TITANOCENE AND ZIRCONOCENE COMPLEXES FOR THE
CARBON-OXYGEN BOND CLEAVAGE OF LIGNIN MODEL COMPOUNDS

by

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Abstract

The development of well-defined transition metal catalysts for the selective cleavage of carbon-oxygen bonds is a critical challenge for the conversion of lignin to useful chemicals. Oxophilic titanocene complexes are particularly attractive for this application. They have been thoroughly studied in a variety of oxidation states and their reactivity can be dramatically altered by simple modifications of the ancillary ligands. Additionally, titanium is earth-abundant, inexpensive, and relatively non-toxic.

Titanocene-mediated carbon-oxygen bond cleavage of the α-aryloxy ketones 2-phenoxy-1-phenylethanone and 2-(2,6-dimethoxyphenoxy)-1-phenylethanone has been demonstrated. In contrast to previously reported C-O bond cleavage reactions of lignin model compounds, this transformation occurs readily at ambient temperature and pressure.

A titanocene phenoxide enolate complex was obtained as a result of the C-O bond cleavage of 2-phenoxy-1-phenylethanone. Selective cleavage of the Ti-enolate bond was achieved with the use of mild acids. Alternatively, both products of the C-O bond cleavage, acetophenone and phenol, can be released from titanium through the use of strong acids, without displacing the cyclopentadienyl ligands.

Titanocene aryloxide enolate complexes with *ortho*-substituted aryloxy ligands were synthesized. A weakening of the Ti-OAr bond was observed as a result of the increased steric bulk. This allowed for partial or complete protonolysis of both Ti-O bonds with the use of the mild acid lutidinium chloride.

A titanocene alkoxide phenoxide complex was prepared. The elimination of phenol from this compound was expected to lead to the formation of a titanaoxirane intermediate, which would then undergo C-O bond cleavage to yield titanocene phenoxide enolate. This reaction is an essential step in the target catalytic cycle for the C-O bond cleavage of lignin model compounds. However, the desired transformation could not be achieved and related titanocene complexes with substituted aryloxy ligands could not be synthesized.

The use of zirconocene was investigated to alleviate to some of the problems encountered with titanocene chemistry. In particular, the ability of zirconium to form 18-electron complexes resulted in different reactivity as compared to titanocene.

Preface

The majority of the results presented in Chapter 2 have been published and some figures and tables were reproduced with permission from: Desnoyer, A. N.; Fartel, B.; MacLeod, K. C.; Patrick, B. O.; Smith, K. M. *Organometallics* **2012**, *31*, 7625-7628 (© 2012 American Chemical Society). Syntheses of compounds **2.1**, **2.2**, **2.3**, **2.5**, reaction of $Cp_2Ti(BTMSA)$ with ketone **2.2**, and reaction of **2.5** with Me_3SiCl were carried out by the following Smith group researchers: Addison N. Desnoyer (undergraduate), K. Cory MacLeod (graduate), and Wen Zhou (graduate). Computational modelling of some of the complexes and presumed intermediates in Chapters 2 and 3 was performed by Dr. W. Stephen McNeil at the University of British Columbia, Okanagan, using density functional theory at the B3LYP/TZVP level. X-ray data collection for Chapter 3 was carried out by Dr. Brian O. Patrick and Anita Lam at the University of British Columbia, Vancouver.

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List of Abbreviations

δ   chemical shift

η^5 eta-5; coordinated to the metal through 5 atoms

^{1}H   proton

Ar   aryl

B   base

BTMSA   bis(trimethylsilyl)acetylene

Cp   cyclopentadienyl

d   doublet

DBU   1,8-diazabicyclo[5.4.0]undec-7-ene

dd   doublet of doublets

dt   doublet of triplets

Et   ethyl

Et$_2$O   diethyl ether

J   coupling constant

Lut   lutidine (2,6-dimethylpyridine)

m   multiplet

Me   methyl

Mes*   super mesityl (2,4,6-tri-*tert*-butylphenyl)

NMR   nuclear magnetic resonance

OTf   triflate, trifluoromethanesulfonate

OTs   tosylate, *p*-toluenesulfonate

Ph   phenyl

ppm   parts per million

s   singlet

t   triplet

T_1 longitudinal relaxation time

tt   triplet of triplets

THF   tetrahydrofuran

^{t}Bu   *tert*-butyl

X   anionic ligand

Acknowledgements

I would like to thank my supervisor, Dr. Kevin M. Smith, for his help and guidance during my graduate studies, Dr. Stephen McNeil and Dr. James Bailey for insightful comments during the writing of this thesis, and the past and present members of the Smith research group for their assistance in the lab. I am grateful to my partner Ben Ward and friend Roger Sherwood for their support and reassurance, and thank my parents for their endless encouragement.

Chapter 1 Introduction

The objective of this thesis is to study fundamental reactions related to the C-O bond cleavage of molecules that model the β-O-4 linkage. The synthesis and reactivity of metallocene complexes based on titanium and zirconium will be investigated.

1.1   Lignin as renewable potential source of aromatic chemicals

Together with cellulose and hemicelluloses, lignin forms the lignocellulosic material found in plant cell walls. Unlike many other natural biomacromolecules, the lignin polymer is not composed of regularly repeating subunits but is instead amorphous. It is the irregular structure of lignin that allows it to serve as the glue giving plants their structural integrity.[1] Lignin makes up 15-30% of lignocellulosic biomass by weight and is removed from wood when making paper. The pulp and paper industry extracted 50 million tons of lignin in 2004 alone, and approximately 98% of this was burned as fuel.[1] However, lignin is one of the few large naturally occurring sources of aromatic chemicals. In recent years, the valorization of lignin has received growing interest.

The conversion of lignin to useful chemicals has been a challenging research area, mainly due to the disordered structure of lignin. The biosynthesis of the polymer is believed to occur via random phenol radical-radical coupling of the three primary monomers: *p*-coumaryl, coniferyl, and sinapyl alcohols, also known as monolignols[1] (Figure 1.1). A variety of linkages are present in lignin (Figure 1.2), with the β-O-4 linkage comprising more than half of them.[1] The depolymerization of lignin via selective cleavage of these linkage structures and other functionalities could result in direct conversion to a variety of bulk and fine chemicals. The development of highly selective catalysts is essential for an economical processing of lignin to valuable aromatics. Recent studies investigating the degradation of lignin or lignin model compounds take advantage of transition metal-based reactions to perform oxidative,[2-4] reductive,[5-6] or redox-neutral[7-9] processes.

p-coumaryl
alcohol

coniferyl
alcohol

sinapyl
alcohol
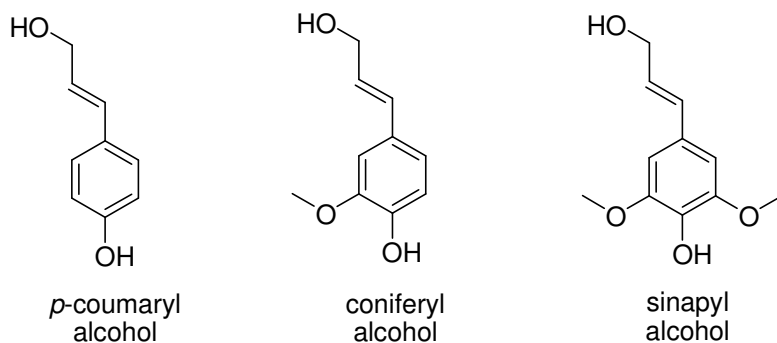
Figure 1.1. The three monolignols.
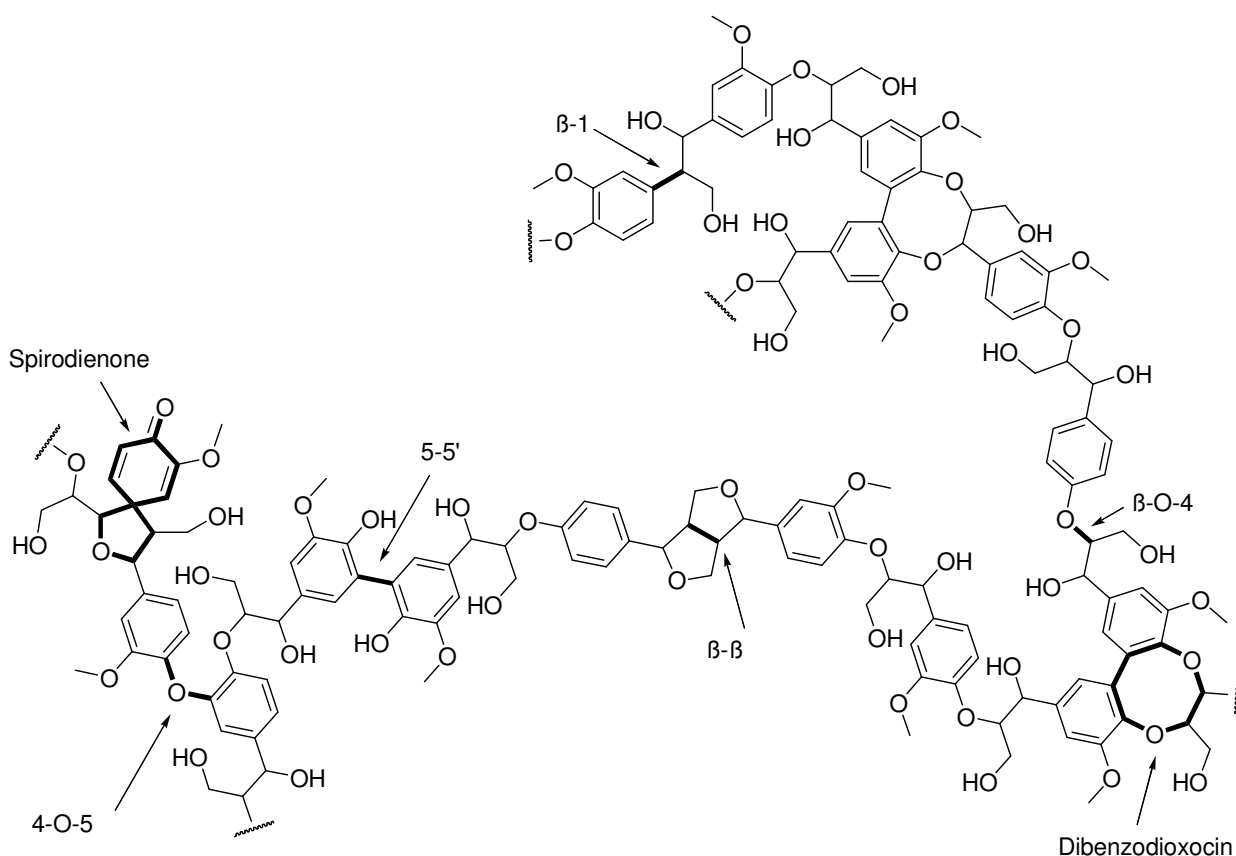
Figure 1.2. Schematic representation of a softwood lignin structure, depicting various linkages.[1]

1.2   Metal-catalyzed redox-neutral C-O bond cleavage of β-O-4 models

Redox-neutral cleavage of the β-O-4 ether bond is particularly attractive because it requires no additional reagents. The reducing equivalents needed to break the C-O bond are obtained from the nearby α-carbinol moiety. To facilitate this move of hydrogen atoms, a suitable catalyst is required. Recent work by Bergmann and Ellman[7] demonstrates the use of a Ru(H)$_2$(CO)(PPh$_3$)(xantphos) catalyst to achieve C-O bond cleavage of 2-phenoxy-1-phenylethanol to yield acetophenone and phenol at 135°C (eq 1.1). The mechanism for this reaction is proposed to proceed via a Ru-catalyzed dehydrogenation of the alcohol to the corresponding α-aryloxyketone, followed by hydrogenolysis of the ketone (Figure 1.3).[10]

$$(1.1)$$
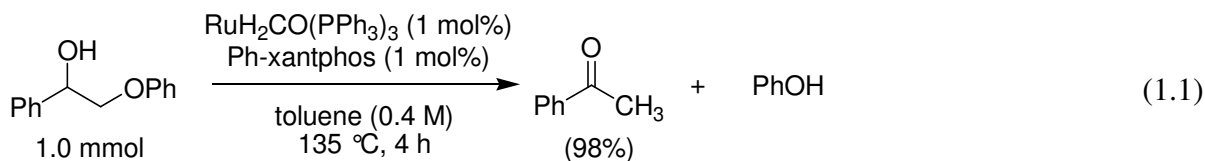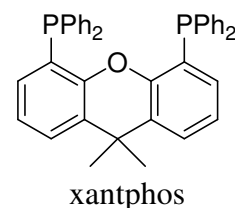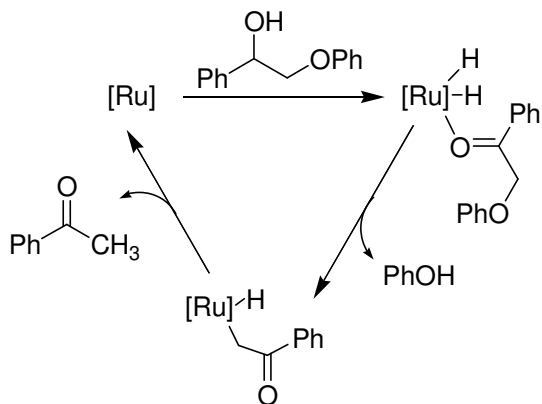
Figure 1.3. Mechanism of ruthenium-catalyzed C-O bond cleavage of 2-phenoxy-1-phenethanol.[7,10]
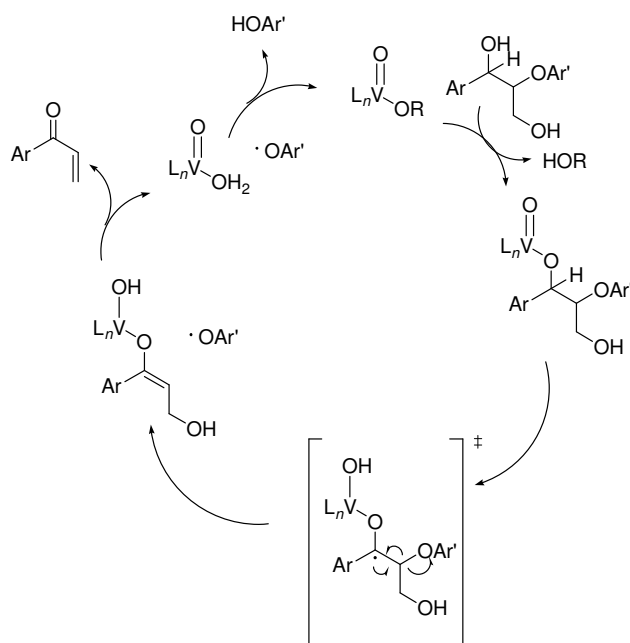
Figure 1.4. Possible mechanism for vanadium-catalyzed C-O bond cleavage. [8]

Another redox-neutral C-O bond cleavage of a β-O-4 lignin model compound with a vanadium catalyst was recently reported by Toste (eq 1.2).[8] Cleavage was achieved at 80°C under aerobic conditions, although the process is formally non-oxidative. The mechanism[8] is thought to proceed via a ligand exchange of the OMe group on vanadium with the benzylic hydroxyl group, followed by hydrogen abstraction from the benzylic position. This forms a vanadium(IV)-hydroxy complex with a ketyl radical, which then eliminates an aryloxy radical. The elimination of the hydroxy group from the resulting enolate, followed by H-atom abstraction from the hydroxo ligand of vanadium by the previously formed ArO· leads to the reforming of the catalyst (Figure 1.4).
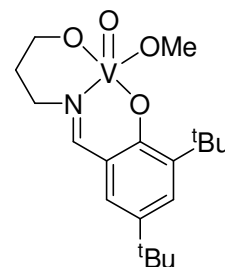
Toste's vanadium catalyst

Unlike in the above example, the corresponding ketone does not undergo C-O bond cleavage under reaction conditions and is thus not an intermediate in the catalytic cycle (eq 1.3). Toste's catalyst was later used by Hanson in an oxidative cleavage of the β-O-4 ether bond (eq 1.4).[3]

$$(1.2)$$

$$(1.3)$$

$$(1.4)$$
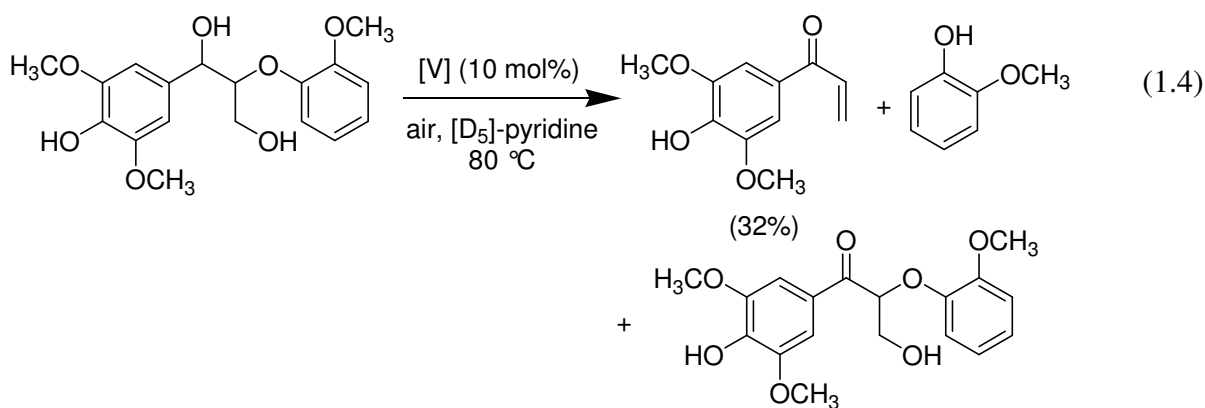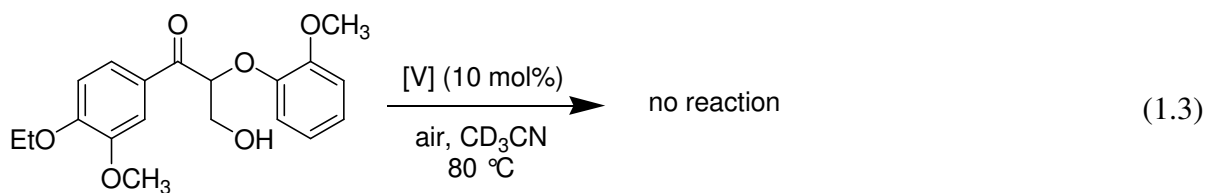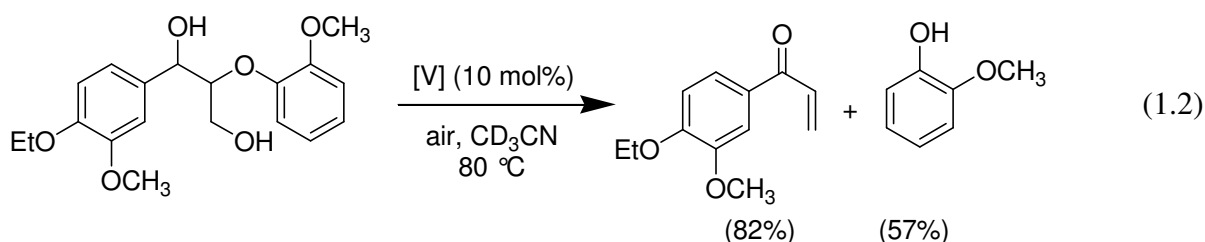
1.3   Titanocene chemistry

These and other recently reported reactions based on ruthenium,[7] nickel,[5,11] and vanadium[2,3,8,12,13] typically require high temperatures for catalysis to occur. The feasibility of a large-scale application of some metal-catalyzed processes is further diminished by their low earth-abundance. In contrast, titanium is the ninth most abundant element in Earth's crust.[14] As an inexpensive transition metal with low toxicity, it is attractive for an industrial application.

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The reactivity of Cp_2Ti complexes has been extensively studied,[15] and can be dramatically altered by simple modifications of the cyclopentadienyl ligands. For example, when compounds of type $(\eta^5-C_5Me_4R)_2Ti(\eta^2-C_2H_4)$, where R = H or Me, are reacted with $MeC\equiv CMe$, insertion of but-2-yne is observed. Instead, when R = ^tBu or $SiMe_3$, $(\eta^5-C_5Me_4R)_2Ti(\eta^2-C_2Me_2)$ is produced by ligand exchange.[16] Titanocene complexes are also remarkably water tolerant. Bis(cyclopentadienyl)titanium perchlorate is prepared by reacting Cp_2TiCl_2 with silver perchlorate in water,[17] and an aqueous workup is employed in the synthesis of dimethyl titanocene.[18] The titanocene framework is also stable with respect to strong acids as demonstrated by Luinstra. A reaction of dimethyltitanocene with excess triflic acid results in the formation of titanocene bis(triflate) with no damage to the 'Cp_2Ti' fragment.[19]

Titanocene complexes are oxophilic due to the formation of a strong Ti-O bond, and may therefore be useful for C-O bond cleavage reactions. While binding of ligands through carbon is preferred for late transition metals such as ruthenium, resulting in ligand rearrangement following C-O bond cleavage (Figure 1.3), ligands are expected to remain bound to titanium through oxygen throughout an entire catalytic cycle, lowering the energy barrier for the bond breaking process. However, Gansäuer demonstrated that protonolysis of a Ti^{IV}-OR bond can be achieved even with mild acids such as lutidinium chloride (pKa 6.65 in water)[20,21] potentially allowing for the release of any C-O bond cleavage products.

1.4   Target catalytic cycle

Initial studies by the Smith group in the use of titanocene complexes for the cleavage of the β-O-4 linkage in lignin employed 2-phenoxy-1-phenethanol (**2.1**) as a model for the ether bond. A target catalytic cycle was proposed (Figure 1.5) based on the chemistry of C-O bond cleavage observed in Toste's vanadium and Bergman's ruthenium systems. It was hypothesized that the coordination of alcohol **2.1** could be achieved by ligand exchange with a suitable $Cp_2Ti(OR)X$ source. It was further assumed that the oxophilic nature of titanium would encourage the coordination of the ether oxygen of the substrate, resulting in the formation of the cationic titanocene complex **A** with an outer-sphere X⁻ ligand. From here, the deprotonation of the alkoxide ligand with an external base B was envisioned. The resulting intermediate would then undergo C-O bond cleavage, forming titanocene enolate phenoxide. The enolate ligand can easily become protonated by HBX. Subsequent ligand

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exchange with **2.1**, followed by protonolysis of the phenoxide ligand would form complex **A**, thus closing the catalytic cycle. Noteworthy, the entire process can be rendered catalytic in base, provided that the conjugate acid HBX can participate in the protonation of enolate.
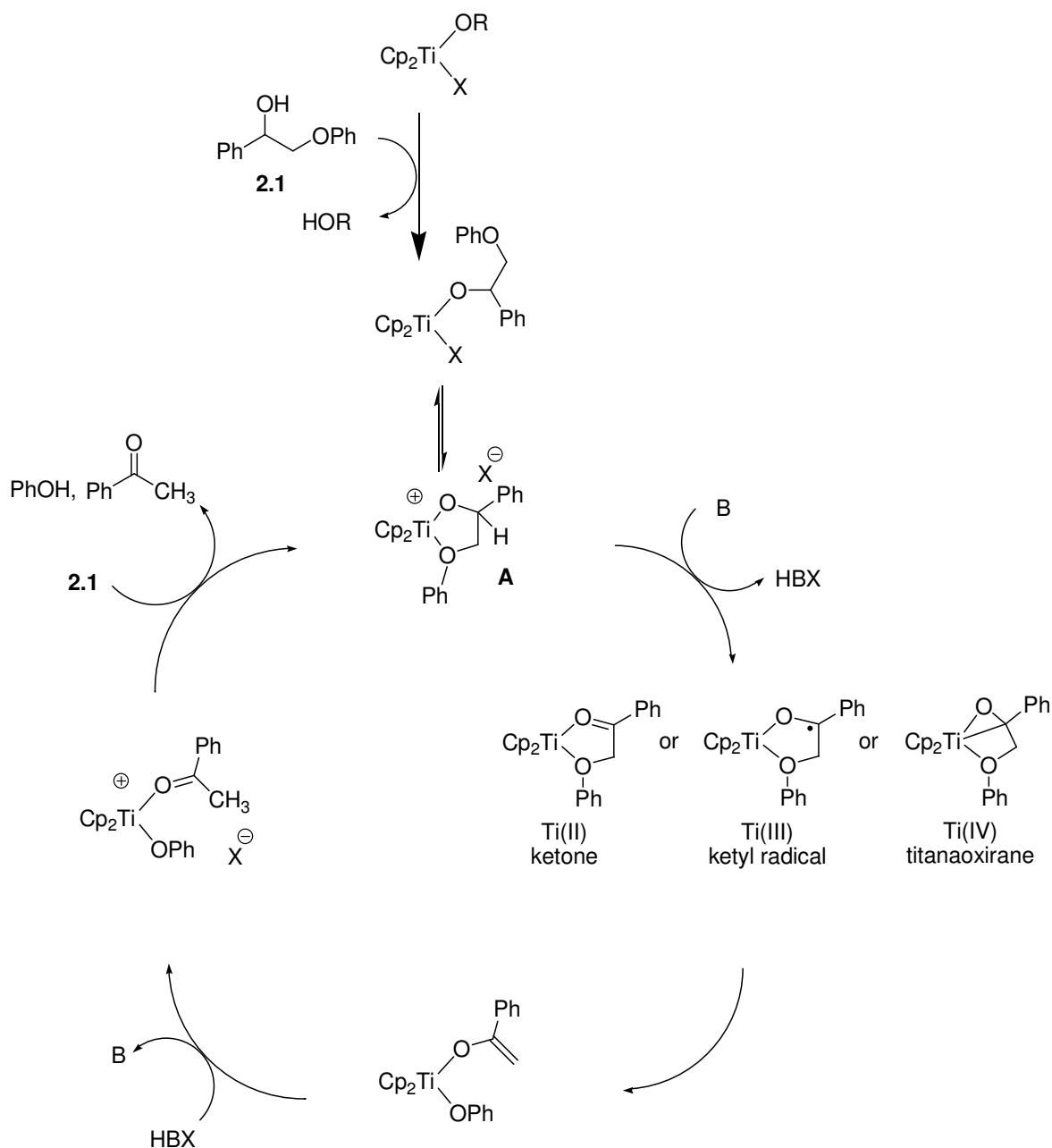
Figure 1.5. Target catalytic cycle for titanocene-catalyzed C-O bond cleavage of 2-phenoxy-1-phenethanol proposed by Smith and coworkers.

1.5   Thesis objectives

In this thesis, C-O bond cleavage of the β-O-4 model compound 2-phenoxy-1-phenethanol will be investigated. The individual steps presented in the above catalytic cycle will be examined in chapter 2. Previous work by Smith and co-workers will be discussed,[22] and the reactivity of titanocene phenoxide enolate with various acids will be studied. In chapter 3, the OAr group in titanocene enolate aryloxide will be modified. Some changes in reactivity will be observed as a result of increased steric bulk of this ligand. Chapter 4 will present initial experiments involving the use of zirconocene for the C-O bond cleavage application.

Chapter 2 Titanocene-Mediated C-O bond Cleavage of Lignin Model Compounds

The target catalytic cycle for the carbon-oxygen bond cleavage of the simple β-O-4 lignin model 2-phenoxy-1-phenylethanol was presented in Figure 1.5. The titanocene complexes believed to be present during catalysis were independently synthesized where possible. The reactivity of these complexes was investigated and results are presented herein.

2.1   Previous work by Smith and co-workers

The synthesis of the cationic titanocene alkoxide complex **A** was attempted by Smith's research group. Titanocene dichloride was reacted with alcohol **2.1** in the presence of DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) to produce titanocene alkoxide chloride **2.3** (eq 2.1). The molecular structure of **2.3** was obtained by X-ray diffraction. The alkoxide ligand was bound solely through the anionic oxygen, with a Ti···O(ether) bond distance over 4.0 Å, demonstrating an absence of chelation in the solid state.[22] Reaction of **2.3** with sodium bis(trimethylsilyl)amide was carried out, but the desired deprotonation of the benzylic position was not observed.[23]

$$(2.1)$$
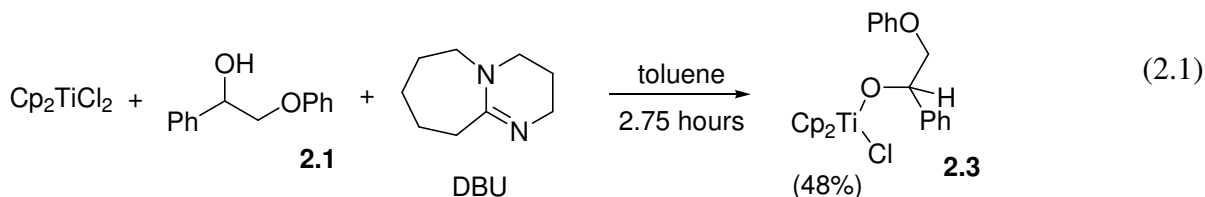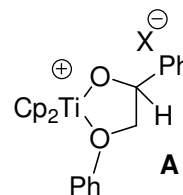
To independently synthesize the ketone-bound titanocene complex **2.4**, Cp$_2$Ti(BTMSA) (BTMSA = bis(trimethylsilyl)acetylene) was employed as a source of titanium. Cp$_2$Ti(BTMSA) is commonly used as a synthon for the reactive bis(cyclopentadienyl)Ti^{II} species.[24] The bis(trimethylsilyl)acetylene ligand is easily substituted with a variety of alkynes and dienes, as well as some ketones. For example, although reactions of Cp$_2$Ti(BTMSA) with formaldehyde, acetone, or benzophenone produce no defined complexes, a reaction with two equivalents of benzaldehyde forms titanadioxacyclopentane (eq 2.2).[25]

$$(2.2)$$
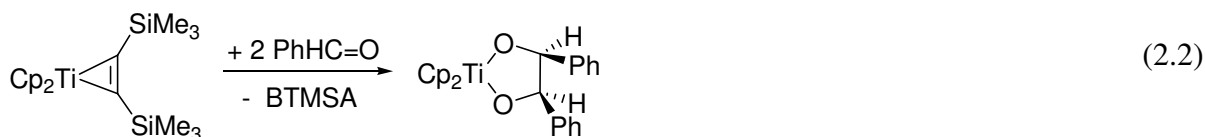
Thus, the α-aryloxy ketone **2.2** was added to Cp$_2$Ti(BTMSA) and a rapid reaction was observed at room temperature (eq 2.3). Although the ketone-bound compound **2.4** was expected to be formed, enolate phenoxide **2.5** was the only observed product by ^{1}H NMR after 20 minutes at room temperature.[22] It was initially presumed that ketone **2.2** binds to titanium to form **2.4** as an intermediate, which then rapidly undergoes C-O bond cleavage to yield the observed enolate phenoxide **2.5**. Attempts at cooling and slowing down the reaction to enable the determination of the intermediate structure were unsuccessful.[26] However, computational studies suggest that a Ti^{IV} titanaoxirane species is the lowest energy electronic structure of the presumed intermediate in the C-O bond cleavage of the α-aryloxy ketone.[27]

$$(2.3)$$
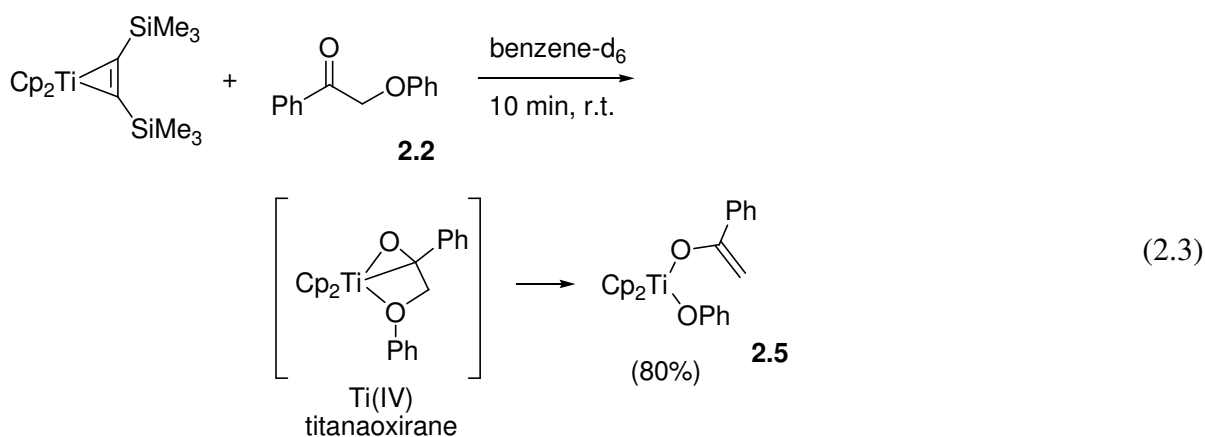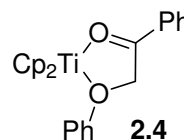
The next step of the target catalytic cycle, the protonation of the enolate ligand in **2.5**, is the subject this chapter. As part of my M.Sc. thesis research, the compound was subjected to various mild and strong acids to observe differences in reactivity. In addition, further attempts were made at the synthesis of the cationic titanocene alkoxide compound **A**. For example, the chloride ligand in titanocene alkoxide chloride **2.3** was replaced with weakly binding anionic ligands to encourage chelation of the alkoxide. Alternatively, reaction of the protonated enolate phenoxide complex with alcohol **2.1** was also tested.

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2.2   Substitution of chloride in Cp$_2$Ti(OR)Cl with weakly coordinating anions

A cationic chelate complex of titanium related to **A** was previously reported by Bosnich.[28] A titanium-catalyzed Mukaiyama reaction of the silyl enol ether PhC(=CH$_2$)OSiMe$_3$ with benzaldehyde in the presence of 2,6-di-*tert*-butyl-4-methylpyridine produced a neutral titanocene aldolate triflate species. This intermediate was found to be in equilibrium with a cationic chelate form, as shown in eq 2.4.

$$(2.4)$$

It was hypothesized that the replacement of chloride with triflate in titanocene alkoxide chloride **2.3** might encourage the chelation of the alkoxide. Thus, compound **2.3** was reacted with silver triflate (eq 2.5). The salt metathesis reaction was rapid, with immediate AgCl precipitate formation and noticeable color change from pale to dark orange within minutes. The ^{1}H NMR of the isolated titanocene alkoxide triflate **2.6** showed diastereotopically split Cp proton resonances at room temperature, similar to the titanocene alkoxide chloride precursor **2.3**. A slight downfield shift of the Cp proton signals relative to compound **2.3** was expected due to the replacement of chloride for the more electron-withdrawing triflate. Such a shift was observed and was not large enough to support chelation of the alkoxide ligand. The methylene proton resonances of **2.6** were found between 4.05-4.14 ppm. For comparison, the methylene protons in Bosnich's related titanocene aldolate triflate appear at 3.23 and 3.59 ppm in CD$_2$Cl$_2$ for the neutral species, yet are separated by more than 1 ppm in the cationic chelate.[28] The closeness of the methylene proton signals for **2.6** is further evidence for a lack of chelation of the alkoxide ligand. Due to disproportionation of **2.6** during recrystalization, an X-ray structure was not obtained.

$$(2.5)$$
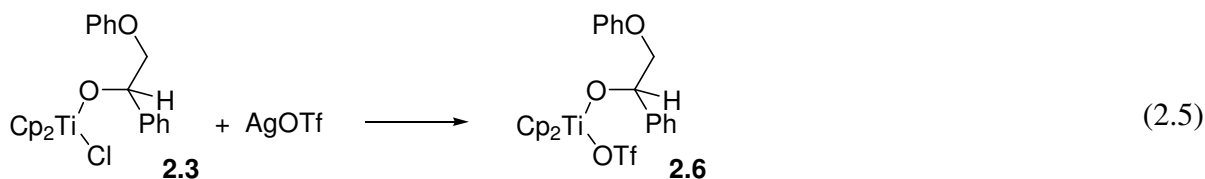
Diasteretopic splitting of the Cp proton resonances was observed in ^{1}H NMR spectra of titanocene alkoxide chloride **2.3** and titanocene alkoxide triflate **2.6**. The appearance of two distinct Cp proton signals is a result of the presence of a chiral centre in the molecule. The benzylic carbon of the alkoxide ligand has four different substituents and is thus chiral. This leads to non-equivalence of the two Cp ring environments, giving rise to two distinct signals. Similarly, the methylene protons of the alkoxide ligand are non-equivalent, although two separate signals are not observed due to overlap. Additionally, although both (*R*) and (*S*) enantiomers are present in the mixture, they are related by symmetry and therefore do not give rise to additional signals. For example H$_A$ in the (*R*) enantiomer is equivalent to H$_B$ in the (*S*) enantiomer (Figure 2.1).
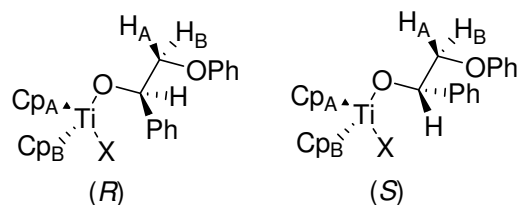
Figure 2.1. The (*R*) and (*S*) enantiomers of Cp$_2$Ti(alkoxide)X.

Unlike the ketone donor of Bosnich's aldolate triflate complex, the weaker ether donor in alkoxide triflate **2.6** does not appear to displace the triflate. Therefore, the OTf$^-$ ligand was replaced with a more weakly coordinating BPh$_4^-$ anion in a reaction of the alkoxide chloride complex **2.3** with sodium tetraphenylborate (eq 2.6).[29] This resulted in the production of multiple species, none of which could be identified as the desired cationic chelate complex **A**.

$$\text{(2.6)}$$
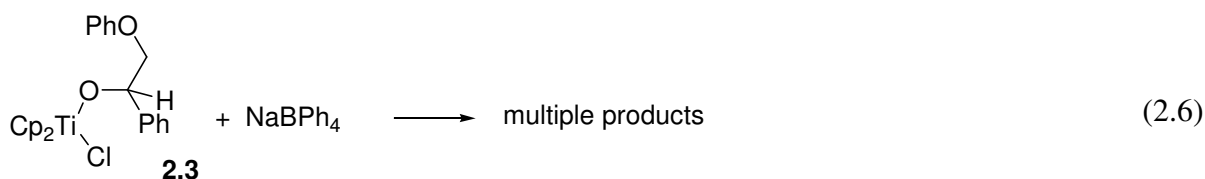
2.3   Protonolysis of titanocene enolate phenoxide

Titanocene enolates have been noted to be sensitive with respect to protonolysis. For example, Cannizzo and Grubbs reported an acidolysis of titanocene enolate with anhydrous HCl as shown in equation 2.7 below.[30]

$$Cp_2Ti \underset{O}{\overset{O}{\langle}} \xrightarrow{\text{HCl}} Cp_2TiCl_2 \ + \ \underset{}{\overset{O}{\text{(acetone)}}} + \ \underset{OH}{\overset{O}{\text{(acetic acid)}}} \tag{2.7}$$
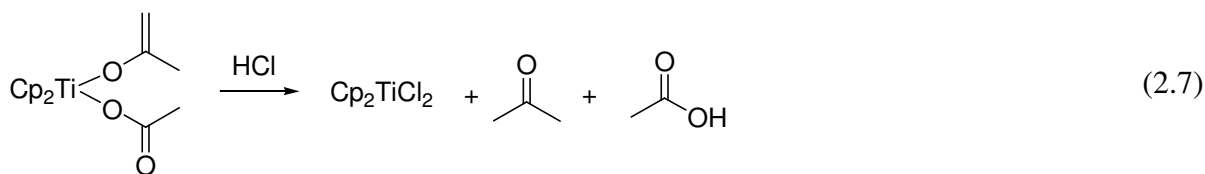
To understand the reactivity of titanocene enolate phenoxide **2.5**, reactions were carried out using various strong and mild acids of the type HX and HNR$_3$X. The effect of the counteranion X on protonation versus protonolysis was also investigated. The results of the experiments are summarized in Table 2.1 below.

Table 2.1. Protonolysis screening of titanocene enolate phenoxide **2.5**
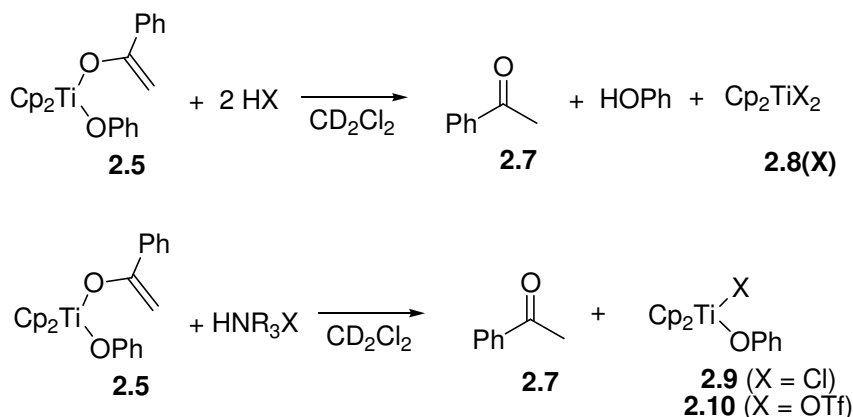
entry	acid	equiv	time	Ti product	Ti yield	yield **2.7**
1	HCl(aq)	2.0	2h	**2.8**(Cl)	99%	99%
2	HOTf	2.0	2h	**2.8**(OTf)	72%	90%
3	HOTs	2.0	2h	**2.8**(OTs)	77%	95%
4	Me$_3$SiCl	2.0	2h	^{b}		
5	Me$_3$SiCl^c	2.0	2h	**2.8**(Cl)	92%	81%
6	[HLut]Cl	1.0	2h	**2.9**	79%	77%
7	[HLut]OTf	1.0	2h	**2.10**	77%	83%
8	[HNEt$_3$]Cl	1.0	2h/24h	**2.9**	82/89%	72/88%
9	[HNEt$_3$]OTf	1.0	2h/24h	**2.10**	70/63%	71/70%
10	[HDBU]Cl	1.0	2h/24h	**2.9**	32/33%	32/26%

^{a} Yields of titanocene product and acetophenone determined by integration relative to 1,3,5-^{t}Bu$_3$C$_6$H$_3$ as internal standard. ^{b} Only unreacted **2.5** observed. ^{c} 2.0 equiv H$_2$O added.

Similar to Cannizzo's findings, when titanocene enolate phenoxide **2.5** is reacted with 2 equivalents of HCl, both Ti-O bonds are cleaved to produce Cp$_2$TiCl$_2$, acetophenone, and

phenol (Table 2.1, entry 1). Excellent yields of titanocene dichloride (99%) and acetophenone (99%) were obtained. It is postulated that the strong coordination of the chloride ion to titanocene prevents the occurrence of side-reactions, resulting in a quantitative conversion.

Luinstra has demonstrated the stability of the titanocene framework to triflic acid in a reaction of dimethyl titanocene with a slight excess of HOTf.[19] The titanocene bis(triflate) product was obtained cleanly after the removal of excess acid by washing and drying under vacuum. Prompted by these results, titanocene phenoxide enolate **2.5** was reacted with two equivalents of HOTf (entry 2). Although compound **2.5** reacted completely, only a 72% yield of the $Cp_2Ti(OTf)_2$ product was obtained. It is postulated that the weaker coordination of the triflate ion allows for the formation of coordinatively unsaturated titanocene intermediates, which might react to yield insoluble (μ-oxo)titanium complexes.[31] This hypothesis is supported by the presence of precipitate in the NMR tube. The yield of acetophenone was nearly quantitative at 90%, consistent with the complete consumption of enolate phenoxide **2.5**.

Reaction of **2.5** with *p*-toluenesulfonic acid monohydrate similarly resulted in the release of acetophenone and formation of $Cp_2Ti(OTs)_2$ (entry 3). The presence of water in the protonolysis reagent seemed to have no adverse effects. Although the formation of acetophenone was nearly quantitative at 95%, a slightly lower yield was observed for the titanocene bis(tosylate) product (77%). The presence of solid in the NMR tube suggests the formation of titanocene bridging phenoxide species due to the weaker coordination of the tosylate ion, as above.

Although enolate phenoxide **2.5** did not react with Me_3SiCl under anhydrous conditions, the addition of water to the reaction led to protonolysis of both Ti-O bonds to yield titanocene dichloride (92%) and acetophenone (81%) (entries 4-5). Similar reactivity was reported for Cr^{III}-OR complexes.[32] The presence of water is proposed to result in the formation of Me_3SiOH and HCl, with HCl being the active species in the protonolysis of titanocene enolate phenoxide **2.5**.[33]

Selective cleavage of the Ti-enolate bond can be achieved through the use of milder acids. Reaction of the enolate phenoxide complex **2.5** with lutidinium chloride (pKa 6.65)[20] produced $Cp_2Ti(OPh)Cl$ and acetophenone (entry 6). Changing of the chloride to a triflate

produced similar results (entry 7). The yields of acetophenone (77% and 83% respectively) and the titanocene products (79% and 77% respectively) were comparable for the two reactions. The relatively low yield in the reaction involving [HLut]Cl is hypothesized to be a result of incomplete consumption of phenoxide enolate **2.5**. Even after 24 hours, 14% of the titanocene starting material remained in the NMR tube. It is postulated that an insufficient amount of [HLut]Cl was added due to contaminants in the acid adding to the weighed mass. Although compound **2.5** was completely consumed in the reaction involving [HLut]OTf, the non-quantitative yield of 77% of $Cp_2Ti(OPh)(OTf)$ is suggested to be a result of titanocene(μ-OPh) formation due to the weakly coordinating triflate ion, as explained above.

The effect of increasing the pKa of the acid was investigated. Reacting compound **2.5** with triethylammonium chloride or triflate (pKa 10.75)[20] resulted in good yields of $Cp_2Ti(OPh)X$ (X = Cl, OTf respectively) and acetophenone (entries 8-9). The titanocene product yields were slightly lower for the triflate reaction as compared to the chloride (70% vs. 82% after 2 hours). Additionally, the yield of $Cp_2Ti(OPh)(OTf)$ decreased with time (70% after 2 hours, 63% after 24 hours). It is hypothesized that (μ-OPh)titanium species or other insoluble byproducts might form due to the reversible coordination of the triflate ion. This is supported by the decrease of $Cp_2Ti(OPh)(OTf)$ concentration over time.

Due to the incorrect stochiometry of titanocene phenoxide enolate **2.5** and [HLut]Cl in entry 6, the yields of this reaction cannot be compared to that of compound **2.5** with [HNEt$_3$]Cl. However, it is observed that an increase in pKa results in a slower reaction for the acids with a triflate counteranion (entry 7 and 9). While phenoxide enolate is completely consumed within 2 hours in the presence of [HLut]OTf, the reaction with [HNEt$_3$]OTf takes more than 2 hours to go to completion. Additionally, the overall yields of acetophenone and titanocene product are lower for the triethylammonium reaction as compared to the lutidinium reaction. These results are in line with expectations of the less acidic triethylammonium salt performing more poorly in protonolysis reactions than lutidinium.

A reaction of **2.5** with DBU·HCl (pKa ~14 in water)[34] was also carried out. With this very mild acid, only approximately 30% of enolate phenoxide **2.5** underwent Ti-enolate bond cleavage (entry 10). This result is consistent with the expected decrease in the protonolysis reactivity with increasing pKa of the acid. Additionally, the related titanocene alkoxide

chloride complex **2.3** is prepared via a reaction of Cp_2TiCl_2 and alcohol **2.1** in the presence of DBU and is stable in the presence of the DBU·HCl byproduct.

The $Cp_2Ti(OPh)X$ products were found to be stable in the presence of excess $HNEt_3X$ or HLutX. This observation was not surprising, since related Ti^{IV} aryloxides can be prepared from Cp_2TiCl_2, NEt_3, and HOAr,[35] generating $HNEt_3Cl$ as a byproduct. Compounds of type $Cp_2Ti(OPh)X$ (X = Cl, OTf) can also be obtained via protonolysis of titanocene enolate phenoxide **2.5** with only one equivalent of HCl or HOTf (eq 2.8).

$$\text{(2.8)}$$
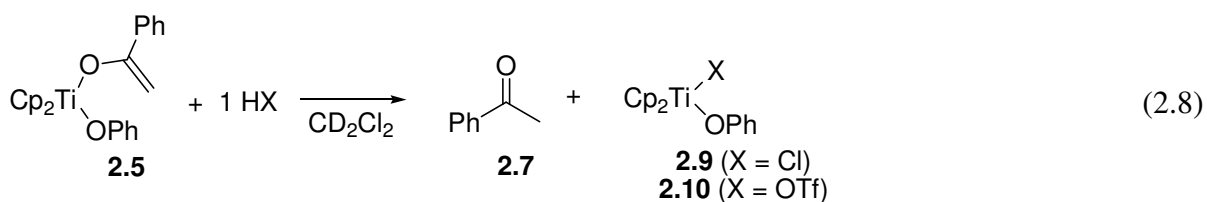
A further comparison of anion effects was made by using acids with Cl and BPh_4 counteranions. Reactions were carried out between **2.5** and acids H_2NCy_2X, $H_2N^iPr_2X$, and HN^iPr_2EtX where X = Cl or BPh_4. Although % yields were not obtained, it was seen that for reactions where X = Cl, **2.5** was consumed rapidly and completely, leading to the production of $Cp_2Ti(OPh)Cl$ and acetophenone. In contrast, reactions where X = BPh_4 resulted in the rapid precipitation of a pale pale solid. After filtration through Celite, the ${}^1H$ NMR spectrum of the solution was recorded. In addition to acetophenone, the solution contained a variety of unidentified titanocene products. This suggests the formation of coordinatively unsaturated titanocene intermediates due to the very weak coordination of the BPh_4 counteranion, which may result in the production of insoluble (μ-OPh)titanium species and other unwanted side-reactions (eq 2.9).

$$\text{(2.9)}$$

+ other products
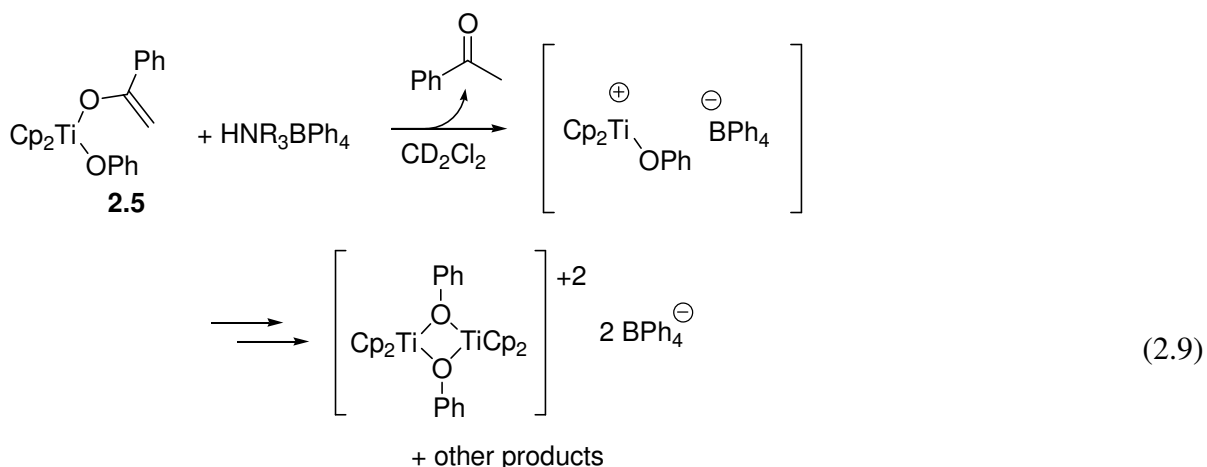
2.4 Synthesis of titanocene alkoxide phenoxide

It was postulated that the product of the protonation of the enolate phenoxide complex **2.5** would react with 2-phenoxy-1-phenethanol (**2.1**) to displace acetophenone. The coordination of the alcohol to titanium was expected to increase the acidity of the OH group, allowing for the protonolysis of the phenoxide ligand by the alcohol to produce phenol and the cationic titanocene alkoxide **A** (Figure 1.5, eq 2.10).

$$(2.10)$$
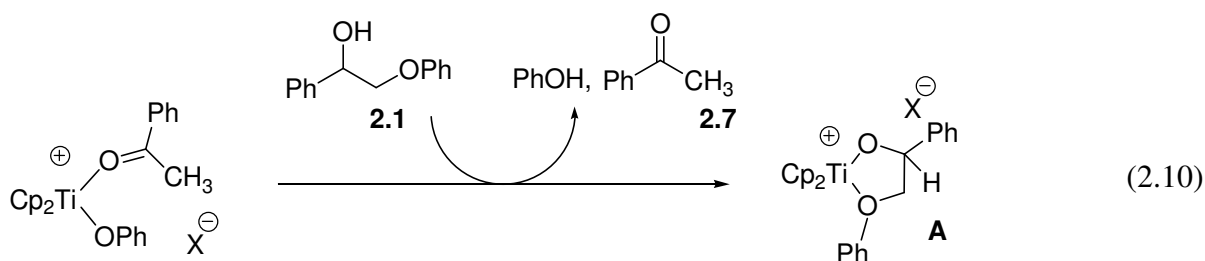
However, the reactions of enolate phenoxide **2.5** did not result in the isolation of the protonated product due to rapid elimination of the acetophenone. Instead, compounds of type Cp$_2$Ti(OPh)X, where X = Cl (**2.9**), OTf (**2.10**), were obtained. Thus, these compounds were used as the starting point for reactions with alcohol **2.1**.

It was hypothesized that the phenoxide chloride compound **2.9** would not react appreciably with alcohol **2.1** due to the strong coordination of the chloride ion. Titanocene phenoxide triflate **2.10** was more likely to undergo a substitution reaction to replace the triflate ligand with the alcohol. Following Luinstra's general procedure,[19] compound **2.10** was prepared via a ligand exchange reaction of Cp$_2$Ti(OPh)$_2$ with Cp$_2$Ti(OTf)$_2$. When an equimolar amount of alcohol **2.1** was added to compound **2.10**, no reaction was observed. However, a subsequent addition of a slight excess of triethylamine resulted in a rapid color change from dark red to orange. Six hours later, all of the alcohol coordinated to titanocene, displacing the triflate ligand and forming titanocene alkoxide phenoxide **2.11** (eq 2.11). As expected, Cp$_2$Ti(OPh)Cl (**2.9**) did not undergo ligand exchange with alcohol **2.1** under the same reaction conditions.

$$(2.11)$$

16
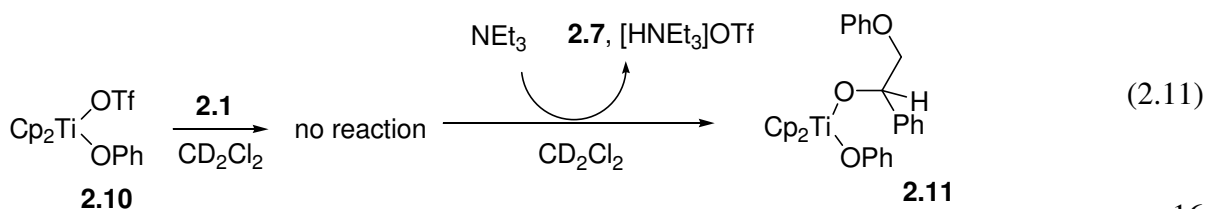
The protonation of titanocene phenoxide enolate **2.5** and reaction with alcohol **2.1** can be done in a one-pot reaction. Although **2.5** does not react with **2.1** in the absence of acid over 48 hours, the addition of equimolar amount of triethylammonium triflate facilitates the release of acetophenone and production of alkoxide phenoxide complex **2.11** (eq 2.12). Since the acid is regenerated in this reaction, it can also be used in a catalytic amount.

$$\text{(2.12)}$$
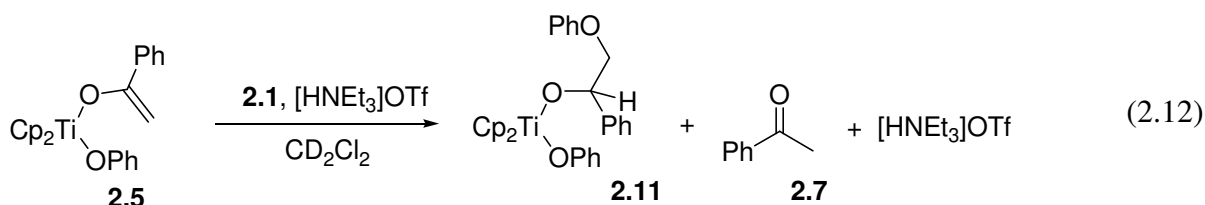
Interestingly, the reaction proceeds cleanly when $[HNEt_3]BPh_4$ is used as an acid. Previous reactions involving the use of tetraphenylborate salts for protonation of the enolate ligand resulted in the formation of multiple unidentified products. Here, following protonation of the enolate, ligand exchange between acetophenone and alcohol **2.1** is presumably faster than the formation of other reactive intermediates (eq 2.13).

$$\text{(2.13)}$$
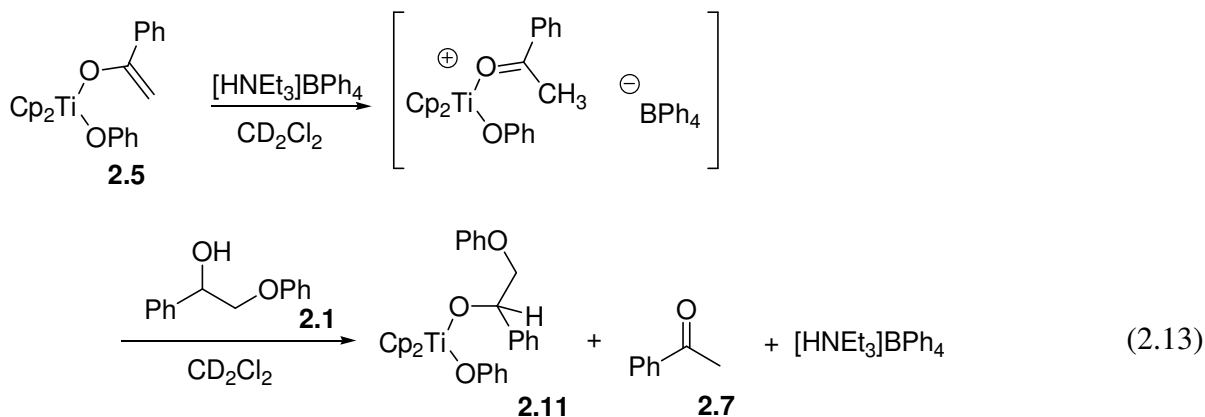
When the reaction of enolate phenoxide **2.5** with alcohol **2.1** is carried out in the presence of $HNEt_3Cl$, titanocene alkoxide phenoxide **2.11** is not obtained. Instead, only the protonolysis of the enolate ligand is achieved, producing $Cp_2Ti(OPh)Cl$ **2.9**. The subsequent ligand exchange with alcohol **2.1** is not successful due to the strong coordination of the chloride ligand (eq 2.14).

17

Ph
$$\text{Cp}_2\text{Ti} \overset{\text{O}}{\underset{\text{OPh}}{<}} \xrightarrow[\text{CD}_2\text{Cl}_2]{\textbf{2.1}, [\text{HNEt}_3]\text{Cl}} \text{Cp}_2\text{Ti} \overset{\text{Cl}}{\underset{\text{OPh}}{<}} \tag{2.14}$$

2.5   **2.9**
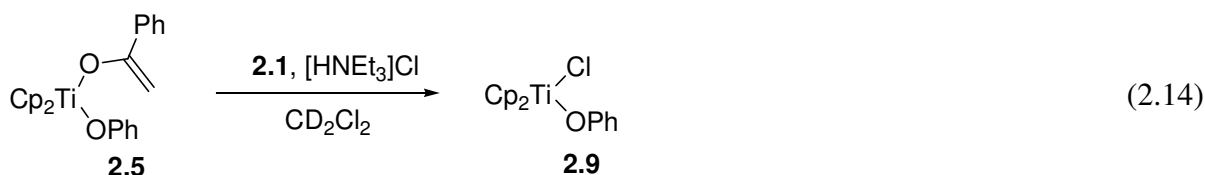
Elimination of phenol from titanocene alkoxide phenoxide **2.11** was expected to result in the formation of the Ti^{IV} titanaoxirane, which would undergo C-O bond cleavage to form the enolate phenoxide complex **2.5** (eq 2.15). Unfortunately, this elimination is not spontaneous at ambient temperature over 24 hours. As shown during protonolysis reactions of titanocene enolate phenoxide **2.5**, the Ti-OPh bond can only be cleaved with strong acids. It is not surprising that the benzylic hydrogen of the 2-phenoxy-1-phenethanol is not acidic enough even when further activated by coordination to titanium. It is possible that sufficient heating might allow one to overcome the energy barrier for phenol elimination; however, this hypothesis was not thoroughly examined.

$$\tag{2.15}$$

2.11   PhOH   Ph   **2.5**
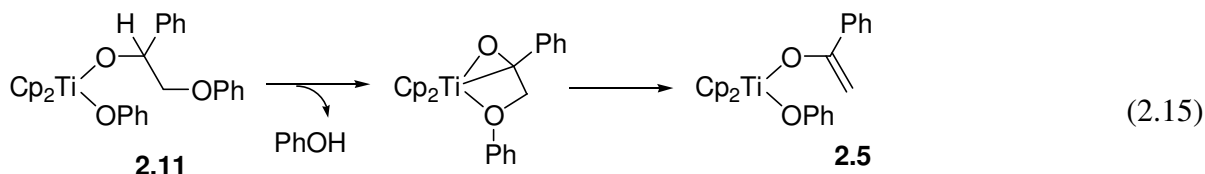
2.5   Experimental section

General Considerations. All reactions were carried out under nitrogen using standard Schlenk and glove box techniques. Hexanes, toluene, CH$_2$Cl$_2$ and THF were purified by passage through activated alumina and deoxygenizer columns from Glass Contour Co. (Laguna Beach, CA, USA). CD$_2$Cl$_2$ was dried with CaH$_2$, purified by vacuum distillation, degassed by three freeze-vacuum-thaw cycles and stored over 4 Å molecular sieves under nitrogen. Celite (Aldrich) was dried overnight at 120 °C before being evacuated and then stored under nitrogen.

PhCH(OH)CH$_2$OPh (**2.1**) and PhC(=O)CH$_2$OPh (**2.2**) were prepared according to the literature procedure.[7] [HNEt$_3$][BPh$_4$] and lutidinium tetraphenylborate were prepared using aqueous HCl and Na[BPh$_4$].[36] Anhydrous NEt$_3$ (≥99.5%) and Me$_3$SiCl (97%) were

purchased from Aldrich, stored under nitrogen and used as received. Triethylamine hydrochloride (>99.0%), silver trifluoromethanesulfonate (99+%), silver *p*-toluenesulfonate (99+%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%), 1,3,5-tri-*tert*-butylbenzene (97%) and collidinium tosylate (98%) were purchased from Aldrich and used as received. Titanocene dichloride (Strem, 99+%) was stored under nitrogen and used as received. $Cp_2Ti(OTf)_2$ was prepared according to the literature procedure.[37] $Cp_2Ti(OPh)Cl$ and $Cp_2Ti(OPh)_2$ were obtained from reaction of Cp_2TiCl_2 with one or two equiv of NaOPh, respectively, according to the literature procedure.[38] NaOPh was prepared from phenol and NaH according to the literature procedure.[39]

^1H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer. Quantitative ^1H NMR spectroscopy for Cp_2TiX_2 complexes required determination of the T_1 for the Cp protons and the use of delays of $5T_1$ between acquisitions.[28] Elemental analyses were performed by the UBC Department of Chemistry Vancouver campus microanalytical services.

Synthesis of titanocene alkoxide triflate (2.6). A solution of silver triflate (5.96 mg, 0.0232 mmol) in 2 mL of diethyl ether was added to a solution of titanocene alkoxide chloride **2.3** (10.0 mg, 0.0234) in 6 mL of diethyl ether. Immediate precipitation of a pale solid was observed. The reaction was stirred for 45 minutes and then filtered through Celite to obtain a clear yellow solution. The solvent was removed in vacuo, yielding a yellow oily residue of **2.6**. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.45-7.27 (m, 6H), 6.98-6.90 (m, 4H), 6.453 (s, 5H), 6.447 (s, 5H), 5.99 (dd, $J = 7.2, 4.4$ Hz, 1H), 4.14-4.05 (m, 2H).

Protonolysis reactions of titanocene enolate phenoxide (2.5). In an inert atmosphere glovebox, **2.5** (8.0 mg, 0.020 mmol) and $1,3,5-tBu_3C_6H_3$ (2.0 mg, 0.0081 mmol) were dissolved in 0.4 mL CD_2Cl_2. An appropriate amount of acid was dissolved in 0.4 mL CD_2Cl_2. The two solutions were combined in a J. Young or Wilmad Screw-Cap NMR tube and allowed to react for 2 hours before recording a ^1H NMR spectrum. In cases where starting material was observed after 2 hours of reaction, a second NMR spectrum was obtained after 24 hours of reaction. The results of these reactions are summarized in Table 2.1.

Synthesis of titanocene phenoxide triflate (2.10). $Cp_2Ti(OTf)_2$ (130.7 mg, 0.275 mmol) and $Cp_2Ti(OPh)_2$ (99.9 mg, 0.274 mmol) were dissolved in 10 mL of toluene. The mixture was stirred for 24 h, and the dark red solution was then filtered through Celite. The solvent was removed in vacuo, and the residue was dissolved in a minimum amount of toluene. Storage at –30 °C for two days resulted in very dark red crystals of **2.10** (89.9 mg, 39%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.28 (dd, *J* = 7.6, 8.8 Hz, 2H), 6.92 (tt, *J* = 7.6, 1.36 Hz, 1H), 6.61 (dd, *J* = 8.8, 1.24 Hz, 2H), 6. 45 (s, 10H), 4.72 (s, 1H), 4.09 (s, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 171.91, 129.87, 121.65, 119.40, 116.80. Anal. Calcd for $C_{17}H_{15}F_3O_4STi$: C, 48.59; H, 3.60. Found: C, 48.94; H, 3.70.

Synthesis of titanocene alkoxide phenoxide (2.11) via titanocene phenoxide triflate. To a solution of AgOTf (41.8 mg, 0.163 mmol) in 3 mL of toluene was added a solution of **2.9** (50.0 mg, 0.163 mmol) dissolved in 3 mL of toluene, resulting in an immediate color change to dark red and formation of a pale precipitate. The mixture was wrapped in foil and stirred for 1 hour, after which the mixture was filtered through Celite, removing the white precipitate and giving a dark red solution of **2.10**. A solution of **2.1** (34.9 mg, 0.163 mmol) in 3 mL toluene and NEt_3 (45 μL, 0.323 mmol) were added to the filtrate and stirred for 72 hours, resulting in an orange solution. The solvent was removed *in* vacuo to give an orange residue. The residue was extracted with Et_2O and filtered through Celite. Recrystallization from 1:2 Et_2O/hexanes at -30 °C yielded dark orange powder of **9** (38.0 mg, 48%). NMR analysis indicated that the product obtained by recrystallization was contaminated with a small amount (~7%) of the intermediate phenoxide triflate, **2.10**. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.48 (dt, *J* = 0.8, 8.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.26-7.34 (m, 4H), 7.07 (dd, *J* = 7.2, 8.4 Hz, 2H), 6.93-6.97 (m, 4H), 6.67 (dd, 7.6, 8.0 Hz, 1H), 6.26 (s, 5H), 6.23 (s, 5H), 5.70 (dd, *J* = 4.4, 7.2 Hz, 1H), 4.09 (dd, *J* = 7.2, 9.6 Hz, 1H), 4.01 (dd, *J* = 4.4, 9.6 Hz, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 170.81, 159.63, 144.12, 130.04, 129.401, 128.77, 127.94, 127.27, 121.17, 118.55, 118.37, 115.94, 115.77, 115.05, 88.60, 68.65.

Chapter 3 Titanocene Complexes with Substituted Aryloxy Ligands

The elimination of phenol from the alkoxide phenoxide complex **2.11** is an essential step for a successful catalytic C-O bond cleavage of 2-phenoxy-1-phenethanol **2.1** (Figure 3.1). However, as mentioned in the previous chapter, initial attempts at achieving this transformation have been unsuccessful, primarily due to the strength of the Ti-OPh bond. Subsequent research was therefore focused on the weakening of this bond, particularly through an increased steric bulk of the aryloxide ligand.
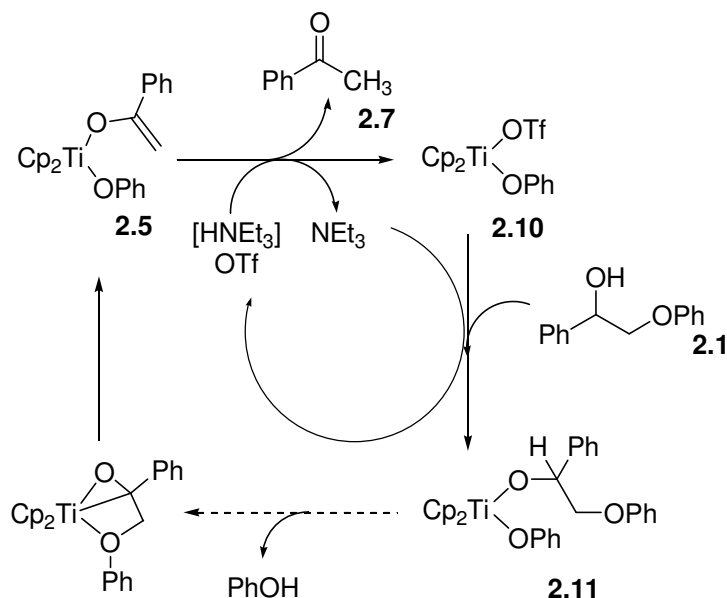
Figure 3.1. Revised target catalytic cycle for C-O bond cleavage of 2-phenoxy-1-phenethanol.

For proof of concept experiments, 2,4,6-tri-*tert*-butylphenoxide (2,4,6-^{t}Bu$_3$(C$_6$H$_2$)OH = HOMes*) was to be used in place of the phenoxide ligand to produce the target compound **3.2** (Figure 3.2). The resulting Ti-OMes* bond was expected to be susceptible to homolytic cleavage since 2,4,6-tri-*tert*-butylphenoxy is a known stable radical.[40] Hydrogen atom abstraction from the benzylic position of the alkoxide ligand by the ·OMes* radical could lead to the formation of the titanaoxirane intermediate and subsequent C-O bond cleavage to yield phenoxide enolate **2.5**.

A second aryloxide ligand of interest was 2,6-dimethoxyphenoxide. This ligand closely resembles the methoxylated phenylpropanoid subunits found especially in hardwood lignin, which contains a higher proportion of sinapyl alcohol as starting material. Additionally, it provides more steric bulk than the unsubstituted phenoxide ligand in **2.11**. It

was expected that the Ti-OAr bond in the hypothetical alkoxide aryloxide complex **3.1** would be weaker than that found in **2.11** but not as weak as the Ti-OMes* bond in **3.2**.
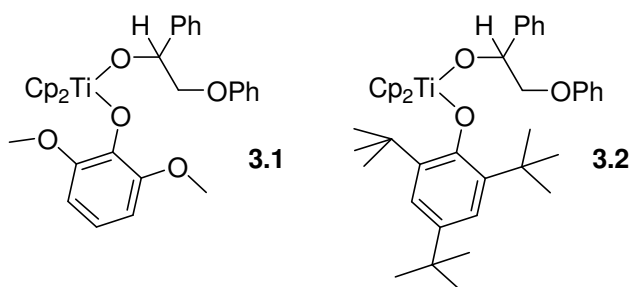
Figure 3.2. Target compounds for studying the effect of increased steric bulk on the elimination of phenol.

3.1   Synthesis of titanocene aryloxide chlorides

To attempt the synthesis of the target alkoxide aryloxide complexes **3.1** and **3.2**, several precursors needed to be synthesized. Sodium salts of 2,6-dimethoxyphenol and 2,4,6-tri-*tert*-butylphenol were prepared during an overnight reaction of sodium hydride with the corresponding phenol. The sodium aryloxides were then reacted with titanocene dichloride over 24 hours to produce the corresponding aryloxide chlorides **3.3** and **3.4** (eq 3.1).[38,41]

$$\text{(3.1)}$$
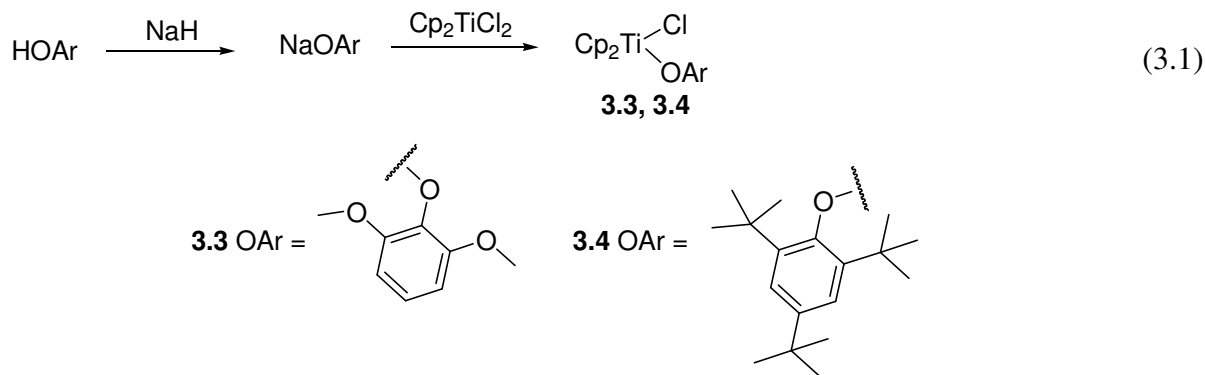
X-ray quality crystals of titanocene aryloxide chloride **3.3** were obtained by recrystallization from diethyl ether, while the less polar Cp$_2$Ti(OMes*)Cl was recrystallized from hexanes. Crystal structures of both were obtained and are discussed below. Additionally, ^{1}H NMR spectra of both compounds were obtained. Similar to the *ortho* hydrogens in the related titanocene phenoxide chloride **2.9**, the *ortho* substituents of the 2,6-dimethoxyaryloxide ligand in **3.3** were found to be equivalent by NMR. However, the *tert-*

butyl substituents of the OMes* ligand in aryloxide chloride **3.4** gave rise to three distinct signals. The non-equivalence of the *ortho* groups suggests a lack of rotation about the O-aryl bond. The rotation might be hindered by the steric interference of the OMes* and cyclopentadienyl ligands.

3.2 X-ray structures of titanocene aryloxide chlorides

Crystal structures of compounds **3.3** and **3.4** are shown below (Figure 3.3, 3.4). Both complexes possess a distorted tetrahedral geometry around titanium. The Ti-O distances are 1.888(4) and 1.9152(17) Å for **3.3** and **3.4** respectively. This is similar to previously reported Ti-O bond distances in related aryloxide chloride complexes, in particular to 1.88 Å found in $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3\text{-}1\text{-Me-}3\text{-CHMe}_2)\text{Ti}(OC_6H_3\text{-}2,6\text{-Me})(Cl)$,[42] 1.896(1) Å for $(\eta^5\text{-}C_5H_4SiMe_3)_2\text{Ti}(OPh)(Cl)$,[43] or 1.880(2) to 1.918(2) in other $(\eta^5\text{-}C_5H_4SiMe_3)_2\text{Ti}(OAr)(Cl)$ complexes.[43] However, these Ti-O distances are all longer than Ti-O bond length of 1.855(2) Å for $(\eta^5\text{-}C_5H_5)_2\text{Ti}(OEt)(Cl)$[44] or 1.835(2) Å for $(\eta^5\text{-}C_5H_5)_2\text{Ti}(OMe)(CN)$,[45] indicating a decreased Ti-O bond order in the aryloxide complexes relative to the monoalkoxide compounds, resulting from a lower degree of electron π donation from O to Ti. Additionally, the Ti-O bond length of titanocene 2,6-dimethoxyphenoxide chloride **3.3** is greater than that observed in a related monocyclopentadienyltitanium dichloride 2,6-dimethoxyphenoxide complex (Ti-O: 1.7781(18) Å).[41] It is postulated that this is due to the steric repulsion between the aryloxide and the two Cp ligands in compound **3.3**. For compound **3.4**, the bulky tert-butyl substituents of the OMes* ligand may be providing additional steric contribution to the lengthening of the Ti-O bond relative to the one found in **3.3**.
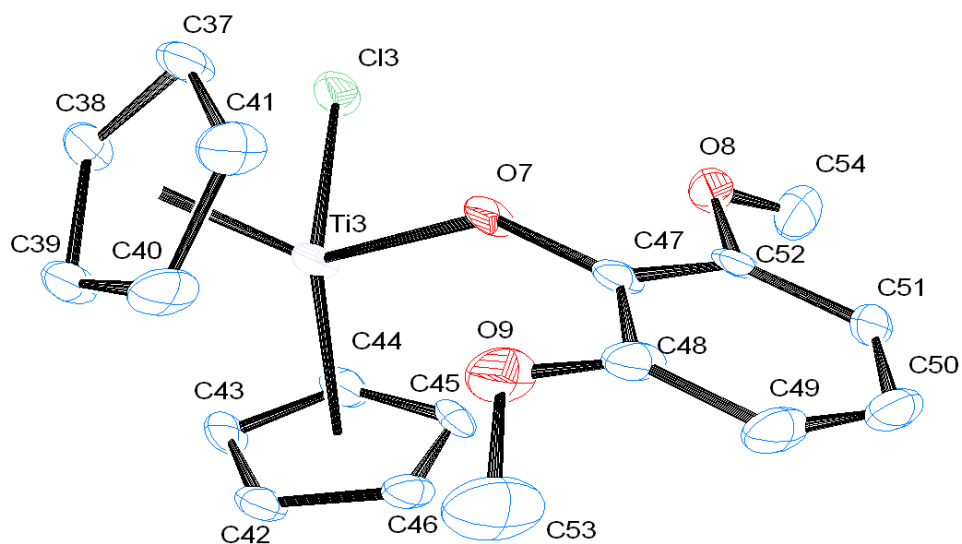
Figure 3.3. Thermal ellipsoid diagram (50% probability level) of **3.3.** Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Ti3-Cl3, 2.4107(18); Ti3-O7, 1.888(4); O7-C47, 1.352(7); Ti3-O7-C47, 142.4(4); Cl3-Ti3-O7, 96.17(16).
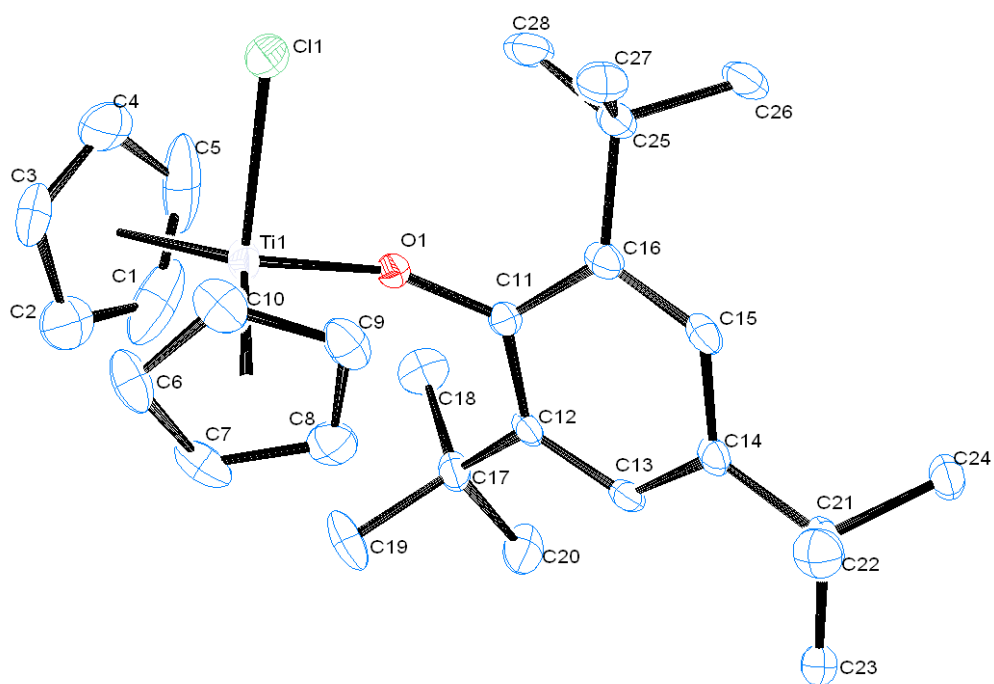
Figure 3.4. Thermal ellipsoid diagram (50% probability level) of **3.4.** Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Ti1-Cl1, 2.391(3); Ti1-O1, 1.9152 (17); O1-C11, 1.362(3); Ti1-O1-C11, 140.44(16); Cl1-Ti1-O1, 100.56(6).

The Ti-Cl bond lengths of 2.4107(18) and 2.391(3) Å for **3.3** and **3.4** respectively are greater than the Ti-Cl distance of 2.364(3) Å found in Cp_2TiCl_2.[46] Elongation of the Ti-Cl bond was also observed in the related complexes $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(OPh)(Cl)$[43] and $(\eta^5\text{-}C_5H_5)_2Ti(OEt)(Cl)$[44] with Ti-Cl bond lengths of 2.3964(6) Å and 2.405(1) Å respectively and is evidence for π bonding competition between the Cl and O atoms. This can be observed for compounds **3.3** and **3.4** where an elongation of the Ti-O bond due to decreased O→Ti π-donation in compound **3.4** is correlated with an increased π-donation from the chloride, resulting in a decreased Ti-Cl bond length.

3.3   Synthesis of titanocene aryloxide triflates

It was previously determined that titanocene phenoxide triflate complex **2.10** can be reacted with 2-phenoxy-1-phenethanol **2.1** in the presence of base to yield the alkoxide phenoxide compound **2.11**. It was therefore hypothesized that the alkoxide aryloxide complexes **3.1** and **3.2** could be prepared via a similar reaction with the corresponding aryloxide triflates. To prepare the desired aryloxide triflates **3.5** and **3.6**, the corresponding aryloxide chlorides were reacted with an equimolar amount of silver triflate for 1 hour, and the silver chloride byproduct was isolated by filtration (eq 3.2).

(3.2)
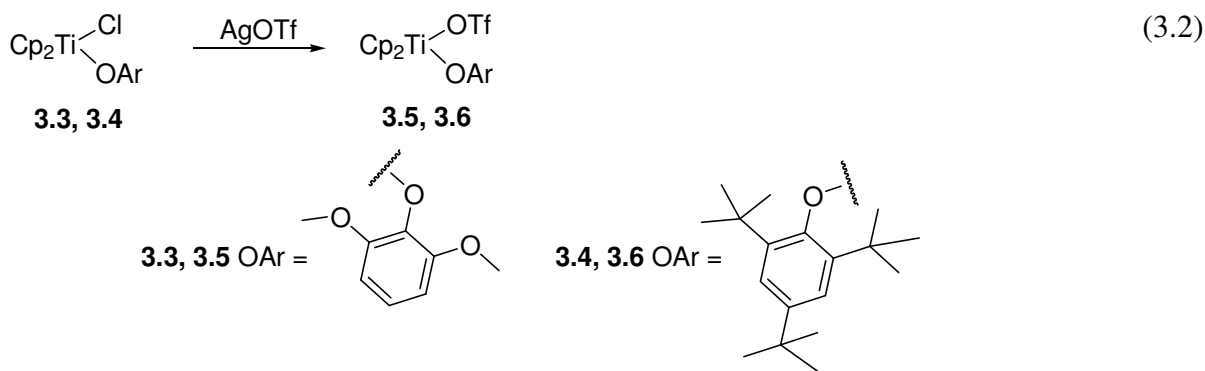
The reaction of the 2,6-dimethoxyaryloxide chloride compound **3.3** with silver triflate resulted in a red solution. The NMR of the product showed a slight downfield shift of the cyclopentadienyl proton peaks relative to those of the starting material, suggesting the replacement of the chloride with the more electron-withdrawing triflate and the formation of the desired aryloxide triflate compound **3.5**.

When $Cp_2Ti(OMes^*)Cl$ was reacted with silver triflate, the solution color changed immediately from the dark red color of the aryloxide chloride to dark green. In previous

reactions, titanocene aryloxide triflates gave rise to orange-red solutions; thus, the color change observed here was unexpected. This dramatic difference in color may indicate significantly different geometry at the titanium centre due to steric demands of the OMes* ligand. Although the product was contaminated with some unreacted starting material, resulting in the overlap of several aryloxide peaks in the ^{1}H NMR, a downfield shift of 0.24 ppm was observed for the cyclopentadienyl proton signal, supporting the formation of the desired OMes* triflate complex **3.6**.

3.4 Synthesis of titanocene aryloxide enolates

Titanocene alkoxide phenoxide **2.11** can also be prepared via a reaction of titanocene enolate phenoxide **2.5** with alcohol **2.1** in the presence of [HNEt$_3$]X (X = OTf, BPh$_4$). It was hypothesized that a similar reaction could be used to prepare alkoxide aryloxide complexes **3.1** and **3.2** from the corresponding enolate aryloxides.

To prepare the desired compounds **3.7** and **3.8**, the corresponding aryloxide triflates **3.5** and **3.6** were reacted overnight with a slight excess of potassium enolate (eq 3.3). In addition to a change in the chemical shift of the cylcopentadienyl protons relative to the starting material, the ^{1}H NMR of both products contained two separate singlets for the methylene protons. This was also observed for the enolate phenoxide complex **2.5**[22] and serves to support the formation of the desired enolate aryloxides **3.7** and **3.8**.

$$(3.3)$$
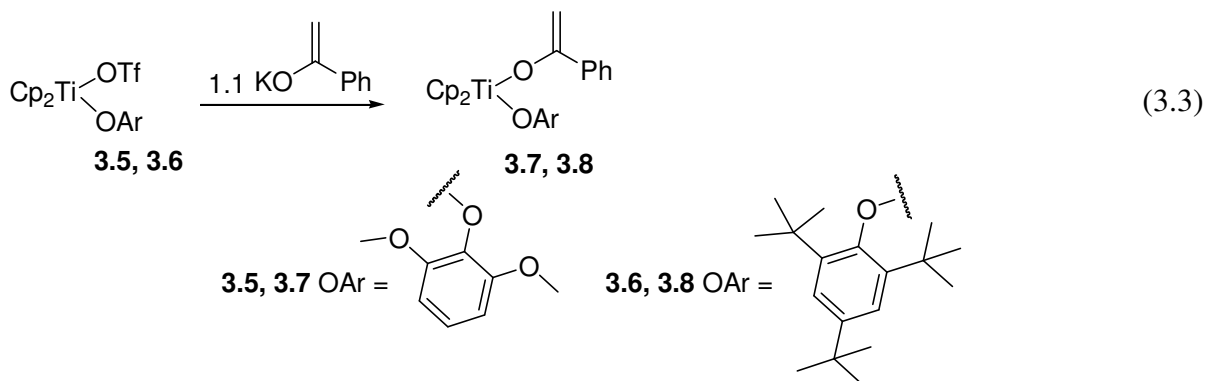
3.5 Protonolysis reactions of titanocene 2,6-dimethoxyphenoxide enolate

To test the hypothesis that *ortho* substituents would weaken the Ti-OAr bond, compound **3.7** was reacted with some mild acids. Triethylammonium chloride was previously used in the protonolysis of phenoxide enolate **2.5** and was shown to cleanly cleave

the Ti-enolate bond, but was ineffective in the protonolysis of the Ti-phenoxide bond. Similar results were observed in the reaction of **3.7** with [HNEt$_3$]Cl (eq 3.4). The first equivalent of the acid cleanly and rapidly cleaved the Ti-enolate bond. When a second equivalent of [HNEt$_3$]Cl was added to the mixture and allowed to react for 20 hours, no further changes were observed. Subsequently, **3.7** was reacted with [HNEt$_3$]OTf to test for counteranion effects. The observed reactivity was the same. The first equivalent of acid cleaved the Ti-enolate bond, yielding approximately 66% yield of acetophenone and titanocene aryloxide triflate. No reaction was achieved with a second equivalent of [HNEt$_3$]OTf over 20 hrs. These experiments do not indicate that *ortho*-disubstitution weakened the Ti-aryloxide bond sufficiently to allow protonolysis by [HNEt$_3$]X (X = Cl, OTf). Since the synthesis of **3.7** required multiple steps over multiple days and the yields were fairly low, further protonolysis reactions of the compound were not carried out.

(3.4)
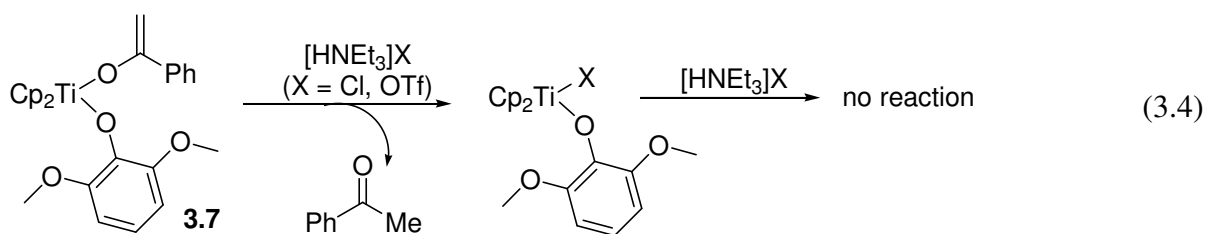
3.6 Protonolysis reactions of titanocene OMes* enolate

The reactivity of **3.8** with mild acids was briefly investigated. As in the case of **3.7**, triethylammonium chloride was the first acid tested. In an NMR scale reaction, **3.8** reacted with an equimolar amount of [HNEt$_3$]Cl to produce acetophenone and Cp$_2$Ti(OMes*)Cl (eq 3.5). Interestingly, this reaction was not as rapid as the one involving enolate phenoxide **2.5** and enolate aryloxide **3.7** (~20 min with **3.8** compared to less than 10 min with **2.5** and **3.7**). It was postulated that this increase in reaction time may be due to the steric bulk of the OMes* ligand preventing access of the acid to the metal. When a second equivalent of [HNEt$_3$]Cl was added to the reaction mixture, no change was observed over 18 hours by NMR, again suggesting that the *ortho tert*-butyl substituents of the aryloxide ligand do not result in sufficient weakening of the Ti-O bond. Since the synthesis of **3.5** required multiple low-yielding steps, further protonolysis reactions of the compound were not carried out.

$$(3.5)$$
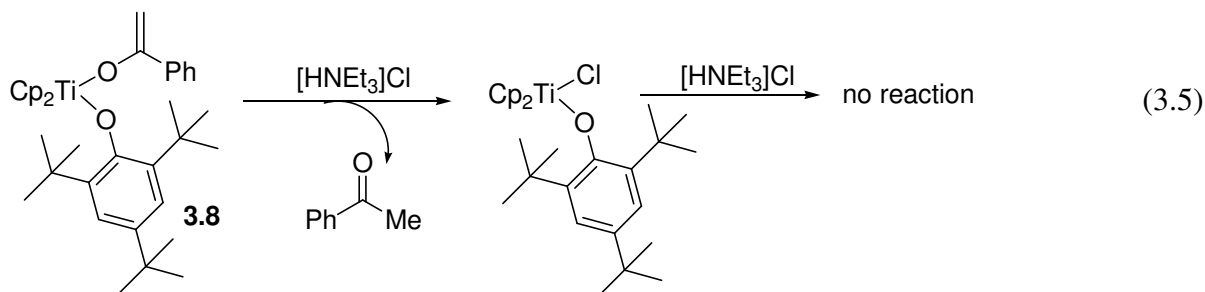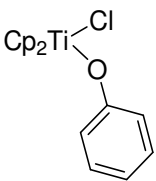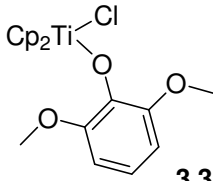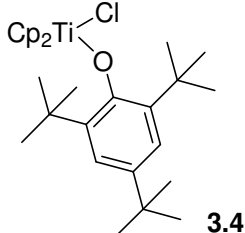
3.7 Protonolysis of titanocene aryloxide chloride complexes

Investigation of the protonolysis of the enolate aryloxide compounds **2.5**, **3.7**, and **3.8** has proven tedious due to the multi-step synthesis of said compounds. However, it has been established that the Ti-enolate bond in all three compounds can be cleaved nearly quantitatively with acids as mild as [HNEt$_3$]Cl (pKa = 10.75).[20] Although it was postulated that the increased steric bulk of the aryloxide ligand in aryloxide enolates **3.7** and **3.8** would weaken the Ti-OAr bond, its protonolysis with [HNEt$_3$]Cl was not observable for either compound.

The products of the Ti-enolate bond protonolysis of titanocene aryloxide enolates **2.5**, **3.7**. and **3.8** with acids of type [HNR$_3$]Cl are the corresponding titanocene aryloxide chloride complexes **2.9**, **3.3**, and **3.4**, which can be synthesized much more rapidly than the enolates. This prompted the investigation of the reactivity of titanocene aryloxide chlorides **2.9**, **3.3**, and **3.4** with acids that are stronger than triethylammonium salts. To allow for a comparison of yields and rates, all three aryloxide chlorides were reacted with [HNEt$_3$]Cl (pKa = 10.75)[20], [HLut]Cl (pKa = 6.65)[20], and 37% aqueous HCl (pKa < 0) in separate NMR tubes containing a known amount of internal standard. The results of the experiment are summarized in Table 3.1 below.

Table 3.1. Protonolysis of titanocene aryloxide chloride compounds with various acids.

Acid used	Reaction time	Conversion to Cp_2TiCl_2 **2.9**	Conversion to Cp_2TiCl_2 **3.3**	Conversion to Cp_2TiCl_2 **3.4**
[HNEt$_3$]Cl (pKa = 10.75)	10 min	0%	0%	Trace
	24 hrs	0%	0%	Trace
[HLut]Cl (pKa = 6.65)	10 min	0%	Trace	Trace
	24 hrs	0%	25%	95%
	6 days	-	50%	100%
HCl (pKa < 0)	10 min	Trace	100%	100%
	24 hrs	100%	-	-

Reactions were monitored by ^{1}H NMR, recorded at 10 min, 24 hrs, and 6 days as necessary. Reaction progress at various times is quoted as percent conversion of titanocene aryloxide chloride complex to Cp_2TiCl_2. The percent conversion was calculated as a ratio of the Cp_2TiCl_2 cyclopentadienyl peak integration over the sum of the starting material and product Cp peaks.

Titanocene phenoxide chloride **2.9** showed no reaction with [HNEt$_3$]Cl or [HLut]Cl over 24 hours. When **2.9** was reacted with concentrated aqueous HCl, traces of the protonolysis products were observable after 10 min, with a full conversion to Cp_2TiCl_2 and phenol after 24 hours.

Titanocene 2,6-dimethoxyaryloxide chloride **3.3** also showed no reactivity in the presence of [HNEt$_3$]Cl after 24 hours. Interestingly, approximately 25% of the starting material converted to Cp_2TiCl_2 and 2,6-dimethoxyphenol when allowed to react with [HLut]Cl for 24 hours. After 6 days, a 50% conversion was observed, suggesting that the reaction slows down and may achieve an equilibrium after several days (eq 3.6). Compound **3.3** also reacted with HCl, much more rapidly than **2.9**, and conversion to products was complete within 10 minutes. These results indicate that the Ti-OAr bond in **3.3** is weakened, likely due to steric effects by the *ortho* methoxy substituents on the aryloxide ligand.

$$\text{(3.6)}$$
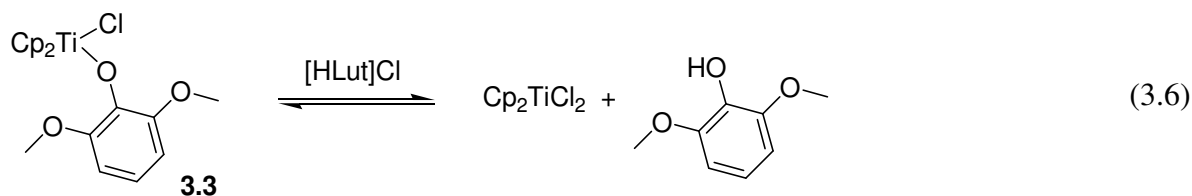
Titanocene OMes* chloride compound **3.4** was also reacted with the selected acids. In the presence of [HNEt$_3$]Cl, trace amounts of **3.4** were converted to Cp$_2$TiCl$_2$ and 2,4,6-tri-*tert*-butylphenoxide after 10 minutes, but no additional reaction was observed after 24 hours. Compound **3.4** was then reacted with [HLut]Cl. After 10 minutes, partial conversion to Cp$_2$TiCl$_2$ was observed in the NMR spectrum. After 24 hours, approximately 95% of the starting material underwent protonolysis to yield Cp$_2$TiCl$_2$ and the corresponding phenol. A subsequent NMR recorded five days later showed complete consumption of the aryloxide chloride **3.4**. This is consistent with the expected weakening of the titanocene-aryloxide bond as a result of increased steric bulk of the aryloxide ligand. Protonolysis of **3.4** with HCl was also carried out. The conversion of starting material to products was complete within 10 minutes. While this reaction is more rapid than the protonolysis of titanocene phenoxide chloride **2.9** by HCl, it is uncertain whether it is faster than the reaction of the 2,6-dimethoxyphenoxide chloride compound **3.3.** Both compounds **3.3** and **3.4** were completely consumed by the time the NMR spectrum was recorded.

3.8   Attempted synthesis of titanocene alkoxide aryloxide complexes

As anticipated, increasing the steric bulk of the aryloxide ligand resulted in a weakening of the Ti-OAr bond. To determine if this weakening was sufficient to allow for protonolysis of the aryloxide ligand by the benzylic proton of the β-O-4 alkoxide, titanocene alkoxide aryloxide complexes **3.1** and **3.2** needed to be synthesized. Synthetic attempts were monitored by NMR. Although the detection of the alkoxide aryloxide complexes was anticipated, these compounds are potentially unstable with respect to loss of the substituted phenol and subsequent carbon-oxygen bond cleavage, as shown in equation 3.7. Thus, the presence of the corresponding phenol and enolate phenoxide **2.5** in the NMR spectrum would equally indicate a successful synthesis of target compounds **3.1** and **3.2**.

(3.7)
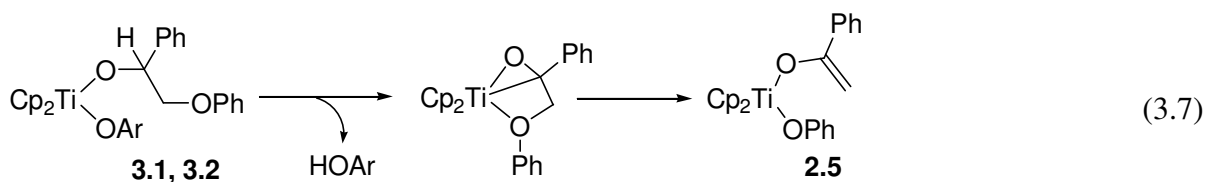
It was postulated that titanocene alkoxide aryloxide compounds **3.1** and **3.2** could be prepared via a reaction of the corresponding aryloxide enolate with alcohol **2.1** in the presence of [HNEt$_3$]X (X = OTf, BPh$_4$), analogous to the synthesis of titanocene alkoxide phenoxide **2.11**. Thus, the 2,6-dimethoxyalkoxide enolate complex **3.7** was combined with alcohol **2.1**. It was expected that no reaction will take place as no acid was added. However, an NMR spectrum recorded 15 minutes after mixing showed traces of acetophenone. This suggested the protonolysis of the Ti-enolate bond by the alcohol. The reaction was thus allowed to proceed without acid addition. After 4 days, a complete disappearance of the enolate aryloxide peaks was noted in the NMR spectrum. By comparison to an internal standard peak, it was determined that all of the starting material underwent Ti-enolate bond cleavage to produce acetophenone. Furthermore, a loss of approximately 50% of cyclopentadienyl-containing compounds was observed. This, coupled with the precipitation of a grey solid in the NMR tube, suggests the formation of some insoluble byproduct as a result of the reaction. The NMR spectrum showed a mixture of previously unobserved titanocene products. The major product possessed an alkoxide ligand bound to titanocene, and the diastereotopically split cyclopentadienyl proton signals were observed at 6.10 and 6.26 ppm in deuterated dichloromethane. While this product was suspected to be the desired titanocene alkoxide aryloxide compound **3.1** (eq 3.8), definitive assignment of peaks was not possible and purification or crystallization was not attempted due to the small scale of the reaction.

(3.8)
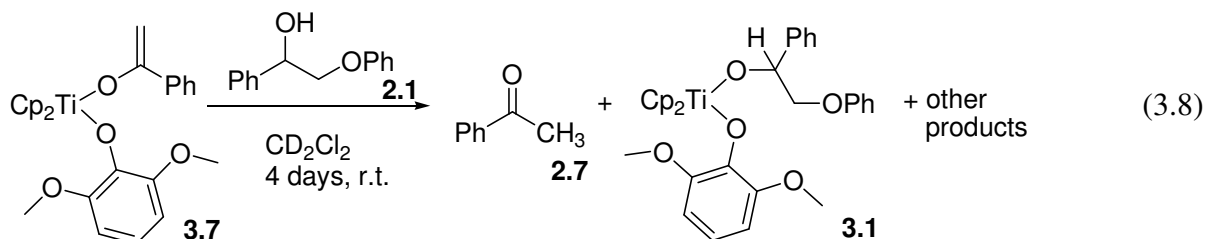
To determine if the presence of acid changes the outcome of the reaction, aryloxide enolate **3.7** was reacted with alcohol **2.1** in the presence of [HNEt$_3$]BPh$_4$. The mixture was allowed to react overnight and filtered to isolate solid byproducts. The ^{1}H NMR spectrum was then recorded. As in the above reaction, a complete disappearance of aryloxide enolate **3.7** was observed along with the formation of a mixture of products, including acetophenone (eq 3.9). Since the protonolysis of the Ti-enolate bond by [HNEt$_3$]X (X = Cl, OTf) was observed previously, this result was not unexpected. Furthermore, it is not surprising that the protonolysis is much more rapid with the use of acid, taking 1 day or less, as compared to the 4 days required for the acid-free reaction above. The major titanocene product in this reaction was the same as above, with cyclopentadienyl proton signals at 6.09 and 6.25 ppm, and is postulated to be the titanocene alkoxide aryloxide compound **3.1**.

(3.9)
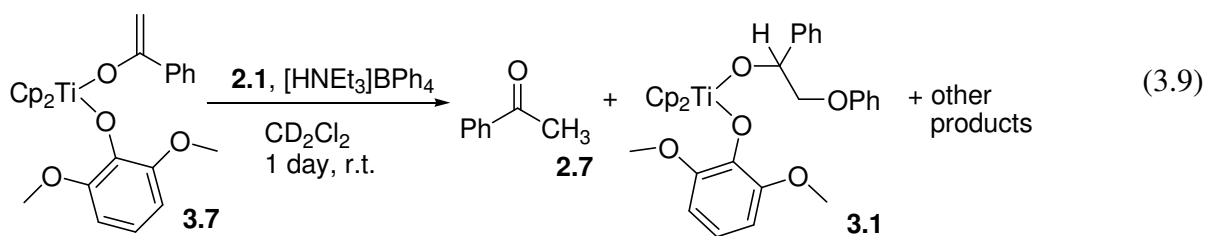
It was postulated that the presumed lack of coordination of the tetraphenylborate ion following the protonolysis of the Ti-enolate bond in the above reaction might be leading to side reactions. This was previously observed in the protonolysis of titanocene phenoxide enolate **2.5** with acids of type [HNR$_3$]BPh$_4$. Thus, the above reaction was repeated with [HNEt$_3$]OTf. The triflate ion was expected to bind to titanium to prevent unwanted side reactions due to an open coordination site, yet the binding should be weak enough such that the triflate is easily displaced by the alkoxide ligand, as was the case in previous reactions of Cp$_2$Ti(OPh)(OTf) (**2.10**) with alcohol **2.1** in the presence of triethylamine. Contrary to expectations, the change of the triethylammonium counteranion did not produce significant improvements in the reaction of 2,6-dimethoxyaryloxide enolate **3.7** with alcohol **2.1**. Although **3.7** was completely consumed and acetophenone was formed, the lack of coordination of alcohol **2.1** indicates that the desired alkoxide aryloxide product **3.1** was not obtained (eq 3.10).

$$\text{(3.10)}$$
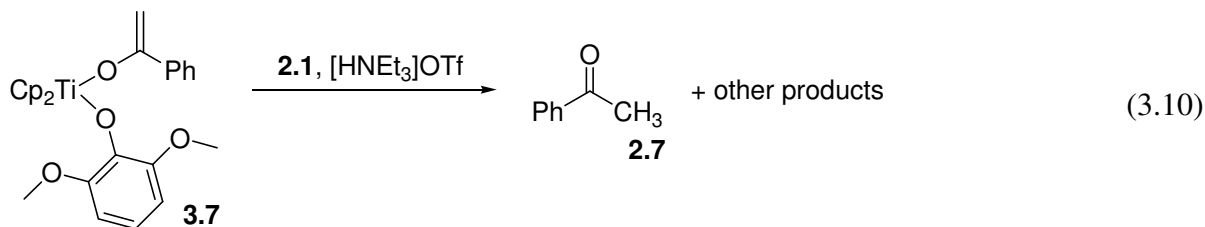
Similarly, synthesis of alkoxide aryloxide **3.2** was attempted using the above route. Titanocene OMes* enolate complex **3.8** was reacted with alcohol **2.1** in the presence of [HNEt₃]OTf. As expected based on previous reactions, protonolysis of the Ti-enolate bond was achieved to form the OMes* triflate complex **3.6**. This compound did not react further (eq 3.11). It is postulated that the steric demands of the OMes* ligand are preventing the access of alcohol **2.1** to the titanium centre.

$$\text{(3.11)}$$
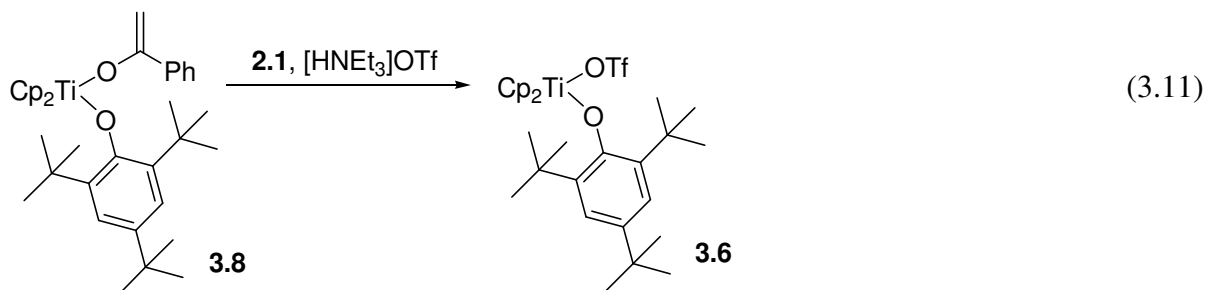
3.9 Study of the reactivity of titanocene alkoxide triflate with phenols

An alternative approach at the synthesis of alkoxide aryloxide complexes **3.1** and **3.2** might involve a reaction of a suitable titanocene alkoxide complex with the corresponding phenol. For this purpose, the titanocene alkoxide triflate complex **2.6** was chosen as the triflate ligand was expected to be easily replaced by an aryloxide ligand. Compound **2.6** was synthesized via a salt metathesis reaction of the titanocene alkoxide chloride complex **2.3** with silver triflate and isolated as a solid. A known amount of **2.6** was then reacted with phenol, 2,6-dimethoxyphenol, or 1,3,5-tri-*tert*-butylphenol. The amounts of the various phenols ranged from 0.5 up to 3 equivalents, relative to **2.6**.

It was discovered that when the alkoxide triflate complex **2.6** is reacted with phenol, titanocene phenoxide triflate **2.10** is formed. Complete conversion to phenoxide triflate **2.10**

can be achieved with two equivalents of phenol (eq 3.12). Similarly, when titanocene alkoxide triflate **2.6** is reacted with 2,6-dimethoxyphenol, titanocene 2,6-dimethoxyphenoxide triflate **3.5** is observed. The addition of two equivalents of 2,6-dimethoxyphenol results in an equilibrium solution where approximately 85% of the starting material is converted to the aryloxide triflate product (eq 3.13). However, when alkoxide triflate **2.6** is combined with 2,4,6-tri-*tert*-butylphenol, no reaction is observed after 24 hours even with a 3-fold excess of the phenol reagent, suggesting an equilibrium which lies heavily to the left (eq 3.14). These results are in agreement with the previously observed trend in the relative stability of the Ti-OAr bond for the three aryloxide ligands.

(3.12)

(3.13)

(3.14)
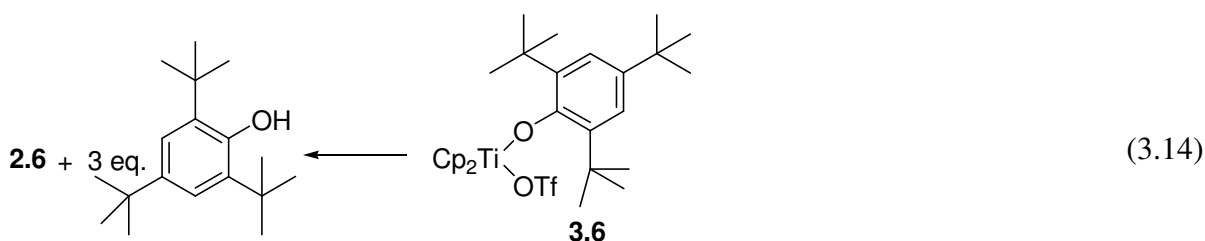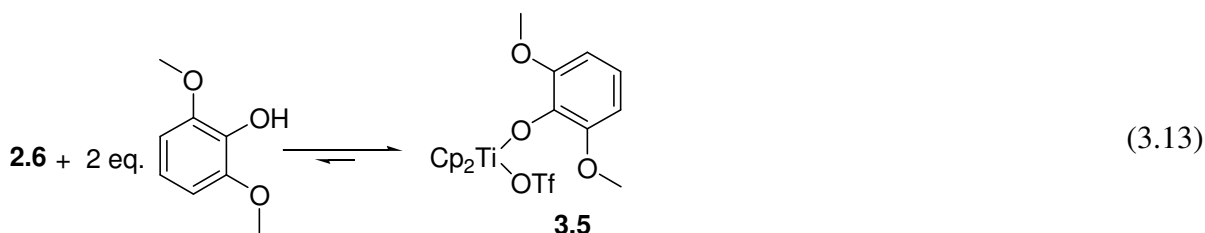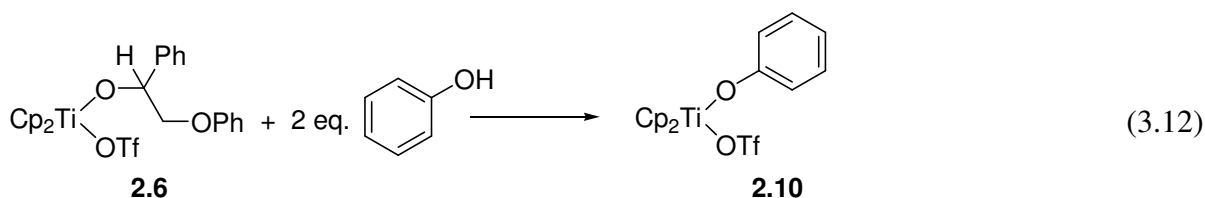
It is postulated that the protonolysis of the Ti-alkoxide bond in titanocene alkoxide triflate **2.6** with phenol occurs via a series of reversible steps as shown in Figure 3.5. The dissociation of the triflate ion and coordination of the phenol results in the formation of the cationic titanocene intermediate **B**. The acidic proton of the phenol becomes well positioned to protonate the oxygen of the alkoxide ligand. Following protonation and elimination of the

alkoxide, triflate recoordinates to titanium, yielding the observed titanocene phenoxide triflate.
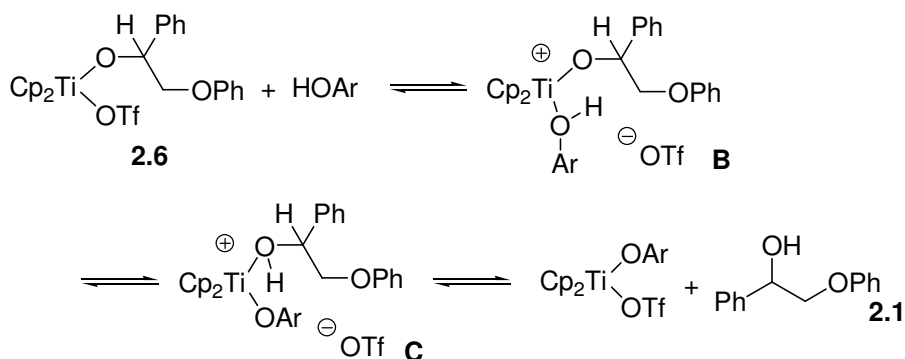
Figure 3.5. Postulated mechanism for the protonolysis of Ti-alkoxide bond by aryl alcohols.

Since the Ti-OPh bond is stronger that the Ti-alkoxide bond, this process is favourable when the alkoxide triflate **2.6** is reacted with phenol. As shown by protonolysis of titanocene aryloxide chlorides, the bond between titanium and 2,6-dimethoxyaryloxide is weaker than the Ti-OPh bond. Thus, the replacement of the alkoxide ligand by 2,6-dimethoxyaryloxide is slightly less favourable, resulting in the observed incomplete conversion to 2,6-dimethoxyphenoxide triflate **3.5**. Due to the large steric bulk of the OMes* ligand, the formation of cationic intermediate **B** is unlikely in the reaction of alkoxide triflate **2.6** with 2,4,6-tri-*tert*-butylphenol. Even if the intermediate did form, the protonolysis of the Ti-alkoxide bond would not be favoured due to the relative weakness of the Ti-OMes* bond.

It was postulated that a similar equilibrium process takes place during the reaction of titanocene phenoxide triflate **2.10** with alcohol **2.1**, where the addition of base is required to produce the alkoxide phenoxide complex **2.11** (eq 3.15). Although compounds **2.10** and **2.1** underwent no observable reaction in the absence of base, a reversible coordination of the alkoxide ligand to produce intermediate **C** might be occuring. The coordination of the alkoxide to titanium increases the acidity of the OH proton, allowing for irreversible deprotonation by a weak base such as triethylamine.

$$(3.15)$$

35
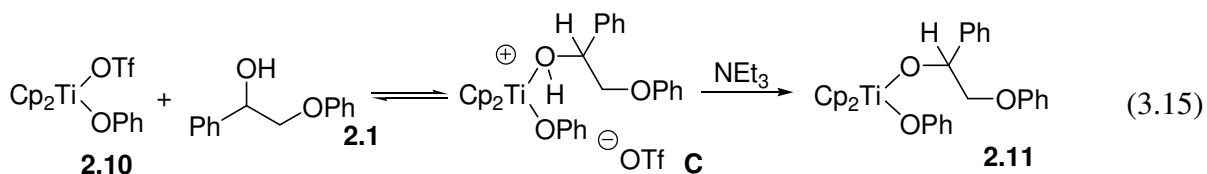
It was hypothesized that in the reaction of titanocene alkoxide triflate with phenols, triethylamine could be used to irreversibly deprotonate intermediate **B** or **C**, leading to the formation of the desired titanocene alkoxide aryloxide complexes. This hypothesis might be tested in the future.

3.10   Carbon-oxygen bond cleavage of 2-(2,6-dimethoxyphenoxy)-1-phenylethanone

While a move towards more realistic lignin model compounds was desirable, it was suspected that the presence of additional oxygen atoms in the molecule might result in different reactivity pathways during the C-O bond cleavage step of the target catalytic cycle. A binding competition between methoxy and aryl ether oxygen atoms could result in a decreased reaction rate or in the generation of unwanted byproducts. Thus, the C-O bond cleavage of a methoxylated β-O-4 model compound, 2-(2,6-dimethoxyphenoxy)-1-phenylethanone (**3.9**), was investigated in parallel with the above reactions.

To study the bond cleavage of α-aryloxy ketone **3.9**, the compound was reacted with $Cp_2Ti(BTMSA)$, a commonly used source of Cp_2Ti^{II} (eq 3.16).[24] Although an immediate color change from brown to red was observed, the mixture was allowed to react for 1 hour. The ^1H NMR spectrum of the resulting product mixture matched that of the independently synthesized titanocene 2,6-dimethoxyphenoxide enolate **3.7**, indicating successful C-O bond cleavage of ketone **3.9**. No other titanocene products were observed, suggesting no side-reactions due to additional oxygen atoms in the substrate.

(3.16)
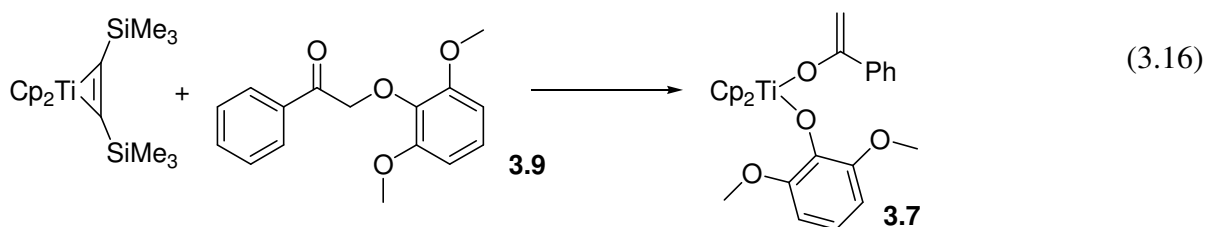
3.11   Experimental section

General considerations. Protocols were identical to those reported in section 2.5. Additionally, C_6D_6 was dried over sodium/benzophenone, purified by vacuum distillation, degassed by three freeze-vacuum-thaw cycles and stored under nitrogen. 2-(2,6-

dimethoxyphenoxy)-1-phenylethanone (**3.9**) was prepared from 2-bromoacetophenone, 2,6-dimethoxyphenol, and K_2CO_3 according to literature procedure.[7] KOC(=CH$_2$)Ph was prepared from acetophenone and KN(SiMe$_3$)$_2$.[47] 2,6-dimethoxyphenol (99%) and 2,4,6-tri-*tert*-butylphenol (98%) were obtained from Aldrich. Aqueous hydrochloric acid (36-38%) was purchased from Fisher Scientific.

Synthesis of titanocene 2,6-dimethoxyphenoxide chloride (3.3). Sodium hydride (46.7 mg, 1.95 mmol) was suspended in 8 mL of THF. A solution of 2,6-dimethoxyphenol (300.4 mg, 1.95 mmol) in 5 mL THF was added dropwise, causing the evolution of gas. The mixture was allowed to react overnight in a Schlenk flask with an opened sidearm to prevent pressure buildup. Cp$_2$TiCl$_2$ (484.6 mg, 1.95 mmol) was then added, resulting in an immediate color change to dark red. After 24 hours, the solvent was removed in vacuo. The red residue was then extracted with 15-20 mL of diethyl ether, filtered through Celite, and taken to dryness again in vacuo. Recrystallization of the crude product from 5 mL of diethyl ether at -30°C for two days yielded dark red X-ray-quality crystals of **3.3** (218.3 mg, 31%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 6.74 (dd, *J* = 8.0, 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 6.31 (s, 10H), 3.80 (s, 6H). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ 151.65, 149.05, 119.59, 118.61, 106.01, 56.55.

Synthesis of titanocene OMes* chloride (3.4). Sodium hydride (27.6 mg, 1.15 mmol) was suspended in 8 mL of THF. A solution of 2,4,6-tri-*tert*-butylphenol (300.1 mg, 1.14 mmol) was added dropwise, resulting in gas formation. The mixture was stirred overnight in a Schlenk flask with an opened sidearm to prevent pressure buildup. Cp$_2$TiCl$_2$ (284.7 mg, 1.14 mmol) was then added, causing an immediate color change to dark red. After stirring for 24 hours, solvent was removed in vacuo. The dark red residue was extracted with hexanes, filtered through Celite, and then again taken to dryness in vacuo. Recrystallization of the crude product from 5 mL of hexanes at -30°C gave dark-red X-ray-quality crystals of **3.4** (170.6 mg, 30%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.16 (d, *J* = 2.7 Hz, 1H), 7.04 (d, *J* = 2.7 Hz, 1H), 6.27 (s, 10H), 1.41 (s, 9H), 1.35 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ 173.02. 140.45, 136.24, 132.90, 123.37, 120.51, 118.38, 36.71, 36.29, 34.54, 32.58, 31.96, 31.89.

Synthesis of titanocene 2,6-dimethoxyphenoxide triflate (3.5). Titanocene 2,6-dimethoxyaryloxide chloride **3.3** (220.3 mg, 0.60 mmol) and AgOTf (154.6 mg, 0.60 mmol) were combined in 20 mL of diethyl ether and stirred for 1 hour. The mixture was then filtered

through Celite, stranding a pale pink solid and giving a dark red filtrate. A 1 mL aliquot of the filtrate was taken to dryness in vacuo, and the red residue was redissolved in CD_2Cl_2 to obtain an NMR spectrum of titanocene 2,6-dimethoxyphenoxide triflate **3.5**. The remaining filtrate was used for the synthesis of titanocene 2,6-dimethoxyphenoxide enolate **3.7** without further purification. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.82 (t, $J = 8.0$ Hz, 1H), 6.60 (d, $J = 8.0$ Hz, 2H), 6.48 (s, 10H), 3.82 (s, 6H).

Synthesis of titanocene OMes* triflate (3.6). Titanocene OMes* chloride **3.4** (6.3 mg, 0.013 mmol) and silver triflate (3.2 mg, 0.012 mmol) were combined in 8 mL of hexanes, resulting in a red-brown solution. No color change and no precipitate formation were observed within an hour due to the low solubility of AgOTf in hexanes. The mixture was therefore allowed to react overnight, resulting in a green solution. The solvent was removed in vacuo. The green-brown residue was redissolved in CD_2Cl_2 and filtered through celite. The contamination of product with starting material resulted in peak overlap of the phenyl and methyl peaks in the ^{1}H NMR spectrum and no chemical shifts are therefore provided. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.50 (s, 10H)

Synthesis of titanocene 2,6-dimethoxyphenoxide enolate (3.7). $KOC(=CH_2Ph)$ (95.4 mg, 0.60 mmol) was added to a solution of crude titanocene 2,6-dimethoxyphenoxide triflate **3.5** (approximately 0.60 mmol) in 20 mL of diethyl ether. The mixture was stirred for 24 hours and then filtered through Celite, giving a red solution. The solvent was removed in vacuo. The orange/red residue was dissolved in 4 mL of diethyl ether and cooled to -30°C. Pure orange-red powder of titanocene 2,6-dimethoxyphenoxide enolate **3.7** was isolated (46.6 mg, 17%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.72 (d, $J = 7.2$ Hz, 2H), 7.33 (t, $J = 7.2$ Hz, 2H), 7.27 (d, $J = 7.2$ Hz, 1H), 6.72 (dd, $J = 7.6$ Hz, 1H), 6.61 (d, $J = 7.6$ Hz, 2H), 6.29 (s, 10H), 4.65 (s, 1H), 4.01 (s, 1H), 3.82 (s, 6H).

Synthesis of titanocene OMes* enolate (3.8). A solution of titanocene OMes* choride **3.4** (101.5 mg, 0.204 mmol) in 8 mL of diethyl ether was added to a suspension of AgOTf (52.5 mg, 0.204 mmol) in 4 mL of diethyl ether. Immediate color change from dark red to dark green accompanied by the formation of a coarse pale precipitate indicated the formation of titanocene OMes* triflate **3.6**. The mixture was stirred for 1 hour and filtered through Celite. The crude solution of **3.6** was added to $KOC(=CH_2Ph)$ (35.5 mg, 0.224 mmol). After 20 hours, the resulting orange-brown mixture was filtered though Celite.

Solvent was removed in vacuo. The residue was redissolved in 1 mL of hexanes and cooled to -30°C for 4 days; however, no solid was isolated. The yield of titanocene OMes* enolate **3.8** was calculated from the ^{1}H NMR of the product by comparison to the 1,3,5-tri-*tert*-butylbenzene internal standard (0.132 mmol, 65% relative to **3.4**). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.50 (m, 2H), 7.32 (m, 3H), 7.09 (s, 2H), 6.35 (s, 10H), 4.24 (s, 1H), 3.80 (s, 1H), 1.28 (m, 27H)

Carbon-oxygen cleavage of 2-(2,6-dimethoxyphenoxy)-1-phenylethanone (3.9). $Cp_2Ti(BTMSA)$ (7.8 mg, 0.22 mmol) in 0.5 mL C_6D_6 was combined with 2-(2,6-dimethoxyphenoxy)-1-phenylethanone **3.9** (6.3 mg, 0.023 mmol) in 0.5 mL C_6D_6, resulting in an immediate color change from orange-brown to red. The mixture was allowed to react for 1 hour, producing titanocene 2,6-dimethoxyphenoxide enolate **3.7** and bis(trimethylsilyl)acetylene. ^{1}H NMR (400 MHz, C_6D_6): δ 8.02 (dd, J = 1.2, 8.4 Hz, 2H), 7.30 (t, J = 8.0 Hz, 2H), 7.20 (tt, J = 1.2, 7.2 Hz, 1H), 6.76 (t, J = 8.4 Hz, 1H), 6.52 (d, J = 8.4 Hz, 2H), 6.12 (s, 10H), 4.91 (s, 1H), 4.14 (s, 1H), 3.42 (s, 6H), 0.16 (s, 18H, $Me_3SiC{\equiv}CSiMe_3$)

Protonolysis of the aryloxide chloride compounds 2.9, 3.3, 3.4. A known amount of 1,3,5-tri-*tert*-butylbenzene internal standard (~3 mg) was added to each titanocene aryloxide chloride (0.08 mmol) dissolved in 0.80 mL CD_2Cl_2 in separate vials. Similarly, separate solutions of [HNEt₃]Cl and [HLut]Cl (0.08 mmol) in 0.80 mL CD_2Cl_2 were prepared. For reactions of aryloxide chlorides with [HNEt₃]Cl or [HLut]Cl, 0.20 mL of the titanocene solution (0.02 mmol) and 0.20 mL of the acid solution (0.02 mmol) were combined in an NMR tube. For reactions of aryloxide chlorides with HCl, 0.20 mL of the titanocene solution (0.02 mmol) was combined with 5 μL of 37% aqueous HCl (0.06 mmol) in an NMR tube. The reactions were monitored by ^{1}H NMR 10 minutes, 24 hours, and 6 days after combination of the reagents. The % conversion values presented in Table 3.1 were calculated as a ratio of the Cp_2TiCl_2 cyclopentadienyl peak integration over the sum of the starting material and product Cp peaks, relative to the internal standard peak.

Reactions of titanocene alkoxide triflate (2.6) with phenol, 2,6-dimethoxyphenol, and 2,4,6-tri-*tert*-butylphenol. Three solutions of titanocene alkoxide triflate **2.6** (0.05 mmol) and 1,3,5-tri-*tert*-butylbenzene internal standard (0.011 mmol) in 0.4 mL CD_2Cl_2 were prepared. Phenol solution was prepared by dissolving phenol (14.1 mg, 0.15 mmol) in

0.60 mL CD_2Cl_2. Phenol solution was added to compound **2.6** in 0.10 mL aliquots (0.025 mmol phenol per aliquot, 0.5 eq) up to 0.50 mL (2.5 eq), with a ^{1}H NMR spectrum recorded after each addition. 2,6-dimethoxyphenol (30.4 mg, 0.20 mmol) was dissolved in 0.80 mL CD_2Cl_2. The 2,6-dimethoxyphenol solution was added to compound **2.6** in 0.10 mL aliquots (0.025 mmol 2,6-dimethoxyphenol per aliquot, 0.5 eq) up to 0.60 mL (3.0 eq), and a ^{1}H NMR spectrum was recorded after each addition. 2,4,6-tri-*tert*-butylphenol (54.1 mg, 0.21 mmol) was dissolved in 0.80 mL CD_2Cl_2. The 2,4,6-tri-*tert*-butylphenol solution was added to compound **2.6** in 0.10 mL aliquots (0.026 mmol 2,4,6-tri-*tert*-butylphenol per aliquot, 0.5 eq) up to 0.2 mL (1 eq), with a ^{1}H NMR spectrum recorded after each addition. The 1:1 mixture of titanocene alkoxide triflate and 2,4,6-tri-*tert*-butylphenol was allowed to react overnight and another ^{1}H NMR spectrum was recorded. The remaining 2,4,6-tri-*tert*-butylphenol solution (0.5 mL, 2.5 eq) was added and allowed to react overnight before the final spectrum was recorded. The results are presented in section 3.9.

Chapter 4 Zirconocene Complexes for the C-O Bond Cleavage of Lignin Model Compounds

As previously noted, the elimination of phenol from the titanocene alkoxide phenoxide complex **2.11** does not occur readily at ambient temperature; however, this conversion represents an important step in the target catalytic cycle presented in Figure 3.1. A possibility to weaken the Ti-aryloxide bond by increasing the steric bulk of the aryloxide ligand and thus encourage the elimination of phenol was examined in Chapter 3. Alternatively, the replacement of titanium with zirconium was proposed.

Similar to titanium, zirconium is an earth-abundant and inexpensive group IV transition metal with low toxicity.[48] However, the two metals have been observed to react differently. Compared to titanium, zirconium more readily forms five-coordinate 18 valence electron complexes. Neutral complexes of the type $[Cp_2ZrX_2L]$[49] (X = anionic ligand (e.g. H, halides, alkyls), L = neutral ligand) and anionic zirconocene-ate $[Cp_2ZrX_3]^-$ complexes[50] have been reported. Unlike the titanocene analogue, the zirconocene complex of bis(trimethylsilyl)acetylene contains a weakly bound solvent molecule, typically THF or pyridine.[51] In addition, $Cp_2Zr(BTMSA)$ is suspected to react via an associative mechanism where the coordination of substrate precedes the elimination of BTMSA, while $Cp_2Ti(BTMSA)$ more likely reacts dissociatively via a $[Cp_2Ti]$ intermediate.[24] The accessibility of 18-electron zirconocene complexes might allow for alternative reaction pathways for the phenol elimination from zirconocene alkoxide phenoxide complex **4.1**.

4.1
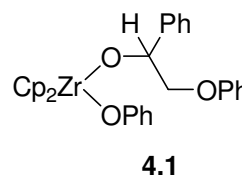
Alternatively, the synthesis of the cationic zirconocene alkoxide chelate complex **4.2** was envisioned. The analogous titanocene alkoxide chelate **A** was proposed as a species in the target catalytic cycle in Figure 1.5. It was postulated that the deprotonation of compound **A** with an external base would lead to the formation of the titanaoxirane intermediate, followed by carbon-oxygen bond cleavage. However, compound **A** could not be synthesized and the proposed reactivity could not be investigated. Related cationic chelate complexes of zirconium have previously been synthesized. Jordan and coworkers isolated crystals of cationic zirconocene chelated by an alkoxide-olefin ligand (Figure 4.1).[52] It was postulated that the ether oxygen of the alkoxide ligand in the hypothetical compound **4.2** might be more

prone to coordination than the vinyl group in Jordan's complex, potentially allowing for the isolation of the cationic chelate species with a bulky non-coordinating counteranion.

Figure 4.1. Cationic chelate complex of zirconium prepared by Jordan and co-workers.[52]

Furthermore, zirconocene alkoxides and aryloxide complexes are readily accessible. The synthesis of zirconocene phenoxide chloride via protonolysis of the commercially available $Cp_2Zr(H)Cl$ with phenol has been reported.[53] Zirconocene bis(alkoxide) complexes can be prepared similarly via reaction of zirconocene dihydride with the corresponding alcohol.[54] To prepare $Cp_2Zr(OR)Me$ compounds, dimethyl zirconocene is reacted with HOR.[54] Compared to the salt metathesis or base-assisted syntheses of titanocene alkoxides, the preparation of zirconocene alkoxides via protonolysis by an alcohol is much more efficient, requiring fewer reagents and generating volatile byproducts, thus eliminating the need for work-up.

4.1   Synthesis of zirconocene alkoxide chloride

It was postulated that the cationic chelate complex **4.2** could be synthesized from zirconocene alkoxide chloride **4.3** by replacing the chloride ligand with less strongly coordinating anions. To prepare the analogous titanocene alkoxide chloride complex **2.3**, Cp_2TiCl_2 was reacted with 2-phenoxy-1-phenethanol **2.1** in the presence of DBU. This route was used to cleanly prepare the zirconocene alkoxide chloride **4.3** from Cp_2ZrCl_2 (eq 4.1). Although crystals of compound **4.3** were obtained, X-ray analysis was not possible. However, the close resemblance to the ^{1}H NMR spectrum of **4.3** to that of the titanocene alkoxide chloride complex **2.3** suggests similarities in bonding. Furthermore, the methylene proton resonances of compound **4.3** are located between 3.91 and 4.02 ppm. The absence of separation in chemical shift of the two proton signals indicates a lack of chelation of the alkoxide ligand.[28] It is therefore postulated that the alkoxide ligand in compound **4.3** binds only through the anionic oxygen, resulting in a neutral four-coordinate species as shown below.

$$Cp_2ZrCl_2 \; + \; \underset{\textbf{2.1}}{\underset{Ph}{\overset{OH}{\diagdown}} \diagdown OPh} \; + \; \text{(DBU structure)} \quad \xrightarrow[\substack{\text{4 hrs}}]{\text{toluene}} \quad \underset{\textbf{4.3}}{Cp_2Zr\underset{Cl}{\overset{O-\overset{\overset{H \; Ph}{|}}{C}-OPh}{\diagup}}} \qquad (4.1)$$
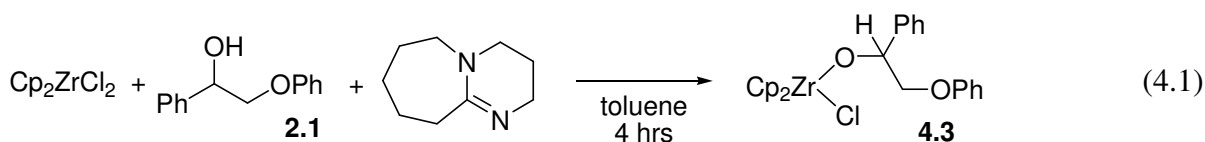
Alternatively, compound **4.3** can be prepared via protonolysis of $Cp_2Zr(H)Cl$ with alcohol **2.1** (eq 4.2). The reaction was first carried out in C_6D_6 in an NMR tube. Immediate gas evolution was observed, but reaction was allowed to proceed overnight to consume all of the $Cp_2Zr(H)Cl$ solid. Although the desired product was obtained as a major component, other zirconocene products were present in the mixture. The concentration of these byproducts increased when the reaction time was extended. It was postulated that a different choice of reaction vessel combined with stirring might accelerate the reaction by allowing the produced hydrogen gas to escape more easily. A shorter reaction time might reduce the formation of unwanted byproducts. The reaction was therefore repeated in an opened vial in an inert atmosphere glovebox with CD_2Cl_2 as the solvent. Compound **4.3** was obtained cleanly within 1.5 hours.

$$Cp_2Zr(H)Cl \; + \; \textbf{2.1} \quad \xrightarrow[\substack{1.5 \text{ hrs}}]{CD_2Cl_2} \quad \underset{\textbf{4.3}}{Cp_2Zr\underset{Cl}{\overset{O-\overset{\overset{H \; Ph}{|}}{C}-OPh}{\diagup}}} \qquad (4.2)$$
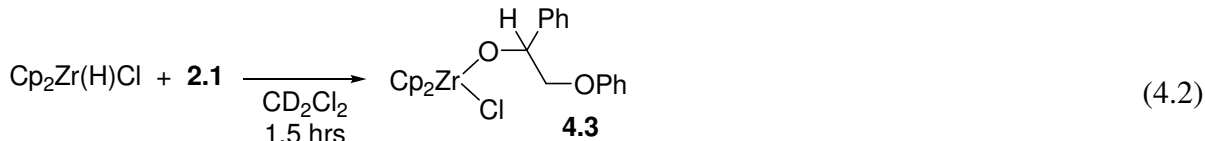
4.2   Substitution of chloride in Cp₂Zr(OR)Cl with weakly coordinating anions

It was hypothesized that a decrease in electron density around zirconium might result in chelation by the alkoxide ligand. To examine this possibility, the chloride ligand in **4.3** was replaced with the less strongly coordinating triflate and tetraphenylborate anions. Both of these ions should form a weaker interaction with the zirconium metal, and might be displaced by the ether oxygen of the alkoxide ligand.

Compound **4.3** and AgOTf were allowed to react in CD_2Cl_2 for approximately 1.5 hours, which is slightly longer than the time needed for the corresponding titanocene reaction to proceed to completion. However, in this time, only a third of **4.3** was converted to a new product, presumed to be the alkoxide triflate **4.4** (eq 4.3). The benzylic proton of the alkoxide ligand as well as the cyclopentadienyl protons of the product are deshielded relative to those of the alkoxide chloride compound **4.3**, consistent with the replacement of the chloride for

43

the more electron-withdrawing triflate. An unusual feature of the ^{1}H NMR of the product is the lack of splitting of the cyclopentadienyl proton signals despite the fact that the alkoxide ligand appears to remain bound to zirconium. Previously synthesized titanocene alkoxide X (X = Cl, OTf) complexes as well as zirconocene alkoxide chloride **4.3** gave rise to diastereotopically split titanocene proton signals; however, the separation of these peaks in the related titanocene alkoxide triflate **2.6** was less than 0.01 ppm. Thus, the lack two distinct Cp proton peaks in compound **4.4** due to peak overlap is not unexpected.

(4.3)
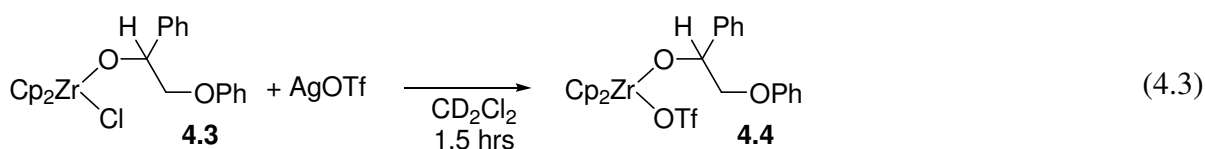
The reaction of zirconocene alkoxide chloride **4.3** with sodium tetraphenylborate was carried out in diethyl ether. After 22 hours, an NMR of the resulting mixture showed mostly unreacted starting material and one new cyclopentadienyl proton signal. It was hypothesized that if the new product were the desired cationic chelate complex **4.2**, addition of a mild base would lead to deprotonation of the alkoxide ligand followed by carbon-oxygen bond cleavage to yield the enolate phenoxide complex **4.5** (eq 4.4). While additions of base to related titanocene alkoxide X (X = Cl, OTf) complexes resulted in no reaction, the addition of a slight excess of triethylamine to the above mixture lead to the formation of a variety of new zirconocene products. Although zirconocene enolate phenoxide **4.5** was not observed in the solution by ^{1}H NMR, the compound is expected to be unstable with respect to protonolysis by the conjugate acid of triethylamine. No other attempts were made to synthesize the cationic zirconocene chelate species **4.2** and its reactivity was not studied further.

(4.4)
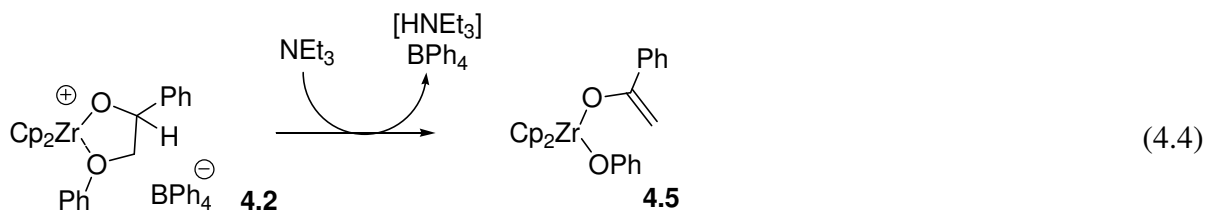
4.3 Attempted synthesis of zirconocene alkoxide phenoxide

In parallel with the above reactions, the synthesis of zirconocene alkoxide phenoxide **4.1** was attempted. The related titanocene alkoxide phenoxide complex **2.11** can be prepared via a reaction of titanocene phenoxide triflate **2.10** with alcohol **2.1** in the presence of triethylamine. To attempt this route for the synthesis of the zirconocene complex **4.1**, zirconocene phenoxide triflate, and its precursor $Cp_2Zr(OPh)Cl$, needed to be synthesized.

Synthesis of zirconocene phenoxide chloride by a salt metathesis reaction of Cp_2ZrCl_2 with NaOPh was first attempted. This route was shown successful in obtaining the analogous titanocene phenoxide chloride compound **2.9**. In the zirconocene reaction, $Cp_2Zr(OPh)Cl$ was obtained as the major product, but contaminants were present. Thus, the compound was instead prepared via a previously reported reaction of $Cp_2Zr(H)Cl$ with $HOPh$.[53] Silver triflate was subsequently added and allowed to react for an hour. The resulting solution of zirconocene phenoxide triflate was then split into two portions and reacted with alcohol **2.1** with or without the addition of base (eq 4.5). When only alcohol **2.1** was added, no reaction occurred over several days. In contrast, when **2.1** was added in combination with triethylamine, a number of unidentified products were obtained. While NMR evidence suggests binding of the deprotonated alcohol to zirconium, formation of alkoxide phenoxide **4.1** by this route is uncertain.

$$Cp_2Zr\genfrac{}{}{0pt}{}{OPh}{Cl} \xrightarrow{\text{AgOTf}} Cp_2Zr\genfrac{}{}{0pt}{}{OPh}{OTf} \begin{array}{l} \xrightarrow{\textbf{2.1}} \text{no reaction} \\ \xrightarrow[\substack{\textbf{2.1,}\\ NEt_3}]{} \text{multiple products} \end{array} \qquad (4.5)$$
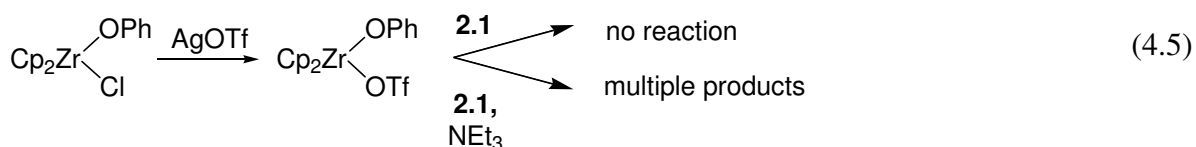
A method for the synthesis of **4.1** by salt metathesis was proposed. Although the combination of titanocene alkoxide chloride **2.3** with NaOPh didn't result in a reaction, zirconocene complex **4.3** may have an associative reaction pathway available to allow for a successful salt metathesis reaction. Indeed, a reaction was observed between the zirconocene alkoxide chloride complex **4.3** and NaOPh (eq 4.6). Multiple products were obtained and not identified. Formation of ate complexes such as $[Cp_2Zr(OCHPhCH_2OPh)(OPh)(Cl)]^-$ is possible.

$$\text{[Cp}_2\text{Zr(OCH(Ph)CH}_2\text{OPh)Cl]} \quad \textbf{4.3} \quad + \text{ NaOPh} \quad \longrightarrow \quad \text{multiple products} \qquad (4.6)$$
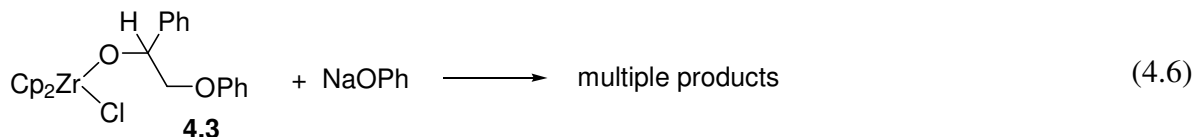
Thirdly, synthesis of zirconocene alkoxide phenoxide **4.1** was attempted via protonolysis of dimethyl zirconocene with alcohol **2.1** and phenol. Reaction of Cp_2ZrMe_2 with **2.1** proceeded cleanly and completely over 1.5 hours to yield a zirconocene alkoxide methyl complex (**4.6**) with methane as a byproduct. Phenol was subsequently added, resulting in the formation of multiple unidentified products (eq 4.7). The reaction was not studied further.

$$Cp_2ZrMe_2 \xrightarrow{\textbf{2.1}} \quad \textbf{4.6} \quad \xrightarrow{\text{PhOH}} \quad \text{multiple products} \qquad (4.7)$$
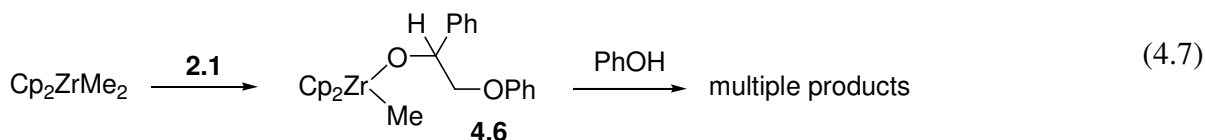
4.4   Attempted Cp$_2$Zr-mediated C-O bond cleavage of 2-phenoxy-1-phenylethanone

The zirconocene-mediated carbon-oxygen bond cleavage of α-aryloxy ketone **2.2** was also investigated. It was anticipated that a reaction of a Cp_2Zr^{II} synthon, such as $Cp_2Zr(BTMSA)$ (BTMSA = bis(trimethylsilyl)acetylene), with ketone **2.2** might result in C-O bond cleavage to produce the zirconocene enolate phenoxide complex **4.5** (eq 4.8).

$$\text{Cp}_2\text{Zr(BTMSA)} \quad + \quad \textbf{2.2} \quad \longrightarrow \quad \textbf{4.5} \qquad (4.8)$$
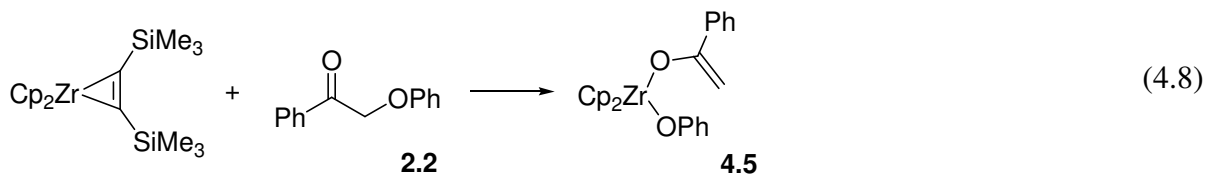
To prepare $Cp_2Zr(BTMSA)(THF)$, zirconocene dichloride was reacted with magnesium and bis(trimethylsilyl)acetylene in THF.[51] Subsequent addition of ketone **2.2** was accompanied by an immediate color change from orange to yellow. However, no zirconocene enolate phenoxide **4.5** was detected in the ^{1}H NMR spectrum of the resulting solution. The main components of the mixture were Cp_2ZrCl_2 and ketone **2.2**. Since no spectrum was recorded prior to the addition of the ketone, it is possible that $Cp_2Zr(BTMSA)(THF)$ was not obtained in the first step of the reaction. Alternatively, a reaction of the product with the

NMR solvent was postulated due to the formation of precipitate when the product was dissolved in CD_2Cl_2.

4.5   Independent synthesis of zirconocene phenoxide enolate

Although the synthesis of zirconocene phenoxide enolate **4.5** was previously reported,[53] the currently known process can be optimized. The reported synthesis of **4.5** involves the reaction of $Cp_2Zr(OPh)Cl$ with $(CO)_5W=CPhO^-Li^+$ to form a zirconooxycarbene complex. The complex is then reacted with $Ph_3P=CH_2$ to yield zirconocene phenoxide enolate **4.5** (Figure 4.2).
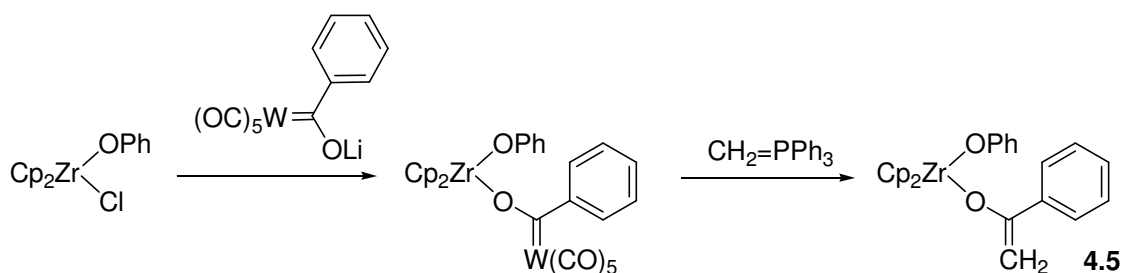
Figure 4.2. Previously reported synthesis of zirconocene phenoxide enolate. [53]

Alternatively, the phenoxide enolate complex **4.5** can be obtained via salt metathesis. Zirconocene phenoxide chloride was prepared via an overnight protonolysis reaction of $Cp_2Zr(H)Cl$ with phenol in benzene. Subsequent reaction with silver triflate in diethyl ether, followed by 48-hour salt metathesis with potassium enolate resulted in the isolation of zirconocene enolate phenoxide **4.5** (eq 4.9).

(4.9)
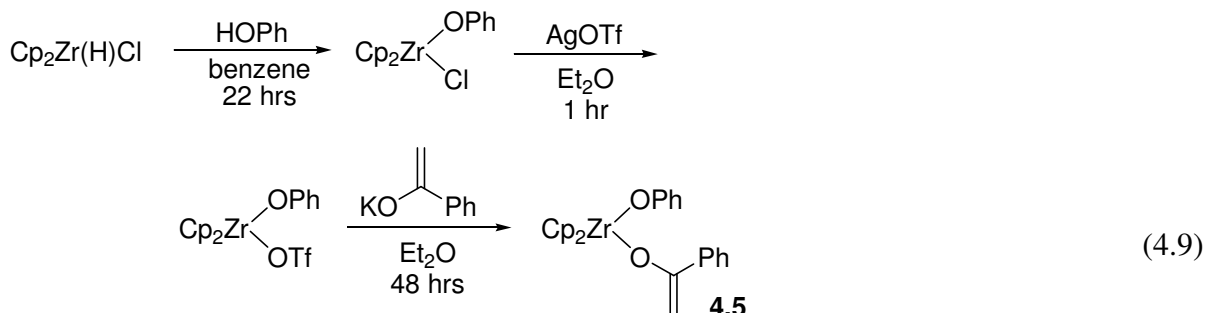
4.6 Experimental section

General considerations. Protocols were identical to those reported in section 2.5. Additionally, C_6D_6 was dried over sodium/benzophenone, purified by vacuum distillation, degassed by three freeze-vacuum-thaw cycles and stored under nitrogen. $KOC(=CH_2)Ph$ was prepared from acetophenone and $KN(SiMe_3)_2$.[47] Bis(cyclopentadienyl)zirconium(IV) dichloride (≥98%), bis(cyclopentadienyl)zirconium(IV) chloride hydride (95%), bis(cyclopentadienyl)zirconium(IV) dihydride (95%), and bis(cyclopentadienyl)dimethylzirconium(IV) (97%) were obtained from Aldrich, stored under nitrogen and used as received.

Synthesis of zirconocene alkoxide chloride (4.3). *Method A: From Cp₂ZrCl₂.* To a suspension of Cp_2ZrCl_2 (207.7 mg, 0.711 mmol) in 10 mL toluene were added alcohol **2.1** (152.6 mg, 0.712 mmol) and DBU (57 μL, 0.38 mmol), resulting in an opaque white mixture. The mixture was stirred at room temperature for 25 minutes, after which time a second aliquot of DBU (60 μL, 0.40 mmol) was added. Stirring was continued for two hours and a final aliquot of DBU (10 μL, 0.067 mmol) was added. After two more hours of stirring, the mixture was filtered through Celite to remove the fine white precipitate. Solvent was removed in vacuo and a colorless oily residue was obtained. Recrystallization from approximately 6:1 diethyl ether/hexanes resulted in the formation of white crystals of zirconocene alkoxide chloride **4.3** (252.4 mg, 76%). Attempted X-ray analysis produced no usable data. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.36 (m, 7H), 6.97 (m, 3H), 6.32 (s, 5H), 6.28 (s, 5H), 5.40 (dd, *J* = 3.5, 8.0 Hz, 1H), 3.97 (m, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 130.19, 128.89, 128.24, 126.76, 121.42, 114.90, 114.60, 114.24, 84.69, 74.42. ^{1}H NMR (400 MHz, C_6D_6): δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 2H), 7.13 (m, 3H), 6.86 (tt, *J* = 1.2, 7.2 Hz, 1H), 6.815 (dt, *J* = 1.2, 8.8 Hz, 2H), 6.06 (s, 5H), 5.95 (s, 5H), 5.24 (dd, *J* = 3.4, 8.0 Hz, 1H), 3.77 (m, 2H).

Method B: From Cp₂Zr(H)Cl. Alcohol **2.1** (6.6 mg, 0.031 mmol) was dissolved in 0.5 mL of CD_2Cl_2 and added to a suspension of $Cp_2Zr(H)Cl$ (8.0 mg, 0.031 mmol) in 0.5 mL of CD_2Cl_2 in an opened vial. Immediate change from an opaque white suspension to a clear yellow solution was accompanied by gas evolution. The mixture was allowed to react for 1.5 hours, after which it was transferred to an NMR tube. The NMR spectrum matched that of **4.3** reported above.

Reaction of zirconocene alkoxide chloride (4.3) with silver triflate. Zirconocene alkoxide chloride **4.3** (9.5 mg, 0.020 mmol) was added to a suspension of AgOTf (5.2 mg, 0.020 mmol) in 1 mL CD_2Cl_2. The mixture was allowed to react for 1.5 hours, after which the gray precipitate was removed by filtration through Celite, resulting in a clear colorless solution. This solution was found to contain a 2:1 mixture of starting material to product. Signal overlap prevented the assignment of all product peaks. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.42 (s, 10H), 5.47 (dd, J = 4.0, 7.6 Hz, 1H).

Reaction of zirconocene alkoxide chloride (4.3) with sodium tetraphenylborate and subsequent addition of triethylamine. Zirconocene alkoxide chloride **4.3** (10.1 mg, 0.022 mmol) was added to a suspension of $NaBPh_4$ (7.4 mg, 0.022 mmol) in 6 mL of diethyl ether. The mixture was stirred for 22 hours. The resulting white opaque suspension was filtered through Celite, giving a clear colorless filtrate. Solvent was removed in vacuo. Residue was redissolved in C_6D_6 and an NMR spectrum was recorded. Due to the presence of a large amount of **4.3** in the mixture, complete assignment of the product peaks was not possible. ^{1}H NMR (400 MHz, C_6D_6): δ 6.02 (s, Cp protons).Triethylamine (4.0 μL, 0.029 mmol) was then added and another NMR spectrum was recorded 20 minutes later. The cyclopentadienyl proton shifts of major products are reported. ^{1}H NMR (400 MHz, C_6D_6): δ 6.18 (s), 6.12 (s), 6.04 (s), 6.02 (s). **4.3** was also detected as a major component of the NMR mixture.

Synthesis of $Cp_2Zr(OPh)Cl$ via salt metathesis. Cp_2ZrCl_2 (49.9 mg, 0.17 mmol) and NaOPh (19.9 mg, 0.17 mmol) were weighed in separate vials. Each compound was dissolved in 5 mL of THF and cooled at -30°C for 10 minutes. The zirconocene solution was then transferred to a flask and NaOPh was added dropwise over 3 minutes while stirring. The reaction was stirred for 28 hours, after which time it was filtered through Celite. The solvent was removed in vacuo. Attempted recrystallization from 4:1 diethyl ether/hexanes did not result in the isolation of solid. The recrystallization solvent was removed in vacuo and the residue was redissolved in C_6D_6. The cyclopentadienyl proton shifts of major products are reported. A few other minor zirconocene products were also detected. ^{1}H NMR (400 MHz, C_6D_6): δ 5.92 (s, 10H).

Attempted synthesis of zirconocene alkoxide phenoxide (4.1) via Cp₂Zr(OPh)(OTf). Cp$_2$Zr(H)Cl (88.7 mg, 0.34 mmol), phenol (32.5 mg, 0.35 mmol) and 2.5 mL benzene were combined in a flask and stirred uncapped for 10 minutes to allow resulting gases to escape. The mixture was then stirred overnight. Solvent was removed in vacuo, and silver triflate (88.3 mg, 0.34 mmol) was added with 8 mL Et$_2$O. After 1 hour, the mixture was filtered through Celite and the residue was redissolved in C$_6$D$_6$. 1,3,5-tri-*tert*-butylbenzene (4.1 mg, 0.017 mmol) was added as an internal standard and the solution was split into two equal volumes. To one sample, alcohol **2.1** (21.1 mg, 0.1 mmol, 1 equiv) was added. No reaction was observed after 10 minutes or 3 days. To the other sample, alcohol **2.1** (21.1 mg, 0.1 mmol, 1 equiv) and NEt$_3$ (15 μL, 0.1 mmol, 1 equiv) were added. After 10 minutes, multiple new products were observed. The cyclopentadienyl proton shifts of major products are reported. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 6.08 (s), 6.01 (s), 5.98 (s).

Attempted synthesis of zirconocene alkoxide phenoxide (4.1) from zirconocene alkoxide chloride. Zirconocene alkoxide chloride **4.3** (41.6 mg, 0.089 mmol) was dissolved in 12 mL THF. A solution of NaOPh (10.9 mg, 0.094 mmol) in 6 mL THF was added dropwise. The mixture was stirred for 28 hours. Solvent was removed in vacuo. The resulting residue was extracted with 2 mL Et$_2$O and filtered through Celite. The diethyl ether was then evaporated and residue was redissolved in C$_6$D$_6$. The cyclopentadienyl proton shifts of major products are reported. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 6.07 (s), 6.00 (s), 5.96 (s).

Attempted synthesis of zirconocene alkoxide phenoxide (4.1) from Cp₂Zr(Me)₂. Cp$_2$ZrMe$_2$ (8.9 mg, 0.035 mmol) was dissolved in 0.5 mL C$_6$D$_6$. A solution of alcohol **2.1** (7.6 mg, 0.035 mmol) in 0.5 mL C$_6$D$_6$ was added. An NMR spectrum of the product, a zirconocene alkoxide methyl complex, was obtained 20 minutes later. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.24 (m, 4H), 7.15 (m, 3H), 6.85 (m, 3H), 5.84 (s, 5H), 5.79 (s, 5H), 5.19 (dd, J = 3.6, 8.0 Hz, 1H), 3.71 (m, 2H). Phenol (3.3 mg, 0.035 mmol) was then added. The mixture was allowed to react for 28 hours. The cyclopentadienyl proton shifts of major products are reported. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 6.07 (s), 6.00 (s), 5.96 (s).

Attempted zirconocene-mediated C-O bond cleavage of 2-phenoxy-1-phenylethanone (2.2). Zirconocene dichloride (14.5 mg, 0.050 mmol), magnesium (1.2 mg, 0.049 mmol), and bis(trimethylsilyl)acetylene (8.3 mg, 0.049 mmol) were combined in a vial with 5 mL of THF. The mixture was allowed to react overnight, resulting in a clear orange

solution. 2-phenoxy-1-phenylethanone (10.6 mg, 0.050 mmol) dissolved in 0.5 mL of THF was then added and allowed to react for 30 minutes, during which time the solution became yellow. The solvent was removed in vacuo and the yellow residue was redissolved in CD_2Cl_2. The NMR mixture was found to contain unreacted ketone **2.2**, Cp_2ZrCl_2, and relatively small amounts of bis(trimethylsilyl)acetylene (0.05 equiv relative to Cp_2ZrCl_2). Upon removal of the NMR sample from the instrument, a white precipitate was observed. The amount of precipitate increased overnight; however, the NMR spectrum remained unchanged.

Synthesis of zirconocene enolate phenoxide (4.5) via Cp₂Zr(OPh)(OTf). A solution of phenol (10.3 mg, 0.109 mmol) in 3 mL benzene was added to $Cp_2Zr(H)Cl$ (27.9 mg, 0.108 mmol), resulting in a cloudy white mixture and gas evolution. The mixture was stirred for 22 hours with a partially opened lid to allow gases to escape. The solvent was then removed, giving a colorless oily residue. The residue was then redissolved in 5 mL of diethyl ether, and a solution of silver triflate (27.8 mg, 0.108 mmol) in 5 mL of diethyl ether was added. Pink-purple precipitate of silver chloride was observed within minutes. After allowing 1 hr for a complete reaction, the mixture was filtered, and the filtrate was added to a solution of potassium enolate (17.2 mg, 0.109 mmol) in 3 mL of diethyl ether. After 48 hours, the mixture was filtered and solvent removed to give a white solid of **4.5**. The NMR spectrum of the product matched that reported by Erker et al.[53]

Chapter 5 Conclusions and Future Work

Although a catalytic carbon-oxygen cleavage of model compounds mimicking the β-O-4 linkage in lignin was not achieved, it was shown that the related α-aryloxy ketones 2-phenoxy-1-phenylethanone and 2-(2,6-dimethoxyphenoxy)-1-phenylethanone undergo titanocene-mediated cleavage of the desired bond at ambient temperature and pressure. Furthermore, the products of the C-O cleavage, acetophenone and the corresponding phenol, can be easily released from titanium with the use of common acids such as HCl, which results in the recovery of titanocene dichloride. Alternately, selective protonolysis of the Ti-enolate bond can be achieved with the use of milder acids. The C-O bond cleavage of the α-aryloxy ketones via a reaction with Cp$_2$Ti(BTMSA), followed by protonolysis of the resulting phenoxide enolate complex with HCl and a reaction of Cp$_2$TiCl$_2$ with Mg and BTMSA constitute a stochiometric cycle for the C-O bond cleavage of the α-aryloxy ketones as shown in Figure 5.1.
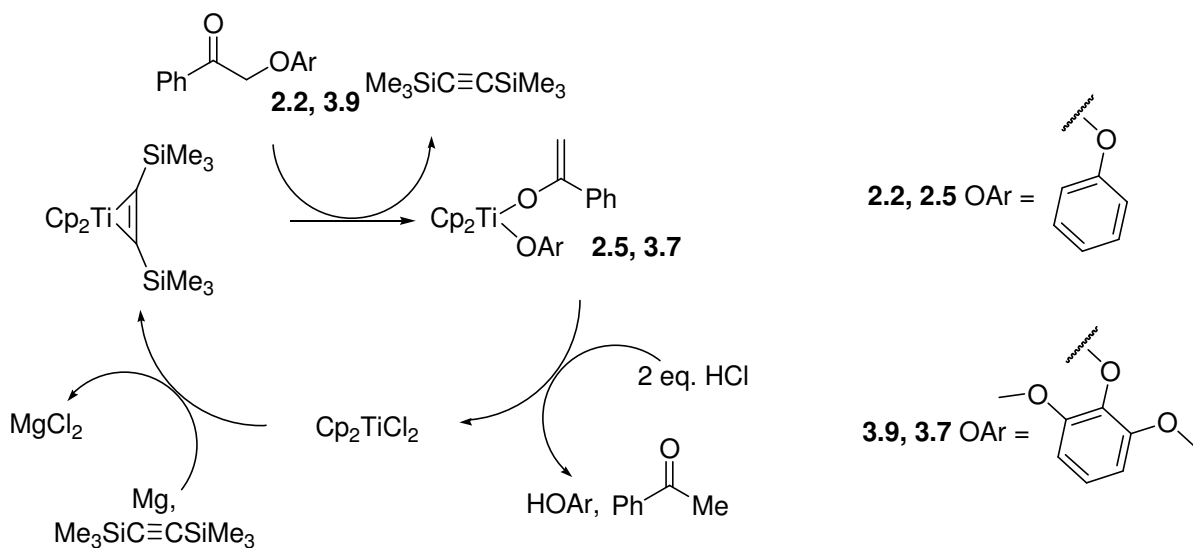
Figure 5.1. Stochiometric cycle for the C-O bond cleavage of α-aryloxy ketones **2.2**, **3.9**.

The challenging step in the target catalytic cycle shown in Figure 3.1 is the elimination of phenol from the alkoxide phenoxide complex **2.11**. It was postulated that a weakening of the Ti-OAr bond through increased steric bulk of the aryloxide ligand was necessary. Protonolysis of titanocene aryloxide chlorides **3.3** and **3.4** with *ortho*-substituted aryloxide ligands confirmed the weakening of the Ti-OAr bond. Additionally, the observed equilibria for the reaction of titanocene alkoxide triflate **2.6** reacting with phenol, 2,6-

dimethoxyphenol, and 2,4,6-tri-*tert*-butylphenol to form $Cp_2Ti(OAr)(OTf)$ indicate the following order for the Ti-OAr bond strength: Ti-OPh > Ti-O(2,6-OMe)C_6H_3 > Ti-OMes*.

A clean synthesis of titanocene aryloxide alkoxide complexes **3.1** and **3.2** could not be accomplished, although future experiments involving a reaction of titanocene alkoxide triflate with the substituted phenols in the presence of base are suggested. It was postulated that the coordination of phenol precedes the Ti-O(alkoxide) bond cleavage (Figure 3.5). If the deprotonation of the coordinated phenol by an external base proceeds faster than the H-transfer from phenol to alkoxide, the desired titanocene aryloxide alkoxide compounds **3.1** and **3.2** might be obtained.

The replacement of cyclopentadienyl ligands on titanium for aryloxide or alkoxide ligands is expected to result in changes in reactivity. Replacing the Cp groups in the alkoxide phenoxide complex **2.11** for OAr or OR might encourage chelation of the ether oxygen of the alkoxide ligand, potentially lowering the energy for HOPh elimination. The investigation of this reactivity is suggested as future work.

Zirconium, known to form five-coordinate 18-electron complexes, was used with the expectation of alternate pathways for phenol elimination from a zirconium analogue of compound **2.11**, zirconocene alkoxide phenoxide **4.1**. The protonolysis route available for the preparation of several zirconocene alkoxide complexes provided a synthetic advantage over titanium due to its decrease in the number of steps, reduction of waste products, and elimination of the need for a work-up. However, attempts at the synthesis of complex **4.1** via protonolysis or salt metathesis route resulted in the formation of multiple unidentified zirconocene complexes. Formation of ate complexes or other unexpected five-coordinate species was postulated.

As noted in chapter 4, a zirconocene alkoxide methyl complex **4.6** can be easily prepared by reacting Cp_2ZrMe_2 with 2-phenoxy-1-phenylethanol (**2.1**). Related zirconocene alkoxide methyl complexes were previously reported by Jordan and co-workers. Depending on the length of the alkyl chain, some of these compounds react with $B(C_6F_5)_3$ to form a cationic zirconocene chelated by an alkoxide-olefin ligand ,with $MeB(C_6F_5)_3^-$ as counteranion.[52] It is recommended that compound **4.6** be reacted with $B(C_6F_5)_3$ as this might encourage the chelation of the alkoxide ligand to yield the desired cationic zirconocene alkoxide species.

Finally, the experiments discussed in this thesis represent an initial investigation of the applicability of titanocene and zirconocene systems to carbon-oxygen bond cleavage of the lignin β-O-4 linkage. Only the simple model compounds 2-phenoxy-1-phenylethanol (**2.1**), 2-phenoxy-1-phenylethanone (**2.6**), and 2-(2,6-dimethoxyphenoxy)-1-phenylethanone (**3.9**) were used in this work. However, the addition of a CH_2OH or OMe substituents in the model compound might result in different reactivity with titanocene or zirconocene. Studies involving the use of model compounds which more closely resemble lignin or reactions with the lignin polymer are an interesting avenue to pursue for future research.

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Appendices

Appendix A: Supplementary X-ray Data

Table A.1. Crystal data and refinement parameters for X-ray structures **3.3** and **3.4**.

	3.3	3.4
Empirical formula	$C_{18}H_{19}ClOTi$	$C_{28}H_{39}ClOTi$
Formula mass	366.67	496.92
Color, habit	Red, irregular	Red, irregular
Crystal dimensions, mm	$0.08 \times 0.12 \times 0.15$	$0.07 \times 0.26 \times 0.35$
Crystal system	Monoclinic	Triclinic
Space Group	$P\, 2_1/n$	$P\bar{1}$ (no. 2)
Z	12	4
a (Å)	10.1454(8)	11.5491(9)
b (Å)	13.363(1)	14.8158(11)
c (Å)	37.244(3)	16.3513(12)
α (°)	90.00	113.3572(34)
β (°)	90.574(1)	92.5033(38)
γ (°)	90.00	92.0499(37)
Collection ranges	$-14 \le h \le 14$; $-18 \le k \le 18$; $-52 \le l \le 52$	$-14 \le h \le 14$; $-18 \le k \le 18$; $-19 \le l \le 19$
Temperature (K)	170(1)	170(1)
V (Å^3)	5049.1(7)	2561.8(5)
D_{calcd} (Mg m^{-3})	1.447	1.231
Radiation	MoKα ($\lambda = 0.71073$ Å)	MoKα ($\lambda = 0.71073$ Å)
Absorption coeff. (μ) (mm^{-1})	0.678	0.455
Absorption correction	Multiscan	Multiscan
F$_{000}$	2280	1016
θ range for data collection (°)	1.9-30.1	1.9 -25.7
Observed reflections	175801	51881
Independent reflections	14824 ($R_{int} = 0.054$)	9663 ($R_{int} = 0.0454$)
Data/restraints/parameters	14824/0/628	9663/0/559
Maximum shift/error	0.00	0.00
Goodness-of-fit on F^2	1.06	1.076
Final R indices [I > 2σ(I)]	$R_1 = 0.038$, $wR_2 = 0.084$	$R_1 = 0.0427$, $wR_2 = 0.0921$
R indices (all data)	$R_1 = 0.053$, $wR_2 = 0.091$	$R_1 = 0.0703$, $wR_2 = 0.1033$
Largest diff. peak and hole (e Å^{-3})	0.45 and –0.43	0.416 and –0.432

Table A.2. Bond lengths [A] and angles [deg] for **3.3**.

C(1)-C(5)	1.395(8)
C(1)-C(2)	1.424(8)
C(1)-Ti(1)	2.400(6)
C(1)-H(1)	0.9500
C(2)-C(3)	1.402(8)
C(2)-Ti(1)	2.393(6)
C(2)-H(2)	0.9500
C(3)-C(4)	1.417(8)
C(3)-Ti(1)	2.419(6)
C(3)-H(3)	0.9500
C(4)-C(5)	1.425(8)
C(4)-Ti(1)	2.384(5)
C(4)-H(4)	0.9500
C(5)-Ti(1)	2.417(6)
C(5)-H(5)	0.9500
C(6)-C(10)	1.400(8)
C(6)-C(7)	1.424(7)
C(6)-Ti(1)	2.391(5)
C(6)-H(6)	0.9500
C(7)-C(8)	1.411(7)
C(7)-Ti(1)	2.376(5)
C(7)-H(7)	0.9500
C(8)-C(9)	1.422(8)
C(8)-Ti(1)	2.377(5)
C(8)-H(8)	0.9500
C(9)-C(10)	1.423(7)
C(9)-Ti(1)	2.364(5)
C(9)-H(9)	0.9500
C(10)-Ti(1)	2.409(5)
C(10)-H(10)	0.9500
C(11)-O(1)	1.325(5)
C(11)-C(16)	1.395(6)
C(11)-C(12)	1.417(6)
C(12)-O(2)	1.377(6)
C(12)-C(13)	1.378(7)
C(13)-C(14)	1.395(10)
C(13)-H(13)	0.9500
C(14)-C(15)	1.389(9)
C(14)-H(14)	0.9500
C(15)-C(16)	1.397(7)
C(15)-H(15)	0.9500
C(16)-O(3)	1.379(6)
C(17)-O(2)	1.437(7)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800

C(17)-H(17C)	0.9800
C(18)-O(3)	1.418(8)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-C(20)	1.404(7)
C(19)-C(23)	1.415(9)
C(19)-Ti(2)	2.392(5)
C(19)-H(19)	0.9500
C(20)-C(21)	1.412(8)
C(20)-Ti(2)	2.416(5)
C(20)-H(20)	0.9500
C(21)-C(22)	1.428(7)
C(21)-Ti(2)	2.355(5)
C(21)-H(21)	0.9500
C(22)-C(23)	1.401(10)
C(22)-Ti(2)	2.373(5)
C(22)-H(22)	0.9500
C(23)-Ti(2)	2.364(6)
C(23)-H(23)	0.9500
C(24)-C(25)	1.385(8)
C(24)-C(28)	1.436(7)
C(24)-Ti(2)	2.398(5)
C(24)-H(24)	0.9500
C(25)-C(26)	1.416(8)
C(25)-Ti(2)	2.404(5)
C(25)-H(25)	0.9500
C(26)-C(27)	1.416(10)
C(26)-Ti(2)	2.379(5)
C(26)-H(26)	0.9500
C(27)-C(28)	1.400(9)
C(27)-Ti(2)	2.422(6)
C(27)-H(27)	0.9500
C(28)-Ti(2)	2.404(6)
C(28)-H(28)	0.9500
C(29)-O(4)	1.335(6)
C(29)-C(30)	1.405(10)
C(29)-C(34)	1.427(10)
C(30)-O(5)	1.374(9)
C(30)-C(31)	1.411(9)
C(31)-C(32)	1.554(15)
C(31)-H(31)	0.9500
C(32)-C(33)	1.294(13)
C(32)-H(32)	0.9500
C(33)-C(34)	1.363(12)
C(33)-H(33)	0.9500

C(34)-O(6)	1.331(11)
C(35)-O(5)	1.436(8)
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-O(6)	1.443(9)
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-C(41)	1.405(9)
C(37)-C(38)	1.420(8)
C(37)-Ti(3)	2.393(7)
C(37)-H(37)	0.9500
C(38)-C(39)	1.401(7)
C(38)-Ti(3)	2.394(6)
C(38)-H(38)	0.9500
C(39)-C(40)	1.428(8)
C(39)-Ti(3)	2.418(7)
C(39)-H(39)	0.9500
C(40)-C(41)	1.414(9)
C(40)-Ti(3)	2.379(8)
C(40)-H(40)	0.9500
C(41)-Ti(3)	2.412(9)
C(41)-H(41)	0.9500
C(42)-C(46)	1.409(9)
C(42)-C(43)	1.427(9)
C(42)-Ti(3)	2.379(6)
C(42)-H(42)	0.9500
C(43)-C(44)	1.409(9)
C(43)-Ti(3)	2.360(6)
C(43)-H(43)	0.9500
C(44)-C(45)	1.416(9)
C(44)-Ti(3)	2.408(8)
C(44)-H(44)	0.9500
C(45)-C(46)	1.419(12)
C(45)-Ti(3)	2.392(8)
C(45)-H(45)	0.9500
C(46)-Ti(3)	2.371(6)
C(46)-H(46)	0.9500
C(47)-O(7)	1.352(7)
C(47)-C(52)	1.401(14)
C(47)-C(48)	1.415(11)
C(48)-O(9)	1.371(11)
C(48)-C(49)	1.396(9)
C(49)-C(50)	1.402(14)
C(49)-H(49)	0.9500

C(50)-C(51)	1.394(13)
C(50)-H(50)	0.9500
C(51)-C(52)	1.400(9)
C(51)-H(51)	0.9500
C(52)-O(8)	1.389(11)
C(53)-O(9)	1.433(9)
C(53)-H(53A)	0.9800
C(53)-H(53B)	0.9800
C(53)-H(53C)	0.9800
C(54)-O(8)	1.415(13)
C(54)-H(54A)	0.9800
C(54)-H(54B)	0.9800
C(54)-H(54C)	0.9800
O(1)-Ti(1)	1.896(3)
O(4)-Ti(2)	1.895(3)
O(7)-Ti(3)	1.888(4)
Cl(1)-Ti(1)	2.4110(15)
Cl(2)-Ti(2)	2.4029(13)
Cl(3)-Ti(3)	2.4107(18)
C(5)-C(1)-C(2)	108.3(5)
C(5)-C(1)-Ti(1)	73.9(3)
C(2)-C(1)-Ti(1)	72.5(3)
C(5)-C(1)-H(1)	125.8
C(2)-C(1)-H(1)	125.8
Ti(1)-C(1)-H(1)	119.7
C(3)-C(2)-C(1)	107.8(5)
C(3)-C(2)-Ti(1)	74.1(3)
C(1)-C(2)-Ti(1)	73.0(3)
C(3)-C(2)-H(2)	126.1
C(1)-C(2)-H(2)	126.1
Ti(1)-C(2)-H(2)	118.8
C(2)-C(3)-C(4)	108.2(5)
C(2)-C(3)-Ti(1)	72.1(3)
C(4)-C(3)-Ti(1)	71.5(3)
C(2)-C(3)-H(3)	125.9
C(4)-C(3)-H(3)	125.9
Ti(1)-C(3)-H(3)	122.3
C(3)-C(4)-C(5)	107.5(5)
C(3)-C(4)-Ti(1)	74.2(3)
C(5)-C(4)-Ti(1)	74.0(3)
C(3)-C(4)-H(4)	126.3
C(5)-C(4)-H(4)	126.3
Ti(1)-C(4)-H(4)	117.6
C(1)-C(5)-C(4)	108.0(5)
C(1)-C(5)-Ti(1)	72.5(3)

C(4)-C(5)-Ti(1)	71.5(3)
C(1)-C(5)-H(5)	126.0
C(4)-C(5)-H(5)	126.0
Ti(1)-C(5)-H(5)	121.8
C(10)-C(6)-C(7)	108.5(5)
C(10)-C(6)-Ti(1)	73.8(3)
C(7)-C(6)-Ti(1)	72.1(3)
C(10)-C(6)-H(6)	125.8
C(7)-C(6)-H(6)	125.8
Ti(1)-C(6)-H(6)	120.2
C(8)-C(7)-C(6)	108.1(5)
C(8)-C(7)-Ti(1)	72.8(3)
C(6)-C(7)-Ti(1)	73.2(3)
C(8)-C(7)-H(7)	125.9
C(6)-C(7)-H(7)	125.9
Ti(1)-C(7)-H(7)	119.9
C(7)-C(8)-C(9)	107.3(4)
C(7)-C(8)-Ti(1)	72.7(3)
C(9)-C(8)-Ti(1)	72.0(3)
C(7)-C(8)-H(8)	126.3
C(9)-C(8)-H(8)	126.3
Ti(1)-C(8)-H(8)	120.8
C(8)-C(9)-C(10)	108.4(5)
C(8)-C(9)-Ti(1)	73.1(3)
C(10)-C(9)-Ti(1)	74.4(3)
C(8)-C(9)-H(9)	125.8
C(10)-C(9)-H(9)	125.8
Ti(1)-C(9)-H(9)	118.6
C(6)-C(10)-C(9)	107.6(5)
C(6)-C(10)-Ti(1)	72.3(3)
C(9)-C(10)-Ti(1)	70.9(3)
C(6)-C(10)-H(10)	126.2
C(9)-C(10)-H(10)	126.2
Ti(1)-C(10)-H(10)	122.3
O(1)-C(11)-C(16)	120.7(4)
O(1)-C(11)-C(12)	120.9(4)
C(16)-C(11)-C(12)	118.4(4)
O(2)-C(12)-C(13)	124.0(5)
O(2)-C(12)-C(11)	114.7(4)
C(13)-C(12)-C(11)	121.3(5)
C(12)-C(13)-C(14)	119.2(5)
C(12)-C(13)-H(13)	120.4
C(14)-C(13)-H(13)	120.4
C(15)-C(14)-C(13)	120.8(5)
C(15)-C(14)-H(14)	119.6
C(13)-C(14)-H(14)	119.6

C(14)-C(15)-C(16)	119.7(5)
C(14)-C(15)-H(15)	120.1
C(16)-C(15)-H(15)	120.1
O(3)-C(16)-C(11)	115.7(4)
O(3)-C(16)-C(15)	123.8(5)
C(11)-C(16)-C(15)	120.6(5)
O(2)-C(17)-H(17A)	109.5
O(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
O(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
O(3)-C(18)-H(18A)	109.5
O(3)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
O(3)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(20)-C(19)-C(23)	108.4(5)
C(20)-C(19)-Ti(2)	74.0(3)
C(23)-C(19)-Ti(2)	71.6(3)
C(20)-C(19)-H(19)	125.8
C(23)-C(19)-H(19)	125.8
Ti(2)-C(19)-H(19)	120.4
C(19)-C(20)-C(21)	107.3(5)
C(19)-C(20)-Ti(2)	72.1(3)
C(21)-C(20)-Ti(2)	70.4(3)
C(19)-C(20)-H(20)	126.3
C(21)-C(20)-H(20)	126.3
Ti(2)-C(20)-H(20)	122.8
C(20)-C(21)-C(22)	108.6(5)
C(20)-C(21)-Ti(2)	75.2(3)
C(22)-C(21)-Ti(2)	73.1(3)
C(20)-C(21)-H(21)	125.7
C(22)-C(21)-H(21)	125.7
Ti(2)-C(21)-H(21)	117.9
C(23)-C(22)-C(21)	106.9(5)
C(23)-C(22)-Ti(2)	72.4(3)
C(21)-C(22)-Ti(2)	71.7(3)
C(23)-C(22)-H(22)	126.6
C(21)-C(22)-H(22)	126.6
Ti(2)-C(22)-H(22)	121.1
C(22)-C(23)-C(19)	108.7(5)
C(22)-C(23)-Ti(2)	73.2(3)
C(19)-C(23)-Ti(2)	73.8(3)
C(22)-C(23)-H(23)	125.7

C(19)-C(23)-H(23)	125.7
Ti(2)-C(23)-H(23)	119.2
C(25)-C(24)-C(28)	107.8(5)
C(25)-C(24)-Ti(2)	73.5(3)
C(28)-C(24)-Ti(2)	72.8(3)
C(25)-C(24)-H(24)	126.1
C(28)-C(24)-H(24)	126.1
Ti(2)-C(24)-H(24)	119.4
C(24)-C(25)-C(26)	108.7(5)
C(24)-C(25)-Ti(2)	73.0(3)
C(26)-C(25)-Ti(2)	71.8(3)
C(24)-C(25)-H(25)	125.6
C(26)-C(25)-H(25)	125.6
Ti(2)-C(25)-H(25)	121.3
C(27)-C(26)-C(25)	107.6(6)
C(27)-C(26)-Ti(2)	74.5(3)
C(25)-C(26)-Ti(2)	73.7(3)
C(27)-C(26)-H(26)	126.2
C(25)-C(26)-H(26)	126.2
Ti(2)-C(26)-H(26)	117.6
C(28)-C(27)-C(26)	108.1(5)
C(28)-C(27)-Ti(2)	72.4(3)
C(26)-C(27)-Ti(2)	71.2(3)
C(28)-C(27)-H(27)	126.0
C(26)-C(27)-H(27)	126.0
Ti(2)-C(27)-H(27)	122.1
C(27)-C(28)-C(24)	107.7(5)
C(27)-C(28)-Ti(2)	73.8(4)
C(24)-C(28)-Ti(2)	72.3(3)
C(27)-C(28)-H(28)	126.1
C(24)-C(28)-H(28)	126.1
Ti(2)-C(28)-H(28)	119.5
O(4)-C(29)-C(30)	120.9(5)
O(4)-C(29)-C(34)	118.2(6)
C(30)-C(29)-C(34)	120.9(6)
O(5)-C(30)-C(29)	115.6(5)
O(5)-C(30)-C(31)	124.4(8)
C(29)-C(30)-C(31)	119.9(8)
C(30)-C(31)-C(32)	112.5(9)
C(30)-C(31)-H(31)	123.8
C(32)-C(31)-H(31)	123.8
C(33)-C(32)-C(31)	127.4(9)
C(33)-C(32)-H(32)	116.3
C(31)-C(32)-H(32)	116.3
C(32)-C(33)-C(34)	116.3(10)
C(32)-C(33)-H(33)	121.9

C(34)-C(33)-H(33)	121.9
O(6)-C(34)-C(33)	119.7(8)
O(6)-C(34)-C(29)	117.2(7)
C(33)-C(34)-C(29)	123.0(8)
O(5)-C(35)-H(35A)	109.5
O(5)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
O(5)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
O(6)-C(36)-H(36A)	109.5
O(6)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
O(6)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(41)-C(37)-C(38)	107.8(5)
C(41)-C(37)-Ti(3)	73.8(4)
C(38)-C(37)-Ti(3)	72.8(4)
C(41)-C(37)-H(37)	126.1
C(38)-C(37)-H(37)	126.1
Ti(3)-C(37)-H(37)	119.2
C(39)-C(38)-C(37)	108.5(5)
C(39)-C(38)-Ti(3)	74.0(4)
C(37)-C(38)-Ti(3)	72.7(4)
C(39)-C(38)-H(38)	125.8
C(37)-C(38)-H(38)	125.8
Ti(3)-C(38)-H(38)	119.3
C(38)-C(39)-C(40)	107.7(5)
C(38)-C(39)-Ti(3)	72.1(4)
C(40)-C(39)-Ti(3)	71.2(4)
C(38)-C(39)-H(39)	126.2
C(40)-C(39)-H(39)	126.2
Ti(3)-C(39)-H(39)	122.2
C(41)-C(40)-C(39)	107.5(5)
C(41)-C(40)-Ti(3)	74.1(5)
C(39)-C(40)-Ti(3)	74.2(4)
C(41)-C(40)-H(40)	126.2
C(39)-C(40)-H(40)	126.2
Ti(3)-C(40)-H(40)	117.5
C(37)-C(41)-C(40)	108.4(5)
C(37)-C(41)-Ti(3)	72.3(5)
C(40)-C(41)-Ti(3)	71.6(5)
C(37)-C(41)-H(41)	125.8
C(40)-C(41)-H(41)	125.8
Ti(3)-C(41)-H(41)	122.1

C(46)-C(42)-C(43)	107.1(6)
C(46)-C(42)-Ti(3)	72.4(3)
C(43)-C(42)-Ti(3)	71.7(3)
C(46)-C(42)-H(42)	126.4
C(43)-C(42)-H(42)	126.4
Ti(3)-C(42)-H(42)	121.2
C(44)-C(43)-C(42)	108.6(5)
C(44)-C(43)-Ti(3)	74.7(4)
C(42)-C(43)-Ti(3)	73.2(3)
C(44)-C(43)-H(43)	125.7
C(42)-C(43)-H(43)	125.7
Ti(3)-C(43)-H(43)	118.3
C(43)-C(44)-C(45)	107.8(7)
C(43)-C(44)-Ti(3)	71.0(4)
C(45)-C(44)-Ti(3)	72.2(5)
C(43)-C(44)-H(44)	126.1
C(45)-C(44)-H(44)	126.1
Ti(3)-C(44)-H(44)	122.4
C(44)-C(45)-C(46)	107.9(6)
C(44)-C(45)-Ti(3)	73.5(4)
C(46)-C(45)-Ti(3)	71.9(5)
C(44)-C(45)-H(45)	126.1
C(46)-C(45)-H(45)	126.1
Ti(3)-C(45)-H(45)	120.4
C(42)-C(46)-C(45)	108.6(6)
C(42)-C(46)-Ti(3)	73.0(3)
C(45)-C(46)-Ti(3)	73.5(4)
C(42)-C(46)-H(46)	125.7
C(45)-C(46)-H(46)	125.7
Ti(3)-C(46)-H(46)	119.6
O(7)-C(47)-C(52)	121.0(7)
O(7)-C(47)-C(48)	119.9(8)
C(52)-C(47)-C(48)	119.2(6)
O(9)-C(48)-C(49)	124.1(8)
O(9)-C(48)-C(47)	115.5(6)
C(49)-C(48)-C(47)	120.4(9)
C(48)-C(49)-C(50)	119.2(8)
C(48)-C(49)-H(49)	120.4
C(50)-C(49)-H(49)	120.4
C(51)-C(50)-C(49)	121.3(7)
C(51)-C(50)-H(50)	119.3
C(49)-C(50)-H(50)	119.3
C(50)-C(51)-C(52)	119.0(9)
C(50)-C(51)-H(51)	120.5
C(52)-C(51)-H(51)	120.5
O(8)-C(52)-C(51)	122.6(9)

O(8)-C(52)-C(47)	116.5(6)
C(51)-C(52)-C(47)	120.8(8)
O(9)-C(53)-H(53A)	109.5
O(9)-C(53)-H(53B)	109.5
H(53A)-C(53)-H(53B)	109.5
O(9)-C(53)-H(53C)	109.5
H(53A)-C(53)-H(53C)	109.5
H(53B)-C(53)-H(53C)	109.5
O(8)-C(54)-H(54A)	109.5
O(8)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5
O(8)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5
C(11)-O(1)-Ti(1)	142.0(3)
C(12)-O(2)-C(17)	115.8(5)
C(16)-O(3)-C(18)	116.6(5)
C(29)-O(4)-Ti(2)	141.6(3)
C(30)-O(5)-C(35)	117.5(6)
C(34)-O(6)-C(36)	117.7(10)
C(47)-O(7)-Ti(3)	142.4(4)
C(52)-O(8)-C(54)	118.5(6)
C(48)-O(9)-C(53)	116.3(6)
O(1)-Ti(1)-C(9)	138.38(17)
O(1)-Ti(1)-C(7)	83.45(17)
C(9)-Ti(1)-C(7)	57.55(19)
O(1)-Ti(1)-C(8)	115.24(18)
C(9)-Ti(1)-C(8)	34.90(19)
C(7)-Ti(1)-C(8)	34.53(18)
O(1)-Ti(1)-C(4)	96.76(18)
C(9)-Ti(1)-C(4)	100.57(18)
C(7)-Ti(1)-C(4)	95.44(19)
C(8)-Ti(1)-C(4)	78.88(18)
O(1)-Ti(1)-C(6)	82.77(17)
C(9)-Ti(1)-C(6)	57.25(17)
C(7)-Ti(1)-C(6)	34.76(17)
C(8)-Ti(1)-C(6)	57.56(17)
C(4)-Ti(1)-C(6)	130.15(19)
O(1)-Ti(1)-C(2)	127.54(18)
C(9)-Ti(1)-C(2)	93.37(19)
C(7)-Ti(1)-C(2)	137.51(19)
C(8)-Ti(1)-C(2)	103.86(19)
C(4)-Ti(1)-C(2)	57.1(2)
C(6)-Ti(1)-C(2)	149.57(19)
O(1)-Ti(1)-C(1)	93.16(18)
C(9)-Ti(1)-C(1)	127.92(19)

C(7)-Ti(1)-C(1)	151.73(19)
C(8)-Ti(1)-C(1)	130.34(18)
C(4)-Ti(1)-C(1)	57.0(2)
C(6)-Ti(1)-C(1)	172.06(19)
C(2)-Ti(1)-C(1)	34.56(19)
O(1)-Ti(1)-C(10)	113.37(17)
C(9)-Ti(1)-C(10)	34.66(16)
C(7)-Ti(1)-C(10)	57.21(19)
C(8)-Ti(1)-C(10)	57.62(18)
C(4)-Ti(1)-C(10)	134.19(19)
C(6)-Ti(1)-C(10)	33.90(18)
C(2)-Ti(1)-C(10)	116.8(2)
C(1)-Ti(1)-C(10)	146.0(2)
O(1)-Ti(1)-Cl(1)	96.76(11)
C(9)-Ti(1)-Cl(1)	96.98(14)
C(7)-Ti(1)-Cl(1)	128.46(14)
C(8)-Ti(1)-Cl(1)	131.09(14)
C(4)-Ti(1)-Cl(1)	135.19(15)
C(6)-Ti(1)-Cl(1)	93.87(13)
C(2)-Ti(1)-Cl(1)	81.08(14)
C(1)-Ti(1)-Cl(1)	79.79(14)
C(10)-Ti(1)-Cl(1)	76.46(14)
O(1)-Ti(1)-C(5)	76.08(17)
C(9)-Ti(1)-C(5)	133.53(18)
C(7)-Ti(1)-C(5)	119.45(19)
C(8)-Ti(1)-C(5)	112.59(18)
C(4)-Ti(1)-C(5)	34.51(19)
C(6)-Ti(1)-C(5)	149.31(19)
C(2)-Ti(1)-C(5)	56.73(19)
C(1)-Ti(1)-C(5)	33.66(18)
C(10)-Ti(1)-C(5)	168.19(18)
Cl(1)-Ti(1)-C(5)	110.34(14)
O(1)-Ti(1)-C(3)	130.00(17)
C(9)-Ti(1)-C(3)	78.61(18)
C(7)-Ti(1)-C(3)	105.09(18)
C(8)-Ti(1)-C(3)	74.35(18)
C(4)-Ti(1)-C(3)	34.31(19)
C(6)-Ti(1)-C(3)	131.04(19)
C(2)-Ti(1)-C(3)	33.87(18)
C(1)-Ti(1)-C(3)	56.56(19)
C(10)-Ti(1)-C(3)	112.21(19)
Cl(1)-Ti(1)-C(3)	112.92(14)
C(5)-Ti(1)-C(3)	56.55(19)
O(4)-Ti(2)-C(21)	138.23(19)
O(4)-Ti(2)-C(23)	83.49(18)
C(21)-Ti(2)-C(23)	57.6(2)

O(4)-Ti(2)-C(22)	115.2(2)
C(21)-Ti(2)-C(22)	35.15(18)
C(23)-Ti(2)-C(22)	34.4(2)
O(4)-Ti(2)-C(26)	97.6(2)
C(21)-Ti(2)-C(26)	100.5(2)
C(23)-Ti(2)-C(26)	95.8(2)
C(22)-Ti(2)-C(26)	78.9(2)
O(4)-Ti(2)-C(19)	82.61(17)
C(21)-Ti(2)-C(19)	57.1(2)
C(23)-Ti(2)-C(19)	34.6(2)
C(22)-Ti(2)-C(19)	57.4(2)
C(26)-Ti(2)-C(19)	130.3(2)
O(4)-Ti(2)-C(24)	92.70(16)
C(21)-Ti(2)-C(24)	128.6(2)
C(23)-Ti(2)-C(24)	151.8(2)
C(22)-Ti(2)-C(24)	130.9(2)
C(26)-Ti(2)-C(24)	56.9(2)
C(19)-Ti(2)-C(24)	171.70(19)
O(4)-Ti(2)-Cl(2)	96.41(11)
C(21)-Ti(2)-Cl(2)	96.78(13)
C(23)-Ti(2)-Cl(2)	128.29(16)
C(22)-Ti(2)-Cl(2)	131.11(14)
C(26)-Ti(2)-Cl(2)	134.92(19)
C(19)-Ti(2)-Cl(2)	93.86(15)
C(24)-Ti(2)-Cl(2)	79.82(13)
O(4)-Ti(2)-C(25)	76.50(18)
C(21)-Ti(2)-C(25)	133.6(2)
C(23)-Ti(2)-C(25)	119.4(2)
C(22)-Ti(2)-C(25)	112.4(2)
C(26)-Ti(2)-C(25)	34.4(2)
C(19)-Ti(2)-C(25)	149.3(2)
C(24)-Ti(2)-C(25)	33.53(19)
Cl(2)-Ti(2)-C(25)	110.55(15)
O(4)-Ti(2)-C(28)	127.38(17)
C(21)-Ti(2)-C(28)	93.8(2)
C(23)-Ti(2)-C(28)	138.1(2)
C(22)-Ti(2)-C(28)	104.5(2)
C(26)-Ti(2)-C(28)	56.9(2)
C(19)-Ti(2)-C(28)	149.83(19)
C(24)-Ti(2)-C(28)	34.80(17)
Cl(2)-Ti(2)-C(28)	80.78(14)
C(25)-Ti(2)-C(28)	56.6(2)
O(4)-Ti(2)-C(20)	113.16(16)
C(21)-Ti(2)-C(20)	34.40(19)
C(23)-Ti(2)-C(20)	57.13(18)
C(22)-Ti(2)-C(20)	57.57(19)

C(26)-Ti(2)-C(20)	134.0(2)
C(19)-Ti(2)-C(20)	33.95(18)
C(24)-Ti(2)-C(20)	146.40(18)
Cl(2)-Ti(2)-C(20)	76.43(13)
C(25)-Ti(2)-C(20)	167.95(19)
C(28)-Ti(2)-C(20)	116.93(18)
O(4)-Ti(2)-C(27)	130.70(19)
C(21)-Ti(2)-C(27)	78.8(2)
C(23)-Ti(2)-C(27)	105.7(2)
C(22)-Ti(2)-C(27)	74.9(2)
C(26)-Ti(2)-C(27)	34.3(2)
C(19)-Ti(2)-C(27)	131.3(2)
C(24)-Ti(2)-C(27)	56.74(19)
Cl(2)-Ti(2)-C(27)	112.32(18)
C(25)-Ti(2)-C(27)	56.5(2)
C(28)-Ti(2)-C(27)	33.7(2)
C(20)-Ti(2)-C(27)	112.07(19)
O(7)-Ti(3)-C(43)	138.4(2)
O(7)-Ti(3)-C(46)	83.1(2)
C(43)-Ti(3)-C(46)	57.7(2)
O(7)-Ti(3)-C(42)	114.72(19)
C(43)-Ti(3)-C(42)	35.1(2)
C(46)-Ti(3)-C(42)	34.5(2)
O(7)-Ti(3)-C(40)	97.2(3)
C(43)-Ti(3)-C(40)	100.0(2)
C(46)-Ti(3)-C(40)	95.9(3)
C(42)-Ti(3)-C(40)	78.7(3)
O(7)-Ti(3)-C(45)	82.8(2)
C(43)-Ti(3)-C(45)	57.4(2)
C(46)-Ti(3)-C(45)	34.7(3)
C(42)-Ti(3)-C(45)	57.5(2)
C(40)-Ti(3)-C(45)	130.4(2)
O(7)-Ti(3)-C(37)	93.3(2)
C(43)-Ti(3)-C(37)	127.7(2)
C(46)-Ti(3)-C(37)	152.3(3)
C(42)-Ti(3)-C(37)	130.7(2)
C(40)-Ti(3)-C(37)	57.2(2)
C(45)-Ti(3)-C(37)	171.7(2)
O(7)-Ti(3)-C(38)	127.7(2)
C(43)-Ti(3)-C(38)	93.3(2)
C(46)-Ti(3)-C(38)	138.2(2)
C(42)-Ti(3)-C(38)	104.4(2)
C(40)-Ti(3)-C(38)	57.2(2)
C(45)-Ti(3)-C(38)	149.4(2)
C(37)-Ti(3)-C(38)	34.5(2)
O(7)-Ti(3)-C(44)	114.0(3)

C(43)-Ti(3)-C(44)	34.4(2)
C(46)-Ti(3)-C(44)	57.3(3)
C(42)-Ti(3)-C(44)	57.5(2)
C(40)-Ti(3)-C(44)	133.5(2)
C(45)-Ti(3)-C(44)	34.3(2)
C(37)-Ti(3)-C(44)	145.3(2)
C(38)-Ti(3)-C(44)	116.0(2)
O(7)-Ti(3)-Cl(3)	96.17(16)
C(43)-Ti(3)-Cl(3)	97.43(16)
C(46)-Ti(3)-Cl(3)	127.7(2)
C(42)-Ti(3)-Cl(3)	131.46(19)
C(40)-Ti(3)-Cl(3)	135.65(16)
C(45)-Ti(3)-Cl(3)	93.1(2)
C(37)-Ti(3)-Cl(3)	79.92(17)
C(38)-Ti(3)-Cl(3)	81.44(15)
C(44)-Ti(3)-Cl(3)	76.37(17)
O(7)-Ti(3)-C(41)	76.5(3)
C(43)-Ti(3)-C(41)	132.8(3)
C(46)-Ti(3)-C(41)	119.6(3)
C(42)-Ti(3)-C(41)	112.2(3)
C(40)-Ti(3)-C(41)	34.3(2)
C(45)-Ti(3)-C(41)	149.6(2)
C(37)-Ti(3)-C(41)	34.0(2)
C(38)-Ti(3)-C(41)	56.7(2)
C(44)-Ti(3)-C(41)	167.2(2)
Cl(3)-Ti(3)-C(41)	110.83(18)
O(7)-Ti(3)-C(39)	130.7(3)
C(43)-Ti(3)-C(39)	77.9(2)
C(46)-Ti(3)-C(39)	105.7(2)
C(42)-Ti(3)-C(39)	74.6(2)
C(40)-Ti(3)-C(39)	34.6(2)
C(45)-Ti(3)-C(39)	131.0(2)
C(37)-Ti(3)-C(39)	56.8(2)
C(38)-Ti(3)-C(39)	33.85(18)
C(44)-Ti(3)-C(39)	111.1(2)
Cl(3)-Ti(3)-C(39)	113.13(15)
C(41)-Ti(3)-C(39)	56.7(2)

Table A.3. Bond lengths [A] and angles [deg] for **3.4.**

_____

C(1)-C(2)	1.360(5)
C(1)-C(5)	1.387(6)
C(1)-Ti(1)	2.391(3)
C(1)-H(1)	0.9300
C(2)-C(3)	1.377(4)
C(2)-Ti(1)	2.407(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.379(5)
C(3)-Ti(1)	2.429(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.399(5)
C(4)-Ti(1)	2.443(3)
C(4)-H(4)	0.9300
C(5)-Ti(1)	2.408(3)
C(5)-H(5)	0.9300
C(6)-C(10)	1.398(4)
C(6)-C(7)	1.410(4)
C(6)-Ti(1)	2.393(3)
C(6)-H(6)	0.9300
C(7)-C(8)	1.396(4)
C(7)-Ti(1)	2.367(3)
C(7)-H(7)	0.9300
C(8)-C(9)	1.401(4)
C(8)-Ti(1)	2.404(3)
C(8)-H(8)	0.9300
C(9)-C(10)	1.404(4)
C(9)-Ti(1)	2.411(3)
C(9)-H(9)	0.9300
C(10)-Ti(1)	2.429(3)
C(10)-H(10)	0.9300
C(11)-O(1)	1.362(3)
C(11)-C(16)	1.424(4)
C(11)-C(12)	1.429(3)
C(12)-C(13)	1.397(4)
C(12)-C(17)	1.545(3)
C(13)-C(14)	1.393(3)
C(13)-H(13)	0.9300
C(14)-C(15)	1.389(3)
C(14)-C(21)	1.531(4)
C(15)-C(16)	1.393(4)
C(15)-H(15)	0.9300
C(16)-C(25)	1.546(3)
C(17)-C(18)	1.528(4)
C(17)-C(20)	1.536(4)

C(17)-C(19)	1.537(4)
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-C(23)	1.529(4)
C(21)-C(22)	1.533(4)
C(21)-C(24)	1.540(3)
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
C(25)-C(28)	1.535(4)
C(25)-C(27)	1.539(4)
C(25)-C(26)	1.546(4)
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600
C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600
C(28)-H(28C)	0.9600
C(29)-C(33)	1.359(6)
C(29)-C(30)	1.396(7)
C(29)-Ti(2)	2.357(4)
C(29)-H(29)	0.9300
C(30)-C(31)	1.377(6)
C(30)-Ti(2)	2.395(3)
C(30)-H(30)	0.9300
C(31)-C(32)	1.380(5)
C(31)-Ti(2)	2.419(3)
C(31)-H(31)	0.9300
C(32)-C(33)	1.331(5)
C(32)-Ti(2)	2.431(3)

C(32)-H(32)	0.9300
C(33)-Ti(2)	2.417(3)
C(33)-H(33)	0.9300
C(34)-C(35)	1.397(4)
C(34)-C(38)	1.407(5)
C(34)-Ti(2)	2.369(3)
C(34)-H(34)	0.9300
C(35)-C(36)	1.382(4)
C(35)-Ti(2)	2.391(3)
C(35)-H(35)	0.9300
C(36)-C(37)	1.383(4)
C(36)-Ti(2)	2.394(3)
C(36)-H(36)	0.9300
C(37)-C(38)	1.383(5)
C(37)-Ti(2)	2.404(3)
C(37)-H(37)	0.9300
C(38)-Ti(2)	2.377(3)
C(38)-H(38)	0.9300
C(39)-O(2)	1.373(3)
C(39)-C(40)	1.422(3)
C(39)-C(44)	1.422(3)
C(40)-C(41)	1.400(4)
C(40)-C(45)	1.547(3)
C(41)-C(42)	1.393(4)
C(41)-H(41)	0.9300
C(42)-C(43)	1.387(3)
C(42)-C(49)	1.536(3)
C(43)-C(44)	1.400(3)
C(43)-H(43)	0.9300
C(44)-C(53)	1.546(3)
C(45)-C(46)	1.532(4)
C(45)-C(47)	1.533(4)
C(45)-C(48)	1.556(3)
C(46)-H(46A)	0.9600
C(46)-H(46B)	0.9600
C(46)-H(46C)	0.9600
C(47)-H(47A)	0.9600
C(47)-H(47B)	0.9600
C(47)-H(47C)	0.9600
C(48)-H(48A)	0.9600
C(48)-H(48B)	0.9600
C(48)-H(48C)	0.9600
C(49)-C(52)	1.528(4)
C(49)-C(50)	1.532(4)
C(49)-C(51)	1.544(3)
C(50)-H(50A)	0.9600

C(50)-H(50B)	0.9600
C(50)-H(50C)	0.9600
C(51)-H(51A)	0.9600
C(51)-H(51B)	0.9600
C(51)-H(51C)	0.9600
C(52)-H(52A)	0.9600
C(52)-H(52B)	0.9600
C(52)-H(52C)	0.9600
C(53)-C(54)	1.533(4)
C(53)-C(56)	1.538(3)
C(53)-C(55)	1.539(3)
C(54)-H(54A)	0.9600
C(54)-H(54B)	0.9600
C(54)-H(54C)	0.9600
C(55)-H(55A)	0.9600
C(55)-H(55B)	0.9600
C(55)-H(55C)	0.9600
C(56)-H(56A)	0.9600
C(56)-H(56B)	0.9600
C(56)-H(56C)	0.9600
O(1)-Ti(1)	1.9152(17)
O(2)-Ti(2)	1.9223(17)
Cl(1)-Ti(1)	2.3994(8)
Cl(2)-Ti(2)	2.3983(8)
C(2)-C(1)-C(5)	108.6(3)
C(2)-C(1)-Ti(1)	74.15(19)
C(5)-C(1)-Ti(1)	73.9(2)
C(2)-C(1)-H(1)	125.7
C(5)-C(1)-H(1)	125.7
Ti(1)-C(1)-H(1)	118.2
C(1)-C(2)-C(3)	108.6(3)
C(1)-C(2)-Ti(1)	72.9(2)
C(3)-C(2)-Ti(1)	74.33(17)
C(1)-C(2)-H(2)	125.7
C(3)-C(2)-H(2)	125.7
Ti(1)-C(2)-H(2)	118.9
C(2)-C(3)-C(4)	108.1(3)
C(2)-C(3)-Ti(1)	72.58(17)
C(4)-C(3)-Ti(1)	74.11(17)
C(2)-C(3)-H(3)	125.9
C(4)-C(3)-H(3)	125.9
Ti(1)-C(3)-H(3)	119.2
C(3)-C(4)-C(5)	107.6(3)
C(3)-C(4)-Ti(1)	72.99(17)
C(5)-C(4)-Ti(1)	71.87(18)

C(3)-C(4)-H(4)	126.2
C(5)-C(4)-H(4)	126.2
Ti(1)-C(4)-H(4)	120.7
C(1)-C(5)-C(4)	107.0(3)
C(1)-C(5)-Ti(1)	72.6(2)
C(4)-C(5)-Ti(1)	74.60(19)
C(1)-C(5)-H(5)	126.5
C(4)-C(5)-H(5)	126.5
Ti(1)-C(5)-H(5)	118.4
C(10)-C(6)-C(7)	107.7(3)
C(10)-C(6)-Ti(1)	74.56(16)
C(7)-C(6)-Ti(1)	71.75(16)
C(10)-C(6)-H(6)	126.1
C(7)-C(6)-H(6)	126.1
Ti(1)-C(6)-H(6)	119.4
C(8)-C(7)-C(6)	108.0(2)
C(8)-C(7)-Ti(1)	74.47(16)
C(6)-C(7)-Ti(1)	73.81(16)
C(8)-C(7)-H(7)	126.0
C(6)-C(7)-H(7)	126.0
Ti(1)-C(7)-H(7)	117.7
C(7)-C(8)-C(9)	108.2(3)
C(7)-C(8)-Ti(1)	71.53(16)
C(9)-C(8)-Ti(1)	73.34(16)
C(7)-C(8)-H(8)	125.9
C(9)-C(8)-H(8)	125.9
Ti(1)-C(8)-H(8)	121.0
C(8)-C(9)-C(10)	107.8(3)
C(8)-C(9)-Ti(1)	72.84(16)
C(10)-C(9)-Ti(1)	73.86(16)
C(8)-C(9)-H(9)	126.1
C(10)-C(9)-H(9)	126.1
Ti(1)-C(9)-H(9)	119.1
C(6)-C(10)-C(9)	108.2(3)
C(6)-C(10)-Ti(1)	71.75(16)
C(9)-C(10)-Ti(1)	72.42(16)
C(6)-C(10)-H(10)	125.9
C(9)-C(10)-H(10)	125.9
Ti(1)-C(10)-H(10)	121.6
O(1)-C(11)-C(16)	122.1(2)
O(1)-C(11)-C(12)	120.1(2)
C(16)-C(11)-C(12)	117.9(2)
C(13)-C(12)-C(11)	117.6(2)
C(13)-C(12)-C(17)	119.0(2)
C(11)-C(12)-C(17)	123.3(2)
C(14)-C(13)-C(12)	123.1(2)

C(14)-C(13)-H(13)	118.4
C(12)-C(13)-H(13)	118.4
C(15)-C(14)-C(13)	115.8(2)
C(15)-C(14)-C(21)	120.3(2)
C(13)-C(14)-C(21)	123.9(2)
C(14)-C(15)-C(16)	124.0(2)
C(14)-C(15)-H(15)	118.0
C(16)-C(15)-H(15)	118.0
C(15)-C(16)-C(11)	117.0(2)
C(15)-C(16)-C(25)	117.4(2)
C(11)-C(16)-C(25)	125.5(2)
C(18)-C(17)-C(20)	105.6(2)
C(18)-C(17)-C(19)	112.1(2)
C(20)-C(17)-C(19)	106.6(2)
C(18)-C(17)-C(12)	109.8(2)
C(20)-C(17)-C(12)	111.2(2)
C(19)-C(17)-C(12)	111.4(2)
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(17)-C(19)-H(19A)	109.5
C(17)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(17)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(17)-C(20)-H(20A)	109.5
C(17)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(17)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(23)-C(21)-C(14)	112.3(2)
C(23)-C(21)-C(22)	108.7(2)
C(14)-C(21)-C(22)	108.2(2)
C(23)-C(21)-C(24)	107.8(2)
C(14)-C(21)-C(24)	110.6(2)
C(22)-C(21)-C(24)	109.2(2)
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5

H(22B)-C(22)-H(22C)	109.5
C(21)-C(23)-H(23A)	109.5
C(21)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(21)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(21)-C(24)-H(24A)	109.5
C(21)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(21)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(28)-C(25)-C(27)	111.8(2)
C(28)-C(25)-C(16)	112.9(2)
C(27)-C(25)-C(16)	110.1(2)
C(28)-C(25)-C(26)	105.4(2)
C(27)-C(25)-C(26)	107.7(2)
C(16)-C(25)-C(26)	108.7(2)
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(25)-C(28)-H(28A)	109.5
C(25)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(25)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(33)-C(29)-C(30)	107.5(3)
C(33)-C(29)-Ti(2)	75.9(2)
C(30)-C(29)-Ti(2)	74.4(2)
C(33)-C(29)-H(29)	126.3
C(30)-C(29)-H(29)	126.3
Ti(2)-C(29)-H(29)	115.6
C(31)-C(30)-C(29)	107.1(3)
C(31)-C(30)-Ti(2)	74.33(19)
C(29)-C(30)-Ti(2)	71.4(2)

C(31)-C(30)-H(30)	126.4
C(29)-C(30)-H(30)	126.4
Ti(2)-C(30)-H(30)	119.7
C(30)-C(31)-C(32)	106.9(3)
C(30)-C(31)-Ti(2)	72.4(2)
C(32)-C(31)-Ti(2)	73.95(18)
C(30)-C(31)-H(31)	126.5
C(32)-C(31)-H(31)	126.5
Ti(2)-C(31)-H(31)	119.1
C(33)-C(32)-C(31)	109.3(3)
C(33)-C(32)-Ti(2)	73.49(19)
C(31)-C(32)-Ti(2)	72.98(17)
C(33)-C(32)-H(32)	125.4
C(31)-C(32)-H(32)	125.4
Ti(2)-C(32)-H(32)	119.9
C(32)-C(33)-C(29)	109.1(4)
C(32)-C(33)-Ti(2)	74.66(19)
C(29)-C(33)-Ti(2)	71.1(2)
C(32)-C(33)-H(33)	125.4
C(29)-C(33)-H(33)	125.4
Ti(2)-C(33)-H(33)	120.5
C(35)-C(34)-C(38)	107.2(3)
C(35)-C(34)-Ti(2)	73.80(16)
C(38)-C(34)-Ti(2)	73.08(18)
C(35)-C(34)-H(34)	126.4
C(38)-C(34)-H(34)	126.4
Ti(2)-C(34)-H(34)	118.7
C(36)-C(35)-C(34)	108.4(3)
C(36)-C(35)-Ti(2)	73.34(16)
C(34)-C(35)-Ti(2)	72.07(16)
C(36)-C(35)-H(35)	125.8
C(34)-C(35)-H(35)	125.8
Ti(2)-C(35)-H(35)	120.6
C(35)-C(36)-C(37)	107.9(3)
C(35)-C(36)-Ti(2)	73.09(16)
C(37)-C(36)-Ti(2)	73.62(18)
C(35)-C(36)-H(36)	126.1
C(37)-C(36)-H(36)	126.1
Ti(2)-C(36)-H(36)	119.1
C(36)-C(37)-C(38)	109.0(3)
C(36)-C(37)-Ti(2)	72.87(17)
C(38)-C(37)-Ti(2)	72.13(19)
C(36)-C(37)-H(37)	125.5
C(38)-C(37)-H(37)	125.5
Ti(2)-C(37)-H(37)	121.2
C(37)-C(38)-C(34)	107.5(3)

C(37)-C(38)-Ti(2)	74.24(19)
C(34)-C(38)-Ti(2)	72.44(18)
C(37)-C(38)-H(38)	126.3
C(34)-C(38)-H(38)	126.3
Ti(2)-C(38)-H(38)	119.0
O(2)-C(39)-C(40)	121.3(2)
O(2)-C(39)-C(44)	120.5(2)
C(40)-C(39)-C(44)	118.2(2)
C(41)-C(40)-C(39)	116.9(2)
C(41)-C(40)-C(45)	116.9(2)
C(39)-C(40)-C(45)	126.2(2)
C(42)-C(41)-C(40)	124.0(2)
C(42)-C(41)-H(41)	118.0
C(40)-C(41)-H(41)	118.0
C(43)-C(42)-C(41)	115.6(2)
C(43)-C(42)-C(49)	123.9(2)
C(41)-C(42)-C(49)	120.5(2)
C(42)-C(43)-C(44)	123.4(2)
C(42)-C(43)-H(43)	118.3
C(44)-C(43)-H(43)	118.3
C(43)-C(44)-C(39)	117.7(2)
C(43)-C(44)-C(53)	119.0(2)
C(39)-C(44)-C(53)	123.1(2)
C(46)-C(45)-C(47)	111.5(2)
C(46)-C(45)-C(40)	113.4(2)
C(47)-C(45)-C(40)	110.3(2)
C(46)-C(45)-C(48)	105.0(2)
C(47)-C(45)-C(48)	107.7(2)
C(40)-C(45)-C(48)	108.6(2)
C(45)-C(46)-H(46A)	109.5
C(45)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
C(45)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
C(45)-C(47)-H(47A)	109.5
C(45)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
C(45)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(45)-C(48)-H(48A)	109.5
C(45)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(45)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5

H(48B)-C(48)-H(48C)	109.5
C(52)-C(49)-C(50)	108.2(2)
C(52)-C(49)-C(42)	112.6(2)
C(50)-C(49)-C(42)	109.0(2)
C(52)-C(49)-C(51)	107.5(2)
C(50)-C(49)-C(51)	109.2(2)
C(42)-C(49)-C(51)	110.2(2)
C(49)-C(50)-H(50A)	109.5
C(49)-C(50)-H(50B)	109.5
H(50A)-C(50)-H(50B)	109.5
C(49)-C(50)-H(50C)	109.5
H(50A)-C(50)-H(50C)	109.5
H(50B)-C(50)-H(50C)	109.5
C(49)-C(51)-H(51A)	109.5
C(49)-C(51)-H(51B)	109.5
H(51A)-C(51)-H(51B)	109.5
C(49)-C(51)-H(51C)	109.5
H(51A)-C(51)-H(51C)	109.5
H(51B)-C(51)-H(51C)	109.5
C(49)-C(52)-H(52A)	109.5
C(49)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52B)	109.5
C(49)-C(52)-H(52C)	109.5
H(52A)-C(52)-H(52C)	109.5
H(52B)-C(52)-H(52C)	109.5
C(54)-C(53)-C(56)	106.2(2)
C(54)-C(53)-C(55)	110.7(2)
C(56)-C(53)-C(55)	106.4(2)
C(54)-C(53)-C(44)	108.5(2)
C(56)-C(53)-C(44)	111.5(2)
C(55)-C(53)-C(44)	113.4(2)
C(53)-C(54)-H(54A)	109.5
C(53)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5
C(53)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5
C(53)-C(55)-H(55A)	109.5
C(53)-C(55)-H(55B)	109.5
H(55A)-C(55)-H(55B)	109.5
C(53)-C(55)-H(55C)	109.5
H(55A)-C(55)-H(55C)	109.5
H(55B)-C(55)-H(55C)	109.5
C(53)-C(56)-H(56A)	109.5
C(53)-C(56)-H(56B)	109.5
H(56A)-C(56)-H(56B)	109.5

C(53)-C(56)-H(56C)	109.5
H(56A)-C(56)-H(56C)	109.5
H(56B)-C(56)-H(56C)	109.5
C(11)-O(1)-Ti(1)	140.44(16)
C(39)-O(2)-Ti(2)	138.85(15)
O(1)-Ti(1)-C(7)	106.49(9)
O(1)-Ti(1)-C(1)	85.35(11)
C(7)-Ti(1)-C(1)	93.88(15)
O(1)-Ti(1)-C(6)	137.07(9)
C(7)-Ti(1)-C(6)	34.45(10)
C(1)-Ti(1)-C(6)	108.19(15)
O(1)-Ti(1)-Cl(1)	100.56(6)
C(7)-Ti(1)-Cl(1)	131.87(7)
C(1)-Ti(1)-Cl(1)	127.75(12)
C(6)-Ti(1)-Cl(1)	101.91(7)
O(1)-Ti(1)-C(8)	80.67(9)
C(7)-Ti(1)-C(8)	34.00(10)
C(1)-Ti(1)-C(8)	113.78(14)
C(6)-Ti(1)-C(8)	56.47(10)
Cl(1)-Ti(1)-C(8)	118.43(7)
O(1)-Ti(1)-C(2)	116.90(11)
C(7)-Ti(1)-C(2)	76.44(11)
C(1)-Ti(1)-C(2)	32.94(13)
C(6)-Ti(1)-C(2)	78.21(12)
Cl(1)-Ti(1)-C(2)	124.19(8)
C(8)-Ti(1)-C(2)	107.74(11)
O(1)-Ti(1)-C(5)	81.08(10)
C(7)-Ti(1)-C(5)	127.16(15)
C(1)-Ti(1)-C(5)	33.59(15)
C(6)-Ti(1)-C(5)	131.88(12)
Cl(1)-Ti(1)-C(5)	95.51(14)
C(8)-Ti(1)-C(5)	143.81(15)
C(2)-Ti(1)-C(5)	55.22(14)
O(1)-Ti(1)-C(9)	90.10(9)
C(7)-Ti(1)-C(9)	56.59(10)
C(1)-Ti(1)-C(9)	147.39(14)
C(6)-Ti(1)-C(9)	56.38(10)
Cl(1)-Ti(1)-C(9)	84.84(7)
C(8)-Ti(1)-C(9)	33.82(10)
C(2)-Ti(1)-C(9)	131.35(11)
C(5)-Ti(1)-C(9)	171.10(11)
O(1)-Ti(1)-C(3)	135.74(9)
C(7)-Ti(1)-C(3)	95.92(11)
C(1)-Ti(1)-C(3)	54.93(11)
C(6)-Ti(1)-C(3)	79.63(11)
Cl(1)-Ti(1)-C(3)	91.31(8)

C(8)-Ti(1)-C(3)	129.84(11)
C(2)-Ti(1)-C(3)	33.09(11)
C(5)-Ti(1)-C(3)	55.25(11)
C(9)-Ti(1)-C(3)	133.65(10)
O(1)-Ti(1)-C(10)	123.46(9)
C(7)-Ti(1)-C(10)	56.40(10)
C(1)-Ti(1)-C(10)	141.73(15)
C(6)-Ti(1)-C(10)	33.69(9)
Cl(1)-Ti(1)-C(10)	75.49(7)
C(8)-Ti(1)-C(10)	55.92(10)
C(2)-Ti(1)-C(10)	110.23(12)
C(5)-Ti(1)-C(10)	154.74(12)
C(9)-Ti(1)-C(10)	33.72(10)
C(3)-Ti(1)-C(10)	100.77(10)
O(1)-Ti(1)-C(4)	110.39(11)
C(7)-Ti(1)-C(4)	128.11(11)
C(1)-Ti(1)-C(4)	55.21(13)
C(6)-Ti(1)-C(4)	110.62(12)
Cl(1)-Ti(1)-C(4)	74.67(8)
C(8)-Ti(1)-C(4)	161.92(11)
C(2)-Ti(1)-C(4)	54.80(11)
C(5)-Ti(1)-C(4)	33.53(13)
C(9)-Ti(1)-C(4)	153.11(12)
C(3)-Ti(1)-C(4)	32.90(11)
C(10)-Ti(1)-C(4)	121.83(12)
O(2)-Ti(2)-C(29)	99.92(17)
O(2)-Ti(2)-C(34)	111.44(10)
C(29)-Ti(2)-C(34)	80.56(16)
O(2)-Ti(2)-C(38)	137.78(10)
C(29)-Ti(2)-C(38)	96.6(2)
C(34)-Ti(2)-C(38)	34.48(13)
O(2)-Ti(2)-C(35)	81.99(8)
C(29)-Ti(2)-C(35)	102.38(13)
C(34)-Ti(2)-C(35)	34.13(10)
C(38)-Ti(2)-C(35)	56.50(10)
O(2)-Ti(2)-C(36)	85.38(9)
C(29)-Ti(2)-C(36)	134.97(14)
C(34)-Ti(2)-C(36)	56.51(11)
C(38)-Ti(2)-C(36)	56.30(11)
C(35)-Ti(2)-C(36)	33.58(10)
O(2)-Ti(2)-C(30)	79.61(10)
C(29)-Ti(2)-C(30)	34.16(16)
C(34)-Ti(2)-C(30)	113.48(18)
C(38)-Ti(2)-C(30)	129.25(17)
C(35)-Ti(2)-C(30)	125.89(16)
C(36)-Ti(2)-C(30)	157.00(13)

O(2)-Ti(2)-Cl(2)	101.32(5)
C(29)-Ti(2)-Cl(2)	130.77(9)
C(34)-Ti(2)-Cl(2)	129.61(9)
C(38)-Ti(2)-Cl(2)	96.60(11)
C(35)-Ti(2)-Cl(2)	124.20(7)
C(36)-Ti(2)-Cl(2)	90.71(8)
C(30)-Ti(2)-Cl(2)	109.19(15)
O(2)-Ti(2)-C(37)	117.22(11)
C(29)-Ti(2)-C(37)	130.1(2)
C(34)-Ti(2)-C(37)	56.23(13)
C(38)-Ti(2)-C(37)	33.62(13)
C(35)-Ti(2)-C(37)	55.58(11)
C(36)-Ti(2)-C(37)	33.51(11)
C(30)-Ti(2)-C(37)	162.02(15)
Cl(2)-Ti(2)-C(37)	75.17(9)
O(2)-Ti(2)-C(33)	131.93(13)
C(29)-Ti(2)-C(33)	33.03(16)
C(34)-Ti(2)-C(33)	77.95(12)
C(38)-Ti(2)-C(33)	76.13(14)
C(35)-Ti(2)-C(33)	110.57(11)
C(36)-Ti(2)-C(33)	130.91(12)
C(30)-Ti(2)-C(33)	54.97(14)
Cl(2)-Ti(2)-C(33)	107.35(12)
C(37)-Ti(2)-C(33)	107.07(15)
O(2)-Ti(2)-C(31)	96.70(10)
C(29)-Ti(2)-C(31)	55.69(13)
C(34)-Ti(2)-C(31)	131.66(11)
C(38)-Ti(2)-C(31)	124.45(12)
C(35)-Ti(2)-C(31)	157.66(11)
C(36)-Ti(2)-C(31)	168.73(12)
C(30)-Ti(2)-C(31)	33.24(14)
Cl(2)-Ti(2)-C(31)	78.02(9)
C(37)-Ti(2)-C(31)	139.99(13)
C(33)-Ti(2)-C(31)	54.40(12)
O(2)-Ti(2)-C(32)	129.50(10)
C(29)-Ti(2)-C(32)	54.44(13)
C(34)-Ti(2)-C(32)	106.13(12)
C(38)-Ti(2)-C(32)	91.43(12)
C(35)-Ti(2)-C(32)	140.23(11)
C(36)-Ti(2)-C(32)	144.63(11)
C(30)-Ti(2)-C(32)	54.64(11)
Cl(2)-Ti(2)-C(32)	78.01(9)
C(37)-Ti(2)-C(32)	111.36(12)
C(33)-Ti(2)-C(32)	31.86(12)
C(31)-Ti(2)-C(32)	33.06(11)