

Marquette University
e-Publications@Marquette

Master's Theses (2009 -)

Dissertations, Theses, and Professional Projects

Synthesis and Reactions of a Tungsten Dioxo Complex

Deborah Bryant
Marquette University

Recommended Citation

Bryant, Deborah, "Synthesis and Reactions of a Tungsten Dioxo Complex" (2010). *Master's Theses (2009 -)*. Paper 57.
http://epublications.marquette.edu/theses_open/57

SYNTHESIS AND REACTIONS OF A
TUNGSTEN DIOXO COMPLEX

by

Deborah M. Bryant, BS

A Thesis Submitted to the Faculty of the Graduate School,
Marquette University,
in Partial Fulfillment of the Requirements for the
Degree of Master of Science

Milwaukee, Wisconsin

August 2010

ABSTRACT
SYNTHESIS AND REACTIONS OF A
TUNGSTEN DIOXO COMPLEX

Deborah M. Bryant, BS

Marquette University, 2010

Metal dioxo complexes are largely known for their ability to epoxidize olefins. The importance of these reactions is reflected in the patents for the ARCO and Halcon processes from the late 1960's. It is very difficult to find literature that shows other indications for metal dioxo complexes.

Catalytic olefin dimerization has become significant in the realm of green chemistry for "atom economical" reactions. Many transition metals have been examined as catalysts for olefin dimerization, but the largest volume of work has been performed using group 8 transition metals, particularly nickel, palladium and platinum. This is especially true for the specific case of styrene dimerization.

Herein, we wish to report the synthesis and X-ray crystal structure for $\text{Cp}^*\text{W}(=\text{O})_2\text{CH}_3$ (**1**), as well as the X-ray crystal structure for $\text{Cp}^*\text{W}(\text{CO})_3\text{CH}_3$ (**2**). The tungsten dioxo complex (**1**) was found to have high selectivity for the dimerization of some *para*-substituted styrenes, yielding the desired *trans*-1,3-diaryl-1-butene products. We also wish to report the X-ray crystal structure of *trans*-1,3-di-(4-bromophenyl)-1-butene which helped to confirm the structure of our products.

ACKNOWLEDGEMENTS

Deborah M. Bryant, BS

All laboratory work was performed in the Department of Chemistry, at Marquette University under the direction of Dr. Chae S. Yi. I would like to sincerely thank Dr. Yi for all of his guidance, patience and encouragement. I would like to thank Dr. William A. Donaldson and Dr. Mark G. Steinmetz for their service on my thesis committee. I would also like to thank Dr. Sergey Lindeman for providing the crystal structures published in this thesis. I am very thankful to all of the graduate students and post-docs that have helped me through this experience, as well.

I would like to extend sincere gratitude to all of my management and coworkers at Abbott Laboratories. This work could not have been achieved without the schedule flexibility they allowed. I would like to personally thank everyone (friends, family, coworkers, etc.) who gave me words of encouragement when I needed them. I would like to acknowledge the Marquette University Graduate School for granting me the extensions I needed to complete this work. Finally, I would like to thank Abbott Laboratories and Marquette University for their financial support.

TABLE OF CONTENTS

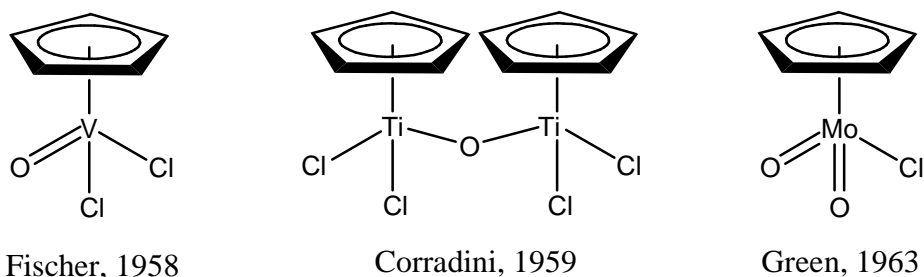
ACKNOWLEDGMENTS	i
TABLE OF CONTENTS	ii
CHAPTER	
I. INTRODUCTION	
A. Catalytic Olefin Epoxidation	1
B. Catalytic Olefin Dimerization	9
C. Catalytic Olefin Codimerization/Cotrimerization	14
II. RESULTS AND DISCUSSION	
A. Research Plan	23
B. Synthesis and Characterization of Cp*W(CO) ₃ CH ₃	24
C. Synthesis and Characterization of Cp*W(=O) ₂ CH ₃	26
D. Catalytic Activity Study of Cp*W(=O) ₂ CH ₃ for Dimerization of <i>Para</i> -Substituted Styrenes	30
E. Proposed Reaction Mechanisms	38
F. Attempted Codimerization of <i>Para</i> -Substituted Styrenes	44
G. Conclusions	46
III. FUTURE RESEARCH	47
IV. EXPERIMENTAL SECTION	49
V. REFERENCES	64
VI. LIST OF SYNTEHSIZED COMPOUNDS	70

I. INTRODUCTION

A. Catalytic Olefin Epoxidation

Metal oxo and dioxo complexes have been studied by many research groups and are largely known for their ability to epoxidize olefins.¹ Some of the first organometallic oxides (shown in Figure 1) were reported in the late 1950's and early 1960's by Fischer,^{2a} Corradini,^{2b} and Green.^{2c} The importance of these metal oxo complexes is reflected in the patents for the ARCO and Halcon processes from the late 1960's.³

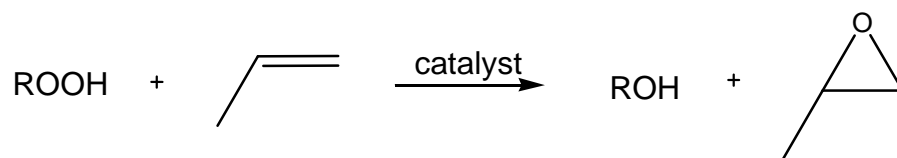
Figure 1. First reported organometallic oxides.



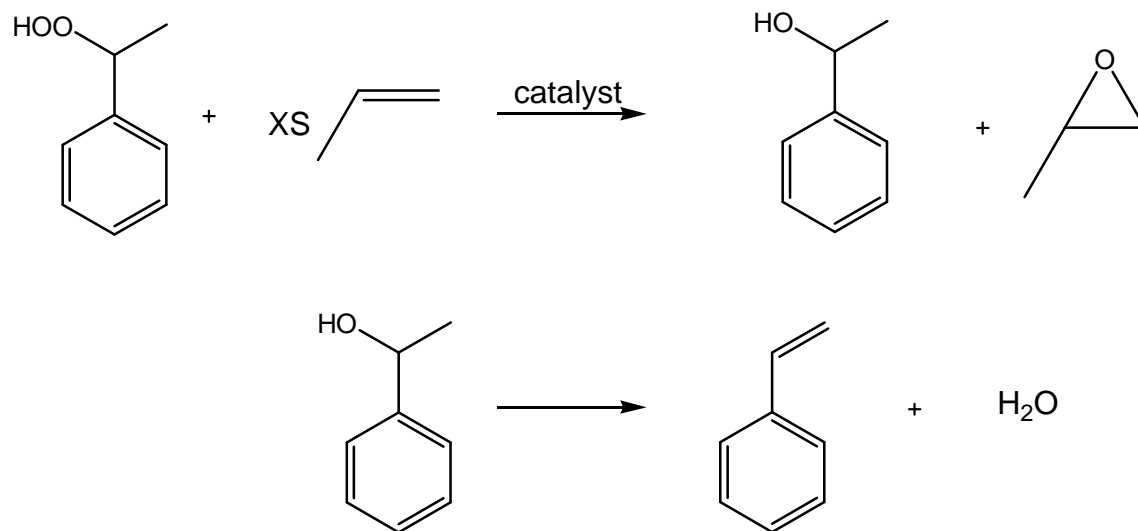
The Halcon process (Scheme 1) for the epoxidation of propylene has received a significant amount of attention in the last 40 years due to its potential for industrially useful co-products by careful selection of the hydroperoxide.^{1g, 4} The first example is the co-production of styrene by using ethylbenzene hydroperoxide (Scheme 2).⁴ The methyl benzyl alcohol by-product is dehydrated to yield styrene. The second, and most significant, example is the co-production of *tert*-butyl alcohol (TBA) by *tert*-butyl hydroperoxide (TBHP) (Scheme 3) in the presence of d^0 metal complexes (such as

Mo(VI) and W(VI) due to the applications of the TBA by-product as a gasoline octane booster.^{1g, 4}

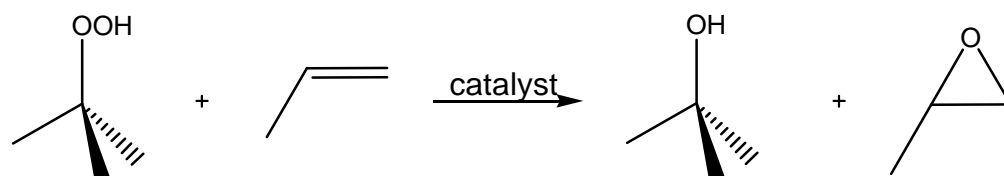
Scheme 1.



Scheme 2.

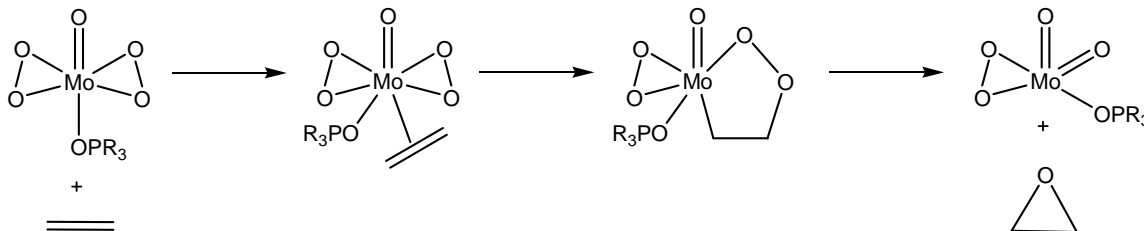


Scheme 3.

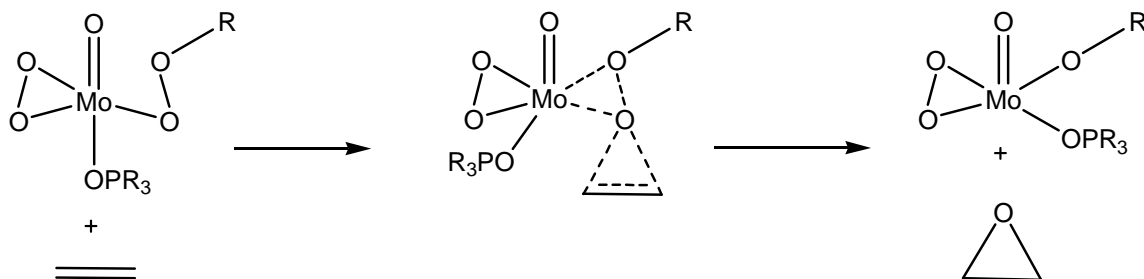


Many high valent transition metal compounds of V(V),^{1g} Cr(VI),^{1h} Mo(VI),^{1b-h} W(VI),^{1b, c, e} and Re(VII)^{1a, d} have been shown to be effective catalysts for epoxidation reactions when combined with organic peroxides such as H₂O₂ and *t*BuOOH. Of these, the most widely studied appear to be molybdenum and tungsten oxides. Despite the amount of study on this reaction since the ARCO/Halcon processes, the actual mechanism for these reactions has not been elucidated. Several theoretical and mechanistic studies have been presented, but there is still much debate over which of the two main mechanisms, proposed by Mimoun⁵ and Sharpless,⁶ is more accurate.⁷

In 1970, Mimoun proposed a mechanism for catalytic epoxidation based on the stoichiometric reaction of molybdenum-peroxo complexes such as Mo(=O)(O₂)₂(OP(NMe₂)₃) with olefins to yield epoxides (Scheme 4).⁶ This led to the belief that metal peroxo compounds could be the intermediates responsible for oxygen transfer in catalytic reactions.^{1f} The first step is coordination of the olefin to the metal center. Next a five-membered metallacycle is formed, followed by formation of the epoxide and a dioxo-peroxo complex.⁸ Mimoun observed that a higher concentration of additional donor ligands inhibits epoxidation. This observation seems to support the initial coordination of the olefin, because additional ligands could block a free coordination site.^{6, 8} Metallacycles are known to exist for late transition metals,⁹ so the second step of the mechanism is not unreasonable.

Scheme 4.

Sharpless studied this mechanism by performing a labeling study by reacting $\text{Mo}(=^{18}\text{O})(\text{O}_2)_2(\text{OP}(\text{NMe}_2)_3)$ with *trans*-cyclododecene.⁶ The results of his study showed that none of the labeled oxygen was incorporated into the epoxide, indicating that it comes exclusively from the peroxo ligands. Initially, this seemed to support the Mimoun mechanism. However, further studies indicated a more concerted mechanism as shown in Scheme 5,^{6, 8, 10} where an intact alkyl hydroperoxide is responsible for the catalytic epoxidation rather than the molybdenum peroxo compound.

Scheme 5.

The epoxidation mechanism remains unclear. Despite that fact, many groups have studied several elements of catalytic epoxidation using high valent metallic oxides such as Mo(VI) and W(VI). One of the elements that these groups have focused on is

increased use of H₂O₂ as the oxidant due to its “green” nature. When H₂O₂ is used, the byproduct is water.^{1b} A second element is developing systems that give higher yield of the desired epoxides when TBHP is used as the oxidant due to the value of its by-product (TBA), as previously mentioned. Another element is more facile synthesis of the catalytic species or synthesis of more stable catalytic species. Metal oxo complexes are known to be difficult to prepare and are not always stable for long periods of time. As would be expected in the course of these studies, there is always some effort to shed light on the reaction mechanism.

Kühn *et al.* performed a series of studies on molybdenum (VI) dioxo compounds of the general formula Mo(=O)₂X₂L₂ where X is Cl, CH₃ or CH₂CH₃, and L₂ is a bidentate ligand.¹¹ Each of the molybdenum complexes was examined as a catalyst precursor in epoxidation of *cis*-cyclooctene with TBHP, and they were all shown to have moderate to high activity. However, when the same tungsten (VI) dioxo compounds were evaluated under similar conditions, the reactivity was noted to be much slower, as shown in Table 1.¹² The major noted benefit of the tungsten complexes is that they appear to be much more stable than their molybdenum counterparts and will continue reacting until almost 100% epoxidation has occurred.

Table 1. Epoxidation of Cyclooctene in the Presence of TBHP.

Metal Complex	M = Mo	M = W
	%epoxidation (reaction time, temp.)	%epoxidation (reaction time, temp.)
M(=O) ₂ Cl ₂ (CYDAB)	20 (4 h, 55 °C)	4 (6 h, 55 °C)
M(=O) ₂ Cl ₂ (BPP)	60 (4 h, 55 °C)	12 (6 h, 70 °C)
M(=O) ₂ Cl ₂ (<i>t</i> Bubipy)	55 (4 h, 55 °C)	19 (6 h, 70 °C)
M(=O) ₂ (Me) ₂ (<i>t</i> Bubipy)	55 (4 h, 55 °C)	30 (6 h, 90 °C)

Luck performed similar experiments with metal-dioxo dichloro species of $M(=O)_2Cl_2(OPMePh_2)_2$ and $M(=O)_2Cl_2dppmO_2$, where $M = Mo$ or W , using TBHP or H_2O_2 as the oxidant for the epoxidation of *cis*-cyclooctene.^{1b} Luck's data, as shown in Table 2, supported the reduced activity noted by Kühn of the tungsten complexes when TBHP was used. However, Luck went further to demonstrate that when H_2O_2 is used, the activity of the molybdenum complexes suffers while the tungsten complexes give >90% epoxide yield after only 6 hours. The combined results of these experiments demonstrates that Mo(VI) complexes are much more effective for Halcon type processes where TBHP is employed and W(VI) complexes can be a much "greener" alternative where H_2O_2 is the desired oxidant.

Table 2. Comparison of Metal Center vs. Oxidant Performed by Luck.

Metal Complex	% Epoxidation After 6 h.	
	TBHP, 55 °C	H_2O_2 , 70 °C
$MoCl_2(=O)_2(OPMePh_2)_2$	100	43
$MoCl_2(=O)_2dppmO_2$	63	26
$WCl_2(=O)_2(OPMePh_2)_2$	30	90
$WCl_2(=O)_2dppmO_2$	22	98

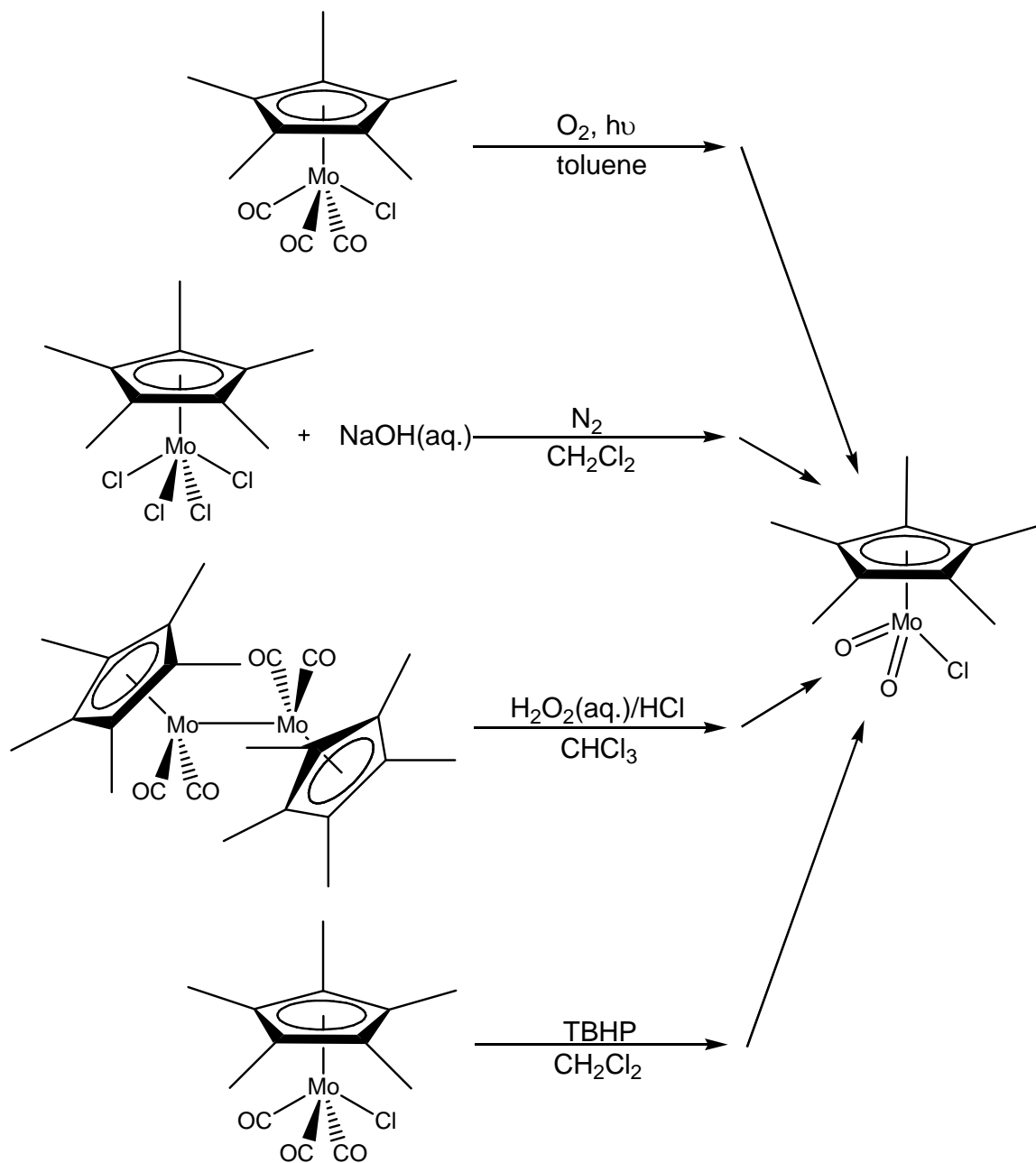
Soluble transition metal-oxo species are often difficult to prepare. Therefore, much attention has been focused on improved synthetic schemes (Scheme 6). In 1991, Trost and Bergman reported the synthesis of $Cp^*Mo(=O)_2Cl$ in 61% yield by irradiating a toluene solution of the carbonyl precursor, $Cp^*Mo(CO)_3Cl$, under an oxygen purge for 2 h.^{1f} Rau later reported the synthesis by reacting Cp^*MoCl_4 with aqueous NaOH in the presence of air. This reaction was found to be sensitive to reaction time and excess base

which would lead to formation of the dimeric product $[\text{Cp}^*\text{MoO}_2]_2\text{O}$.¹³ In 1994, Bottomley reported high yields (86%) by oxidizing $[\text{Cp}^*\text{Mo}(\text{CO})_2]_2$ with 30% aq. H_2O_2 followed by addition of HCl.¹⁴ Recently, a more general method has been reported by Kühn, Romão, *et al.* for the reaction of $\text{Cp}'\text{Mo}(\text{CO})_3\text{Cl}$ ($\text{Cp}' = \text{Cp}, \text{Cp}^*, \text{C}_5\text{Bz}_5$) with TBHP.¹⁵ The resulting dioxo complexes were formed in moderate yields (55-75%), but the authors consider this a better route since it is more general and accommodates different substituents on the Cp ring.^{1d, 15}

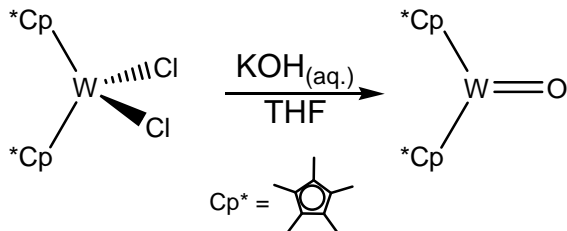
It has been noted in the literature that metal oxo compounds can be highly reactive and are not always very stable at ambient conditions.^{14, 15, 16} Bercaw reported the preparation of the highly reactive $\text{Cp}^*_2\text{W}=\text{O}$ from the more stable $\text{Cp}^*_2\text{WCl}_2$ using aqueous KOH (Scheme 7).^{16a} A few years later, he reported preparation of the closely related $\text{Cp}^*_2\text{Ta}(=\text{O})\text{Cl}$ and $\text{Cp}^*_2\text{Ta}(=\text{O})\text{H}$ compounds via $\text{Cp}^*_2\text{TaCl}(\text{THF})$ starting from $\text{Cp}^*_2\text{TaCl}_2$ (Scheme 8).^{16b}

Since dioxo complexes were recently synthesized from their carbonyl precursors using TBHP,¹⁵ and TBHP is commonly used as the oxidant in olefin epoxidation reactions, Kühn *et al.* recently evaluated the use of the metal carbonyl precursors in olefin epoxidation (Scheme 9).¹⁷ They found that the carbonyl precursors were just as active as the dioxo complexes. Since the carbonyl precursors are much more stable than their dioxo analogues, they are ideal for long term storage.^{17a}

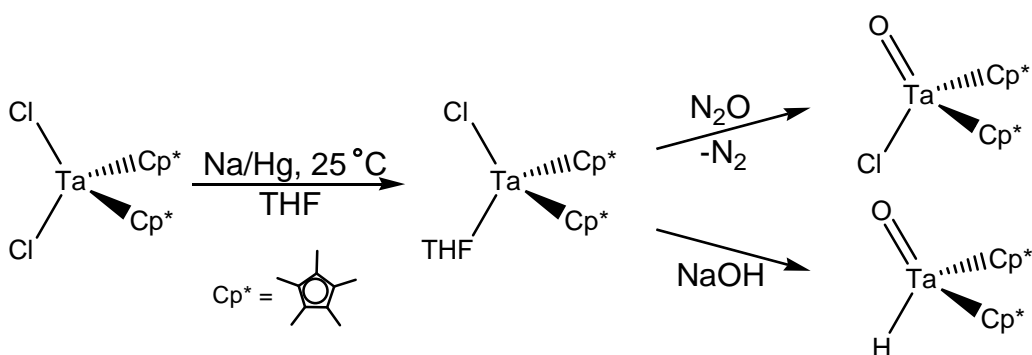
Scheme 6.



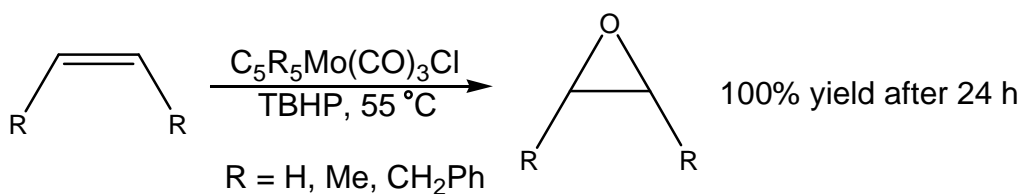
Scheme 7.



Scheme 8.



Scheme 9.



B. Catalytic Olefin Dimerization

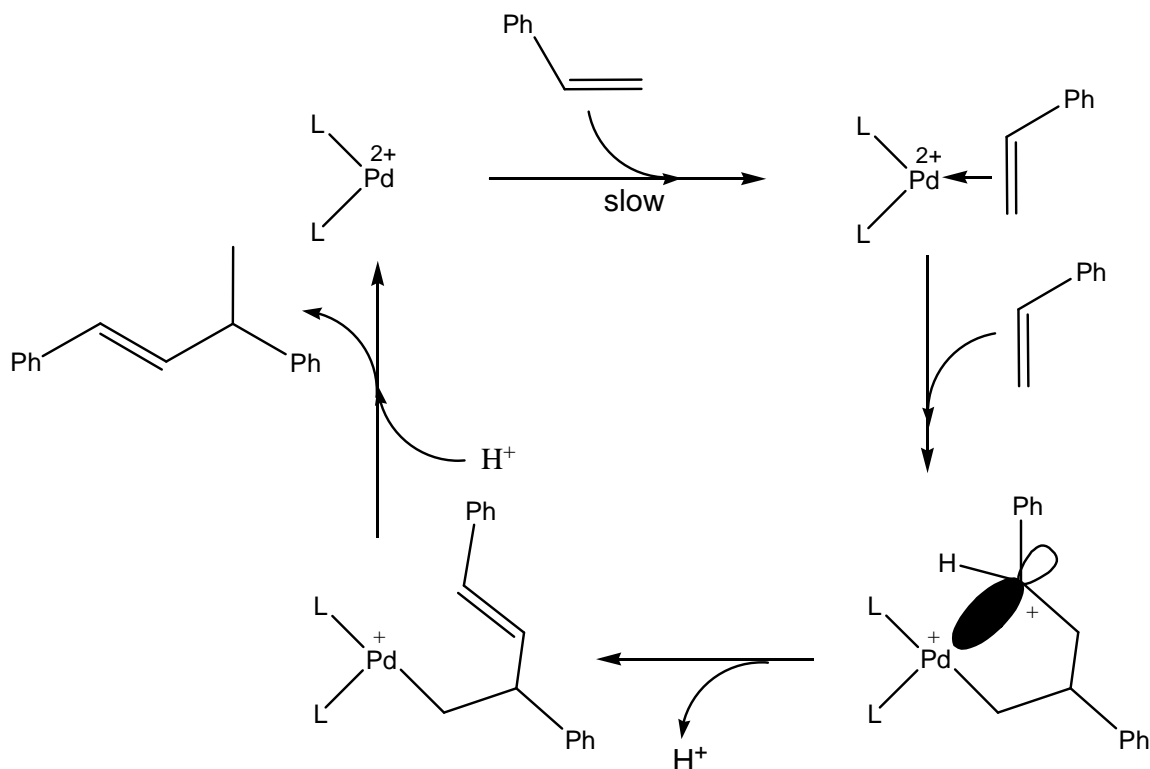
Methods of olefin dimerization have become significant reactions in the realm of green chemistry. In theory, all atoms from the starting materials are reincorporated into the final product and there are no byproducts. “Atom economy” is a term started by Trost,¹⁸ and used by other groups, to describe these types of reactions. Catalytic olefin

dimerization by transition metals was significantly studied through the 1960's, and then interest seemed to be minimal through the next couple of decades, but a renewed interest in this topic appeared in the late 1990's.

While many transition metals have been examined as catalysts for olefin dimerization,¹⁹ by far, the largest volume of work has been performed using group 8 transition metals,²⁰ particularly nickel, palladium and platinum.²¹ This is especially true for the specific case of styrene dimerization.^{22, 23}

The Sen group spent a period of about 12 years examining a series of electrophilic Pd(II) compounds and their activity in styrene dimerization.²² Their reactions proceeded at reasonable temperatures (25 °C to 45 °C) with greater than 90% yield of 1,3-diphenyl-1-butene.^{22d, g} They proposed a cationic mechanism (Scheme 10) where the carbocation intermediate is stabilized by electron density from a Pd(II) d-orbital.^{22h} They proposed that, since the carbocation is stabilized, it is no longer susceptible to electrophilic attack on the γ -phenyl group to form a cyclic indan, or an olefin to form a higher oligomer. Strongly donating ligands, such as pyridine or tertiary phosphines, were shown to aid styrene dimerization^{22d, g} by increasing the ability of the palladium center to donate electron density to the carbocation, while weaker ligands, such as CH₃CN demonstrated styrene polymerization.^{22a, b, c}

Scheme 10.

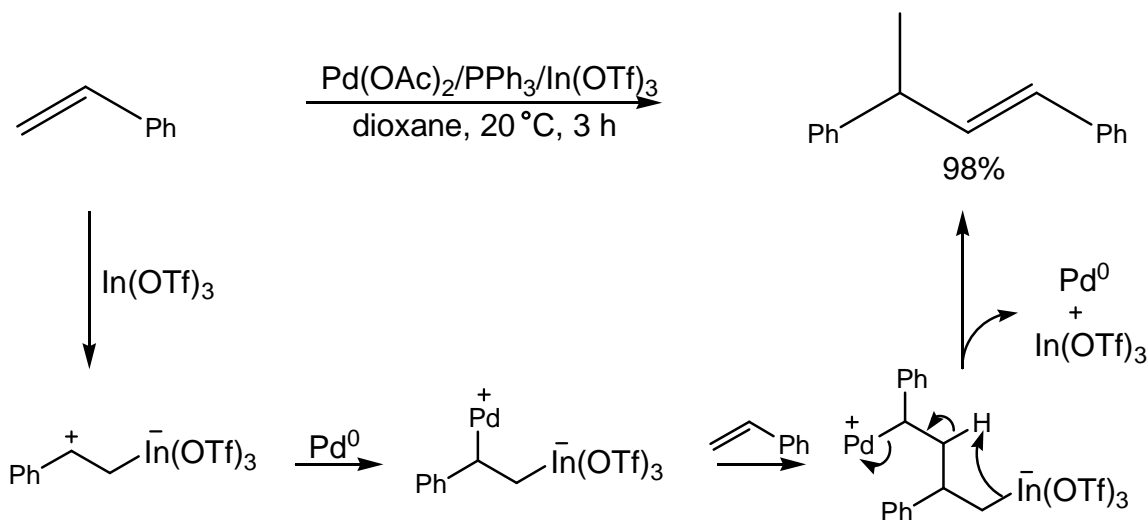


Shirakawa *et al.* found a palladium-indium triflate catalyst that was much more active for styrene dimerization than the previously used cationic palladium (II) catalysts.^{23a} The reaction (outlined in Scheme 11) uses $Pd(OAc)_2/PPh_3/In(OTf)_3$ in a 1:1:5 ratio as the catalyst. 1,3-Diphenyl-1-butene is obtained in 98% isolated yield after 3 h at 20 °C.

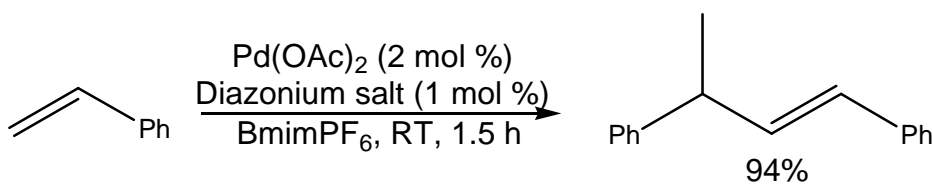
Shortly thereafter, Kabalka *et al.* reported the dimerization of styrene using $Pd(OAc)_2$ with a small amount of diazonium salt (*p*-nitro-phenyldiazonium tetrafluoroborate) in ionic solvent ($BmimPF_6$) (Scheme 12).^{23b} The reaction proceeded at room temperature and yielded 94% of (E)-1,3-diphenyl-1-butene after just 1.5 h. The mechanism of this reaction remains unclear since control reactions without the diazonium

salt yielded no traceable dimer product. However, they have ruled out a free radical mechanism since no dimerization product is formed when AIBN is used in place of the diazonium salt.

Scheme 11.



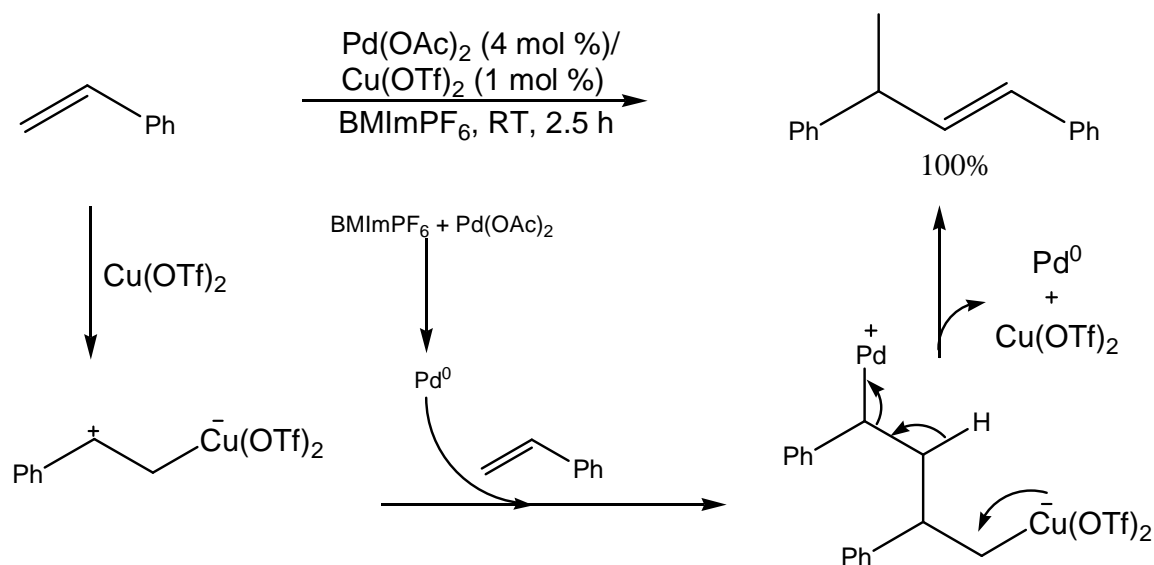
Scheme 12.



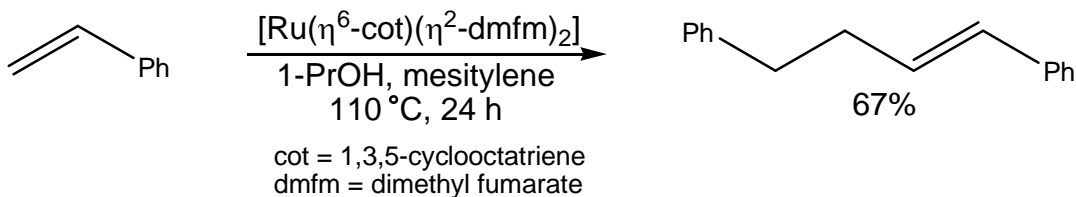
Lai *et al.* also evaluated styrene dimerization in an ionic solvent (BMImPF_6) using $\text{Pd}(\text{OAc})_2$ with $\text{Cu}(\text{OTf})_2$ as the cocatalyst.^{23c} The reaction (outlined in Scheme 13) proceeded at room temperature with greater than 98% conversion to 1,3-diphenyl-1-butene within 4.5 h. Their studies found that when other ionic liquids were used as the reaction medium, the $\text{Pd}(\text{OAc})_2/\text{Cu}(\text{OTf})_2$ system was completely inactive. Study of the

reaction mechanism is currently in progress, but the authors currently believe that styrene is activated with copper (II) triflate to accept nucleophilic attack of the palladium(0) complexes which are generated from the 1,3-dialkylimidazolium salt. This mechanism is similar to what Shirakawa proposed.^{23a}

Scheme 13.



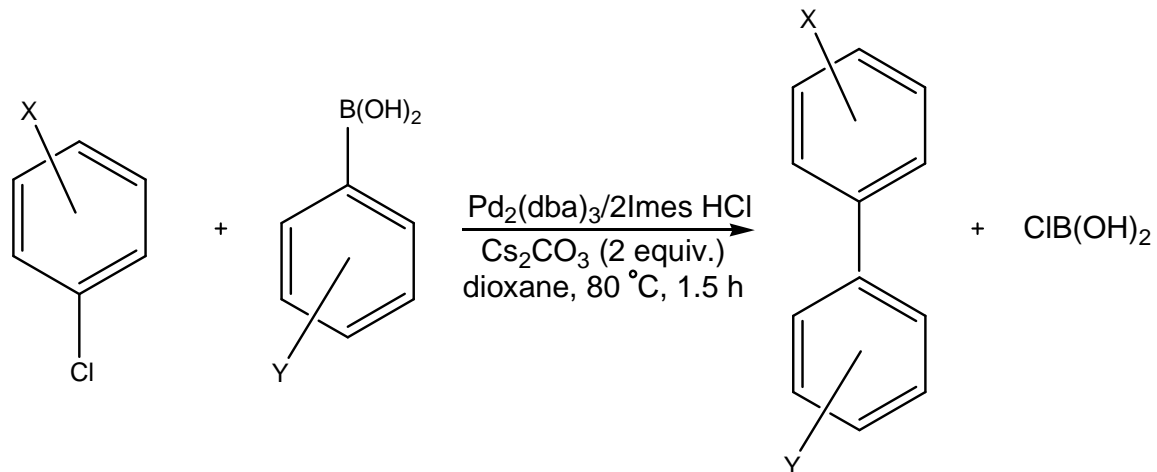
Most recently, Kondo *et al.* reported the selective dimerization of styrene using Ru(0) complexes.^{23d} However, unlike the previously cited reactions, Kondo's system yields an unusual linear head-to-head dimer (Scheme 14). Dimerization was performed by using [Ru(η^6 -cot)(η^2 -dmfm)₂] (cot = 1,3,5-cyclooctatriene, dmfm = dimethyl fumarate) at 80 °C for 24 h, which gave 53% isolated yield of (E)-1,4-diphenyl-1-butene. When other zero-valent complexes with modified ligands were examined, the catalytic activity was reduced. When Ru(II) complexes were examined, no reaction occurred.

Scheme 14.

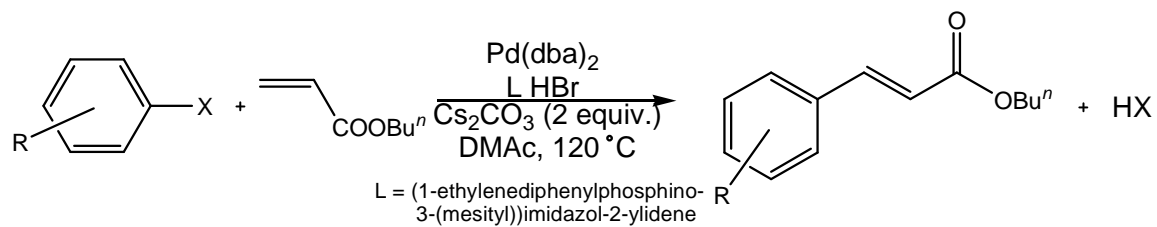
C. Catalytic Olefin Codimerization/Cotrimerization

As mentioned above for olefin dimerization, catalytic codimerization is a desirable transformation in the realm of “green” chemistry. Dozens of cross-coupling reactions have been developed over the years, but they typically have significant (usually stoichiometric) production of side products such as acids or alcohols.²⁴ Some notable examples include the Suzuki-Miyaura reaction (Scheme 15), the Heck reaction (Scheme 16), the Sonogashira reaction (Scheme 17), the Kumada-Tamao-Corriu reaction (Scheme 18), the Stille reaction (Scheme 19), and amination (Scheme 20). These reactions have been established as being very versatile reactions with high product yields, but they lack the atomic conservation of a codimerization reaction. In the case of the Stille reaction, there is some difficulty removing tin from the desired product which is a major issue given the toxicity of tin.

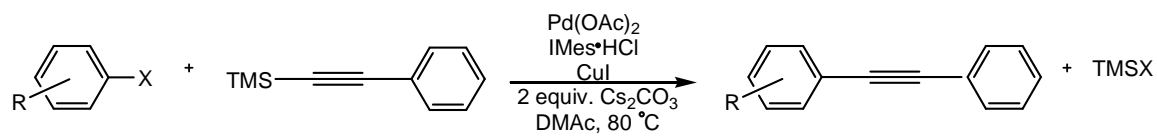
Scheme 15.



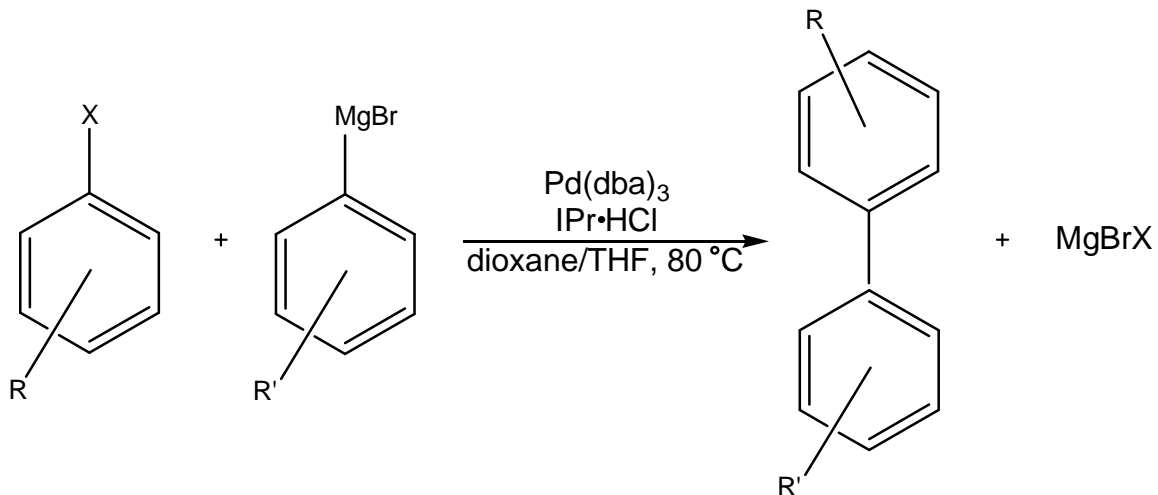
Scheme 16.



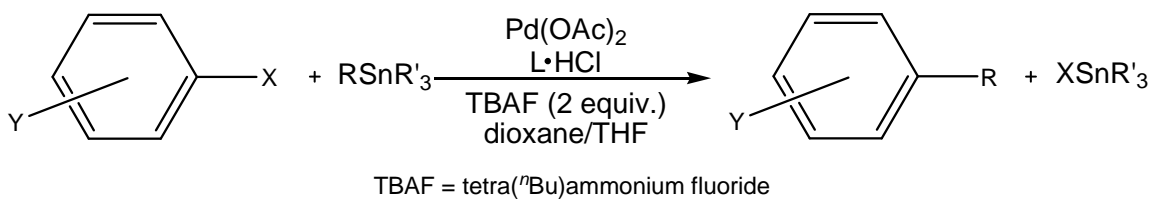
Scheme 17.



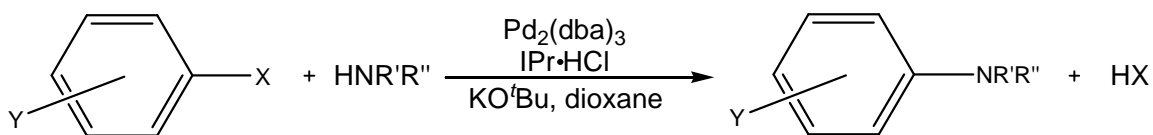
Scheme 18.



Scheme 19.



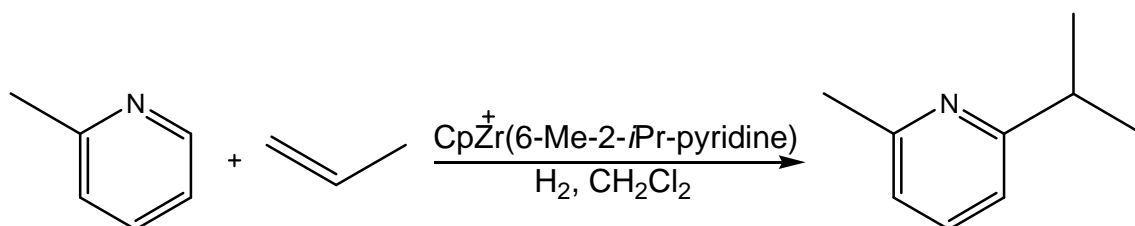
Scheme 20.



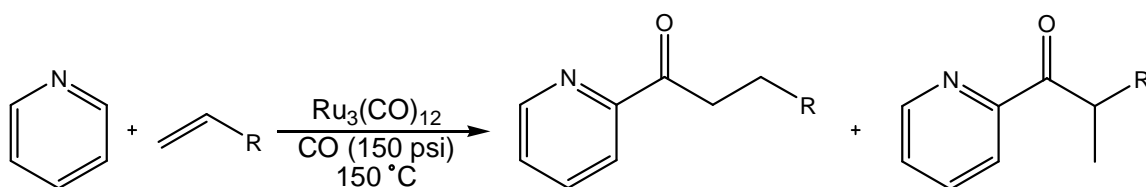
Although codimerization reactions conserve the atoms in the starting materials, one disadvantage that is often faced is lack of selectivity.^{25, 26} Jordan and Taylor²⁵ reported the zirconium catalyzed addition of propene to α -picoline in high yield (Scheme 21), but there was also about 10% formation of propane. Shortly thereafter, Moore *et al.*²⁶ reported the acylation of pyridine with carbon monoxide and olefins using a

ruthenium cluster complex (Scheme 22). The reaction was highly regioselective, with only ortho-substituted products observed. However, a combination of linear and branched products were obtained (~13:1 ratio).

Scheme 21.

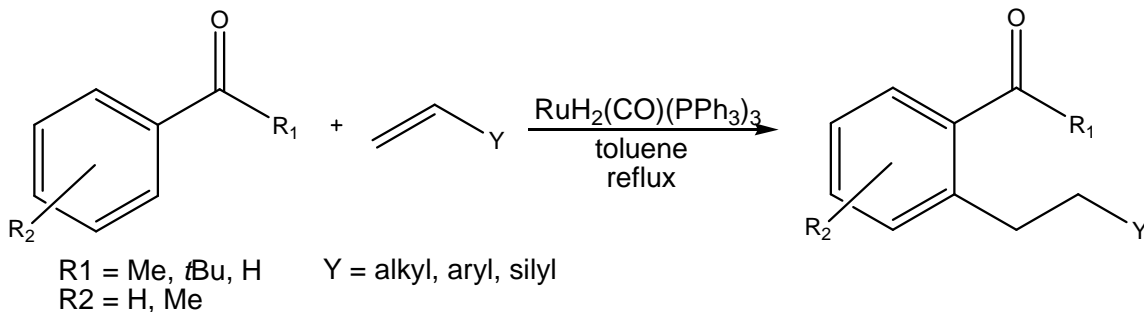


Scheme 22.



The precedent for effective codimerization seemed to be established by Murai²⁷ in the early 1990s. He used a ruthenium hydride catalyst to add olefins to aromatic ketones (Scheme 23). Almost quantitative yields were obtained for many of the cross-coupling products. His reaction also showed remarkable generality, whereas many previous cases were limited to a small combination of reactants.

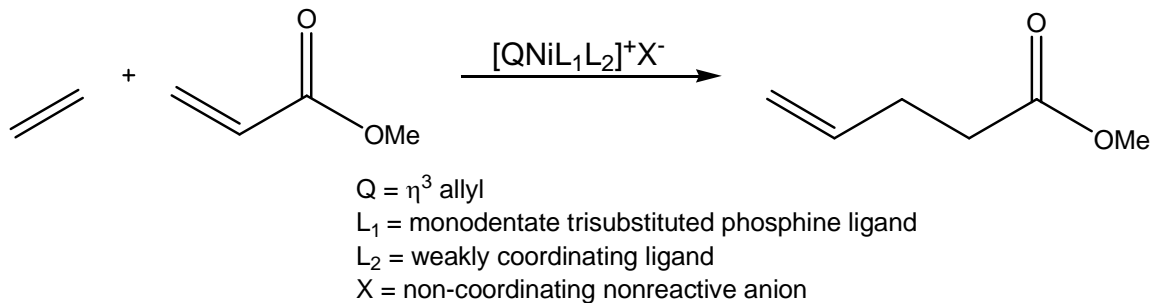
Scheme 23.



Codimerization of olefins is an area that is of great synthetic interest, but is one of the most challenging due to the large production of unwanted homodimers and isomers. Despite this challenge, many groups continue to attempt these reactions. Nickel seems to be one of the most used metals in these reactions.²⁸⁻³¹ In the 1970's, Jones and Symes²⁸ attempted the linear dimerization of 1-olefins using a nickel-aluminum catalyst. They were able to achieve linear products, but the reactions were not overly selective and they had high yields of homodimers along with the codimers.

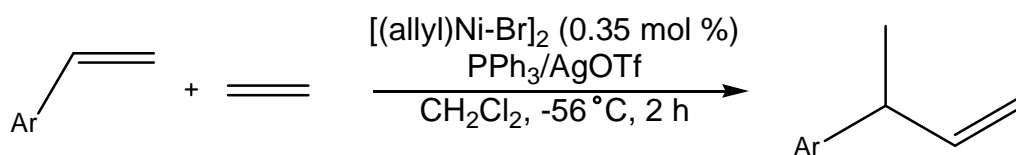
In the late 1990's, Brookhart published a US Patent for the preparation of methyl 4-pentenoate (a synthetic precursor for nylon 6,6) using a nickel catalyst (Scheme 24),²⁹ but the reaction is not without some of the problems noted above. Large amounts of homodimer products as well as undesired isomers were formed during the reactions.

Scheme 24.

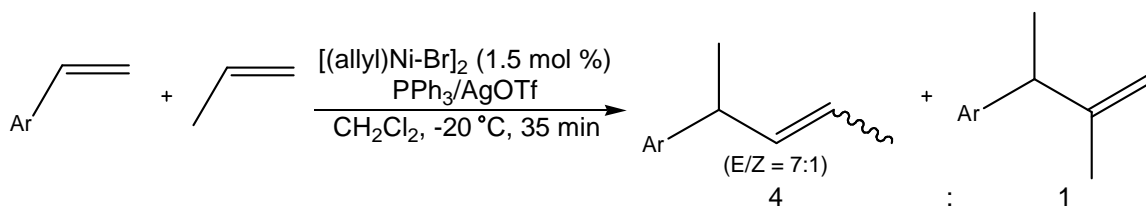


About the same time, RajanBabu *et al.*³⁰ demonstrated extremely high yield and selectivity for the hydrovinylation of vinylarenes using an allylnickel bromide dimer (Scheme 25). Then they attempted the same reaction with propylene.³¹ They obtained the same high product yields as previously noted, but the result was a mixture of isomeric products (Scheme 26).

Scheme 25.

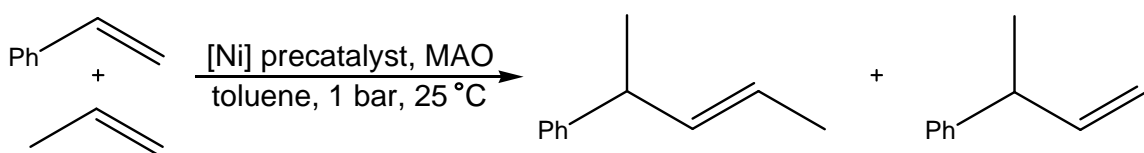


Scheme 26.

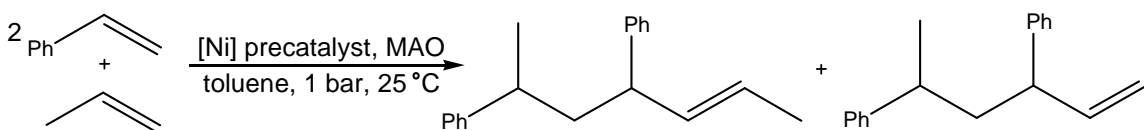


More recently, Faissner and Huttner demonstrated a similar issue with the codimerization and cotrimerization of styrene and propene using nickel catalysts that contained chelating ligands (Schemes 27 and 28).³² Both reactions yielded a combination of (E) and (Z) isomers; approximately 9:1 for dimerization and approximately 8:2 for trimerization. They also noted the formation of a cotrimerization byproduct, 4,6-diphenyl-2-heptene during the codimerization reaction.

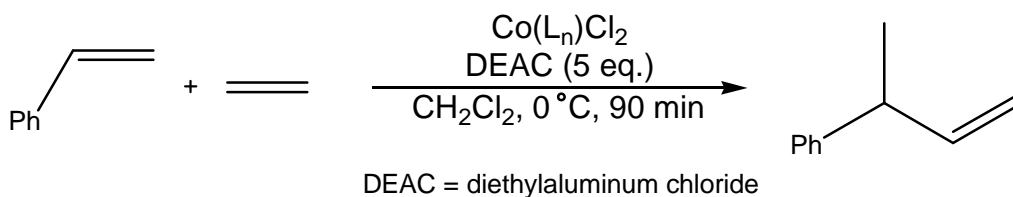
Scheme 27.



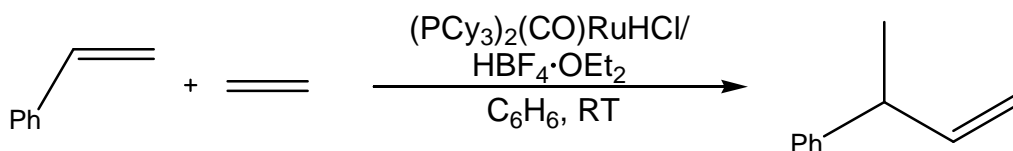
Scheme 28.



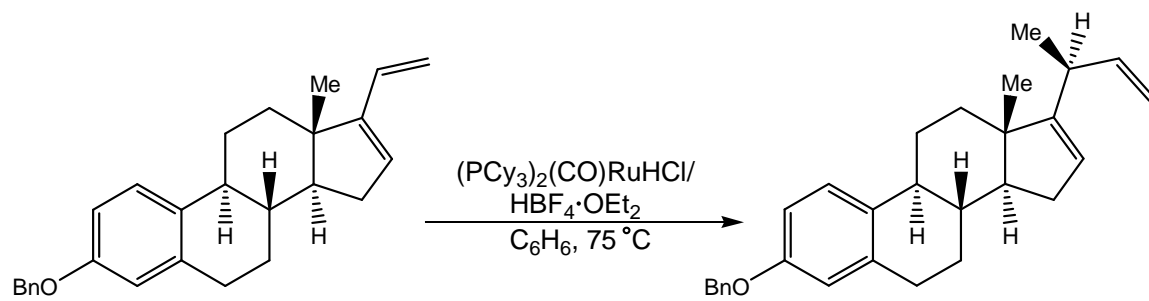
One of the most recent examples of highly selective hydrovinylation was reported by Vogt *et al.*³³ They used cobalt based catalysts of the type $\text{Co}(\text{L}_n)\text{Cl}_2$ where L_n is either monophosphine or diphosphine ligands (Scheme 29). This reaction is very unique because cobalt based systems have been rarely studied in codimerization reactions except for the addition of ethene to 1,3-butadiene or norbornadiene. It is also run at 0 °C which is mild compared to the lower temperatures needed for many of the nickel based systems to prevent isomerization or oligomerization of the product.

Scheme 29.

Our own group has explored a unique system for hydrovinylation using ruthenium catalysts.³⁴ We have demonstrated high product yield (>90%) and selectivity for many substrates using a ruthenium hydride that was prepared in-situ using $\text{HBF}_4 \cdot \text{OEt}_2$ (Scheme 30).^{34a} Remarkably, this reaction occurs at room temperature. The same ruthenium hydride was shown to catalyze the hydrovinylation of unsymmetrically substituted 1,3-dienes, including a steroidal diene yielding a single diastereomer of the 20(S) configuration in high yield (Scheme 31).^{34b} The 20(S) configuration of the steroid derivative has been shown to have therapeutic effects, but there is a lack of reactions that will selectively yield this configuration.

Scheme 30.

Scheme 31.



II. RESULTS AND DISCUSSION

A. Research Plan

Metal oxo and dioxo complexes have been studied by many research groups and are largely known for their ability to epoxidize olefins.¹ Some of the first organometallic oxides (shown in Figure 1) were reported in the late 1950's and early 1960's. The importance of these metal oxo complexes is reflected in the patents for the ARCO and Halcon processes from the late 1960's.³

Most metal oxo complexes are largely known for their ability to epoxidize olefins,¹ but that seems to be the limitation of their reaction scope. A literature search does not reveal other catalytic applications for these compounds. In particular, our metal dioxo complex, **1** (Figure 3), has only been used as a synthetic precursor for other metal complexes since its discovery.^{36, 37, 38}

Metal carbonyl complexes have been known for their long shelf life,^{17a} and relative ease of preparation from commercially available sources.³⁵ They are good sources in the preparation of metal oxo complexes,^{1f, 14, 15} which are known to have less stability than their carbonyl precursors.^{17a}

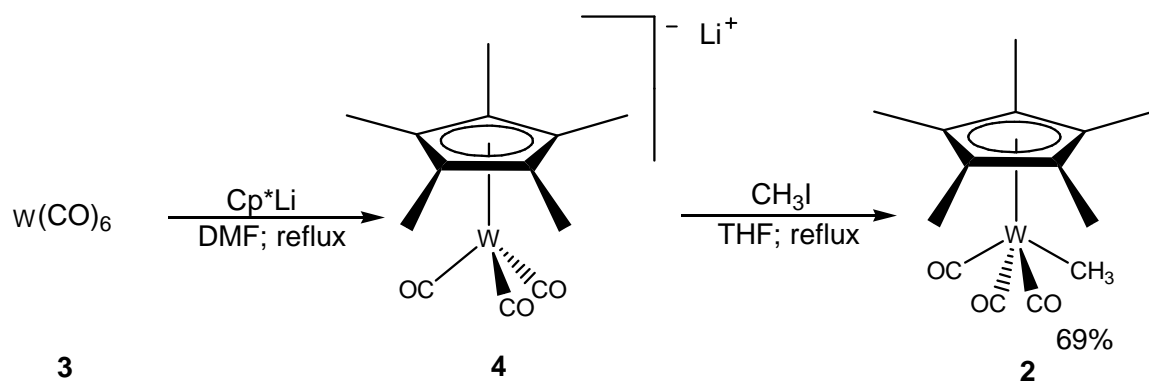
Our research plan was to prepare complex **1** from its carbonyl precursor, **2**, which has been previously prepared in our laboratory. Our initial goal was to examine the catalytic activity of **1** for olefin oxidation and other C-C bond forming reactions. We found that complex **1** showed a high activity for olefin dimerization, which is unprecedented for metal-dioxo compounds. After finding suitable conditions and

substrates for olefin dimerization, we then wanted to see if selective codimerization was possible with this catalytic system.

B. Synthesis and Characterization of $\text{Cp}^*\text{W}(\text{CO})_3\text{CH}_3$

The preparation of tricarbonyl methyl η^5 -pentamethylcyclopentadienyl tungsten (**2**) dates back to 1971 when King and Efraty^{39a} reacted 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene with the acetonitrile complex $(\text{CH}_3\text{CN})_3\text{W}(\text{CO})_3$. This reaction yielded only 4% of **2**. Less than a year later, they reported an improved reaction using the same starting materials and were able to obtain 41% yield of **2**.^{39b} We used a general procedure described by Mahmoud and Rest³⁵ in our preparation of **2** which gave us significantly higher yields from $\text{W}(\text{CO})_6$ (**3**) (Scheme 32). **3** was heated at reflux with Cp^*Li in DMF for 1.5 h. After the solvent was evaporated, the residue (**4**) was heated at reflux with CH_3I in THF for 2 h to give yellow crystals of **2** in good yield (69%).

Scheme 32.

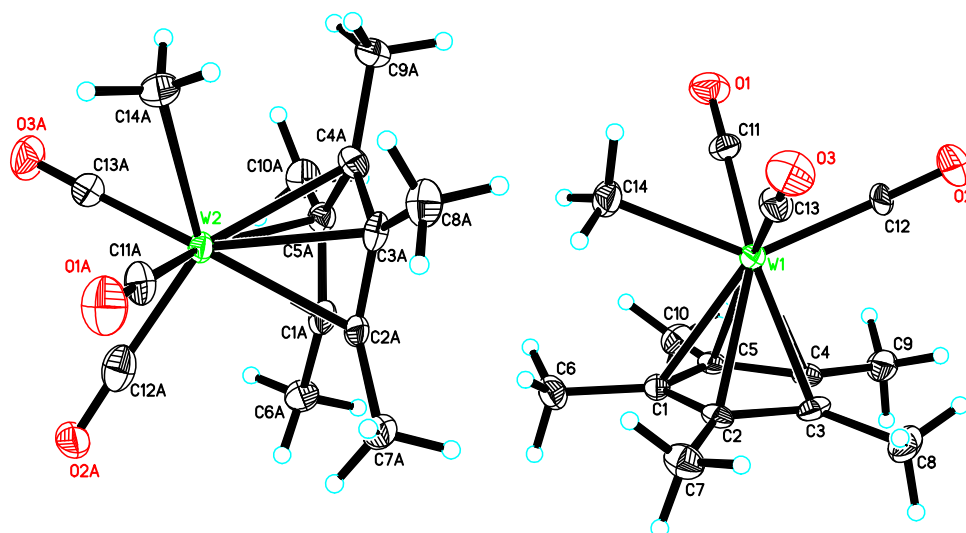


The product appeared to be relatively stable in ambient laboratory conditions for several months. The product was characterized by ^1H and ^{13}C NMR spectroscopy and X-ray crystallography. The ^1H NMR spectrum exhibited the Cp* signal at δ 1.97 ppm and the methyl hydrogens at δ 0.10 ppm. The ^{13}C NMR spectrum showed the carbonyl carbons at δ 233.2 ppm (1 CO) and δ 220.3 ppm (2 COs). Also, the metal bound methyl carbon appeared at δ -24.0 ppm.

Although the product (**2**) has been known since at least the 1970s,³⁹ its characterization has been limited to spectroscopic data of similar structures which have been confirmed by X-ray crystallography.⁴⁰ A literature search failed to reveal the published crystal structure for **2**. The yellow orthorhombic crystals were grown by adding hexanes to a concentrated solution of **2** in Et₂O and subsequent slow evaporation at reduced temperature (refrigeration).

Complex **2** crystallizes as twin racemates in Pna21 space group (Figure 2), exhibiting the expected four-legged piano stool arrangement. The W-C distance for the methyl groups (W1-C(14) = 2.306(5) Å, W2-C(14A) = 2.307(6) Å) are extremely close to that of CpBzW(CO)₃CH₃ (2.306(3) Å).^{40c} In the racemate on the right (W1), the distance from tungsten to a carbonyl carbon cis to the methyl ligand (W1-C(11) = 1.987(5) Å) is shorter than the other two tungsten-carbonyl distances (W1-C(12) = 1.993(7) Å, W1-C(13) = 1.998(5) Å). For the racemate on the left (W2), the shortest tungsten-carbonyl distance is for the carbonyl *trans* to the methyl group (W2-C(12A) = 1.975(9) Å). While the two carbonyls *cis* to the methyl group have longer W-C bonds (W2-C(11A) = 1.992(5) Å, W2-C(13A) = 1.994(5) Å). Based on the W-C (ring) distances, the Cp* plane is slightly tilted away from the methyl group in both racemates.

Figure 2. Crystallographic structure of Cp*W(CO)₃CH₃ (**2**).

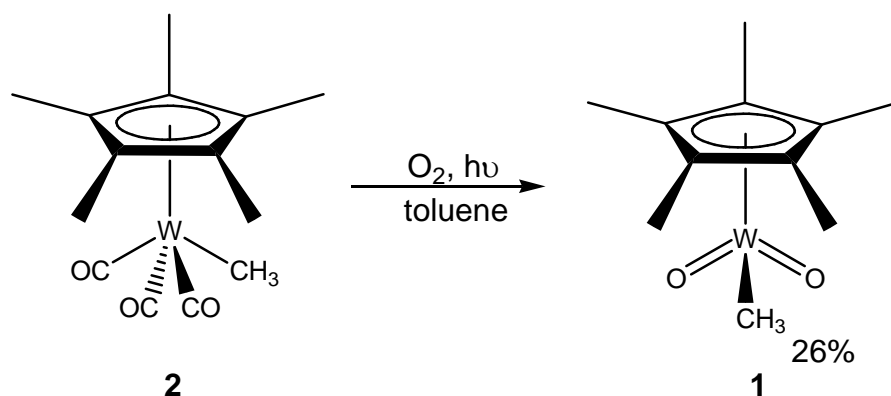


C. Synthesis and Characterization of Cp*W(=O)₂CH₃

UV irradiation of metal carbonyl complexes under oxygen atmosphere has been a common approach in the preparation of metal oxo compounds.^{1f, 41} In 1964, Cousins and Green^{41a} reported the preparation of CpMo(=O)₂Cl (**6**) in 25% yield by exposing a chloroform solution of [CpMo(CO)₃]₂ (**5**) to UV light and air. Bergman^{1f} reported the preparation of the pentamethylcyclopentadienyl analogue of this compound, Cp*Mo(=O)₂Cl, in 61% yield by exposing a toluene solution of Cp*Mo(CO)₃Cl to UV light and oxygen. The tungsten analogue of this compound, Cp*W(=O)₂Cl, was prepared by Faller and Ma⁴² in 27% yield by refluxing a chloroform solution of [Cp*W(CO)₂]₂ under oxygen. A few years later, Rau¹³ *et al.* reported the preparation of the same compound in 44% yield by adding aqueous NaOH to an acetone solution of Cp*WCl₄ in air.

In 1988, Faller and Ma³⁶ reported the preparation of **1** in 15% yield by reacting Cp*W(=O)₂Cl with 1.5 eq. of 2 M MeMgCl. Just a year later, Legzdins³⁷ *et al.* prepared **1** in 50% yield by adding a MeLi solution to a suspension of Cp*W(NO)I₂ followed by addition of 30% H₂O₂. We prepared complex **1** from complex **2** (Scheme 33). O₂ was bubbled through a solution of **2** (~700 mg) in toluene while the solution was exposed to UV light at reduced temperature (cold water bath). Isolation on a silica gel column yielded off-white crystals in relatively moderate yield (20-25%).

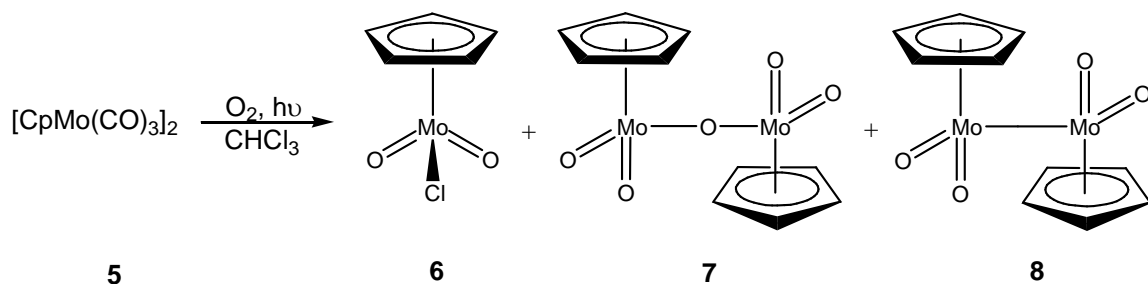
Scheme 33.



Initial attempts at this reaction resulted in very low yields of ~10%. In this case the unreacted starting material (**2**) was easily recovered in high yield (69%) and recrystallized for reuse. However, as the yield of **1** increased to above 20%, **2** was no longer recoverable from the reaction. There are many possible reasons for this occurrence. During the isolation process, the first band to come off of the column is yellow. In the cases when the yield of **1** is ~10%, the yellow band is simply unreacted starting material (**2**) which is easily recrystallized from Et₂O/hexanes. However, as the yield of **1** increases, it is very likely that there are side reactions occurring that inhibit the

recovery of **2**. Cousins and Green^{41a} prepared the compound, $\text{CpMo(=O)}_2\text{Cl}$, under similar reaction conditions, but also noted the formation of the two dimolybdenum complexes as shown in Scheme 34. They noted that the bridged μ -oxo complex **7** is pale yellow, and the tetraoxide complex **8** is brown. It is possible that Cp^*W complexes analogous to **7** and **8** are being formed during the reaction. We already know that the Cp^*W complex $[\text{Cp}^*\text{W}_2\text{O}_5]$ analogous to **7** has been previously documented to be a yellow compound⁴³ and it is likely that the Cp^*W compound analogous to **8** has a similar color to the dimolybdenum complex. It is very possible that if these side products are formed during the reaction that they are eluting in the yellow band along with, or instead of, any unreacted **2**.

Scheme 34.

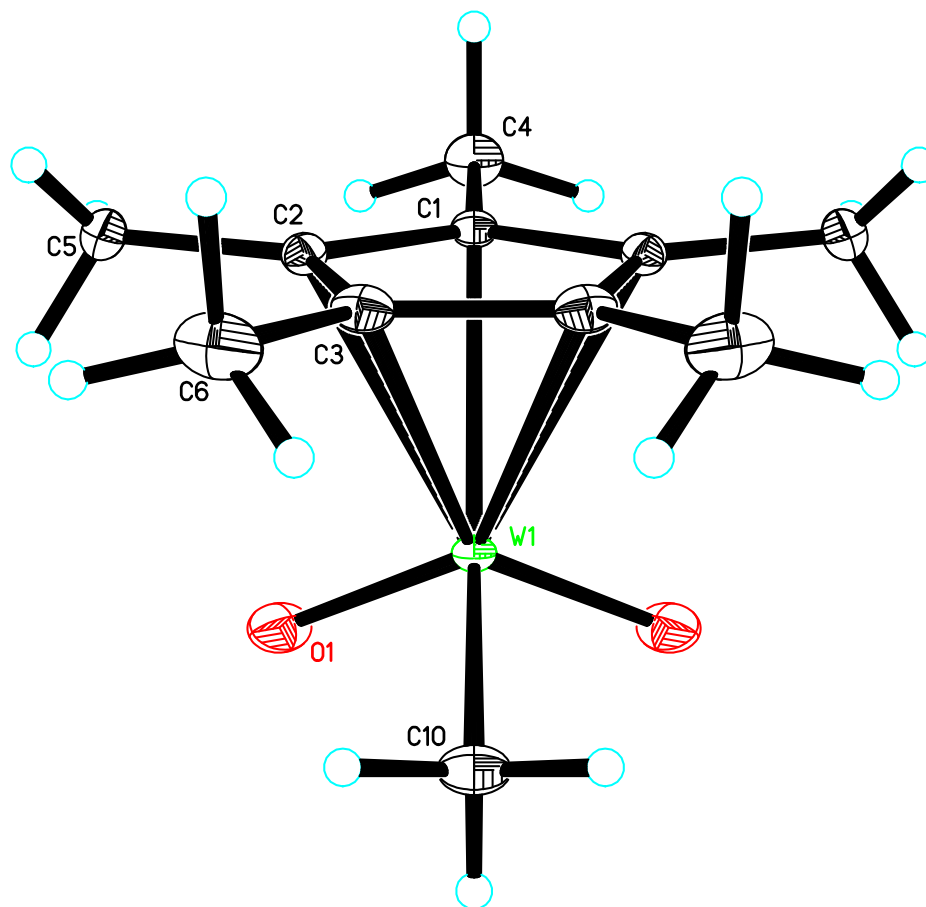


Although many dioxo complexes are noted to lack stability,^{14, 15, 16} the product (**1**) is relatively stable for several months when stored at ambient conditions in a desiccator. The crystals appear to pick up moisture and clump together if stored outside a desiccator. The product was characterized by ^1H and ^{13}C NMR spectroscopy and X-ray crystallography. The ^1H NMR spectrum exhibited the Cp^* signal at δ 2.09 ppm and the methyl hydrogens at δ 0.99 ppm, which is consistent with data previously reported by

Faller and Ma.³⁶ The ^{13}C NMR spectrum showed the Cp* ring carbons at δ 117.8 ppm, along with the Cp* methyl carbons at δ 11.1 ppm and the metal bound methyl carbon at δ 15.6 ppm.

The off-white monoclinic crystals were grown by adding hexanes to a concentrated solution of **1** in Et₂O and subsequent slow evaporation at reduced temperature (refrigeration). The compound crystallizes in the P21/m space group with a three-legged piano stool arrangement (Figure 3) which exhibits perfect symmetry in a plane containing C(1), C(4), C(10) and W. The tungsten-carbon bond distance for the metal bound methyl group is 2.136(2) Å. The two W=O bonds are both 1.7298(13) which is very similar to other similar tungsten dioxo compounds.^{1b, 41c} Based on the W-C (ring) distances, the Cp* plane is slightly tilted away from the methyl group as noted above for **2**.

Figure 3. Crystallographic structure of Cp*W(=O)₂CH₃ (**1**).



D. Catalytic Activity Study of Cp*W(=O)₂CH₃ for Dimerization of *Para*-Substituted Styrenes

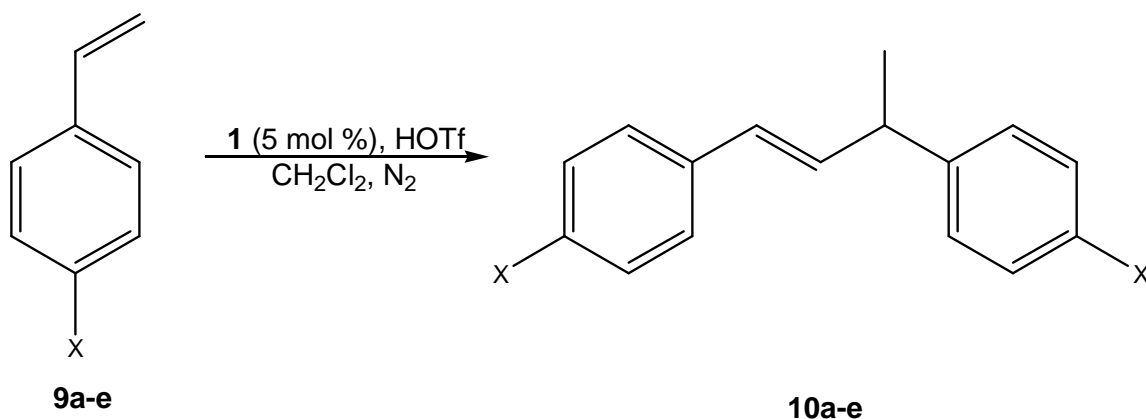
Since its discovery in 1988,³⁶ complex **1** has only been used as a precursor to create new organometallic complexes.^{36, 37, 38} Faller and Ma used **1** to make the corresponding peroxy [Cp*W(=O)(O₂)Me], sulfido [Cp*W(=O)(=S)Me] and Cp*W(=S)₂Me], and persulfido [Cp*W(=O)(S₂)Me and Cp*W(=S)(S₂)Me] complexes.³⁶

^{38b, 38c} Legzdins *et al.* also made the corresponding peroxy complex, as well as $\text{Cp}^*\text{W}(=\text{O})(\text{Cl})_2\text{Me}$ and $\text{Cp}^*\text{W}(=\text{O})(\text{Me})(\text{CH}_2\text{Ph})_2$ using **1** as a precursor.^{37, 38a} We were not able to find any published reactions where **1** was used to prepare organic compounds, whether as a catalyst or otherwise.

Unlike many dioxo complexes which are known for their ability to epoxidize olefins,^{1b, c, f} **1** has been shown to selectively dimerize some *para*-substituted styrenes following the general reaction shown in Scheme 35. While there are other catalytic systems noted for the dimerization of styrenes, many of them require a co-catalyst or other additives.²³ Complex **1** merely needs to react with an equimolar amount of triflic acid for about an hour prior to adding the styrene substrate. (Caution: It is very important that the reaction of **1** with triflic acid is maintained under nitrogen atmosphere to prevent explosion. It is thought that exposure to air may form an unstable metal-peroxy complex which is responsible for the explosion.^{1f})

Most of the styrene derivative substrates react at room temperature to yield the dimer products. In some cases, the reactions were found to be highly dependent on temperature. For example, when 4-bromostyrene (**9d**) was reacted at 50 °C, the GC-MS spectrum showed mostly starting material with several unidentified peaks of $m/e \sim 355$. However, when the reaction was carried out at 70 °C, the GC-MS spectrum showed one peak corresponding to the dimer (**10d**). A similar case was observed for 4-vinylbenzylchloride (**9e**) where the reaction at 40 °C resulted in the formation of higher oligomers, while the reaction at room temperature yielded a single isolable dimer (**10e**).

Scheme 35.



X	Reaction Temp.	Reaction Time (h.)	Product	Isolated % Yield
H (9a)	50 °C	21	10a	36
F (9b)	RT	23	10b	58
Cl (9c)	RT	26	10c	56
Br (9d)	70 °C	21	10d	84
CH ₂ Cl (9e)	RT	26	10e	53

In one case, the temperature was found to strongly affect the outcome of the reaction where the substrate was reacted only with HOTf. When 4-chlorostyrene (**9c**) was reacted at about 50 °C, both the reaction with **1** and the reaction with only HOTf showed a single dimeric product (**10c**) in the GC-MS spectrum (it is useful to note that, although the control reaction showed a single dimer product in the GC-MS, the ¹H NMR spectrum of this reaction was not clean and contained very broad peaks). This initial result was somewhat disappointing. However, when the reactions were repeated at room temperature, the reaction with **1** still resulted in a clean product while the control reaction resulted in the dimer along with several trimer peaks.

In all cases for the reaction conditions noted in Scheme 35, the control reactions without **1** did not result in clean, isolable products. The resulting ¹H NMR spectra

contained several broad peaks. Figure 4 and Figure 5 show example ^1H NMR spectra for the reaction of **9d** with (**10d**) and without **1**, respectively.

Figure 4. ^1H NMR spectrum for **10d**.

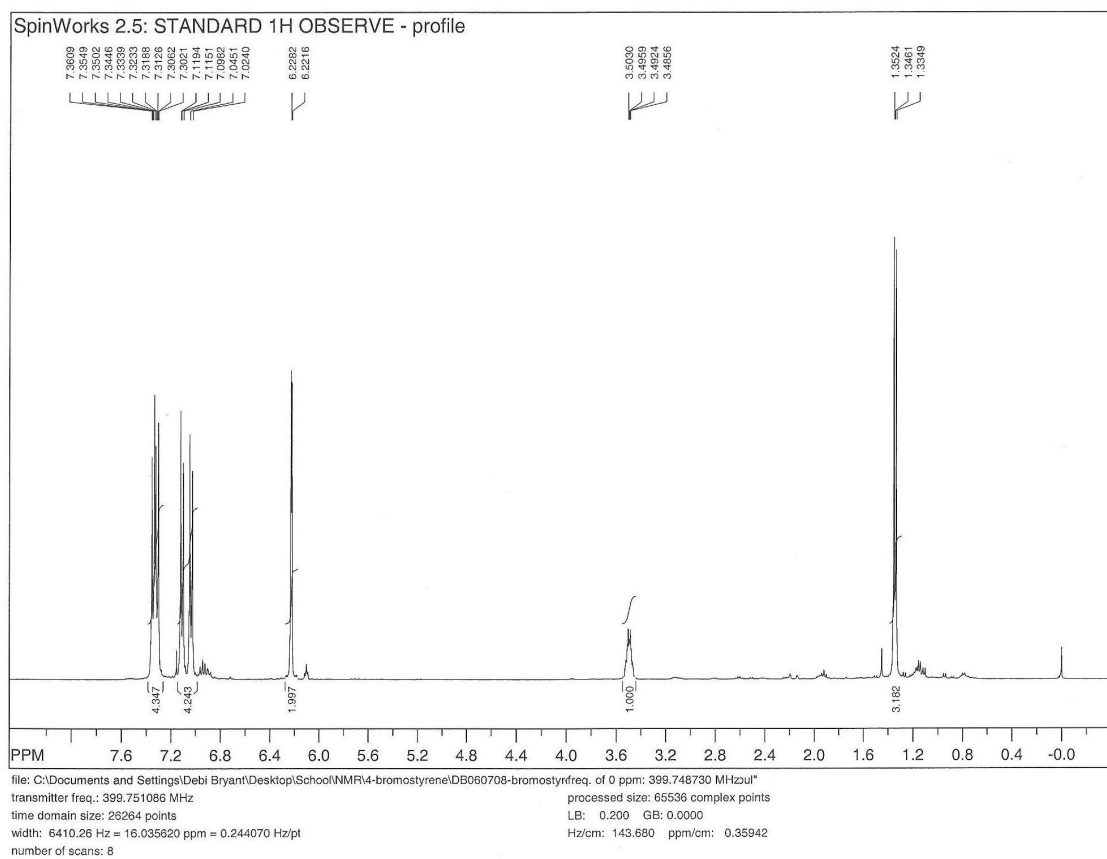
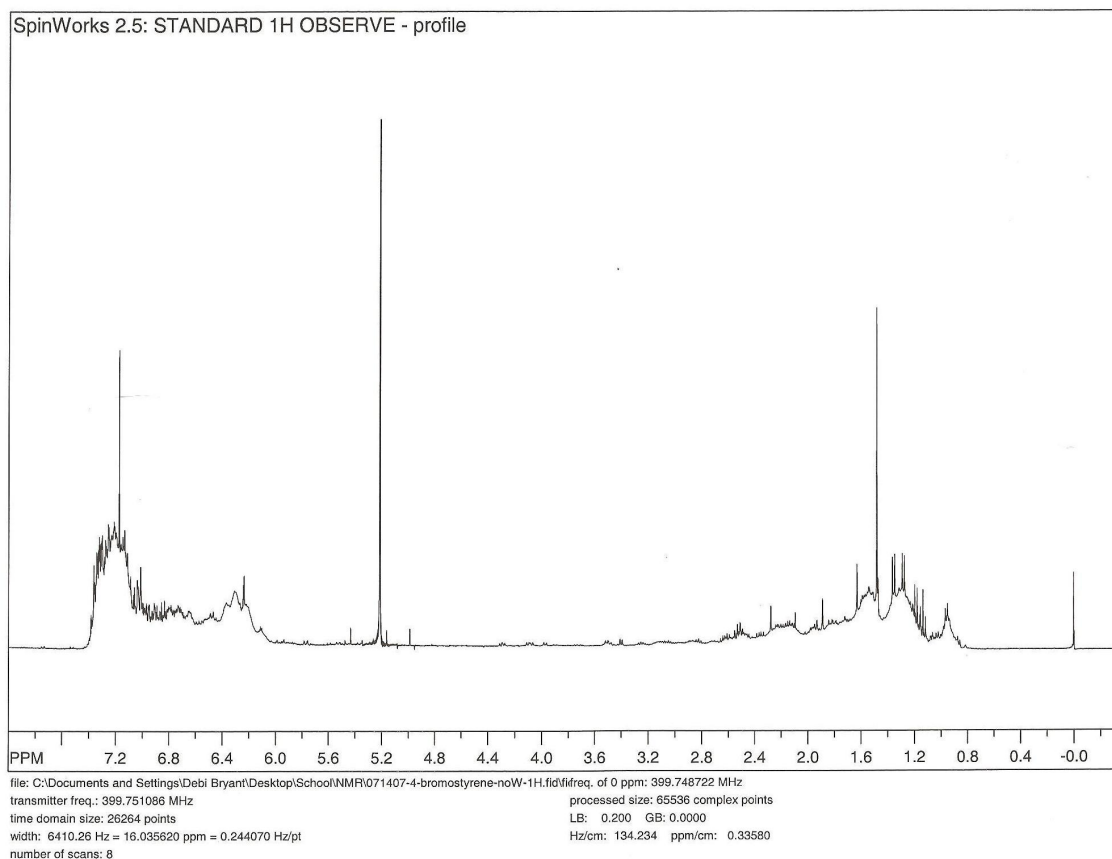


Figure 5. ^1H NMR spectrum for the reaction of **9d** with HOTf.



As demonstrated in Figure 4, all of the dimer products (**10a-e**) have two sets of similar characteristic peaks in their ^1H NMR spectra. The first one is a doublet that occurs at about δ 1.4 ppm with a $J_{\text{H-H}}$ of about 7 Hz which corresponds to the methyl hydrogens (attached to C(10) in Figure 7). The second one is a multiplet at about δ 3.5 ppm which also has a $J_{\text{H-H}}$ of about 7 Hz. This multiplet corresponds to a single hydrogen which neighbors the methyl group (attached to C(9) in Figure 7).

We expected a third set of peaks that occurs at about δ 6.2 ppm, corresponding to the hydrogens in a C-C double bond (attached to C(7) and C(8) in Figure 7), in each of **10a-e** to be our key in determining the exact structure of the products. We expected our

products to be one of 3 possible isomers as shown in Figure 6. We assumed that the hydrogen coupling constant would tell us whether the double bond was *cis* ($J_{\text{H-H}} \sim 6\text{-}15$ Hz), *trans* ($J_{\text{H-H}} \sim 11\text{-}18$ Hz) or terminal ($J_{\text{H-H}} \sim 0\text{-}5$ Hz).⁴⁴ However, the $J_{\text{H-H}}$ for this set of peaks ranged from 2.9 to 16.0 Hz as shown in Table 3. Based on the data in Table 3, it initially appeared that we may have had all three isomers.

Figure 6. Possible dimer products for the reaction of **9a-e** with **4**.

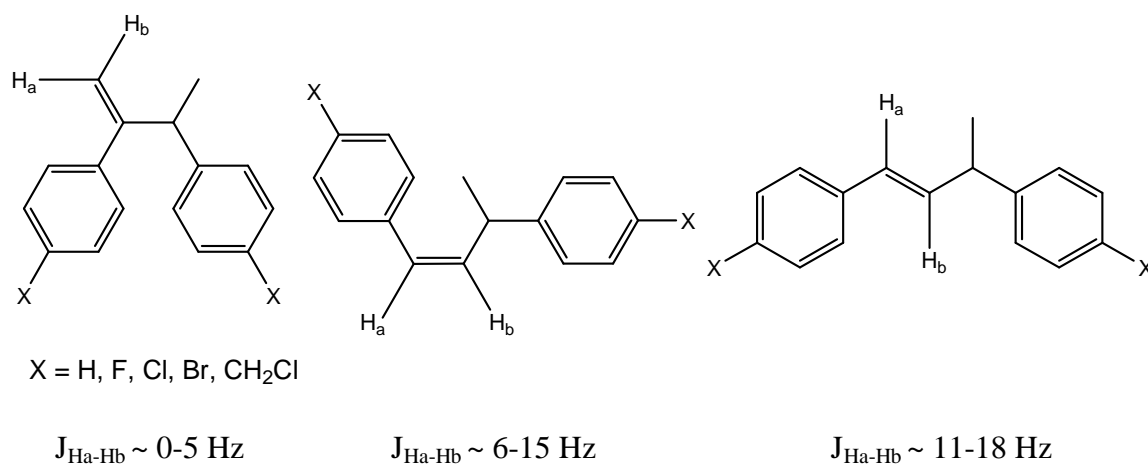


Table 3. $J_{\text{Ha-Hb}}$ for **10a-e** peaks at δ 6.2 ppm (corresponding to C-C double bond).

X	Product	$J_{\text{Ha-Hb}}$ (Hz)*
Br	10d	2.9
H	10a	4.9
Cl	10c	5.0
CH ₂ Cl	10e	6.5
F	10b	16.0

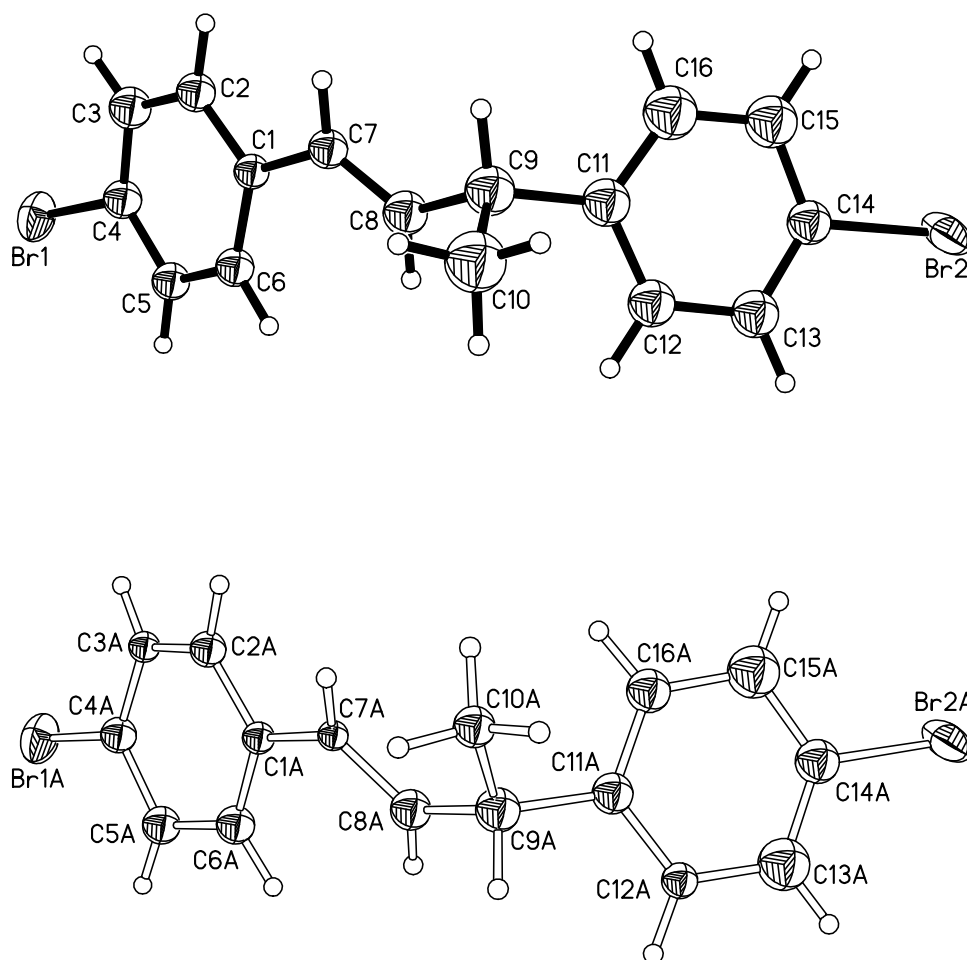
*CDCl₃ was used as the NMR solvent.

In the case where X is fluorine (**10b**), the $J_{\text{Ha-Hb}}$ is 16.0 Hz indicating the possibility of a *trans* double bond. When X is bromine (**10d**), the $J_{\text{Ha-Hb}}$ is 2.9 Hz indicating the possibility of geminal hydrogens. It seems that the electron donating

power of the *para* substituent would determine the structure of the dimer. However, the crystal structure of **10d** confirmed that the terminal methylene group was not an option for the products of our dimerization reaction. As seen in Figure 7, **10d** is very clearly the *trans* isomer rather than the terminal double bond as indicated by the $J_{\text{Ha-Hb}}$ coupling constant. It appears that there is something about the molecules that yields unexpected coupling constants for the double bond.

This structure is consistent with those proposed by other groups for styrene dimers.^{22, 23} However, there does not appear to be a previously published crystal structure for any styrene dimer. This may be due to the fact that many styrene dimers are oils rather than solids. In our experiments, we only observed crystal formation for the higher molecular weight dimers of 4-chlorostyrene (**10c**), 4-bromostyrene (**10d**) and 4-vinylbenzyl chloride (**10e**).

Figure 7. Crystallographic Structure of *trans*-1,3-Di-(4-Bromophenyl)-1-Butene (**10d**)

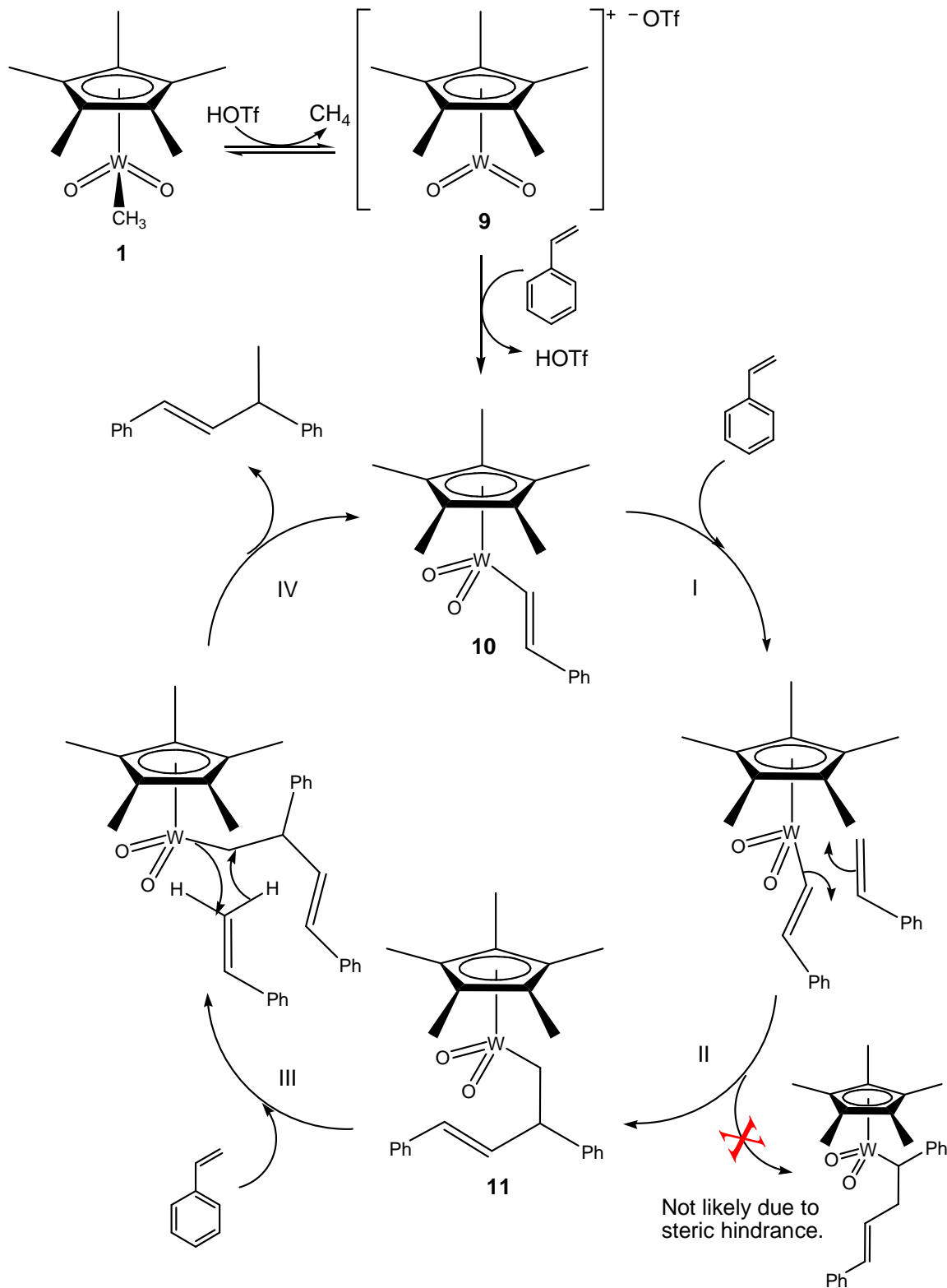


The off-white orthorhombic crystals were grown from a slowly evaporated solution of **10d** in CDCl₃. The enantiomers crystallize neither as a racemate nor separately, but in a chiral space group P2₁2₁2₁ randomly substituting each other, which is a very uncommon occurrence.

E. Proposed Reaction Mechanisms

Kondo *et al.*^{23d} proposed mechanisms for the dimerization of styrene, but these are for a linear product. The Sen group^{22g, h} had previously reported a cationic mechanism for the formation of 1,3-diphenyl-1-butene (Scheme 10). However, this mechanism was proposed based on a square planar palladium complex with a +2 charge on the metal atom. Legzdins^{19d} proposed a σ -bond metathesis-like mechanism for C-H activation by tungsten hydrocarbyl hydrido complexes $[\text{Cp}^*\text{W}(\text{NO})(\text{R})(\text{H})(\text{PMe}_3)]$, R = alkyl, aryl] which is followed by reductive elimination of the product. All three of these mechanisms are based on more than one bonding site available at the metal center. Roy and Sunoj^{21c} recently proposed a mechanism involving σ -bond metathesis using a nickel hydride or a nickel alkyl active species. We initially predicted a similar version of Roy and Sunoj's mechanism in Scheme 36 which is a possibility to account for the formation of **10a-e**.

First, this mechanism makes it very easy to justify the lack of a linear dimerization product due to the steric hindrance demonstrated in Step II of the reaction. Second, since tungsten is at its highest oxidation state and the Cp* ligand and the doubly bonded oxygens are not very labile, it is difficult to assume that the metal center will have any extra bonding sites available. In other words, σ -bond metathesis would be the only way that the second styrene molecule could attach to the metal center. However, one major problem with the mechanism proposed in Scheme 36 is the assumption that the methyl group is lost as methane gas, which means that the starting catalyst would not be recoverable from the reaction.

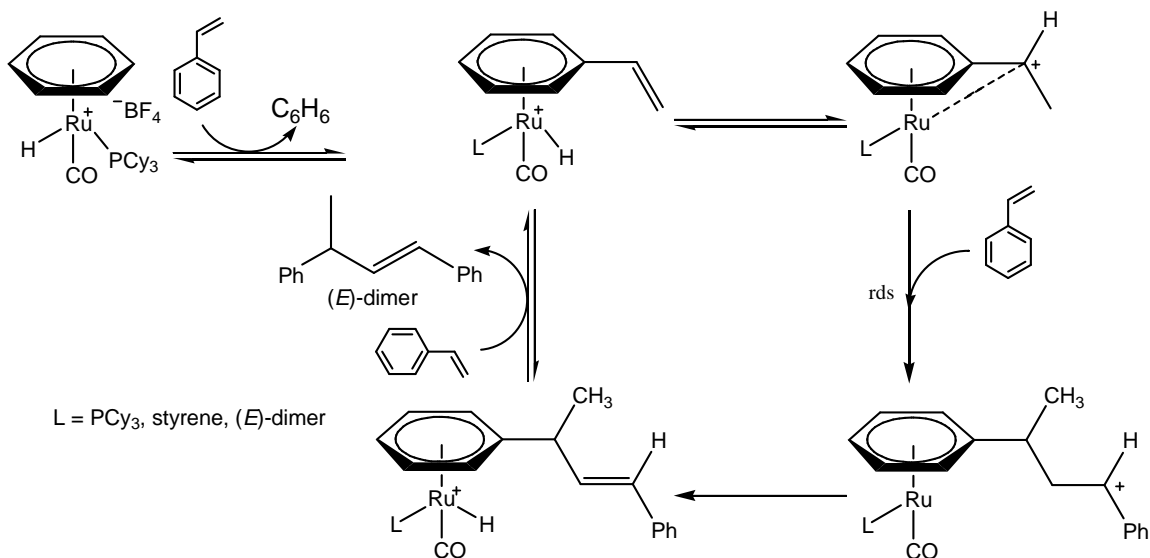
Scheme 36. Initial Proposed Mechanism for Styrene Dimerization

Based on unsuccessful attempts to isolate the “active” cationic catalyst species (**9**), reductive elimination of the product (as proposed by Legzdins^{19d}) did not seem a likely option. Attempts to isolate **9** have resulted in brown solutions or residues indicating that this intermediate may be extremely unstable. If that is the case, it should be possible to isolate compounds **10** and **11** by adding 1 or 2 equivalents, respectively, of styrene to a solution of **9**. If the methyl analog (**1**) is stable, then, theoretically, the styrene analog (**10**) and the diphenyl butene analog (**11**) should also be stable.

Unfortunately, initial attempts at isolating **10** or **11** resulted in almost full recovery of **1** (~80%) along with styrene dimer products. The ¹H NMR spectra of the recovered **1** from these reactions indicates that all ligands remained intact. Although we do not have enough evidence to fully rule out the mechanism proposed in Scheme 36, we need to consider other alternatives that would leave the molecule intact after the reaction.

Our own group has recently proposed a possible mechanism for styrene dimerization that is catalyzed by a cationic ruthenium hydride complex (Scheme 37).⁴⁵ This mechanism involves displacement of a neutral benzene ligand by another neutral ligand leaving a metal complex intact after the reaction. In order for this to work, we would have to assume displacement of the negatively charged Cp* ligand by a neutral styrene molecule. This seems unlikely given the electrophilicity of the tungsten center. We would also need some additional source of hydrogen in order to act as a counter-ion for the Cp* displacement, the presumed triflate ions in solution, and to form the carbocation on the styrene molecule.

Scheme 37. Proposed Styrene Dimerization Mechanism Catalyzed by a Cationic Ruthenium-Hydride Complex

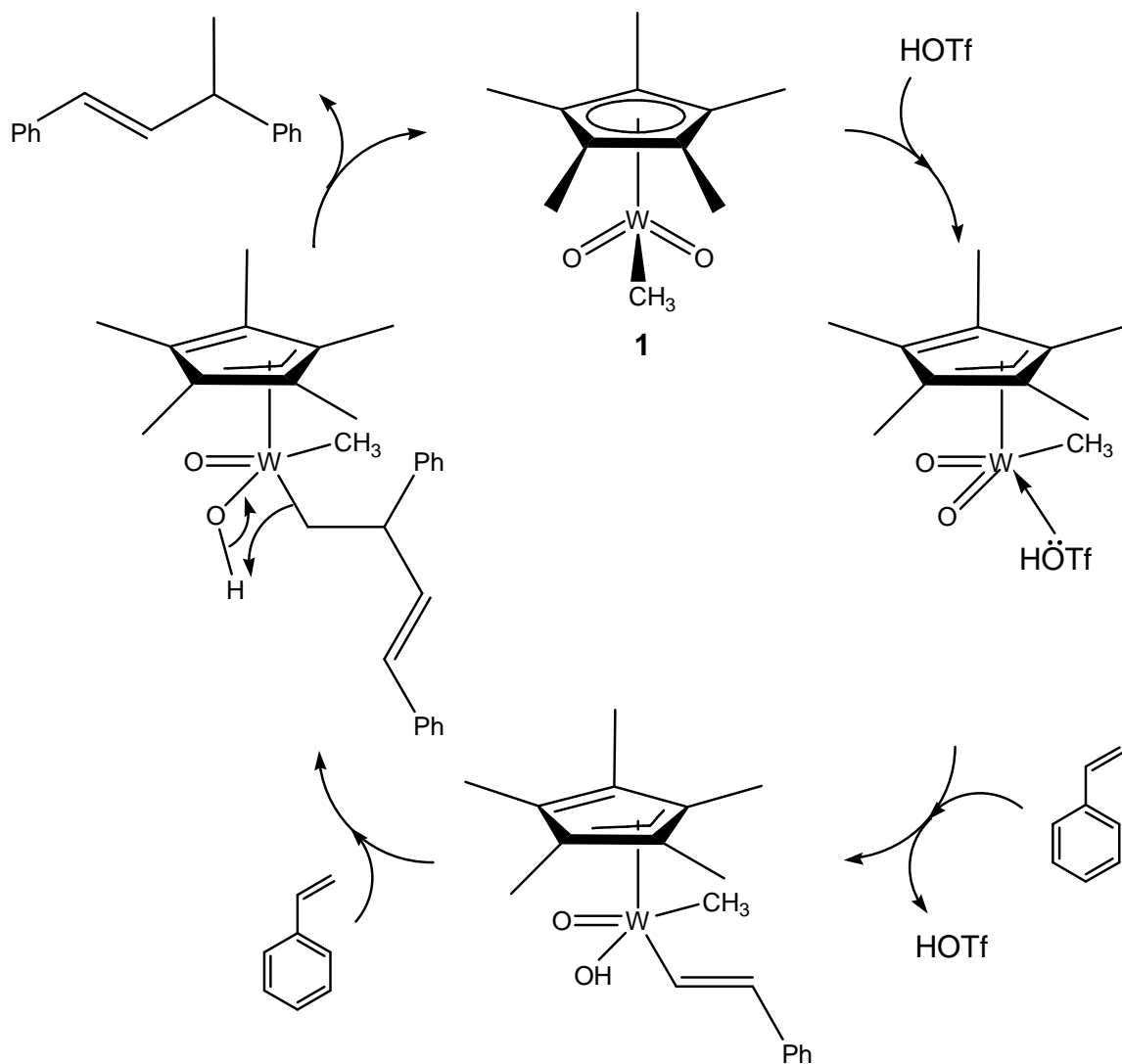


Another possible mechanism that could leave the metal complex intact would involve ring slippage of the Cp* ligand. Ring slippage has been noted as a mechanism for ligand exchange in organometallic complexes,⁴⁶ and, more recently, has been documented as a mechanism for alcohol racemization.⁴⁷ For this type of mechanism to work for our system, some assumptions have to be made. One assumption is that the triflic acid would be strong enough to cause the ring slippage. Another assumption is that one of the oxo ligands will become a hydroxyl ligand in order to accommodate the styrene ions, and, in turn, provide the hydrogen needed for reductive elimination of the product.

Scheme 38 shows a possible mechanism for styrene dimerization which might account for the catalyst remaining intact at the end of the cycle. This cycle might also account for not being able to isolate the “active” complex or any intermediates because all of the intermediates shown in Scheme 38 are only 14 electron complexes which are

not known to be stable for 6-coordinate metal compounds. However, given the electrophilicity of the tungsten center, this mechanism is not a likely possibility.

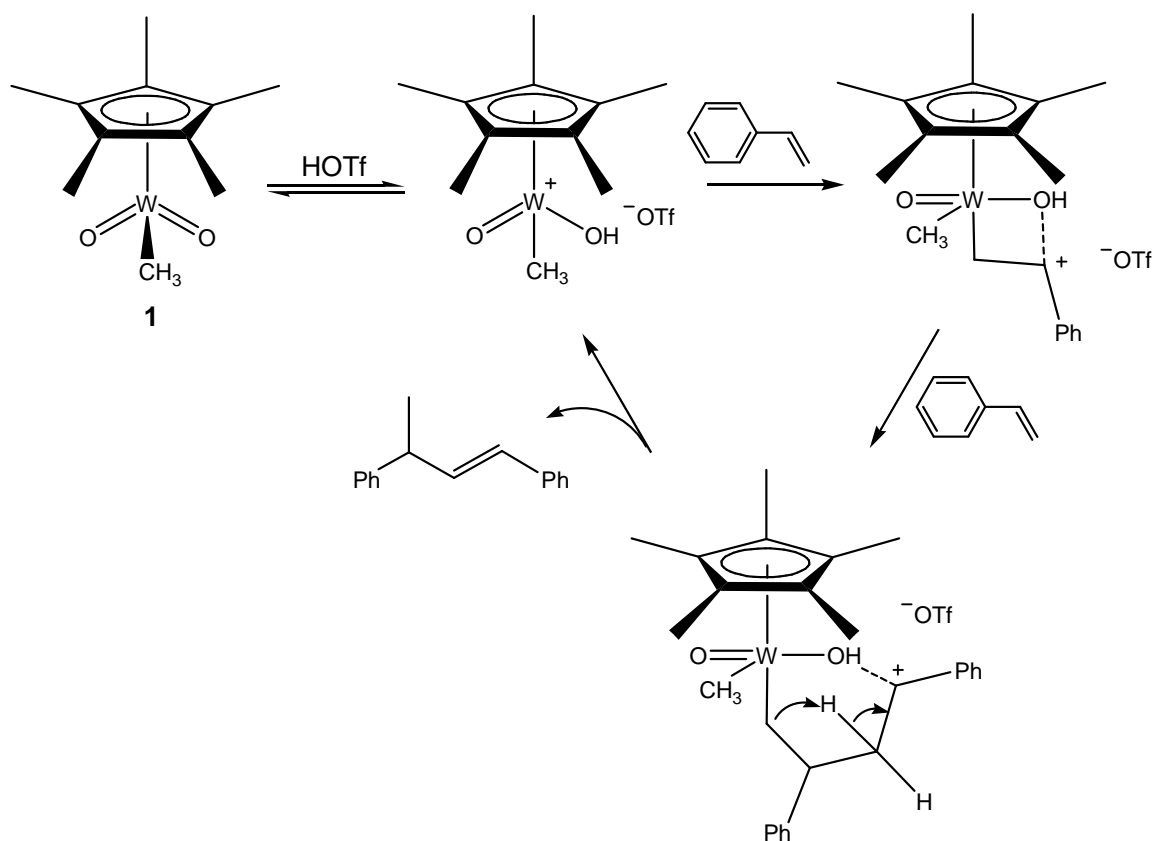
Scheme 38. Proposed Ring-Slippage Mechanism for Styrene Dimerization



An alternative proposal shown in Scheme 39 would account for recovery of the starting catalyst, as well as accommodate the lack of open bonding sites on the metal center. It is a carbocation mechanism based on Sen's (Scheme 10) that would depend on

the lone pair electrons from one of the oxygen atoms bonded to the metal center for stabilization. This mechanism can account for the lack of linear dimer due to steric hindrance from the Cp* ligand, and can also account for the inability to isolate any intermediate species due to the instability of the carbocations. We would propose that the addition of the first styrene molecule is the rate limiting step for this reaction. Although we do not have enough evidence to fully rule out or confirm any of the proposed mechanisms, it appears that the carbocation mechanism may be the most likely.

Scheme 39. Proposed Carbocation Mechanism for Styrene Dimerization



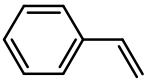
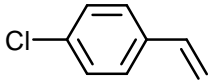
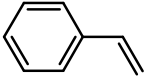
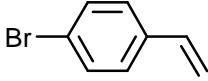
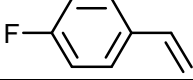
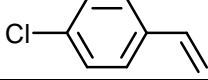
F. Attempted Codimerization of *Para*-Substituted Styrenes

Dozens of cross-coupling reactions exist, but they are not without problems. They typically have significant (usually stoichiometric) production of side products such as acids or alcohols.²⁴ Codimerization of olefins is an area that is of great synthetic interest, but is one of the most challenging due to the large production of unwanted homodimers and isomers. One of the most common codimerization reactions involving styrene is hydrovinylation, which is the addition of ethene in order to obtain 3-aryl-1-butenes. These compounds are desired intermediates in the production of 2-arylpropionic acids,^{30c, 33} which are anti-inflammatories, and are monomers for the production of syndiotactic polymers.³³

We attempted to codimerize the various *para*-substituted styrenes, **9a-d**, using the same conditions for the homodimerization reactions (outlined in Scheme 35) hoping that some selectivity might occur in the products. For each set of substrates, the reaction was run at conditions that were ideal for one component or the other. For example, in the case of styrene (**9a**) and 4-bromostyrene (**9d**), the reaction was run at 50 °C which is the favored temperature for styrene (**9a**), and at 70 °C which is the favored temperature for 4-bromostyrene (**9d**). The results are summarized in Table 4.

In all cases, there seemed to be some preference for the higher molecular weight dimers. In most cases (except for the reaction of **9a** with **9d** at 50 °C), there was a slight preference for the codimer products. For the case of styrene (**9a**) combined with 4-chlorostyrene (**9c**), there is virtually no change in the product ratios when the reaction conditions are altered. In this case, there seems to be a selectivity for defined product ratios.

Table 4. Product ratios for styrene codimerization reactions.

Substrates		Reaction Conditions	Product Ratios ^a		
A	B		2A	AB	2B
		RT, 21.5 h.	1	2.0	1.7
		50 °C, 22 h.	1	1.9	1.6
		50 °C, 22 h.	1	2.4	2.7
		70 °C, 22 h.	1 ^b	2.8	3.2
		RT, 21.5 h.	1	1.8	1.5

^aProduct ratios are based on GC-MS peak area.

^bThe styrene homodimer is a combination of 3 small isomer peaks. There was no preference for one isomer in this reaction.

Interestingly, for the reaction of styrene (**9a**) with 4-bromostyrene (**9d**) at 50 °C, there was no unreacted **9d**. As noted previously for the homodimerization of **9d**, the reaction at 50 °C resulted in a large amount of unreacted starting material and very little product, which is why the reaction needed to be run at 70 °C. In this case, somehow the presence of styrene influenced the homodimerization of **9d** under milder conditions than were previously required. Another thing to note from this reaction is that the lack of significant production of styrene dimer (**10d**) at 70 °C indicates the likelihood of polymerization under harsher reaction conditions.

Due to the lack of selectivity we were hoping for, we did not attempt to isolate the codimer products at this time. It is likely that they could be isolated on a long silica gel column using hexanes as defined in the procedure for isolating the homodimers. The lack of selectivity could be attributed to the speed at which the dimerization would presumably occur in the proposed mechanism in Scheme 39.

G. Conclusions

We have successfully prepared, isolated and obtained the crystal structures for $\text{Cp}^*\text{W}(\text{CO})_3\text{CH}_3$ (**2**) and $\text{Cp}^*\text{W}(=\text{O})_2\text{CH}_3$ (**1**) which have not been previously published. Although the reaction scope appears to be limited, **1** has been shown to successfully dimerize styrene and some *para*-substituted styrenes to the desired 1,3-diaryl-1-butene products which has never been previously documented for a metal dioxo complex. The crystal structure was obtained for *trans*-1,3-di-(4-bromophenyl)-1-butene which confirmed the presence of the *trans* double bond in the dimer products.

We attempted to selectively codimerize these *para*-substituted styrenes. Although the selectivity we were hoping for was not obtained, there was some selectivity demonstrated in the product ratios. Although we did not isolate these codimers, they would be easily isolated by column chromatography.

III. FUTURE RESEARCH

The work presented in this thesis provides many opportunities for continued research. One item to focus on would be elucidation of the reaction mechanism. One way to do this might be to modify the Cp* ligand to CpBz or Cp*i*Pr (or any other Cp') to see if the reaction can be opened to a broader class of olefins. Monitoring the ¹H NMR signal of the methyl protons during the reaction might help to indicate which possible mechanism is occurring.

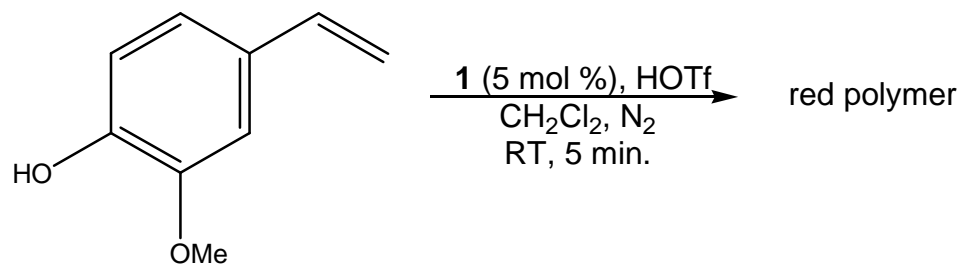
Another item would be a comparison with the analogous molybdenum complexes. It would be interesting to see if Cp*Mo(=O)₂CH₃ can also be utilized as a dimerization catalyst. Alternatively, it would be useful to see if **1** is an effective epoxidation catalyst compared to other metal dioxo complexes. Also, it has been shown that Cp*Mo(CO)₃CH₃ is an effective catalyst precursor for olefin epoxidation,^{17a} but we have not found documentation where the same tungsten carbonyl complex (**2**) has been evaluated for this purpose. (The analogous complex CpW(CO)₃CH₃ has been evaluated and found to have much lower activity than Cp*Mo(CO)₃CH₃).

One of the most interesting items for future research is the potential for living polymerization using **1**. Tungsten complexes are known to form living polymer chains during ring-opening reactions.⁴⁸ Somewhat more recently, a tungsten complex has been documented to form a living polymer using a phenylacetylene derivative.⁴⁹

We observed the polymerization of 4-methoxystyrene and 4-methylstyrene in their NMR spectra. More remarkably, we have visually observed the formation of an insoluble polymer when using 2-methoxy-4-vinylphenol as the substrate (Scheme 40). Upon addition of a second charge of substrate, the previously formed polymer appears to

re-react with the newly added substrate. Because of this observation, samples have been isolated and prepared for GPC analysis to determine if the molecular weight of the polymer can be controlled.

Scheme 40.



IV. EXPERIMENTAL SECTION

General Comments. All operations were carried out under N₂ using either a Vacuum Atmospheres glove box or standard Schlenk techniques on a double manifold vacuum line. Reagent grade solvents were distilled from an appropriate drying agent under N₂ before use. THF and toluene were distilled from sodium/benzophenone. CH₂Cl₂ was distilled from CaH₂. Hexanes were stirred with concentrated H₂SO₄, washed with water, saturated aqueous Na₂CO₃, and again with water, pre-dried with anhydrous MgSO₄ and distilled from sodium benzophenone ketyl with tetraethylene glycol dimethyl ether added. DMF was dried of 4 Å molecular sieves, vacuum transferred and stored under N₂. HOTf was stored under N₂. CH₃I was stored over 4 Å molecular sieves and purged with N₂ immediately prior to use. Et₂O, CDCl₃, Cp*H, *n*BuLi (2.5 M in hexanes), W(CO)₆, Al₂O₃, silica gel, styrene, 4-fluorostyrene, 4-chlorostyrene, 4-bromostyrene and 4-vinylbenzylchloride were used without further purification. ¹H and ¹³C NMR spectra were recorded on a Varian 300 MHz or 400 MHz FT-NMR spectrometer. Mass spectroscopy (GC-MS) data were obtained on a Hewlett-Packard 6850 Gas Chromatograph.

Preparation of 2. THF (50 mL) was added to a round bottom Schlenk flask equipped with a magnetic stirring bar and a rubber septum under N₂. Cp*H (2 mL, 13 mmol) was added via syringe through the septum. The solution was cooled to -78 °C and *n*-butyl lithium (5.5 mL of a 2.5 M solution in hexanes, 14 mmol) was added dropwise via syringe through the septum. The solution was allowed to come to room temperature with constant stirring for 1 h. The solvent was evaporated and the pale yellow residue dried

for 1 h under vacuum. **3** (4.481 g, 12.73 mmol) and DMF (50 mL) were added to the flask, and the rubber septum was replaced with a reflux condenser. The mixture was heated at reflux for 1.5 h. The resulting orange solution was cooled to room temperature and the reflux condenser was replaced with a rubber septum. The solvent was removed under vacuum to give an orange oil which was dried under vacuum at 60 °C for 1 h. The residue was dissolved in THF (50 mL) and methyl iodide (3 mL, 48 mmol) was added via syringe through the septum. The septum was replaced with a reflux condenser and the mixture was heated at reflux for 2 h. The solvent was evaporated from the yellow-brown solution and the resulting yellow-brown precipitate was dried under vacuum for 1 h. The following operations were done in the air. The precipitate was extracted with several portions of hexanes, the extracts were passed through filter paper and combined. The solvent was evaporated under vacuum to give a crude yellow product. The crude product was dissolved in Et₂O (100 mL) and filtered through a short Al₂O₃ (5 g) column. The filtrate was evaporated under vacuum to give a yellow solid. Recrystallization from Et₂O/hexanes and drying under vacuum for 2 h afforded 3.678 g (69%) of yellow crystals. ¹H NMR (CDCl₃) δ 1.97 (s, 15H, CCH₃), 0.10 (s, 3H, W-CH₃); ¹³C{¹H} NMR (CDCl₃) δ 233.2 (s, CO), 220.3 (s, 2 CO's), 102.9 (s, CCH₃), 10.8 (s, CCH₃), -24.0 (s, W-CH₃).

Preparation of 1. Compound **2** (0.727 g, 1.74 mmol) was dissolved in toluene (25 mL) in a round bottom Schlenk flask equipped with a stir bar and a rubber septum. The flask was placed in a cold water bath, and O₂ was bubbled through the solution while being exposed to UV light (Hanovia mercury lamp) for 1.5 h. The solvent was evaporated

under vacuum and the greenish yellow residue was dried under vacuum for 1 h. The residue was dissolved in CH_2Cl_2 and the crude product was separated on a silica gel column using Et_2O as the eluent. The second, colorless band was collected. The solvent was evaporated under vacuum, and the residue was recrystallized in Et_2O /hexanes to afford 0.157 g (25%) of off-white crystals. ^1H NMR (CDCl_3) δ 2.09 (s, 15H, CCH_3), 0.99 (s, 3H, W-CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 117.8 (s, CCH_3), 15.6 (s, W-CH_3), 11.1 (s, CCH_3).

Catalytic Dimerization of Styrene (9a). Compound **1** (0.037 g, 0.10 mmol) was added to a 50 mL Schlenk tube equipped with a stir bar. CH_2Cl_2 (10 mL) was added, and the mixture was cooled to $-78\text{ }^\circ\text{C}$, degassed, and HOTf (9 μL , 0.1 mmol) was added under N_2 . The mixture was warmed to room temperature and stirred for 1 h. Styrene (0.212 g, 2.04 mmol) was added under N_2 at $-78\text{ }^\circ\text{C}$. The solution was degassed, N_2 reintroduced and the mixture was placed in a $50\text{ }^\circ\text{C}$ oil bath for 21 h. The following operations were done in the air. The solution was filtered through a short silica gel column with CH_2Cl_2 to remove the catalyst. The filtrate was evaporated under vacuum leaving an oily residue. The residue was dissolved in hexane and separated on a silica gel column with 10:1 hexane: CH_2Cl_2 . The solvent was evaporated and the residue dried under vacuum for 4 h yielding 0.077 g (36%) of a clear oil (**10a**). GC-MS [40 $^\circ\text{C}$ (3 min.); 10 $^\circ\text{C}/\text{min}$. \rightarrow 250 $^\circ\text{C}$ (15 min.)] retention time 19.00 min., m/e 208. ^1H NMR (CDCl_3) δ 7.19 (m, 10H, aromatic), 6.30 (d, $J_{\text{H-H}} = 4.9\text{ Hz}$, 2H, $=\text{CH}$), 3.55 (m, $J_{\text{H-H}} = 6.6\text{ Hz}$, 1H, CHCH_3), 1.38 (d, $J_{\text{H-H}} = 7.1\text{ Hz}$, 3H, CHCH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 145.6, 137.6, 135.3, 128.6, 127.4, 127.1, 126.3, 126.2 (aromatic/vinylic), 42.6 (s, CCH_3), 21.3 (s, CCH_3).

Reaction of Styrene with HOTf. CH_2Cl_2 (4 mL) was added to a 50 mL Schlenk tube equipped with a stir bar. The solution was cooled to $-78\text{ }^\circ\text{C}$, degassed, and HOTf (3 μL , 0.03 mmol) introduced under N_2 . Compound **9a** (65 μL , 0.57 mmol) was added under N_2 at $-78\text{ }^\circ\text{C}$. The solution was degassed, N_2 reintroduced and the mixture was placed in a $50\text{ }^\circ\text{C}$ oil bath for 45 h. The following operations were done in the air. The solution was filtered through a short silica gel column, and the resulting solution analyzed by GC-MS. GC-MS [40 $^\circ\text{C}$ (3 min.); 10 $^\circ\text{C}/\text{min.}$ \rightarrow 250 $^\circ\text{C}$ (15 min.)] several peaks retention time 16.35 to 19.32 min, m/e 208; 21.00 min., m/e 280; 22.91 min., m/e 279.

Catalytic Dimerization of 4-Fluorostyrene (9b). Tungsten compound **1** (0.035 g, 0.096 mmol) was added to a 50 mL Schlenk tube equipped with a stir bar. CH_2Cl_2 (10 mL) was added. The mixture was cooled to $-78\text{ }^\circ\text{C}$, degassed, and HOTf (9 μL , 0.1 mmol) was added under N_2 . The mixture was warmed to room temperature and stirred for 1 h. 4-Fluorostyrene (0.250 g, 2.05 mmol) was added under N_2 at $-78\text{ }^\circ\text{C}$. The solution was degassed, N_2 reintroduced and the mixture was stirred at room temperature for 23 h. The following operations were done in the air. The solution was filtered through a short silica gel column with CH_2Cl_2 to remove the catalyst. The filtrate was evaporated under vacuum leaving an oily residue. The residue was dissolved in CH_2Cl_2 and separated on a silica gel column with hexane. The solvent was evaporated and the residue dried under vacuum for 4 h yielding 0.144 g (58%) of a clear oil (**10b**) that glows under UV light. GC-MS [40 $^\circ\text{C}$ (3 min.); 10 $^\circ\text{C}/\text{min.}$ \rightarrow 250 $^\circ\text{C}$ (15 min.)] retention time 18.91 min., m/e 244. ^1H NMR (CDCl_3) δ 7.30 and 7.03 (m, 8H, aromatic), 6.35 (m, $J_{\text{H-H}} = 16.0\text{ Hz}$, 6.5 Hz, 2H, =CH), 3.65 (m, $J_{\text{H-H}} = 6.8\text{ Hz}$, 1H, CHCH₃), 1.49 (d, $J_{\text{H-H}} = 6.9\text{ Hz}$, 3H, CHCH₃);

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 163.5, 162.8, 161.0, 160.4, 141.1, 134.9, 133.7, 128.9, 127.7, 115.5 (aromatic/vinylic), 42.0 (s, CCH_3), 21.5 (s, CCH_3).

Reaction of 9b with HOTf. CH_2Cl_2 (3.5 mL) was added to a 50 mL Schlenk tube equipped with a stir bar. The solution was cooled to $-78\text{ }^\circ\text{C}$, degassed, and HOTf (3 μL , 0.03 mmol) introduced under N_2 . Compound **9b** (70 μL , 0.59 mmol) was added under N_2 at $-78\text{ }^\circ\text{C}$. The solution was degassed, N_2 reintroduced and the mixture was allowed to stir for 20 h. The following operations were done in the air. The solution was filtered through a short silica gel column, and the resulting solution analyzed by GC-MS and NMR. GC-MS [40 $^\circ\text{C}$ (3 min.); 10 $^\circ\text{C}/\text{min}$. \rightarrow 250 $^\circ\text{C}$ (15 min.)] retention time 19.47 min, m/e 244; several peaks 24.80 to 28.627 min., m/e 488. ^1H NMR (CDCl_3) δ 7 (very broad aromatic peaks), 1.4 (broad methyl peaks).

Catalytic Dimerization of 4-Chlorostyrene (9c). Tungsten complex **1** (0.037 g, 0.10 mmol) was added to a 50 mL Schlenk tube equipped with a stir bar. CH_2Cl_2 (10 mL) was added. The mixture was cooled to $-78\text{ }^\circ\text{C}$, degassed, and HOTf (9 μL , 0.1 mmol) was added under N_2 . The mixture was warmed to room temperature and stirred for 1 h. 4-Chlorostyrene (0.273 g, 2.24 mmol) was added under N_2 at $-78\text{ }^\circ\text{C}$. The solution was degassed, N_2 reintroduced and the mixture was stirred at room temperature for 26 h. The following operations were done in the air. The solution was filtered through a short silica gel column with CH_2Cl_2 to remove the catalyst. The filtrate was evaporated under vacuum leaving an oily residue. The residue was dissolved in hexane and separated on a silica gel column with hexane. The solvent was evaporated and the residue dried under

vacuum for 4 h yielding 0.157 g (56%) of a white solid (**10c**) which glows under UV light. GC-MS [40 °C (3 min.); 10 °C/min. → 250 °C (30 min.)] retention time 23.47 min., m/e 276. ¹H NMR (CDCl₃) δ 7.15 (m, 8H, aromatic), 6.22 (d, J_{H-H} = 5.0 Hz, 2H, =CH), 3.50 (m, J_{H-H} = 7.0 Hz, 5.1 Hz, 1H, CHCH₃), 1.34 (d, J_{H-H} = 7.3 Hz, 3H, CHCH₃); ¹³C{¹H} NMR (CDCl₃) δ 143.8, 135.8, 135.3, 132.8, 132.0, 128.7, 127.8, 127.4 (aromatic/vinylic), 42.0 (s, CCH₃), 21.1 (s, CCH₃).

Reaction of 9c with HOTf. CH₂Cl₂ (3.5 mL) was added to a 50 mL Schlenk tube equipped with a stir bar. The solution was cooled to -78 °C, degassed, and HOTf (3 μL, 0.03 mmol) introduced under N₂. Compound **9c** (72 μL, 0.60 mmol) was added under N₂ at -78 °C. The solution was degassed, N₂ reintroduced and the mixture was stirred at room temperature for 20 h. The following operations were done in the air. The solution was filtered through a short silica gel column, and the resulting solution analyzed by GC-MS and ¹H NMR. GC-MS [40 °C (3 min.); 10 °C/min. → 250 °C (35 min.)] retention time 23.62 min, m/e 276; 28.29 min., m/e 281; 37.63, 40.43, 41.74 and 50.77 min., m/e 416; 47.48 and 47.76 min., m/e 414. ¹H NMR (CDCl₃) δ 6.8 (very broad aromatic peaks), 1.6 (broad methyl peaks).

Catalytic Dimerization of 4-Bromostyrene (9d). Tungsten complex **1** (0.038 g, 0.10 mmol) was added to a 50 mL Schlenk tube equipped with a stir bar. CH₂Cl₂ (10 mL) was added. The mixture was cooled to -78 °C, degassed, and HOTf (9 μL, 0.1 mmol) was added under N₂. The mixture was warmed to room temperature and stirred for 1 h. 4-Bromostyrene (0.390 g, 2.13 mmol) was added under N₂ at -78 °C. The solution was

degassed, N₂ reintroduced and the mixture was placed in a 70 °C oil bath for 21 h. The following operations were done in the air. The solution was filtered through a short silica gel column with CH₂Cl₂ to remove the catalyst. The filtrate was concentrated and the resulting solution was separated on a silica gel column with hexane. The solvent was evaporated and the residue dried under vacuum for 3 h yielding 0.327 g (84%) of an off-white solid (**10d**) which glows under UV light. GC-MS [40 °C (3 min.); 10 °C/min. → 250 °C (15 min.)] retention time 25.80 min., m/e 366. ¹H NMR (CDCl₃) δ 7.21 (m, 8H, aromatic), 6.22 (d, J_{H-H} = 2.9 Hz, 2H, =CH), 3.49 (m, J_{H-H} = 7.3 Hz, 2.8 Hz, 1H, CHCH₃), 1.34 (d, J_{H-H} = 7.0 Hz, 3H, CHCH₃); ¹³C{¹H} NMR (CDCl₃) δ 144.2, 136.2, 135.3, 131.6, 129.0, 127.8, 127.7 (aromatic/vinylic), 42.0 (s, CCH₃), 20.9 (s, CCH₃).

Reaction of 9d with HOTf. CH₂Cl₂ (3.5 mL) was added to a 50 mL Schlenk tube equipped with a stir bar. The solution was cooled to -78 °C, degassed, and HOTf (3 μL, 0.03 mmol) introduced under N₂. Compound **9d** (79 μL, 0.60 mmol) was added under N₂ at -78 °C. The solution was degassed, N₂ reintroduced and the mixture was placed in a 70 °C oil bath for 20.5 h. The following operations were done in the air. The solution was filtered through a short silica gel column, and the resulting solution analyzed by GC-MS and ¹H NMR. GC-MS [40 °C (3 min.); 10 °C/min. → 250 °C (15 min.)] retention times 24.79, 24.94 and 26.49 min, m/e 366. ¹H NMR (CDCl₃) δ 6.8 (very broad aromatic peaks), 1.6 (broad methyl peaks).

Catalytic Dimerization of 4-Vinylbenzyl Chloride (9e). Tungsten complex **1** (0.037 g, 0.10 mmol) was added to a 50 mL Schlenk tube equipped with a stir bar. CH_2Cl_2 (10 mL) was added. The mixture was cooled to $-78\text{ }^\circ\text{C}$, degassed, and HOTf (9 μL , 0.1 mmol) was added under N_2 . The mixture was warmed to room temperature and stirred for 1 h. 4-Vinylbenzyl chloride (0.326 g, 2.14 mmol) was added under N_2 at $-78\text{ }^\circ\text{C}$. The solution was degassed, N_2 reintroduced and the mixture was stirred at room temperature for 26 h. The following operations were done in the air. The solution was filtered through a short silica gel column with CH_2Cl_2 to remove the catalyst. The filtrate was concentrated and the resulting solution was separated on a silica gel column with 4:1 hexane: CH_2Cl_2 . The solvent was evaporated and the residue dried under vacuum for 3 h yielding 0.172 g (53%) of a clear oil (**10e**) which glows under UV light. GC-MS [40 $^\circ\text{C}$ (3 min.); 10 $^\circ\text{C}/\text{min}$. \rightarrow 250 $^\circ\text{C}$ (30 min.)] retention time 27.68 min., m/e 304. ^1H NMR (CDCl_3) δ 7.36 (m, 8H, aromatic), 6.45 (d, $J_{\text{H-H}} = 6.5\text{ Hz}, 5.4\text{ Hz}, 2\text{H}, =\text{CH}$), 4.61 (d, $J_{\text{H-H}} = 9.0\text{ Hz}, 4\text{H}, \text{Ph-CH}_2\text{Cl}$), 3.71 (m, $J_{\text{H-H}} = 6.9\text{ Hz}, 5.1\text{ Hz}, 1\text{H}, \text{CHCH}_3$), 1.52 (d, $J_{\text{H-H}} = 7.1\text{ Hz}, 3\text{H}, \text{CHCH}_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 145.7, 137.5, 136.1, 135.5, 135.3, 128.8, 128.7, 128.0, 127.6, 126.4 (aromatic/vinylic), 46.1 (s, PhCH_2Cl), 42.2 (s, CCH_3), 21.0 (s, CCH_3).

Reaction of 9e with HOTf. CH_2Cl_2 (3.5 mL) was added to a 50 mL Schlenk tube equipped with a stir bar. The solution was cooled to $-78\text{ }^\circ\text{C}$, degassed, and HOTf (3 μL , 0.03 mmol) introduced under N_2 . Compound **9e** (85 μL , 0.60 mmol) was added under N_2 at $-78\text{ }^\circ\text{C}$. The solution was degassed, N_2 reintroduced and the mixture was stirred at room temperature for 24 h. The following operations were done in the air. The solution

was filtered through a short silica gel column, and the resulting solution analyzed by GC-MS and ^1H NMR. GC-MS [40 °C (3 min.); 10 °C/min. \rightarrow 250 °C (30 min.)] retention time 27.86 min. (very small peak), m/e 304. ^1H NMR (CDCl_3) δ 6.8 (very broad aromatic peaks), 4.5 (broad PhCH_2Cl), 1.6 (broad methyl peaks).

Catalytic Codimerization of 9a with 9c.

Method A. Tungsten complex **1** (0.010 g, 0.027 mmol) was added to a 50 mL Schlenk tube equipped with a stir bar. CH_2Cl_2 (3.5 mL) was added. The mixture was cooled to -78 °C, degassed, and HOTf (3 μL , 0.03 mmol) was added under N_2 . The mixture was warmed to room temperature and stirred for 1 h. Compound **9a** (35 μL , 0.31 mmol) and compound **9c** (35 μL , 0.29 mmol) were added under N_2 at -78 °C. The solution was degassed, N_2 reintroduced and the mixture was stirred at room temperature for 21.5 h. The following operations were done in the air. The solution was filtered through a short silica gel column with CH_2Cl_2 to remove the catalyst and the filtrate was analyzed by GC-MS. GC-MS [40 °C (3 min.); 10 °C/min. \rightarrow 250 °C (35 min.)] retention time 18.95 min., m/e 208; 21.13 min., m/e 242; 23.36 min., m/e 276.

Method B. Tungsten complex **1** (0.010 g, 0.027 mmol) was added to a 50 mL Schlenk tube equipped with a stir bar. CH_2Cl_2 (3.5 mL) was added. The mixture was cooled to -78 °C, degassed, and HOTf (3 μL , 0.03 mmol) was added under N_2 . The mixture was warmed to room temperature and stirred for 1 h. Compound **9a** (35 μL , 0.31 mmol) and compound **9c** (35 μL , 0.29 mmol) were added under N_2 at -78 °C. The solution was degassed, N_2 reintroduced and the mixture was placed in a 50 °C oil bath for 22 h. The following operations were done in the air. The solution was filtered through a short silica

gel column with CH_2Cl_2 to remove the catalyst and the filtrate was analyzed by GC-MS. GC-MS [40 °C (3 min.); 10 °C/min. → 250 °C (30 min.)] retention time 18.91 min., m/e 208; 21.11 min., m/e 242; 23.34 min., m/e 276.

Reaction of 9a and 9c with HOTf.

Method A. CH_2Cl_2 (3.5 mL) was added to a 50 mL Schlenk tube equipped with a stir bar. The mixture was cooled to -78 °C, degassed, and HOTf (3 μL , 0.03 mmol) was added under N_2 . Compound **9a** (35 μL , 0.31 mmol) and compound **9c** (35 μL , 0.29 mmol) were added under N_2 at -78 °C. The solution was degassed, N_2 reintroduced and the mixture was stirred at room temperature for 21.5 h. The following operations were done in the air. The solution was filtered through a short silica gel column with CH_2Cl_2 to remove the catalyst and the filtrate was analyzed by GC-MS. GC-MS [40 °C (3 min.); 10 °C/min. → 250 °C (35 min.)] retention time 21.49 min. (small peak), m/e 242; 23.50 min. (small peak), m/e 276.

Method B. CH_2Cl_2 (3.5 mL) was added to a 50 mL Schlenk tube equipped with a stir bar. The mixture was cooled to -78 °C, degassed, and HOTf (3 μL , 0.03 mmol) was added under N_2 . Compound **9a** (35 μL , 0.31 mmol) and compound **9c** (35 μL , 0.29 mmol) were added under N_2 at -78 °C. The solution was degassed, N_2 reintroduced and the mixture was placed in a 50 °C oil bath for 22 h. The following operations were done in the air. The solution was filtered through a short silica gel column with CH_2Cl_2 to remove the catalyst and the filtrate was analyzed by GC-MS. GC-MS [40 °C (3 min.); 10 °C/min. → 250 °C (35 min.)] retention time 21.28 min. (small peak), m/e 242; 23.40 min. (small peak), m/e 276.

Catalytic Codimerization of 9a and 9d.

Method A. Tungsten complex **1** (0.010 g, 0.027 mmol) was added to a 50 mL Schlenk tube equipped with a stir bar. CH₂Cl₂ (3.5 mL) was added. The mixture was cooled to -78 °C, degassed, and HOTf (3 μL, 0.03 mmol) was added under N₂. The mixture was warmed to room temperature and stirred for 1 h. Compound **9a** (35 μL, 0.31 mmol) and compound **9d** (40 μL, 0.31 mmol) were added under N₂ at -78 °C. The solution was degassed, N₂ reintroduced and the mixture was placed in a 50 °C oil bath for 22 h. The following operations were done in the air. The solution was filtered through a short silica gel column with CH₂Cl₂ to remove the catalyst and the filtrate was analyzed by GC-MS. GC-MS [40 °C (3 min.); 10 °C/min. → 250 °C (20 min.)] retention time 18.91 min., m/e 208; 22.19 min., m/e 286; 25.60 min., m/e 366.

Method B. Tungsten complex **1** (0.010 g, 0.027 mmol) was added to a 50 mL Schlenk tube equipped with a stir bar. CH₂Cl₂ (3.5 mL) was added. The mixture was cooled to -78 °C, degassed, and HOTf (3 μL, 0.03 mmol) was added under N₂. The mixture was warmed to room temperature and stirred for 1 h. Compound **9a** (35 μL, 0.31 mmol) and compound **9d** (40 μL, 0.31 mmol) were added under N₂ at -78 °C. The solution was degassed, N₂ reintroduced and the mixture was placed in a 70 °C oil bath for 22 h. The following operations were done in the air. The solution was filtered through a short silica gel column with CH₂Cl₂ to remove the catalyst and the filtrate was analyzed by GC-MS. GC-MS [40 °C (3 min.); 10 °C/min. → 250 °C (20 min.)] retention time 18.97 min. (small peak), m/e 208; 22.19 min., m/e 286; 25.60 min., m/e 366.

Catalytic Codimerization of 9c and 9b. Tungsten complex **1** (0.010 g, 0.027 mmol) was added to a 50 mL Schlenk tube equipped with a stir bar. CH₂Cl₂ (3.5 mL) was added. The mixture was cooled to -78 °C, degassed, and HOTf (3 μL, 0.03 mmol) was added under N₂. The mixture was warmed to room temperature and stirred for 1 h. Compound **9c** (35 μL, 0.29 mmol) and compound **9b** (35 μL, 0.29 mmol) were added under N₂ at -78 °C. The solution was degassed, N₂ reintroduced and the mixture was stirred at room temperature for 22 h. The following operations were done in the air. The solution was filtered through a short silica gel column with CH₂Cl₂ to remove the catalyst and the filtrate was analyzed by GC-MS. GC-MS [40 °C (3 min.); 10 °C/min. → 250 °C (35 min.)] retention time 18.92 min., m/e 244; 21.18 min., m/e 260; 23.33 min., m/e 276.

Table 5. Crystal Data and Structure Refinement for **2**.

Identification code	yicac	
Empirical formula	C ₁₄ H ₁₈ O ₃ W	
Formula weight	418.13	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 22.6322(4) Å	α = 90°.
	b = 12.7771(2) Å	β = 90°.
	c = 9.8184(2) Å	γ = 90°.
Volume	2839.23(9) Å ³	
Z	8	
Density (calculated)	1.956 Mg/m ³	
Absorption coefficient	15.070 mm ⁻¹	
F(000)	1600	
Crystal size	0.38 x 0.27 x 0.13 mm ³	
Theta range for data collection	3.97 to 67.08°.	
Index ranges	0 ≤ h ≤ 25, 0 ≤ k ≤ 14, 0 ≤ l ≤ 11	
Reflections collected	23195	
Independent reflections	2615 [R(int) = 0.0242]	
Completeness to theta = 67.08°	97.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.2447 and 0.0693	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2615 / 7 / 338	
Goodness-of-fit on F ²	1.135	
Final R indices [I > 2σ(I)]	R1 = 0.0146, wR2 = 0.0375	
R indices (all data)	R1 = 0.0147, wR2 = 0.0376	
Absolute structure parameter	0.00	
Extinction coefficient	0.000202(10)	
Largest diff. peak and hole	1.230 and -0.573 e.Å ⁻³	

Table 6. Crystal Data and Structure Refinement for **1**.

Identification code	yib	
Empirical formula	C ₁₁ H ₁₈ O ₂ W	
Formula weight	366.10	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /m	
Unit cell dimensions	a = 7.7677(10) Å	α = 90°.
	b = 8.8575(11) Å	β = 107.0390(10)°.
	c = 8.7206(11) Å	γ = 90°.
Volume	573.66(13) Å ³	
Z	2	
Density (calculated)	2.119 Mg/m ³	
Absorption coefficient	10.042 mm ⁻¹	
F(000)	348	
Crystal size	0.28 x 0.26 x 0.18 mm ³	
Theta range for data collection	3.09 to 31.94°.	
Index ranges	-11 ≤ h ≤ 10, 0 ≤ k ≤ 12, 0 ≤ l ≤ 12	
Reflections collected	9207	
Independent reflections	1954 [R(int) = 0.0226]	
Completeness to theta = 31.94°	93.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2651 and 0.1654	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1954 / 0 / 108	
Goodness-of-fit on F ²	0.956	
Final R indices [I > 2σ(I)]	R1 = 0.0119, wR2 = 0.0319	
R indices (all data)	R1 = 0.0124, wR2 = 0.0321	
Largest diff. peak and hole	0.664 and -1.563 e.Å ⁻³	

Table 7. Crystal Data and Structure Refinement for **10d**.

Identification code	yiva	
Empirical formula	C ₁₆ H ₁₄ Br ₂	
Formula weight	366.09	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.4642(2) Å	α = 90°.
	b = 7.8503(3) Å	β = 90°.
	c = 33.4920(10) Å	γ = 90°.
Volume	1436.66(9) Å ³	
Z	4	
Density (calculated)	1.693 Mg/m ³	
Absorption coefficient	6.974 mm ⁻¹	
F(000)	720	
Crystal size	0.52 x 0.35 x 0.07 mm ³	
Theta range for data collection	2.64 to 67.50°.	
Index ranges	-6 ≤ h ≤ 6, 0 ≤ k ≤ 9, 0 ≤ l ≤ 40	
Reflections collected	11346	
Independent reflections	2555 [R(int) = 0.0436]	
Completeness to theta = 67.50°	98.7 %	
Absorption correction	Numerical	
Max. and min. transmission	0.6410 and 0.1222	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2555 / 44 / 150	
Goodness-of-fit on F ²	1.101	
Final R indices [I > 2σ(I)]	R1 = 0.0742, wR2 = 0.1918	
R indices (all data)	R1 = 0.0747, wR2 = 0.1921	
Absolute structure parameter	0.13(10)	
Largest diff. peak and hole	0.840 and -1.634 e.Å ⁻³	

V. REFERENCES

1. (a) Vezzosi, S.; Ferré, A. G.; Crucianelli, M.; Crestini, C.; Saladino, R. *J. Catal.* **2008**, *257*, 262. (b) Jimtaisong, A.; Luck, R. L. *Inorg. Chem.* **2006**, *45*, 10391. (c) Martins, A. M.; Romão, C. C.; Abrantes, M.; Azevedo, M. C.; Cui, J.; Dias, A. R.; Duarte, M. T.; Lemos, M. A.; Lourenço, T.; Poli, R. *Organometallics* **2005**, *24*, 2582. (d) Kühn, F. E.; Santos, A. M.; Herrmann, W. A. *Dalton Trans.* **2005**, 2483. (e) Abrantes, M.; Valente, A.; Pillinger, M.; Gonçalves, I. S.; Rocha, J.; Romão, C. C. *J. Catal.* **2002**, *209*, 237. (f) Trost, M. K.; Bergman, R. G. *Organomet.* **1991**, *10*, 1172. (g) Mimoun, H. *Catal. Today* **1987**, 281. (h) Rappé, A. K.; Goddard III, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 5115.
2. (a) Fischer, E. O.; Vigoureux, S. *Chem. Ber.* **1958**, *91*, 1343. (b) Corradini, P.; Allegra, G. *J. Am. Chem. Soc.*, **1959**, *81*, 5510. (c) Cousins, M.; Green, M. L. H.; *J. Chem. Soc.* **1963**, 889.
3. (a) Sheng, M. N.; Zajacek, G. J. (ARCO), GB 1.136.923, **1968**. (b) Kollar, J. (Halcon), US 3.351.635, **1967**.
4. (a) Landau, R.; Sullivan, G. A.; Brown, D. CHEMTECH **1979**, 602. (b)
5. Mimoun, H.; de Roch, I. S.; Sajus, L. *Tetrahedron*, **1970**, *26*, 37.
6. Sharpless, K. B.; Townsend, J. M.; Williams, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 295.
7. Kühn, F. E.; Groarke, M.; Bencze, É.; Herdtweck, E.; Prazeres, A.; Santos, A. M.; Calhorda, M. J.; Romão, C. C.; Gonçalves, I. S.; Lopes, A. D.; Pillinger, M. *Chem. Eur. J.* **2002**, *8*, 2370.
8. Deubel, D. V.; Frenking, G.; Gisdakis, P.; Herrmann, W. A.; Rösch, N.; Sundermeyer, J. *Acc. Chem. Res.* **2004**, *37*, 645.

9. (a) Mimoun, H. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 734. (b) Sheldon, R. A.; Van Doorn, J. A. *Organomet. Chem.* **1975**, *94*, 115.
10. Chong, A. O.; Sharpless, K. B. *J. Org. Chem.* **1977**, *42*, 1587.
11. (a) Santos, A. M.; Kühn, F. E.; Bruus-Jensen, K.; Lucas, I.; Romão, C. C.; Herdtweck, E. *J. Chem. Soc., Dalton Trans.* **2001**, 1332. (b) Kühn, F. E.; Santos, A. M.; Lopes, A. D.; Gonçalves, I. S.; Herdtweck, E.; Romão, C. C. *J. Mol. Catal. A: Chemical* **2000**, *164*, 25. (c) Kühn, F. E.; Lopes, A. D.; Santos, A. M.; Herdtweck, E.; Haider, J. J.; Romão, C. C.; Gil Santos, A. *J. Mol. Catal. A: Chemical* **2000**, *151*, 147.
12. Kühn, F. E.; Xue, W.; Al-Ajlouni, A.; Santos, A. M.; Zang, S.; Romão, C. C.; Eickerling, G.; Herdtweck, E. *Inorg. Chem.* **2002**, *41*, 4468.
13. Rau, M. S.; Kretz, C. M.; Geoffroy, G. L. *Organomet.* **1993**, *12*, 3447.
14. Bottomley, F.; Boyle, P. D.; Chen, J. *Organomet.* **1994**, *13*, 370.
15. Abrantes, M.; Santos, A. M.; Mink, J.; Kühn, F. E.; Romão, C. C. *Organomet.* **2003**, *22*, 2112.
16. (a) Parkin, G.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 2053. (b) Antonelli, D. M.; Schaefer, W. P.; Parkin, G.; Bercaw, J. E. *J. Organomet. Chem.* **1993**, *462*, 213.
17. (a) Zhao, J.; Santos, A. M.; Herdtweck, E.; Kühn, F. E. *J. Mol. Catal. A: Chemical* **2004**, *222*, 265. (b) Zhao, J.; Herdtweck, E.; Kühn, F. E. *J. Organomet. Chem.* **2006**, *691*, 2199. (c) Freund, C.; Abrantes, M.; Kühn, F. E. *J. Organomet. Chem.* **2006**, *691*, 3718.
18. (a) Trost, B. M. *Science* **1991**, *254*, 1471. (b) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259.

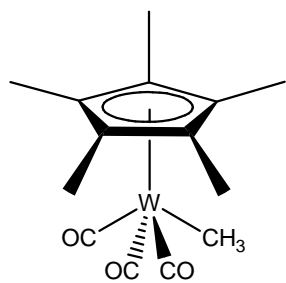
19. (a) Trecker, D. J.; Foote, R. S.; Henry, J. P.; McKeon, J. E. *J. Am. Chem. Soc.* **1966**, *88*:13, 3021. (b) McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*:4, 1315. (c) van der Heijden, H.; Hessen, B.; Orpen, A. G. *J. Am. Chem. Soc.* **1998**, *120*, 1112. (d) Lee, K.; Legzdins, P.; Pamplin, C. B.; Patrick, B. O.; Wada K. *Organometallics* **2005**, *24*, 638. (e) Tobisch, W. *Organometallics* **2007**, *26*, 6529.
20. (a) Small, B. L.; Marcucci, A. J. *Organometallics* **2001**, *20*, 5738. (b) Small, B. L. *Organometallics* **2003**, *22*, 3178. (c) Bhalla G.; Oxgaard, J.; Goddard, W. A. III; Periana, R. A. *Organometallics* **2005**, *24*, 5499.
21. (a) DiRenzo, G. M.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 6225. (b) Doherty, S.; Knight, J. G.; Smyth, C. H.; Harrington, R. W.; Clegg, W. *Organometallics* **2007**, *26*, 5961. (c) Roy, D.; Sunoj, R. B. *Org. Biomol. Chem.* **2010**, *8*, 1040.
22. (a) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627. (b) Sen, A.; Lai, T.-W. *Inorg. Chem.* **1981**, *20*, 4036. (c) Sen, A.; Lai, T.-W. *Organomet.* **1982**, *1*, 415. (d) Sen, A.; Lai, T. *Organometallics* **1983**, *2*, 1059. (e) Sen, A.; Lai, T.-W.; Thomas, R. *J. Organomet. Chem.* **1988**, *358*, 567. (f) Sen, A. *Acc. Chem. Res.* **1988**, *21*, 421. (g) Jiang, Z.; Sen, A. *J. Am. Chem. Soc.* **1990**, *112*, 9655. (h) Jiang, Z.; Sen, A. *Organometallics* **1993**, *12*, 1406.
23. (a) Tsuchimoto, T.; Kamiyama, S.; Negoro, R.; Shirakawa, E.; Kawakami, Y. *Chem. Commun.* **2003**, 852. (b) Kabalka, G. W.; Dong, G.; Venkataiah, B. *Tetrahedron Lett.* **2004**, *45*, 2775. (c) Peng, J.; Li, J.; Qiu, H.; Jiang, J.; Jiang, K.; Mao, J.; Lai, G. *J. Mol. Catal. A: Chemical* **2006**, *225*, 16. (d) Kondo, T.; Takagi, D.; Tsujita, H.; Ura, Y.; Wada, K.; Mitsudo, T. *Angew. Chem. Int. Ed.* **2007**, *46*, 5958.

24. Hillier, A. C.; Grasa, G. A.; Viciu, M. S.; Lee, H. M.; Yang, C.; Nolan, S. P. *J. Organomet. Chem.* **2002**, *653*, 69.
25. Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 778.
26. Moore, E. J.; Pretzer, W. R.; O'Connell, T. J.; Harris, J.; LaBounty, L.; Chou, L.; Grimmer, S. S. *J. Am. Chem. Soc.* **1992**, *114*, 5888.
27. Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529.
28. Jones, J. R.; Symes, T. J. *J. Chem. Soc.* **1971**, 1124.
29. Brookhart, M. S.; Hauptman, E. M. (E. I. du Pont de Nemours and Company) U.S. Pat. 5892101, **1999**.
30. (a) Nomura, N.; Jin, J.; Park, H.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1998**, *120*, 459. (b) Nandi, M.; Jin, J.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1999**, *121*, 9899. (c) RajanBabu, T. V.; Nomura, N.; Jin, J.; Radetich, B.; Park, H.; Nandi, M. *Chem. Eur. J.* **1999**, *5*, 1963.
31. Jin, J.; RajanBabu, T. V. *Tetrahedron* **2000**, *56*, 2145.
32. Faissner, R.; Huttner G. *Eur. J. Inorg. Chem.* **2003**, 2239.
33. Grutters, M. M. P.; van der Vlugt, J. I.; Pei, Y.; Mills, A. M.; Lutz, M.; Spek, A. L.; Müller, C.; Moberg, C.; Vogt, D. *Adv. Synth. Catal.* **2009**, *351*, 2199.
34. (a) Yi, C. S.; He, Z.; Lee, D. W. *Organometallics* **2001**, *20*, 802. (b) He, Z.; Yi, C. S.; Donaldson, W. A. *Org. Lett.* **2003**, *5*, 1567.
35. Mahmoud, K. A.; Rest, A. J. *J. Chem. Soc. Dalton Trans.* **1984**, 187.
36. Faller, J. W.; Ma, Y. *Organometallics* **1988**, *7*, 559.
37. Legzdins, P.; Phillips, E. C.; Sánchez, L. *Organometallics* **1989**, *8*, 940.

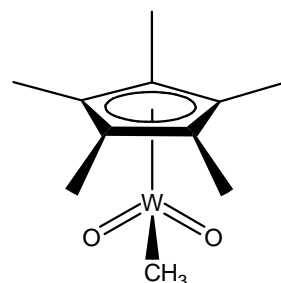
38. (a) Legzdins, P.; Phillips, E. C.; Rettig, S. J.; Sánchez, L.; Trotter, J.; Yee, V. C. *Organometallics* **1988**, *7*, 1877. (b) Faller, J. W.; Ma, Y. *Organometallics* **1989**, *8*, 609. (c) Faller, J. W.; Kucharczyk, R. R.; Ma, Y. *Inorg. Chem.* **1990**, *29*, 1662.
39. (a) King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1971**, *93:19*, 4950. (b) King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1972**, *94:11*, 3773.
40. (a) Yi, C. S.; Wódka, D. *Organometallics* **1996**, *15*, 2 (crystal structure of $[\text{Cp}^*\text{W}(\text{CO})_3(\text{OEt}_3)]^+$). (b) Koola, J. D.; Roddick, D. M. *Organometallics* **1991**, *10*, 591 (crystal structure of $\text{Cp}^*\text{Mo}(\text{CO})_3\text{CF}_3$). (c) Martins, A. M.; Branquinho, R.; Cui, J.; Dias, A. R.; Duarte, T.; Fernandes, J.; Rodrigues, S. S. *J. Organomet. Chem.* **2004**, *689*, 2368 (crystal structure of $\text{CpBzW}(\text{CO})_3\text{CH}_3$).
41. For some examples of this reaction, see: (a) Cousins, M.; Green, M. L. H. *J. Chem. Soc.* **1964**, 1567. (b) Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1984**, *3*, 1313. (c) Legzdins, P.; Rettig, S. J.; Sánchez, L. *Organometallics* **1985**, *4*, 1470. (d) Burkhardt, E. R.; Doney, J. J.; Bergnam, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022.
42. Faller, J. W.; Ma, Y. *J. Organomet. Chem.* **1988**, *340*, 59.
43. Dinoi, C.; Taban, G.; Sözen, P.; Demirhan, F.; Daran, J.; Poli, R. *J. Organomet. Chem.* **2007**, *692*, 3743.
44. Pavia, D. L.; Lampman, G. M.; Kriz, G. S. *Introduction to Spectroscopy*, 3rd Ed.; Thomson Learning, Inc.: United States, **2001**; p. 237.
45. Lee, D. W.; Yi, C. S. *Organometallics* **2010**, *29*, ASAP.
46. (a) Glueck, D. S.; Bergman, R. G. *Organometallics* **1991**, *10*, 1479. (b) Bang, H.; Lynch, T. J.; Basolo, F. *Organometallics* **1992**, *11*, 40.

47. Nyhlén, J.; Privalov, T.; Bäckvall, J.-E. *Chem. Eur. J.* **2009**, *15*, 5220.
48. (a) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1985**, 874. (b) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169. (c) Bazan, G. C.; Schrock R. R. *Macromolecules* **1991**, *24*, 817.
49. Hayano, S.; Masuda, T. *Macromolecules* **1999**, *32*, 7344.

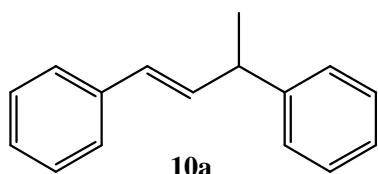
VI. LIST OF SYNTHESIZED COMPOUNDS



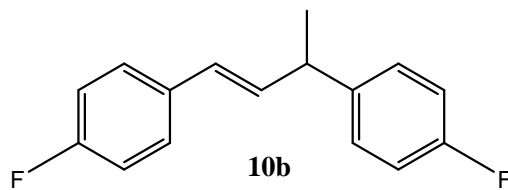
3



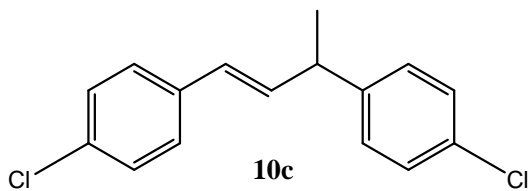
4



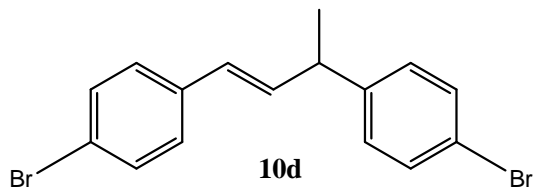
10a



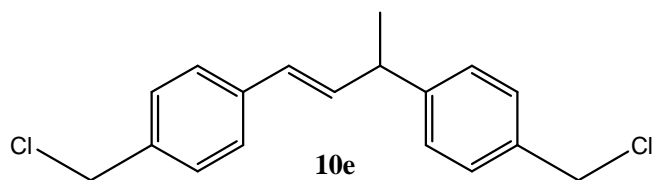
10b



10c



10d



10e