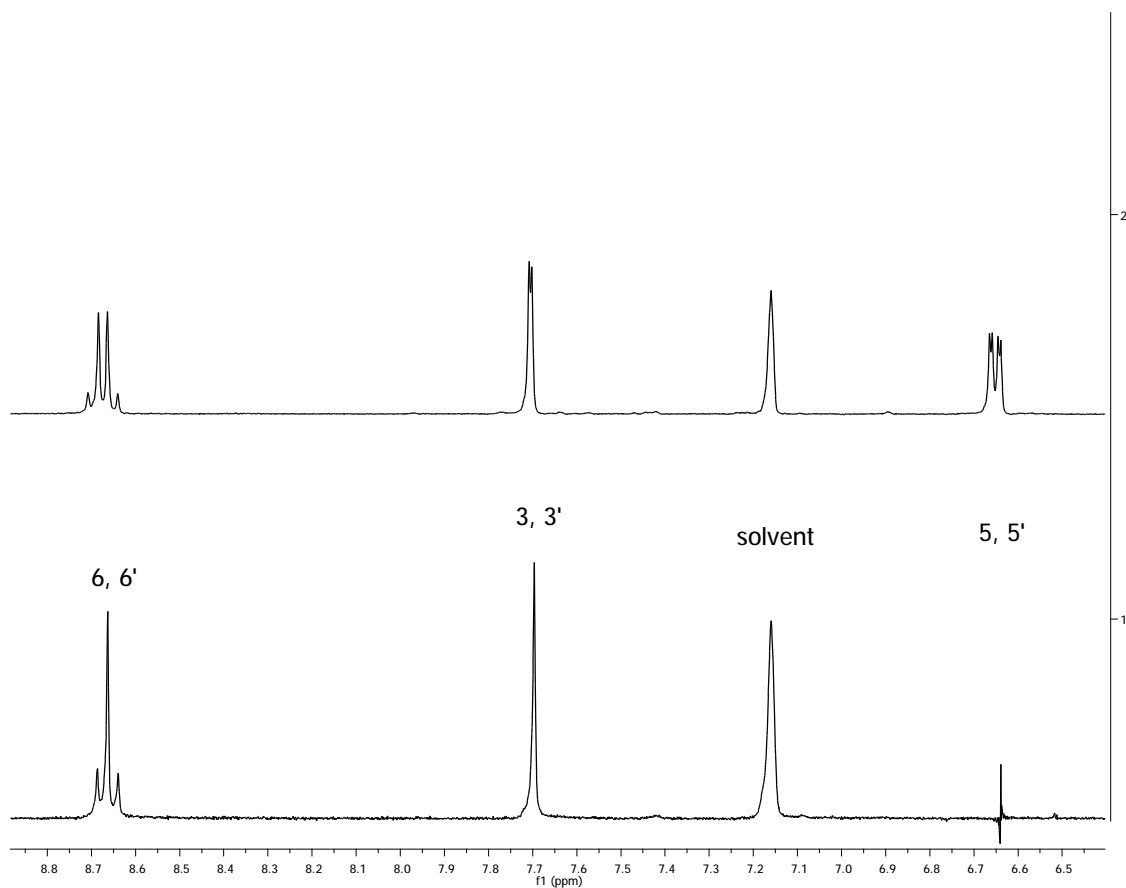


Figure 5. Homonuclear decoupling experiment to verify assignments of ^1H bpy resonances as well as assign Pt satellites on the ^1H bpy 2,2' protons (**2.8** in C_6D_6).

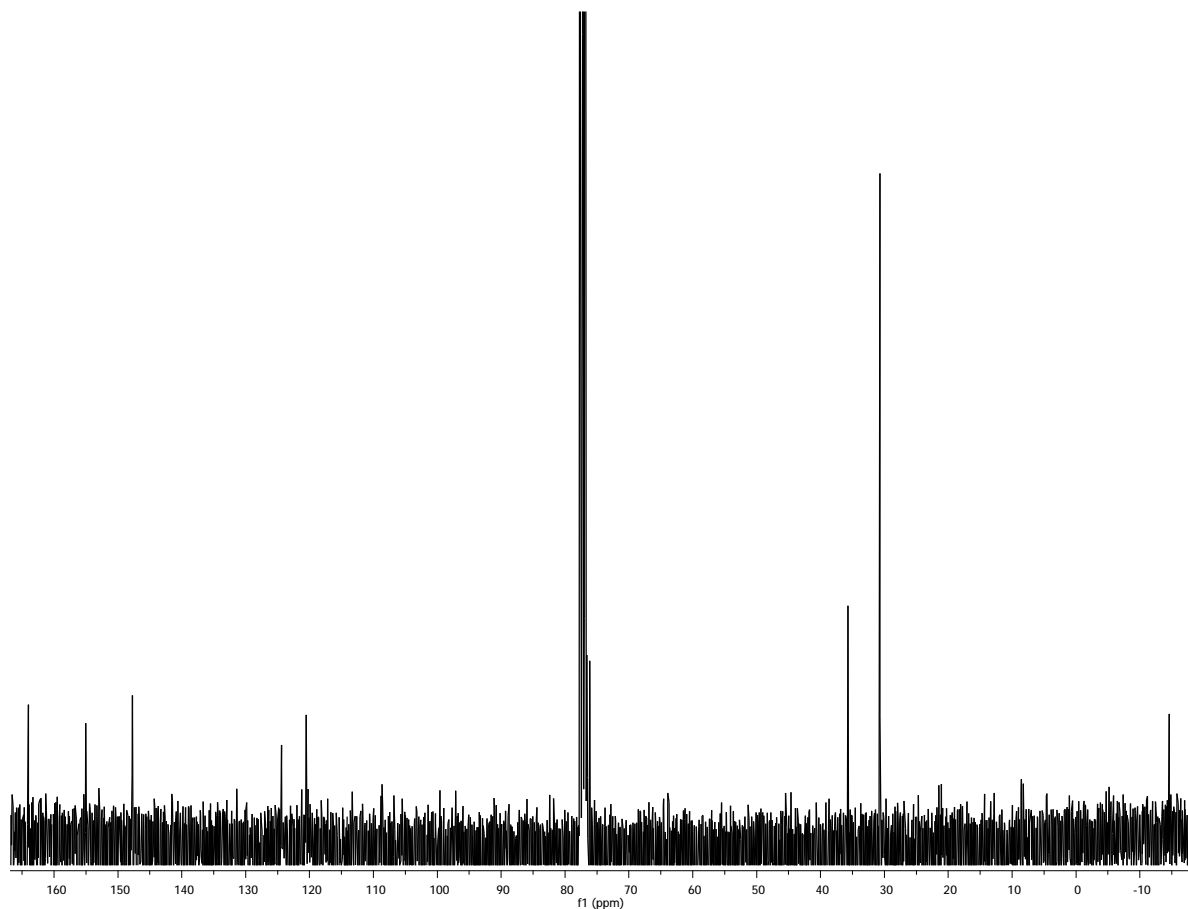


Figure 6. ^{13}C NMR spectrum of $(^t\text{bpy})\text{Pt}(\text{Me})_2(\text{I})_2$ in CDCl_3 .

Complex **2.8** has been characterized by ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, elemental analysis, and an X-ray diffraction study. The observation of a single resonance for the *tert*-butyl groups as well as a single resonance due to the methyl groups is consistent with a geometry of *trans*-methyl or *trans*-iodide ligands. The lack of evidence of inequivalent methyl or ^tbpy ligands rules out the possibility of a *cis*-methyl-*cis*-iodide product. The equivalent ^tbpy and Me groups suggest one of the two isomers depicted in Scheme 13 and is inconsistent with an isomer that has a configuration with a methyl and iodide trans to the pyridyl fragment.

Relative to the Pt(II) complex, the oxidized complex exhibits a downfield Pt-CH₃ shift from 2.12 ppm to 3.12 ppm in the ¹H NMR spectrum as well as a decrease ²J_{Pt-H} coupling constant from 86 Hz to 73 Hz. The value of the coupling constant for complex **2.8** is similar to those noted by Templeton *et al.* where the octahedral Pt(IV) complex Tp'PtPh₂Me shows a ²J_{Pt-H} of 70.4 Hz (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate).¹³¹ An analogous, more recently reported complex (t⁴bpy)Pt(Me)₂(Br)₂ has a similar ²J_{Pt-H} of 70.6 Hz.¹³² The ¹³C NMR spectrum revealed 5 downfield resonances assigned to the t⁴bpy aromatic carbons. Additionally, a resonance at 35.67 ppm was assigned to the quaternary *tert*-butyl carbon and a peak at 30.66 ppm which is due to the *tert*-butyl methyls. Complex **2.8** has a resonance assigned to the methyls attached to the platinum at -14.7 ppm in the ¹³C NMR spectrum. The (t⁴bpy)Pt(Me)₂(Br)₂ complex also exhibits a ¹J_{Pt-C} of 515.7 Hz compared to 506.5 Hz for **2.8**.

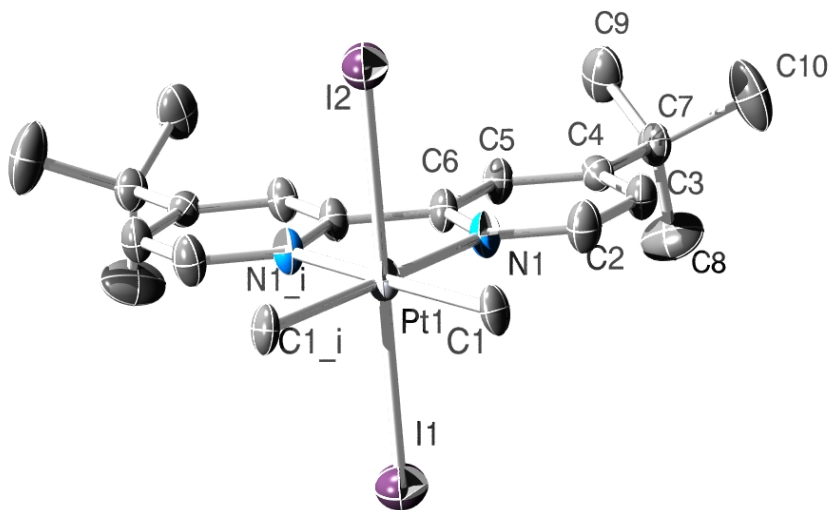


Figure 7. ORTEP of (t⁴bpy)Pt(Me)₂(I)₂ (30% probability, H atoms excluded for clarity). Selected bond lengths(Å) and angles(°): Pt1-N1, 2.168(4); Pt1-N1_i, 2.167(4); Pt1-C1, 2.183(5); Pt1-C1_i, 2.208(5); Pt1-I1, 2.640(1); Pt1-I2, 2.652(1); N1-Pt1-N1_i, 75.5(2); N2-Pt1-C1_i, 100.92(2); N1-Pt1-C1, 101.13(2); C1_i-Pt1-C1, 82.2(3).

A crystal suitable for X-Ray diffraction study was grown of (^tbpy)Pt(Me)₂(I)₂ from layered THF/pentane. The crystal revealed *trans* iodide ligands (Figure 7). The analogous (^tbpy)Pt(Me)₂(Br)₂ (see above) exhibits a Pt-N bond length of 2.172(6) Å, which is roughly equal to the 2.168(4) Å for **2.8**. The Pt-C bonds are also nearly identical with an average length of 2.200(5) Å for (**2.8**) and 2.081(7) Å for the dibromide complex. As expected, the Pt-halide bond length is greater for Pt-I [2.65(1) Å] vs. Pt-Br [2.45(1) Å]. The N-Pt-N bond angles are roughly identical at 75.5(2)° for **2.8** and 75.2(3)° for (^tbpy)Pt(Me)₂(Br)₂. The bromide complex exhibits a greater C-Pt-C bond angle at 87.3(4)° relative to the 82.2(3)° for (^tbpy)Pt(Me)₂(I)₂. Finally the C-Pt-N bonds of the dibromide complex are slightly smaller at 98.7(3)° versus 101.0(2)° average for **2.8**.

Table 2. Crystallographic parameters for (^tbpy)Pt(Me)₂(I)₂ (**2.8**).

	(^t bpy)Pt(Me) ₂ (I) ₂
Empirical formula	C ₂₀ H ₃₀ N ₂ PtI ₂
Formula weight	747.35
Crystal system	orthorhombic
a, Å	17.074(1)
b, Å	14.267(1)
c, Å	20.097(2)
α, β, γ, °	90
V, Å ³	4895.5(7)
Z	8
D _{calcd}	2.028 g/cm ³
Crystal size, mm	0.10 x 0.24 x 0.42
R1, wR2 {I>2σ(I)}	0.0487, 0.1332
GOF	1.088

Reactivity of (^tbpy)Pt(Me)₂(I)₂. Heating (^tbpy)Pt(Me)₂(I)₂ in benzene-d₆ at temperatures up to 100°C for up to a week showed no change by ¹H NMR spectroscopy. However, heating (^tbpy)Pt(Me)₂(I)₂ in benzene-d₆ with NaBAR^F₄ shows decomposition of the

complex and likely production of CH_3D (indicated by a 1:1:1 triplet at ~ 0.15 ppm) by ^1H NMR spectroscopy. GC-MS analysis of the reaction solution showed evidence of $\text{C}_6\text{D}_5\text{CH}_3$ ($m/z = 98$), biphenyl- d_{10} ($m/z = 164$), and PhI-d_5 ($m/z = 209$). To verify that these compounds were not a result of impurities in the solvent, a GC-MS of C_6D_6 was taken and no evidence of any of the previously listed compounds was found. Although not definitive, the production of these species indicates that $[(^i\text{bpy})\text{Pt}(\text{Me})_2(\text{I})]^+$ may carry out C-H activation; however, C-C reductive elimination also appears to be a problem. The resultant platinum decomposition products have not been identified (Figure 8).

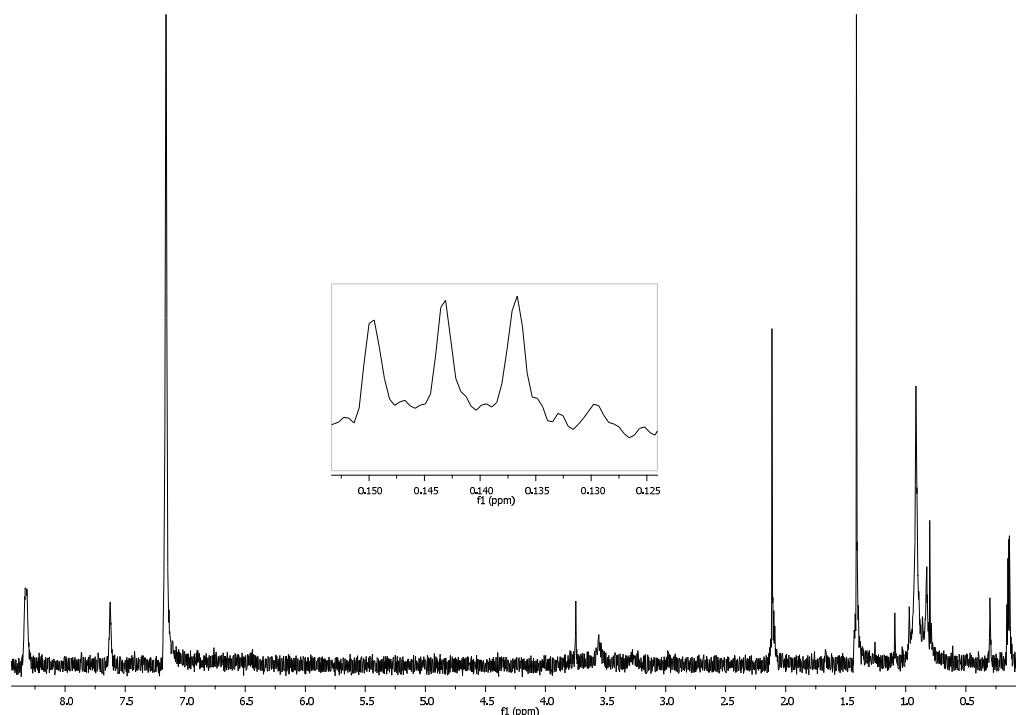


Figure 8. ^1H NMR spectrum of reaction of $(\text{tbpy})\text{Pt}(\text{Me})_2(\text{I})_2$ with $\text{NaBAR}_4^{\text{F}}$ with inset of 1:1:1 triplet of CH_3D in benzene- d_6 .

In an attempt to synthesize complexes of the type $(^i\text{bpy})\text{Pt}(\text{Me})_2(\text{I})(\text{X})$ ($\text{X} = \text{OMe}$, OH), **2.8** was allowed to react with excess NaOMe and CsOH . In a screw cap NMR tube

containing a THF- d_8 solution of **2.8**, excess NaOMe was added. The farthest downfield ^1H resonance is shifted from 8.6 ppm to 9.4 ppm. Further the methyl resonance moves upfield from 2.1 ppm to 1.2 ppm with an increase in $^2J_{\text{Pt-H}}$ coupling constant to 86 Hz from 73 Hz (Figure 9). The shift in the methyl resonance coupled with the return to an 86 Hz coupling constant (the same as **2.1**) suggest a reversion to a Pt(II) complex. Removal of the solvent and reconstitution in C_6D_6 revealed that, the complex has reverted to **2.1**, and free ^1H was produced [^1H NMR (C_6D_6 , δ): 9.043 (d), 8.633 (d), 6.932 (dd), 1.141 (s)].

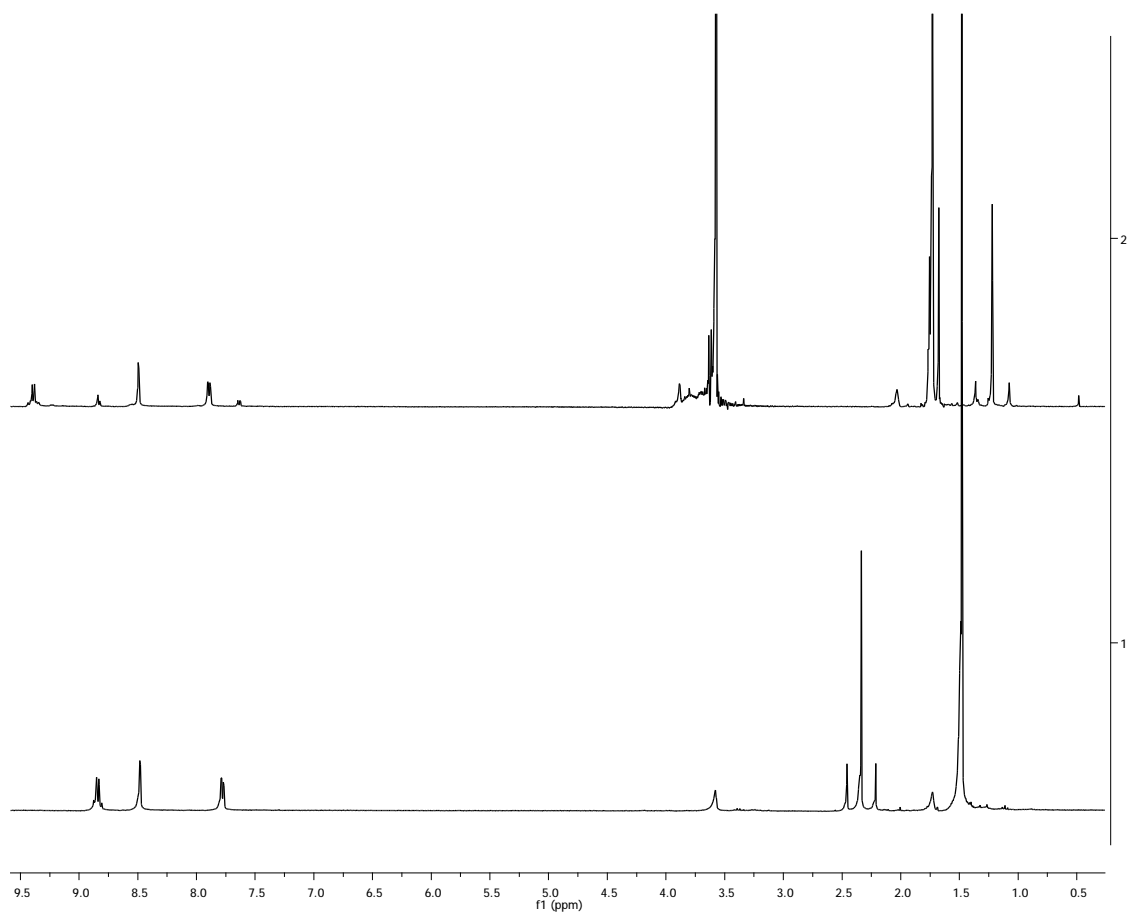


Figure 9. ^1H NMR spectra of $(^1\text{H})\text{Pt}(\text{Me})_2(\text{I})_2 + \text{NaOMe}$ (bottom before addition of NaOMe, top after addition of NaOMe) in THF- d_8 .

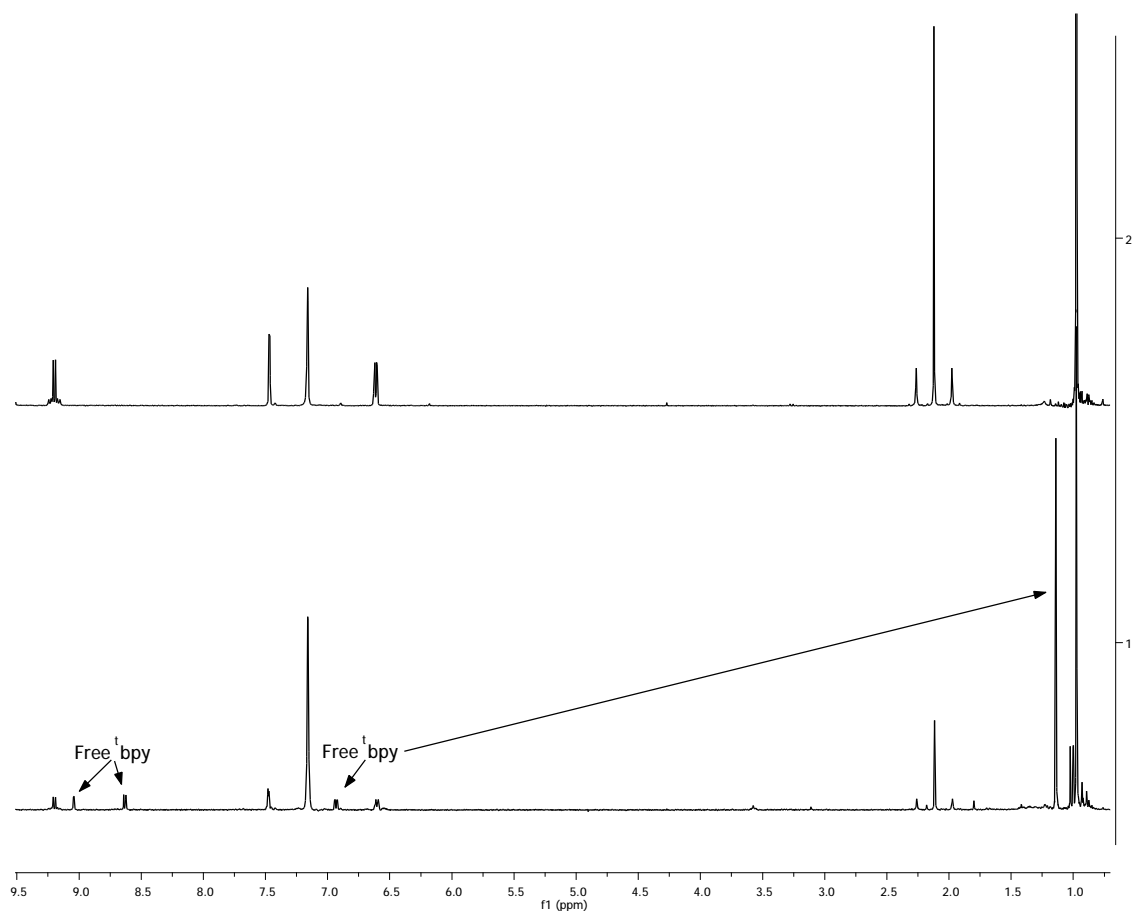


Figure 10. Complex **2.8** when reacted with NaOMe (bottom) in THF- d_8 reverts to complex **2.1** and releases free t' bpv (top) (^1H NMR spectra in C_6D_6).

In contrast, the reaction with CsOH seems to yield decomposition showing the methyl singlet with Pt-satellites having disappeared. The downfield t' bpv resonance also moves upfield (Figure 11). No evidence of methanol was present in the ^1H NMR spectrum. The solvent was removed and the residuals taken up in C_6D_6 . The ^1H NMR spectrum showed no methyl resonance and free t' bpv.

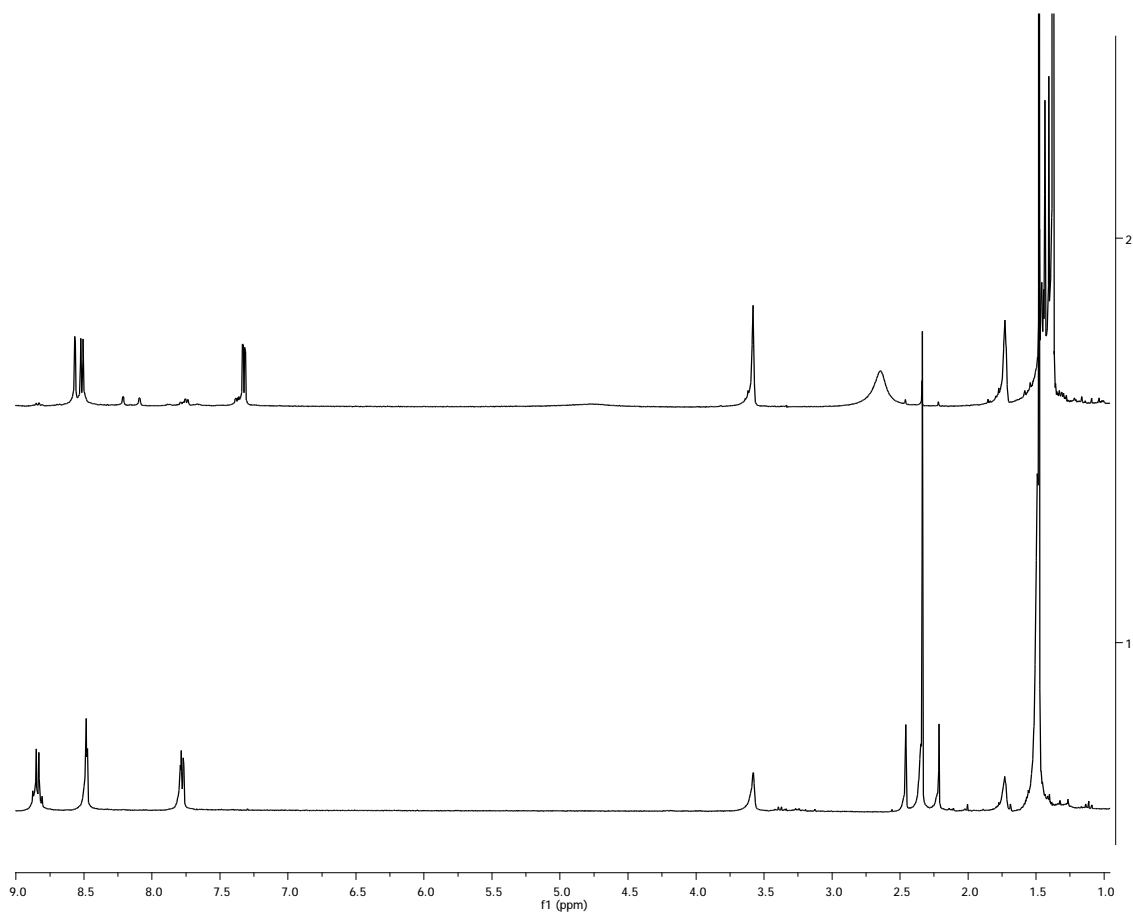


Figure 11. ^1H NMR spectra of $(t'\text{bpv})\text{Pt}(\text{Me})_2(\text{I})_2 + \text{CsOH}$ in $\text{THF-}d_8$ (bottom nmr – initial; top nmr – final).

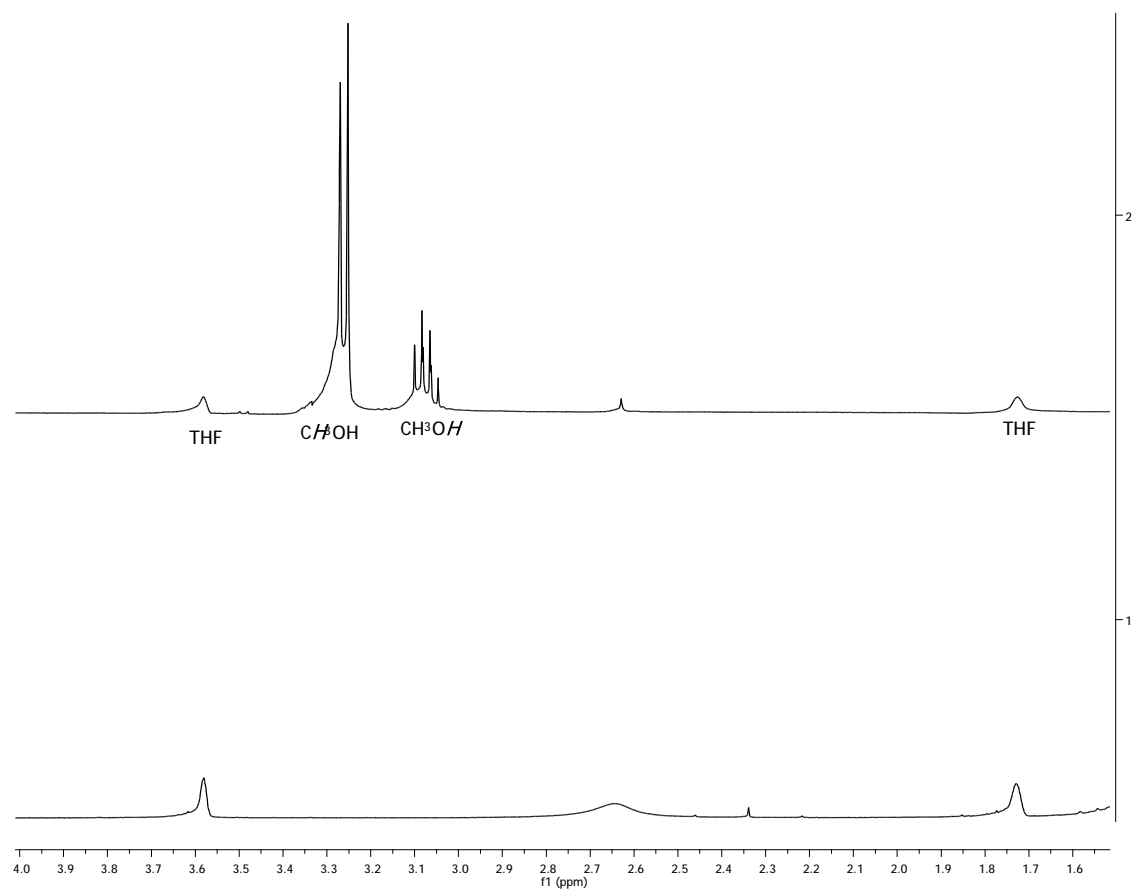


Figure 12. Expansion of the ^1H NMR spectrum of $(t\text{-bpy})\text{Pt}(\text{Me})_2(\text{I})_2 + \text{CsOH}$ in $\text{THF-}d_8$ (bottom) with reference spectrum of MeOH in $\text{THF-}d_8$ (top).

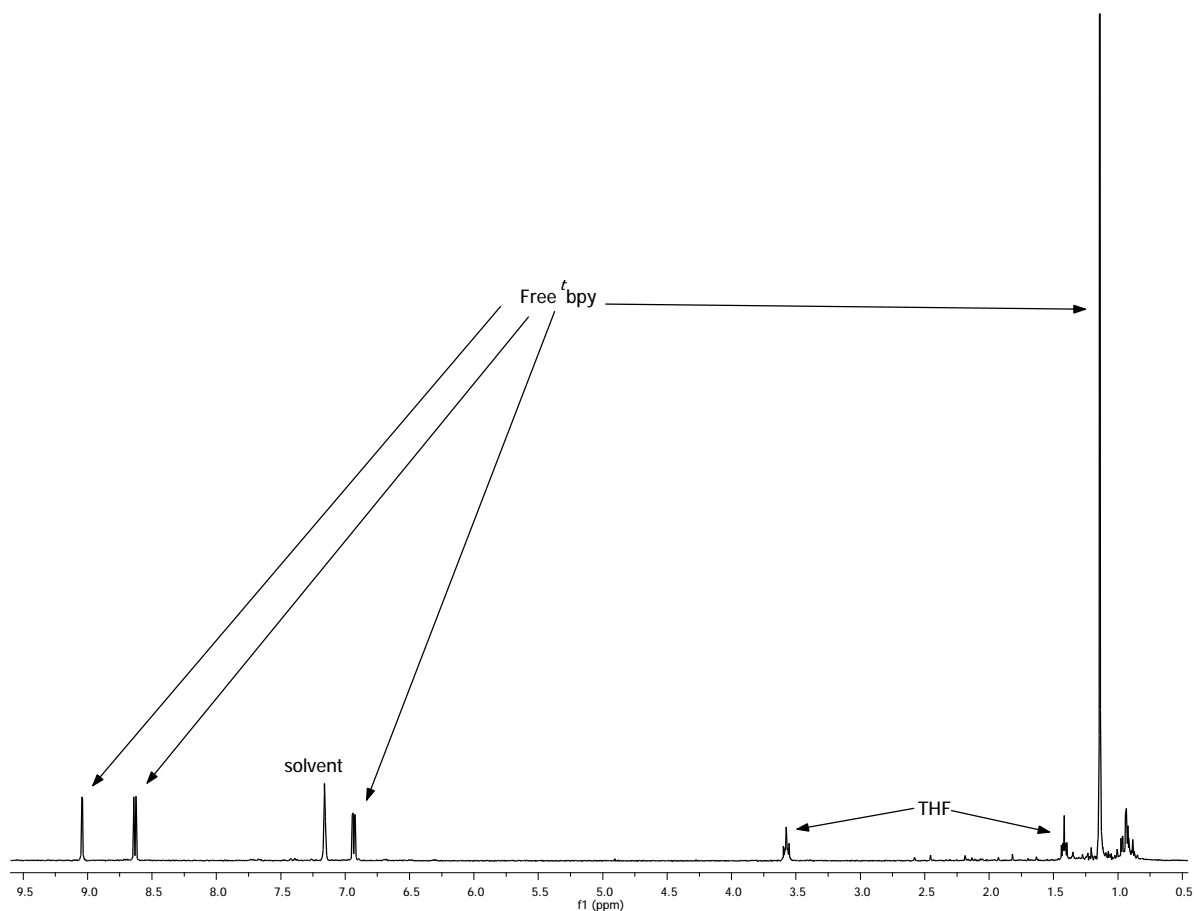


Figure 13. Products of the reaction of **2.8** and CsOH in benzene- d_6 .

Oxidation of (*t*-bpy)Pt(Me)(NPh) with elemental iodine. In a screw cap NMR tube, elemental iodine was added to a C_6D_6 solution of (*t*-bpy)Pt(Me)(NPh) (**2.3**). This gives a product with an NMR spectrum consistent with (*t*-bpy)Pt(Me)(NPh)(I)₂ (**2.9**) (Figure 14). The most salient details which indicate production of complex **2.9** include a downfield shift of the methyl resonance in the 1H NMR spectrum from 1.85 ppm to 3.87 ppm and a decrease in the frequency of the Pt satellites on the methyl resonance from 84 Hz to 72 Hz. Scaling up this reaction in benzene, however, yields unclear conversion. Therefore a series

of NMR scale reactions were attempted to determine alternate solvents for conversion. These reactions are summarized in Table 3.

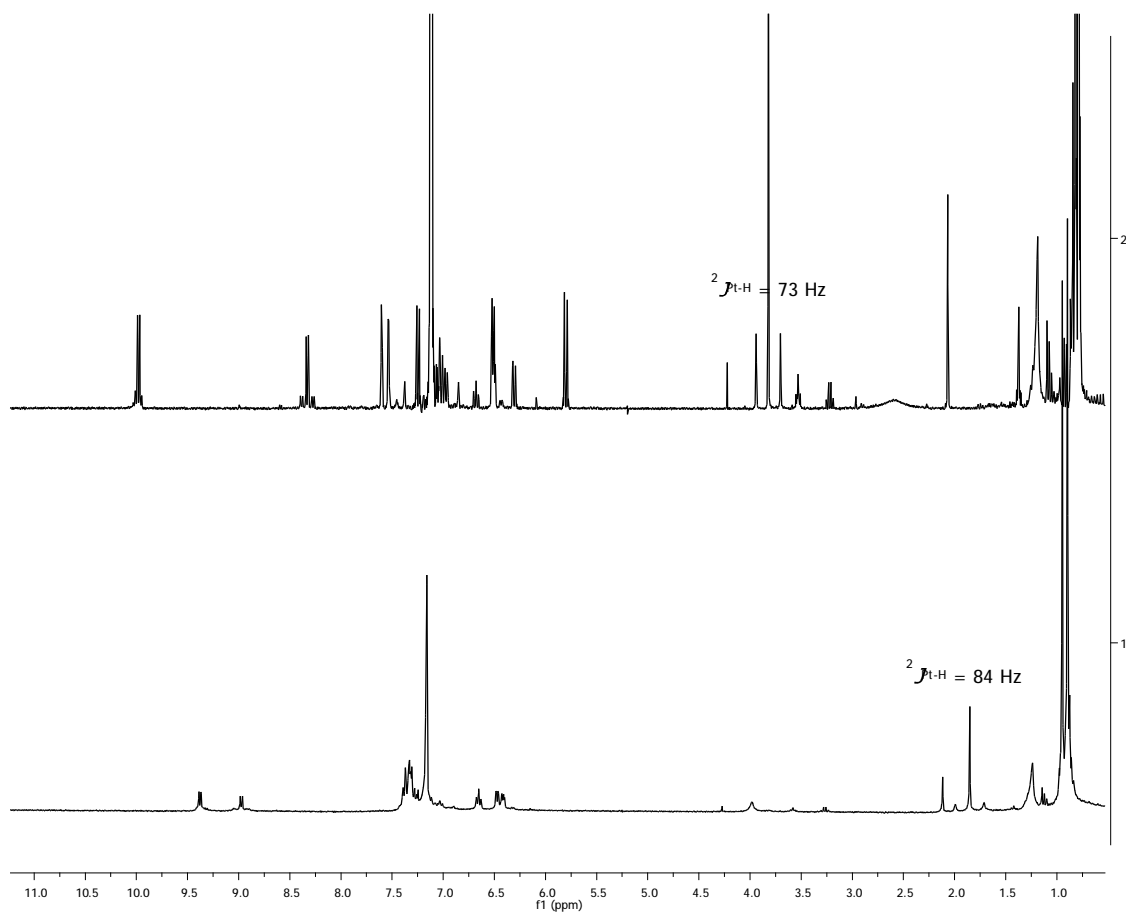


Figure 14. ^1H NMR spectra of (tbpy)Pt(Me)(NHPh) [bottom] and (tbpy)Pt(Me)(NHPh)(I) $_2$ [top] in benzene- d_6 .

Table 3. Summary of solvents in which the reaction of **2.3** and I $_2$ was attempted to form **2.9** and whether the reaction cleanly produced the expected product.

Solvent	Clean Production?
CDCl $_3$	No
Acetone- d_6	No
CD $_3$ CN	Yes
CD $_3$ NO $_2$	No
C $_6$ D $_6$	No

Since the cleanest production resulted from using CD_3CN , an attempt was made to scale up the reaction in acetonitrile. Stirring **2.3** in acetonitrile overnight with a slight excess of I_2 resulted in a color change from green to black-brown. The solvent was removed and the product isolated (Figure 15). The product undergoes decomposition in both CD_3CN and C_6D_6 through an unknown route to yield aniline in about 20 hours. Anticipating a possible C-N reductive elimination route to produce MeNHPh , a ^1H NMR spectrum of *N*-methylaniline revealed a singlet at 2.27 ppm which is conspicuously absent from the NMR spectrum of the decomposition (Figure 16).

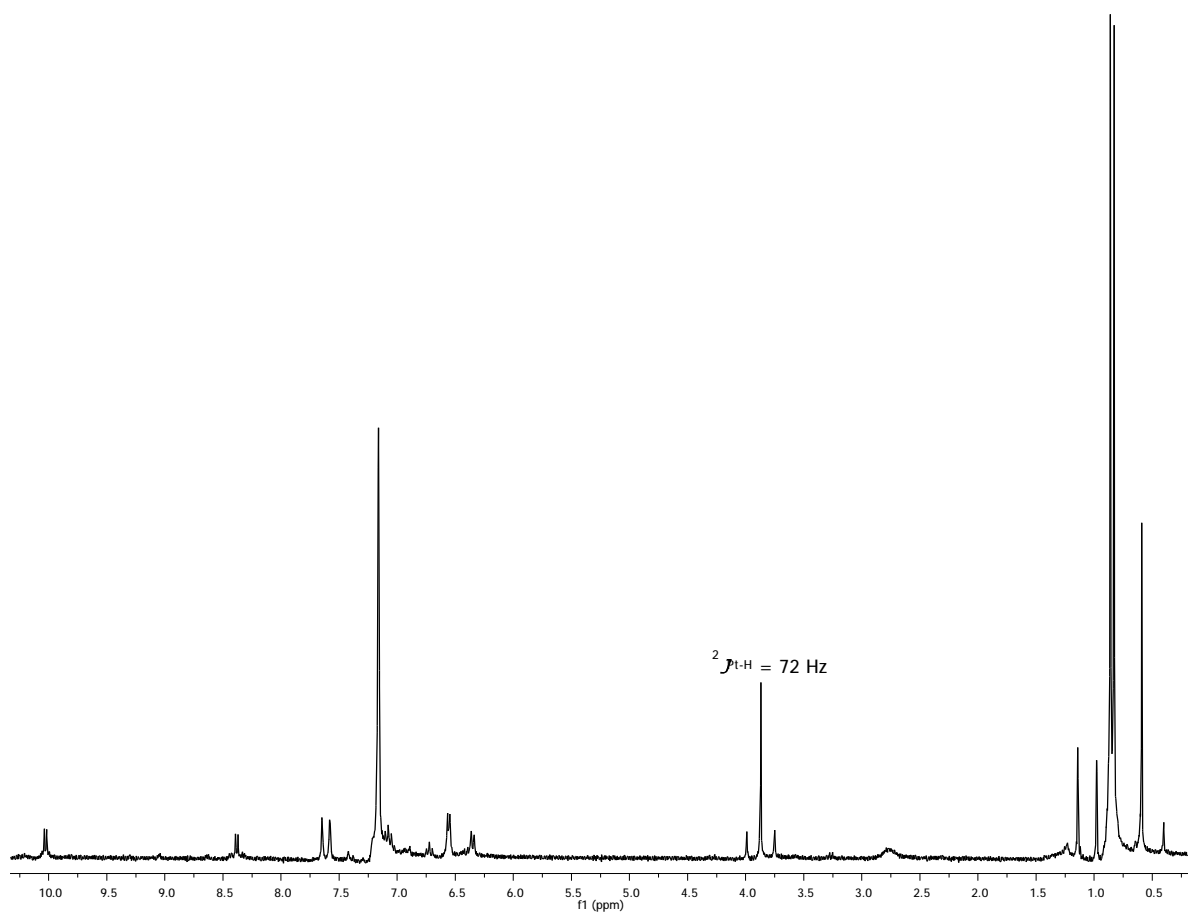


Figure 15. ^1H NMR spectrum of **2.9** in benzene- d_6 synthesized in acetonitrile.

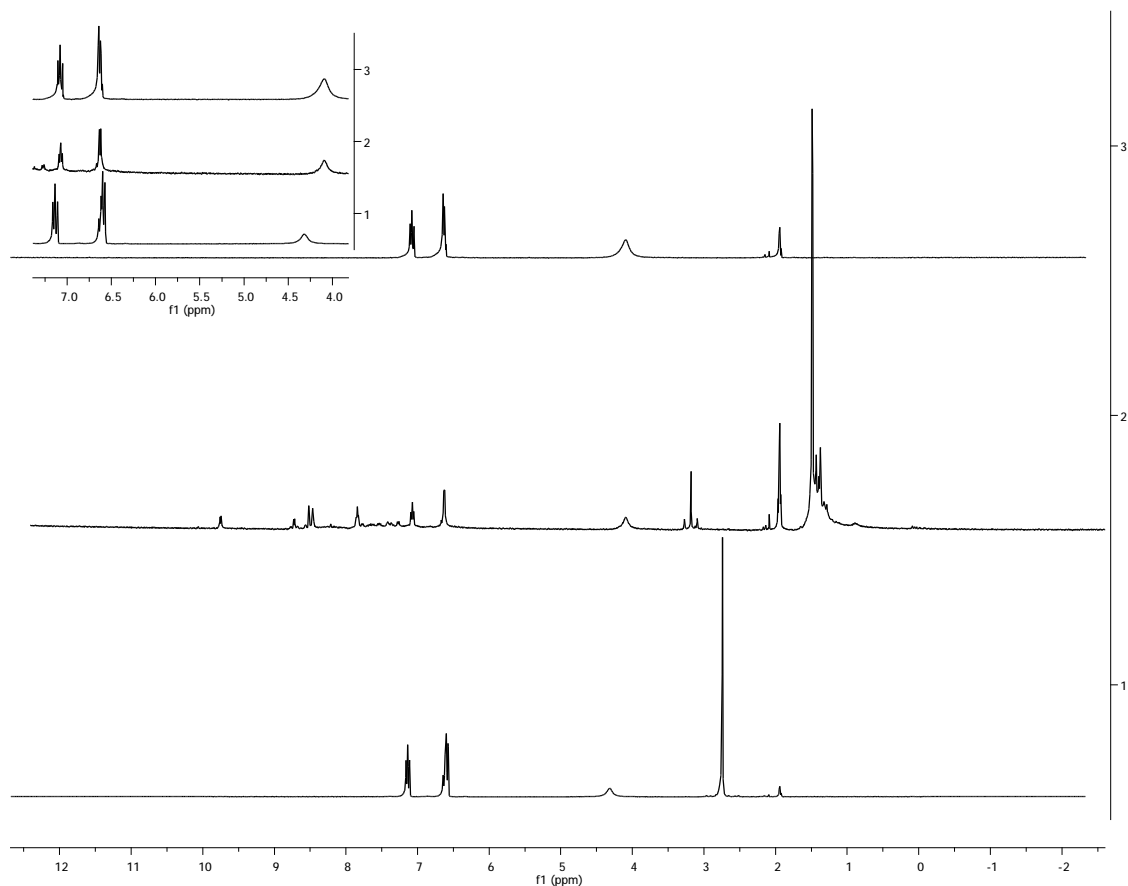


Figure 16. ^1H NMR spectra of *N*-methylaniline (bottom), **2.9** (middle), and aniline (top) in CD_3CN .

Attempts to grow X-ray quality crystals of the (*t*bpy)Pt(Me)(NHPH)(I)₂ complex from layers of benzene/pentane, THF/pentane, and toluene/pentane, as well as slow evaporation from THF and diethylether have yielded no suitable X-ray quality crystals.

Attempted oxidation of (*t*bpy)Pt(NHPH)₂ (2.6). The complex (*t*bpy)Pt(NHPH)₂ was added to a screw cap NMR tube with a slight excess of I₂ in C₆D₆. Periodic ^1H NMR spectra were taken. After observing little to no reactivity at room temperature as the previous complexes had shown, the NMR tube was heated to 60° C and further periodic NMR spectra

were taken. The complex shows minimal reactivity with mostly starting material remaining (Figure 17). Additionally decomposition producing aniline and free 'bpy is noted (Figure 18). An attempt to scale this reaction for product characterization resulted in decomposition to an insoluble black powder.

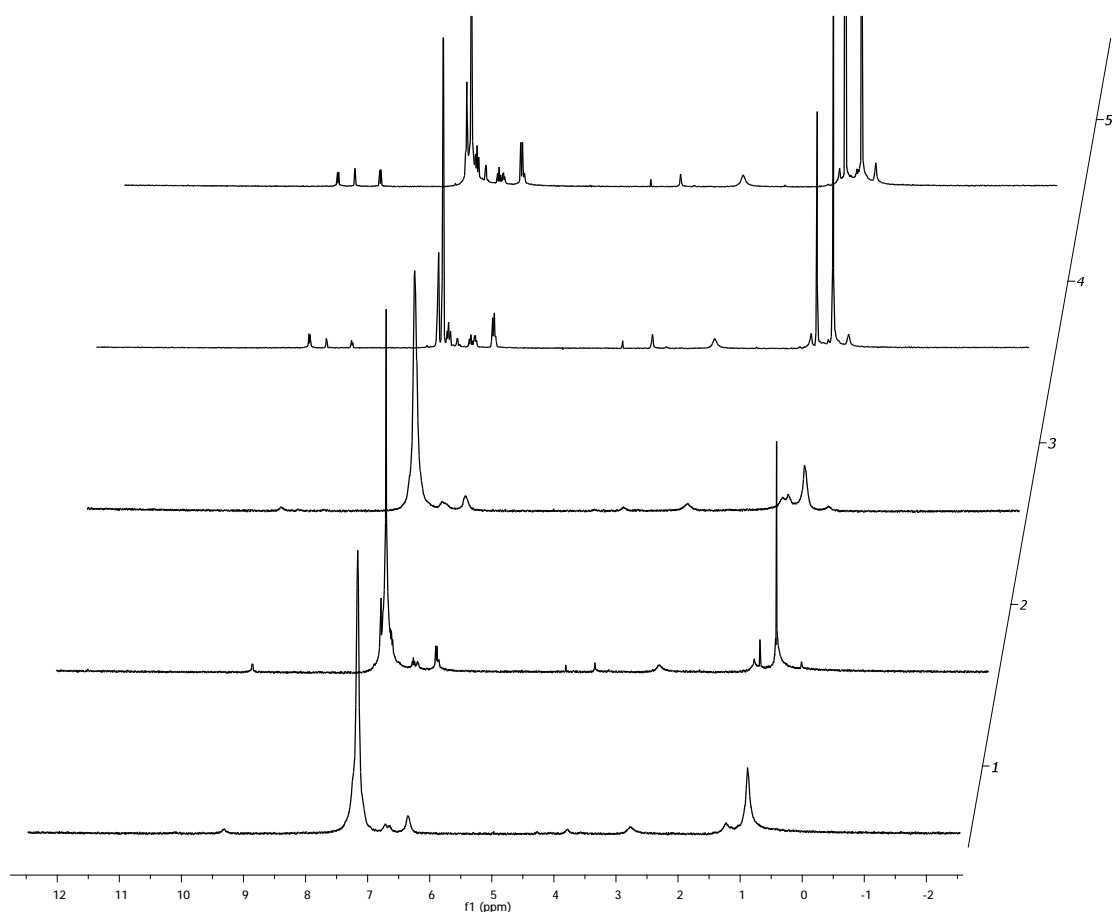


Figure 17. ^1H NMR spectra of $(^i\text{bpy})\text{Pt}(\text{NHPh})_2$ (spectrum #1), $(^i\text{bpy})\text{Pt}(\text{NHPh})_2 + \text{I}_2$ (spectrum #2), after 2 days at room temperature (spectrum #3), after heating for 1 day (spectrum #4), after heating for 2 days (spectrum #5) in benzene- d_6 .

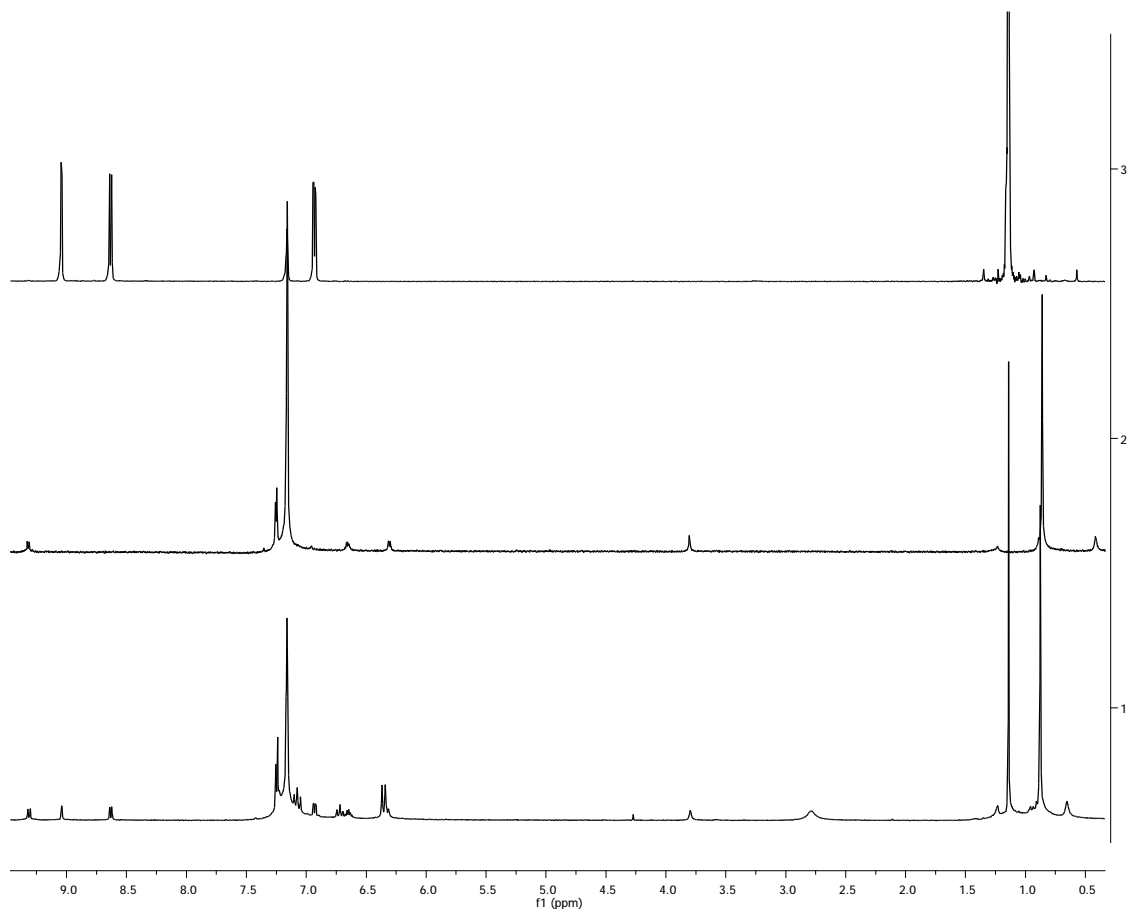


Figure 18. ^1H NMR spectra of $(^i\text{bpy})\text{Pt}(\text{NHPh})_2 + \text{I}_2$ (bottom), **2.6** (middle), and free ^ibpy (top) in C_6D_6 (resonances not due to starting material or free ^ibpy in spectrum #1 are assigned to free aniline).

Attempted oxidation of $(^i\text{bpy})\text{Pt}(\text{NHPh})(\text{Cl})$ (2.7). The complex $(^i\text{bpy})\text{Pt}(\text{NHPh})(\text{Cl})$ was added to a screw cap NMR tube with a slight excess of I_2 in C_6D_6 . The ^1H NMR spectrum showed instantaneous conversion to a new complex. The tert-butyl peaks are observed to go from two doublets to a singlet which is likely a result of coincidental overlap. Nine aromatic resonances are observed which would be consistent with the expected complex $(^i\text{bpy})\text{Pt}(\text{NHPh})(\text{Cl})(\text{I})_2$; however, the integrations are inconsistent with that product. Most notable is the integration of the assigned NH peak for 10H. None of the

resonances, however, are consistent with free aniline or with free ^tbpy. Attempts to scale up this reaction for characterization resulted in decomposition to unknown species.

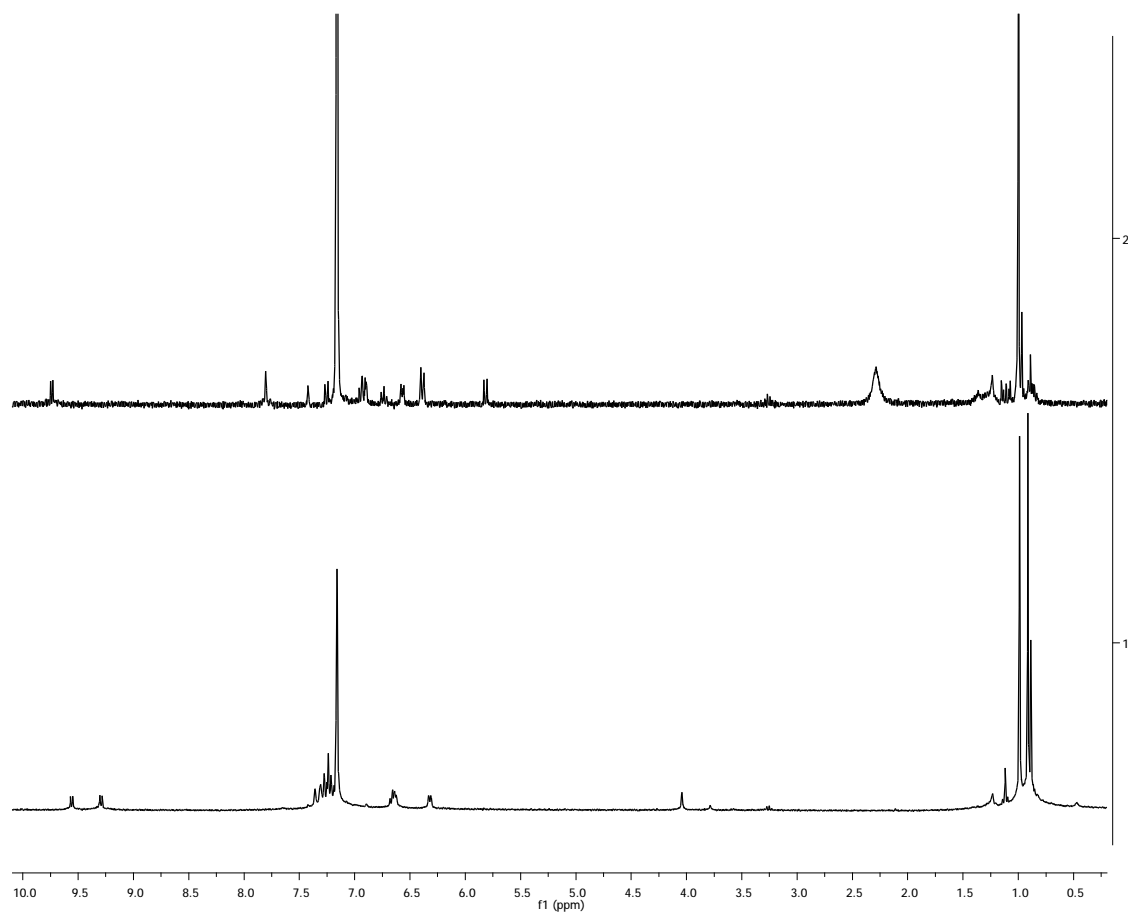


Figure 19. ¹H NMR spectra of (t)bpyPt(NHPh)(Cl) (**2.7**) (bottom) and **2.7** + I₂.

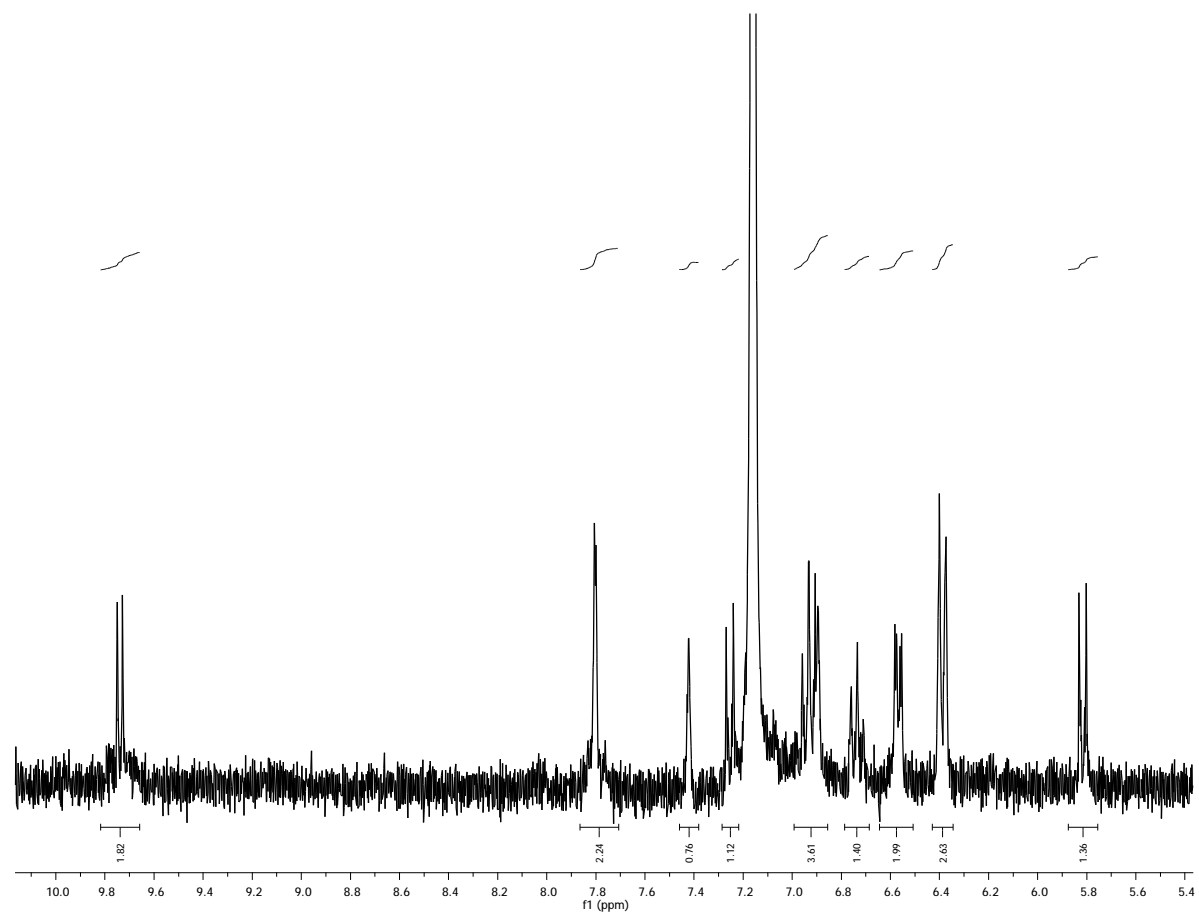


Figure 20. ^1H NMR spectrum (downfield region) of $(t\text{-bpy})\text{Pt}(\text{NHPh})(\text{Cl}) + \text{I}_2$ in C_6D_6 (with integrations normalized to 18H total for the upfield $t\text{-bpy-}t\text{-Bu}$ peaks).

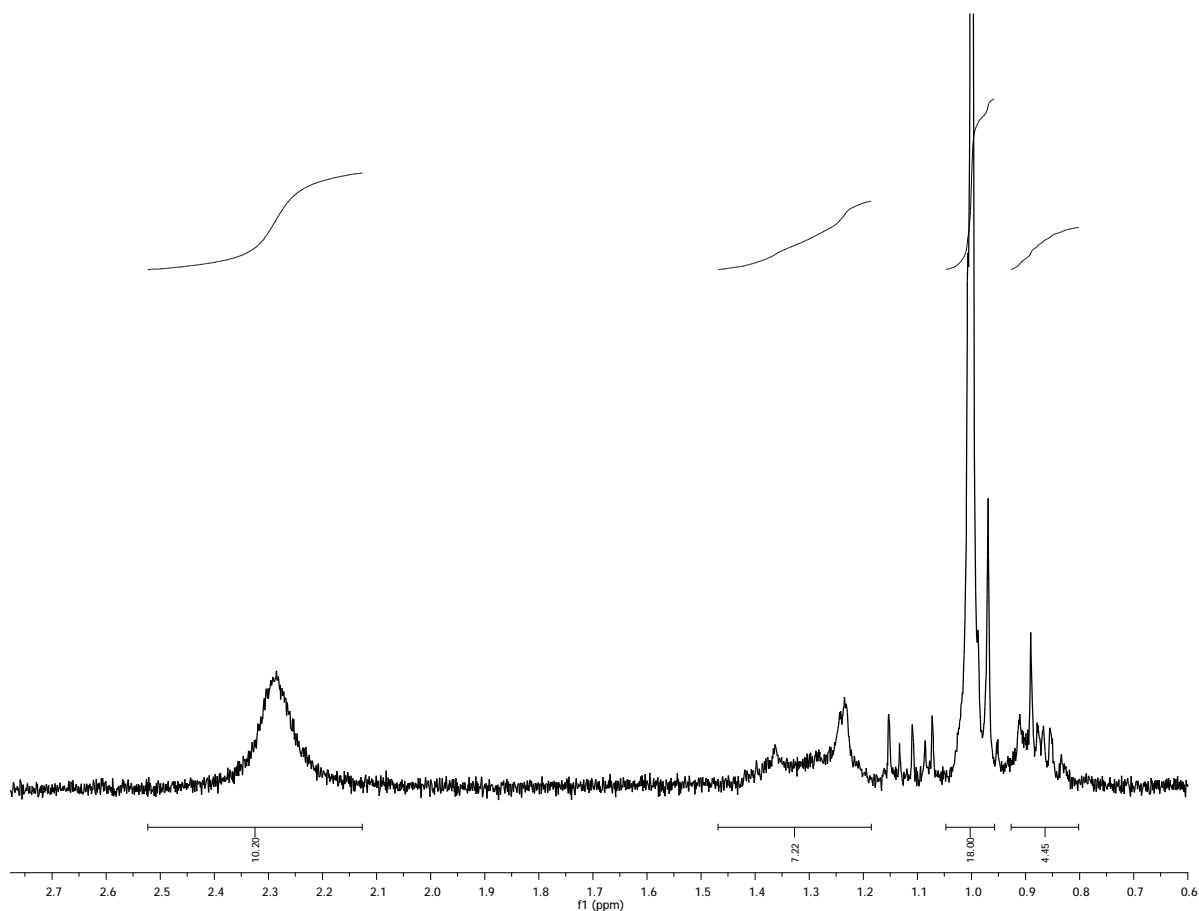


Figure 21. ^1H NMR spectrum (downfield region) of $(^t\text{bpy})\text{Pt}(\text{NHPh})(\text{Cl}) + \text{I}_2$ in C_6D_6 (with integrations normalized to 18H total for the upfield ^tbpy - ^tBu peaks).

3 Conclusions

The oxidation of $(^t\text{bpy})\text{Pt}(\text{Me})_2$ to $(^t\text{bpy})\text{Pt}(\text{Me})_2(\text{I})_2$ is easily achieved; however, the oxidation of Pt(IV)-amido complexes is a more difficult task. Two of the amido complexes appears to eliminate aniline through an as yet unknown pathway. While the $(^t\text{bpy})\text{Pt}(\text{NHPh})_2$ complex quickly produce aniline upon reaction with I_2 , the $(^t\text{bpy})\text{Pt}(\text{Me})(\text{NHPh})$ produces aniline with extended time (>20 hours) in CD_3CN and C_6D_6 . The M-X π -disruption appears to render the basic lone pairs of the amido complexes too reactive at room temperature to

remain stable. Metathesis of an iodide ligand of **2.8** for a hydroxide or methoxide utilizing CsOH and NaOMe respectively resulted not in the anticipated metathesis but in reversion to **2.1**. Further studies will be explored to determine if alternative synthesis routes or auxiliary ligands will allow isolation of stable late transition metals complexes possessing M-amido bonds. Further study into the C-H activation ability of (^tbpy)Pt(Me)₂(I)₂ should be explored to determine the production of the possible C-H activation products relative to complex.

4 Experimental

General Methods. Unless otherwise noted all procedures were performed under an inert atmosphere of dinitrogen in a nitrogen-filled glovebox or using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges. Benzene, toluene, and tetrahydrofuran were purified by distillation over sodium/benzophenone. Pentane was distilled over sodium prior to use. Hexanes and methylene chloride were purified by passage through a column of activated alumina. Acetonitrile and methanol were dried by distillation from CaH₂. Aniline was purified by vacuum distillation from CaH₂. Benzene-*d*₆, chloroform-*d*, nitromethane-*d*₃, acetone-*d*₆, and methylene chloride-*d*₂ were degassed via three freeze-pump-thaw cycles and stored under a dinitrogen atmosphere over 4Å molecular sieves. ¹H and ¹³C NMR spectra were acquired using Varian Mercury spectrometers operating at 300 or 400 MHz (¹H NMR) and 75 or 100 MHz (¹³C NMR), respectively and referenced to TMS using residual proton signals or the ¹³C resonances of the deuterated solvent. Electrochemical experiments were performed under a nitrogen atmosphere using a BAS Epsilon Potentiostat. Cyclic voltammograms were recorded in a standard three-

electrode cell from -2.50 V to + 2.50 V with a glassy carbon working electrode and tetrabutylammonium hexafluorophosphate as electrolyte. Tetrabutylammonium hexafluorophosphate was dried under dynamic vacuum at 100 °C for 48 h prior to use. All potentials are reported versus NHE (normal hydrogen electrode) using ferrocene or cobaltocenium hexafluorophosphate as an internal standard. Elemental analyses were performed by Atlantic Microlab, Inc. GC-MS was performed using a HP GCD system with a 30 m x 0.25 mm HP-5 column with 0.25 µm film thickness. The following reagents were synthesized as previously reported: $\{\text{PtMe}_2(\text{SEt}_2)\}_2$,¹²⁹ sodium tetrakis[(3,5-trifluoromethyl)phenyl]borate ($[\text{Na}][\text{BAR}'_4]$),¹³³ $(^t\text{bpy})\text{Pt}(\text{Me})_2$,¹¹⁸ $(^t\text{bpy})\text{Pt}(\text{Me})(\text{TFA})$,¹¹⁹ $[(^t\text{bpy})\text{Pt}(\text{Me})(\text{NH}_2\text{Ph})][\text{TFA}]$ (**2.2**),¹³⁰ $(^t\text{bpy})\text{Pt}(\text{Me})(\text{NHPh})$ (**2.3**),¹³⁰ $(^t\text{bpy})\text{Pt}(\text{OTf})_2$ (**2.4**),¹¹⁹ $[(^t\text{bpy})\text{Pt}(\text{NH}_2\text{Ph})_2][\text{OTf}]_2$ (**2.5**),¹³⁰ $(^t\text{bpy})\text{Pt}(\text{NHPh})_2$ (**2.6**)¹³⁰, and $(^t\text{bpy})\text{Pt}(\text{NHPh})(\text{Cl})$ (**2.7**)¹³⁰. All other reagents were used as purchased from commercial sources.

$(^t\text{bpy})\text{Pt}(\text{Me})_2(\text{I})_2$ (2.8**).** To a 50 mL round bottom flask charged with $(^t\text{bpy})\text{Pt}(\text{Me})_2$ (**2.1**) (69.0 mg, 0.14 mmol) was added 15 mL of benzene. I_2 (38.1 mg, 0.015 mmol) was added. After stirring for 18 hours, the solvent was removed *in vacuo*. The flask was scraped to obtain the product (82.1mg, 73% yield). A crystal suitable for X-ray diffraction study was grown by layering a THF solution of **2.8** and pentane. Anal Calcd. for $\text{C}_{20}\text{H}_{30}\text{I}_2\text{N}_2\text{Pt}$: C, 32.14; H, 4.05; N, 3.75. Found: C, 32.38; H, 4.01; N, 3.70. ^1H NMR (C_6D_6 , δ): 8.34 (dd, $^3J_{\text{H6-H5}} = 5.9$ Hz, $^3J_{\text{Pt-H6}} = 13.1$ Hz, 2H, ^tbpy 6/6'), 7.94 (d, $^4J_{\text{H3-H5}} = 1.8$ Hz, 2H, ^tbpy 3/3'), 6.76 (dd, $^3J_{\text{H6-H5}} = 5.9$, $^4J_{\text{H3-H5}} = 1.8$ Hz, 2H, ^tbpy 5/5'), 2.63 (s with Pt satellites, 6H, Pt- CH_3 , $^2J_{\text{Pt-H}} = 73$ Hz), 1.04 (s, 18H, ^tbpy - ^tBu). ^{13}C NMR (CDCl_3 , δ): 163.99 (^tbpy 6/6'), 154.93

(¹bpy 4/4'), 147.65 (¹bpy 2/2'), 124.38 (¹bpy 3/3'), 120.50 (¹bpy 5/5'), 35.67 (¹bpy-CMe₃), 30.66 (¹bpy-CMe₃), -14.70 (Pt-CH₃ with Pt satellites, ¹J_{Pt-C} = 506.5 Hz).

(¹bpy)Pt(Me)(NHPh)(I)₂ (2.9). To a 50 mL round bottom flask charged with (¹bpy)Pt(Me)(NHPh) (**2.3**) (153.0 mg, 0.310 mmol) was added 25 mL of acetonitrile. I₂ (80.1 mg, 0.315 mmol) was added. After stirring for 20 hours, the solvent was removed *in vacuo*. The flask was scraped to obtain the product (178.80 mg, 77% yield). ¹H NMR (C₆D₆, δ): 10.03 (d w/Pt satellites, 1H, ³J_{H6-H5} = 5.7 Hz, ³J_{Pt-H6} = 12 Hz, ¹bpy 6 or 6'), 8.38 (d w/ Pt satellites, 1H, ³J_{H6-H5} = 6 Hz, ³J_{Pt-H6} = 34 Hz, ¹bpy 6 or 6'), 7.64 (d, 1H, ⁴J_{H3-H5} = 2 Hz, ¹bpy 3 or 3'), 7.58 (d, 1H, ⁴J_{H3-H5} = 2 Hz, ¹bpy 3 or 3'), 7.12-7.02 (t, J_{HH} = 8 Hz, overlap of solvent and anilido-*meta*), 6.72 (tt, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.9 Hz, anilido-*para*), 6.56 (d, ³J_{HH} = 6 Hz, anilido-*ortho*), 5.96, 5.94 (each a d, each 1H, ⁴J_{H3-H5} = 2Hz, ¹bpy 5/5'), 3.87 (s w/ Pt satellites, ²J_{Pt-H} = 72.3 Hz, Pt-CH₃), 0.86, 0.83 (each a s, 9H each, ¹bpy-¹Bu).

NMR Scale Reaction of (¹bpy)Pt(Cl)(NHPh) + I₂. To a screw cap NMR tube were added (¹bpy)Pt(Cl)(NHPh) (5 mg, 0.008 mmol) and I₂ (5 mg, 0.020 mmol). Changes were noted in the ¹H NMR spectrum immediately. The following characterization is based on the analysis presented above. One caveat is the large integration of the amido/aniline NH/NH₂ peak as well as the fact that the aniline integrations are relative to the metal complex. ¹H NMR (C₆D₆, δ): 9.74 (d, 2H, ³J_{H5-H6} = 6Hz, ¹bpy 6/6'), 7.81 (d, 2H, ⁴J_{H3-H5} = 2Hz, ¹bpy 3/3'), 7.42 (s, 1H, anilido-*para*), 7.26 (d, 2H, ³J_{HH} = 7Hz, anilido-*ortho*), 6.93 (dt, ²J_{HH} = ²J_{HH} = 8Hz, 3H, aniline-*meta*), 6.73 (t, J_{HH} = 8 Hz, 1.5H, aniline-*para*), 6.57 (dd, 2H, ²J_{HH} = 2Hz, ²J_{HH} = 8Hz, anilido-*meta*), 6.37 (d, J_{HH} = 8 Hz, 3H, aniline-*ortho*), 5.82 (dd, 2H, ³J_{H5-H6} =

6Hz, $^4J_{\text{H3-H5}} = 2\text{Hz}$, t**bp**y 5/5'), 2.30 (very br s, 10H, aniline/anilido NH/NH₂), 1.00 (s, 18H, t**bp**y-tBu).

Scaled-Up Reaction of (tbp**y)Pt(Cl)(N**HP**h) + I₂.** In a 50mL round bottom flask, (t**bp**y)Pt(Cl)(N**HP**h) (76.9mg, 0.130mmol) was taken up in benzene and I₂ (35.1 mg, 0.138 mmol) was added. The mixture was stirred for an hour. The solvent was removed and the product scraped from the flask walls. A ¹H NMR spectrum of the product in C₆D₆ showed only upfield peaks and nothing in the aryl t**bp**y region.

NMR Scale Reaction of (tbp**y)Pt(N**HP**h)₂(I)₂.** (t**bp**y)Pt(N**HP**h)₂ (28.3 mg, 0.044 mmol) were taken up in C₆D₆ and I₂ (12.3 mg, .049 mmol) was added. After several days, minimal change was noted. Heating to 60 °C for 1 day caused new resonances to appear (see NMR spectrum above); however prolonged heating did not carry the reaction to completion.

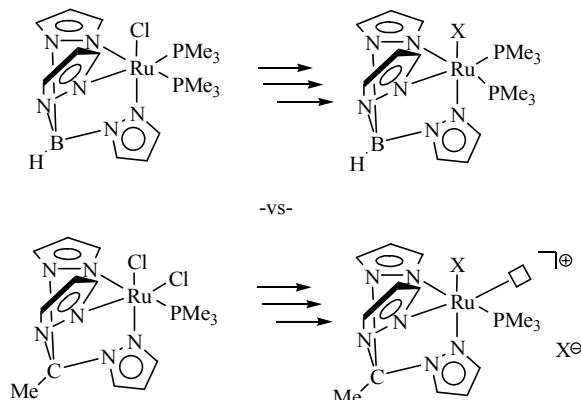
Attempted Synthesis of (tbp**y)Pt(Me)₂(I)(OMe) or (t**bp**y)Pt(Me)₂(OMe)₂.** To an orange solution of **2.8** in THF-*d*₈ was added to excess of NaOMe. An immediate change was noted in the ¹H NMR spectrum (see above). The contents of the tube were transferred to a shell vial and the solvent removed. The resultant solid was taken up in C₆D₆ and the ¹H NMR spectrum revealed that the complex had been reduced to **2.1**.

Attempted Synthesis of (tbp**y)Pt(Me)₂(I)(OH) or (t**bp**y)Pt(Me)₂(OH)₂.** To an orange solution of **2.8** in THF-*d*₈ was added an excess of CsOH·H₂O. After 3 days, a change was noted in the ¹H NMR spectrum (see above). The contents of the tube were transferred to a shell vial and the solvent removed. The resultant solid was taken up in C₆D₆ and the ¹H NMR spectrum revealed that the complex had been reduced to **2.1**.

CHAPTER 3

1 Rationale for Pyrazolyl Alkane Chemistry

The Gunnoe Group has studied complexes possessing the Tp ligand framework for some time {Tp = hydridotris(pyrazolyl)borate}.^{62,74-76,81,82,85-87,89} When coordinated to charge neutral systems of Ru(II), the monoanionic nature of Tp allows only one other anionic ligand. In previous TpRu complexes, this anionic ligand was typically an alkyl, aryl, or heteroatomic ligand wherein reactivity was centered. Because the other coordination sites on Tp based complexes are occupied by neutral ligands, reversible ligand dissociation (often achieved through thermal displacement) results in competition for the coordination of hydrocarbons (Scheme 8). Also including a ligand dissociation step in the kinetic studies prohibits the *direct* observation and therefore *direct* study of the C-H activation step. To circumvent this requirement, a new ligand backbone is needed.



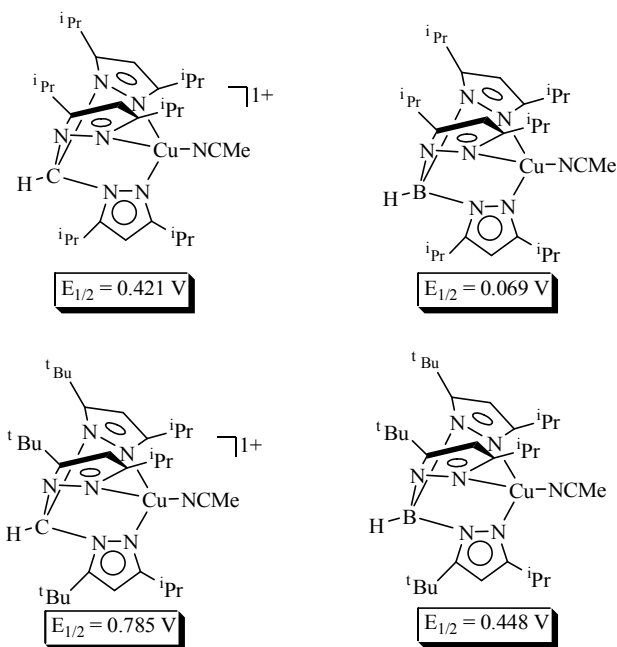
Scheme 14. Poly(pyrazolyl)alkanes allow access to an open coordination site without the need for thermal displacement of a neutral ligand.

Using a poly(pyrazolyl)alkane backbone allows two anionic ligands in the starting material (Scheme 14). One of these ligands can be metathesis for a reactive moiety (*e.g.*,

alkyl, aryl, alkoxo, amido, *etc.*) while the other can be removed utilizing the salt of a non-coordinating anionic counterion (*e.g.*, NaBF₄, NaBPh₄, *etc.*). Using a non-coordinating counterion keeps the necessary coordination site open. To that end, we have made synthetic efforts toward complexes that are analogous to our previously reported Tp-based complexes, but which possess poly(pyrazolyl) alkanes.

2 Introduction to Pyrazolyl Alkanes

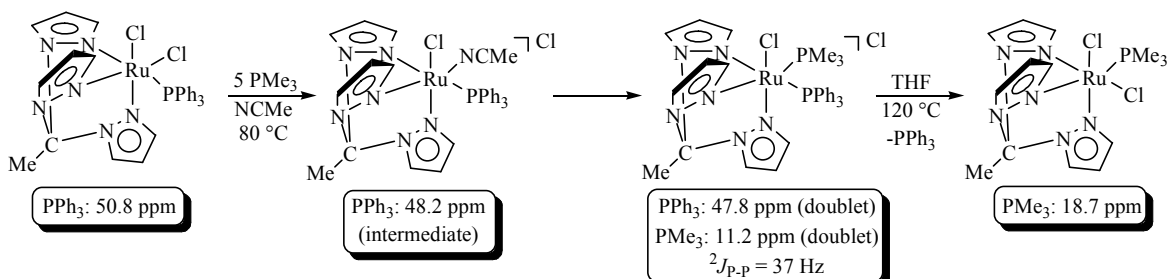
Poly(pyrazolyl) alkanes are neutral analogs of the polypyrazolyl borates.¹³⁴ Herein, the Ep {Ep = 1,1,1-tris(pyrazolyl)ethane} ligand was studied. The coordination and geometry of Ep has been shown to approximate related polypyrazolyl borates.¹³⁴⁻¹³⁸ The major difference between the polypyrazolyl borates and the polypyrazolyl alkanes is that the exchange of the Group 3 boron for a Group 4 carbon renders the ligand neutral rather than monoanionic as is the case with the borates.¹³⁹



Scheme 15. Redox potentials for four representative complexes, two possessing poly(pyrazolyl) borates and two with poly(pyrazolyl) alkanes. Note that for corresponding complexes, the ones possessing neutral ligands have a greater potential (potentials reported vs nonaqueous Ag/AgCl).

A key consequence of this electronic change is that the metal center is rendered less electron rich as observed by the more positive II/I redox potential shown in for the poly(pyrazolyl)alkane based complexes versus those with poly(pyrazolyl)borates in Scheme 15.¹³⁹ This increased electrophilicity should facilitate the coordination and activation of C-H bonds. Dr. Karl Pittard¹⁴⁰ completed initial studies on poly(pyrazolyl)alkanes in the Gunnoe group and determined the synthetic methods for $\text{EpRu}(\text{PPh}_3)(\text{Cl})_2$ and $\text{EpRu}(\text{PMe}_3)(\text{Cl})_2$. Dr. Pittard determined that in the synthesis of $\text{EpRu}(\text{PMe}_3)(\text{Cl})_2$ a progression through $[\text{EpRu}(\text{PPh}_3)(\text{NCMe})(\text{Cl})][\text{Cl}]$ and $[\text{EpRu}(\text{PPh}_3)(\text{PMe}_3)(\text{Cl})][\text{Cl}]$ intermediate complexes was required. Additionally, he determined that these reactions are easily followed by ^{31}P NMR spectroscopy. The complexes exhibit characteristic resonances which aid in the

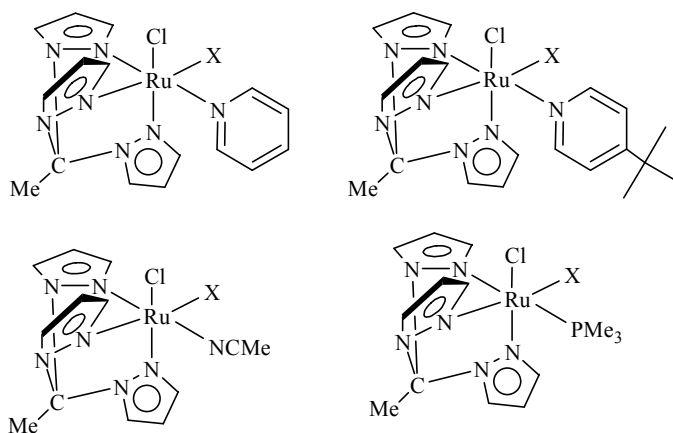
determination of reaction progress (Scheme 16). Here, we sought to prepare $\text{EpRu}(\text{X})(\text{Cl})(\text{L})$ precursors (Scheme 17), abstract the chloride in exchange for a non-coordinating counterion and study subsequent C-H activation reactions.



Scheme 16. Synthetic method for $\text{EpRu}(\text{PMe}_3)(\text{Cl})_2$ with identifying ^{31}P NMR resonances.

3 Synthetic Efforts

A series of Ep complexes was envisioned (Scheme 17). One major drawback of the Ep complexes is their lack of solubility in most common organic solvents. For example, the $\text{EpRu}(\text{Cl})_2\text{PPh}_3$ complex is soluble in chloroform and only very sparingly soluble in DMSO; however, ligand metathesis reactions (*e.g.*, OH^- or OMe^- for Cl^-) attempted in chloroform yielded decomposition products.



Scheme 17. Target Ep complexes ($\text{X} = \text{NHPh}$, OH , OMe).

Initially the complex $\text{EpRu}(\text{py})(\text{Cl})_2$ was targeted as a precursor to $\text{EpRu}(\text{py})(\text{Cl})(\text{X})$. (py = *N*-pyridyl, X = anionic heteroatomic ligand). Utilizing the synthetic technique developed for production of $\text{EpRu}(\text{PMe}_3)(\text{Cl})_2$, preparation of $\text{EpRu}(\text{py})(\text{Cl})_2$ was attempted by heating $\text{EpRu}(\text{PPh}_3)(\text{Cl})_2$ in deuterated acetonitrile with excess pyridine. Following this reaction by ^{31}P NMR showed no conversion to a new product and only showed evidence of $\text{EpRu}(\text{PPh}_3)(\text{Cl})_2$ (50.8 ppm) and a small amount of $[\text{EpRu}(\text{PPh}_3)(\text{Cl})(\text{NCCD}_3)][\text{Cl}]$ (48.2 ppm) (Figure 22).

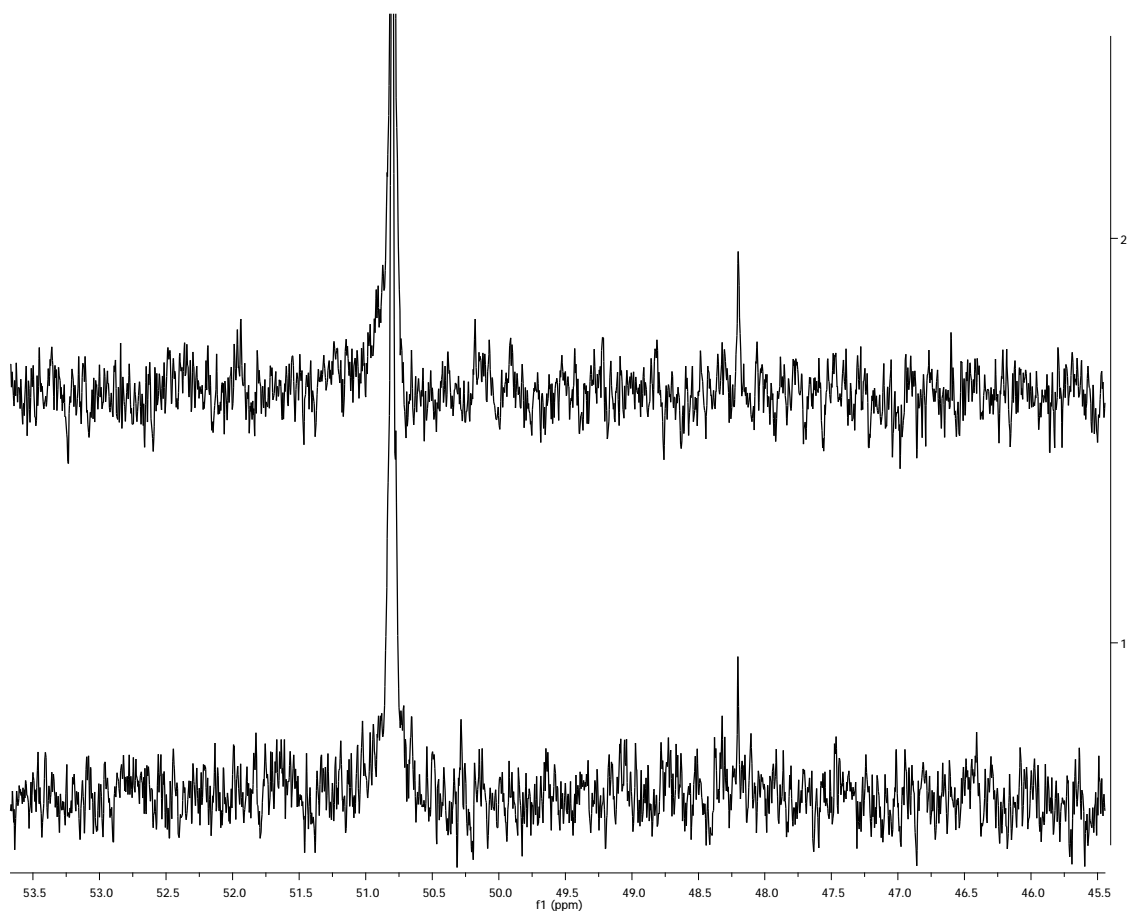
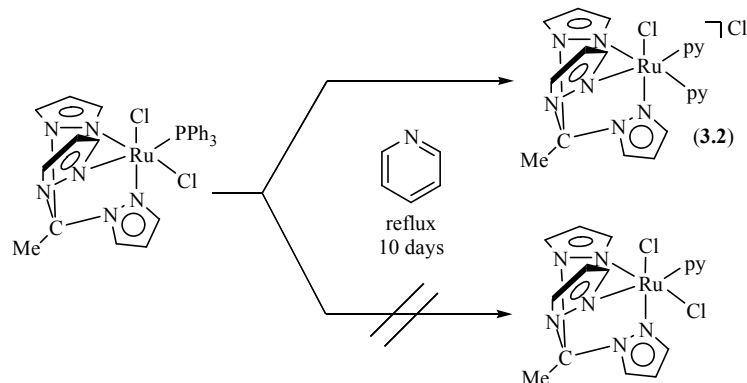


Figure 22. ^{31}P NMR spectra of $\text{EpRu}(\text{PPh}_3)(\text{Cl})_2$ and pyridine in CD_3CN (initial – bottom, after 3 days heating – top).

In an alternative attempt, $\text{EpRu}(\text{PPh}_3)(\text{Cl})_2$ was refluxed in neat pyridine for ten days. The product was isolated by reducing the solvent volume under reduced pressure and a nitrogen stream due to the high boiling point of pyridine followed by precipitation upon addition of diethyl ether. A ^1H NMR spectrum of the resultant solid revealed a complex possessing a mirror plane of symmetry which was assigned as $[\text{EpRu}(\text{py})_2(\text{Cl})][\text{Cl}]$ (**3.2**). Six resonances were assigned to the Ep ligand (with 2:1 ratio for the side arms versus the center arm) as opposed to the nine (all integrating for 1H) that would be present if the complex had no symmetry. Additionally the pyridine resonances integrate to 4:4:2 (*o:m:p*) relative to 1H for the farthest downfield resonance. Finally the ^{31}P NMR spectrum revealed no resonances, which indicates that all $\text{EpRu}(\text{PPh}_3)(\text{Cl})_2$ has been consumed.



Scheme 18. Refluxing $\text{EpRu}(\text{Cl})_2(\text{PPh}_3)$ in neat pyridine yields the bispyridine not the monoppyridine complex.

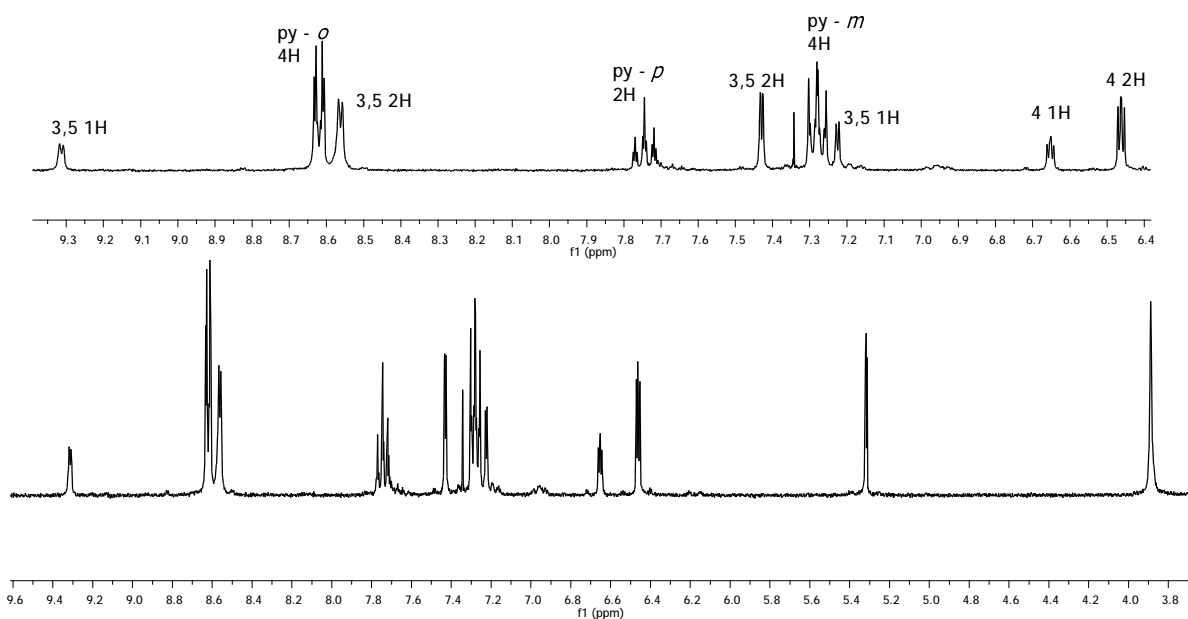


Figure 23. ^1H NMR spectrum of complex **3.2** in CD_2Cl_2 with expansion of aromatic region to show mirror symmetry of the complex.

Attempts to remove one of the pyridine ligands from $[\text{EpRu}(\text{py})_2(\text{Cl})][\text{Cl}]$ to produce $\text{EpRu}(\text{py})(\text{Cl})_2$ resulted in no change or decomposition by ^1H NMR spectroscopy (Table 4). In solvents where the complex was insoluble, evidence of pyridine in the solvent would have provided evidence for removal from the complex.

Table 4. Summary of thermolysis attempts to remove one pyridine from [EpRu(Cl)(py)₂][Cl] to produce EpRu(py)(Cl)₂.

Solvent	Temperature	Duration	Soluble?	Evidence of Pyridine?
Toluene- <i>d</i> ₈	120 °C	3 days	No	No
C ₆ D ₆	120 °C	3 days	No	No
THF ^a	100 °C	2 days	No	No – decomp.

^aProtio THF was used during heating. The solvent was removed and the ¹H NMR spectrum was taken in DMSO-*d*₆.

Because of the inability to remove one pyridine ligand, an attempt to synthesize [EpRu(py)₂(OMe)][Cl] was made. Adding excess NaOMe to an NMR tube containing a CD₃OD solution of [EpRu(py)₂(Cl)][Cl] resulted in no reactivity. Further heating to 70 °C also caused no observable change.

Using *trans*-Cl₂Ru(py)₄¹⁴¹ as an alternative starting material EpRu(py)(Cl)₂ synthesis was attempted. Ep and *trans*-Cl₂Ru(py)₄ readily dissolved in THF and were refluxed for 3 days. No visible changes were observed over the course of the reaction. Following isolation of the product, the ¹H NMR spectrum revealed only the original *trans*-Cl₂Ru(py)₄ and no evidence of Ep coordination.

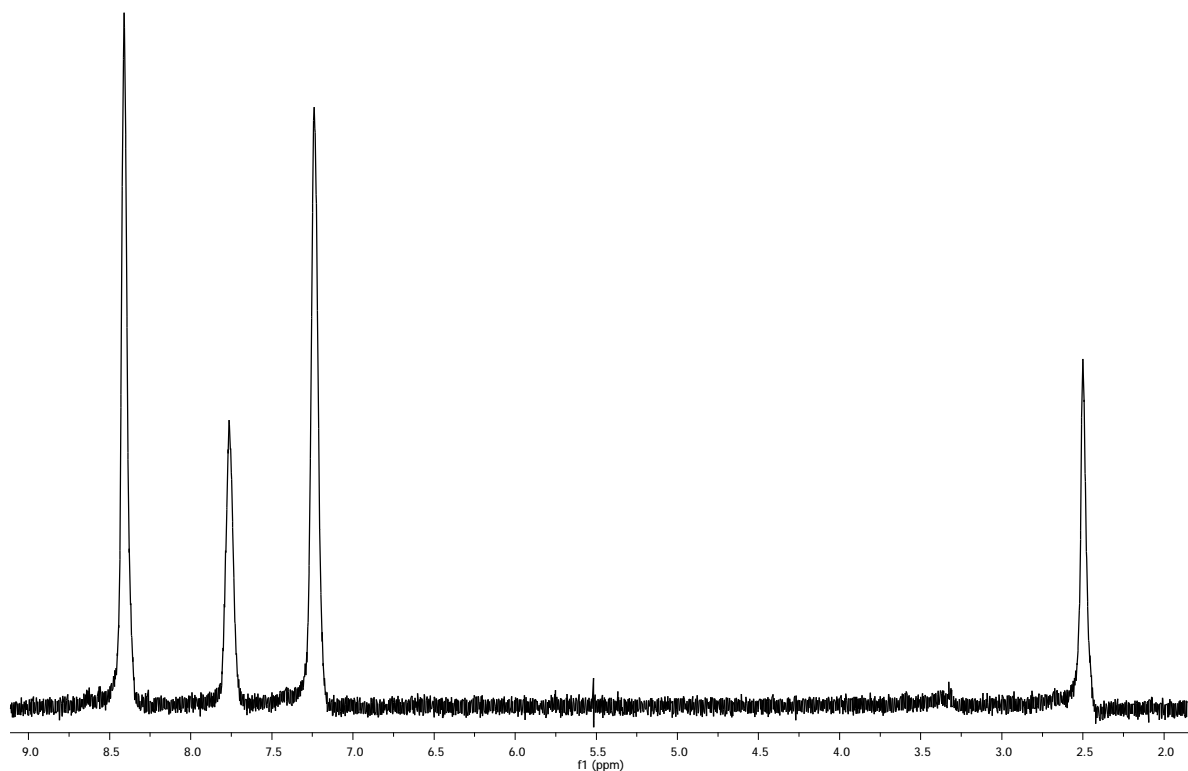
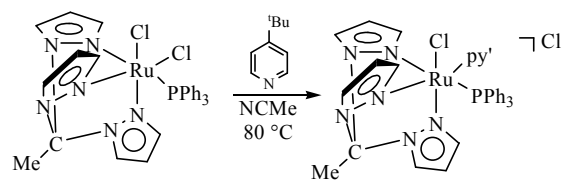


Figure 24. ^1H NMR spectrum of $\text{trans-Cl}_2\text{Ru}(\text{py})_4$ in $\text{DMSO-}d_6$ after attempted coordination of Ep.

Attempts were made to duplicate the reactivity observed for pyridine utilizing 4-*tert*-butylpyridine (py') with the anticipation that the *tert*-butyl group would enhance solubility. Similar to the reactivity discussed above, heating $\text{EpRu}(\text{PPh}_3)(\text{Cl})_2$ in acetonitrile with excess 4-*tert*-butylpyridine (eq 25) for up to eight days results in only incomplete conversion and a mixture of products (Figure 25 & Figure 26).



(25)

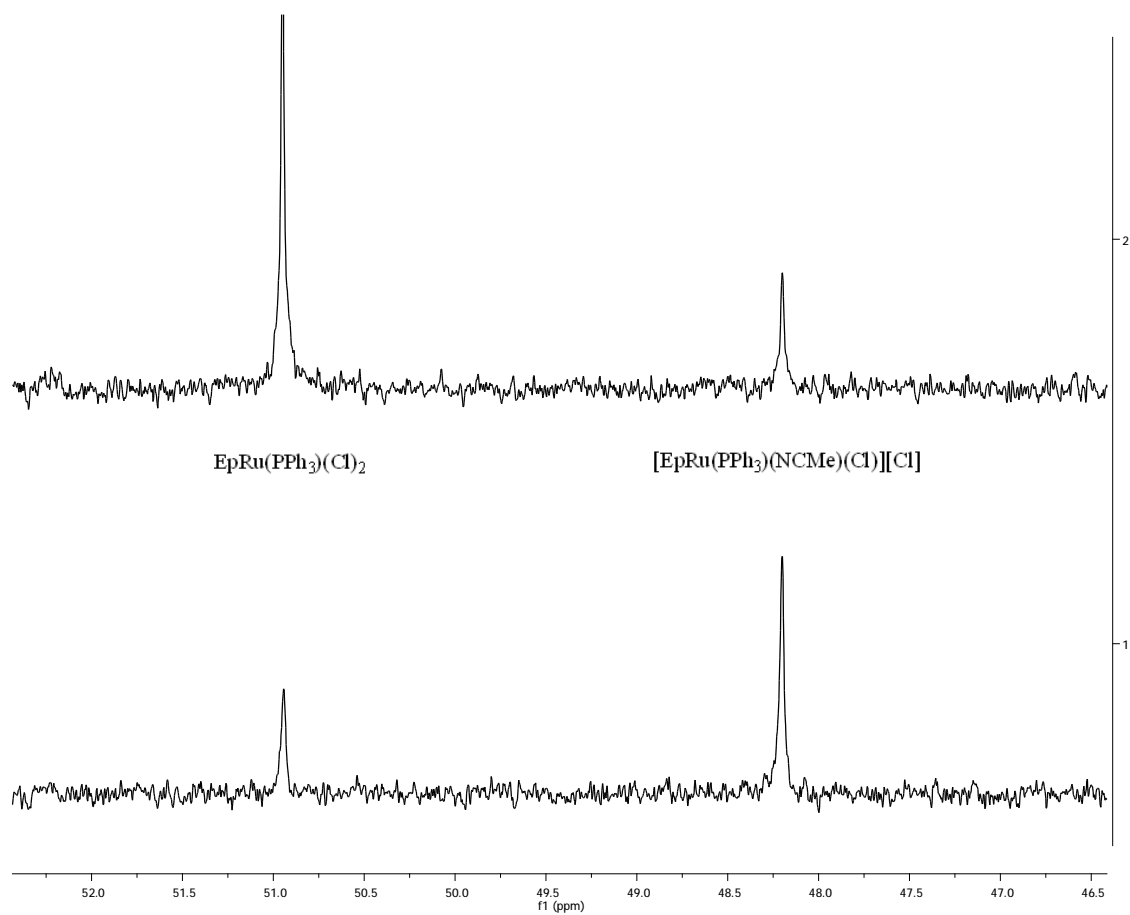


Figure 25. ^{31}P NMR spectrum of the reaction of $\text{EpRu}(\text{PPh}_3)(\text{Cl})_2$ and 4-*tert*-butylpyridine in $\text{DMSO}-d_6$ (bottom after 3 days, top after 8 days).

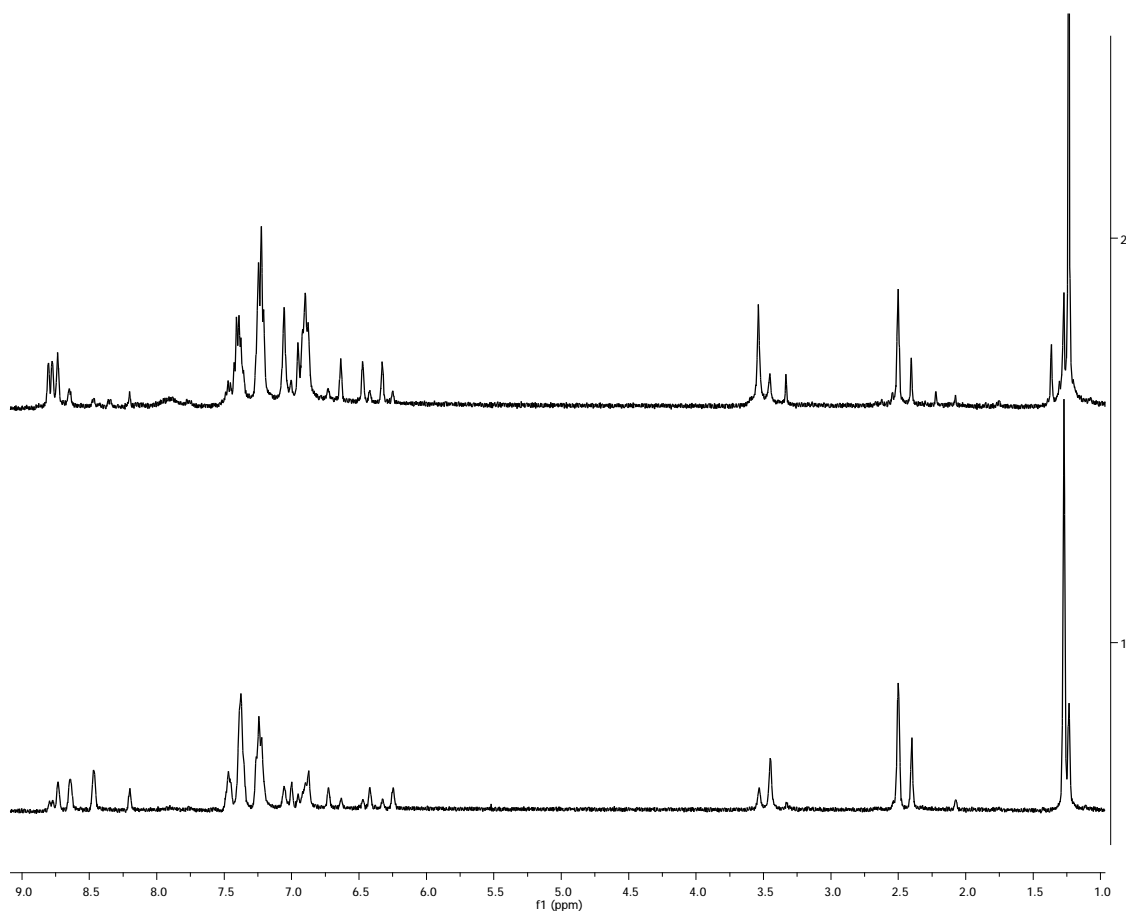


Figure 26. ^1H NMR spectra of the reaction of $\text{EpRu}(\text{PPh}_3)(\text{Cl})_2$ and 4-*tert*-butylpyridine in $\text{DMSO-}d_6$ (bottom after 3 days, top after 8 days).

Due to the incomplete conversion, synthesis of $\text{EpRu}(\text{py}')(\text{Cl})_2$ or $\text{EpRu}(\text{py}')_2(\text{Cl})$ was attempted by heating $\text{EpRu}(\text{PPh}_3)(\text{Cl})_2$ in neat py' for ten days (Figure 27). Following heating solvent removal was achieved by placing the solution under vacuum and allowing a small stream of nitrogen to bubble through the solution. The product was precipitated with diethyl ether. ^1H NMR spectroscopy revealed a lack of solubility in CD_2Cl_2 (Figure 28). Since enhancing solubility was a key goal of this reaction and due to the difficulty in solvent removal, this synthesis method was abandoned.

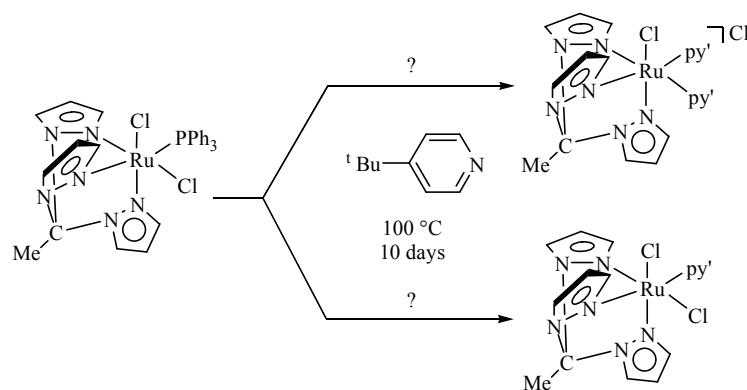


Figure 27. Attempted synthesis of $\text{EpRu}(\text{py}')_x(\text{Cl})_{2-x}$ complexes.

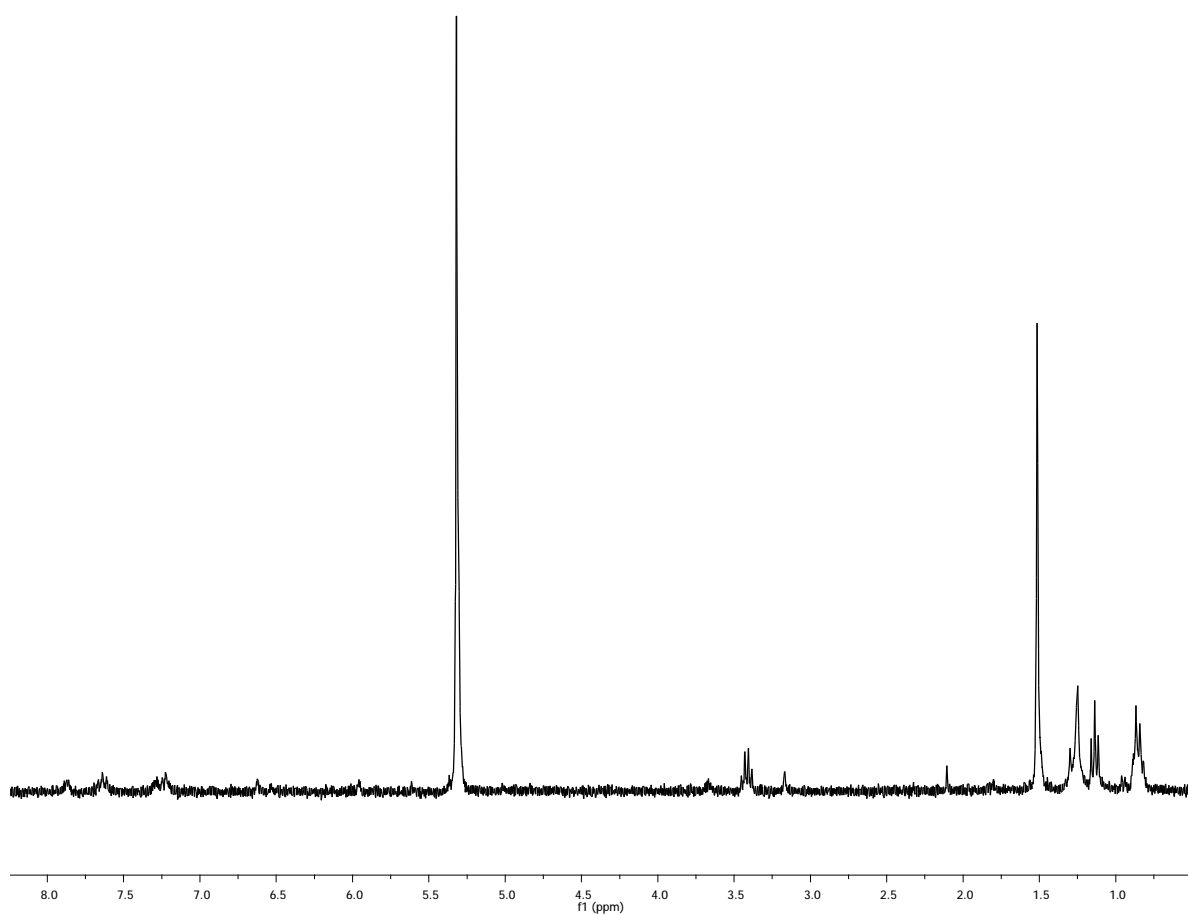
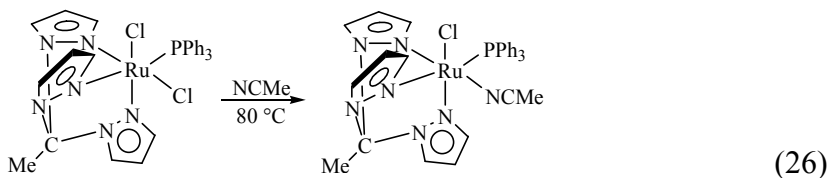


Figure 28. ^1H NMR spectrum in CD_2Cl_2 of product from heating $\text{EpRu}(\text{PPh}_3)(\text{Cl})_2$ in neat 4-*tert*-butylpyridine.

With the inability to access systems containing pyridine or 4-*tert*-butylpyridine, $\text{EpRu}(\text{NCMe})(\text{Cl})_2$, which could be utilized to produce $\text{EpRu}(\text{NCMe})(\text{Cl})(\text{X})$, was approached. Having observed the production of $[\text{EpRu}(\text{Cl})(\text{PPh}_3)(\text{NCMe})][\text{Cl}]$ as an intermediate in other synthesis reactions (see above), this complex was approached as a starting point.



Heating a slurry of $\text{EpRu}(\text{PPh}_3)(\text{Cl})_2$ in MeCN for three days at 80°C resulted in the formation of $[\text{EpRu}(\text{Cl})(\text{PPh}_3)(\text{NCMe})][\text{Cl}]$ (eq 26), which was purified by removing all solvent *in vacuo*, reconstituting the resultant solid in minimal methylene chloride, and affecting precipitation with hexanes (Figure 29). Using ^1H NMR spectroscopy, an asymmetric complex with nine Ep aromatic resonances was observed. A ^{13}C NMR spectrum was also taken revealing resonances consistent with $[\text{EpRu}(\text{Cl})(\text{PPh}_3)(\text{NCMe})][\text{Cl}]$ (Figure 30). The ^{13}C NMR spectrum revealed resonances similar to those reported for $\text{EpRu}(\text{PPh}_3)(\text{Cl})_2$. The resonances which were assigned to the symmetric Ep 3/5's and 4's for $\text{EpRu}(\text{PPh}_3)(\text{Cl})_2$ were split into two resonances. Additionally, the quaternary Ep apical position was observed to shift downfield from 83.8 ppm to 84.3 ppm as well as the Ep methyl resonance shifting from 21.2 ppm downfield to 21.5 ppm. The ^{31}P NMR spectrum revealed only a singlet at 48.2 ppm. Attempts to isolate a crystal suitable for X-ray diffraction study failed. The resultant solid was found to be soluble in chloroform,

methylene chloride, DMSO, and acetonitrile; however, extended time in chloroform and methylene chloride led to decomposition.

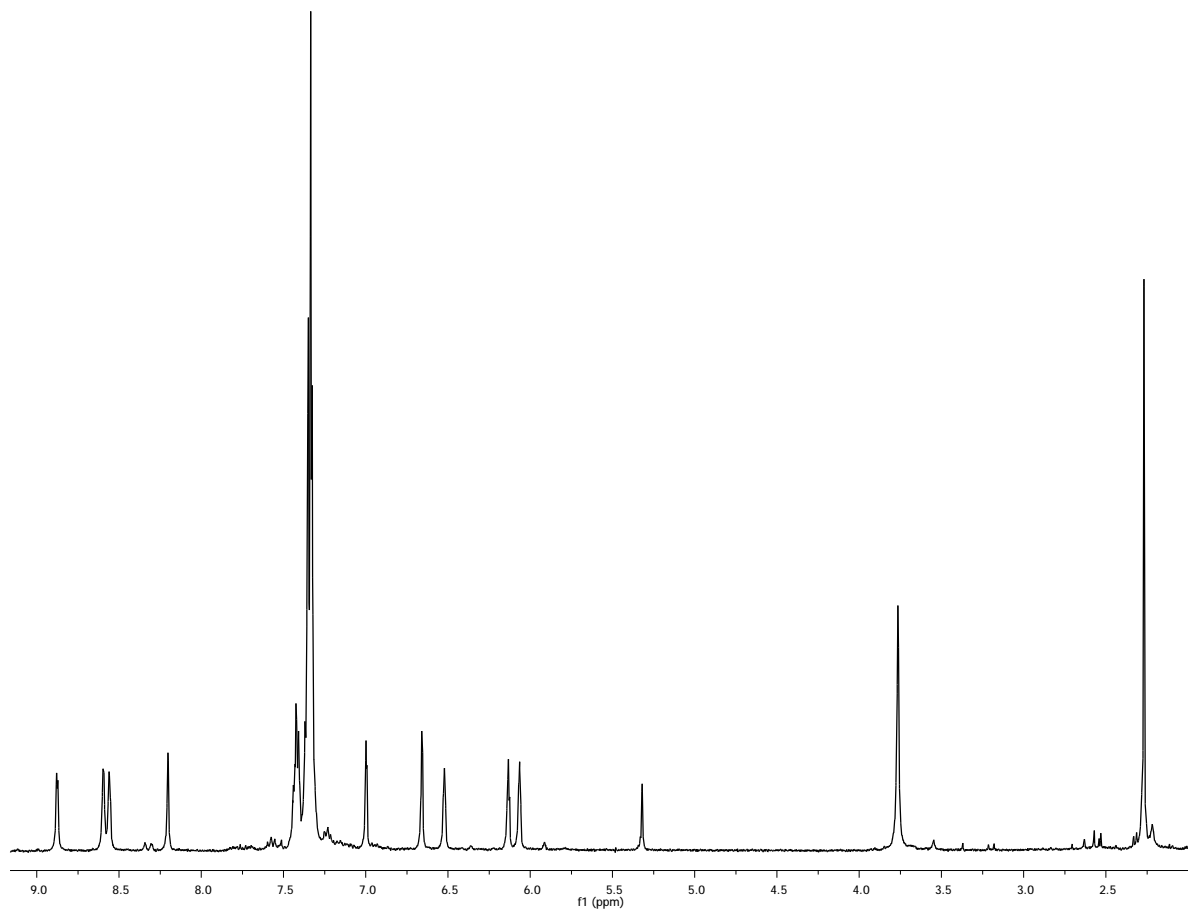


Figure 29. ^1H NMR spectrum of $[\text{EpRu}(\text{Cl})(\text{PPh}_3)(\text{NCMe})][\text{Cl}]$ in CD_2Cl_2 .

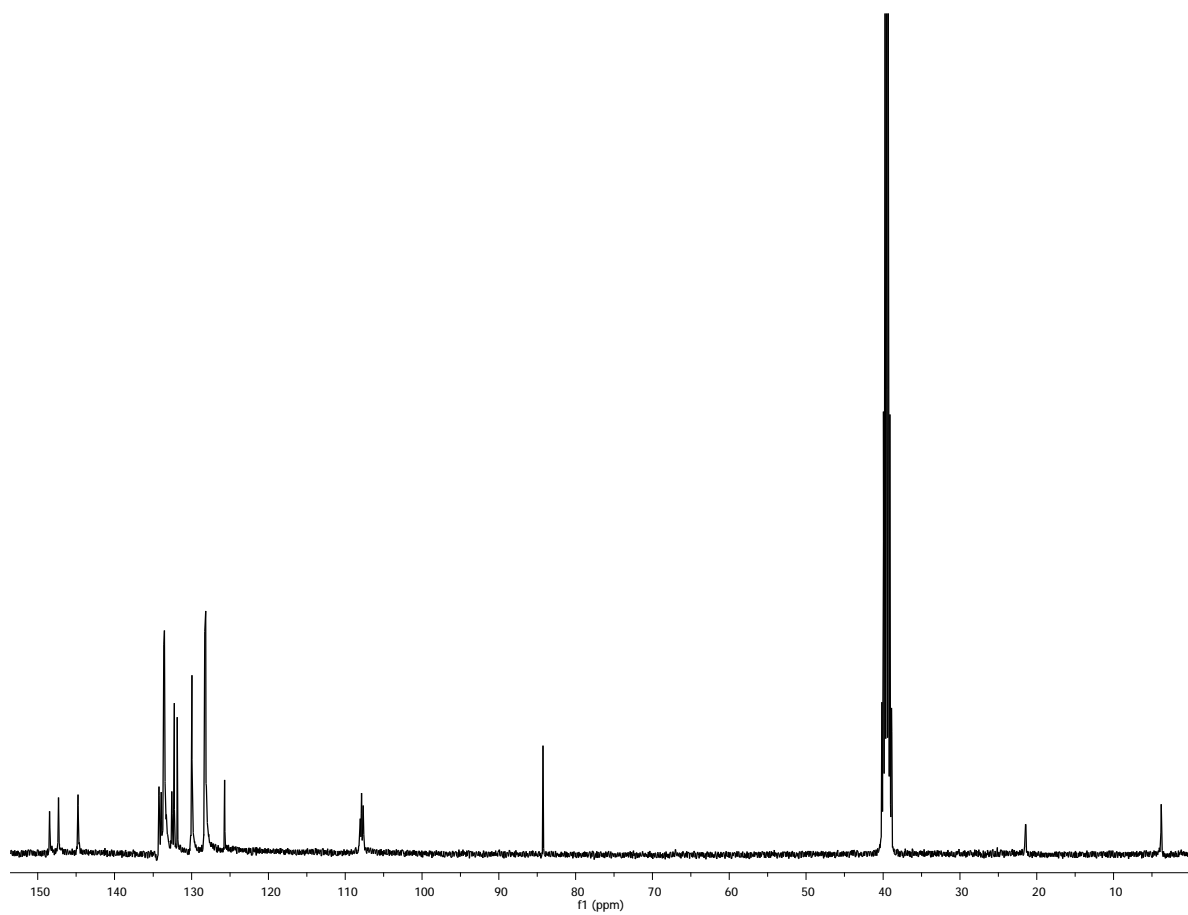


Figure 30. ^{13}C NMR spectrum of $[\text{EpRu}(\text{Cl})(\text{PPh}_3)(\text{NCMe})][\text{Cl}]$ in $\text{DMSO-}d_6$.

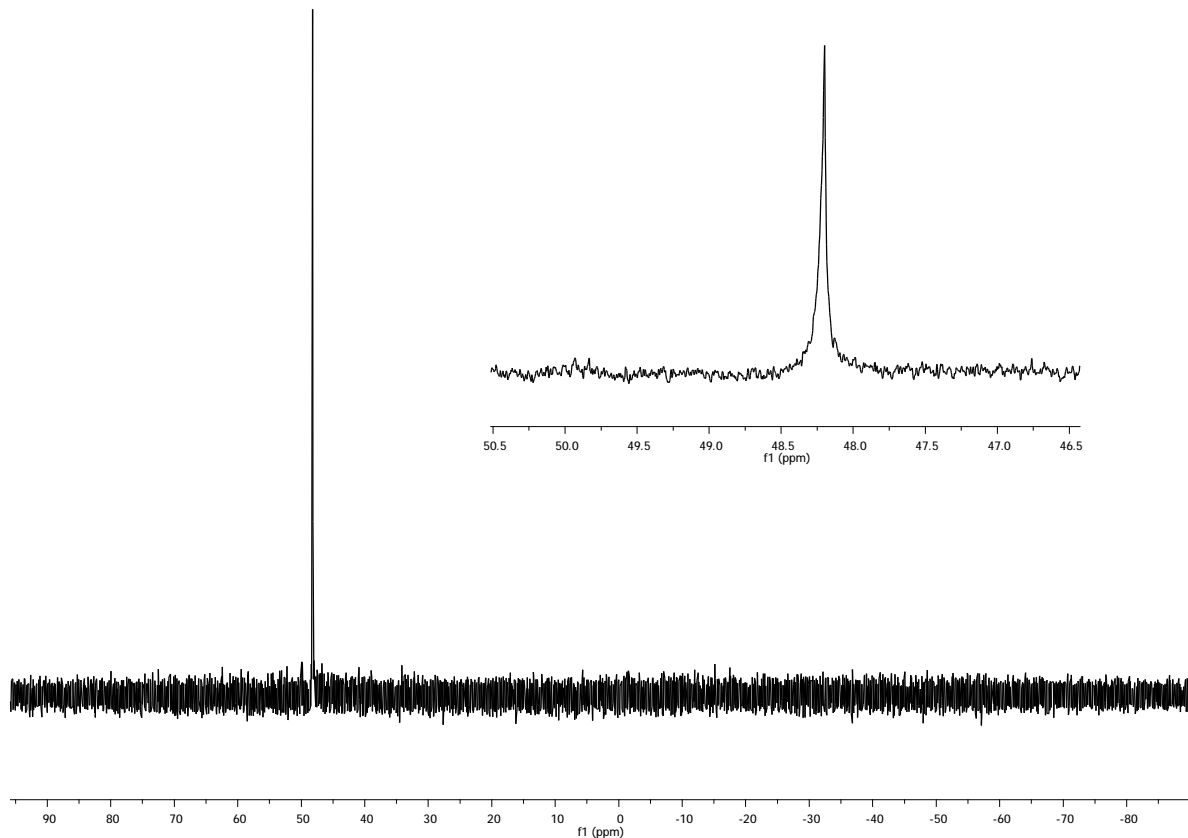


Figure 31. ^{31}P NMR spectrum of $[\text{EpRu}(\text{Cl})(\text{PPh}_3)(\text{NCMe})][\text{Cl}]$ in CD_2Cl_2 .

Attempts to abstract the triphenylphosphine ligand to return to a dichloride species, $\text{EpRu}(\text{NCMe})(\text{Cl})_2$ were unfruitful. Heating for extended times (up to 1 week) in toluene and THF at temperatures from 80 °C to 130 °C yielded no reaction.

Ep was added to a toluene solution of *trans*-(Cl) $_2\text{Ru}(\text{NCMe})_4$.¹⁴¹ The solution remained heterogeneous. After 2 days an aliquot was isolated. Notably absent in the ^1H NMR spectrum were any resonances in the aromatic region. The solution was then heated to reflux for 3 hours. The solution remained heterogeneous and the solid was collected on a

fine frit after cooling. The ^1H NMR spectrum revealed resonances in the aromatic region; however, these resonances were determined to be toluene remaining from the reaction.¹⁴²

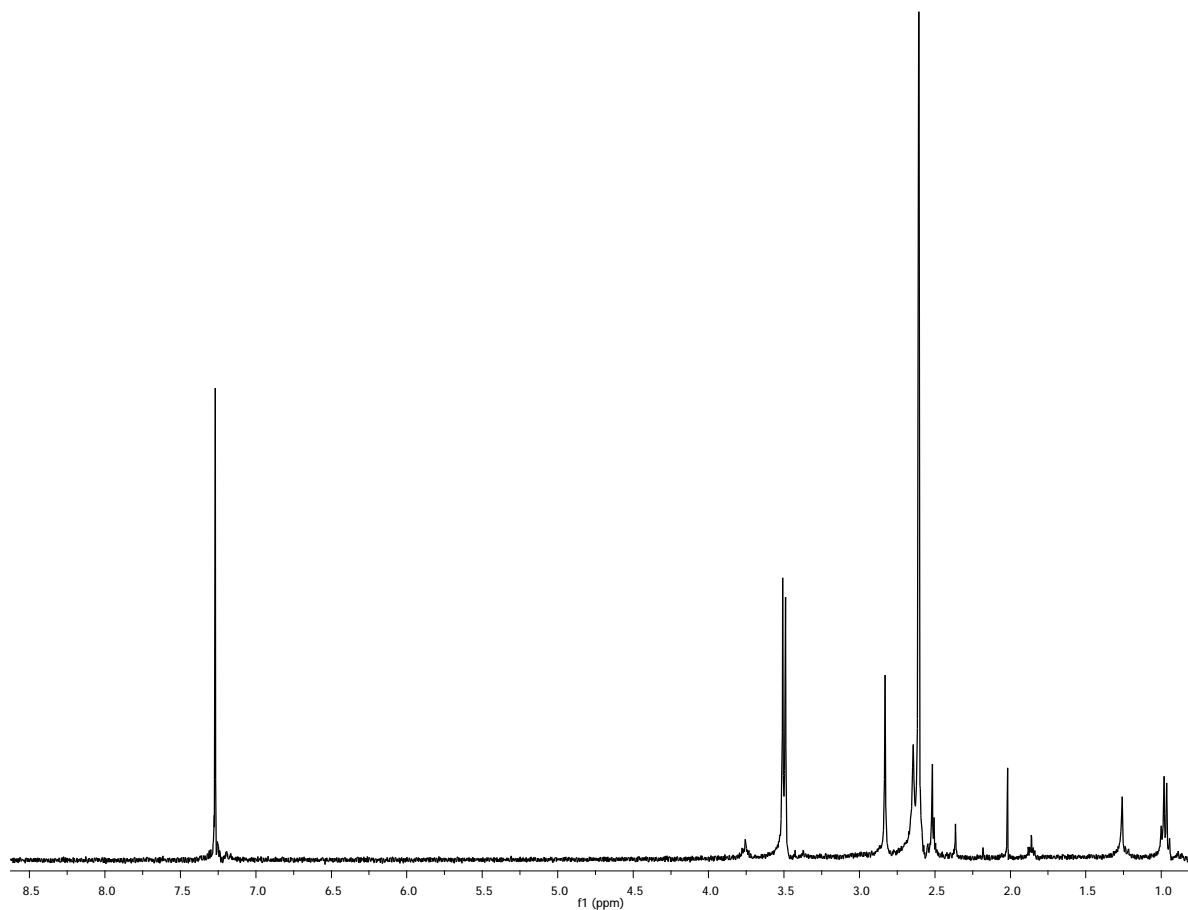


Figure 32. ^1H NMR spectrum in CDCl_3 of the product of $\text{trans}-(\text{Cl})_2\text{Ru}(\text{NCMe})_4$ and Ep after stirring for two days.

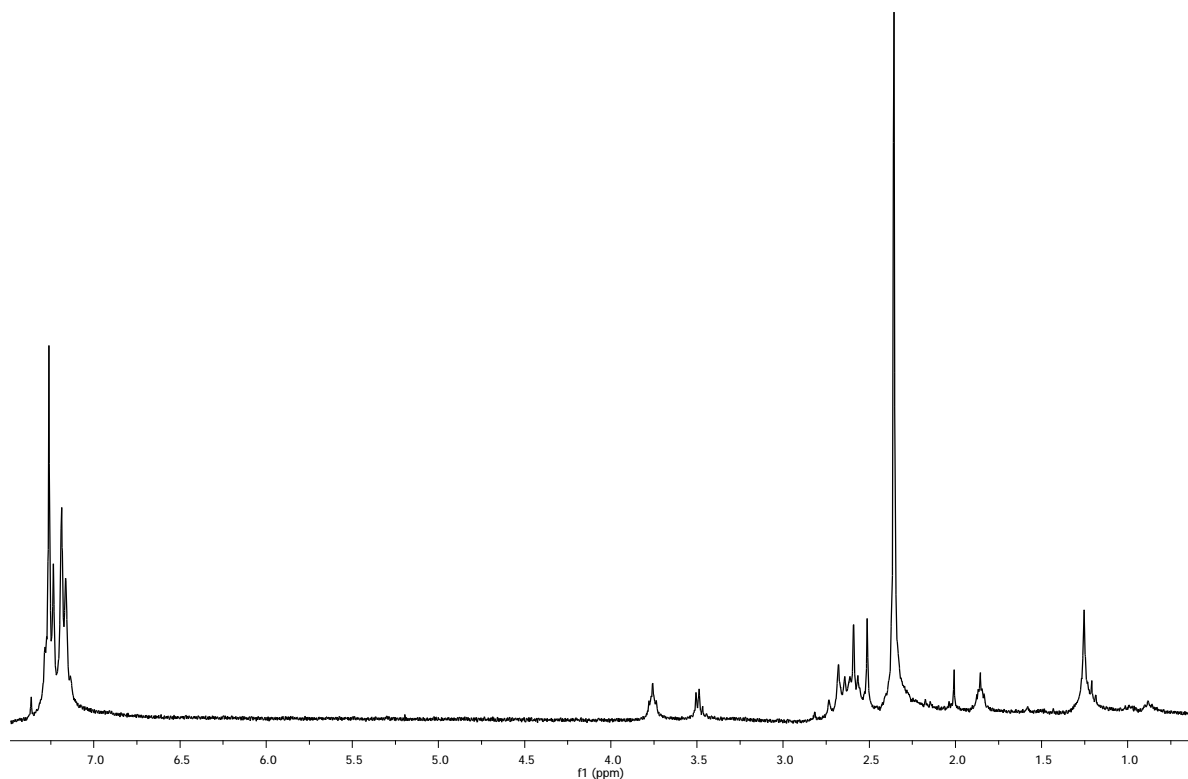


Figure 33. ^1H NMR spectrum in CDCl_3 of the product of $\text{trans}-(\text{Cl})_2\text{Ru}(\text{NCMe})_4$ and Ep after heating for three hours.

In unpublished work by Dr. Karl Pittard, $\text{EpRu}(\text{PMe}_3)(\text{Cl})_2$ was found to be unreactive with methylating reagents as well as ligand metathesis of the chloride for hydroxide or methoxide. The Gunnoe group has previously prepared $\text{TpRu}(\text{X})(\text{PMe}_3)_2$ ($\text{X}=\text{NHPh}$, OH) from $\text{TpRu}(\text{OTf})(\text{PMe}_3)_2$ (OTf = trifluoromethanesulfonate).^{74,75,77} In an attempt to achieve similar Ep analogues of the type $\text{EpRu}(\text{OTf})(\text{PMe}_3)(\text{Y})$ ($\text{Y} = \text{Cl}$ or OTf), Dr. Pittard attempted chloride metathesis of $\text{EpRu}(\text{PMe}_3)(\text{Cl})_2$ using silver triflate was attempted in various solvents. In most solvents the complex $\text{EpRu}(\text{PMe}_3)(\text{Cl})_2$ was found to

be insoluble and unreactive. However, upon heating the complex in methanol- d_4 the ^1H NMR spectrum of the complex revealed that the mirror plane of symmetry was broken. This yielded evidence for replacement of one of the chlorides for another ligand.

Coordination of methanol, rather than triflate, to form $[\text{EpRu}(\text{PMe}_3)(\text{Cl})(\text{DOCD}_3)][\text{Cl}]$ was confirmed by heating $\text{EpRu}(\text{PMe}_3)(\text{Cl})_2$ in neat CD_3OD with no added triflate (Figure 34). Small amounts of impurities were noted in the ^1H NMR spectrum after 17 hours of heating. The impurities coincided with the starting complex (Figure 35). A ^{31}P NMR spectrum confirmed that the starting material was still present in a small amount (Figure 36). In order to complete conversion to one product, excess NaBPh_4 was added (eq 27). Both ^1H and ^{31}P NMR spectroscopy revealed that one complex was formed.

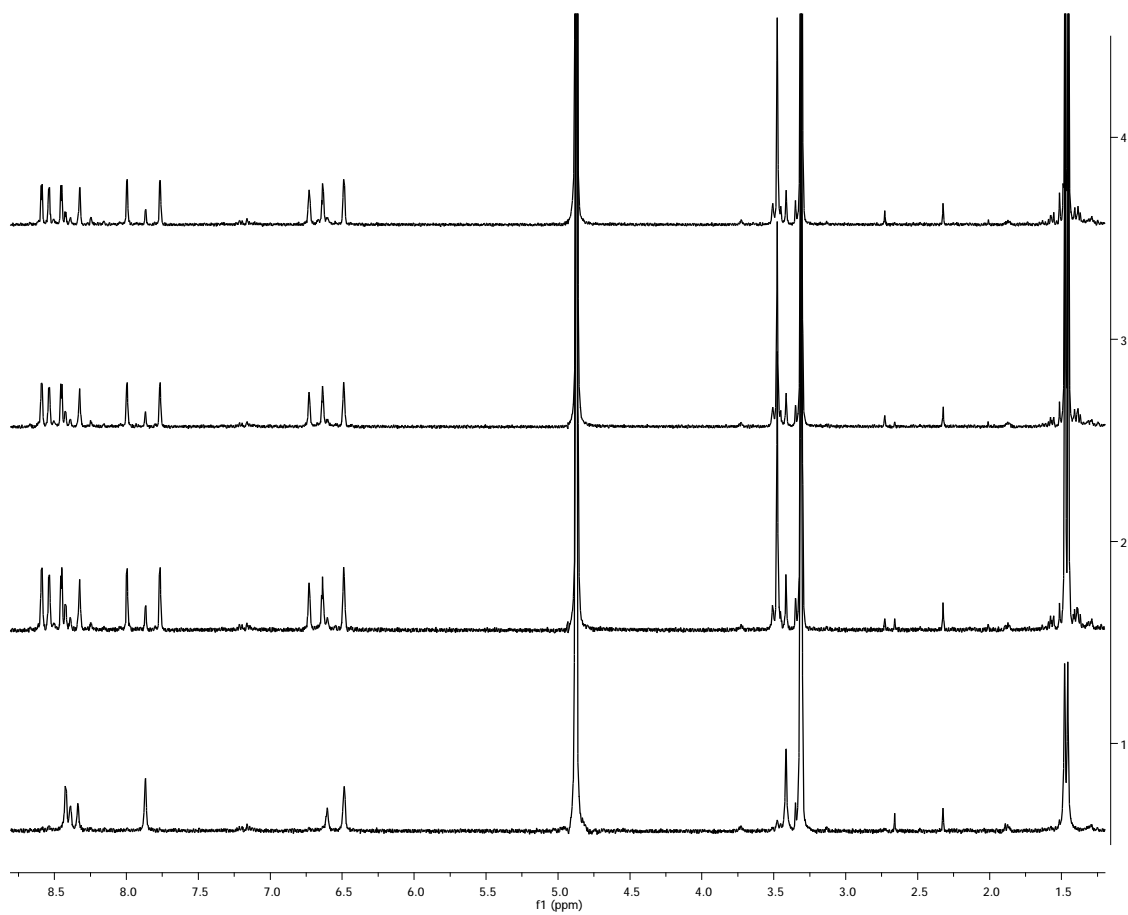


Figure 34. ^1H NMR spectra of heating $\text{EpRuPMe}_3(\text{Cl})_2$ in CD_3OD (1 – initial; 2 – 2 hours; 3 – 4.5 hours; 4 – 17 hours).

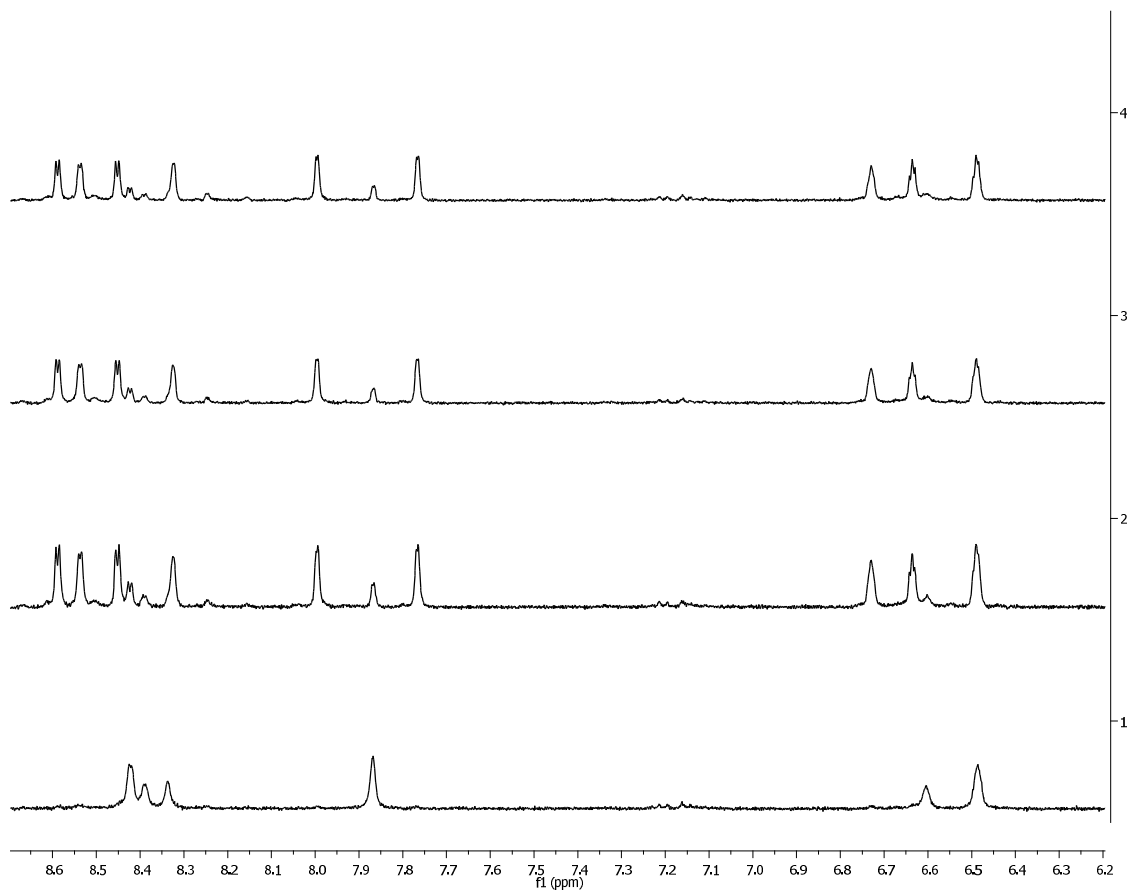


Figure 35. ^1H NMR spectra (expansion of 6.2 – 8.7 ppm) of heating $\text{EpRuPMe}_3(\text{Cl})_2$ in CD_3OD (spectrum #1 – initial; spectrum #2 – 2 hours; spectrum #3 – 4.5 hours; spectrum #4 – 17 hours).

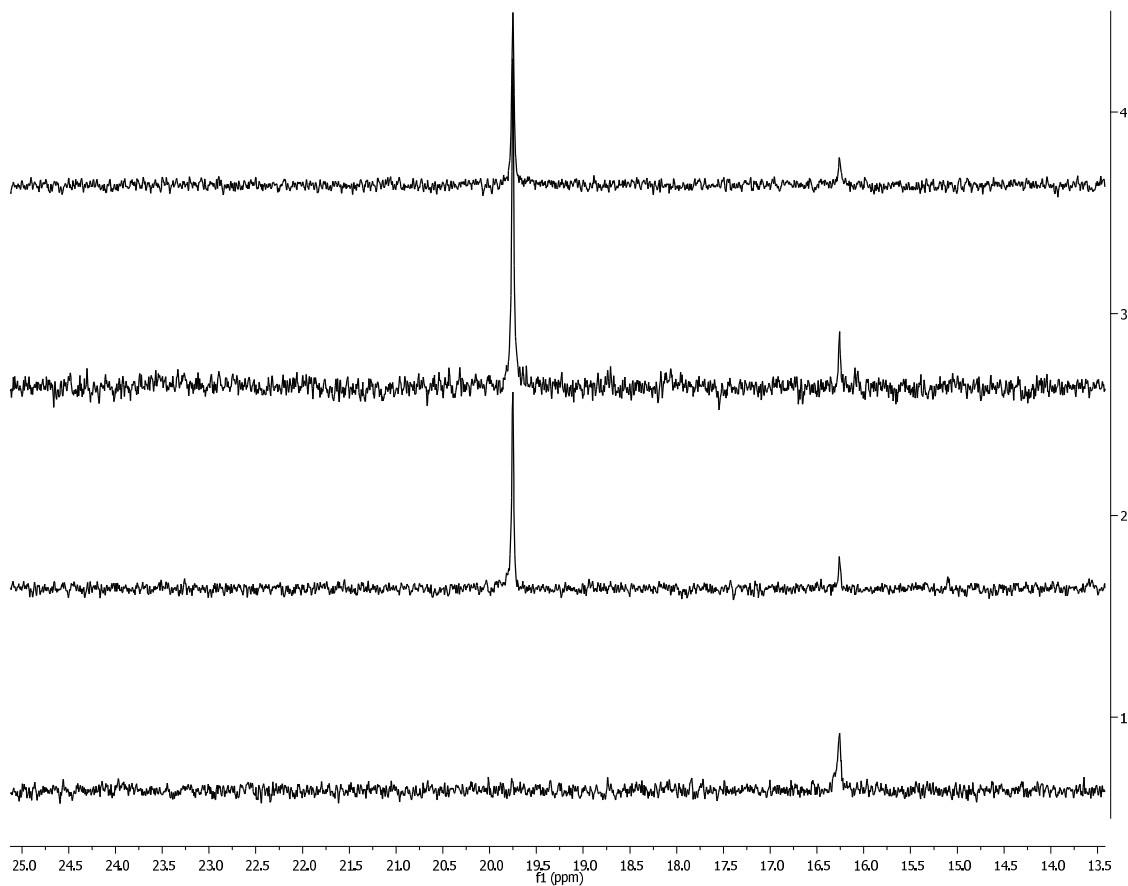
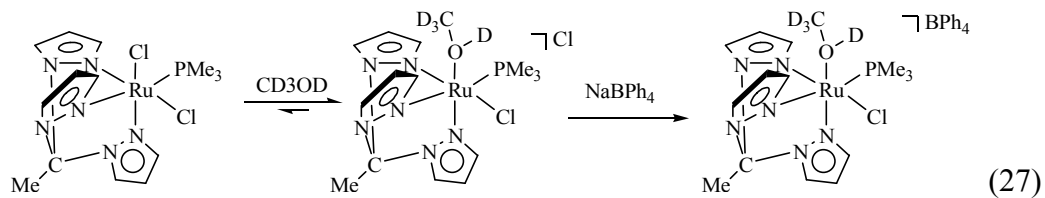


Figure 36. ^{31}P NMR spectra of heating $\text{EpRuPMe}_3(\text{Cl})_2$ in CD_3OD (spectrum #1 – initial; spectrum #2 – 2 hours; spectrum #3 – 4.5 hours; spectrum #4 – 17 hours).



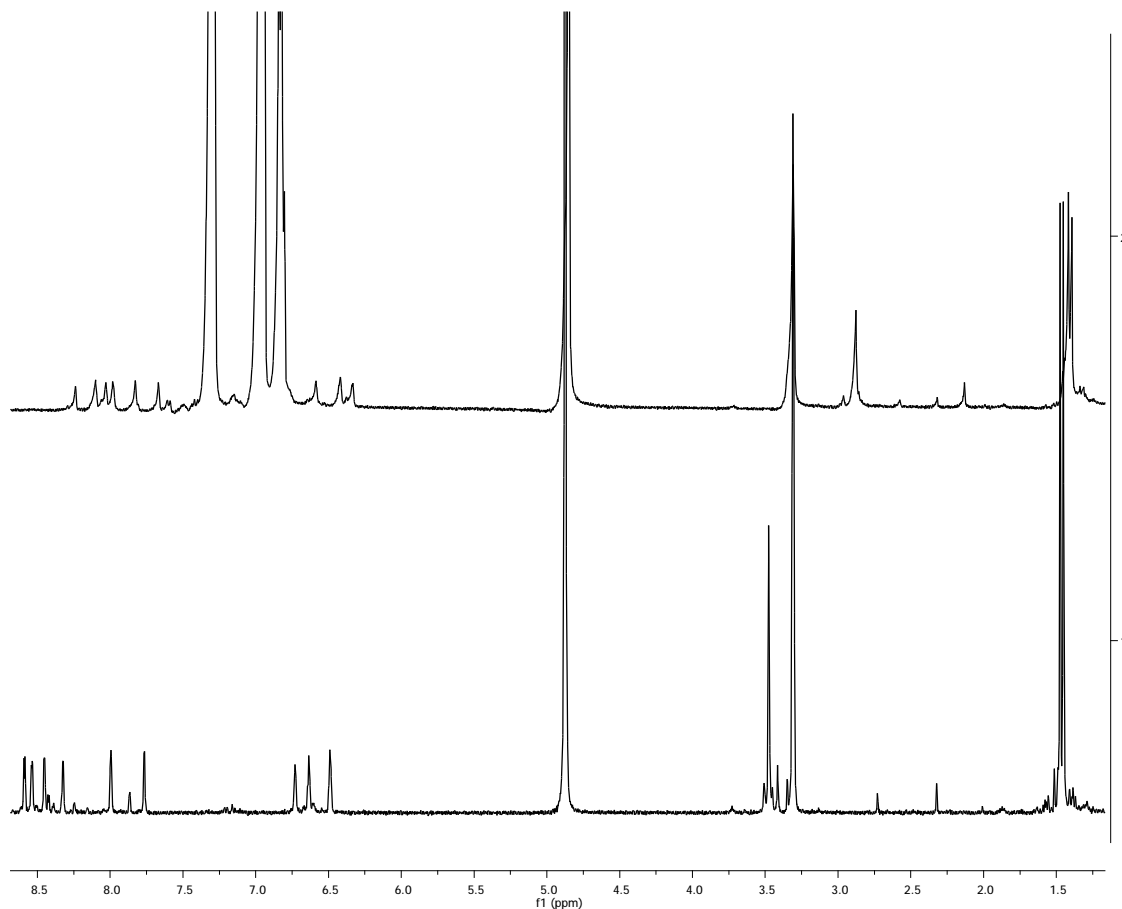


Figure 37. ^1H NMR spectra in CD_3OD of $[\text{EpRu}(\text{DOCD}_3)(\text{PMe}_3)(\text{Cl})][\text{Cl}]$ (bottom) and $[\text{EpRu}(\text{DOCD}_3)(\text{PMe}_3)(\text{Cl})][\text{BPh}_4]$ (top).

With clean preparation of $[\text{EpRu}(\text{DOCD}_3)(\text{PMe}_3)(\text{Cl})][\text{BPh}_4]$ (**3.4**), a new route toward preparation of $\text{EpRu}(\text{OMe})(\text{PMe}_3)(\text{Cl})$ was possible. Scale up and isolation of $[\text{EpRu}(\text{HOMe})(\text{PMe}_3)(\text{Cl})][\text{BPh}_4]$ was attempted. Upon isolation of $[\text{EpRu}(\text{HOMe})(\text{PMe}_3)(\text{Cl})][\text{BPh}_4]$ a deprotonation reaction could be carried out (eq 28). However upon scale-up of the reaction depicted in equation 27 and isolation by precipitation, the product was found to be impure. Although it possessed some resonances similar to the

NMR scale reaction, many resonances that were expected were not present including most importantly the apical Ep-CH₃ peak.

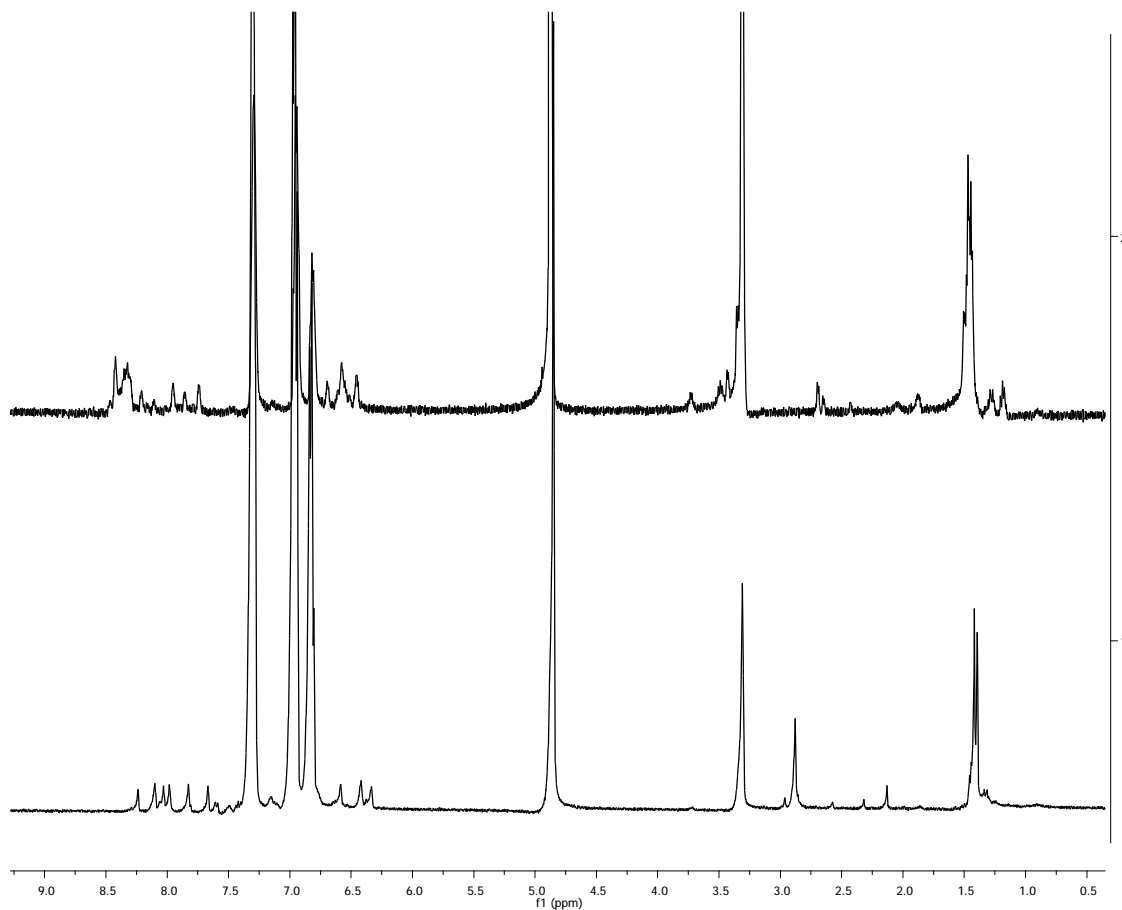
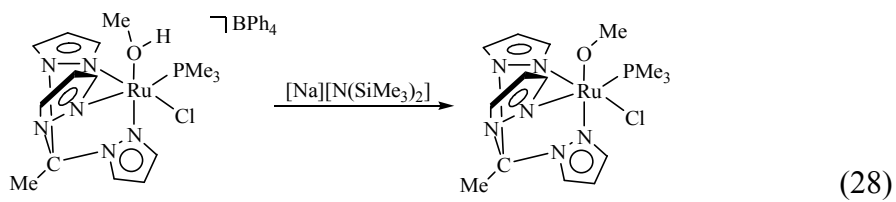
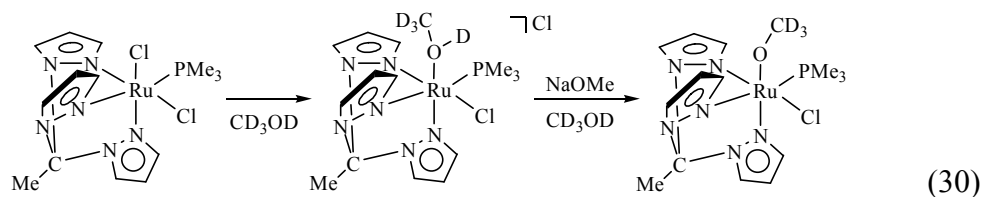
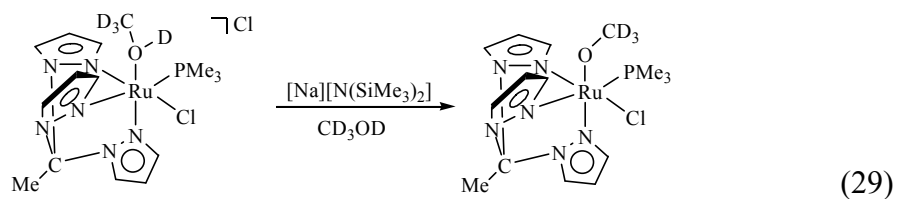


Figure 38. ¹H NMR spectra for comparison of [EpRu(DOCD₃)(PMe₃)(Cl)][BPh₄] generated *in situ* (bottom) and scaled-up product, [EpRu(HOCH₃)(PMe₃)(Cl)][BPh₄] (not cleanly formed).





Without isolation of clean [EpRu(HOMe)(PMe₃)(Cl)][BPh₄], deprotonation of [EpRu(PMe₃)(Cl)(HOMe)][Cl] in methanol was attempted to form EpRu(PMe₃)(Cl)(OMe). A solution of EpRu(PMe₃)(Cl)₂ was heated in methanol-*d*₄ for 3 hours, the solution was then cooled to -78 °C and 1 equivalent of NaN(SiMe₃)₂ was added dropwise (eq 29). A ¹H NMR spectrum showed two unknown products inconsistent with EpRu(PMe₃)(Cl)(OMe). Only six resonances of equal integration are noted in the downfield aromatic region where the pyrazolyl protons of the Ep ligand are usually found. The PMe₃ resonance (1.37 ppm) remains unchanged; however, a small peak is noted just downfield (1.45 ppm).

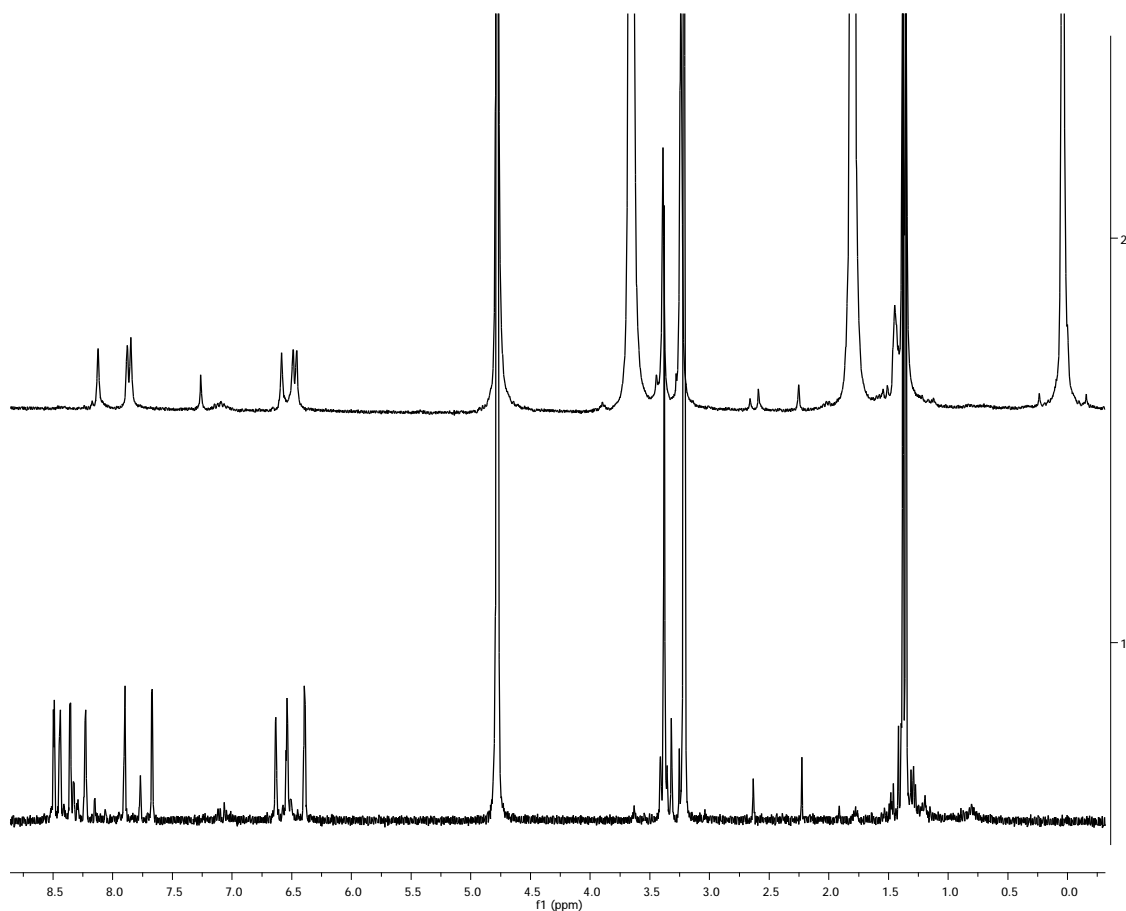


Figure 39. ^1H NMR spectra (in CD_3OD) of $[\text{EpRu}(\text{PMe}_3)(\text{Cl})(\text{DOCD}_3)][\text{Cl}]$ (bottom) and after addition of $[\text{Na}][\text{N}(\text{SiMe}_3)]$ (top).

In a further attempt to isolate a ruthenium methoxide complex, a solution of $\text{EpRu}(\text{PMe}_3)(\text{Cl})_2$ in methanol- d_4 was heated with excess NaOMe (eq 30). After several days of heating, incomplete reaction and decomposition were observed by ^1H NMR spectroscopy (Figure 40).

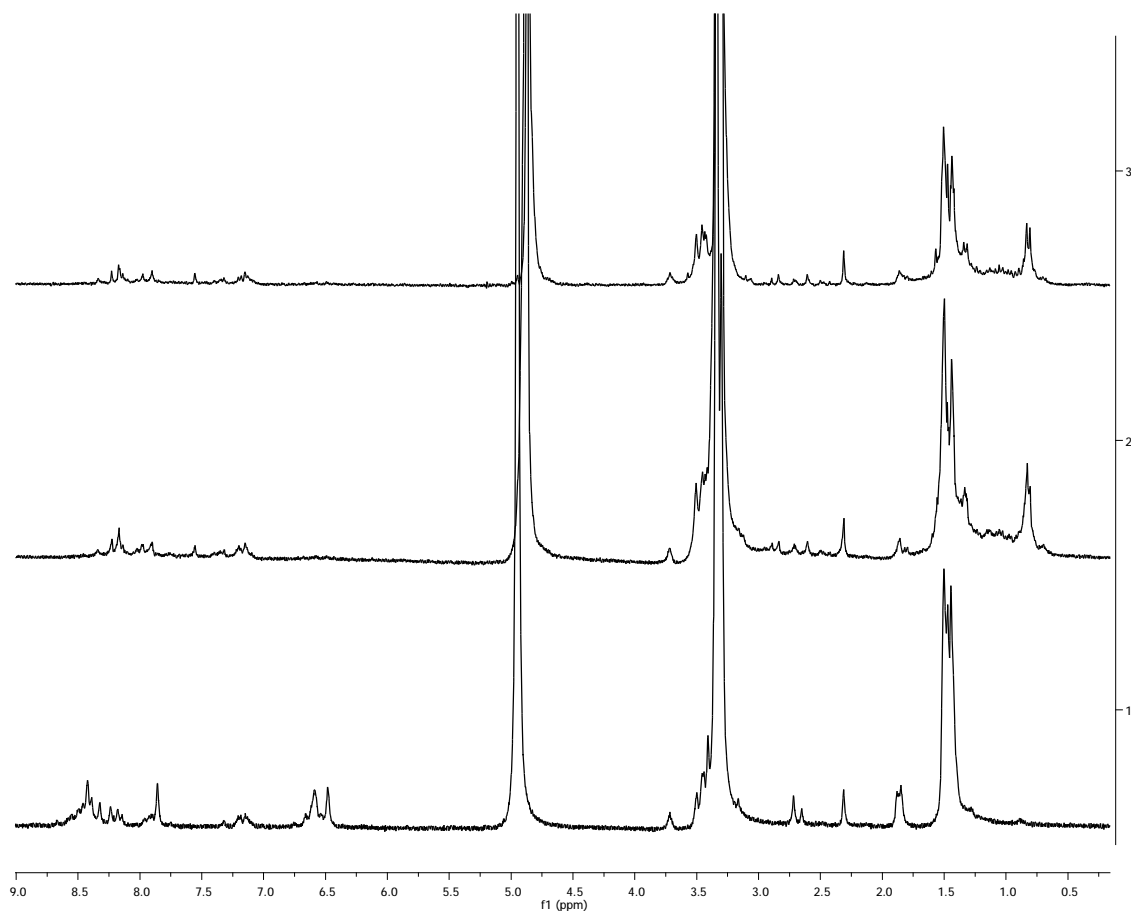


Figure 40. ^1H NMR spectra (in CD_3OD) of the reaction of $\text{EpRu}(\text{PMe}_3)(\text{Cl})$ and NaOMe (immediately after adding reagents and sonication – 1; after heating 3 days at $60\text{ }^\circ\text{C}$ – 2; after 4 days at $60\text{ }^\circ\text{C}$ – 3).

4 Conclusions

While in theory, the tris(pyrazolyl)alkane complexes envisioned herein could result in highly reactive species due to the possibility of a highly electrophilic metal center and the capability for *in situ* generation of an open coordination site. This reactivity, however, could not be developed due to a lack of solubility in many solvents making proper functionalization difficult.

5 Experimental

Unless otherwise stated, all procedures were performed under anaerobic conditions in a nitrogen-filled glovebox or by using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer ($O_2 < 15$ ppm for all reactions). Acetonitrile and methanol were dried by distillation from CaH_2 . Hexanes, methylene chloride, and tetrahydrofuran were purified by passage through a column of activated alumina. Acetone- d_6 , benzene- d_6 , acetonitrile- d_3 , dimethylsulfoxide- d_6 , and chloroform- d were degassed with three freeze-pump-thaw cycles and stored under a dinitrogen atmosphere over 4 Å molecular sieves. 1H and ^{13}C NMR spectra were acquired using Varian Mercury spectrometers operating at 300 or 400 MHz (1H NMR) and 75 or 100 MHz (^{13}C NMR), respectively and referenced to TMS using residual proton signals or the ^{13}C resonances of the deuterated solvent. ^{19}F and ^{31}P NMR spectra were acquired on Varian Mercury 300 or 400 MHz spectrometers and referenced against the external standards of perfluorobenzene and phosphoric acid respectively. $Ru(PPh_3)_3(Cl)_2$, $NaBAR'_4$, *trans*- $Cl_2Ru(py)_4$, *trans*- $Cl_2Ru(NCMe)_4$, and Ep were prepared according to published procedures ($py = N$ -pyridyl).^{133,141,143-147} $EpRu(PPh_3)(Cl)_2$, $[EpRu(Cl)(PPh_3)(PMe_3)][Cl]$, and $EpRu(PMe_3)(Cl)_2$ were developed by Dr. Karl Pittard.¹⁴⁰ All other reagents were used as purchased from commercial sources.

Attempted synthesis of $[EpRu(PPh_3)(py)(Cl)][Cl]$. To a shell vial were added $EpRu(PPh_3)(Cl)_2$ (10.3 mg, 0.016 mmol), pyridine (0.1 mL, 0.12 mmol) and CD_3CN . The contents of the vial were transferred to a screw cap NMR tube and the tube sealed. The tube

was heated at 80 °C for 5 days with periodic ^1H NMR spectra being taken. Incomplete conversion was observed.

[EpRu(py)₂(Cl)][Cl] (3.1). EpRu(PPh₃)(Cl)₂ (298.1 mg, 0.450 mmol) was added to a round bottom flask with pyridine (50 mL). The flask was equipped with an air cooled condenser and refluxed for 10 days. After heating, the solvent was removed by pulling vacuum with a pierced septum to allow a stream of N₂ into the flask due to the high boiling point of pyridine. The resultant solid was taken up in minimal pyridine and diethyl ether was added to precipitate the solid. The solid was collected on a fine frit and dried *in vacuo*. ^1H NMR (CD₂Cl₂, δ) 9.33 (d, J = 2.9 Hz, 1H, Ep 3/5), 8.67 – 8.61 (m, 4H py-*ortho*), 8.58 (d, J = 3.0 Hz, 2H, Ep 3/5), 7.76 (tt, J = 7.6, 1.5 Hz, 2H, py-*para*), 7.45 (d, J = 1.8 Hz, 2H, Ep 3/5), 7.30 (ddd, J = 7.5, 5.3, 1.2 Hz, 4H, py-*meta*), 7.24 (d, J = 2.1 Hz, 1H, Ep 4), 6.67 (t, 1H, Ep 4), 6.48 (dd, J = 3.0, 2.2 Hz, 2H, Ep 4), 3.91 (s, 3H, Ep-CH₃).

Thermolysis of [EpRu(py)₂(Cl)][Cl] in Toluene-*d*₈. [EpRu(py)₂(Cl)] (10.1 mg, 0.018 mmol) was taken up in toluene-*d*₈ (0.5 mL) and placed to a screw cap NMR tube. The tube was sealed and heated for 24 hours at 120 °C with periodic ^1H NMR spectra being taken. No production of free pyridine was observed.

Thermolysis of [EpRu(py)₂(Cl)][Cl] in Benzene-*d*₆. [EpRu(py)₂(Cl)] (5.1 mg, 0.009 mmol) was taken up in benzene-*d*₆ (0.5 mL) and placed to a screw cap NMR tube. The tube was sealed and heated for 24 hours at 80 °C with periodic ^1H NMR spectra being taken. No production of free pyridine was observed.

Thermolysis of [EpRu(py)₂(Cl)][Cl] in THF. [EpRu(py)₂(Cl)] (5.1 mg, 0.009 mmol) were taken up in THF (0.5 mL) and placed to a screw cap NMR tube. The tube was sealed and heated for 24 hours at 80 °C. After heating, the solvent was removed *in vacuo* and replaced with DMSO-*d*₆. A ¹H NMR spectrum was taken.

Reaction of [EpRu(py)₂(Cl)][Cl] and NaOMe. [EpRu(py)₂(Cl)][Cl] (21.0 mg, 0.037 mmol) and NaOMe (59 mg, 1.50 mmol) were taken up in CD₃OD and placed in a screw cap NMR tube. The tube was sealed and heated to 70 °C for 2 days with periodic ¹H NMR spectra being taken. No conversion was observed.

Attempted synthesis of [EpRu(py)₂(Cl)][Cl] or EpRu(py)(Cl)₂ utilizing a new method. To a 50 mL round bottom flask were added *trans*-Cl₂Ru(py)₄ (58.7 mg, 0.120 mmol) and Ep (43.1mg 0.180 mmol) in toluene to produce an orange heterogeneous mixture. The flask heated to reflux for six hours. The mixture remained heterogeneous, and after cooling, an orange solid was collected on a fine frit. The filtrate was yellow in color; the solvent was removed. ¹H NMR of both the solid and the filtrate revealed starting material.

Attempted synthesis of [EpRu(py')(PPh₃)(Cl)][Cl]. EpRu(PPh₃)(Cl)₂ (111.0 mg, 0.176 mmol) was added to a pressure tube with 4-*tert*-butylpyridine (0.150 mL) and NCMe was added as the solvent. The tube was sealed and heated to 90 °C for 10 days. After heating, the solution was concentrated under reduced pressure. Diethyl ether was added to precipitate the solid. The solid was collected on a fine frit and dried *in vacuo*. ¹H NMR revealed a mixture of products.

Attempted synthesis of [EpRu(py)₂(Cl)][Cl] or EpRu(py)(Cl)₂. EpRu(PPh₃)(Cl)₂ (108.2 mg, 0.163 mmol) was added to a round bottom flask with 4-*tert*-butylpyridine (27 mL). The flask was equipped with an air cooled condenser and refluxed for 10 days. After heating, the solvent was reduced by pulling vacuum while a needle allowing a stream of N₂ to bubble through the solution due to the high boiling point of 4-*tert*-butylpyridine. Diethyl ether was added to precipitate the solid. The solid was collected on a fine frit and dried *in vacuo*. ¹H NMR showed no apparent production of the expected product.

[EpRu(PPh₃)(NCMe)(Cl)][Cl] (3.2). EpRu(PPh₃)(Cl)₂ (198.8 mg, 0.300 mmol) was taken up in acetonitrile (50 mL) and placed in a pressure tube. The tube was sealed and heated for 3 days at 80 °C. The volatiles were removed *in vacuo* and the resultant solid was taken up in minimal methylene chloride. Hexanes were added to precipitate the solid. The yellow product was collected on a fine frit, washed with hexanes, and dried *in vacuo* (148.4 mg, 70.3% yield). ¹H NMR (CD₂Cl₂, δ): 8.88 (d, *J* = 3.0 Hz, 1H, Ep 3/5), 8.59 (d, *J* = 2.8 Hz, 1H, Ep 3/5), 8.56 (s, 1H Ep 3/5), 8.20 (s, 1H, Ep 3/5), 7.47 – 7.32 (m, 15H, PPh₃), 7.00 (d, *J* = 2.0 Hz, 1H, Ep 4), 6.66 (d, *J* = 2.0 Hz, 1H Ep 3/5), 6.52 (br s, 1H Ep 3/5), 6.13 (t, *J* = 3 Hz 1H, Ep 4), 6.07 (t, *J* = 3 Hz 1H, Ep 4), 3.76 (s, 3H, Ep CH₃), 2.27 (s, 3H, NCCH₃). ¹³C{¹H} NMR (DMSO-*d*₆, δ) 148.48 (s, PPh₃ - *para*), 147.33 (s, Ep 3/5), 144.80 (s, Ep 3/5), 134.09 (d, ¹*J*_{P-C} = 29Hz, PPh₃ - *ipso*), 133.58 (d, *J* = 9.2 Hz, PPh₃ - *ortho*), 132.57 (s, Ep 3/5), 132.26 (s, Ep 3/5), 131.86 (s, Ep 3/5), 129.98 (s, Ep 3/5), 128.23 (d, *J* = 9.0 Hz, PPh₃ - *meta*), 125.69 (s, NCCH₃), 108.1, 107.9, 107.7 (each a s, Ep 4 x 3), 84.27 (s, Ep apical C), 21.47 (s, Ep CH₃), 3.80 (s, NCCH₃). ³¹P{¹H} NMR (CD₂Cl₂, δ): 48.0 (s, PPh₃).

Attempted synthesis of $\text{EpRu}(\text{NCMe})(\text{Cl})_2$ utilizing a new method. To a 50 mL round bottom flask were added *trans*- $\text{Cl}_2\text{Ru}(\text{NCMe})_4$ (149.5 mg, 0.445 mmol) and Ep (111.4 mg 0.488 mmol) in toluene to produce an orange heterogeneous mixture. The flask heated to reflux for two. The mixture remained heterogeneous, and after cooling, a yellow solid was collected on a fine frit. ^1H NMR spectroscopy revealed starting material.

$[\text{EpRu}(\text{PMe}_3)(\text{Cl})(\text{DOCD}_3)][\text{Cl}]$ (3.3). $\text{EpRu}(\text{PMe}_3)(\text{Cl})_2$ was placed in a screw cap nmr tube with CD_3OD . The tube was heated overnight. Slight impurities are present by ^1H NMR and ^{31}P NMR spectroscopy. ^1H NMR (CD_3OD , δ) 8.58 (d, $J = 3.0$ Hz, 1H, Ep 3/5), 8.53 (d, $J = 2.6$ Hz, 1H, Ep 3/5), 8.45 (d, $J = 3.0$ Hz, 1H, Ep 3/5), 8.32 (d, $J = 1.1$ Hz, 1H, Ep 3/5), 7.99 (d, $J = 1.9$ Hz, 1H, Ep 3/5), 7.76 (d, $J = 1.9$ Hz, 1H, Ep 4), 6.72 (s, 1H, Ep 3/5), 6.63 (s, 1H, Ep 4), 6.48 (s, 1H, Ep 4), 3.47 (s, 3H, Ep- CH_3), 1.46 (d, $J = 9.1$ Hz, 9H, $\text{P}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ (CD_3OD , δ): 19.7.

$[\text{EpRu}(\text{DOCD}_3)(\text{PMe}_3)(\text{Cl})][\text{BPh}_4]$ (3.4). To complete conversion of **3.3** a metathesis was initiated. $\text{EpRu}(\text{PMe}_3)(\text{Cl})_2$ and excess NaBPh_4 were added to a screw cap NMR tube in CD_3OD . The tube was heated for 24 hours. ^1H NMR (CD_3OD , δ) 8.24 (s, 1H, Ep 3/5), 8.10 (s, 1H, Ep 3/5), 8.03 (s, 1H, Ep 3/5), 7.98 (s, 1H, Ep 3/5), 7.83 (s, 1H, Ep 3/5), 7.67 (s, 1H, Ep 4), 6.59 (s, 1H, Ep 3/5), 6.42 (s, 1H, Ep 4), 6.33 (s, 1H, Ep 4), 2.88 (s, 3H, Ep- CH_3), 1.40 (d, $J = 9.1$ Hz, 9H, $\text{P}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ (CD_3OD , δ): 20.0.

Scale up of $[\text{EpRu}(\text{HOME})(\text{PMe}_3)(\text{Cl})][\text{BPh}_4]$. To a pressure tube charged with $\text{EpRu}(\text{PMe}_3)(\text{Cl})_2$ (137.3 mg, 0.288 mmol) and NaBPh_4 (100.1 mg, 0.293 mmol) was added MeOH (50 mL). The tube was sealed and heated for 3 hours. The yellow solution was

filtered through Celite to remove any NaCl generated. The filtrate was reduced to dryness and the resultant solid taken up in minimal chloroform. Diethyl ether was added to precipitate the solid. The yellow solid was collected on a fine frit and dried *in vacuo*. ^1H NMR spectroscopy revealed a product inconsistent with the expected complex.

Attempted deprotonation of $[\text{EpRu}(\text{DOCD}_3)(\text{PMe}_3)(\text{Cl})][\text{Cl}]$. $\text{EpRu}(\text{PMe}_3)(\text{Cl})_2$ (10.3 mg, 0.022 mmol) was taken up in CD_3OD (0.5 ml). The solution was heated to $60\text{ }^\circ\text{C}$ for an hour. The tube was then cooled to $-78\text{ }^\circ\text{C}$ in a cold well cooled by a dry ice/acetone bath. $[\text{Na}][\text{N}(\text{SiMe}_3)_2]$ (21.6 μl , 0.022 mmol) was added dropwise. The tube was allowed to sit for 3 days with ^1H NMR spectra taken immediately, after one day, and after three days. The ^1H NMR spectra did not reveal conversion to the expected product.

Attempted synthesis of $[\text{EpRu}(\text{OCD}_3)(\text{PMe}_3)(\text{Cl})][\text{Cl}]$ using NaOMe. $\text{EpRu}(\text{PMe}_3)(\text{Cl})_2$ (15.3 mg, 0.032 mmol) and NaOMe (3.2 mg, 0.059 mmol) were taken up in CD_3OD (0.5 ml) and placed in a screw cap NMR tube. The tube was sealed and heated to $60\text{ }^\circ\text{C}$ for 4 days with periodic ^1H NMR spectra being taken. The ^1H NMR spectra did not reveal the expected product.

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