

University of Tennessee at Chattanooga

UTC Scholar

---

Honors Theses

Student Research, Creative Works, and  
Publications

---

8-2017

## Octahedral ruthenium(II) complexes for C-H bond activation and olefin hydroarylation

Patrick Z. Zdunek

University of Tennessee at Chattanooga, [hqz791@mocs.utc.edu](mailto:hqz791@mocs.utc.edu)

Follow this and additional works at: <https://scholar.utc.edu/honors-theses>

 Part of the [Chemistry Commons](#)

---

### Recommended Citation

Zdunek, Patrick Z., "Octahedral ruthenium(II) complexes for C-H bond activation and olefin hydroarylation" (2017). *Honors Theses*.

This Theses is brought to you for free and open access by the Student Research, Creative Works, and Publications at UTC Scholar. It has been accepted for inclusion in Honors Theses by an authorized administrator of UTC Scholar. For more information, please contact [scholar@utc.edu](mailto:scholar@utc.edu).

Octahedral Ruthenium(II) Complexes for C-H Bond Activation and Olefin  
Hydroarylation

Patrick Zdunek

Departmental Honors Thesis  
The University of Tennessee at Chattanooga  
Department of Chemistry and Physics

Examination Date: April 4, 2017

---

John P. Lee  
Assistant Professor of Chemistry  
Thesis Director

---

Kyle Knight  
Professor of Chemistry  
Department Examiner

## Abstract

The study of inert C-H bond activation of hydrocarbons has been gaining interest. As these hydrocarbons are used in the production of many consumables such as fuel, plastics, and detergents, it is necessary to efficiently utilize the finite quantity of petroleum feedstocks. Transition metal complexes are incorporated as catalysts into synthetic routes to create new C-X (X = C, N, O) bonds in order to increase the chemical value of organic molecules. The complex  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}(\text{Ph})(\text{OTf})]$  (**1**) ( $\text{P}\{\text{OCH}_2\text{CF}_3\}_3$  = tris(2,2,2-trifluoroethyl) phosphite, Ph = phenyl, OTf = trifluoromethanesulfonate) was prepared and tested for functionality as a catalyst in olefin hydroarylation. Catalytic reactions were attempted with 5 mol % of **1** in ethylene (15 psi) and benzene- $\text{d}_6$  at a varying temperatures, which resulted in the decomposition of **1** and no formation of an organic product. With the observed decomposition of the complex in catalytic attempts, three different directions were pursued: the coordination of ligands 1,4,7-trimethyl-1,4,7-triazacyclononane ( $9\text{N}3_{\text{Me}}$ ) and 1,4,7-trithiacyclononane ( $9\text{S}3$ ) to complex **1** to replace  $\eta^6\text{-}p\text{-cymene}$  as the ancillary ligand, the synthesis of a  $\text{Ru}(\eta^6\text{-}p\text{-cymene})$  complex that had the caged phosphite ligand trimethylolpropane phosphite  $\{\text{P}(\text{OCH}_2)_3\text{CEt}\}$  coordinated, and the synthesis of Ru complexes containing the anionic ancillary ligand pentamethylcyclopentadiene ( $\text{Cp}^*$ ). The ligands  $9\text{S}3$  and  $9\text{N}3_{\text{Me}}$  did not coordinate to complex **1**. The new complex  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\{\text{P}(\text{OCH}_2)_3\text{CEt}\}(\text{Ph})(\text{Cl})]$  (**2**) was synthesized. The new complex  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}_2(\text{Cl})]$  (**3**) was synthesized, characterized, and reactivity with AgOTf, AgOAc, PhMgBr, PhLi, and MeLi has been tested (AgOAc = silver acetate).

*List of abbreviations:*

BArF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ( $C_{32}H_{12}BF_{24}^-$ )

CO = carbon monoxide (CO)

Cp\* = pentamethylcyclopentadiene ( $C_{10}H_{16}$ )

NCMe = acetonitrile ( $C_2H_3N$ )

OAc = acetate ( $C_2H_3O_2^-$ )

OTf = trifluoromethanesulfonate ( $CF_3SO_3^-$ )

Tp = tris(pyrazolyl)borate ( $HB(C_3N_2H_3)_3^-$ )

9N3Me = 1,4,7-trimethyl-1,4,7-triazacyclononane ( $C_9H_{21}N_3$ )

9S3 = 1,4,7-trithiacyclononane ( $C_6H_{12}S_3$ )

## Table of Contents

<b>Chapter 1. Catalytic Activation of C-H Bonds and Ruthenium (II) Complexes</b> .....	7
Introduction .....	7
Inert Bond Activation .....	7
Friedel Craft's Catalysis .....	7
Olefin Hydroarylation .....	9
Ruthenium (II) Catalysts .....	11
References .....	14
<b>Chapter 2. Reactivity of [Ru(<math>\eta^6</math>-<i>p</i>-cymene){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>}(Ph)(OTf)] and Further Synthesis of Ru(<i>p</i>-cymene) Complexes</b> .....	17
Introduction: [Ru( $\eta^6$ - <i>p</i> -cymene){P(OCH <sub>2</sub> CF <sub>3</sub> ) <sub>3</sub> }(Ph)(OTf)] .....	17
Reactivity of [Ru( $\eta^6$ - <i>p</i> -cymene){P(OCH <sub>2</sub> CF <sub>3</sub> ) <sub>3</sub> }(Ph)(OTf)] .....	18
Dissociation of $\eta^6$ - <i>p</i> -cymene .....	21
<u>Reactivity of [Ru(NCMe)<sub>3</sub>{P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>}(Ph)(OTf)]:</u>	
Coordination of Ancillary Ligands 9S3 and 9N3 <sub>Me</sub> .....	22
Coordination of Caged Phosphite {P(OCH <sub>2</sub> ) <sub>3</sub> CEt} .....	23
Conclusions: Future Work with Ru( $\eta^6$ - <i>p</i> -cymene) complexes .....	25
Methods .....	26

Experimental .....	26
<i>[Ru(η<sup>6</sup>-p-cymene)(P{OCH<sub>2</sub>CF<sub>3</sub>})<sub>3</sub>(Ph)(OTf)]<sup>1</sup></i> .....	26
<i>Catalysis Reaction w/ [Ru(η<sup>6</sup>-p-cymene)(P{OCH<sub>2</sub>CF<sub>3</sub>})<sub>3</sub>(Ph)(OTf)]</i> .....	26
<i>[Ru(NCMe)<sub>3</sub>{P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>(Ph)(OTf)}</i> .....	27
<i>[Ru(9S3){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>(Ph)(OTf)]</i> .....	28
<i>[Ru(9N3Me ){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>(Ph)(OTf)]</i> .....	28
<i>[Ru(η<sup>6</sup>-p-cymene)(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(Cl)<sub>2</sub>]<sup>3</sup></i> .....	28
<i>[Ru(η<sup>6</sup>-p-cymene)(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(Ph)(Cl)]<sup>3</sup></i> .....	29
References.....	30

### Chapter 3. Ruthenium(II) Complexes with Coordinated Ancillary Ligand

<b>Pentamethylcyclopentadienyl Anion (Cp*)</b> .....	<b>31</b>
Introduction: Anionic Ruthenium(II) Catalysts .....	31
Synthesis of [Ru(Cp*){P(OCH <sub>2</sub> CF <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> (Cl)].....	32
<u>Reactivity of [Ru(Cp*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(Cl)]:</u>	
Grignard and Organolithium Reagents .....	35
<u>Reactivity of [Ru(Cp*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(Cl)]:</u>	
Silver Salts .....	37
Conclusions: Future Work with [Ru(Cp*){P(OCH <sub>2</sub> CF <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> (Cl)] .....	38
Methods .....	40
Experimental .....	40
<i>[Ru(Cp*)Cl<sub>2</sub>]<sub>2</sub></i> .....	40

$[Ru(Cp^*)\{P(OCH_2CF_3)_3\}_2(Cl)]$ .....	40
$[Ru(Cp^*)\{P(OCH_2CF_3)_3\}_2(Cl)]$ w/ AgOTf.....	41
$[Ru(Cp^*)\{P(OCH_2CF_3)_3\}_2(Cl)]$ w/ AgOAc.....	41
$[Ru(Cp^*)\{P(OCH_2CF_3)_3\}_2(Cl)]$ w/ PhMgBr .....	42
$[Ru(Cp^*)\{P(OCH_2CF_3)_3\}_2(Cl)]$ w/ PhLi .....	42
$[Ru(Cp^*)\{P(OCH_2CF_3)_3\}_2(Cl)]$ w/ MeLi.....	43
References .....	44

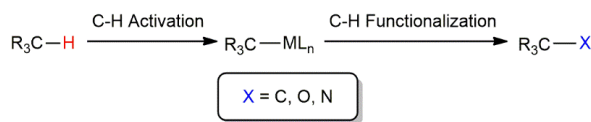
# Chapter 1. Catalytic Carbon-Hydrogen Bond Activation Using Ruthenium(II) Complexes

## Introduction

The focus of this project is the catalyst-assisted activation of inert carbon-hydrogen bonds. The activation of C-H bonds and creation of C-C bonds allows for more efficient use of hydrocarbons obtained from petroleum-based feedstocks, as these hydrocarbons can be modified in their structure and functionality to create compounds necessary for the production of other goods.<sup>1</sup> These hydrocarbons can become sources of stored energy as petroleum products, such as gasoline and natural gas, as well as plastic and detergent, and it is important to efficiently use these hydrocarbons as they are of a finite quantity. Plastics and detergents are made from the bi-products of petroleum when it is refined to produce natural gas. The use of metal complexes in the activation of these bonds allows for increased selectivity, and the production of a desired hydrocarbon, such as ethylbenzene or styrene, can be more efficient than current methods such as Friedel-Crafts catalysis.

## Inert Bond Activation

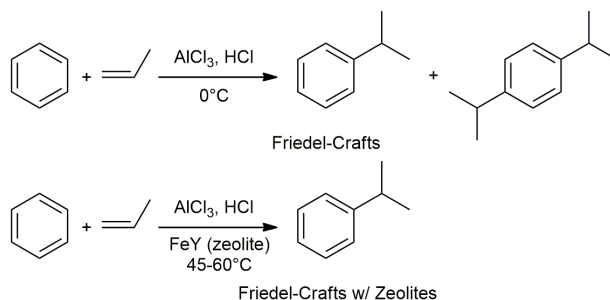
The study of the activation and functionalization of inert bonds (i.e., C-H, H<sub>2</sub>, CO<sub>2</sub>) has been gaining attention as environmental concerns have risen over the years.<sup>1</sup> Depicted in Scheme 1, the activation of inert C-H bonds is a reaction in which a carbon-hydrogen bond is cleaved and subsequently the bond is replaced by a carbon-X bond, where X is usually a



**Scheme 1.** General C-H Activation and Functionalization



carbon, nitrogen, oxygen, or halogen.<sup>2</sup> To cleave the C-H bond, a transition metal complex, a molecule consisting on a metal central atom and a surrounding array of ions or molecules known as ligands, is often used. The metal interacting in the reaction is usually part of an organometallic complex: a complex with at least a single metal-carbon bond present. Carbon-carbon bond formation is the fundamental approach to adding complexity and value to a molecule.<sup>3</sup> The addition of a carbon chain to an aromatic substrate for example benzene, is a method to produce value-added alkyl arenes such as styrene, ethylbenzene, and cumene (isopropylbenzene). Ethylbenzene is

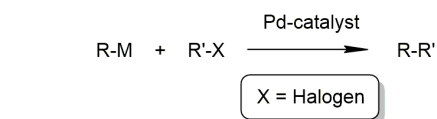


**Scheme 2.** C-C Bond Formation with Benzene

primarily utilized in the production of styrene, and in 2010, > 15 million tons of ethylbenzene and approximately 25 million tons of styrene were produced.<sup>4,5,6</sup> At the industrial scale, the production of alkyl arenes is done through Friedel-Crafts catalysis.<sup>3,6,7</sup> Friedel-Crafts utilizes a main-group Lewis acid with a Brønsted acid.<sup>7</sup> There are several disadvantages to this reaction. The first issue is the over alkylation of the aromatic. This is due to the nucleophilic nature of the mono-alkylated product, which makes it more likely to substitute a second hydrogen atom with an alkyl chain before the more electrophilic, non-substituted aromatic is alkylated (Scheme 2).<sup>9</sup> The inclusion of zeolites, microporous aluminosilicate minerals, into the reaction process has allowed for improved selectivity and less waste. However, the zeolites require unique design for specific applications and still do not permit the formation of linear products.<sup>8</sup> The second issue is the formation of a branched product, as the increased stability of tertiary and secondary carbocations

influences a carbocation rearrangement. This prevents the formation of primary carbocations, therefore preventing linearly alkylated products.<sup>7-9</sup> A third issue is the requirement of an alkyl halide reagent. This can require additional synthetic measures to halogenate a reactant, and in an industrial scope, it is a less economical method. For example, other reactions, namely Suzuki,

Sonogashira, Negishi, and Stille, are able to provide alternative methods for C-C bond formation for aromatic substrates.<sup>3,10,11</sup>



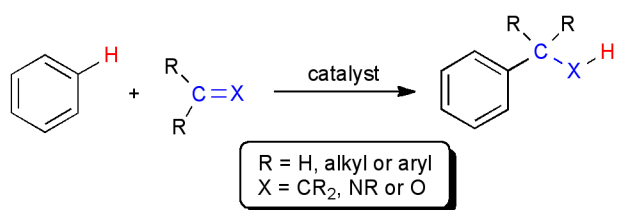
**Scheme 3.** Cross-Coupling Reaction via Pd Catalyst

Suzuki palladium catalysts are reported to facilitate cross-coupling reactions with organoboron compounds and aromatic compounds (Scheme 3). Though these catalysts provide alternate routes for C-C formation, they require the incorporation of halides into the aromatic substrate, which often is a multistep synthesis.<sup>11,12</sup>

### Olefin Hydroarylation

The specific activation reaction to be studied is olefin hydroarylation. Hydroarylation is defined as the addition of an aromatic C-H bond across an unsaturated substrate (*i.e.*, C=X double bond, where X = CR<sub>2</sub>, NR, or O) (Scheme 4).<sup>3,13,14</sup> A proposed

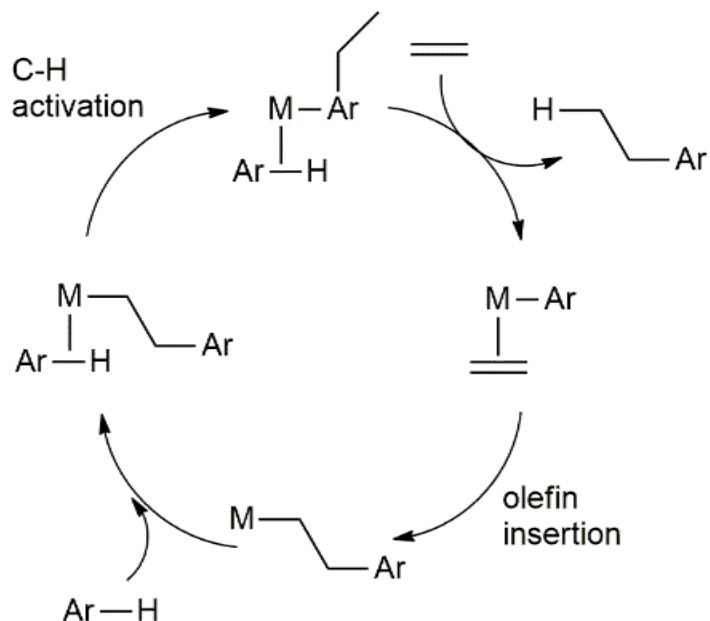
catalytic cycle is shown in Scheme 5. The catalytic cycle begins with the coordination of an olefin to the metal center.<sup>3,13-15</sup> The succeeding step is the insertion of the olefin into the metal-aryl



**Scheme 4.** General C=X hydroarylation reaction using **benzene** as the aromatic source

bond. With a metal coordination site available, an aromatic is able to coordinate to the metal center. The C-H bond activation of the alkyl arene returns coordination to the

aromatic portion of the hydrocarbon, allowing the dissociation of the alkyl arene product. Opening a new coordination site, the metal is subject to the coordination of ethylene, and the catalytic cycle reinitiates.

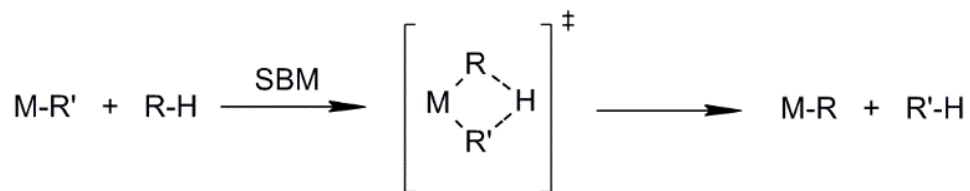


**Scheme 5.** Catalytic Cycle for Ethylene Hydroarylation

A list of undesirable side reactions can occur in this cycle, so the design of a catalyst requires forethought in order to avoid such reactions. As the six coordinate metal catalyst is designed to contain a phenyl ligand and to contain only a single leaving group, only one equivalent of the olefin is able to bond to the metal center. To prevent the coordination of a second phenyl ligand, the steric profile of the other coordinated ligands can be modified to allow the coordination of a smaller olefin but restrict the coordination of a phenyl ligand. A second issue is the formation of a catalyst resting state following olefin insertion, as an equivalent of the olefin could coordinate to the metal center rather than the phenyl ligand. A few other side reactions  $\beta$ -hydride elimination, C-H oxidative addition, C-H activation of substrates other than the selected arene, and multiple olefin

insertions resulting in polymerization.<sup>3</sup> Published kinetic studies provide insight into these side reactions, which can further assist the design of a catalyst for olefin hydroarylation.

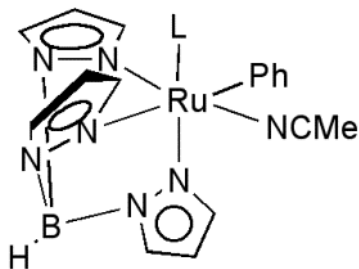
It is through this cycle that ethylbenzene can be produced through the reaction of ethylene, benzene, and a transition metal catalyst. Two steps in this olefin hydroarylation cycle are considerable improvements over Friedel Crafts catalysis: olefin insertion and metal-mediated aromatic C-H bond activation.<sup>3,13</sup> Reported computational and experimental studies confirm the metal-mediated C-H bond activation mechanism is through a concerted  $\sigma$ -bond metathesis (SBM) pathway (Scheme 6).<sup>3</sup>



**Scheme 6.** Sigma Bond Metathesis (SBM)<sup>3</sup>

### Ruthenium (II) Catalysts

Complexes of the type  $[\text{Ru}(\text{Tp})(\text{L})(\text{Ph})(\text{NCMe})]$  (Tp = tris(pyrazolyl)borate, L = neutral ligand, Ph = phenyl, NCMe = acetonitrile) (Figure 1) as well as  $\text{Ru}(\text{Cp}^*)$  and  $\text{Ru}(\text{Tpm}^{5-\text{Me}})^{16}$  ( $\text{Cp}^*$  = pentamethylcyclopentadienyl,  $\text{Tpm}^{5-\text{Me}}$  = tris(5-



**Figure 1.** General Structure of Reported Tp(Ru) Catalysts

methylpyrazolyl)methane) have been reported to have turnovers of ethylbenzene when utilized in olefin hydroarylation. The ancillary ligand is the anionic ligand tris(pyrazolyl)borate (Tp). Tris(pyrazolyl)borate is a tridentate ligand, and it occupies an entire face of the octahedral geometry

of the complex. A phenyl ligand (Ph) is also coordinated to the metal center. Its preliminary

coordination to the metal center is required for the catalytic cycle. The third ligand is acetonitrile (NCMe), and its purpose is to serve as a leaving group. Acetonitrile is the most labile ligand of the four ligands coordinated to the metal center, and in the presence of an olefin, it will dissociate to make available a coordination site for the ligand. The neutral ligand denoted  $L$  can be modified for desired electronic and steric characteristics.<sup>16</sup>

Of the five reported ligands  $L$ , carbon monoxide with the smallest cone angle ( $95^\circ$ ) is reported to have the highest number of turnovers of ethylbenzene when in the complex  $[\text{Ru}(\text{Tp})(\text{CO})(\text{Ph})(\text{NCMe})]$ .<sup>16,17,18</sup> This is due to a combination of carbon monoxide's small cone angle (sterics), which provides the least steric hindrance and has the highest  $\pi$ -accepting character (electronics).<sup>16</sup> Ligand cone angle is used to measure the size of a ligand and is the measure of the angle formed between the metal at the vertex of the cone and the outer perimeter that is formed by the rotating ligand.<sup>17,18</sup> Along with molecular modeling, the cone angles are measured through a reaction between  $\text{Ni}(\text{CO})_4$  and an excess of  $L$ , which was monitored through IR spectroscopy. As the cone angle of a ligand decreases, more equivalents of  $L$  are able to coordinate to the Ni metal center.<sup>17</sup> Steric hindrance and electronic effects are key factors in the performance of these catalysts, as the complex containing  $L = \text{P}(\text{pyr})_3$  (cone angle =  $145^\circ$ ) is too sterically hindered to allow coordination of an olefin to the metal center.<sup>17</sup>

As suggested in Foley *et al*, ancillary ligands such as Tp and Cp\* are stable once coordinated to the metal center due to their anionic nature, but these electron dense ligands also provide certain limitations in the variability of the ligand  $L$  that can be coordinated to the metal center.<sup>3</sup> As suggested, less electron-rich metals and neutral ancillary ligands

could provide a greater variance in the electronic and steric profile of the ligands coordinated to the metal center.

A ruthenium complex with the neutral ligand  $\eta^6$ -*p*-cymene has been synthesized and fully characterized. Its proposed function is to catalyze the hydrophenylation of ethylene. The proposed work is to test the viability of this complex to act as a catalyst in a variety of reaction conditions.

## References

1. Goldman, A. S.; Goldberg, K. I. “In Activation and Functionalization of C-H Bonds” American Chemical Society: Washington, D. C., **2004**, 885, 1-43.
2. Crabtree, R. H. “Alkane C–H activation and functionalization with homogeneous transition metal catalysts: a century of progress – a new millennium in prospect” *J. Chem. Soc.: Dalton Trans.*, 2001, 2437-2450.
3. Foley, N. A.; Lee, J. P.; Ke, Z.; Gunnoe, T. B.; Cundari, T. R. “Ru(II) Catalysts Supported by Hydridotris(pyrazolyl)borate for the Hydroarylation of Olefins: Reaction Scope, Mechanistic Studies, and Guides for the Development of Improved Catalysts” *Acc. Chem. Res.* **2009**, *42*, 585-597.
4. Ceresana. “Market Study: Benzene”; <http://www.ceresana.com/en/market-studies/chemicals/benzene/>
5. U.S. Department of Energy. “New Process for Producing Styrene Cuts Costs, Saves Energy, and Reduces Greenhouse Gas Emissions”; [https://www1.eere.energy.gov/office\\_eere/pdfs/exelus\\_case\\_study.pdf](https://www1.eere.energy.gov/office_eere/pdfs/exelus_case_study.pdf)
6. Perego, C.; Ingallina, P. “Combining alkylation and transalkylation for alkylaromatic production” *Green Chem.* **2004**, *6*, 274–279.
7. Roberts, R. M.; Khalaf, A. A. “Friedel-Crafts Alkylation Chemistry: A Century of Discovery” Marcel Dekker, Inc.: New York, **1984**.

8. Joslin, E. E.; McMullin, C. L.; Gunnoe, T. B.; Cundari, T. R.; Sabat, M.; Myers, W. H. "Coordination Chemistry of 4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2,2,1]heptane: Preparation and Characterization of Ru(II)Complexes" *Inorg.Chem.* **2012**, *51*, 4791-4801.
9. Smith, M. B.; March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure* (6th ed.); Wiley-Interscience: New York, **2007**.
10. Miyaura, N.; Suzuki, A. "Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds" *Chem. Rev.* **1995**, *95*, 2457-2483.
11. Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. "Aryl-Aryl Bond Formation One Century after the Discovery of the Ullmann Reaction" *Chem. Rev.* **2002**, *102*, 1359-1470.
12. Lail, M.; Bell, C. M.; Mei, J.; Conner, D.; Cundari, T. R.; Gunnoe, T. B.; Petersen, J. L. "Experimental and Computational Studies of Ruthenium(II)-Catalyzed Addition of Arene C-H Bonds to Olefins" *Organometallics* **2004**, *23*, 5007-5020.
13. Goj, L. A.; Gunnoe, T. B. "Developments in Catalytic Aromatic C-H Transformations: Promising Tools for Organic Synthesis" *Curr. Org. Chem.* **2005**, *9*, 671-685.
14. Joslin, E. E.; McMullin, C. L.; Gunnoe, T. B.; Cundari, T. R.; Sabat, M.; Myers, W. H. "Catalytic Hydroarylation of Ethylene Using TpRu(L)(NCMe)Ph(L) = 2,6,7-Trioxa-1-phosphabicyclo[2,2,1]heptane): Comparison to



TpRu(L')(NCMe)Ph Systems (L' = CO, PMe<sub>3</sub>, P(pyr)<sub>3</sub>, or P(OCH<sub>2</sub>)<sub>3</sub>CEt)”  
*Organometallics* **3023**, 31 (19), 6851-6860.

15. Ritleng, V.; Sirlin, C.; Pfeffer, M. “Ru-, Rh-, and Pd-Catalyzed C–C Bond Formation Involving C–H Activation and Addition on Unsaturated Substrates: Reactions and Mechanistic Aspects” *Chem. Rev.* **2002**, 102, 1731–1769.
16. McKeown, B. A.; Lee, J. P.; Mei, J. Cundari, T. R.; Gunnoe, T. B. “Transition Metal Mediated C–H Activation and Functionalization: The Role of Poly(pyrazolyl)borate and Poly(pyrazolyl)alkane Ligands” *Eur. J. Inorg. Chem.* **2016**, 15-16, 2296-2311.
17. Tolman, C. A. “Steric Effects of Phosphorus Ligands in Organometallic Chemistry and Homogeneous Catalysis” *Chem. Rev.* **1977**, 77, 313–348.
18. Moloy, K. G.; Petersen, J. L. “N-Pyrrolyl Phosphines: An Unexploited Class of Phosphine Ligands with Exceptional  $\pi$ -Acceptor Character” *J. Am. Chem. Soc.* **1995**, 117, 7696–7710.

## Chapter 2. Reactivity of $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}(\text{Ph})(\text{OTf})]$ and Further Synthesis of Additional Ru(*p*-cymene) Complexes

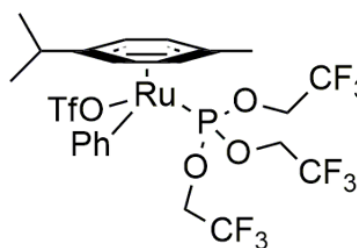
### Introduction: $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}(\text{Ph})(\text{OTf})]$

The work of Ms. Ashley Riner resulted in the synthesis and full characterization of the piano-stool complex  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}(\text{OTf})(\text{Ph})]$  (**1**). Pictured in Figure 1, complex **1** contains a ruthenium (II) metal center and a facially coordinating *p*-cymene ligand.  $\eta^6\text{-}p\text{-Cymene}$  ( $\text{C}_{10}\text{H}_{14}$ ) is an

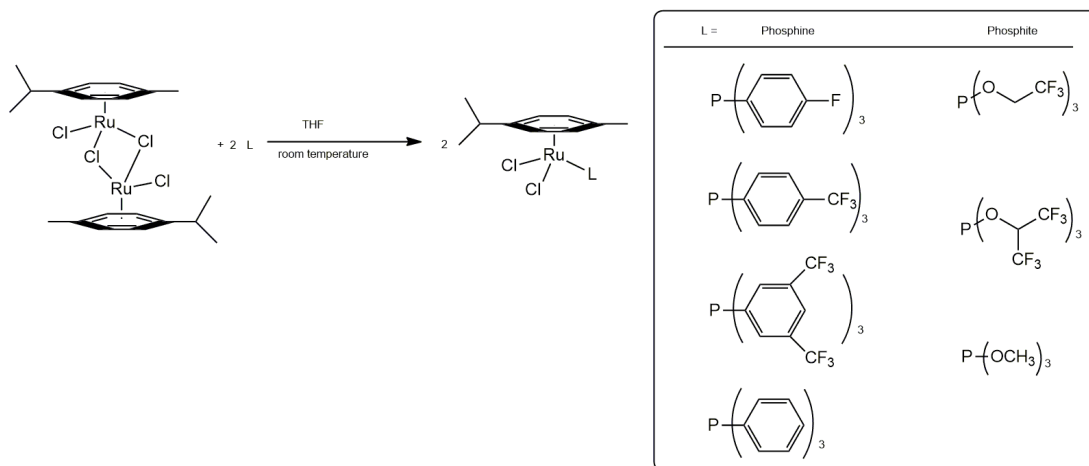
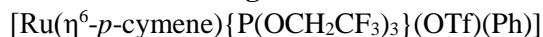
alkylbenzene *para*-substituted with an isopropyl group and a methyl group.

Considered one of the legs in the mixed sandwich piano stool structure, tris(2,2,2-

trifluoroethyl) phosphite is coordinated to the metal center. This specific phosphite was selected after a series of three phosphites and four phosphines were analyzed for their electronic donating ability through HOMO-LUMO

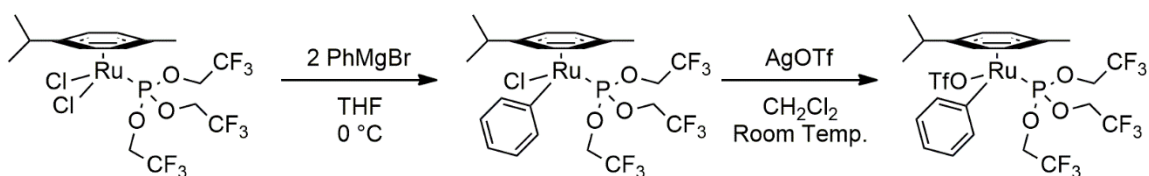


**Figure 1.**



**Scheme 1.** Synthesis of  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{L})(\text{Cl})_2]$  Complexes

gap calculations and their sterics through single-crystal X-ray diffraction; the seven analyzed complexes were of the type  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{L})(\text{Cl})_2]$  ( $\text{L} = \text{Scheme 1}$ ).<sup>1</sup> The phosphite was selected as it has the second largest HUMO-LUMO energy gap of  $8.37 \times 10^4 \text{ cm}^{-1}$  and is the least sterically encumbering. The value calculated for the energy gap is directly indicative of the electronic influence of the respective ligand  $\text{L}$  on the metal center. Ligands with larger field split values represent higher  $\pi$  acceptance, which reflects a less electron-rich metal center. It has been shown that less electron-rich  $\text{Tp}(\text{Ru})$  complexes are more active for ethylene hydrophenylation.<sup>2</sup> Crucial to the architecture of a catalyst, maintaining a low steric hindrance can significantly increase the coordination of olefins to the metal center during catalysis. The coordinated phenyl ligand is required for the catalytic cycle. The triflate ( $\text{OTf}^-$ ) ligand is likely to be the most labile in the complex and could act as a leaving group. If loaded into solution with an olefin and reaction conditions are ideal for catalysis, the triflate ligand would dissociate from the metal center and open a coordination site for an olefin. The synthesis of **1** was optimized (Scheme 2) and fully characterized through multi nuclear NMR and elemental analysis.



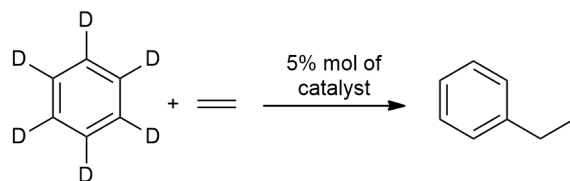
**Scheme 2.** Synthesis of  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}(\text{Ph})(\text{OTf})]$  (**1**)

### Reactivity of $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}(\text{Ph})(\text{OTf})]$

The first experiments regarding the reactivity of complex **1** began with the utilization of valved NMR sample tubes. The sample tubes allowed for the evacuation of  $\text{N}_2$  gas from the tube, enabling the sample to be refilled with a selected gas. In this set of

experiments, the gas of choice was ethylene (C<sub>2</sub>H<sub>4</sub>). The sample tubes were charged with a solution comprised of 5 mol % of **1** and anhydrous benzene-d<sub>6</sub> (C<sub>6</sub>D<sub>6</sub>). The sample tubes were then degassed three times with the freeze-pump-thaw method to be finally pressurized with ethylene gas to 15 psi. Displayed in

Scheme 3, the proposed reaction would produce ethylbenzene. Initial <sup>1</sup>H, <sup>19</sup>F, and <sup>31</sup>P NMR experiments were run to obtain baseline spectra of the complex in a



**Scheme 3.** Proposed reaction of benzene-d<sub>6</sub>, ethylene, and complex **1**

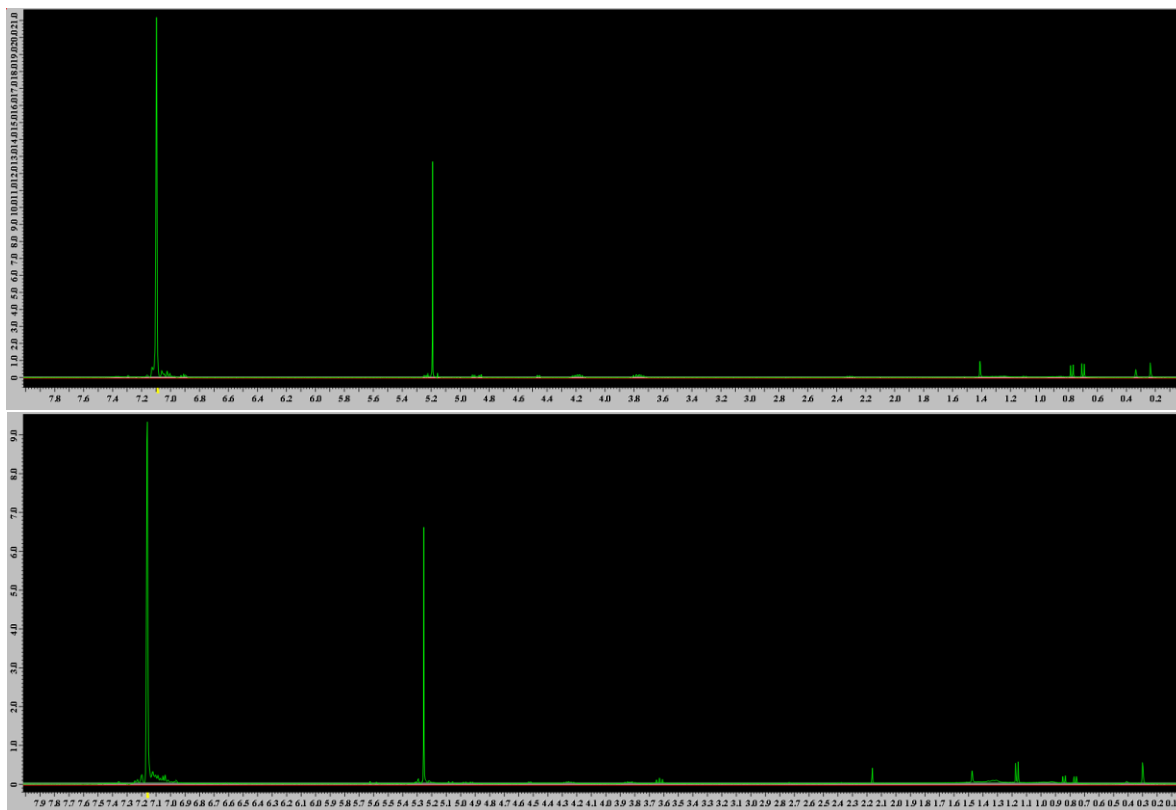
deuterated benzene (not observed through NMR) and ethylene solution before any heat was applied to the tubes. The first set of experiments involved immersing the tubes in an oil bath to be exposed to heat for varying times. The reaction time and temperature data is displayed in Table 1. After being heated, the samples were analyzed through NMR again to observe the formation of any products. The immediate observation was that the integration of the ethylene peak at 5.24 ppm increased relative to the signals of complex **1** (Figure 2), suggesting the decomposition of **1**.

**Table 1.** Experimental Data for Catalysis Utilizing



Aromatic	Olefin (15 psi)	Additive	Time	Temperature	Products
Benzene	Ethylene	None	80 min	90°C	None
Benzene	Ethylene	None	2 hrs	120°C	None
Benzene	Ethylene	None	24 hrs	90°C	None
Benzene	Ethylene	NaBARf	24 hrs	90°C	None
Benzene	Ethylene	NaBARf	24 hrs	65°C	None

A hypothesis was formed that the complex was decomposing at temperatures at or above 60 °C, resulting in a complete dissociation of the ligands from the metal. After the sample tubes had been heated, it was observed that a brown film had formed on the top of



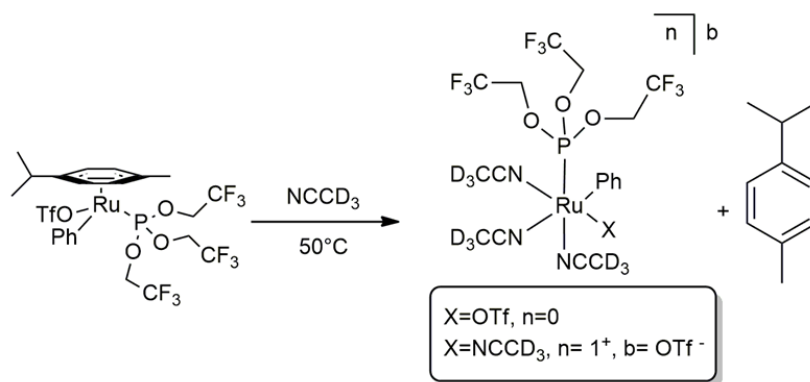
**Figure 2.**  $^1\text{H}$  NMR Spectra of  $[\text{Ru}(p\text{-cymene})\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}(\text{Ph})(\text{OTf})]$  (**1**) and Ethylene gas (15 psi) in Benzene- $d_6$  before (top) and after (bottom) heating to 90 °C for 80 minutes

the originally yellow-gold solution. Under the pretense that the complex's inert character resulted from the lack of expected lability from the triflate ligand, a similar set of experiments was run, except the NMR tubes additionally were charged with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ( $\text{NaBAR}^{\text{F}}$ ). The purpose of including the  $\text{BAR}^{\text{F}}_4^-$  anion was to promote the dissociation of the triflate ligand via irreversible formation of  $\text{NaOTf}$ , as  $\text{BAR}^{\text{F}}_4^-$  will behave as an outer-sphere non-coordinating anion. Two similar ethylene experiments were attempted with the inclusion of  $\text{NaBAR}^{\text{F}}$  into the reaction of ethylene, benzene, and complex **1**. In one experiment, the sample was allowed to heat to

90 °C, while the second reaction was only heated to 60 °C. Through analysis of the resulting NMR spectra, it was concluded that NaBAR<sup>F</sup> did not promote the dissociation of triflate, and catalysis did not occur. Instead, it was observed that a thin brown film formed in the reaction tube, and the integration in the <sup>1</sup>H NMR spectrum revealed the decomposition of **1**.

### Dissociation of $\eta^6$ -*p*-cymene

To understand what was occurring to the complex in the reactions attempting catalysis, complex **1** was loaded into an NMR tube with the solvent acetonitrile-d<sub>3</sub> (NCCD<sub>3</sub>) and monitored through <sup>1</sup>H NMR spectroscopy in between intervals of heating the tube to 50 °C. With no benzene or ethylene present in the sample tube, the direct effect of heat on the complex could be observed in the presence of a coordinating solvent. It was found that after heating the sample to 50 °C for 24 hours, the *p*-cymene ligand dissociated from the metal center as observed by <sup>1</sup>H NMR, and three acetonitrile-d<sub>3</sub> groups likely



**Scheme 4.** Dissociation of *p*-cymene and presumed coordination of acetonitrile-d<sub>3</sub> coordinate to the metal center (Scheme 4) as the phosphite resonance indicated one new complex. This is because the only noticeable shifts in the resonances of complex **1** were of

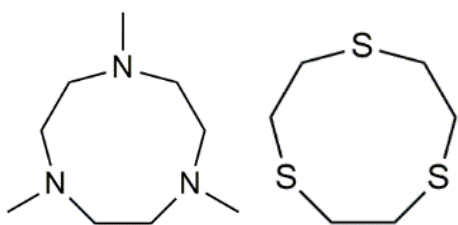
the *p*-cymene complex, and as the acetonitrile- $d_3$  is not visible through  $^1\text{H}$  NMR, it cannot be observed if coordinated to the ruthenium.

With the confirmation of the lability of *p*-cymene, two different directions for further research were considered: to synthesize a ruthenium complex similar to **1** with a different ancillary ligand or replace  $\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}$  in the synthesis of **1** with a different phosphite or phosphine ligand.

### Reactivity of $[\text{Ru}(\text{NCMe})_3\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}(\text{Ph})(\text{OTf})]$ :

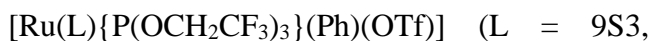
#### Coordination of Ancillary Ligands 9S3 and 9N3<sub>Me</sub>

It was then hypothesized that the coordination of three labile acetonitrile ligands could be utilized for further synthesis by providing coordination sites for a tridentate



**Figure 3.** 1,4,7-trimethyl-1,4,7-triazacyclononane (9N<sub>3Me</sub>) and 1,4,7-trithiacyclononane (9S3)

ancillary ligand: electron rich amine 1,4,7-trimethyl-1,4,7-triazacyclononane (9N<sub>3Me</sub>) and electron poor thioether 1,4,7-trithiacyclononane (9S3) (Figure 3). The proposed complexes would have been of the type



9N<sub>3Me</sub>) (Figure 4). These two ancillary ligands

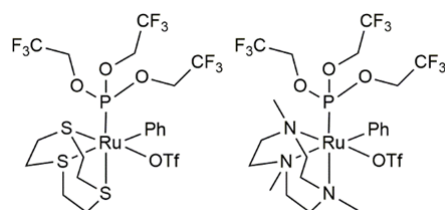
were selected as 9S3 is an electron poor thioether,

and 9N<sub>3Me</sub> is an electron rich amine.<sup>3,4</sup> These

electronic properties could prevent the ancillary

ligand dissociation experienced with *p*-cymene while providing the desired electronic

influence on the metal center.

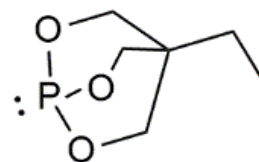


**Figure 4.** Proposed Ru(9S3) and Ru(9N<sub>3Me</sub>) Complexes

A series of reactions between **1** and 9S3 in acetonitrile, which causes the formation of intermediate **2**, were performed at room temperature, 50 °C, and 70 °C. These experiments were monitored through <sup>1</sup>H NMR. In all three reaction conditions, decomposition of **1** occurred, and 9S3 did not coordinate to the metal center. This was clear as the resonances in the <sup>1</sup>H NMR of 9S3 had not shifted relative to their free ligand resonances, and the resonances of complex **1** had drastically decreased in integration. In a reaction with 9N3<sub>Me</sub> set at room temperature overnight, complex **1** was seen to have decomposed. Once again, the integration of the resonances of complex **1** had decreased, and the resonances of 9N3<sub>Me</sub> had not shifted from their free ligand shifts. This suggests that the acetonitrile ligands are not labile as coordination of either ligand proved unsuccessful. The reactions were repeated in toluene with 9S3 heated at 100°C for 24 hours and 9N3<sub>Me</sub> at 60°C for 5 hours in an attempt to bypass acetonitrile coordination. Neither 9S3 or 9N3<sub>Me</sub> successfully coordinated to the metal center.

### Coordination of Caged Phosphite {P(OCH<sub>2</sub>)<sub>3</sub>CEt}

The cone angle of triethyl phosphite is reported to be 109°, and the structurally similar tris(2,2,2-trifluoroethyl) phosphite is ~109°.<sup>6</sup> It was hypothesized that this was sterically hindering the association of ethylene, therefore preventing the disassociation of the triflate anion in complex **1**. Because of this, the ancillary ligand η<sup>6</sup>-*p*-cymene dissociated from the metal center



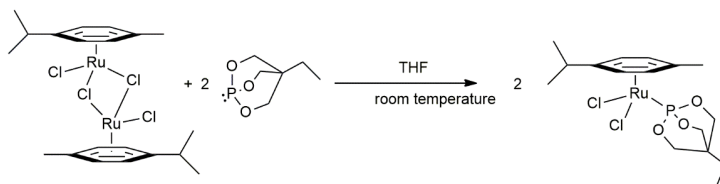
**Figure 5.** {P(OCH<sub>2</sub>)<sub>3</sub>CEt}

before any of the other three coordinated ligands. The phosphite selected to replace the trifluoroethyl phosphite was trimethylolpropane phosphite {P(OCH<sub>2</sub>)<sub>3</sub>CEt}, a caged phosphite (Figure 5). This phosphite has a cone angle of 101°, a difference of 8°.<sup>6</sup> In



addition to the smaller cone angle, this ligand differs in its lack of fluorine atoms. In regards to spectroscopy, the  $^{19}\text{F}$  NMR handle available in **1** from the trifluoroethyl phosphite ligand has been lost as well as the electron withdrawing property of the three trifluoromethyls. However, in previous complexes, the trifluoromethyl groups have also appeared to be the cause of oil products, which are more difficult to work with than solid products.

Similar to the synthesis of complex **1**, the synthesis of  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\{\text{P}(\text{OCH}_2)\text{CEt}\}(\text{Cl})_2]$  (Scheme 5) began with the



**Scheme 5.** Synthesis of  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\{\text{P}(\text{OCH}_2)\text{CEt}\}(\text{Cl})_2]$

splitting of the chloride bridges in  $[\text{Ru}(p\text{-cymene})(\text{Cl})_2]_2$ .<sup>5</sup> The product of this reaction was analyzed through  $^1\text{H}$  and  $^{31}\text{P}$  NMR, and it was confirmed that complex had been produced. In order to produce the complex  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\{\text{P}(\text{OCH}_2)\text{CEt}\}(\text{Ph})(\text{Cl})]$  **2**, the complex  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\{\text{P}(\text{OCH}_2)\text{CEt}\}(\text{Cl})_2]$  reacted with  $\text{PhMgBr}$ . An NMR sample was prepared with complex **2**. Analyzed through  $^1\text{H}$  and  $^{31}\text{P}$  NMR, the formation of complex **2** was confirmed with a yield of 76.6%, and the complex was characterized.

Future characterization work with **2** includes elemental analysis and a single-crystal X-ray crystal structure data for the complex. Along with the characterization of complex **2**, improving the synthesis and yield for the complex would be included in the future work. Complex **2** could display catalytic reactivity. If catalytic activity is not detected, the replacement of the  $\text{Cl}^-$  for a different labile ligand such as acetonitrile could result in a catalyst.

### Conclusions: Future Work with Ru( $\eta^6$ -*p*-cymene) complexes

As complex **1** did not prove to be a viable catalyst, there are three different directions for future work. The first would be to utilize the dissociation of *p*-cymene for association of a different ancillary ligand while avoiding the acetonitrile coordination to ruthenium(II). The second direction would be the synthesis of Ru(*p*-cymene) catalysts that do not contain tris(2,2,2-trifluoroethyl) phosphite. The synthesis of complex **2** requires optimization for a higher product yield, along with experiments that test its catalytic potential and further characterization. The third direction is the utilization of a ruthenium starting material containing an anionic ancillary coordinated to the ruthenium metal center and circumventing the use of Ru(*p*-cymene) starting material. As the neutral ancillary ligand  $\eta^6$ -*p*-cymene is too labile, the inclusion of an anionic ancillary ligand may provide a more stable complex for catalysis.

## Methods

Reactions were carried out in a glovebox with inert N<sub>2</sub> gas environment. Reactions requiring temperature different than ambient conditions were prepared in the glovebox and then performed outside of the glovebox on a Schlenk line. NMR samples were prepared in the glovebox, and experiments were conducted on the JEOL ECX-400 NMR Spectrometer.

## Experimental

*[Ru(η<sup>6</sup>-p-cymene)(P{OCH<sub>2</sub>CF<sub>3</sub>})<sub>3</sub>(Ph)(OTf)] (1)*

A 100 mL Schlenk flask was charged with 0.140 g [Ru(p-cymene){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>}(Cl)<sub>2</sub>] (0.220 mmol) and 20 mL of THF in the inert nitrogen glovebox. The flask was then connected to the Schlenk line. The line was evacuated and opened to N<sub>2</sub>. To the orange solution was added 81.6 mg (0.15 mL, 0.4500 mmol) PhMgBr at ice water conditions, and the mixture was left to stir at room temperature for 15 minutes. It was then allowed to warm to room temperature and stir for 45 minutes. Approximately 2 mL of “wet” THF was added, and the flask was disconnected from the Schlenk line and brought back into the glovebox. The volatiles were removed in vacuo to leave an oil that was then dissolved in CH<sub>2</sub>Cl<sub>2</sub>. This solution was filtered through silica gel, producing a bright yellow liquid. Assuming 100% yield, approximately 1 equivalent of AgOTf was added. The solution was left to stir at room temperature in the dark in the glovebox overnight. The dark yellow solution was filtered through celite and reduced to a minimal volume in vacuo, forming a bright yellow solution. Hexanes were used to precipitate a product, and the solution was reduced to dryness in vacuo, producing a yellow powder (0.115 g, 0.145 mmol, 66.0% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.35-7.61, 6.94 ppm (m, 5H, C<sub>6</sub>H<sub>5</sub>), 5.36-5.59 ppm (q of d, 4H, <sup>3</sup>J<sub>HH</sub> = 5.95 Hz,

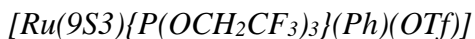
*p*-cym C<sub>6</sub>H<sub>4</sub>), 3.83, 4.36 ppm (d of m, 6H, <sup>3</sup>J<sub>HH</sub> = 225.3 Hz), 2.73 ppm (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.02 ppm (s, 3H, Ar-CH<sub>3</sub>), 1.21 ppm (q, 6H, <sup>3</sup>J<sub>HH</sub> = 6.87 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>): δ -75.1 ppm (-CF<sub>3</sub>), -77.8 ppm (OTf). <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>): δ 133.7 ppm (P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>).

*Catalysis Reaction w/ [Ru(η<sup>6</sup>-p-cymene)(P{OCH<sub>2</sub>CF<sub>3</sub>})<sub>3</sub>(Ph)(OTf)]*

In an inert N<sub>2</sub> environment, a pressurizable NMR tube was charged with 2.6 mg (mmol) and 0.7 mL of Benzene-d<sub>6</sub>. The tube was sealed and attached to the Schlenk line. The tube underwent a freeze-pump-thaw three times: the tube was frozen in liquid nitrogen, the gas in the tube was evacuated, and then the tube was thawed to release more gas bubbles from the solution. After evacuating the tube the final time, it was filled with 15 psi ethylene gas. An initial <sup>1</sup>H NMR spectrum was obtained. The tube was then immersed in a 90°C oil bath for 80 minutes, and then an <sup>1</sup>H NMR spectrum was taken. The spectrum revealed no significant change from the initial spectrum, so the tube was heated at 120°C for 2 hours. Analysis of the <sup>1</sup>H spectrum obtained after the heating revealed decomposition of the complex.

*[Ru(NCMe)<sub>3</sub>{P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>}(Ph)(OTf)]*

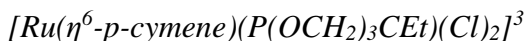
In an inert N<sub>2</sub> environment, a pressure tube was loaded with 48.1 mg (0.0609 mmol) of [Ru(η<sup>6</sup>-*p*-cymene){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>}(Ph)(OTf)] **1** and 30 mL of acetonitrile. This tube was sealed and placed into an oil bath set at 50 °C for one hour. The orange solution was observed to fade into a faint, tan color. An NMR sample was prepared from the solution. Through loss of integration of the complex **1** peaks and the formation of free phosphite and triflate ligand resonances in the <sup>1</sup>H, <sup>19</sup>F, and <sup>31</sup>P, it was revealed that decomposition of complex **1** was occurring, and [Ru(NCMe)<sub>3</sub>{P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>}(Ph)(OTf)] was not isolated.



In an inert N<sub>2</sub> environment, a pressure tube was loaded with 49.1 mg (0.0621 mmol) [Ru( $\eta^6$ -*p*-cymene){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>}(Ph)(OTf)] **1**, ~12 mL of acetonitrile, and 12.3 mg of 9S3 (0.0682 mmol). The tube was sealed and placed into an oil bath set at 50 °C for three hours. An NMR sample was prepared and analyzed. Data revealed the decomposition of complex **1** and formation of free phosphite ligand.



In an inert N<sub>2</sub> environment, a pressure tube was loaded with 48.1 mg (0.0609 mmol) [Ru( $\eta^6$ -*p*-cymene){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>}(Ph)(OTf)] **1**, ~12 mL of acetonitrile, and 3.54 mg of 9N3<sub>Me</sub> (0.0207 mmol). The tube was sealed and placed into an oil bath set at 50 °C for three hours. An NMR sample was prepared and analyzed. Data revealed the decomposition of complex **1** and formation of free phosphite ligand.



In an inert N<sub>2</sub> environment, a round-bottom flask was loaded with a stir bar, 0.2124 g (0.347 mmol) of [Ru( $\eta^6$ -*p*-cymene)(Cl)<sub>2</sub>]<sub>2</sub>, 0.124 g (0.765 mmol, 2.2 eq.) of P(OCH<sub>2</sub>)<sub>3</sub>CEt, and 25 mL of THF. The solution stirred for 3 hours. The solvent was then reduced by vacuum to a minimum volume, and hexanes were added to precipitate an orange solid. This was then filtered through a porous glass frit. An orange product was collected with a yield of 248.5 mg (0.531 mmol, 76.6%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  4.40 (d, 6H, <sup>3</sup>J<sub>HP</sub> = 5.04 Hz, P(OCH<sub>2</sub>)<sub>3</sub>-R), 1.27 (q, 2H, <sup>3</sup>J<sub>HH</sub> = 7.68 Hz, -CCH<sub>2</sub>CH<sub>3</sub>), 0.88 (t, 3H, <sup>3</sup>J<sub>HH</sub> = 7.79 Hz, -CCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  90.0 (s, C<sub>6</sub>H<sub>6</sub>), 89.3 (s,

P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>), 75.5 (s, P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>), 22.1 (s, P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>), 7.3 (s, P(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P (400 MHz, CDCl<sub>3</sub>): δ 111.4 ppm (s, -P(OCH<sub>2</sub>)CEt)

*[Ru(η<sup>6</sup>-p-cymene)(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(Ph)(Cl)](2)*

In an inert N<sub>2</sub> environment, a Schlenk flask was charged with 146.5 mg (0.313 mmol) of [Ru(η<sup>6</sup>-p-cymene)(P(OCH<sub>2</sub>)<sub>3</sub>CEt)(Ph)(OTf)], 20 mL of THF, and a stir bar. The flask was sealed and attached to a Schlenk line. The line was evacuated and backfilled with N<sub>2</sub> gas three times. With a syringe 0.113 g (0.113 mL, 0.623 mmol) of PhMgBr was added to the flask that was submerged in an ice bath. This was allowed in the ice bath conditions for 15 minutes and then at room temperature. The flask was removed from the Schlenk line and returned to the N<sub>2</sub> inert environment of the glovebox. The volatiles of the solution were removed until an oil had formed. This was dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, and this solution was filtered through celite. The filtrate was collected in a round-bottom flask, and hexanes were added to precipitate a product. The solvent was removed, and 43.3 mg (0.0849 mmol, 36.9%) of [Ru(*p*-cymene){P(OCH<sub>2</sub>)<sub>3</sub>CEt}(Ph)(Cl)] were collected. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.82 ppm (m, 5H, C<sub>6</sub>H<sub>5</sub>), 4.40 (d, 6H, <sup>3</sup>J<sub>HP</sub> = 5.04 Hz, P(OCH<sub>2</sub>)<sub>3</sub>-R), 1.27 (q, 2H, <sup>3</sup>J<sub>HH</sub> = 7.68 Hz, -CCH<sub>2</sub>CH<sub>3</sub>), 0.88 (t, 3H, <sup>3</sup>J<sub>HH</sub> = 7.79 Hz, -CCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P (400 MHz, CDCl<sub>3</sub>): δ 123.3 ppm (s, -P(OCH<sub>2</sub>)CEt).

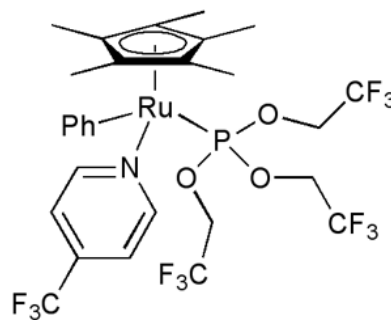
## References

1. Lee, J.P.; Hankins, M.J.; Riner, A. D.; Albu, T. V. “Synthetic, structural, and spectroscopic studies of mixed sandwich Ru(II) complexes involving  $\eta^6$ -*p*-cymene with monodentate fluorine-containing phosphines or phosphites” *J. Coord. Chem.*, **2016**, *69*, 20-38.
2. Joslin, E. E.; McMullin, C. L.; Gunnoe, T. B.; Cundari, T. R.; Sabat, M.; Myers, W. H. “Catalytic Hydroarylation of Ethylene Using TpRu(L)(NCMe)Ph(L= 2,6,7-Trioxa-1-phosphabicyclo[2,2,1]heptane): Comparison to TpRu(L')(NCMe)Ph Systems (L' = CO, PMe<sub>3</sub>, P(pyr)<sub>3</sub>, or P(OCH<sub>2</sub>)<sub>3</sub>CEt)” *Organometallics* **3023**, *31* (19), 6851-6860.
3. Ward, M. D. “The Coordination Chemistry of Macrocyclic Ligands” *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **1990**, *87*, 303-339.
4. Blake, A. J.; Gould, R. O.; Greig, J. A.; Holder, A. J.; Hyde, T. I.; Schroder, M; “Gold Thioether chemistry: synthesis, structure, and redox interconversion of [Au([9]aneS<sub>3</sub>)<sub>2</sub>]<sup>+2+/3+</sup>([9]aneS<sub>3</sub>= 1,4,7-trithiacyclononane)” *J. Chem. Soc., Chem. Commun.* **1989**, *13*, 876-878.
5. Joslin, E. E.; McMullin, C. L.; Gunnoe, T. B.; Cundari, T. R.; Sabat, M.; Myers, W. H. “Coordination Chemistry of 4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2,2,1]heptane: Preparation and Characterization of Ru(II) Complexes” *Inorg. Chem.*, **2012**, *51* (8), 4791–4801.
6. Tolman, C. A. “Steric Effects of Phosphorus Ligands in Organometallic Chemistry and Homogeneous Catalysis” *Chem. Rev.* **1977**, *77*, 313–348.

## Chapter 3: Ruthenium(II) Complexes with the Ancillary Ligand Pentamethylcyclopentadienyl Anion (Cp\*)

### Introduction: Anionic Ruthenium(II) Catalysts

In light of the work done with Ru(*p*-cymene) systems, the goal became to synthesize similar Ru(II) complexes with the anionic ligand pentamethylcyclopentadienyl (Cp\*). The anionic ligand is a more electron-rich system that would prove less labile than *p*-cymene, and *p*-cymene ruthenium complexes are generally utilized in reactions where the *p*-cymene is replaced by a stronger coordinating ligand.<sup>1</sup> The use of anionic ligands as the ancillary ligand in complexes designed for C-H bond activation is of literary precedent; a series of trispyrazolylborate ruthenium (Tp{Ru}) catalysts were synthesized and used in a catalytic cycle for the production of ethylbenzene.<sup>2</sup> The



**Figure 1.** Proposed Complex [Ru(Cp\*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>}(4-(trifluoromethyl)pyridine)(Ph)]

ligands of the proposed catalyst [Ru(Cp\*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>}(4-(trifluoromethyl)pyridine)(Ph)] (Figure 1) can be related structurally to the general structure of the aforementioned Tp(Ru) catalysts.<sup>3</sup> The Cp\* and Tp ligands facially coordinate, consequently directing reactivity to the other half of the octahedral metal center. Both complexes contain labile ligands, i.e. NCMe and 4-(trifluoromethyl)pyridine, that serve as leaving groups which open coordination sites for olefins such as ethylene to coordinate and take part in catalysis.<sup>2</sup> The coordinated phenyls (Ph) are required for their inclusion in the catalytic cycle to produce ethylbenzene. The final ligand in the proposed

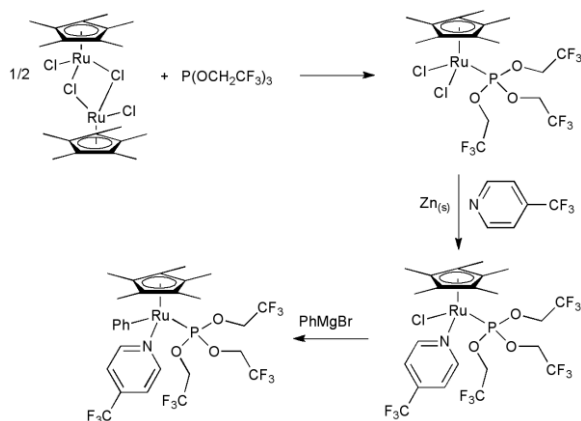


complex, tris(2,2,2-trifluoroethyl) phosphite, is equivalent in role to the numerous L ligands in the Tp(Ru) system, which provide various steric environments for the complex.

### Synthesis of $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}_2(\text{Cl})]$

The synthesis of proposed complex  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}(4\text{-trifluoromethylpyridine})(\text{Ph})]$  begins with the reaction of hydrated ruthenium trichloride with pentamethylcyclopentadiene.<sup>4</sup> The product of this reaction was pentamethylcyclopentadienylruthenium(III) dichloride,  $[\text{Ru}(\text{Cp}^*)(\text{Cl})_2]_2$  (Scheme 1).<sup>4</sup> Each ruthenium metal center formerly assigned a +3 oxidation state, is paramagnetic due to the two unpaired electrons, and exhibits pseudo-octahedral geometry. The purity of  $[\text{Ru}(\text{Cp}^*)(\text{Cl})_2]_2$  was confirmed by

carbon and hydrogen elemental analysis. This geometry results from the  $\text{Cp}^*$  ligand facially coordinating, occupying three coordination sites to the metal center, and imitating an imperfect octahedral geometry with three chloride ions. The splitting of the



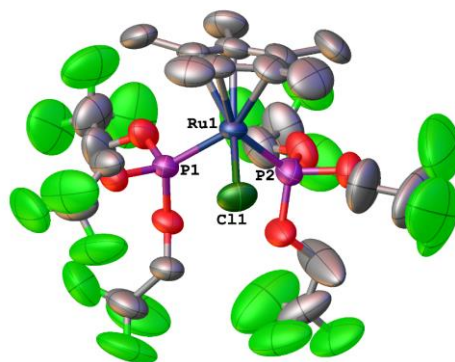
**Scheme 1.** Proposed Synthesis of  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}(\text{py})(\text{Ph})]$

bridging chlorides between the  $\text{Ru}(\text{Cp}^*)$  dimer was performed in a reaction with the ligand tris(2,2,2-trifluoroethyl) phosphite for the expected formation of two equivalents of the complex  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}(\text{Cl})_2]$  (Scheme 1). A yellow solid was obtained and upon analysis through multi-nuclear NMR spectroscopy, signals were present, suggesting that the product was a ruthenium(II) complex (diamagnetic) and not the expected paramagnetic ruthenium(III) product. A hypothesis was formed that two chlorines

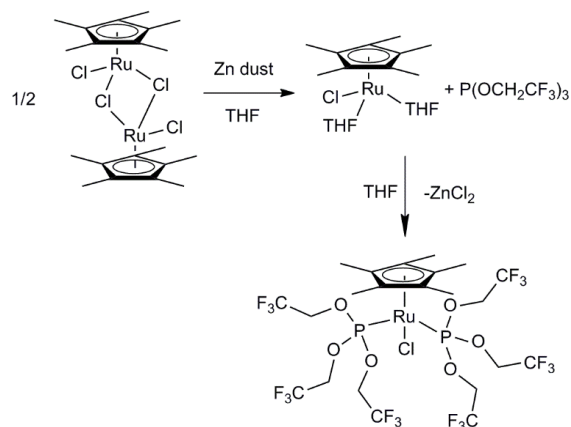
dissociated from each ruthenium and two equivalents of the phosphite ligand had bonded to each ruthenium, resulting in the complex  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}_2(\text{Cl})]$  (**3**). There were two ways to confirm this hypothesis: the first was to look at the integration of the phosphite ligands in the  $^1\text{H}$  NMR. If the hypothesis was correct, the signal for these two phosphite ligands would equate to twelve hydrogens instead of the six hydrogens in the mono-substituted complex. This was confirmed in the NMR with an integration of 12H for the multiplet at 4.33 ppm in  $\text{CDCl}_3$ . The second indicator is a preliminary crystal structure

acquired through single crystal X-ray crystallography. A sample was prepared for single-crystal X-ray diffraction on a Bruker SMART X2S benchtop diffractometer, and the resulting sample data was resolved into a crystal structure

using diffraction software Olex2 (Figure 2). Looking at the crystal structure, there was noticeable disorder with the fluorines in the phosphite ligand. Though we were unable to model the disorder, these data did confirm the coordination of two phosphite ligands to the ruthenium metal center. With knowledge of the high steric interference from the two coordinated phosphites, further synthesis would

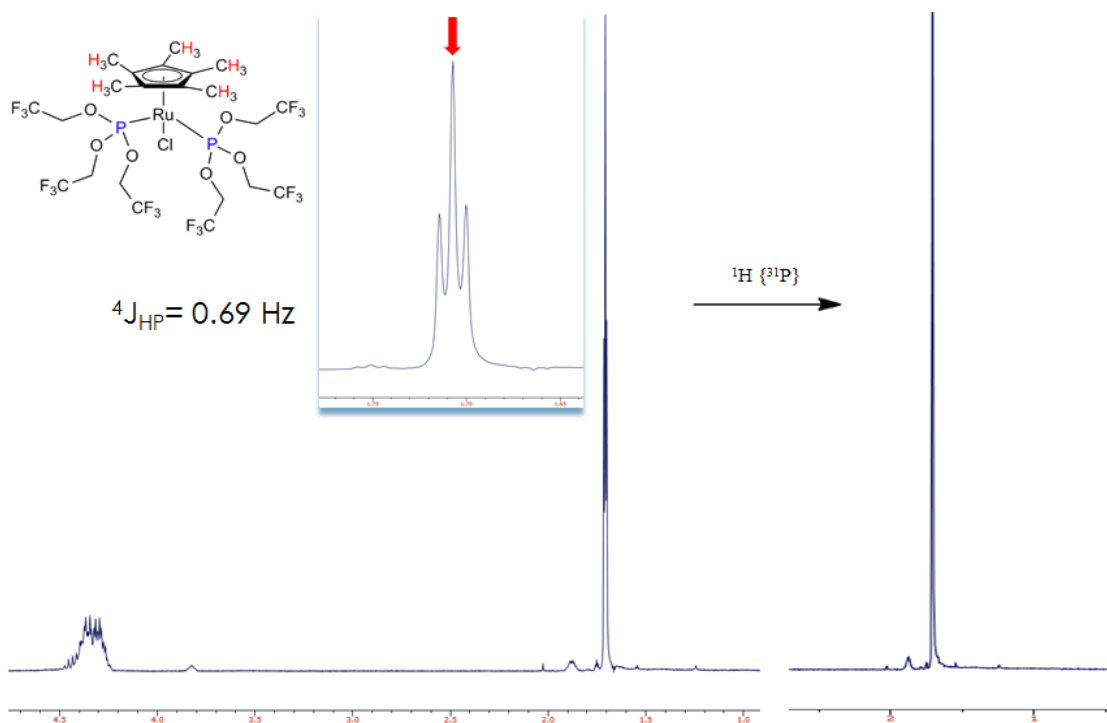


**Figure 2.** Crystal Structure of  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}_2(\text{Cl})]$  (**3**)



**Scheme 2.** Optimized Synthesis of  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}_2(\text{Cl})]$  (**3**)

require a different approach. To improve the yield of  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}_2(\text{Cl})]$  **3**, the initial reduction of the ruthenium metal was facilitated with the addition of Zn dust into the reaction (Scheme 2). This improved the yields of complex **3** to 89%. In the reduction reaction with Zn dust, the  $[\text{Ru}(\text{Cp}^*)(\text{Cl})_2]_2$  solution began with a brown color. As the reduction progressed, a pine green color was observed, followed by an aquamarine color. The reaction then returned to a pine green color, and the solution was then filtered through celite to remove  $\text{ZnCl}_2$  salt.



**Figure 3.**  $^1\text{H} \{^{31}\text{P}\}$  NMR of  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}_2(\text{Cl})]$  (**3**)

The  $^1\text{H}$  NMR spectra of complex **3** revealed a triplet at 1.71 ppm ( $^4J_{\text{HP}} = 0.69$  Hz) (Figure 3). This signal integrated to fifteen hydrogen atoms, characteristic of the fifteen equivalent hydrogen atoms on the methyl groups of the  $\text{Cp}^*$  ligand. The triplet splitting was not typical of the  $\text{Cp}^*$  ligand, and there were not two atoms within a three bond distance that were coupling to the hydrogens. It was suspected that the hydrogens were

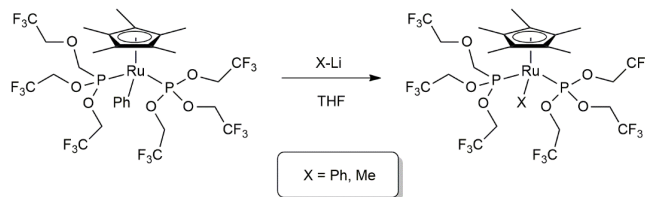
coupling to the two phosphorous nuclei, and this was tested through a phosphorous-decoupled  $^1\text{H}$  NMR experiment (Figure 3). The resulting spectrum was identical to the previous, differing only in the triplet at 1.71 ppm had collapsed to a singlet. This confirmed the proposition. Though hydrogen-phosphorous coupling is not atypical, this find was intriguing especially upon considering the distance between hydrogens and phosphorous nuclei. Similar reported complexes  $[\text{Ru}(\text{Cp}^*)(\text{PEt}_3)_2(\text{Cl})]^5$ ,  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2)_3\text{CEt}\}_2(\text{Cl})]^5$   $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{O}^i\text{Pr})_3\}_2(\text{Cl})]^5$ , and  $[\text{Fe}(\text{Cp}^*)\{\text{P}(\text{OCH}_2)_3\text{CEt}\}_2(\text{Cl})]^6$  have not exhibited the hydrogen-phosphorous coupling from the  $\text{Cp}^*$  methyl hydrogens to the phosphine ligands, while the complex  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{O}-o\text{-MeC}_6\text{H}_4)_3\}_2(\text{Cl})]^5$  did experience four bond H-P coupling. This suggests that the cause of coupling is related to the structure of the coordinated phosphine or phosphite. At this time we do not know if the coupling is through-bond or through-space coupling between the two nuclei.

Reactivity of  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}_2(\text{Cl})]$ :

### Grignard and Organolithium Reagents

With the confirmed and optimized synthesis of complex **3**  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}_2(\text{Cl})]$ , **3** was placed in a reaction with 1.4 molar equivalents of  $\text{PhMgBr}$  similar to the preparation of  $[\text{Ru}(p\text{-cym})\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}(\text{Ph})(\text{Cl})]$ . This was done in order to replace the chlorine with a phenyl, possibly preparing a complex ready to test for use as a catalyst. The recovery of starting material from the attempted reaction was confirmed through  $^1\text{H}$  NMR, revealing that the phenyl ligand did not coordinate to the metal.

The next direction was led by the hypothesis that a Grignard reagent was too weak in replacing the coordinated chlorine. So the organolithium reagents



**Scheme 3.**  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}_2(\text{Cl})]$  Reactions with Organolithium Reagents

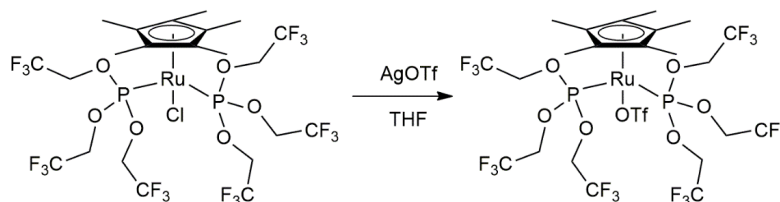
phenyllithium (PhLi) and methyllithium (MeLi) were selected because organolithium reagents could be more effective in removing the chlorine (Scheme 3). This is because of the greater difference in electronegativity between the lithium atom and the carbon atom of the alkyl, which correlates to a higher reactivity. The reaction between **3** and PhLi was performed in expectation of the product  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}_2(\text{Ph})]$ . The reaction was prepared in an inert  $\text{N}_2$  environment, and 2 molar equivalents of PhLi were added to the flask through a syringe to maintain an oxygen- and water-free environment. The product was analyzed through  $^1\text{H}$  NMR, and starting material was recovered. These results suggest either that the phenyl is too bulky to successfully coordinate to the ruthenium due to the two sterically hindering phosphite ligands and/or the Ru-Cl bond is inert to substitution.

The second organolithium reagent MeLi was selected to produce  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}_2(\text{Me})]$ . MeLi was selected because the methyl would not be as sterically hindered as the attempted phenyl ligand. Once the methyl has been coordinated, the complex could be implanted in further synthetic routes to replace the methyl with other ligands that could not previously coordinate. The reaction was prepared in an inert  $\text{N}_2$  environment, and the MeLi (2.1 molar equivalents) was added to the reaction flask via syringe. Analysis of the reaction through  $^1\text{H}$  NMR revealed that starting material was recovered, and the reaction was unsuccessful. This suggests that the Ru-Cl bond is inert.

## Reactivity of $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}_2(\text{Cl})]$ :

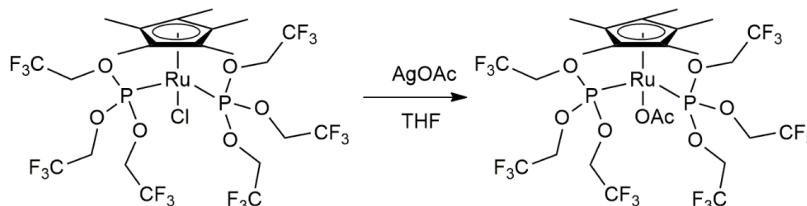
### Silver Salts

The next focus was to explore reactivity between **3** and silver salts. To promote coordination to the ruthenium metal center, it is expected that the silver cation would bond with the chloride ion of complex **3** and precipitate out of solution. The precipitation of silver chloride salt would drive the reaction forward. The silver salts chosen were silver acetate ( $\text{AgOAc}$ ) and silver trifluoromethanesulfonate, triflate ( $\text{OTf}$ ). The successful coordination of triflate in the place of chlorine would allow for the utilization of triflate as a leaving group in a catalytic cycle. In the reaction, 1.1 molar eq. of  $\text{AgOTf}$  was added to a THF (tetrahydrofuran) solution of complex **3** and was allowed to stir overnight (Scheme 4). After filtration through celite to remove silver precipitates, the solvent was removed. Through analyzing the  $^{19}\text{F}$  spectrum in search for a second fluorine resonance from the triflate, it was determined that the triflate did not coordinate to the ruthenium in place of the chlorine, and the complex  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}_2(\text{OTf})]$  was not synthesized and all resonances in the  $^1\text{H}$  NMR confirmed the recovery of the starting complex.



**Scheme 4.** Reaction between **1** and  $\text{AgOTf}$  in THF

In a similar reaction, 1.2 eq. of silver acetate was loaded into a flask to react with **3**. If OAc<sup>-</sup> successfully coordinated as in Scheme 5 then the complex could be used to facilitate acetate-assisted C-H bond activation.<sup>7</sup> Upon inspection of <sup>1</sup>H data, it was observed that acetate had not coordinated to the metal center and starting material had been recovered.



**Scheme 5.** Reaction between **1** and AgOAc in THF

With a more clear understanding of the lability of the chloride ion, or lack thereof, in **3**, it remained unclear if even the phosphite would be labile under higher thermal conditions. In a set of experiments to determine this, two flasks were each loaded with 10 mg of **3** and 5 mL of acetonitrile-d<sub>3</sub> and were heated to 60 °C and 80 °C respectively in an oil bath. After being heated overnight, an NMR sample was prepared from the solution, and a <sup>1</sup>H NMR was run. The data confirmed that the complex in an excess ligand (acetonitrile) environment was not labile, even when heat was applied to help facilitate the dissociation of a phosphite ligand.

#### Conclusion: Future Work with [Ru(Cp\*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(Cl)]

The future of this project lies in two different directions. The first would be the dissociation of a phosphite ligand from the ruthenium metal center in order to synthesize complexes of the type [Ru(Cp\*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>](L)(Cl)]. The removal of a phosphite could allow for the coordination of a leaving group and a phenyl, in order to produce a complex

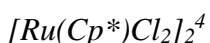
of the type  $[\text{Ru}(\text{Cp}^*)\{\text{P}(\text{OCH}_2\text{CF}_3)_3\}(\text{L})(\text{Ph})]$ . This would cause an overall increase in the lability of the complex and potential catalytic activity in an olefin and benzene rich environment. The second direction would be the coordination of other phosphine and phosphite ligands. Two Ru(II) complexes of the type  $[\text{Ru}(\text{Cp}^*)(\text{NCMe})(\text{PPh}_3)_2]$  and  $[\text{Ru}(\text{Cp}^*)(\text{NCMe})(\text{bpy})]$  (bpy = bipyridine) have been reported as active, cocatalyst-free, and tunable catalysts for metal-catalyzed living radical polymerization.<sup>8</sup> The starting complex in the synthesis of either complex is  $[\text{Ru}(\text{Cp}^*)(\text{PPh}_3)_2(\text{Cl})]$ , which is similar in structure to complex **3**. This offers a promising direction into future work with complex **3** as well as the future design of Ru(Cp\*) complexes.



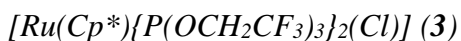
## Methods

Reactions were carried out in a glovebox with inert N<sub>2</sub> gas environment. Reactions requiring temperature different than ambient conditions were prepared in the glovebox and then performed outside of the glovebox on a Schlenk line. NMR samples were prepared in the glovebox, and experiments were conducted on the JEOL ECX-400 NMR Spectrometer.

## Experimental



In an N<sub>2</sub> environment, a 200 mL Schlenk flask was loaded with 3.3015 g of RuCl<sub>3</sub> \* 3 H<sub>2</sub>O (0.0159 mol), 100 mL of MeOH, and a stir bar. Once attached on the Schlenk Line, the line leading to the flask was cleared and backfilled with N<sub>2</sub> gas three times. This line was then opened to the flask. 5.00 g (~5.7 mL, 0.0367 mol) of C<sub>5</sub>Me<sub>5</sub>H (HCp<sup>\*</sup>) were added to the flask. This mixture refluxed for 6 hours, and then cooled at -80 °C for 12 hours. This black solution was then filtered through a porous frit. The light gold-amber precipitate was washed with ~80 mL hexanes. The <sup>1</sup>H NMR revealed impurities, so the filtrate was then washed with 100 mL of pentane. There was a yield of 2.6084 g (4.23 mmol) at 79.9%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.81 ppm (s, 30H, Cp<sup>\*</sup>)



In an N<sub>2</sub> environment, a 100 mL flask was loaded with a stir bar, 0.1076 g (0.1746 mmol) of [Ru(Cp<sup>\*</sup>)Cl<sub>2</sub>]<sub>2</sub>, and 25 mL of THF. Upon the addition of 0.02283 g (0.3492 mmol) of Zn, the reaction was allowed to stir for four hours. The following color changes were exhibited due to the reduction of the Ru: brown to aquamarine to green. After stirring,

the mixture was filtered through celite to remove ZnCl<sub>2</sub> salt. The green filtrate was collected in a 100 mL flask, and 0.252 g (0.169 mL, 0.768 mmol) of tris(2,2,2-triethyl) phosphite were added to the flask to stir overnight. In this time, the solution turned a yellow color. The solvent was reduced in vacuo, and a solid was collected. The yield was 165.9 mg (1.788 mmol, 51.2%). Into a test tube, roughly ten milligrams of the sample were dissolved in 10mL of diethyl ether. The test tube was then covered with punctured aluminum foil and set into a jar to evaporate in a contained system. Once the solvent evaporated, crystals had formed on the sides of the test tube and were retrieved for analysis. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.33 (m, 12H, -CH<sub>2</sub>CF<sub>3</sub>), 1.72 (t, 15H, *J*<sub>HP</sub> = 0.69 Hz, Cp\*). <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>): δ -74.5 ppm (-CF<sub>3</sub>). <sup>31</sup>P NMR (400 MHz, CDCl<sub>3</sub>): δ 154.5 ppm (Ru-P). Anal. Calcd for RuP<sub>2</sub>C<sub>22</sub>H<sub>27</sub>: H, 2.61; C, 26.52. Found: H, 2.43; C, 27.1.

*[Ru(Cp\*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(Cl)] w/ AgOTf*

In an inert N<sub>2</sub> environment, a flask was loaded with a stir bar, 0.0991 g (0.107 mmol) of [Ru(Cp\*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(Cl)] (**3**), 0.0232 g (0.139 mmol) of AgOAc, and 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The flask was sealed and allowed to stir for 4 days. The solution was then filtered through celite, and the solvent was removed from the filtrate. The data revealed the recovery of starting materials.

*[Ru(Cp\*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(Cl)] w/ AgOAc*

In an inert N<sub>2</sub> environment, a flask was loaded with a stir bar, 0.0991 g (0.107 mmol) of [Ru(Cp\*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(Cl)] (**3**), 0.0232 g (0.139 mmol) of AgOAc, and 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The flask was sealed and allowed to stir for 4 days. The solution was then

filtered through celite, and the solvent was removed from the filtrate. The data revealed the recovery of the reactants.

*[Ru(Cp\*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(Cl)] w/ PhMgBr*

In an inert N<sub>2</sub> environment, a flask was loaded with a stir bar, 45.3 mg (0.433 mmol) of [Ru(Cp\*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(Cl)] (**3**), and 20 mL of THF. This flask was sealed, submerged in an ice water bath, and attached to a Schlenk line. The line was evacuated and backfilled with N<sub>2</sub> gas three times. Using a syringe, 17.3 mg (0.0173 mL, 0.0954 mmol) of PhMgBr were added to the flask. This was allowed to stir for 15 minutes at 0°C and then at room temperature for an hour. No color changes were observed. The reaction flask was returned to the glove box, where the solution was filtered through celite. The filtrate was collected in a flask, and the solvent was reduced to a minimum volume. CH<sub>2</sub>Cl<sub>2</sub> was added to the flask to crash out a product. Upon collected a solid on a porous glass frit, an NMR sample was prepared with the product. The sample was analyzed, and it was revealed that only starting material had been recovered.

*[Ru(Cp\*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(Cl)] w/ PhLi*

In an inert N<sub>2</sub> environment, a Schlenk flask was charged with 31.1 mg (0.0335 mmol) of [Ru(Cp\*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(Cl)] (**3**), a stir bar, and 15 mL of THF. The flask was sealed and attached to the Schlenk Line. The line was evacuated and backfilled with N<sub>2</sub> gas three times, and then the flask was opened to the line in an N<sub>2</sub> environment. The flask was placed in an ice bath, and with a syringe, 2.82 mg (0.07 mL, 0.162 mmol) of PhLi were added to the flask. This solution was allowed to stir overnight. The flask was then return to the N<sub>2</sub> environment of a glovebox, and the solvent was reduced in vacuo to give an oil.

A crude NMR sample was prepared with the oil, and upon analysis, the data revealed that multiple products have been formed along with the recovery of starting material.

*[Ru(Cp\*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>}<sub>2</sub>(Cl)] w/ MeLi*

In an inert N<sub>2</sub> environment, a Schlenk flask was charged with 35.6 mg (0.0384 mmol) of [Ru(Cp\*){P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>}<sub>2</sub>(Cl)] (**3**), a stir bar, and 15 mL of THF. The flask was sealed and attached to the Schlenk Line. The line was evacuated and backfilled with N<sub>2</sub> gas three times, and then the flask was opened to the line in an N<sub>2</sub> environment. The flask was placed in an ice bath, and with a syringe, 13.6 mg (0.09 mL, 0.162 mmol) of PhLi were added to the flask. This solution was allowed to stir overnight. The flask was then return to the N<sub>2</sub> environment of a glovebox, and the solvent was reduced in vacuo to give an oil. A crude NMR sample was prepared with the oil, and upon analysis, the data revealed the recovery of starting material.

## References

1. Bennett, M. A.; Huang, T. N.; Matheson, T. W.; Smith, A. K. (1982). "( $\eta^6$ -Hexamethylbenzene)ruthenium Complexes". *Inorganic Syntheses*: John Wiley & Sons, Inc.: Hoboken, NJ, 1982, 74–78.
2. McKeown, B. A.; Lee, J. P.; Mei, J.; Cundari, T. R.; Gunnoe, T. B. "Transition Metal Mediated C–H Activation and Functionalization: The Role of Poly(pyrazolyl)borate and Poly(pyrazolyl)alkane Ligands" *Eur. J. Inorg. Chem.* **2016**, 15-16, 2296–2311.
3. Joslin, E. E.; McMullin, C. L.; Gunnoe, T. B.; Cundari, T. R.; Sabat, M.; Myers, W. H. "Catalytic Hydroarylation of Ethylene Using  $\text{TpRu(L)(NCMe)Ph}$  ( $L = 2,6,7$ -Trioxa-1-phosphabicyclo[2,2,1]heptane): Comparison to  $\text{TpRu(L')}(NCMe)Ph$  Systems ( $L' = \text{CO}$ ,  $\text{PMe}_3$ ,  $\text{P}(\text{pyr})_3$ , or  $\text{P}(\text{OCH}_2)_3\text{CEt}$ )" *Organometallics* **3023**, 31 (19), 6851-6860.
4. Koelle, U.; Kossakowski, J. "Di- $\mu$ -Chloro-Bis[( $\eta^5$ -Pentamethylcyclopentadienyl)Chlororuthenium(III)],  $[\text{Cp}^*\text{RuCl}_2]_2$  and Di- $\mu$ -methoxo-Bis( $\eta^5$ -Pentamethylcyclopentadienyl)diruthenium(II),  $[\text{Cp}^*\text{RuOMe}]_2$ " *Inorg. Synth.* **1992**, 29, 225-228.
5. Serron, S. A.; Luo, L.; Stevens, E. D.; Nolan, S. P.; Jones, N. L.; Fagan, P. J. "Organoruthenium Thermochemistry. Enthalpies of Reaction of  $\text{Cp}'\text{Ru}(\text{COD})\text{Cl}$  ( $\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$  and  $\eta^5\text{-C}_5\text{Me}_5$ ) with Tertiary Phosphite Ligands" *Organometallics* **1996**, 15, 5209-5215.
6. Mei, J.; Pardue, D. B.; Kalman, S. E.; Gunnoe, T. B.; Cundari, T. R.; Sabat, M. "Oxygen Atom Insertion into Iron(II) Phenyl and Methyl Bonds: A Key Step for Catalytic Hydrocarbon Functionalization" *Organometallics* **2014**, 33, 5597-5605.

7. Maleckis, A.; Kampf, J. W.; Sanford, M. S. "A Detailed Study of Acetate-Assisted C-H Activation at Palladium(IV) Centers" *J. Am. Chem. Soc.* **2013**, *135*, 6618-6625.
8. Fujimura, K.; Ouchi, M.; Tsujita, J.; Sawamoto, M.; "Cationic Cp\*-Ruthenium Catalysts for Metal-Catalyzed Living Radical Polymerization: Cocatalyst-Independent Catalysis Tuned by Counteranion" *Macromolecules* **2016**, *49*, 2962-2970.