Synthesis And Reactivity Of Metal Bis(alkoxide) Complexes In Nitrene Coupling And Polymerization Of Polar Monomers

Duleeka Chamini Wannipurage

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SYNTHESIS AND REACTIVITY OF METAL BIS(ALKOXIDE) COMPLEXES IN NITRENE COUPLING AND POLYMERIZATION OF POLAR MONOMERS

by

DULEEKA C. WANNIPURAGE

DISSERTATION

Submitted to the Graduate School of Wayne State University, Detroit, Michigan in partial fulfillment of the requirements for the degree of

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Advisor Date

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CHAPTER 1: INTRODUCTION


1.1. General

My dissertation focuses primarily on two projects: iron-mediated homocoupling of nitrenes to produce azoarenes, and magnesium-mediated polymerization and copolymerization of cyclic esters. These projects addressed two specific problems in homogeneous catalysis. The first problem is the scarcity of efficient and broad-range catalysts for the synthesis of symmetric and asymmetric azoarenes, which are very commonly used in the chemical industry. The second problem is the need to develop efficient and sustainable catalysts for the polymerization of polar monomers to produce biodegradable and biorenewable alternatives to polyolefins. In both projects, I developed complexes in bis(alkoxide) ligand environments and explored their catalytic reactivity.

The introduction to this dissertation will provide background information to both projects, while also discussing the chemistry of the alkoxide-ligated metal complexes. In the first part of this introduction (subchapters 1.2-1.5), my goal is to introduce the reader to the chemistry of azoarenes. The following topics will be discussed: What are azoarenes and what are the uses? What are synthetic pathways towards azoarenes? What are the advantages of the catalytic transition metal-mediated synthesis of azoarenes, which catalysts had been used toward this goal, and why do we pursue alkoxide-ligated catalysts for the synthesis of azoarenes?

My second project focuses on the design of magnesium alkoxide catalysts towards the synthesis of polyesters. Therefore, in the second part of the introduction (subchapters 1.6-1.10), I
will discuss different syntheses of polyesters in the general context of polymerization. Different types of polyesters and their properties will be discussed as well. 

1.2. Background on Azoarenes

Azoarenes are organic compounds that contain one or more azo (-N=N-) groups linked to various aromatic moieties (Scheme 1).\(^1\) Due to their \(\pi\)-electron delocalization, azoarenes typically display intense colors. The color of an azoarene can be generally modified by the modification of aromatic rings. In addition, azoarenes show light-sensitive \textit{cis-trans} isomerization (Scheme 2). Due to these structural properties, azoarenes are widely applied in various fields. Azoarenes are used in the chemical industry as dyes and pigments.\(^1\) The emerging applications of azoarenes include molecular photoswitches, optical storage media, and drug delivery agents.\(^2-4\) Azoarenes are the most important class of commercial dyes (“azo dyes”) which covers more than 50% of the industrial dyes (see Figure 1.1 for the selected examples of azo dyes).\(^1\) Azorubine, Sunset Yellow, Lemon Yellow, Yellow 2G are common food colors. Sudan 1 (orange-red) is used to colorize waxes, oils, petrol, solvents, and polishes. Direct Blue 1 is a common textile dye. Light-sensitive \textit{cis-trans} isomerization of azoarene is used in the medical field. Azoarenes can act as reversible “gate-keeper” systems in the drug delivery matrix. In this application, azoarenes are capable of undergoing reversible switching from “on” to “off” via \textit{cis-trans} isomerization by alternating irradiation of UV and visible light.\(^5\)
1.2. Azoarenes can be synthesized by many different synthetic pathways including azo coupling of the diazonium salt with activated aromatic compounds, condensation of aromatic nitroso derivatives with aniline (Mills reaction), reductive coupling of nitro derivatives, and transformation of azoxybenzene to 4-hydroxy substituted azo derivative (Wallach reaction). Many of these synthetic pathways require stoichiometric amounts of chemical oxidants and produce significant amounts of toxic by-products. On the other hand, these reactions are not catalytic, produce limited types of azoarenes with stoichiometric amounts.
1.3. Organoazides as Nitrene Precursors

Organoazides (RN₃) are considered excellent nitrene precursors due to several reasons. The majority of organoazides are commercially available or can be easily synthesized. Furthermore, the only by-product of the conversion of organoazides to nitrene is environmentally friendly dinitrogen N₂. Transition metal catalysis is essential to cleave the RN-N₂ bond of an organic azide to form metal-bound nitrene functionality under mild reaction conditions. Formally, the initial coordination of an organoazide to the electrophilic transition metal center is followed by the two-electron reductive splitting to give metal-imido and the release N₂ (Figure 1.2). Metal-coordinated nitrenes serve as reactive intermediates in C-H bond amination, aziridination, and formation of carbodiimides, isocyanates, and azoarenes (Figure 1.3).
1.4. Transition Metal-Mediated Azoarene Synthesis

Transition metal-mediated azoarene formation takes place via nitrene homocoupling (dimerization). While nitrene homocoupling is a common side reaction in the reactive nitrene chemistry that accompanies other nitrene-transfer reactions (such as C-H activation or aziridination), it is rarely the main reaction route following metal-nitrene (imido) formation. Therefore, catalytic formation of azoarenes by nitrene homocoupling using metal-imido complexes is relatively rare. Figure 1.4 below demonstrates selected metal complexes which exhibit the formation of azoarenes stoichiometrically or catalytically. Hillhouse, Cundari, and co-
workers introduced a nickel-diphosphine complex which showed formation of azomesitylene but the reaction was not catalytic due to azomesitylene coordination to the metal.\textsuperscript{10} Peters and co-workers have described iron and ruthenium catalytic systems which could catalytically convert several aryl azides $\text{ArN}_3$ ($\text{Ar} = \text{Ph}, \text{4-MePh}, \text{4-MeOPh}, \text{Mes}$) to azoarenes in moderate yields.\textsuperscript{11} Heyduk and co-workers reported a tantalum catalyst with the redox-active amine bis(phenoxide) ligand, which showed catalytic conversion of phenyl azide to azobenzene (10 equiv).\textsuperscript{12} Recently Uyeda and coworkers reported a dinickel catalyst that showed the catalytic formation of azoarene efficiently with broad substrate scope.\textsuperscript{13} Uyeda’s catalyst produced azoarenes via the reaction of dinickel-bridging nitrene with an additional equivalent of aryl azide, which resulted in the formation of metal-bound (initially) \textit{cis}-azoarene. Following its dissociation, \textit{cis} azoarene would relax into the energetically favorable \textit{trans} form. The only limitation of Uyeda’s catalyst was the inability of a bulky nitrene to react with the second equivalent of a bulky azide.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{transition-metal-complexes.png}
\caption{Selected transition-metal complexes involved in stoichiometric and catalytic nitrene coupling to form azoarenes.}
\end{figure}
1.5. Alkoxide-Ligated Complexes for Nitrene Transfer Reactivity

The reactivity of transition metal nitrene complexes is determined by their electronic nature, which is regulated, in part, by the ancillary ligand type. A significant number of studies during the last decade demonstrated that strong-field ligands, that combine strong $\sigma$-donation and some degree of $\pi$-acceptance (e.g. N-heterocyclic carbenes or phosphines), form surprisingly stable high-valent late metal imido and nitrido complexes (Figure 1.5). In a sharp contrast, relatively weak-field nitrogen-based ligands (e.g., dipyrrromethene) led to reactive electrophilic nitrenes.

Figure 1.5. Examples of complexes with strong-field ligand that form stable high-valent late metal imido and nitride.

Alkoxides are among the simplest, oldest, and easily synthesizable ligands for the transition metals. Until recently, however, the major focus of the alkoxide chemistry was on oxophilic early transition metals, for which alkoxides were considered to be a natural fit. Recent years
witnessed an increase in the use of alkoxides as supporting ligands for later transition metals, particularly 3d, due to several considerations presented below.\textsuperscript{18} Alkoxides generally form relatively strong bonds with 3d transition elements, including middle and late metals, which makes them viable ligands for such elements. The higher electronegativity of oxygen (compared with nitrogen and carbon), however, should result in an alkoxide being a weaker $\sigma$-donor than amide and alkyl. The presence of the occupied $\pi$-symmetry orbitals on the oxygen leads to the $\pi$-donor character of the alkoxide (\textbf{Figure 1.6}). Due to the combination of weak $\sigma$-donation and $\pi$-donation, alkoxides could be considered among the weakest-field ligands. This weak-field nature should subsequently lead to reactive nitrene functionalities due to the anticipated high-spin configuration of the metal centers in these complexes.

\textbf{Figure 0.6}. Steric and electronic aspects of the alkoxide coordination in \(\text{M(OR)}\textsubscript{2}(=X)\) complexes (\(X = \text{Nitrene}\)).

The steric aspect of the alkoxide ligation also merits consideration, as it has a significant effect on the design of alkoxide-based group-transfer catalysts. Unlike related amide ligands \([\text{NR}\textsubscript{2}]\), alkoxide \([\text{OR}]\) features a single substituent.\textsuperscript{19} The lack of steric protection and the presence of the lone pairs on the oxygen often results in cluster formation, particularly for the $\pi$-basic later metals. Extreme bulk at the \(R\) group constitutes one of the solutions to this problem. Several bulky \([\text{OCR}\textsubscript{3}]\) ligands were designed in the recent decade, allowing the formation of well-defined
mononuclear platforms for the installation of the reactive functionality (Figure 1.6). Furthermore, the steric bulk of the alkoxide can be carefully modified to allow the selective formation of bis(alkoxide) [M(OR)₂] and tris(alkoxide) [M(OR)₃] platforms.

There has been significant interest in the design of low-coordinate nitrene (imido) complexes featuring alkoxide ligand environments. As discussed earlier, the weak-field π-donating nature of alkoxide ligands is expected to render such complexes highly reactive. Low coordination is desirable to enable substrate coordination prior to the N-substrate bond formation.

Given the well-established activity of iron-nitrene functionalities in group transfer reactions, nitrene-transfer reactivity of iron complexes in alkoxide and related O-based ligand environments drew particularly close attention. Early on, Kawaguchi and coworkers described reactivity of two-coordinate Fe(OAr)₂ (Ar = 2,6-Ad-4-Me₆H₂ or Ar = 2,6-Ad-4-iPr-C₆H₄) with adamantyl azide.²⁰ The reaction formed pale green Fe(II) products Fe(OAr)(OAr’-NHAd) products (Figure 1.7). It was hypothesized that the reaction proceeded via a reactive transient electrophilic Fe(IV)-imido complex [Fe⁴(OR)₂(NAd)] which inserts nitrene into the C-H bond of the neighboring adamantyl group.

![Figure 1.7](image_url)  
**Figure 1.7.** Insertion of nitrene into an aryloxide C-H bond demonstrated by Kawaguchi and coworkers.

Our group has investigated the reactivity of Fe(OR)₂(THF)₂ (OR = OC’Bu₂Ph) (1) with an alkyl (adamantyl) azide.²¹ The reaction led to the reductive coupling of the azide via the terminal nitrogens to yield an iron(III) hexazene complex (RO)₂Fe(μ-κ²:κ²-AdN₆Ad)Fe(OR)₂ (2) (Figure...
Remarkably, reductive coupling of azides by Fe(OR)$_2$(THF)$_2$ did not require the reducing power of Fe(I)/Mg(I)/Zn(I) metalloradicals, as in the previous instances. DFT calculations suggested that the initial azide coordination to mononuclear [Fe$^{II}$(OR)$_2$] species may form an azide-bridged dimer with significant azide reduction; the dimerization event places azide radicals in near proximity and allows for the subsequent reductive coupling.

**Figure 0.8.** Possible mechanism for the reductive coupling of adamantyl azide to give Fe(OR)$_2$-hexazene.

Treatment of Fe(OR)$_2$(THF)$_2$ with aryl azides N$_3$Ar led to the reductive splitting of N$_3$Ar and likely formation of nitrene intermediates. For bulky aryl azides (e.g., mesityl, 2,6-diethylphenyl), the reaction yielded corresponding azoarenes quantitatively (**Figure 1.9**). Mesityl nitrene coupling is selective for the [Fe(OR)$_2$] system even in the presence of a large excess (solvent) of a weak C-H bond donor, cyclohexadiene. For aryl azides lacking ortho substituents (e.g., phenyl, 3,5-dimethylphenyl), the initial nitrene formation resulted in alkoxide disproportionation to give Fe$_2$(μ$_2$-NAr)$_2$(OR)$_2$(THF)$_2$ (3) and Fe(OR)$_3$ (4). The resulting bridging imido complexes Fe$_2$(μ$_2$-NAr)$_2$(OR)$_2$(THF)$_2$ did not produce azoarenes upon thermolysis. Their treatment with additional azide or isocyanide similarly produced no additional products, emphasizing the stability of the [Fe$_2$(μ$_2$-NAr)] core. Thus, while our first-generation nitrene
homocoupling catalyst was highly reactive, its reactivity scope was narrow and limited to bulky aryl nitrenes only. My subsequent work in this project focused on the development of new iron-alkoxide catalysts for nitrene coupling with wider substrate scope.

![Diagram of reaction](image)

**Figure 0.9.** Reactivity of Fe(OR)₂(THF)$_2$ (1) (OR = OC$^2$Bu$_2$Ph) with aryl azides: formation of azoarenes for Ar = 2,4,6-Me$_3$PhN$_3$ and 2,6-Et$_2$PhN$_3$, and iron-imido dimers for Ar = Ph and 4-MePh.

### 1.6. Types of Polymerizations

The second part of my dissertation focuses on the design of new magnesium alkoxide catalysts for the polymerization of polar monomers. Overall, there are two major types of polymerizations based on polymerization mechanism: (1) step-growth polymerization, (2) chain-growth polymerization. Step-growth polymerization proceeds via a stepwise reaction between functional groups in bifunctional monomers (Figure 1.10). The size of the polymer increases slowly in this polymerization and different sizes of the species present (monomers react with each other or with dimers, trimers, or $n$-mers to produce different sizes of polymers) in the reaction medium will react with each other to form different sizes of the polymers until it forms large-size polymer chain. At lower monomer conversions, a significant distribution in polymer sizes is
observed in step-grown polymerization. Step-growth polymerization generally requires harsh reaction conditions and produces small molecular byproducts as water or small alcohol. Polyester formation using dicarboxylic acid with dialcohol and polyamide synthesis using dicarboxylic acid with diamine provide examples for the step-growth polymerization.\textsuperscript{24}

In chain-growth polymerization, an initiator or a catalyst with a reactive site is required (Figure 1.11). A reactive site can be a cation, an anion, or a free radical. In propagation, each monomer will react with the reactive site when the addition of the monomers to the polymer chain takes place. In contrast to the step-growth polymerization, in chain-growth polymerization the monomers only react with the reactive site of the initiator. Therefore, better control over the polymerization can be seen with similar sizes of the polymers at lower monomer conversions. Chain growth polymerization produces high molecular weight polymers and the molecular weight of the polymer builds up rapidly.\textsuperscript{23,24} Synthesis of polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), and ring-opening polymerization of lactide are examples of chain-growth polymerization.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11.png}
\caption{Demonstration of step-growth polymerization.}
\end{figure}
1.7. Polyesters: Types and Biodegradability

Polyesters are polymers that contain an ester functional group in the main chain as the repeating unit (Scheme 3). Polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polylactic acid (PLA), polyglycolic acid (PGA), polycaprolactone (PCL), poly-2-hydroxy butyrate (PHB) are examples of commercially available polyesters. Polyesters can be broadly divided into three major types as aromatic polyesters, semi-aromatic polyesters, and aliphatic polyesters. Aromatic polyesters contain aromatic ring and ester linkage in every repeating unit in the main polymer chain. Polybisphenol-A terephthalate and poly(-p-hydroxybenzoate) are the most common aromatic polyesters. Aromatic polyesters have attractive properties such as very high glass transition temperature, good strength, ductility, stiffness, higher transparency, resistance for degradation from UV light, and hardness. Due to their excellent mechanical and electrical properties and chemical stability, aromatic polyesters are used in different industries including the
production of medical devices, automobiles, electronic displays, semiconductor molding compounds, and solar-energy panels. Semi-aromatic polyesters contain one aromatic monomer and one aliphatic monomer in the repeating unit of the polymer chain. Poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are the most common semi-aromatic polyesters used in the polymer industry. Semi-aromatic polyesters have intermediate properties between aromatic and aliphatic polyesters. Due to the aromatic component, semi-aromatic polyesters show high strength and toughness. Due to the aliphatic component, they also demonstrate flexibility. Aliphatic polyesters are constructed from aliphatic monomers and contain aliphatic repeating units in the main polymer chain. Aliphatic polyesters show lower thermal stability and poor hydrolytic stability. However, they demonstrate higher flexibility, and higher biocompatibility and biodegradability. Polylactic acid (PLA) and poly(glycolic acid) (PGA) are some of the most common aliphatic polyesters used in many different fields. Due to the higher biodegradability and biocompatibility, aliphatic polyesters are used in the production of medical devices, packaging materials, food containers, and drinking water bottles.

Biodegradability is an important feature of a polymer in today’s economy. Classified by the parameter of biodegradability, there are three types of polyesters: (1) biodegradable polyesters, (2) semi-biodegradable polyesters, and (3) non-biodegradable polyesters. Biodegradable polyesters are constructed with fully renewable, biodegradable monomers. Polylactic acid (PLA), polyglycolic acid (PGA), and polycaprolactone (PCL) are common examples of biodegradable polyesters. Semi-biodegradable polyesters contain renewable monomers, in addition to non-renewable monomers. Poly(limonene phthalate) is a semi-biodegradable polyester containing a fully renewable monomer (limonene oxide) and a non-renewable monomer (phthalic anhydride). Non-biodegradable polyesters are synthesized using non-renewable, typically petroleum-based
monomers. Poly(ethylene terephthalate) PET is one of the most common non-biodegradable polyesters that is synthesized using ethylene glycol and terephthalic acid.\textsuperscript{28}

1.8. Synthesis of Polyesters

Polyester synthesis can be done via different methods, including step-growth mechanism via condensation of diacids or diesters with diols, chain-growth ring-opening polymerization of cyclic esters, and chain-growth ring-opening copolymerization of epoxides with anhydrides.\textsuperscript{29} Conventional condensation process requires difunctional monomers such as dialcohols, dicarboxylic acids or diesters (Figure 1.12a). For example, the synthesis of PET uses terephthalic acid (TPA) or dimethyl terephthalate (DMT), and ethylene glycol (EG).\textsuperscript{25} In contrast, lactide, β-butyrolactone, and glycolide are examples of renewable cyclic esters which are used in chain-growth ring-opening polymerization to give poly(lactide) (PLA), poly(3-hydroxybutyrate) (PHB), and poly(glycolic acid) (PGA), respectively (Figure 1.12b).\textsuperscript{30} Generally, Ring-Opening Polymerization (ROP) releases ring strain in the monomers. Due to this thermodynamic driving force, it takes place under milder reaction conditions. Ring-Opening COPolymerization of epoxide and anhydrides (ROCOP) enables the formation of a variety of polyesters (exhibiting different properties) due to the large monomer library of epoxides and anhydrides. Fully and partially biodegradable polyesters can be synthesized by selecting different epoxides and anhydrides. Cyclohexene oxide, propylene oxide, isobutylene oxide, limonene oxide, phthalic anhydride, succinic anhydride, maleic anhydride, and cyclohexene anhydride are some of the common epoxides and anhydrides used in polyester synthesis in ROCOP (Figure 1.12c).\textsuperscript{31}
Figure 0.12. Selected monomers used in polyester synthesis: (a) monomers used in step-growth polymerization to produce PET, (B) monomers used in ring-opening polymerization of cyclic esters, (c) monomers used in ring-opening copolymerization of epoxide and anhydrides.

Figure 0.13. Ring-opening polymerization of lactide.
1.9. Synthesis of Polylactide via Ring-Opening Polymerization Lactide

Polylactide (PLA) is a biodegradable, biocompatible, aliphatic polyester made via ring-opening polymerization of lactide (LA) (Figure 1.13). Lactide is a renewable monomer derived from corn, sugar cane, or beet sugar. PLA is a sustainable alternative to petroleum-based polymers that has good mechanical properties, fabricability, and biocompatibility. Due to its biodegradability and biocompatibility, PLA has numerous applications as a recyclable plastic in biomedical applications such as sutures, stents, dental implants, bone screws, and pins. In addition, PLA is used in the production of packaging materials, production of water bottles and cups, and fiber technology.29,32,33

![Diagram of PLA synthesis and degradation](image)

**Figure 0.14.** Life cycle of PLA33

PLA is an eco-friendly polyester due to rapid biodegradation compared with other plastics (Figure 1.14). Lactides are formed via fermentation of sugars in agricultural biomass. PLA is produced via ROP of lactide. In degradation, the first step is to hydrolyze PLA to short polymers followed by the formation of lactic acid. Finally, microorganisms decompose lactic acid into CO$_2$ and water.

ROP of lactide proceeds via a coordination-insertion mechanism in the presence of metal
alkoxide catalyst to produce PLA (Figure 1.15). Initially, the lactide monomer is coordinated to the metal center. Next, it is inserted into the metal alkoxide bond through the acyl-oxygen bond. This event forms a new metal alkoxide bond for the next insertion of the lactide monomer.

![Coordination-insertion mechanism for ROP of lactide](image)

**Figure 0.15.** The coordination-insertion mechanism for ROP of lactide.$^{34}$

1.10. Tacticity of the PLA

The properties of PLA depend on the tacticity of the polymer. Tacticity represents the stereochemistry at the adjacent chiral centers of the polymer chain. Lactide molecules have two chiral centers. Depending on the stereocenters present in the LA molecule, three different stereoisomers are possible: L-lactide, D-lactide, and meso-lactide (Figure 1.16). According to the stereocenters present in the polymer chain, PLA can have different tacticities (Figure 1.17). The tacticity of the PLA will be determined by the polymerization catalyst, co-catalyst, stereoisomer used for polymerization. Physical properties of the polymer such as crystallinity, flexibility, and the melting point will be determined by the tacticity of PLA microstructures. Syndiotactic, isotactic, and heterotactic polymers are ordered polymers which leads to the their crystalline nature. In atactic polymers, stereocenters will be arranged without any order. Therefore, atactic
polymers are amorphous.

Figure 0.16. Stereoisomers of lactides.
Figure 0.17. Stereochemistry of PLA microstructure.\textsuperscript{35}
1.11. Ring-Opening Copolymerization of Epoxide and Anhydride for the Synthesis of Polyesters

Alternating ring-opening copolymerization (ROCOP) of epoxide and anhydride constitutes an important general pathway to produce various types of polyesters (Figure 1.18). A large variety of materials featuring different properties are available due to the large library of monomers. Furthermore, as a result of the low cost and high availability of many of these monomers, ROCOP is an inexpensive pathway to synthesize polyesters under mild reaction conditions. ROCOP of epoxide and anhydride can produce unsaturated polyesters by using unsaturated monomers such as limonene oxide and maleic anhydride. These polymers can be functionalized in post-polymerization modification to increase the polymer scope. Formation of polyethers via homopolymerization of epoxide is one of the commonly associated problems of ROCOP that depends on the concentration of monomers, catalyst, and co-catalyst systems used in ROCOP. Smaller alcohol as benzyl alcohol, 4-dimethylaminopyridine (DMAP), and bis(triphenylphosphine)iminium chloride (PPNCl) are well known to be efficient co-catalysts used in ROCOP of epoxides and anhydrides. Co-catalyst increases the selectivity and the efficiency of the metal catalyst in polymerization. Biodegradable polyester can be synthesized by choosing the correct monomers. Limonene oxide, alpha-pinene oxide, and cyclohexene oxide are some of the renewable monomers which can be used to synthesize biodegradable polyesters.

Similarly, to the ROP of LA, ROCOP of epoxide and anhydride proceeds via coordination insertion mechanism (Figure 1.19). In the initiation step, epoxide coordinates to the metal center
and then reacts with the initiator to generate metal-alkoxide intermediates. The subsequent coordination of the anhydride to the metal center is followed by attack of the metal alkoxide intermediate to generate the metal carboxylate intermediate. In the propagation step, this process will be repeated to produce a long polyester chain.

![Coordination-insertion mechanism for the ring-opening copolymerization (ROCOP) of epoxide and anhydride](image)

**Figure 0.19.** Coordination-insertion mechanism for the ring-opening copolymerization (ROCOP) of epoxide and anhydride

### 1.12. Previous ROP and ROCOP Catalysts

ROP and ROCOP require metal initiators or catalysts for the polymerization process. Main group and transition metal catalysts with different ligand environments were reported for both processes. Compared with pure stereoisomers of LA, rac-LA is cheaper but the synthesis of stereoselective PLA from rac-LA can be challenging and generally requires some sort of asymmetric induction, either via a chiral nature of the catalyst, or via a chain-end control. Williams and coworkers reported a single-site β-diketiminate tin(II) catalyst that exhibited polymerization of rac-LA to give heterotactic PLA with narrow molecular weight distribution ([Figure 1.20A](#)). 38 Arnold and coworkers reported a racemic mixture of chiral indium catalyst ([Figure 1.20B](#)) which
shows stereoselective ROP for *rac*-LA by giving isotactic PLA with higher molecular weight polymers.\(^{39}\) Iminomethylpirididine-based copper complex, reported by Lee and coworkers, exhibited heterotactic PLA formation from *rac*-LA.\(^{40}\)

**Figure 0.20.** Selected examples for (A) ROP of LA and (B) ROCOP of epoxides and anhydrides.

Several groups have reported the main group and transition metal catalysts for ROCOP of epoxide and anhydride (Figure 1.20C). Williams and coworkers reported di-magnesium and dizinc catalysts with macrocyclic ancillary ligand system for ROCOP of phthalic anhydride and cyclohexene oxide.\(^{41}\) Dutachateau and coworkers reported several transition metal (Cr, Mn, Co) and Al catalysts with salen and tetraphenylporphyrin ligand (Figure 1.20D) for ROCOP of styrene oxide and several anhydrides.\(^{42}\)
1.13. Benefits of Homoleptic Magnesium Alkoxide Complexes for Polymerization Reactivity

For both ROP of LA and ROCOP of epoxide and anhydride, main group alkoxide complexes offer significant advantages since it is not necessary to remove the catalyst residues that contaminate the polymer matrix after polymerization due to the colorless nature of the complexes." Magnesium alkoxide complexes are particularly attractive catalysts from both economic and environmental points of view due to their low cost and toxicity as well as the high natural abundance. Either homoleptic alkoxide/alkyl complexes or heteroleptic complexes in which the metal center is stabilized by multidentate ancillary ligands have been reported as efficient catalysts for the ROP of cyclic esters. Otherwise, the examples of magnesium catalysts that exhibit catalytic behavior toward the ROCOP of epoxides and anhydrides are relatively rare. Homoleptic magnesium alkoxide complexes such as polymeric magnesium ethoxide (Mg(OEt)2) and mononuclear magnesium 2,6-di-tert-butyl-4-methylphenoxide (Mg(BHT)2(THF)2) were shown to be active in the copolymerization of maleic anhydride and propylene oxide. Recently, Williams reported the first example of a well-defined heteroleptic bimetallic magnesium complex that demonstrated ROCOP of phthalic anhydride and cyclohexene oxide. It was also active in copolymerizations of epoxides with anhydrides and CO2. Subsequently, heterobimetallic complexes of magnesium and zinc, with improved performances in comparison to the related homometallic species, were reported by the same author. Homoleptic, well-defined and single-site main group metal alkoxide complexes can be of significant advantage to the fields of ROP and ROCOP.


Our group investigates the catalytic nitrene transfer reactivity to synthesize azoarenes using aryl azides as nitrene precursors. Our previous Fe(OR)2(THF)2 showed efficient azoarene
formation for the di-ortho substituted aryl azides. However, it was unable to produce azoarenes for the mono-ortho, meta, and para- substituted aryl azides. It is likely that the insufficient steric bulk of our first-generation alkoxide ligand [OC'Bu₂Ph] led to the formation of an unreactive Fe(OR)₃ by-product that prevented further catalytic reactivity. The major goal of the first part of my dissertation is to improve the nitrene transfer reactivity of our iron alkoxide catalytic system via the alkoxide ligand modification. In addition to the nitrene transfer reactivity, synthetic pathways towards iron- and other alkoxide complexes, as well as their spectroscopic characterization will be also described.

In the second part of my dissertation, my goals include design of efficient and sustainable Mg(OR)₂ complexes for ROP of LA and ROCOP of epoxide and anhydride. There were many catalytic systems found in the literature for both ROP and ROCOP processes for the synthesis of polyesters. However, most of the systems include expensive ligand systems or/or toxic elements. Design and synthesis of non-toxic, earth-abundant, highly efficient, and inexpensive catalysts were needed. As described above, magnesium is among the most abundant, inexpensive, and eco-friendly elements to be used in catalysis. Furthermore, my design of the [Mg(OC'Bu₂Ph)₂] precatalyst features “naked”, or the ancillary-ligand-free pre-catalyst, in which both alkoxide groups can serve as initiators. As a result, the catalyst is expected to be more efficient, and no ancillary ligand contamination will be left within the polymer matrix.

Accordingly, my dissertation includes several chapters as described below. **Chapter 2** will discuss nitrene coupling catalyzed by an iron(II) complex featuring a modified monodentate alkoxide ligand [OC'Bu₂(3,5-Ph₂C₆H₃)]. Both homocoupling and heterocoupling of nitrenes will be described. **Chapter 3** will present nitrene homocoupling mediated by an iron(II) complex of a chelating bis(alkoxide) ligand [OO]^{Ph}. Fe[OO]^{PhTHF)₂ replicates most of the structural
features of the earlier systems containing two bulky monodentate alkoxide but is significantly more stable due to the chelate effect. Chapter 4 will describe nitrene hetero-coupling mediated by an Fe(OC'Bu₂(3,5-Ph₂C₆H₃)₂(THF)₂ and combination of Fe(OC'Bu₂(3,5-Ph₂C₆H₃)₂(THF)₂ and Fe[OO]PbTHF)₂. Chapter 5 will describe structural and spectroscopic comparison of different iron alkoxide pre-catalysts, and chapter 6 will present a novel synthetic route towards iron (and ruthenium) alkoxide complexes using thallium alkoxide precursor. Chapter 7 will describe synthesis and characterization of new achiral magnesium bis(alkoxide) complex Mg(OR)₂(THF)₂ (OR = OC'Bu₂Ph) and the investigation of its polymerization and copolymerization reactivity. Chapter 8 will present the synthesis of several new chiral alkoxide ligands, and their magnesium complexes, and their resulting reactivity in ROP of lactide, and ROCOP of epoxide and anhydride. Chapter 9 will conclude this dissertation and will present future directions.
CHAPTER 2: THE CATALYTIC NITRENE COUPLING BY AN IRON(II) BIS(ALKOXIDE) COMPLEX


2.1. Introduction

Our group investigates group-transfer reactivity of organoazides and related substrates at transition metal centers in weak-field bis(alkoxide) ligand environments. We have previously demonstrated that iron bis(alkoxide) complex Fe(OR)₂(THF)₂ (OR = OC\textsubscript{2}Bu\textsubscript{2}Ph, 1, Figure 2.1) catalyzed efficiently transformation of bulky aryl azides ArN\textsubscript{3} (Ar = 2,4,6-Me\textsubscript{3}Ph or 2,6-Et\textsubscript{2}Ph) to the corresponding azoarenes.\textsuperscript{22} Intriguingly, no azoarene formation was observed for smaller aryl azides (Ar = 2-MePh, 3,5-Me\textsubscript{2}Ph, 4-MePh). Instead, formation of bridging imido mono(alkoxide) complexes Fe\textsubscript{2}(μ\textsubscript{2}-NAr)\textsubscript{2}(OR)\textsubscript{2}(THF)\textsubscript{2} (3) was observed, along with tris(alkoxide) Fe(OR)\textsubscript{3} by-product. We postulated that favorable alkoxide disproportionation was responsible for the lack of catalysis with smaller aryl azides.

\textbf{Figure 2.1.} Reactivity of complex 1 with aryl azides as a function of Ar group substituents.
To prevent the disproportionation and to shed light into the reaction mechanism, Dr. Maryum Yousif has designed bulkier alkoxide [OR’] (OR’ = OC'Bu₂(3,5-Ph₂Ph) and its iron(II) complex (Figure 2.2).\textsuperscript{49,50} Fe(OR’\textsubscript{2})(THF)\textsubscript{2} (5) is synthesized by one-step approach, that involves protonolysis of Fe(N(SiMe\textsubscript{2})\textsubscript{2})(THF)\textsubscript{x}. It was anticipated that the larger size of [OR’] would preclude the formation of hypothetical “Fe(OR’\textsubscript{3})” species, and as a result would prevent alkoxide disproportionation and enable better-defined catalytic performance with organoazides.

\[
\text{Fe(N(SiMe\textsubscript{2})\textsubscript{2})\textsubscript{2}(THF)\textsubscript{2}} \xrightarrow{2 \text{ HOR'}} \text{Fe}^{\text{II}}\text{OR'}
\]

\[
\text{R'}O\text{Fe}^{\text{II}}\text{OR'}\text{THF} \quad \text{THF}
\]

5, 95% yield

**Figure 2.2.** Design of Fe(OR’\textsubscript{2})(THF)\textsubscript{2}

The reaction of 5 with a stoichiometric amount (two equivalents) of the corresponding aryl azide shows the formation of azoarenes as the only organic products for the bulkier aryl azides (Ar = mesityl, 2,6-diethylphenyl). In contrast, formation of tetrazene complexes Fe(OR’\textsubscript{2})(ArNNNNAr) (6-9) is observed for the less bulky aryl azides (Ar = phenyl, 4-methylphenyl, 4-methoxyphenyl, 3,5-dimethylphenyl). Tetrazene complexes Fe(OR’\textsubscript{2})(ArNNNNAr) produce the corresponding azoarenes (ArNNAr) upon heating Figure 2.3.
Figure 2.3. Stoichiometric reactivity of azides with 5: synthesis of Fe(OR')₂(ArNNNNAr) complexes 6-9 vs. nitrene coupling for the bulkier mesityl azide.

2.2. Catalytic Nitrene Homo-Coupling Reactivity by Fe(OC'Bu₂(3,5-Ph₂C₆H₃))₂(THF)₂ complex

Similarly, to complex 1, complex 5 is also able to efficient couple mesityl and 2,6-diethylphenyl nitrenes to give the corresponding azoarenes (Table 2.1) in high yields. As previously observed for 1, catalysis with 5 proceeds at RT to give azomesitylene and azo(2,6-diethylbenzene) in nearly quantitative yields. More significantly, 5 is also capable of nitrene coupling with other azide precursors, albeit higher catalyst loadings and heating is required in these cases. Thus, 3,5-dimethylphenylazide forms azo(3,5-dimethylbenzene) in 47% yield after 8 hours at 60 °C; heating for 24 h brings the yield of the product to about 70%. Similarly, azoarene formation is observed for aryl azides featuring only one substituent in the ortho position (2-Me, 2-Et, 2-‘Pr). For example, 2-ethylphenyl azide gives 65% yield after 8 h. Finally, 4-methylphenyl, 4-trifluoromethylphenyl, or 4-isopropyl azide give comparable yields of 16%, 15%, and 14%, respectively (approximately one turnover), after 8 h at 60 °C; longer heating (24 h) improves the azoarene yield for 4-methylphenyl azide to 33%. In contrast, longer heating times do not improve the yields of 4-trifluoromethylphenyl or 4-isopropylphenyl azides, producing instead black
insoluble material, which we were unable to identify. No product formation was observed for 4-methoxyphenyl azide.

Table 2.1. Complex 5-catalyzed formation of azoarenes from the corresponding azides.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Azide</th>
<th>Catalytic Loading (mol%)</th>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Yield(^a) (%)</th>
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<td>10</td>
<td>8</td>
<td>60(^c)/100</td>
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</table>

\(^a\)The reactions were conducted in C\(_6\)D\(_6\) in the presence of an internal standard (trimethoxybenzene or hexamethylbenzene) and the yields were determined by \(^1\)H NMR spectroscopy. GCMS yields were similar and are given in the SI. \(^b\)Longer heating of these samples produced insoluble materials; no yield improvement was observed by \(^1\)H NMR spectroscopy. \(^c\)The reaction at 100 °C was conducted in C\(_7\)D\(_8\) in the presence of an internal standard.

2.3. Computational Mechanistic Studies of the Nitrene Coupling Reactivity by Fe(OC\(^1\)Bu\(_2\)(3,5-Ph\(_2\)C\(_6\)H\(_3\)))\(_2\)(THF)\(_2\)

QM/MM calculations were employed to probe the reaction mechanism of tetrazene and azoarene formation, in collaboration with the group of Prof. Lord. Although these results employ the less sterically bulky first-generation alkoxide ligand (OC\(^1\)Bu\(_2\)Ph), this choice allowed for a more complete data set to be obtained. The thermodynamics of the full model (see Appendix B) are nearly identical suggesting that the conclusions reached for this small model are also valid for the experimental system. Multiple rotational conformations within the alkoxide arms were probed for each species/spin state. Typically, these rotamers fell within 3–5 kcal/mol of the lowest energy rotamer (see Appendix B). Only the lowest energy spin state and rotamer are reported in here. The 4-methoxyphenyl azide substrate was used for all calculations.
Figure 2.4. (left) shows the optimized structure of the lowest energy iron mono(imido) complex (i). This quintet was calculated to be nearly isoenergetic with the triplet imido complex ($\Delta G = 0.7$ kcal/mol). The tetrazene (ii) favors the quintet (Figure 2.4, middle) that was calculated to be 12.6 and 3.3 kcal/mol lower in energy than the triplet and septet tetrazenes, respectively, consistent with spectroscopy and full model DFT calculations. The transition state for tetrazene formation (i–ii–TS, Figure 2.4 right) has a barrier of 20.9 kcal/mol leading to ii that is $-8.5$ kcal/mol relative to free azide and i. This transition state is consistent with 1,3-dipolar addition of the azide to i. The exergonic formation of ii is consistent with isolation of the tetrazene, yet the reverse barrier of 29.4 kcal/mol is accessible meaning that under appropriate conditions, and assuming that azoarene formation directly from i does not have a lower barrier, then the tetrazene may act as a masked iron mono(imido) complex similar to the Mn complex reported by Zdilla and co-workers.

Next, we explored how azoarene can form: (i) through formation of the 1,2-tetrazene proposed by Hillhouse and Cundari, (ii) directly from ii through N$_2$ loss, (iii) from i and azide with N$_2$ loss, and (iv) by dimerization of two equivalents of i. The 1,2-tetrazene was found to be endergonic by 19.4 kcal/mol vs. ii (and 10.9 kcal/mol higher in energy than free azide and i). Moreover, its barrier
is 9.4 kcal/mol higher than $i$–$ii$–TS, meaning that it is neither kinetically nor thermodynamically competitive allowing us to rule out pathway (i). $N_2$ loss from $ii$ to form a quintet bis(imido) complex $iii$, Figure 2.5 (left), is found to be slightly endergonic relative to $ii$ by 5.2 kcal/mol, but with a prohibitive barrier of 45.3 kcal/mol for $ii$–$iii$–TS (Figure 2.5 middle). Coupling of the imidos in this putative intermediate to form the azoarene complex $iv$ is quite exergonic at −43.7 kcal/mol vs $iii$, and with a reasonable barrier of 3.0 kcal/mol. Thus, if the bis(imido) can be formed then azoarene formation should proceed smoothly, but pathway (ii) is not kinetically feasible on the quintet surface. The formation of $iii$ directly from $i$ and azide was also found to have a prohibitive barrier of 40.7 kcal/mol ($i$–$iii$–TS, Figure 2.5 right), ruling out pathway (iii). Calculation of alternative spin states for the bis(imido) complex demonstrated that the triplet is favored over the quintet by 10.5 kcal/mol. Unfortunately, formation of this intermediate from the triplet form of $ii$ or $i$ and azide is found to have a barrier of 35.1 and 41.2 kcal/mol, respectively, ruling out pathways (ii) and (iii) on the triplet surface as well. Not only are all of these barriers higher than the reverse barrier to azide and $i$ from the tetrazene, but these barrier heights are also inconsistent with the experimental conditions. Finally, dimerization of $i$ to form a bridging azoarene between two equivalents of $\text{Fe(OR)}_2$ (v) was probed on the nonet surface. A reasonable barrier of 19.8 kcal/mol is calculated and the reaction is exergonic by −21.6 kcal/mol. Therefore, pathway (iv) is predicted to be the most feasible pathway for azoarene formation.
Figure 2.5. Optimized structures of the quintet iron bis(imido) (iii, left), tetrazene (ii–iii–TS, middle), and transition state between these structures (i–iii–TS, right). Solid atoms are those included in the QM region, while those that are partially transparent are in the MM region.\textsuperscript{46}

Figure 2.6 summarizes all of these thermodynamics for both the quintet and triplet surfaces. This potential energy surface suggests that azoarene and tetrazene formation are kinetically competitive. If ii is formed then i can be reformed, though endergonically, such that the lost azide could be activated by another Fe(OR)\textsubscript{2} equivalent to make i irreversibly (due to N\textsubscript{2} loss). Moreover, this proposed mechanism is consistent with the formation of mixed azoarenes in an approximately statistical ratio from tetrazene under heating. While this mechanism has been probed with the first-generation alkoxide ligand, as shown in (see Appendix B) the reaction thermodynamics are nearly identical for the second-generation alkoxide ligand (OR’ = OC\textsuperscript{t}Bu\textsubscript{2}(3,5-Ph\textsubscript{2}Ph)).
Figure 2.6. Summary of reaction thermodynamics for the formation of tetrazene and azoarene from i and azide. The transition state labelled with * was unable to be located. OR = OC('Bu)_2Ph and Ar = 4-methoxyphenyl.

2.4. Summery and Conclusions

Our 1st generation bis(alkoxide) complex Fe(OR)_2(THF)_2 (OR = OC('Bu)_2Ph) catalyzed homocoupling of aryl nitrenes to give azoarenes. However, this reactivity was limited to bulky (featuring two groups in the ortho positions) aryl azides only; no coupling was observed for the less bulky precursors. We demonstrated that the increase in the size of the alkoxide ligand in Fe(OR')_2(THF)_2 (OR' = OC('Bu)(3,5-Ph_2Ph)) enables significantly broader range of reactivity. Both bulky and non-bulky aryl nitrenes are coupled with Fe(OC('Bu)(3,5-Ph_2Ph)_2(THF)_2, albeit the coupling of the less bulky substrates requires higher temperatures and longer reaction times. We explain this difference in reactivity by the increased stability of the Fe(OR')_2-type system: while Fe(OR)_2 catalysts disproportionated to catalytically inactive mono(alkoxide) and tris(alkoxide)
species, only catalytically competent bis(alkoxide) complexes were observed for [OR’]. No reaction intermediates were observed for Fe(OR)₂(THF)₂ system. In contrast, stoichiometric reactions of Fe(OR’)₂(THF)₂ with non-bulky aryl azides led to the observation of the iron(III) tetrazene radical anion complexes, that can produce azoarene products after heating. Tetrazene complexes likely serve as a “masked form” of the reactive nitrene complex based on these observations and the QM/MM modeling of the reaction mechanism. These calculations suggest that the tetrazene complex is more stable than nitrene and free azide by 8.5 kcal/mol, which may explain the sluggish reactivity of the less bulky aryl azides.

2. Experimental Section

2.5. General Methods and Procedures

All reactions involving air-sensitive materials were executed in a nitrogen-filled glovebox. The synthesis of HOR’ has been previously reported.⁴⁹ Fe(OR’)₂(THF)₂ was synthesized as described by Dr. Maryum Yousif.⁵⁰ Mesityl azide, 2-isopropylphenyl azide, 4-isopropylphenyl azide, 2,6-diethylphenyl azide, 3,5-dimethylphenyl azide, 2-phenylphenyl azide, 2-ethylphenyl azide, 2-methoxyphenyl azide, and Fe[N(SiMe₃)₂]₂(THF) were synthesized according to previously reported procedures.⁵¹-⁵³ (Caution: organic azides are potentially shock-sensitive and should be handled with care!) Iron(II) chloride was purchased from Strem. Potassium bis(trimethylsilyl)amide, azidobenzene solution, 4-azidotoluene, 4-(trifluoromethyl)phenyl azide solution, 4-azidoanisole solution, 2-methylphenyl azide were purchased from Aldrich and used as received. All solvents were purchased from Fisher Scientific and were of HPLC grade. The solvents were purified using an MBraun solvent purification system and stored over 3 Å molecular sieves. NMR spectra were recorded at the Lumigen Instrument Center (Wayne State University) on a Varian Mercury 400 MHz NMR spectrometer in C₆D₆ at room temperature. Chemical shifts
and coupling constants (J) are reported in parts per million (δ) and hertz, respectively. GCMS was performed at the Lumigen Instrument Center using Agilent 6890N spectrometer.

2.5.2. Computational Details

Electronic structure calculations were performed using the Gaussian 09 (revisions A02, C01, and D01) quantum chemical software package. For the computational investigation of the electronic structure and spectroscopy of the tetrazene complex we used the spin unrestricted formalism, the B3LYP/6-311G functional/basis set combination, and an unabridged structural model. Single point self-consistent field (SCF) calculations and geometry optimizations were completed using standard convergence criteria. The ground state character of a particular electronic configuration was assessed on the basis of time-dependent DFT calculations, that is, all one-electron excitations were found to be positive. The theoretical exchange coupling constants, J, were estimated by comparing the predicted SCF energies of the ferromagnetic (F) and broken-symmetry (BS) states.\textsuperscript{54} The initial electronic guesses of the starting SCF calculations were obtained using the default guess option in the case of the F configuration and the \textit{fragment} option of the \textit{guess} keyword for the BS states. While the F state had a septet, S\textsubscript{T} = 3 configuration, the BS state corresponds to a S\textsubscript{T} = 2 configurations for which 5α, spin-up, electrons are localized on the iron site while 1β, spin-down, electron was localized on the tetrazene ligand. The value of the exchange coupling constant was obtained using the expression \( J = 2(E_F - E_{BS})/5 \) where the E\textsubscript{BS} and E\textsubscript{F} energies were obtained from single-point calculations performed using either on the x-ray structure or on the geometry optimized structures (using the \( \hat{H} = J\hat{S}_1 \cdot \hat{S}_2 \) spin Hamiltonian). Charge and spin distributions were assessed based on the Mulliken atomic spin densities and charges. The predicted ΔE\textsubscript{Q} and η values describing the electric field gradient and the predicted \textsuperscript{57}Fe hyperfine coupling constants were estimated using the standard \textit{prop} keyword of the Gaussian
code. The predicted isomer shift values were determined using the calibration given by Vrajmasu et al.\textsuperscript{55}

Mechanistic investigations were performed using QM/MM methods at the ONIOM(OPBE/6-311G(d):UFF) level of theory.\textsuperscript{56} Models of both the first (OC(‘Bu)\textsubscript{2}Ph) and second (OC(‘Bu)\textsubscript{2}(3,5-Ph\textsubscript{2}Ph)) generation alkoxide ligands were studied. The tBu and aryl groups of the alkoxide ligand were placed in the MM region. Most geometry optimizations took advantage of the quadratic macrostep option in Gaussian09.\textsuperscript{57} Optimized structures were verified to be minima by analyzing the harmonic frequencies, transition states had a single imaginary frequency corresponding to the molecular motion of that mechanistic step.

\textbf{2.5.3. General Procedure for Catalytic Formation of Azoarenes}

All of the reactions were performed by adding 10 or 20 equiv of organic azide and 1,3,5-trimethoxybenzene (TMB) standard solution in C\textsubscript{6}D\textsubscript{6} to a solution of complex 2 (approximately 30-35 mg) in C\textsubscript{6}D\textsubscript{6} in an N\textsubscript{2}-filled glovebox. The reaction mixture was then stirred at the noted temperature for 8 or 24 hours. The yields of azoarene products were determined by \textsuperscript{1}H NMR spectroscopy and GCMS (see Appendix B).
CHAPTER 3: CATALYTIC NITRENE HOMOCOUPLING BY AN IRON(II) COMPLEX OF A CHELATING BIS(ALKOXIDE) LIGAND

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3.1. Introduction

Our group investigates group-transfer chemistry at [M(OR)₂] platforms, generally featuring two bulky monodentate alkoxide ligands. As described in Chapter 1, we have reported that Fe(OR)₂(THF)₂ (OR = OC'Bu₂Ph) (1) served as an efficient catalyst for nitrene dimerization, although its reactivity was restricted to bulky aryl nitrenes featuring two ortho substituents (1). Mechanistic studies suggested that alkoxide disproportionation (to yield tris(alkoxide) Fe(OR)₃ and bridging imido species [Fe₂(OR)₂(µ₂-NAr)]) was at least in part responsible for this limitation. As described in the previous chapter, to overcome this problem, we designed Fe(OR’₂)(THF)₂ with a bulkier alkoxide ligand OR’ (OR’ = OC'Bu₂(3,5-Ph₂C₆H₃) (5). Consistent with our expectations, arresting the disproportionation route increased the overall scope of substrates to single ortho as well as meta-substituted aryl nitrenes, although the substrates lacking such substituents still exhibited poor reactivity (generally one turnover or less).

A different approach to the design of the more robust catalyst involves linking two monodentate alkoxides into a chelating ligand. This chapter describes nitrene homocoupling reactivity with a newly designed iron(II) complex of a chelating bis(alkoxide) ligand.
3.2. Design of the Chelating Bis(alkoxide) Complex Fe[OO]^{Ph}(THF)_{2} for Nitrene Transfer Reactivity

![Figure 3.1](image1.png)

**Figure 3.1.** Newly design chelating alkoxide ligand and iron(II) chelating alkoxide complex

To further improve the stability of our iron(II) bis(alkoxide) catalytic system, our group has designed a new chelating bis(alkoxide) ligand H_{2}[OO]^{Ph} (10) The ligand and its corresponding iron(II) chelating complex (11) (**Figure 3.2**) were initially synthesized by my coworker. The structure of the complex revealed the overall similar coordination chemistry to the iron complexes of two monodentate alkoxides (**Figure 3.3**), allowing me to conduct a comparative structure-activity study of different “Fe(OR)_{2}” systems for nitrene coupling.

![Figure 3.2](image2.png)

**Figure 3.2.** Comparison of interalkoxide angles of iron(II) alkoxide complexes 1, 5 and 11.

3.3. Catalytic Nitrene Homo-Coupling Reactivity by Fe[OO]^{Ph}(THF)_{2} Complex

The reactivity of 11 in nitrene coupling was investigated and the results are presented in **Figure 3.4**. All reactions were carried out in C_{6}D_{6} at 60 °C for 24 h using 10 mol% catalyst. The reactions were monitored by NMR spectroscopy, using trimethoxybenzene, hexamethylbenzene,
or hexafluorobenzene as an internal standard. The products were identified by $^1$H NMR spectroscopy and confirmed by GC-MS; selected azoarenes were isolated and further characterized. Most notably, nitrene coupling reactivity exhibited by Fe[OO]$_{\text{Ph}}$(THF)$_2$ (11) is almost perfectly complementary to the reactivity exhibited by 1 or 5: while the previous catalysts were selective for the coupling of bulky aryl nitrenes, the present catalyst (11) demonstrates high to moderate yields for non-bulky substrates featuring para alkyl, trifluoro, or halo substituents; the conversion is quantitative for the phenyl azide (Figure 3.4). The formation of halosubstituted azoarenes is particularly noteworthy, as these groups can be later functionalized via cross-coupling. Although lower yields were observed for the $p$-nitro, $p$-acetyl, or $p$-methoxy groups, these are uncommon functional groups for metal-mediated formation of azoarenes. In contrast, Fe(OR)$_2$(THF)$_2$ (1) did not exhibit any reactivity with phenyl azide or para-substituted azides, and Fe(OR')$_2$(THF)$_2$ (5) exhibited low reactivity at best. meta-Substituted 3,5-dimethylphenyl azide and 3-trifluoromethylphenyl azide exhibited relatively high yields (69% and 64% yields, respectively). In a sharp contrast, no reactivity with ortho-substituted (e.g. mesityl) azides was observed for Fe[OO]$_{\text{Ph}}$(THF)$_2$ (11), whereas both Fe(OR)$_2$(THF)$_2$ and Fe(OR')$_2$(THF)$_2$ demonstrated quantitative yield with mesityl azide.
Figure 3.3. Nitrene coupling reactivity exhibited by 11.
3.4. Computational Studies to Understand the Reaction Mechanism

What is the origin of the observed reactivity differences between Fe[OO] Ph and Fe(OR) 2/Fe(OR’) 2 (1/2) systems? Due to the overall similarity of the three iron bis(alkoxide) systems, it is probable that the reaction of Fe[OO] Ph with aryl azides also proceeds via a metal-nitrene intermediate, whose formation and reactivity were computationally interrogated for the Fe(OR) 2/Fe(OR’) 2 systems. Putative iron nitrenes with Ar = Ph and Ar = 2,6-Me 2 Ph (Mes surrogate) were optimized as quintets, based on our earlier modeling efforts, 50 for [OO] Ph and OR (Figure 3.5). In the less sterically bulky NPh species, the N of the nitrene is exposed for reactivity whereas it is blocked by one of the alkoxide phenyl groups for the ortho-substituted aryl substituent when the iron nitrene is supported by the [OO] Ph ligand (Figure 3.5, top). In contrast, the nitrene N remains accessible for both aryl substituents when FeNAr is supported instead by two OR groups (Figure 3.5, bottom). Therefore, we hypothesize that the inaccessibility of the nitrene when ortho-substituents are present may be responsible for the lack of azoarene formation in the presence of our new chelating ligand. Moreover, the Fe–N bond is mostly accessible by an incoming substrate from either face of the plane defined by the alkoxides and nitrene in Fe(OR) 2(NAr), whereas the back face is blocked by the bridging terphenyl group and the front face is at least partially blocked by the alkoxide phenyl groups in Fe[OO] PhNAr. Even though these ligands give a similar trigonal planar coordination environment in both bis(alkoxide) environments, the spatial constraints imposed by the chelating ligand may provide an opportunity to control reactivity by limiting the approach of reactants to the nitrene moiety.
Mononuclear complex Fe[OO]$_{\text{Ph}}$(THF)$_2$ is closely related to the previously reported Fe(OR)$_2$(THF)$_2$ complexes with bulky monodentate alkoxides (OR = OC$_{\text{tBu}}$$_2$Ph and OC$_{\text{tBu}}$$_2$(3,5-Ph$_2$Ph)). Whereas the overall donors disposition at the iron(II) center is maintained, tying the alkoxides with the terphenyl bridge changed somewhat the steric nature of the metal site, which is illustrated by a nearly linear ArO–Fe–OAr angle (156°), as compared with ~140° in the more relaxed structures with monodentate ligands. Whereas the present “OCPh$_3$” motif is not bulkier than the previously utilized OC$_{\text{tBu}}$$_2$Ar, it is likely the rigidity of the chelating system that prevents the rearrangement (i.e. rotation or geometry change) of the alkoxides. This difference in the nature of the active site is manifested in the reactivity of the resulting nitrene coupling catalysts. While

**Figure 3.4.** Optimized structures of putative iron nitrenes [Fe(L)(NAr)] supported by chelating [OO]$_{\text{Ph}}$ ligand (top) or untethered OR ligands (bottom), using Ar=Ph (left) and Ar=2,6-Me$_2$Ph (right). All species were modeled as quintets

### 3.5. Summary and Conclusions

Mononuclear complex Fe[OO]$_{\text{Ph}}$(THF)$_2$ is closely related to the previously reported Fe(OR)$_2$(THF)$_2$ complexes with bulky monodentate alkoxides (OR = OC$_{\text{tBu}}$$_2$Ph and OC$_{\text{tBu}}$$_2$(3,5-Ph$_2$Ph)). Whereas the overall donors disposition at the iron(II) center is maintained, tying the alkoxides with the terphenyl bridge changed somewhat the steric nature of the metal site, which is illustrated by a nearly linear ArO–Fe–OAr angle (156°), as compared with ~140° in the more relaxed structures with monodentate ligands. Whereas the present “OCPh$_3$” motif is not bulkier than the previously utilized OC$_{\text{tBu}}$$_2$Ar, it is likely the rigidity of the chelating system that prevents the rearrangement (i.e. rotation or geometry change) of the alkoxides. This difference in the nature of the active site is manifested in the reactivity of the resulting nitrene coupling catalysts. While
Fe(OR)$_2$(THF)$_2$ complexes were able to couple bulky aryl nitrenes only (for OR = OC'Bu$_2$Ph) or mostly (for OR' = OC'Bu$_2$(3,5-Ph$_2$Ph)), Fe[OO]$^\text{Ph}$(THF)$_2$ is selective for coupling aryl nitrenes lacking ortho substituents; no reactivity with ortho-substituted (i.e. mesityl) azide took place. Successful formation of 13 different azobenzenes is presented. The difference in the reactivity is hypothesized to be due to the sterically congested active site of Fe[OO]$^\text{Ph}$, which interferes with the reactivity of putative ‘‘Fe[OO]$^\text{Ph}(=\text{NMe})$’’ species.

3.6. Experimental Section

3.6.1. Computational Details

DFT calculations were performed in collaboration with the Lord group at GVSU using ORCA version 4.0.1.2.$^{59}$ Geometry optimizations were performed at the BP86-D3/def2-SVP level of theory using default numerical settings (ensuring proper numerical convergence), Becke-Johnson damping, and the RI-J algorithm.$^{60-66}$ Stationary points were verified as minima by analyzing the harmonic frequencies at the same level of theory. Standard approximations were used to derive the Gibbs free energies at 298.15 K, with the vibrational entropy calculated using the quasi-RRHO algorithm.$^{67}$ Subsequent single point energy refinements at the BP86-D3/def2-TZVP and B3LYP-D3/def2-TZVP levels of theory.$^{68-71}$ The B3LYP single points employed the RJCOSX algorithm. Triple-zeta free energies were estimated as $G_{TZ} = G_{DZ} - E_{DZ} + E_{TZ}$. Orbital and spin density isosurfaces were created by generating cube files with the ORCA utilities, then visualized using GaussView version 6.0.16.$^{72}$

3.6.2. General Methods and Procedures

Air-sensitive reactions were carried out in a nitrogen-filled glovebox. Benzene-d$_6$ was purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves. HPLC grade non-deuterated solvents were purchased from Sigma-Aldrich and purified using an MBraun
solvent purification system. Compounds were generally characterized by $^1$H and $^{13}$C NMR, high-resolution mass spectrometry. Chemical Shifts and coupling constants ($J$) were reported in parts per million and Hertz respectively. Thermofisher Scientific LTQ Orbitrap XL mass spectrometer at the Lumigen Instrument Centre was used for high resolution mass spectra. GC-MS analysis were done using Agilant 6890N spectrometer, Thermo TG5MS 30m × 0.32mm × 0.25μm column, 7683 series injector, and Agilant 5973 detector.

3.6.3. General Procedure for Catalytic Formation of Azoarenes

Fe[OO]$^{Ph}$(THF)$_2$ was synthesized as described elsewhere.$^{58}$ All azides were synthesized using previously reported procedures. Catalytic reactions were performed by adding 10 equiv of organic azide and 1,2,3-trimethoxy benzene (TMB), hexafluorobenzene (HFB) or hexamethyl benzene (HMB) internal standard solution in C$_6$D$_6$ to a C$_6$D$_6$ solution of 10.0-12.0mg (0.0126-0.0151 mmol) catalyst (Fe[OO]$^{Ph}$(THF)$_2$) in N$_2$ filled glovebox. The reaction mixture was stirred in 60 °C for 24 h. Yields of azoarenes were calculated by $^1$H NMR; the spectra were compared to the previously published NMR spectra of the corresponding azoarenes. Formation of azoarenes was confirmed by GC-MS. Representative azoarenes were isolated in a pure state using silica gel column chromatography (hexane).

3.6.4. Isolation of (4-MePh)N=N(4-MePh)

Reactions were done according to the general procedure by reacting 28.0 mg (0.0354 mmol) of catalyst with 47.1 mg (0.354 mmol, 10 equiv) of 4-methylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene was isolated in 76% yield (28.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, $J$ = 7.6 Hz, 4H), 7.31 (d, $J$ = 7.8 Hz, 4H), 2.43 (s, $J$ = Hz, 6H); $^{13}$C NMR (400 MHz, CDCl$_3$) δ 150.61, 140.97,
129.48, 122.49, 21.26, HR-MS m/z calcd for C_{14}H_{15}N_{2}[M+H]^+: 211.1230, found: 211.1224.

3.6.5. Isolation of (4-PrPh)N=N(4-PrPh)

Reactions were done according to the general procedure by reacting 34.9mg (0.0441mmol) of catalyst with 71.0 mg (0.441 mmol, 10 equiv) of 4-methylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene was isolated in 42% yield (20.0 mg). ¹H NMR (400 MHz, C₆D₆) δ 8.10 (d, J = 8.0 Hz, 4H), 7.12 (d, J = 8.0 Hz, 4H), 2.66 (sept, J = 8.0 Hz, 2H), 1.08 (d, J = 8.0 Hz, 6H). ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8.6 Hz, 4H), 7.34 (d, J = 8.2 Hz, 4H), 3.03-2.96 (m, 2H) 1.3 (d, J = 7.0 Hz, 12H); ¹³C NMR (400MHz, CDCl₃) δ 151.68, 150.84, 126.74, 122.45, 33.80, 23.55, HRMS m/z calcd for C_{18}H₂₃N₂[M+H]^+: 267.1855, found: 267.1856.

3.6.6. Isolation of (3,5-Me₂Ph)N=N(3,5-Me₂Ph)

Reactions were done according to the general procedure by reacting 33.8mg (0.0427 mmol) of catalyst with 63.0mg (0.428 mmol, 10 equiv) of 4-methylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene was isolated in 61% yield (31.1 mg). ¹H NMR (400 MHz, C₆D₆) δ 7.82 (s, 4Hz 4H), 6.82 (s, 2H), 2.14 (s, 12H) (trans form). ¹H NMR (400 MHz, CDCl₃) δ 7.52 (s, 4Hz 4H), 7.11 (s, 2H), 2.41 (s, 12H); ¹³C NMR (400 MHz, CDCl₃) δ 138.71, 132.48, 120.51, 118.02, 21.24, HRMS m/z calcd for C₁₆H₁₉N₂ [M+H]^+: 239.1543, found: 239.1535.

3.6.7. Isolation of (4-FPh)N=N(4-FPh)

Reactions were done according to the general procedure by reacting 30.2 mg (0.0381mmol) of catalyst with 52.3 mg (0.381mmol, 10 equiv) of 4-methylphenyl azide; no internal standard was
used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene was isolated in 74% yield (30.8 mg). $^1$H NMR (400MHz, CDCl$_3$) δ 7.94-7.91 (m, 4H), 7.21-7.18 (m, 4H); $^{13}$C NMR (400MHz, CDCl$_3$) δ 164.99, 148.88, 124.63, 115.77, HRMS m/z calcd for C$_{12}$H$_9$N$_2$F$_2$ [M+H]$^+$:219.0728, found: 219.0731
CHAPTER 4: HETERO-COUPLED AZOARENE SYNTHESIS USING IRON(II) ALKOXIDE COMPLEXES

4.1. Introduction

As discussed in introduction, azoarenes are important highly colored chemical compounds which are used in different fields.\textsuperscript{1-4} Several groups have recently reported catalytic synthesis of symmetric azoarenes from organoazides using transition metal catalysis.\textsuperscript{10-13} In general, this synthetic route uses environmentally friendly base transition metal catalyst, avoids using toxic co-reactants, and produces only N\textsubscript{2} as a by-product. The reaction generally proceeds via a transition metal mediated formation of aryl nitrene, which undergoes homocoupling. However, most industrially important azoarenes are asymmetric, featuring two different aryl groups. It is unclear whether a single transition metal catalyst, or a combination thereof, can demonstrate selectivity in the formation of asymmetric azoarenes from two different organoazide precursors.

Our group has previously reported three different iron-alkoxide pre-catalysts of the Fe(OR)\textsubscript{2}(THF)\textsubscript{2} general form that displays different reactivity in nitrene homocoupling (Figure 4.1).\textsuperscript{22,50,58} Our first-generation catalyst Fe(OC\textsuperscript{t}Bu\textsubscript{2}Ph)\textsubscript{2}(THF)\textsubscript{2} was able to couple efficiently mesityl nitrene to produce azomesitylene. However, its reactivity was limited to bulky azides only; its reaction with less bulky aryl azides generally produced μ-imido complexes that failed to demonstrate nitrene coupling. Our second-generation catalyst, featuring bulkier alkoxide ligand, Fe(OC\textsuperscript{t}Bu\textsubscript{2}(3,5-Ph\textsubscript{2}C\textsubscript{6}H\textsubscript{3}))\textsubscript{2}(THF)\textsubscript{2}, exhibited a broader range of substrates in nitrene
homocoupling. Although the reaction with ortho-substituted nitrenes was the most efficient (nearly quantitative yields), this catalyst also exhibited homocoupling of less bulky meta-substituted and even para-substituted aryl nitrenes, with yields between 30-70%. Our chelating Fe[OO]Ph(THF)₂ exhibited nitrone homocoupling only for meta and para-substituted aryl azides. Following these results, we became interested in the heterocoupling reactivity of this catalyst and decided to investigate its reactivity with a 1:1 combination of various aryl azides. Herein we demonstrate that Fe(OC'Bu₂(3,5-Ph₂C₆H₃))₂(THF)₂ is capable of forming several new hetero-coupled azoarenes. The products were isolated and their cis:trans isomerization is studied.

In addition to studying the heterocoupling reactivity of Fe(OC'Bu₂(3,5-Ph₂C₆H₃))₂(THF)₂ by itself, we decided to investigate the combination of Fe(OC'Bu₂(3,5-Ph₂C₆H₃))₂(THF)₂ and Fe[OO]Ph(THF)₂ catalysts. As Fe(OC'Bu₂(3,5-Ph₂C₆H₃))₂(THF)₂ was able to couple preferentially bulky nitrenes, and Fe[OO]Ph(THF)₂ coupled preferentially non-bulky substrates, we postulated that the combination of these catalysts may be able to produce hetero-coupled azoarene combining bulky and non-bulky aryl groups

4.2. Catalytic Nitrene Hetero-Coupling Reactivity by Fe(OC'Bu₂(3,5-Ph₂C₆H₃))₂(THF)₂

Complex 5

Scheme 4.1. Heterocoupled (asymmetric) azoarene synthesis using Fe(OC'Bu₂(3,5-Ph₂C₆H₃))₂(THF)₂ 5.

We have studied heterocoupling reactivity of Fe(OC'Bu₂(3,5-Ph₂C₆H₃))₂(THF)₂ (5) using 10% of the catalyst with 5 equivalents of two different substituted aryl azides (Scheme 4.1). We
have investigated a combination of di-ortho, mono-ortho, para, and meta substituted arylazides with this catalyst. A simple statistical distribution of the products for the combination of Ar₁N₃ and Ar₂N₃ would entail the formation of Ar₁N=NAr₁:Ar₁N=NAr₂:Ar₂N=NAr₂ in 25:50:25 ratio. Slight differences in the products distributions were observed for the different combinations of aryl azides. Thus, a combination of di-ortho substituted aryl azide with mono-ortho substituted aryl azide follows the expected statistical distribution (entry 2, 3 and 5, Table 4.1). A combination of mesityl azide with 2-ethylphenyl azide, mesityl azide with 2-methylphenyl azide, 2,6-diethylphenyl azide with 2-i-propylazide produced 25% of each homocoupled azoarene and 50% of the respective heterocoupled azoarene product. The combination of two di-ortho-substituted azides, mesityl azide with 2,6-diethylphenyl azide, produced larger proportion (40%) of each homocoupled product and smaller proportion (20%) of the heterocoupled product (entry 4, Table 4.1). In contrast, the combination of mesityl azide with 2-isopropylphenyl azide produced a higher percentage of the heterocoupled azoarene product (60%) and a lower percentage of each homocoupled azoarene product (20%) (entry 1, Table 4.1). A combination of 2,6-diethylphenyl azide and 2-methylphenyl azide led to the formation of approximately 33% of each product (entry 6, Table 4.1).
Table 4.1. Hetero-coupling reactivity of Fe(OC\'Bu$_2$(3,5-Ph$_2$C$_6$H$_3$)$_2$(THF)$_2$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Azide 1</th>
<th>Azide 2</th>
<th>Homocoupled Product of Azide 1</th>
<th>Homocoupled Product of Azide 2</th>
<th>Heterocoupled product</th>
<th>Unreacted azide 1</th>
<th>Unreacted azide 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MesN$_3$</td>
<td>2'-PrPhN$_3$</td>
<td>20</td>
<td>20</td>
<td>60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>MesN$_3$</td>
<td>2-CH$_3$PhN$_3$</td>
<td>25</td>
<td>25</td>
<td>50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>MesN$_3$</td>
<td>2-EtPhN$_3$</td>
<td>25</td>
<td>25</td>
<td>50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>MesN$_3$</td>
<td>2,6-EtPhN$_3$</td>
<td>40</td>
<td>40</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>2,6-EtPhN$_3$</td>
<td>2'-PrPhN$_3$</td>
<td>25</td>
<td>25</td>
<td>50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>2,6-EtPhN$_3$</td>
<td>2-CH$_3$PhN$_3$</td>
<td>33</td>
<td>33</td>
<td>33</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>3,5-Me$_2$PhN$_3$</td>
<td>4-CH$_3$PhN$_3$</td>
<td>11</td>
<td>13</td>
<td>12</td>
<td>33</td>
<td>31</td>
</tr>
<tr>
<td>8</td>
<td>2-EtPhN$_3$</td>
<td>2'-PrPhN$_3$</td>
<td>16</td>
<td>16</td>
<td>30</td>
<td>15</td>
<td>18</td>
</tr>
<tr>
<td>9</td>
<td>MesN$_3$</td>
<td>3,5-Me$_2$PhN$_3$</td>
<td>2</td>
<td>40</td>
<td>10</td>
<td>38</td>
<td>0</td>
</tr>
</tbody>
</table>

We have previously demonstrated the reaction of Fe(OC\'Bu$_2$(3,5-Ph$_2$C$_6$H$_3$)$_2$(THF)$_2$ with non-bulky aryl azides led initially to the formation of green tetrazene complexes Fe(OC\'Bu$_2$(3,5-Ph$_2$C$_6$H$_3$)$_2$(ArNNNNAr), which were characterized by X-ray crystallography, Mossbauer spectroscopy and EPR. Similarly, A combination of meta- and para-substituted azides (3,5-dimethylphenyl azide and 4-methylphenyl azide) in the present case produced reaction color change from light brown to dark green, suggesting tetrazene formation. The reaction exhibited overall lower reactivity, producing 11% and 13% of the homocoupled products, and 12% of the heterocoupled product (entry 7, Table 4.1). The combination of the mono-ortho-substituted azides (2-ethylphenyl azide and 2'-propylphenyl) produced 16% of each homocoupled azoarene and 30% of the heterocoupled azoarene product (entry 8, Table 4.1). Surprisingly, the reaction between mesityl azide and 3,5-dimethylphenyl azides showed much higher yield of homocoupled product of 3,5-dimethylphenyl azide (40%) (entry 9, Table 4.1). The reaction color change to dark green suggested formation of the stable tetrazene complex with 3,5-dimethylphenyl azide (Fe(OC\'Bu$_2$(3,5-Ph$_2$C$_6$H$_3$)$_2$((3,5-Me$_2$C$_6$H$_3$))NNNN(3,5-Me$_2$C$_6$H$_3$)) as previously observed.[ref].
This stable tetrazene complex likely prevents nitrene formation with mesityl azide for homocoupling reactivity. The results above suggest (Table 4.1) that to produce the heterocoupled product in high (approximately statistical) yield, one of the aryl azides azide should be di-ortho-substituted and the other azide should be mono-ortho-substituted.

4.3. Catalytic Nitrene Hetero-Coupling Reactivity by Combination of Fe(Oc’Bu2(3,5-Ph2C6H3))2(THF)2 and Fe[OO]Ph(THF)2 Catalysts

Fe[OO]Ph(THF)2 itself showed very good reactivity with the non-bulky aryl azides to produce homocoupled azo arenes in high yield.58 Herein we have studied the combination of Fe(OC’Bu2(3,5-Ph2C6H3))2(THF)2 (3) and Fe[OO]Ph(THF)2 (11) catalysts for the heterocoupling reactivity. The catalytic reactivity of the combination of Fe(OC’Bu2(3,5-Ph2C6H3))2(THF)2 and Fe[OO]Ph(THF)2 was investigated using 5% of each catalyst with 5 equivalents of mesityl azide and 5 equivalent of several different para-substituted aryl azides (Scheme 4.2). We specifically selected mesityl azide because it showed the highest reactivity for Fe(OC’Bu2(3,5-Ph2C6H3))2(THF)2. 4-Methylphenyl azide, 4-bromophenyl azide, 4-chlorophenyl azide, and 4-floromethylphenyl azide were selected as the non-buly partners for this study due to their higher reactivity for Fe[OO]Ph(THF)2.

Scheme 4.2. Heterocoupled azoarene synthesis using combination of Fe(OC’Bu2(3,5-Ph2C6H3))2(THF)2 (3) and Fe[OO]Ph(THF)2 (11).
catalysts exhibited reaction color change from light brown to dark green, suggesting tetrazene formation of Fe(OC'Bu₂(3,5-Ph₂C₆H₃))₂(THF)₂ with para-substituted azides. The reactions exhibited overall lower reactivity for the homocoupling of mesityl azide and the heterocoupling of mesityl azide with para-substituted azides likely due to the stability of this tetrazene intermediate. The major products in these reactions are homocoupled azoarenes of para-substituted azides: 36%, 23%, 27% and 24% for 4-methylphenyl azide, 4-chlorophenyl azide, 4-bromophenyl azide, and 4-floromethylphenyl azide, respectively (entry 1-4, table 4.2). Azomesitylene production was around 1% in each reaction (entry 1-4, table 4.2). The yields of the heterocoupled azoarenes were 14%, 8%, 9%, and 8% for the reactions between mesityl azide with 4-methylphenyl azide, 4-chlorophenyl azide, 4-bromophenyl azide, and 4-floromethylphenyl azide, respectively (entry 1-4, table 4.2).

Table 4.2. Hetero-coupling reactivity of combination of Fe(OC'Bu₂(3,5-Ph₂C₆H₃))₂(THF)₂ and Fe[OO]²⁺(THF)₂

<table>
<thead>
<tr>
<th>Entry</th>
<th>Azide 1</th>
<th>Azide 2</th>
<th>Homocoupled Product of Azide 1</th>
<th>Homocoupled Product of Azide 2</th>
<th>Heterocoupled product</th>
<th>Unreacted azide 1</th>
<th>Unreacted azide 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MesN₃</td>
<td>4-CH₃PhN₃</td>
<td>1</td>
<td>36</td>
<td>14</td>
<td>35</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>MesN₃</td>
<td>4-CIPhN₃</td>
<td>1</td>
<td>23</td>
<td>8</td>
<td>41</td>
<td>19</td>
</tr>
<tr>
<td>3</td>
<td>MesN₃</td>
<td>4-BrPhN₃</td>
<td>1</td>
<td>27</td>
<td>9</td>
<td>40</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>MesN₃</td>
<td>4-CF₃PhN₃</td>
<td>1</td>
<td>24</td>
<td>8</td>
<td>41</td>
<td>18</td>
</tr>
</tbody>
</table>

4.4. Light Sensitive Cis-Trans Isomerization

Light-sensitive cis-trans isomerization is one of the most important properties of azoarenes. Due to this property, azoarenes are used as molecular photoswitches and drug delivery agents. Generally, trans-isomer of an azoarene is more stable. However, the stability of cis-isomer was reported to increase with the ortho substitution of the azoarene. While most of the previously reported symmetric azoarenes were observed in the form of trans isomer at room
temperature,11-13, 22, 50 relatively little is known about asymmetric azoarenes. To shed light on the cis-trans isomerism of the asymmetric azoarenes, we have isolated heterocoupled products which were obtained in relatively high yields (Table 4.3). Heterocoupled azoarenes from entry 1-6, Table 4.1 were purified by column chromatography and isolated in higher yields. 1H NMR spectroscopy (C6D6) revealed the presence of both cis and trans isomers at room temperature. While the trans isomer was dominant (between 69-86%, depending in the azoarene, see Table 4.3), a relatively significant amounts of cis isomers (14-31%) were observed.

**Table 4.3. Cis-trans isomerization of isolated heterocoupled azoarenes**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Heterocoupled azoarene</th>
<th>Isolated from column</th>
<th>Heating at 60 ºC for 2 h</th>
<th>Irradiation with UV light for 2 h</th>
<th>Irradiation with UV light for 6 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MesN=N(2-PrC6H4)</td>
<td>75 25</td>
<td>100 0</td>
<td>60 40</td>
<td>11 89</td>
</tr>
<tr>
<td>2</td>
<td>MesN=N(2-CH3C6H4)</td>
<td>81 19</td>
<td>100 0</td>
<td>59 41</td>
<td>33 67</td>
</tr>
<tr>
<td>3</td>
<td>MesN=N(2-EtC6H4)</td>
<td>86 14</td>
<td>100 0</td>
<td>66 34</td>
<td>10 90</td>
</tr>
<tr>
<td>4</td>
<td>MesN=N(2,6-Et2C6H3)</td>
<td>80 20</td>
<td>100 0</td>
<td>67 33</td>
<td>40 60</td>
</tr>
<tr>
<td>5</td>
<td>(2-PrPh)N=N(2,6-Et2PhC6H3)</td>
<td>69 31</td>
<td>100 0</td>
<td>59 41</td>
<td>16 84</td>
</tr>
<tr>
<td>6</td>
<td>(2,6-Et2C6H3)N=N(2-CH3C6H4)</td>
<td>74 26</td>
<td>100 0</td>
<td>69 31</td>
<td>25 75</td>
</tr>
</tbody>
</table>

**Scheme 4.3. Cis-trans isomerization observed for azoarenes in Table 4.3.**

Relative stability of cis and trans isomers was studied at higher temperature and/or under irradiation (Scheme 4.3). Heating all azoarenes to 60 ºC for 2 h results in a complete transformation of the mixture to the trans form. Pure trans products were characterized by 1H and 13C NMR spectroscopy at 60 ºC. Thus, Figure 4.2 demonstrates that while MesN=N(2-PrC6H4 is
obtained in a 75:25 trans:cis ratio at room temperature, heating at 60 °C produces clean spectrum of the trans product only. Upon cooling down to room temperature, the spectrum of the cis/trans mixture is observed again. In contrast, exposure of the samples to the UV light (365 nm) for 2 hours increases significantly the amount of the cis isomer in the sample. Further exposure (for 6 h) makes the cis isomer predominant in the mixture, although the exact ratio depends on the azoarene. As Figure 4.2 demonstrates, only traces of the trans product are observed for MesN=N(2-‘PrC₆H₄) after the irradiation for 6 h. A similar trend was observed for all other isolated hetero-coupled azoarenes after exposure to UV light (entry 2-6, Table 4.3 and Appendix D).
Figure 4.2. Spectrum of MesN=N(2-iprPh): A = after exposure to the UV (365 nm) light for 4 hours, B = at room temperature, C = heating after 2 h at 60 °C

4.5. Summary and Conclusions

Fe(OC′Bu2(3,5-Ph2C6H3))2(THF)2 has demonstrated a rare capability to catalyze heterocoupling reactivity for a combination of mono-ortho-substituted aryl azides with di-ortho substituted aryl azides. The products were generally produced in >50% yields and thus could be easily separated and characterized. In contrast, any combination involving less bulky meta/para substituted aryl azide did not lead to the production of the heterocoupled product in a good yield due to the formation of the stable tetrazene complexes with paral/meta substituted aryl azides.
Mixed catalyst reactivity of \( \text{Fe} \left( \text{OC}^\text{Bu}_2(3,5-\text{Ph}_2\text{C}_6\text{H}_3) \right)_2(\text{THF})_2 \) and \( \text{Fe}[\text{OO}]^\text{Ph}(\text{THF})_2 \) was not successful again likely due to the stable tetrazene formation of \( \text{Fe} \left( \text{OC}^\text{Bu}_2(3,5-\text{Ph}_2\text{C}_6\text{H}_3) \right)_2(\text{ArNNNNAr}) \). A variety of new asymmetric azoarenes were isolated and their \textit{cis-trans} isomerism was investigated. All azoarenes were shown to demonstrate the presence of both isomers in solution at room temperature, with the trans isomer being the predominant one. Thermal conditions lead to the full conversion of the mixture to the \textit{trans} isomer only in all cases, while the irradiation of the mixture with the UV light leads to the predominant formation of the \textit{cis} isomer.

4.6. Experimental Section

4.6.1. General Methods and Procedures

Air-sensitive reactions were carried out in a nitrogen-filled glovebox. Benzene-\( \text{d}_6 \) was purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves. HPLC grade non-deuterated solvents were purchased from Sigma-Aldrich and purified using an MBraun solvent purification system. Compounds were generally characterized by \( ^1\text{H} \) and \( ^{13}\text{C} \) NMR, high-resolution mass spectrometry. Chemical Shifts and coupling constants (\( J \)) were reported in parts per million and Hertz respectively. Thermofisher Scientific LTQ Orbitrap XL mass spectrometer at the Lumigen Instrument Centre was used for high resolution mass spectra. GC-MS analysis were done using Agilent 6890N spectrometer, Thermo TG5MS 30m \( \times \) 0.32mm \( \times \) 0.25μm column, 7683 series injector, and Agilent 5973 detector.

4.6.2. General Procedure for Catalytic Formation of Azoarenes

\( \text{Fe} \left( \text{OC}^\text{Bu}_2(3,5-\text{Ph}_2\text{C}_6\text{H}_3) \right)_2(\text{THF})_2 \) was synthesized according to the original publication.\(^{50}\) All azides were synthesized using previously reported procedures. Catalytic reactions were performed by adding 5 equiv of each organic azide and 1,2,3-trimethoxy benzene (TMB), and hexafluorobenzene (HFB) internal standard solution in \( \text{C}_6\text{D}_6 \) to a \( \text{C}_6\text{D}_6 \) solution of 30 mg (0.032 mmol) catalyst \( \text{Fe} \left( \text{OC}^\text{Bu}_2(3,5-\text{Ph}_2\text{C}_6\text{H}_3) \right)_2(\text{THF})_2 \) in \( \text{N}_2 \) filled glovebox. The reaction mixture was
stirred in 60 °C for 24 h. Yields of azoarenes were calculated by 1H NMR; the spectra were compared to the previously published NMR spectra of the corresponding homocoupled azoarenes and some of heterocoupled azoarenes were isolated and fully characterized using 1H NMR, 13C NMR, UV and HRMS. Formation of azoarenes was confirmed by GC-MS. Representative azoarenes were isolated in a pure state using silica gel column chromatography (hexane).

To check mixed catalysts reactivity for hetero-coupled azoarene formation Fe(OC'Bu2(3,5-Ph2C6H3))2(THF)2 and Fe[OO]Ph(THF)2 were used. Fe[OO]Ph(THF)2 was synthesized according to the original publication.58 Catalytic reactions were performed by adding 5 equiv of each organic azide and 1,2,3-trimethoxy benzene (TMB), or hexafluorobenzene (HFB) internal standard solution in C6D6 to a C6D6 solution of 15 mg (0.015 mmol) of Fe(OC'Bu2(3,5-Ph2C6H3))2(THF)2 and 12 mg (0.015 mmol) (Fe[OO]Ph(THF)2) in N2 filled glovebox. The reaction mixture was stirred in 60 °C for 24 h. Yields of azoarenes were calculated by 1H NMR; the spectra were compared to the previously published NMR spectra of the corresponding azoarenes. Formation of azoarenes was confirmed by GC-MS.

4.6.3. Isolation of MesN=N(2-iPrC6H4)

Reactions were done according to the general procedure by reacting 30.0 mg (0.032 mmol) of Fe(OC'Bu2(3,5-Ph2C6H3))2(THF)2 catalyst with 25.8 mg (0.159 mmol, 5 equiv) of mesityl azide and 25.8 mg (0.159 mmol, 5 equiv) of 2-2-propylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene was isolated in 43% yield (19.0 mg). Trans isomer: 1H NMR (600 MHz, C6D6) δ 7.81 (d, J = 7.9 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.21(t, J = 7.9 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 6.79 (s, 2H). 4.22 (m, 1H), 2.46 (s, 6H), 2.10 (s, 3H), 1.26 (d, J = 7.0 Hz, 6H); 13C NMR (150 MHz, C6D6) δ 151.15, 149.84, 148.51,
139.03, 132.56, 131.59, 130.83, 126.91, 126.84, 115.78, 27.97, 24.29, 21.43, 20.23. *Cis* isomer: 

\[ \text{H NMR (600 MHz, C}_6\text{D}_6 \] \( \delta \) 7.16 (d, 1H), 6.84 (t, \( J = 7.6 \) Hz, 1H), 6.52 (s, 2H) 6.48 (t, \( J = 8.4 \) Hz, 1H), 6.22 (d, \( J = 7.9 \) Hz, 1H), 3.89 (m, 1H), 2.00 (s, 3H), 1.89 (s, 6H), 1.33 (d, \( J = 6.7 \) Hz, 6H); \[ \text{C NMR (150 MHz, C}_6\text{D}_6 \] \( \delta \) 152.10, 150.84, 145.95, 136.22, 129.74, 129.68, 127.18, 126.11, 125.41, 115.64, 28.54, 23.75, 21.12, 18.12. \[ \text{HR-MS m/z calcd for C}_{18}\text{H}_{23}\text{N}_2[M+H]^+: 267.1856, found: 267.1852. \]

**UV-Vis:** \( \lambda_{\text{max}}, \text{nm (}\varepsilon_{\text{M}}, \text{Lmol}^{-1}\text{cm}^{-1}): 237 \text{ (sh, 1584), 242 (sh, 1523), } 330 \text{ (2147), 463 (143).} \]

### 4.6.4. Isolation of MesN=N(2-CH₃C₆H₄)

Reactions were done according to the general procedure by reacting 30.0 mg (0.032 mmol) of Fe(OC'Bu₂(3,5-Ph₂C₆H₃))₂(THF)₂ catalyst with 25.8 mg (0.159 mmol, 5 equiv) of mesityl azide and 21.3 mg (0.159 mmol, 5 equiv) of 2-methylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene was isolated in 36% yield (14.3 mg). *Trans* isomer: 

\[ \text{H NMR (600 MHz, C}_6\text{D}_6 \] \( \delta \) 7.81 (d, \( J = 7.6 \) Hz, 2H), 7.1 (m, 3H), 6.79 (s, 2H), 2.6 (s, 3H), 2.46 (s, 6H), 2.10 (s, 3H); \[ \text{C NMR (150 MHz, C}_6\text{D}_6 \] \( \delta \) 152.10, 150.84, 145.95, 136.22, 129.74, 129.68, 127.18, 126.11, 125.41, 115.64, 28.54, 23.75, 21.12, 18.12. \[ \text{HR-MS m/z calcd for C}_{18}\text{H}_{23}\text{N}_2[M+H]^+: 267.1856, found: 267.1852. \]

**UV-Vis:** \( \lambda_{\text{max}}, \text{nm (}\varepsilon_{\text{M}}, \text{Lmol}^{-1}\text{cm}^{-1}): 237 \text{ (sh, 1584), 242 (sh, 1523), } 330 \text{ (2147), 463 (143).} \]

### 4.6.5. Isolation of MesN=N(2-EtC₆H₄)

Reactions were done according to the general procedure by reacting 30.0 mg (0.032 mmol)
of Fe(OC\textsuperscript{t}Bu\textsubscript{2}(3,5-Ph\textsubscript{2}C\textsubscript{6}H\textsubscript{3}))\textsubscript{2}(THF)\textsubscript{2} catalyst with 25.8 mg (0.159 mmol, 5 equiv) of mesityl azide and 23.5 mg (0.159 mmol, 5 equiv) of 2-ethylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene was isolated in 34% yield (14.1 mg). Trans isomer: \textsuperscript{1}H NMR (600 MHz, C\textsubscript{6}D\textsubscript{6}) δ 7.87 (d, J = 7.9 Hz, 1H), 7.15 (m, 2H), 7.09 (m, 1H), 6.78 (s, 2H), 3.1 (q, J = 7.6 Hz, 2H), 2.46 (s, 6H), 2.10 (s, 3H), 1.23 (t, J = 7.6 Hz, 3H); \textsuperscript{13}C NMR (150 MHz, C\textsubscript{6}D\textsubscript{6}) δ 151.77, 149.63, 144.59, 139.11, 132.72, 131.41, 130.87, 130.41, 127.13, 115.76, 25.41, 21.43, 20.32, 16.87. Cis isomer: \textsuperscript{1}H NMR (600 MHz, C\textsubscript{6}D\textsubscript{6}) δ 7.04 (d, J = 7.6 Hz, 1H), 6.8 (m. 1H), 6.51 (s, 2H), 6.49 (t, J = 8.4 Hz, 1H), 6.23 (d, J = 8.2 Hz, 1H), 3.00 (q, J =7.5 Hz, 2H), 2.00 (s, 3H), 1.15 (t, J = 7.5 Hz, 3H); \textsuperscript{13}C NMR (150 MHz, C\textsubscript{6}D\textsubscript{6}) δ 152.12, 141.43, 136.16, 130.11, 129.72, 129.43, 126.19, 125.57, 115.74, 24.83, 21.11, 18.09, 15.06, HR-MS m/z calcd for C\textsubscript{17}H\textsubscript{21}N\textsubscript{2} [M+H]\textsuperscript{+}: 253.1699, found: 253.1697. UV-Vis: λ\textsubscript{max}, nm (ε\textsubscript{M}, Lmol\textsuperscript{-1}cm\textsuperscript{-1}): 236 (sh, 4808), 331 (7320), 465 (370)

\textbf{4.6.6. Isolation of MesN=N(2,6-Et\textsubscript{2}C\textsubscript{6}H\textsubscript{4})}

Reactions were done according to the general procedure by reacting 30.0 mg (0.032 mmol) of Fe(OC\textsuperscript{t}Bu\textsubscript{2}(3,5-Ph\textsubscript{2}C\textsubscript{6}H\textsubscript{3}))\textsubscript{2}(THF)\textsubscript{2} catalyst with 25.8 mg (0.159 mmol, 5 equiv) of mesityl azide and 27.9 mg (0.159 mmol, 5 equiv) of 2,6-diethylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene was isolated in 16% yield (7.2 mg). Trans isomer: \textsuperscript{1}H NMR (600 MHz, C\textsubscript{6}D\textsubscript{6}) δ 7.09 (m, 1H), 7.04 (m, 2H), 6.78 (s, 2H), 2.73 (q, J = 7.6 Hz, 4H), 2.48 (s, 6H), 2.09 (s, 3H), 1.15 (t, J = 7.5 Hz, 6H); \textsuperscript{13}C NMR (150 MHz, C\textsubscript{6}D\textsubscript{6}) δ 152.37, 149.57, 139.44, 137.20, 132.86, 131.04, 130.29, 128.81, 26.08, 21.38, 20.47, 16.71. Cis isomer: \textsuperscript{1}H NMR (600 MHz, C\textsubscript{6}D\textsubscript{6}) δ 6.93 (m, 1H), 6.82 (d, J=7.6 Hz, 2H), 6.48
(s, 2H), 2.73 (q, 7.6× Hz, 4H), 1.95 (s, 3H), 1.92 (s, 6H), 1.00 (t, J = 7.6×(2) Hz, 6H); \(^{13}\)C NMR (150 MHz, C\(_6\)D\(_6\)) δ 153.81, 152.15, 137.52, 133.81, 127.13, 25.31, 21.04, 19.24, 14.39 HR-MS m/z calcd for C\(_{15}\)H\(_{22}\)N\(_2\)[M+H]\(^{+}\): 281.2012, found: 281.2011.

4.6.7. Isolation of (2-iPrPh)N=N(2,6-Et\(_2\)C\(_6\)H\(_4\))

Reactions were done according to the general procedure by reacting 30.0 mg (0.032 mmol) of Fe(OC\(^{t}\)Bu\(_2\)(3,5-Ph\(_2\)C\(_6\)H\(_3\)))\(_2\)(THF)\(_2\) catalyst with 28.0 mg (0.159 mmol, 5 equiv) of 2,6-diethylphenyl azide and 25.8 mg (0.159 mmol, 5 equiv) of 2-i-propylphenyl; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene was isolated in 37\% yield (17.2 mg). Trans isomer: \(^1\)H NMR (600 MHz, C\(_6\)D\(_6\)) δ 7.72 (d, J = 8.2 Hz, 1H), 7.25 (d, J = 7.3 Hz, 1H), 7.16 (t, J = 7.0×(2) Hz, 1H), 7.03 (m, 2H), 6.98 (m, 2H), 4.2 (m, 1H), 2.69 (q, J = 7.3×(3) Hz, 4H), 1.20 (d, J = 7.0 Hz, 6H), 1.09 (t, J = 7.5×(2) Hz, 6H); \(^{13}\)C NMR (150 MHz, C\(_6\)D\(_6\)) δ 152.27, 150.95, 148.83, 137.27, 132.01, 128.94, 127.03, 27.74, 26.01, 24.40, 16.32. Cis isomer: 7.12 (m, 2H), 6.91 (m, 1H), 6.80 (d, J = 7.6 Hz, 2H), 6.42 (m, 1H), 6.24 (d, J = 9.1 Hz, 1H), 3.95 (m, 1H), 2.36 (m, 2H), 2.07 (m, 2H), 1.29 (d, J = 6.7 Hz, 6H), 0.95 (t, J = 7.6×(2) Hz, 6H); \(^{13}\)C NMR (150 MHz, C\(_6\)D\(_6\)) δ 151.54, 148.74, 146.83, 137.94, 134.15, 131.86, 131.77, 129.45, 127.36, 127.32, 127.15, 126.97, 125.34, 115.81, 28.45, 24.85, 23.82, 14.07. HR-MS m/z calcd for C\(_{19}\)H\(_{25}\)N\(_2\)[M+H]\(^{+}\): 281.2012, found: 281.2010. UV-Vis: \(\lambda_{\text{max}}, \text{nm} (\epsilon_{M}, \text{Lmol}^{-1}\text{cm}^{-1})\): 226 (sh, 1170), 240 (sh, 1272), 280 (sh, 1166), 316 (1421) 465 (102).

4.6.8. Isolation of (2-MePh)N=N(2,6-Et\(_2\)C\(_6\)H\(_4\))

Reactions were done according to the general procedure by reacting 30.0 mg (0.032 mmol) of Fe(OC\(^{t}\)Bu\(_2\)(3,5-Ph\(_2\)C\(_6\)H\(_3\)))\(_2\)(THF)\(_2\) catalyst with 28.0 mg (0.159 mmol, 5 equiv) of 2,6-
diethylphenyl azide and 21.3 mg (0.159 mmol, 5 equiv) of 2-methylphenyl azide; no internal standard was used for this reaction. After the reaction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using hexane as an eluent. Azoarene was isolated in 25% yield (10.5 mg). Trans isomer: \(^1\)H NMR (600 MHz, C\(_6\)D\(_6\)) \(\delta\) 7.77 (d, \(J = 7.2\) Hz, 1H), 7.08 (m, 4H), 7.02 (m, 2H), 2.74 (q, \(J = 7.3\times(3)\)Hz, 4H), 2.6 (s, 3H), 1.14 (t, \(J = 7.5\times(2)\) Hz, 6H); \(^{13}\)C NMR (150 MHz, C\(_6\)D\(_6\)) \(\delta\) 152.25, 151.93, 138.71, 137.54, 132.03, 131.52, 129.06, 128.31, 127.17, 26.13, 18.23, 16.42. Cis isomer: \(^1\)H NMR (600 MHz, C\(_6\)D\(_6\)) \(\delta\) 6.94 (m, 2H), 6.82 (d, \(J = 7.6\) Hz, 2H), 6.73 (t, \(J = 7.5\times(2)\) Hz, 1H), 6.47 (t, \(J = 7.8\times(2)\) Hz, 1H), 6.26 (d, \(J = 7.9\) Hz, 1H), 2.56 (s, 3H), 2.38 (m, 2H), 2.08 (m, 2H), 0.98 (t, \(J = 7.5\times(2)\) Hz, 6H); \(^{13}\)C NMR (150 MHz, C\(_6\)D\(_6\)) \(\delta\) 152.09, 136.20, 129.23, 128.47, 127.26, 126.88, 125.62, 116.07, 115.83, 32.30, 24.70, 23.39, 18.00, 14.68, 14.07. HR-MS m/z calcd for C\(_{17}\)H\(_{21}\)N\(_2\) [M+H]: 253.1694, found: 253.1699. UV-Vis: \(\lambda_{\text{max}}, \text{nm (}\varepsilon_{\text{M}}, \text{Lmol}^{-1}\text{cm}^{-1})\): 251 (sh, 3290) 320 (2580), 460 (170).
CHAPTER 5: A SPECTROSCOPIC AND THEORETICAL INVESTIGATION OF HIGH-SPIN, SEE-SAW FE(II) COMPLEXES SUPPORTED BY BULKY ALKOXIDES

5.1. Introduction

Due to the low toxicity, high abundance, and low cost of the metal, the chemistry of iron compounds is an active area of research. Moreover, the increased reactivity of low-coordinate high-spin iron(II) complexes is often harnessed for catalytic applications.\textsuperscript{22,50,58} Alkoxides are easy to synthesize, environmentally benign ligands which, because of their weak field character with weak $\sigma$- and strong $\pi$-donation, are excellent platforms for supporting high-spin iron(II) complexes.\textsuperscript{18} To date, iron(II)-alkoxides have been used in the catalysis of nitrene transfer including the synthesis of azoarenes and, also, the catalysis of lactide polymerization.\textsuperscript{22,50,58} Typically, four coordinate iron(II) complexes exhibit either a tetrahedral or a square-planar geometry which is often imposed by the steric demands of the supporting ligands.\textsuperscript{74, 75, 76} Iron(II) square planar complexes are common with porphyrin, salicylaldoxime, and phthalocyanine ligands.\textsuperscript{74} Tetrahedral complexes are often formed by monodentate non-chelating ligands. In contrast, the alkoxides of iron(II) complexes with $S = 2$ ground state exhibit an unusual \textit{see-saw} geometry.\textsuperscript{22,50,58}

To elucidate the electronic structure of these compounds, including the factors that determine their unusual geometry, this chapter describes the spectroscopic investigation of a series of the four-coordinate high-spin iron(II) alkoxide complexes with different alkoxide ligands, see Scheme 5.1.\textsuperscript{22,50,58,77}
Scheme 5.1. Structures of 1, 5, 11, and 12.

Here we use complexes with three different monodentate alkoxide ligands and one chelating alkoxide ligand. Bis(alkoxide) complexes featuring two bulky monodentate ligands generally exhibit a relatively large-angle between the alkoxides (RO-M-OR~ 138° – 148°). Complex 1 incorporates two THF groups and two monodentate bulky alkoxide ligands (HOC′Bu2Ph) which have two tert-butyl groups and one phenyl group. The inter-alkoxide angle is 139°, which leads to seesaw geometry at the metal center. Complexes 5 and 12 were synthesized using HOC′Bu2(OC′Bu2(3,5-Ph2C6H3)) and HOC′Bu2(OC′Bu2(3,5-Me2C6H3)) respectively. Compound 12 can be also synthesized using the corresponding Tl precursor TlOC′Bu2(OC′Bu2(3,5-Me2C6H3)), as described in Chapter 5. Compared with 1, the alkoxide ligands of 5 and 12 have meta-substituted phenyl rings. The O-Fe-O alkoxide angles of 5 and 12 are 148.1° and 141.5°, respectively. The structure of 11 resembles that of 1, 5 and 12 albeit with a significantly wider inter-alkoxide angle of 155.5(2) degrees.
This research was conducted in collaboration with Prof. Sebastian Stoian’s group at the University of Idaho.

5.2. Zero-field Mössbauer Spectra of 1, 5, 11 and 12

To evaluate the electronic structures of 1, 5, 11 and 12, we have recorded a series of zero-field $^{57}$Fe Mössbauer spectra at 100 K. Inspection of Figure 5.1 shows that for these compounds we observe spectra dominated by two resonances that is, a quadrupole doublet which for 1 is characterized by an isomer shift $\delta = 1.112$ mm/s, quadrupole splitting $\Delta E_Q = 0.924$ mm/s, and relatively narrow linewidths $\Gamma = 0.292$ mm/s.

![Figure 5.1](image)

**Figure 5.1.** Zero-field Mössbauer spectra recorded at 100 K for samples 1, 5, 11 and 12. The parameters used to obtain these simulations are listed in Table 5.1.

Inspection of Table 5.1 shows that even though 1, 5, 11 and 12 are supported by different alkoxide ligands, the differences between their zero-field Mössbauer parameters, $\delta$ and $\Delta E_Q$, are very small. This observation suggests that these compounds have very similar electronic structures.
Furthermore, their isomer shift values are typical of high-spin iron(II) sites which suggests that these complexes have an $S = 2$ ground state. This electronic configuration is consistent with that anticipated based on the relatively low ligand field strength of the alkoxide and THF ligands and on the four-coordinate character of these compounds. Interestingly, the quadrupole splitting value is smaller than that of typical high-spin ferrous sites, $\Delta E_Q > 1.5 \text{ mm/s}$, which suggests that perhaps, analogous to square-planar complexes, we observe a large ligand contribution to the electric field gradient (EFG) tensor. Finally, inspection of Figure 1 shows that while for 1 and 12 we can identify only one quadrupole doublet which accounts for > 92% of the spectral area and thus of the iron contained in the sample, for 5 and 11 we observe an additional doublet. This minor spectral component accounts for ~ 20% of the iron present in these samples. Although the isomer shift of these species is typical of high-spin ferrous sites, just like that of the major spectral component, their quadrupole splitting is much larger. The large linewidths, $\Gamma \geq 0.5 \text{ mm/s}$, observed for this minor component suggest that it originates from a heterogeneous chemical species perhaps formed by the loss of one or both THF molecules.

**Table 5.1.** Zero-field Mössbauer parameters derived from the analysis of the spectra presented in Figure 5.1.

<table>
<thead>
<tr>
<th>#</th>
<th>$\delta$ [mm/s]</th>
<th>$\Delta E_Q$ [mm/s]</th>
<th>$\Gamma$ [mm/s]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.112</td>
<td>0.924</td>
<td>0.292</td>
<td>92</td>
</tr>
<tr>
<td>12</td>
<td>1.141</td>
<td>0.968</td>
<td>0.324</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>1.15</td>
<td>1.05</td>
<td>0.27</td>
<td>75</td>
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<tr>
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<td>1.03</td>
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<td>0.5</td>
<td>22</td>
</tr>
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<td>11</td>
<td>1.16</td>
<td>1.034</td>
<td>0.32</td>
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</tr>
<tr>
<td></td>
<td>1.1</td>
<td>2.1</td>
<td>0.5</td>
<td>22</td>
</tr>
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</table>

**5.3. Field-Dependent Mössbauer Spectra of 12**

A representative series of field- and temperature-dependent Mössbauer spectra recorded for 12 is presented in Figure 5.2. These spectra were recorded while the magnetic field was applied parallel to the direction of the 14.4 keV gamma-rays. The set of field-dependent spectra considered
in our study is presented in Figures E.1-E.3 (see Appendix E) and was analyzed using the standard $S = 2$ spin-Hamiltonian, equations 1a-b. For these equations, all symbols have their standard meanings.

\[
\hat{H} = D \left( S_z^2 - 2 \right) + \frac{E}{D} \left( S_x^2 - S_y^2 \right) + \mu_B \vec{S} \cdot \vec{g} \cdot \vec{B} + \delta + \vec{H}_Q + \vec{S} \cdot \vec{A} \cdot \vec{I} + \mu_n g_n \vec{I} \cdot \vec{B} \quad (1a)
\]

\[
\hat{H}_Q = \frac{eQV_ZZ}{2} \left[ 3I_z^2 - \frac{15}{4} + \eta (I_x^2 - I_y^2) \right] \quad (1b)
\]

**Figure 5.2.** Field- and temperature-dependent $^{57}$Fe Mössbauer spectra were recorded for $^{12}$.

Inspection of Figures 5.2 and Figure E.1 (see Appendix E) shows that applying a relatively small field of 1 T induces a large magnetic hyperfine splitting. Moreover, increasing the field further, up to 8 T, leads to a more gradual development of the observed hyperfine splitting. This behavior is indicative of a negative $D$ and a positive internal field along the easy axis of
magnetization. The negative D leads to a ground state consisting of a quasi-doublet, \(|\pm\rangle \approx (|2,2\rangle \pm |2, -2\rangle)/\sqrt{2}\), which is essentially thermally isolated at \(\sim 4\) K. The fast rise of the magnetic hyperfine splitting observed at low fields is due to the competition between the Zeeman interaction and the ZFS of the ground quasi-doublet, \(\delta_{zfs} \approx 3 \cdot D \cdot (E/D)^2\), which becomes overwhelmed for \(B > 1\) T.

**Table 5.2.** Fine and hyperfine structure parameters derived from the analysis of the field-dependent data recorded for 12.a

<table>
<thead>
<tr>
<th>(D) [cm(^{-1})]</th>
<th>E/D</th>
<th>(g_x)</th>
<th>(g_y)</th>
<th>(g_z)</th>
<th>(\delta^a) [mm/s]</th>
<th>(\Delta E_{Q}^{a,b}) [mm/s]</th>
<th>(\eta^b)</th>
<th>(A_x/g_n\beta_n) [T]</th>
<th>(A_y/g_n\beta_n) [T]</th>
<th>(A_z/g_n\beta_n) [T]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-14.0(4)</td>
<td>0.10(5)</td>
<td>2.1(1)</td>
<td>2.1(1)</td>
<td>2.3(1)</td>
<td>1.14</td>
<td>0.99</td>
<td>0.7(2)</td>
<td>-13.4(2.0)</td>
<td>-28.1(2.0)</td>
<td>3.9(1)</td>
</tr>
</tbody>
</table>

a) The numbers in parentheses provide estimates of uncertainties for the corresponding significant digits.

b) The EFG tensor is rotate from the reference frame of the ZFS tensor by a standard set of Euler angles \(\alpha = \gamma = 0^\circ\), \(\beta = 15^\circ\).

The observed magnetic hyperfine splitting pattern is determined by an effective field that acts on \(^{57}\)Fe nuclei. This field originates from the vector sum of the internal and applied fields, \(\vec{B}_{\text{effective}} = \vec{B}_{\text{internal}} + \vec{B}_{\text{applied}}\), such that \(\vec{B}_{\text{internal}} = -\vec{A} \cdot \langle \hat{S}\rangle / g_n\mu_n\). The spin expectation values, \(\langle \hat{S}\rangle\), are dependent on the specific values of the spin-Hamiltonian parameters. In this case, because the ground quasi-doublet is magnetically uniaxial, with an easy axis along \(z\), we find that \(\langle \hat{S}_z\rangle \gg \langle \hat{S}_x\rangle \approx \langle \hat{S}_y\rangle \approx 0\). Consequently, the low-temperature spectra are most sensitive to the \(A_z\) component of the hyperfine coupling tensor and, for \(B < 4\) T, independent to \(A_x\) and \(A_y\). Analysis of the low-field spectra, \(B < 0.5\) T (data not shown), showed that the simulations of these spectra are very sensitive to E/D and that this parameter is distributed such that \(\sigma(E/D) = 0.05\). For most of the other experimental conditions the theoretical spectra are not very sensitive to this parameter and the experimental data could be well reproduced using a single value, E/D = 0.1. This behavior can be traced to the dramatic changes induced by small changes in \(\delta_{zfs}\), which is quadratically dependent on E/D, to the steepness with which \(\langle \hat{S}_z\rangle\) rises at low fields and reaches its \(\langle \hat{S}_z\rangle \sim - 2.0\).
saturation value, (see Figure E.3). The observation that at low temperature the observed magnetic hyperfine splitting increases with the applied field, even after $\langle \hat{S}_z \rangle$ reaches its saturation value, demonstrates that $A_z$ is positive, that is, along the easy axis of magnetization the $B_{int,z}$ is parallel to the applied field.

Inspection of Figure E.3 shows that at high temperatures, $T > 100$ K, we observe a Curie-like behavior, that is, $\langle \hat{S} \rangle \sim 1/T$. Furthermore, the magnetic anisotropy is considerably smaller $\langle \hat{S}_z \rangle_{th} \approx \langle \hat{S}_x \rangle_{th} \approx \langle \hat{S}_y \rangle_{th}$. This behavior allowed us to use the 8 T, 100–180 K spectra to establish that $\Delta E_Q$ is positive, the asymmetry parameter of the EFG tensor $\eta \sim 0.7$, and the $A_{x,y}$ components of the hyperfine coupling tensor. Our best estimate of the zfs parameter $D$ was determined from the analysis of the high-field spectra obtained at intermediate temperatures. The theoretical spectra of Figures 5.2, Figure E.1 – E.2 (see Appendix E) were obtained by using the parameters presented in Table 5.2 which were obtained from an exhaustive series of spectral fits and simulations of the entire data set.

5.4. Theoretical Investigation of Iron(II)-Alkoxide Complexes

To rationalize the parameters obtained from the spectroscopic characterization of 1, 5, 11, and 12 we have performed a series of DFT and CASSCF calculations. Our calculations show that the electronic structure of our compounds shares many similarities with that of quasi-linear, two-coordinate iron(II) complexes. Specifically, the strong steric repulsion between the two alkoxide ligands forces them in a near colinear arrangement which, in turn, leads to a $x^2-y^2$ ground orbital state and a low-lying $xy$ excited state, vide infra. The spin-orbit interaction between these orbital states leads to an unquenching of the angular momentum along the $z$-axis, found approximately along the direction of the alkoxide ligands, which produces a negative $D$ and an easy axis of magnetization along this direction. Finally, considering that the interactions between the alkoxide
ligands force them as far away from each other as possible, it is then surprising that the interactions between the THF ligands do not lead to a similar result, that is, instead of square-planar geometry, these complexes adopt a *seesaw* conformation.

**Figure 5.3.** Crystal-field splitting diagram derived from the CAS(5,6) calculations.

Our DFT calculations were performed using the B3LYP/6-311G functional/basis set combination and used an unabridged structural model derived from the experimental X-ray structure of 12. The cartesian coordinate system used for these calculations was chosen such that the $x$-axis bisected the O-Fe-O angle spanned by the two THF molecules and the $z$-axis is found in the O-Fe-O plane of the alkoxide ligands. Inspection of the Löwding atomic charges shows that
the atomic charges predicted for oxygen atoms belonging to the alkoxide ligands, ~ -0.59, are twice as large when compared to those predicted for the oxygen atoms belonging to the THF ligands, ~-0.31. Moreover, the four unpaired electrons of the formal iron(II) site are localized mainly on the iron site corresponding to an iron atomic spin density of +3.66 and ~ +0.11 for the alkoxide ligands. This pattern is reproduced by the atomic charges and spin densities derived from Mulliken and natural population analysis and is consistent with the presence of dominant metal-ligand interactions between the iron and alkoxide ligands. Analysis of the reduced orbital populations shows that the ground state configuration is best described using the \( |(x^2 - y^2)^2(xy)^a(xz)^a(yz)^a(z^2)^a| \) Slater determinant. Finally, while the DFT-predicted \( \eta = 0.31 \) obtained for 12 is somewhat smaller than that observed experimentally the theoretical \( \Delta E_Q = 1.27 \) mm/s and \( \delta = 0.951 \) mm/s compare very well with the experimental values.

The CASSCF calculations were performed using a simplified structural models derived from the experimental X-ray structure of 12 for which the mesityl substituents of the alkoxide ligands were replaced with phenyl and the 'Bu groups with hydrogen atoms. Inspection of Table 5.3 shows that in contrast to CP DFT our \textit{ab initio} CASSCF and CASSCF/NEVPT2-predicted D values are in good agreement with the experimental values. Comparing the theoretical values obtained when only the quintet states are considered with those derived when \( S = 1 \) are also included in the spin-orbit calculations we find that the triplet states account for ~ 20% of the total D value. Furthermore, as expected from the crystal field splitting diagram presented in Figure 5.3, these calculations show that the dominant quintet contribution to ZFS originates from the interaction of the \( x^2-y^2 \) ground state with the low-lying \( xy \) excited orbital state.
Table 5.3. Theoretical ZFS parameters and g values obtained for 12.

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<th>g_{min}</th>
<th>g_{mid}</th>
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<td>2.1(1)</td>
<td>2.1(1)</td>
<td>2.3(1)</td>
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</table>

5.5. Summary and Conclusion

In collaboration with the group of Prof. Sebastian Stoian, we investigated the electronic structures of four iron(II) alkoxide complexes which exhibit an unusual seesaw geometry. Analysis of the zero-field $^{57}$Fe Mössbauer spectra indicates that these compounds have very similar electronic structures. The field- and temperature dependent Mössbauer spectra obtained for 12 revealed a $S = 2$ ground state characterized by a negative D. The theoretical investigation of 12 suggests that its magnetic anisotropy is due primarily to the spin orbit interaction between the orbital states obtained by populating either the $x^2 - y^2$ or $xy$ orbitals by a single spin-down, $\beta$ electron and leads to an easy axis of magnetization aligned with the two alkoxide ligands.

5.6. Experimental Section

5.6.1. Synthesis of Iron Complexes

Complexes 1, 5, 11, and 12 were synthesized according to published protocols. The samples were prepared at WSU and were shipped to UI, while kept at 77 K, using a shipping dewar.

5.6.2. $^{57}$Fe Mössbauer Spectroscopy

The absorbers used in this study were prepared by packing ~ 50 mg ground powder of neat compounds, dispersed Nujol, in custom polyethylene containers. Because of their increased reactivity toward oxygen, these samples were handled and stored under liquid nitrogen. The field- and temperature-dependent $^{57}$Fe nuclear gamma resonance (Mössbauer) spectra of 1, 5, 11, and 12
have been recorded using a spectrometer operated in a constant acceleration mode. This instrument was equipped with a Janis 8DT cryostat and a superconducting coil capable of producing magnetic fields up to 8 T. The cryostat was cooled with liquid helium and was connected to a LHeP22-based Cryomech® helium recovery system. Because of this recovery system the cryostat was pressurized to ~ 2 psi over ambient pressure which increased the boiling temperature of liquid He to 4.35 K. Therefore, spectra recorded at ~ 4.3 K were obtained by submerging samples in liquid helium. Data collected at higher temperatures, up to 220 K, were obtained using a Cryocon® 22 C-120 temperature controller by placing the sample in a stream of He gas and measuring the temperature using a calibrated Cernox® sensor. The 14.4 keV γ-rays used to detect the Mössbauer effect propagated parallel to the applied magnetic field. Isomer shifts are reported with respect to the centroid of a spectrum recorded for a foil of α-iron metal recorded at room temperature. Spectral simulations were performed using the WMOSS program (See Co., formerly Web Research Co., Edina, MN).

5.6.3. Computational Studies

Density functional theory (DFT) and complete active space self-consistent field (CASSCF) calculations were performed using ORCA 5.0.0 quantum-mechanics software package. The DFT calculations used the B3LYP/6-311G functional/basis-set combination and unabridged structural models derived from the experimental X-ray structures. Predicted isomer shift values were obtained using the calibration provided by Vrajmasu et al. Predicted spectroscopic properties, including electric field gradients and hyperfine coupling constants were obtained using the eprnmr module implemented in ORCA. DFT-predicted theoretical zero-field splitting (ZFS) parameters and the orbital contributions to the hyperfine coupling tensor (\(A_L\)) were estimated using the coupled-perturbed (CP) SCF approach, the spin-orbit coupling operator was implemented using
the mean-field approximation (SOMF). SCF calculations used the RIJCOSX approximation and the auxiliary basis sets generated using the *autoaux* keyword. The nature of the ground state was established by inspecting the theoretical atomic charges, atomic spin densities, and orbital populations predicted by the Mulliken, Löwdin, and natural population analysis. The ground state character of the electronic configuration was established based on time-dependent (TD) DFT calculations which predicted that all one-electron excitations were positive.

CASSCF calculations were performed using an abridged structural model derived from the experimental structure of 12 for which the 'Bu side groups of the alkoxide ligands were replaced with hydrogen atoms and the mesityl with phenyl. The active space of the CAS(5,6) spanned the five canonical d orbitals and comprised six electrons according to the expected 3d\(^6\) configuration of the iron(II) ion. Two calculations were run, one which considered only the five quintet states and another which also considered the 35 triplet states. These calculations used the def2-TZVPP basis set in conjunction with the def2/JK auxiliary basis set and the RI-JK approximation. The orientation of the cartesian coordinates used was selected such that the z-axis bisected the OFeO angle formed by the two THF molecules and the x axis was roughly aligned with the alkoxide ligands. The dynamic correlations were included using the N-electron valence 2\(^{nd}\) order perturbation theory (NVEPT2) approach. The initial guesses were obtained from restricted open shell DFT calculations performed at the B3LYP/def2-TZVPP level of theory. Theoretical ZFS parameters were obtained using the quasi-degenerate perturbation theory (QDPT) and effective spin-Hamiltonian approach implemented in ORCA.
CHAPTER 6: SYNTHESIS AND CHARACTERIZATION OF THALLIUM ALKOXIDES AND THEIR APPLICATION IN SYNTHESIS OF TRANSITION METAL ALKOXIDES

Parts of the text in this chapter were reprinted or adapted with permission from: Grass, A.; Kulathungage, L. W.; Wannipurage, D.; Ward, C. L.; Groysman. S. *Dalton Trans.* 2021, 50, 2501-2509.

6.1. Introduction

Alkoxides are among the most common ligands in coordination chemistry and homogeneous catalysis, and therefore it is important to develop general, efficient, and reliable routes towards alkoxide-supported transition metal complexes. Two general routes to the transition metal alkoxide complexes include salt metathesis between transition metal halide sources \((\text{MX}_n)\) and alkali metal alkoxides \((\text{M'}\text{OR})\), or protonolysis of transition metal amide/alkyl precursors with more acidic alcohols. Both routes exhibit advantages and drawbacks. While the salt metathesis route employs commercially available transition metal halide precursors, it often yields mixed-metal “ate” complexes of \([\text{MM'}\text{OR}_n\text{X}]\) composition as a result of incomplete removal of \(\text{M'}\text{X}\) \((\text{M'} = \text{Li}, \text{Na}, \text{K})\). In contrast, protonolysis route generally forms \(\text{M(OR)}_n\) complexes cleanly. However, it requires the corresponding transition metal amide/alkyl precursors (often commercially unavailable). An alternative, less explored synthetic route to the metal-alkoxide complexes involves salt metathesis between thallium alkoxides \(\text{TlOR}\) and transition metal halides \(\text{MX}_n\). As the reaction of \(\text{TlOR}\) with halide-containing complexes yields insoluble \(\text{TIX}\) salts, this route generally avoids the formation of the mixed-metal species. This route also employs commercially available transition metal halide complexes; \(\text{TlOR}\) can be synthesized in one step using the combination of \(\text{TlPF}_6\) (or other non-coordinating anion) with alkali metal alkoxides. We have previously explored salt metathesis and protonolysis routes towards well-define mononuclear metal alkoxide complexes.
these routes are generally quite efficient, sometimes they require two separate synthetic steps which result in relatively poor yields. In certain cases (particularly for heavier 4d/5d middle and late metals), these routes fail to produce desired products. Herein we demonstrate that the efficient synthesis of a selected 3d (Fe) and 4d (Ru) complexes is possible using a Tl alkoxide precursor. These studies were carried out using a bulky alkoxide ligand [OC′Bu₂(3,5-Me₂C₆H₃)], that is closely related to [OC′Bu₂Ph] and [OC′Bu₂(3,5-Ph₂C₆H₃)] which were discussed earlier in my dissertation.

6.2. Synthesis and Characterization of LiOC′Bu₂(3,5-Me₂C₆H₃)

Treatment of 1-bromo-3,5-dimethylbenzene with two equivalents of t-butyllithium followed by the addition of hexamethylacetone formed the lithium salt of the ligand, LiOC′Bu₂(3,5-Me₂C₆H₃). Colorless crystals of LiOC′Bu₂(3,5-Me₂C₆H₃) were obtained by recrystallization from hexane in 81% yield (Scheme 6.1). We note that the structure of HOC′Bu₂(3,5-Me₂C₆H₃) was previously reported, by Dr. Maryam Yousif but its reactivity was not investigated.

Scheme 6.1. Synthesis of LiOC′Bu₂(3,5-Me₂C₆H₃) (13).

LiOC′Bu₂(3,5-Me₂C₆H₃) was characterized by ¹H NMR, ¹³C NMR, and IR spectroscopy, and X-ray crystallography. Solid-state structure revelas the overall dimeric Li₂(OC′Bu₂(3,5-
Me$_2$C$_6$H$_3$)$_2$(THF)$_2$ structure. Each lithium center is coordinated by two (bridging) alkoxide ligands, in addition to one THF ligand (Figure 6.1 and Appendix F).

Figure 6.1. ORTEP diagram (50% probability ellipsoids) of the X-ray structure of 13. H atoms were omitted for clarity.
Table 6.1. Experimental crystallographic parameters for 13

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6.3. Synthesis and Characterization of \( \text{TL}_2(\text{OC' Bu}_2(3,5-\text{Me}_2\text{C}_6\text{H}_3))_2 \)

\[
\text{LiOR} + \text{TIPF}_6 \xrightarrow{\text{THF/ether}} \text{0.5} \xrightarrow{-\text{LiPF}_6} \text{R} - \text{O} - \text{Tl} - \text{O} - \text{R} \]

\[
\text{OR} = \text{OC' Bu}_2(3,5-\text{Me}_2\text{C}_6\text{H}_3)
\]

**Scheme 6.2.** Synthesis of \( \text{TL}_2(\text{OC' Bu}_2(3,5-\text{Me}_2\text{C}_6\text{H}_3))_2 \) (14).

Mixing THF solutions of TIPF\(_6\) and LiOC'Bu\(_2\)(3,5-Me\(_2\)C\(_6\)H\(_3\)) at room temperature produced silver-gray suspension that was stirred for 2 hours (Scheme 6.2). Subsequent solvent removal followed by recrystallization from hexane resulted in the crystalline 14 in 69% yield. 14 is stable in the solid state in the absence of light at -35 °C over at least one month. It slowly decomposes in solution as indicated by the formation of a silver precipitate. Characterization of freshly crystallized \( \text{TL}_2(\text{OC' Bu}_2(3,5-\text{Me}_2\text{C}_6\text{H}_3))_2 \) by \(^1\)H NMR spectroscopy revealed the presence of two isomers (see Appendix F). Notably, prolonged storage (4 weeks) of 14 in solution at -35 °C led to the formation of a single isomer (see Appendix F), whose structure is shown in Figure 6.2. The structure of 14 is featuring non-planar \( \text{TL}_2\text{O}_2 \) ring and staggered conformation between the alkoxides.

**Figure 6.2.** X-ray structures of 14 (top, side view and front view), 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond distances (Å): Tl1-O1 2.361(4), Tl1-O2 2.394(4), Tl2-O2 2.366(4), Tl2-O1 2.406(4), Tl1---Tl 3.6256(4), O1---O2 2.959(4).
Table 6.2. Experimental crystallographic parameters for 14

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</table>
Formally two-coordinate dimeric homoleptic Tl alkoxides are rare. Selected structures of homoleptic [TlOR]_n complexes are given in Figure 6.3. For non-bulky alkoxides, TlOR generally assumes tetrameric cubane structures [Tl(OR)]_4 (in which Tl is three-coordinate), or leads to higher-nuclearity clusters [Tl(OR)]_n (Tl featuring coordination number of 4 or higher). Bulkier [OC(CH_3)_3] and [O(C(CF_3)_3)] ligands have been also shown to form tetrameric cubane structures [Tl(OR)]_4 featuring a three-coordinate Tl. In contrast, bulky 2,6-disubsituted aryloxides were shown to form dimeric formally two-coordinate Tl_2(OAr)_2 readily. Less bulky aryloxides typically formed higher-nuclearity clusters or polymers, except for the noteworthy example of electron-deficient aryloxides, such as in Tl_2(O(p-C_6H_4F))_2.

Figure 6.3. Selected examples of homoleptic TlOR/TlOAr structures.
6.4. Alkoxide-Transfer Reactivity of Tl₂(OC'Bu₂(3,5-Me₂C₆H₃))₂

Complex 14 serves as a convenient precursor for the synthesis of transition metal alkoxide complexes. Treatment of 14 with FeCl₂ produced Fe(OC'Bu₂(3,5-Me₂C₆H₃))(THF)₂ (12). Complex 12 is obtained as light-gold crystals isolated in 61% yield by recrystallization from hexanes. Fe(OC'Bu₂(3,5-Me₂C₆H₃))(THF)₂ was characterized by X-ray crystallography, IR, and UV. X-ray crystal structure of compound 12 (Figure 6.4) demonstrates highly distorted tetrahedral geometry with a wide inter-alkoxide O1-Fe-O2 angle of 148.1(1)°. Selected structural parameters are given in Figure 6.4.
Figure 6.4. X-ray structure of 12, 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond distances (Å): Fe-O1 1.846(2), Fe-O2 1.851(2), Fe-O3 2.171(2), Fe-O4 2.232(2). Selected bond angles (°): O1-Fe-O2 148.1(1), O3-Fe-O4 88.8(1).
Table 6.3. Experimental crystallographic parameters for 12

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We have also explored the reactivity of $\text{Tl}_2(\text{OC’Bu}_2(\text{3,5-Me}_2\text{C}_6\text{H}_3))_2$ towards heavier (4d) middle/late metals in the alkoxide ligand environment. This work specifically focused on the heavier group 8 congener of Fe(II), Ru(II). Ru(II) complexes with unsupported alkoxide ligands are relatively rare.\textsuperscript{1,46-50} Treatment of $[\text{RuCl}_2(\text{cymene})]_2$ with $\text{Tl}_2(\text{OC’Bu}_2(\text{3,5-Me}_2\text{C}_6\text{H}_3))_2$ resulted in the formation of a magenta solution, from which dark-purple crystals were isolated. $^1\text{H NMR}$ characterization of the crystalline product 16 (81% yield) demonstrated the presence of only four aromatic alkoxide signals, instead of the expected three phenyl protons of $\text{Tl}_2(\text{OC’Bu}_2(\text{3,5-Me}_2\text{C}_6\text{H}_3))_2$. In addition, the NMR spectrum contained cymene aromatic protons as two doublets at 5.55 and 5.42 ppm, one $^3\text{Bu}$ resonance (18 protons overall) at 1.20 ppm, cymene $^3\text{Pr}$ resonances at 0.97 ppm, and the cymene Me peak at 1.43 ppm. X-ray diffraction study disclosed the structure of C-H activated product 16 (Figure 6.5). Complex 16 features bidentate coordination of the alkoxide through oxygen and the ortho-carbon to Ru(II) center, in addition to the $\eta^6$-bound cymene ligand.

Figure 6.5. X-ray structures of 16 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond distances (Å) and angles (°) for 16: Ru-O 1.910(1), Ru-C1 2.068(2), O-Ru-C1 81.32(5).
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<td><strong>GOF (F²)</strong></td>
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</table>
6.5. Summary and Conclusions

In summary, we have reported the synthesis of rare dimeric thallium-alkoxide complex bearing bulky alkoxide \([\text{OC}^\prime \text{Bu}_2(3,5-\text{Me}_2\text{C}_6\text{H}_3)]\). The complex is observed as two different conformers; the distinct conformers are supported by \(^1\text{H}\) NMR spectroscopy. \(\text{Tl}_2(\text{OR})_2\) precursors allow a one-step formation of transition metal complexes with bulky alkoxide ligand, \([\text{OC}^\prime \text{Bu}_2(3,5-\text{Me}_2\text{C}_6\text{H}_3)]\), which is generally more efficient and higher-yielding compared with the previously described two-step synthesis. Furthermore, the use of \(\text{Tl}_2(\text{OR})_2\) enabled preparation of a rare example of the second-row complex (Ru) with \([\text{OC}^\prime \text{Bu}_2(3,5-\text{Me}_2\text{C}_6\text{H}_3)]\).

6.6. Experimental Section

6.6.1. General Methods and Procedures

All reactions involving air-sensitive materials were executed in a nitrogen-filled glovebox or by standard Schlenk line procedures. Thallium hexafluorophosphate was purchased from Strem. All solvents were purchased from Fischer Scientific and were of HPLC grade. The solvents were purified using an MBRAUN solvent purification system and stored over 3 Å molecular sieves. Deuterated benzene \((\text{C}_6\text{D}_6)\) and toluene \((\text{C}_7\text{D}_8)\) were purchased from Cambridge Laboratories, degassed under argon, and stored over 3 Å molecular sieves. NMR spectra were recorded at the Lumigen Instrument Center (Wayne State University). NMR was performed on Agilent 400 MHz or Agilent 600 MHz Spectrometers in \(\text{C}_6\text{D}_6\) and \(\text{C}_7\text{D}_8\) at room temperature unless otherwise noted. Chemical shifts and coupling constants \((J)\) were reported in parts per million \((\delta)\) and Hertz \((\text{Hz})\), respectively. IR spectra were recorded on Shimadzu IR-Affinity1 FT-IR spectrometer as paratone oil mull suspensions. UV-Vis spectra were obtained using Shimadzu UV-1800 spectrometer.

Warning: Thallium hexafluorophosphate and other thallium salts are highly toxic, can be fatal if swallowed or inhaled and should be handled with utmost care! All reactions that involved
thallium precursors or products were conducted in the glovebox. All thallium-contaminated waste (including glassware such as vials and pipets or kimwipes) was separated from the other glovebox waste and discarded separately labelled “thallium waste”.

6.6.2. X-ray Crystallographic Details

The structures of 12, 13, 14, and 16 were determined by X-ray diffraction analysis. The crystals were mounted on a Bruker APEXII/Kappa three circle goniometer platform diffractometer equipped with an APEX 2 detector. A graphic monochromator was employed for wavelength selection of the Mo Kα radiation (λ = 0.71073 Å). The data were processed, and the structure was solved using the APEX 2 software supplied by Bruker AXS. The structure was refined with the program ShelXL using Olex2. Hydrogen atoms were placed in calculated positions using a standard riding model and refined isotropically; all other atoms were refined anisotropically. The structure of 16 exhibited tert-butyl groups disorder which was successfully modeled by two alternating conformations. Selected crystal and structure refinement data is given in Table 6.4.

6.6.3. Synthesis of LiOC\textsuperscript{t}Bu\textsubscript{2}(3,5-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3}) (1)

To a solution of 1-bromo-3,5-dimethylbenzene (0.430 g, 2.33 mmol) in 4 ml ether and 2 ml THF, a solution of t-BuLi in pentane (2.7 ml, 1.7 M) was added dropwise at -35 °C. The solution changed color from colorless to yellow. The reaction was allowed to slowly warm to room temperature while stirred for one hour, after which it was cooled again to -35 °C and added to a cold solution of hexamethylacetone (0.4 mL, 2.31 mmol) in 2 ml of ether. The reaction was stirred for 24 hours, after which all solvents were removed under in vacuo to yield yellowish white residue. The residue was dissolved in hexanes and kept at -35 °C to get colorless crystals of 13 (428 mg, 81% yield). \textsuperscript{1}H NMR (600 MHz, C\textsubscript{6}D\textsubscript{6}, room temperature) δ 7.67 (s, 1H, Ph), δ 7.43 (s, 1H, Ph), δ 6.75 (s, 1H, Ph), δ 2.30 (s, 3H), δ 2.19 (s, 3H), δ 1.19 (s, 18H). \textsuperscript{13}C NMR (C\textsubscript{6}D\textsubscript{6}, 150
MHz) δ 152.80, 137.63, 136.02, 125.46, 85.46, 43.04, 32.05, 22.42. IR (cm\(^{-1}\)): 2962 (m), 2870 (m), 2816 (w), 1604 (w), 1388 (w), 1365 (w), 1126 (w), 1080 (s), 1010 (m), 849 (s), 764 (s), 709 (s). The structure of 13 was also determined by the X-ray structure determination (see ESI).

### 6.6.4. Synthesis of Tl\(_2\)(OC\(_t\)Bu\(_2\)(3,5-Me\(_2\)C\(_6\)H\(_3\)))\(_2\) (14)

A solution of TlPF\(_6\) (89 mg, 0.255 mmol) in THF was added to a stirred clear THF solution of LiOC\(_t\)Bu\(_2\)(3,5-Me\(_2\)Ph) (65 mg, 0.256 mmol) at room temperature. The reaction turned silver-grey and was stirred at room temperature for two hours. The volatiles were removed \textit{in vacuo}. The resulting solid was dissolved in hexane, filtered, and concentrated. Subsequent recrystallization at -35 °C yields colorless crystals of 14 (79 mg, 69% yield). \(^1\)H NMR (600 MHz, C\(_6\)D\(_6\), room temperature) δ 8.14 (bs, 1H, Ph), δ 7.42 (bs, 1H, Ph), δ 6.74 (bs, 1H, Ph), δ 2.25 (s, 6H) δ 1.26 (s, 18H). \(^{13}\)C NMR (C\(_6\)D\(_6\), 150 MHz) δ 153.35, 136.17, 135.52, 129.69, 128.84, 127.89, 90.42, 44.65, 32.65, 22.66. UV: \(\lambda_{\text{max}}, \text{nm} (\varepsilon_M, \text{L mol}^{-1}\text{cm}^{-1})\): 316 (900 L mol\(^{-1}\) cm\(^{-1}\)), 297 (1200 L mol\(^{-1}\) cm\(^{-1}\)). The structure of 14 was also determined by the X-ray structure determination.

### 6.6.5. Synthesis of Fe(OC\(_t\)Bu\(_2\)(3,5-Me\(_2\)C\(_6\)H\(_3\)))\(_2\)(THF)\(_2\) (12)

A solution of Tl\(_2\)(OC\(_t\)Bu\(_2\)(3,5-Me\(_2\)C\(_6\)H\(_3\)))\(_2\) (190 mg, 0.210 mmol) in THF was added to a stirred THF solution of FeCl\(_2\) (27 mg, 0.210 mmol) at room temperature. The solution color turned into light brown, and white precipitate formation was observed. The reaction was stirred at room temperature for one hour. The volatiles were removed \textit{in vacuo}. The resulting residue was dissolved in hexane, filtered, and concentrated. Recrystallization from hexane at -35 °C yielded light yellow X-ray quality crystals of 12 (82 mg, 61% yield). UV: \(\lambda_{\text{max}}, \text{nm} (\varepsilon_M, \text{L mol}^{-1}\text{cm}^{-1})\): 407 (sh, 250 L mol\(^{-1}\) cm\(^{-1}\)). IR (cm\(^{-1}\)): 2970 (w), 2978 (m), 2885 (m), 2831 (w), 1597(w), 1481 (w), 1388 (w), 1350 (w), 1134 (m), 1087 (s), 1033 (s), 894 (m), 848 (s), 763 (m), 702 (s). The structure
of 12 was also determined by the X-ray structure determination.

6.6.6. Synthesis of Ru(cymene)[(κ²-OC'Bu₂Me₂C₆H₂)] (16)

A solution of Tl₂(OC'Bu₂(3,5-Me₂C₆H₃))₂ (133 mg, 0.147 mmol) in THF was added to a stirred THF solution of [Ru(p-cymene)Cl₂]₂ (45 mg, 0.074 mmol) at room temperature. Following the addition, the solution turned magenta and precipitate formation was observed. The reaction was stirred at room temperature for one hour. The volatiles were removed in vacuo. The resulting residue was dissolved in hexane, filtered, and concentrated. Recrystallization from hexane at -35°C yielded dark purple X-ray quality crystals of 16 (59 mg, 81% yield).<sup>1</sup>H NMR (C₆D₆, 600 MHz) δ 7.27 (s, 1H, Ph), 7.01 (s, 1H, Ph), 5.55 (d, J_HH = 6.2 Hz, 2H), 5.42 (d, J_HH = 6.2 Hz, 2H), 3.09 (s, 3H), 2.21 (s, 3H), 1.57 (s, 3H), 1.95 (m, 1H) 1.43 (s, 3H) 1.20 (s, 18H), 0.97(d, J_HH = 6.7 Hz, 6H)

<sup>13</sup>C NMR (C₆D₆, 150 MHz) δ 176.88, 171.10, 149.55, 131.34, 127.73, 123.06, 106.48, 90.20, 84.55, 82.99, 78.88, 39.96, 32.54, 31.45, 30.56, 23.37, 22.35, 20.44. UV: λ<sub>max</sub>, nm (ε<sub>M</sub>, Lmol⁻¹cm⁻¹): 545 (5200 Lmol⁻¹cm⁻¹), 361 (15400 Lmol⁻¹cm⁻¹), 263 (30000 Lmol⁻¹cm⁻¹). The structure of 16 was also determined by the X-ray structure determination.
CHAPTER 7: SYNTHESIS AND CHARACTERIZATION OF NEW ACHIRAL MAGNESIUM ALKOXIDE COMPLEXES Mg(OR)_2(THF)_2 AND INVESTIGATION OF THEIR POLYMERIZATION AND COPOLYMERIZATION REACTIVITY

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7.1. Introduction

There is a significant current interest in polyesters as biodegradable and renewable alternatives to polyolefins.\textsuperscript{99,100} In the last decade, the ring-opening copolymerization (ROCOP) of cyclic anhydrides with epoxides is emerging as a promising alternative route for the synthesis of polyesters.\textsuperscript{101,102} Compared to ring-opening polymerization ROP, ROCOP provides access to more structurally diverse polyesters, due to the availability of large libraries for both monomers. For both synthetic processes, catalysts based on coordination compounds of benign metals such as group 2 and 12 metals offer significant advantages since it is not necessary to remove the catalyst residues that eventually contaminate the resulting material.\textsuperscript{103-106} Magnesium complexes, because of their low cost and toxicity as well as the high abundance of the chemical element, are attractive from both an economic and environmental point of view. Herein we describe a new well-defined monomeric magnesium complex supported by bulky bis(alkoxide) ligand environment, Mg(OR)_2(THF)_2 (OR = OC\textsubscript{6}Bu\textsubscript{2}Ph), that exhibits active ROCOP of various anhydride/epoxide mixtures, in addition to active ROP of lactide. The sustainable and non-toxic nature of the complex (containing a non-toxic metal and easily synthesizable ligand) contribute to its biocompatibility, and constitute an attractive feature of the newly reported catalytic system.
7.2. Synthesis and Characterization of Achiral Mg(OR)$_2$ Complexes

7.2.1. Synthesis of Mg(OC'Bu$_2$Ph)$_2$(THF)$_2$ (17)

We have previously demonstrated that the bulky alkoxide ligand [OC'Bu$_2$Ph] (OR hereafter) enables formation of well-defined mononuclear complexes M(OC'Bu$_2$Ph)$_2$(THF)$_2$ with middle and late 3d transition metals (M = Mn-Co) in M(II) oxidation states.\textsuperscript{82} As Mg(II) features similar ionic radius to Mn(II) and Fe(II), the formation of a similar complex was hypothesized. Mg(OC'Bu$_2$Ph)$_2$(THF)$_2$ complex 17 can be synthesized in via two synthetic pathways.\textsuperscript{107} One step synthesis of Mg(OC'Bu$_2$Ph)$_2$(THF)$_2$ complex 17 was done via treatment of n-butyl-sec-butylmagnesium (0.7 M solution in hexane) with two equivalents of HOR.\textsuperscript{107} The reaction proceeds via Mg(OC'Bu$_2$Ph)(sec-Bu)(THF)$_2$ intermediate (18), that can be isolated in high yield from the reaction of n-butyl-sec-butylmagnesium with one equivalent of HOR (Figure 7.1). The selectivity of the protonolysis of n-butyl vs. sec-butyl likely originates in the steric difference between the two alkyl groups. The intermediate nature of 18 in the synthesis of 17 is further demonstrated by the reaction of 18 with HOR, which forms 17 in 95\% isolated yield.

![Figure 7.1](image-url)
Complex 17, as well as the intermediate 18, was characterized by proton and carbon NMR spectroscopy, X-ray crystallography, and elemental analysis. Proton NMR spectrum of complex 17 demonstrates five aromatic signals for the ligand phenyl group, consistent with its restricted rotation. In contrast, four tert-butyl groups give rise to one singlet, suggesting effective $C_{2v}$ symmetry in solution. The spectrum of 18 contains four resonances attributable to the sec-butyl group (Mg-CH(Me)(Et) at 0.19 ppm), in addition to the resonances attributable to one OR ligand and two THF ligands. Solid-state structures of 17 and 18 are also given in Figure 7.1; selected bond distances and angles are provided in the Figure caption. X-ray crystallography reveals mononuclear structure for both 17 and 18. Both complexes exhibit distorted tetrahedral geometry, with narrow THF-Mg-THF angles (91° (1) and 89° (2), and broader RO-Mg-OR/RO-Mg-C angles (127° (1) and 131°). Complex 17 exhibits crystallographic $C_2$ symmetry; the $C_2$-symmetric structure of 17 is isomorphous with previously reported structures of other M(OR)$_2$(THF)$_2$ complexes (M = Mn, Fe, Co), all crystallizing in $F_{dd2}$ space group. We note that 17 is a rare example of a mononuclear magnesium bis(alkoxide) complex; several comparable bis(aryloxide) complexes were also reported. We also note that related mono(aryloxide)mono(alkyl) magnesium complexes [Mg(OAr)(R)] had been previously reported by Carpentier and coworkers (Ar = 2,6-t-Bu$_2$-4-MeC$_6$H$_2$, R = hexyl), Henderson and coworkers (Ar = 2,6-t-Bu$_2$C$_6$H$_3$, R = n-Bu), Kuhn, Laufer and coworkers (Ar = 2,4,6-t-Bu$_3$C$_6$H$_2$, R = n-Bu), and Nifant'ev and coworkers (Ar = 2,6-t-Bu$_2$-4-MeC$_6$H$_2$, R = n-Bu). Most complexes exhibited dimeric structures Mg$_2$(μ$_2$-OAr)$_2$R$_2$; Nifant'ev and coworkers also described structurally similar monomeric complex Mg(O-2,6-t-Bu$_2$-4-MeC$_6$H$_2$)(n-Bu)(THF)$_2$ Mg(O-2,6-t-Bu$_2$-4-MeC$_6$H$_2$)(n-Bu)(THF)$_2$ exhibited close structural parameters to 18, with slightly wider THF-Mg-THF angle (99° vs. 89° in 18).
Table 7.1. Experimental crystallographic parameters for 18.

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<th>Value</th>
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<tr>
<td>space group</td>
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<td>Z</td>
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<tr>
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<tr>
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<td>V, Å&lt;sup&gt;3&lt;/sup&gt;</td>
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</tr>
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<tr>
<td>GOF (F&lt;sup&gt;2&lt;/sup&gt;)</td>
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7.2.2. Synthesis and Characterization of Mg(OC'Bu₂(3,5-Ph₂C₆H₃))₂(THF)₂

Our group have previously demonstrated that the bulky alkoxide ligand (OR' = OC'Bu₂(3,5-Ph₂C₆H₃)) enables formation of well-defined mononuclear complexes M(OR)₂(THF)₂ with middle and late 3d transition metals (M = Cr, Fe, Co) in M(II) oxidation states.⁴⁹,⁵⁰ Similarly to Mg(OR)₂(THF)₂, we have explored the reactivity of sterically bulky (OR' = OC'Bu₂(3,5-Ph₂C₆H₃)) ligand with n-butyl-sec-butylmagnesium. One step synthesis of Mg(OR')₂(THF)₂ complex 19 was done via treatment of n-butyl-sec-butylmagnesium (0.7 M solution in hexane) with two equivalents of HOR' (Figure 7.2).

![Synthesis and structure of complexes 19.](image)

**Figure 7.2.** Synthesis and structure of complexes 19. Selected bond distances (Å) and angles (°) for 19: Mg O1 1.829(4), Mg O2 1.829(3), O1 Mg O1' 131.75(16), O2 Mg1 O2' 95.33(16).
X-ray crystallography reveals mononuclear structure for 19. Complexes 19 exhibit distorted tetrahedral geometry, with narrow THF-Mg-THF angles (95.3(1) °, and broader RO-Mg-OR angle (131.7(1) °). Complex 19 exhibits $P\overline{1}$ space group.

**Table 7.2.** Experimental crystallographic parameters for 19.

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<td>GOF ($F^2$)</td>
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7.3. Reactivity of Mg(OC′Bu₂Ph)₂(THF)₂ Towards Lactide Polymerization and Characterization of the Resulting Polymers

To test the reactivity of 17 in the ring-opening polymerization of cyclic esters, we conducted ROP studies using rac-lactide precursor. Polymerization runs were carried out using 10 µmol of the catalyst using different ratios of lactide:catalyst precursor (100:1, 200:1, 300:1) in dichloromethane and toluene. Monomer conversion was monitored by ¹H NMR spectroscopy. The catalyst exhibited moderate polymerization activity; the reaction was slightly faster in dichloromethane compared with toluene. For example, approximately 30% consumption of LA was observed in dichloromethane after 30 minutes, and in toluene after 1 hour, when 200 equivalents of the monomer were used. However, the polymerization does not appear to be well-controlled, giving relatively large molecular weight distribution (D= 1.79 ÷ 4.89), and lower than expected $M_n$ values (Table 7.3). Moreover, in most of the cases, with the increase of the conversion molecular weights decrease, while the dispersity values increase, thus suggesting that transesterification reactions do occur during the polymerization reactions. To prevent possible catalyst aggregation and enable better polymerization control, we have attempted polymerization in a coordinating solvent, THF (Table 7.3). The activity in THF was relatively high (very similar to DCM), and some decrease in the PDI values was obtained. Cui, Chen and coworkers have demonstrated that the addition of relatively non-bulky alcohols (as initiators) to Mg(n-Bu)₂ resulted in a more controlled behavior.¹⁰⁸ Lactide polymerization with 17 in the presence of one equivalent or ten equivalents of added PhCH₂OH has resulted in a significantly higher activity, and significantly lower PDI values, consistent with the previous reports (Table 7.4). Finally, we have also compared the reactivity of 18 with the reactivity of 17 (Table 7.5). While the overall polymerization reactivity of 18 is similar to 17, it appears less reactive, exhibiting somewhat lower monomer conversion.
Table 7.3. Catalytic reactions employing Mg(OR)$_2$(THF)$_2$ (17) with rac-lactide in different solvents.$^a$

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<th>Entry</th>
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<th>Eq of lactide</th>
<th>Time (h)</th>
<th>Temp (°C)</th>
<th>Conversion $^b$</th>
<th>$^cM_n$(10$^3$)</th>
<th>$^dM_n^{exp}$(10$^3$)</th>
<th>$^dD$</th>
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<td>19.0</td>
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<td>n.d.$^e$</td>
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</table>

$^a$Reaction conditions: [Mg] = 10 µmol; solvent = 10 mL. $^b$Conversion of lactide determined by $^1$H NMR spectroscopy (400 MHz, CDCl$_3$) of the reaction mixture. $^c$Calculated $M_n$ of PLA (in gmol$^{-1}$) = 144.14 x ([LA]/[Mg]) x conversion LA $^d$Experimental $M_n$ (corrected using factor 0.58) and $D$ values were determined by GPC analysis in THF using polystyrene standards. $^e$Not determined (due to the insufficient amount of material).
Table 7.4. Catalytic reactions employing 17 with rac-lactide and PhCH2OH as a co-catalyst. The reactions were conducted in DCM.

<table>
<thead>
<tr>
<th>Entry</th>
<th>1:PhCH2OH</th>
<th>Eq of lactide</th>
<th>Time (h)</th>
<th>Conversion %</th>
<th>$^cM_n^{th}$ (10^3)</th>
<th>$^dM_n^{exp}$ (10^3)</th>
<th>$^dD$</th>
</tr>
</thead>
<tbody>
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<td>3.4</td>
<td>1.48</td>
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</table>

*aReaction conditions: [Mg] = 10 µmol; DCM = 10 mL. *bConversion of lactide determined by $^1$H NMR spectroscopy (400 MHz, CDCl3) of the reaction mixture. *cCalculated $M_n$ of PLA (in gmol⁻¹) = 144.14 x ([LA]/([Mg]+[PhCH2OH])) x conversion LA. *dExperimental $M_n$ (corrected using factor 0.58) and $D$ values were determined by GPC analysis in THF using polystyrene standards.

In order to observe the end groups of the polymer chains, a polymerization experiment was carried out in the presence of 25 equivalents of the monomer. The sample was analyzed by $^1$H NMR (see Figure G.9 in Appendix G) which showed the presence of HOCH(CH3)CO- and -CH(CH3)COOH terminal groups as prevailing chain end groups.118 The HOCH(CH3)CO- groups can be generated during the termination reaction by the hydrolysis of the metal-growing chain bond while the formation of the carboxylic acid end groups can be attributable both to the hydrolysis of the magnesium-alkoxide bond by reaction with adventitious molecules of water and...
to chain transfer reactions occurring during the polymerization reaction in which water molecules act as the chain transfer agent.

$^1$H NMR analysis of the methine region of the homonuclear decoupled protonic spectra of the polymer samples obtained from rac-lactide showed the formation of atactic polymers (see Figure G.8. in Appendix G), as predictable by considering the non chiral nature of the catalyst.

Overall, LA polymerization activity exhibited by Mg(OR)$_2$(THF)$_2$ appears similar to the LA polymerization activity exhibited by a related Mg(OCPh$_3$)$_2$(THF)$_2$ complex, reported by Cui, Chen, and coworkers.$^{108}$ Following these experiments, we turned to investigate ROCOP.

7.4. Reactivity of Mg(OC'tBu$_2$Ph)$_2$(THF)$_2$ Towards Ring-Opening Copolymerization of Epoxide and Anhydride and Characterization of the Resulting Polymers

Ring-opening copolymerization was done with collaboration with Prof. Mazzeo group Department of Chemistry and Biology of the University of Salerno, Italy.

7.4.1 Copolymerization of CHO with Cylic Anhydrides

Initially, we explored the copolymerization of cyclohexene oxide (CHO) with phthalic (PA) and succinic anhydride (SA) using the magnesium complex 17 under different reaction conditions (Scheme 7.1). The polymers produced were characterized by $^1$H NMR, GPC and MALDI-ToF-MS analyses. Selected data are reported in Table 7.6. The composition of the obtained polymers was estimated by $^1$H NMR analysis, by comparing the integrals of the signals of epoxide/anhydride sequences with those of sequential enchainment of epoxides.
Scheme 7.1. Synthesis of polyesters from cyclohexene oxide (CHO) and succinic (SA) or phthalic anhydride (PA).

Table 7.6. Ring Opening co-Polymerization promoted by Mg(OR)$_2$(THF)$_2$.$^{a}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Anhydride (equiv)</th>
<th>CHO (equiv)</th>
<th>Cocat (equiv)</th>
<th>Time (h)</th>
<th>T (°C)</th>
<th>$^{b}$conv. (%)</th>
<th>$^{c}$Ester (%)</th>
<th>$^{d}$M$_n$ (KDa)</th>
<th>$^{e}$</th>
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<td>&gt;99</td>
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<td>BnOH(1)</td>
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<td>&gt;99</td>
<td>5.9</td>
<td>1.33</td>
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<td>3$^e$</td>
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<td>BnOH(1)</td>
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<td>110</td>
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<td>1.8</td>
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<td>250</td>
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<td>1.16</td>
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<tr>
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<td>250</td>
<td>PPNCl (1)</td>
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<td>68</td>
<td>93</td>
<td>1.7</td>
<td>1.24</td>
</tr>
<tr>
<td>7</td>
<td>SA (100)</td>
<td>800</td>
<td>BnOH(1)</td>
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<td>110</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>4.6</td>
<td>1.22</td>
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</table>

$^a$Reaction conditions: Mg = $1.0 \times 10^{-5}$ mol; solvent = 1 mL of toluene. $^b$Conversion of anhydride determined by $^1$H NMR spectroscopy (400 MHz, CDCl$_3$) of reaction mixture. $^c$Determined by integrating the normalized resonances for ester linkages (4.80–5.26 ppm) and ether linkages (3.22–3.64 ppm). $^d$Experimental $M_n$ and $D$ values were determined by GPC analysis in THF using polystyrene standards. $^e$Solvent free.

The ring-opening copolymerization of phthalic anhydride and cyclohexene oxide using the magnesium complex 17 as a catalyst in the presence of benzyl alcohol (BnOH) was investigated (entry 1, Table 7.6). Initially, an epoxide: anhydride: catalyst ratio of 100:100:1, with the concentration of both monomers at 1.0 M in toluene solution was used. Under these reaction conditions, the catalytic activity was relatively low, comparable with that obtained with the bimetallic magnesium catalyst reported by Williams for which 19 equiv. of PA were converted in 22 h at 100 °C producing a polyester with about 20% of ether junctions.$^{119}$ Surprisingly, the poly(1,2-cyclohexylene-1,2-phthalate) obtained by 17 showed a perfectly alternating structure, with a percentage of ether linkages lower than of 0.3% (see Figure 7.3). A significant increase of
the catalytic activity was registered when the copolymerization was performed in the presence of an excess of cyclohexene oxide (entry 2, Table 7.6), in agreement with the well-documented first-order dependence of ROCOP with respect to the epoxide monomer.\textsuperscript{120} However, even under these reaction conditions, the selectivity was preserved. In contrast, when the polymerization was performed in the absence of solvent, the percentage of ester linkages decreased dramatically (entry 3, Table 7.6).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7_3}
\caption{\textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6} 298 K) of PA/CHO copolymer obtained in entry 1 of Table 7.6.}
\end{figure}

Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF MS) was used in order to confirm the chain end-group fidelity. For samples obtained in the presence of benzyl alcohol, two major distributions were observed attributable to a full polymeric repeat unit or a half polymeric repeat unit (i.e., one extra epoxide incorporated on the chain end), as expected from an alternating copolymerization system. The end-groups for both major distributions were calculated to correspond to BnOH initiation (Figure 7.4). A third family of
signals of lower intensity was observed for polymer chains having as chain end groups the alkoxy fragment originally coordinated to the magnesium center.

To gain additional insight about the initiation steps, a polymerization experiment in the absence of alcohol, under the same reaction conditions described by entry 1, was performed. After 96 h, a conversion of 46% of PA was achieved, showing an activity lower than that obtained in the presence of BnOH. The NMR analysis of the polymer revealed the production of copolymer with a perfectly alternating structure and a percentage of polyether sequences lower than 1%. As for the chain-end group analysis, OH end-capped chains were the prevailing product while the percentage of polymeric chains with OR ligand as the chain-end group was less than 5% (see Figure G.15 in Appendix G). A reasonable hypothesis about the initiation step is that the first opening of the epoxide was mainly performed by the nucleophilic species that are present in the polymerization medium (such as alcohol or as traces of water) while the insertion on the metal-ligand bond is only a sporadic phenomenon.

**Figure 7.4.** MALDI-ToF-MS spectrum of PA/CHO copolymer synthesized by 17 (entry 1, Table 7.6).
According to several reports, various metal catalysts exhibit remarkably higher activity and selectivity when used in combination with a cocatalyst that is neutral nucleophilic species such as 4-(dimethylamino)pyridine (DMAP) or onium salts such as bis(triphenylphosphine)iminium chloride (PPNCl). Thus, the copolymerization reactions of CHO/PA were subsequently performed by using complex 17 in combination with one equivalent of PPNCl. As expected, the presence of the onium salt had beneficial effects on the catalytic activity: at 100 °C, after 24 hours, the magnesium catalyst 17 was able to convert about 207 equivalents of both monomers (entry 4, Table 7.6). Surprisingly, the catalytic system formed by 17 and PPNCl revealed to be less selective, producing a polymer containing a moderate percentage of ether linkages. A lower activity was observed when the reaction was performed at lower temperature (entry 5, Table 7.6) with a moderate benefit on the selectivity.

![Figure 7.5. MALDI-ToF-MS spectrum of PA/CHO copolymer synthesized by 17/PPNCl (entry 5, Table 7.6).](image-url)
The MALDI-ToF spectrum of polymer obtained by 17/PPNCl (Figure 7.5) showed clearly patterns for polymer chains with a significantly higher CHO than PA content, coherently with that observed from $^1$H NMR analysis. Two families of distributions were detected corresponding to ligand or OH end-capped chains (designed by circles and triangles, respectively). Neither linear polymer chains with Cl end groups nor cyclic polymers were detected. This could mean that the initiation reactions in the ROCOP of CHO with PA are performed by different groups depending on the nature of the cocatalyst: when BnOH was used, the first nucleophilic attack was performed preferentially by the exogeneous alcohol. In the presence of PPNCl, the nucleophilic attack was performed by the traces of water or by the alkoxide ligand OR originally coordinated to magnesium. Therefore, in contrast to the other catalytic systems, the chlorine atom of PPNCl was not an efficient initiating group.

Subsequently, the reactivity of complex 17 was extended to the copolymerization of cyclohexene oxide with succinic anhydride (SA). Under the same reaction conditions explored for PA, complex 17 showed an analogous behavior: the polymerization was selective only when BnOH was used as activator (entry 6 vs entry 7, Table 7.6).

The GPC analysis of all obtained polymers displayed distributions with moderately narrow dispersities ($D<1.33$). The number average molecular weight values ($M_n$) measured by GPC (without any calibration correction) were always lower than the theoretical ones expected for a living system. This could be a consequence of the presence of protic impurities present within monomers that can act as chain transfer agents.
7.4.2. Copolymerization of Phthalic Anhydride with Limonene Oxide

Scheme 7.2. Synthesis of polyesters from limonene oxide (LO) and phthalic anhydride (PA).

Considering the structural analogy between CHO and LO (limonene oxide), we decided next to explore the reactivity of the commercial LO, a mixture of cis and trans R isomers, derived mainly from the R-limonene isomer present in orange oils (Scheme 7.2). As a monomer, it has been used in the copolymerization with CO$_2$ and, less frequently, with cyclic anhydrides. Complex 17, activated by PPNCl, showed a good activity in toluene solution (entry 1, Table 7.7). The catalyst did not show any preference toward one of the two isomers of limonene oxide. A similar activity was achieved by using benzyl alcohol as activator (entry 2, Table 7.7).

Table 7.7. Ring Opening co-Polymerization of LO promoted by Mg(OR)$_2$(THF)$_2$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>PA (equiv)</th>
<th>CHO (equiv)</th>
<th>LO (equiv)</th>
<th>Time (h)</th>
<th>bPA conv. (%)</th>
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<tr>
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<td>-</td>
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<td>45</td>
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<td>72</td>
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</tr>
</tbody>
</table>

a Reaction conditions: [PA]: [LO]: [Mg]: [PPNCl] = 250:250:1:1 and Mg = 1.0 $\times$ 10$^{-5}$ mol; Solvent = 1 mL of toluene. T=80 °C b Determined by $^1$H NMR spectroscopy (400 MHz, CDCl$_3$) of crude reaction. c BnOH was used as cocatalyst instead of PPNCl.
The H NMR analysis of the obtained copolymer (Figure 7.6) confirmed the absence of ether linkages, as expected because of the bulky nature of LO. The microstructure of the LO/PA copolymer, elucidated by the $^{13}$C NMR analysis (Figure 7.7), showed an atactic polymer, coherently with the achiral structure of the catalyst.

Next, the catalytic activity of complex 17 in the terpolymerization of phthalic anhydride with both epoxides, CHO and LO, was tested (entry 3, Table 7.7). The reaction was performed under the same reaction conditions used for the related copolymerizations and monitored by H NMR. Aliquots of the reaction mixture were taken at different times to evaluate the conversions of all the monomers. After 24 hours a conversion of about 30% of CHO was achieved while no conversion of LO was observed. The intensity of resonances of the anhydride within the polymer was consistent with the intensity of resonances of the CHO reacted. After 48 hours, conversions of 60% of CHO, 18% of LO and 40% of PA were achieved (18 LO and 40 PA). After additional 24 hours, an almost complete conversion of CHO was achieved (95%) while the conversions of
LO and PA were 44% and 61%, respectively. During terpolymerization, the rate of incorporation of cyclohexene oxide was faster compared with that of limonene oxide. Thus, the CHO incorporation was preferred although a gradual consumption of LO was observed, as evident by evaluating the conversions of the two epoxides versus time. These data supported the hypothesis of gradient microstructure for the terpolymer in which a gradual change in epoxide composition from CHO predominantly to predominantly LO. The $^1$H NMR spectrum of the crude polymer accounted for a terpolymer containing a 1:1.4 ratio of LO and CHO (Figure 7.8).

**Figure 7.7.** $^{13}$C NMR (100 MHz, CDCl$_3$ 298 K) of PA/LO copolymer obtained in entry 1 of Table 7.5.

GPC analysis of the obtained polymer revealed a bimodal molecular weight distribution. To clarify if the obtained sample was a mechanical mixture of the two copolymers or a true terpolymer a DOSY experiment was performed (Figure 7.9). The DOSY experiment showed that the signals of all the monomeric units lay at the same diffusion coefficient, and therefore belonged to the same polymeric chains, thus confirming the formation of a terpolymer.
Figure 7.8. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) of PA/CHO-PA/LO copolymer obtained in run 2 of Table 7.5.

Figure 7.9. $^2$D DOSY NMR (600 MHz, CDCl$_3$, RT) of poly[[cyclohexene phthalate]-block-\textendash poly[[limonene phthalate]].
7.4.3. Copolymerization of Limonene Oxide with Dihydrocoumarin

Finally, aiming to develop novel functional polymers, we tested the reactivity of complex 17 in the copolymerization of LO with dihydrocoumarin, an aromatic 6-member lactone that cannot be homopolymerized by ROP because of the low ring strain. The copolymer of LO with dihydrocoumarin is an attractive material: since both monomers are derived from renewable resources, this product represents an example of totally biorenewable polyester.

Scheme 7.3. Synthesis of polyesters from limonene oxide (LO) and dihydrocoumarin (DHC).

Because of the low reactivity of both monomers, the reaction was performed at high temperature (100 °C) for seven days. After this time, a solid product was obtained after precipitation in wet hexane. The polymer was analyzed by NMR spectroscopy and MALDI ToF. The $^1$H NMR analysis of the reaction mixture demonstrated a polymeric chain with an alternating sequence of the two monomers. The alternating structure was confirmed by the MALDI-ToF-MS spectrum (Figure G.14 in Appendix G). No stereoselectivity for the incorporation of a specific stereoisomer of limonene oxide was observed. The opening of the epoxide was not regioselective as demonstrated by the presence of two different signals for the methine proton of the limonene portion (protons 1 and 2 of Figure G.10, see also Figure G.13 in Appendix). This was further confirmed by the presence of two signals for the corresponding methine carbons. A complete assignment of the resonances of the $^{13}$C spectrum was also performed (Figure G.14 in Appendix).

The thermal stability of the oligomeric sample of DHC/LO (as determined through
thermogravimetric analysis (TGA) showed a complete degradation obtained at temperature higher than 270 °C (see Figure G.16 in Appendix).

Figure 7.10. $^1$H NMR (600 MHz, CDCl$_3$, 298 K) of DHC/LO copolymer.

7.5. Summary and Conclusions

We have reported synthesis, ROP, and ROCOP with a new well-defined mononuclear magnesium complex Mg(OR)$_2$(THF)$_2$ (OR = OC‘Bu$_2$Ph). The complex led to active albeit not well controlled ROP of lactide precursor; utilization of coordinating solvent (THF) or benzyl alcohol as a co-catalyst leads to somewhat better control of polymerization. In contrast, well-behaved ROCOP was obtained with a variety of different monomers. While the use of PPNCl as nucleophilic initiator leads to an efficient copolymerization CHO with PA or SA, the structure of the resulting copolymers was found to be only moderately alternating, demonstrating small amount of ether linkages. In contrast, the use of BnOH as an initiator forms perfectly alternating copolymer of PA with CHO. More challenging biorenewable monomer, LO, was also co-polymerized with PA. The combination of PA with both CHO and LO leads to the formation of terpolymer, whose integrity was confirmed by DOSY. Finally, the combination of two biorenewable precursors, LO
and dihydrocumarin, formed a fully biorenewable novel copolymer. No stereoselectivity was observed in all the above reactions, likely due to the achiral nature of the catalyst. Our future plans include investigation of additional monomers, as well as the design of chiral metal pre-catalysts, which could lead to the stereospecific enchainment of monomers in the copolymer structure.

7.6. Experimental Section

7.6.1 General

All reactions involving air-sensitive materials were carried out in a nitrogen-filled glovebox. Di-tert-butyl-phenylmethanol (HOR) were synthesized according to previously published procedures.\textsuperscript{134} n-Butyl-sec-butylmagnesium (0.7 M solution in hexane) was purchased from Sigma and used as received. All non-deuterated solvents were purchased from Aldrich and were of HPLC grade. The non-deuterated solvents were purified using an MBraun solvent purification system. C\textsubscript{6}D\textsubscript{6} and CDCl\textsubscript{3} were purchased from Cambridge Isotope Laboratories. rac-Lactide was obtained from Sigma Aldrich and purified by recrystallization from toluene, following by drying over P\textsubscript{2}O\textsubscript{5} for 72 h, as previously described.\textsuperscript{135,136} CHO was purchased from Aldrich and purified by distillation by CaH\textsubscript{2}. Anhydrides were purchased from Aldrich and purified by crystallization from toluene. All solvents were stored over 3 Å molecular sieves. Complexes were characterized by \textsuperscript{1}H and \textsuperscript{13}C NMR, X-ray crystallography, and elemental analysis. NMR spectra for metal complexes were recorded at the Lumigen Instrument Centre (Wayne State University) on an Agilent 400 and 600 MHz spectrometers in C\textsubscript{6}D\textsubscript{6} at room temperature. Chemical shifts and coupling constants (\textit{J}) were reported in parts per million (\textit{\delta}) and Hertz respectively. Elemental analysis was performed under ambient air-free conditions by Midwest Microlab LLC.

The molecular weights (\textit{M}_\text{n} and \textit{M}_\text{w}) and the molecular mass distribution (\textit{Đ}) of polymer samples were measured by gel permeation chromatography (GPC) at 30 °C using THF as the solvent, a flow rate of the eluent of 1 mL min\textsuperscript{-1}, and narrow polystyrene standards as the reference. The
measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four Styragel columns (range 1000–100000 Å). GPC analyses were done at the Department of Chemistry and Biology of the University of Salerno.

Mass spectra were acquired using a Bruker solariX XR Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 T refrigerated actively-shielded superconducting magnet (Bruker Biospin, Wissembourg, France). The polymer samples were ionized in positive ion mode using the MALDI ion source. The mass range was set to m/z 200 – 5000. The laser power was 12% and 18 laser shots were used for each scan. Mass spectra were calibrated externally using a mix of peptide clusters in MALDI ionization positive ion mode. A linear calibration was applied. The polymer samples were dissolved in THF at a concentration of 1 mg/mL. The cationization agent used was potassium trifluoroacetate (Fluka, > 99 %) dissolved in THF at a concentration of 5 mg/mL. The matrix used was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (Fluka) and was dissolved in THF at a concentration of 40 mg/mL. Solutions of matrix, salt and polymer were mixed in a volume ratio of 4:1:4, respectively. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry.

7.6.2. X-ray Crystallographic Details

The structures of Mg(OR)(sec-Bu)(THF)$_2$ (18) and Mg(OR')$_2$(THF)$_2$ (19) were determined by X-ray crystallography; the structure of Mg(OR)$_2$(THF)$_2$ was previously reported, by Dr. Thilini Hollingsworth. A Bruker APEXII/Kappa three circle goniometer platform diffractometer with an APEX-2 detector was used for data collection. A graphic monochromator was employed for the wavelength selection (MoKα radiation, λ = 0.71073 Å). The data were processed, and the structure was solved using the APEX-2 software. The structure was refined by standard difference Fourier techniques with SHELXL (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms were placed in calculated positions using a standard riding model and refined
isotropically; all other atoms were refined anisotropically. The structure of 18 contained disordered sec-butyl group; the disorder was modeled using two alternating positions. Detailed crystal and structure refinement data are given in Table 7.1.

7.6.3. Preparation of Mg(OR)(sec-butyl)(THF)₂ (18)

A 1 mL solution of HOR (142 mg, 0.64 mmol, 1.0 equiv.) in diethyl ether and a 0.92 mL solution of Mg(n-butyl)(sec-butyl) (89 mg, 0.64 mmol, 1.0 equiv.) in hexane were prepared. The solution of HOR was then added dropwise to a stirring solution of Mg(n-butyl)(sec-butyl). 0.5 ml of THF was then added to the reaction mixture. The reaction mixture was stirred for 2 hours, upon which the volatiles were removed in vacuo. X-ray quality crystals were obtained from a saturated hexane solution of Mg(OR)(sec-Bu)(THF)₂ kept at −35 °C (254 mg, 0.57 mmol, 89%). ¹H NMR (C₆D₆, 600 MHz) δ 8.14 (d, 3J_HH = 8.2 Hz, 1H), 7.93 (d, 3J_HH = 8.2 Hz, 1H), 7.43 (m, 1H), 7.24 (m, 2H), 3.62 (m, 8H), 2.15 (m, 2H), 1.78 (d, 3J_HH = 7.81 Hz, 3H), 1.42 (t, 3J_HH = 7.2 Hz, 3H), 1.35 (s, 18H), 1.26 (m, 8H), 0.19 (q, 3J_HH = 7.4 Hz, 1H); ¹³C{¹H} NMR (C₆D₆, 150 MHz) δ 153.59, 129.35, 128.81, 124.92, 124.29, 83.47, 68.66, 42.48, 33.10, 31.03, 24.82, 22.02, 19.11, 17.13. Anal. Calcd for C₃₈H₆₂MgO₄: C, 72.88; H, 10.87. Found: C, 72.92; H, 10.65.

7.6.4. Preparation of Mg(OR)₂(THF)₂ (17) via the Reaction of Mg(OR)(sec-butyl)(THF)₂ (18) with HOR

A 1 mL solution of HOR (176.2 mg, 0.397 mmol, 1.0 equiv) in diethyl ether and a 1 mL solution of Mg(OR)(sec-butyl)(THF)₂ (18, 87.0 mg, 0.395 mmol, 1.0 equiv.) in THF were prepared. The solution of HOR was then added dropwise to a stirring solution of Mg(OR)₁(sec-butyl)(THF)₂. The reaction mixture was stirred for 2 hours, upon which the volatiles were removed in vacuo. Colorless crystals of 17 were obtained from a saturated diethyl ether solution kept at −35 °C (228.5 mg, 0.376 mmol, 95%). The nature and purity of the product was confirmed by its ¹H NMR spectrum, identical to the spectrum of 17 described above.
7.6.5. Preparation of Mg(OR’)\(_2\) (THF)\(_2\) (19)

A 1 mL solution of HOR’ (142 mg, 0.38 mmol, 2.0 equiv.) in THF and a 1 mL solution of Mg(n-butyl)(sec-butyl) (27 ml, 0.19 mmol, 1 equiv.) in hexane were prepared. The solution of HOR’ was then added dropwise to a stirring solution of Mg(n-butyl)(sec-butyl). 0.5 ml of THF was then added to the reaction mixture. The reaction mixture was stirred for 2 hours, upon which the volatiles were removed in vacuo. The resulting oily solid was extracted to diethyl ether, filtered and concentrated in vacuo to about 0.5 ml. X-ray quality crystals were obtained from a saturated diethyl ether solution of Mg(OR)\(_2\) (THF)\(_2\) kept at −35 °C (161 mg, 0.18 mmol, 93%). \(^{1}\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz) \(\delta\) 8.18 (s, 2H), 7.94 (s, 2H), 7.69 (d, \(^{3}\)J\(_{HH}\) = 8.0 Hz, 4H), 7.59 (d, \(^{3}\)J\(_{HH}\) = 8.0 Hz, 4H), 7.53 (s, 2H), 7.47 (t, \(^{3}\)J\(_{HH}\) = 8.0 Hz, 4H), 7.42 (t, \(^{3}\)J\(_{HH}\) = 8.0 Hz, 4H), 7.35 (t, \(^{3}\)J\(_{HH}\) = 8.0 Hz, 4H), 4.02 (m, 8H), 1.73 (m, 8H), 1.14 (s, 36H); \(^{13}\)C\\(_{\{^1\}H}\) NMR (C\(_6\)D\(_6\), 100 MHz) \(\delta\) 155.13, 143.93, 143.18, 140.26, 138.33, 129.27, 128.93, 128.20, 128.03, 127.76, 127.32, 122.81, 84.48, 70.84, 42.99, 31.66, 25.63. Anal. Calcd for C\(_{38}\)H\(_{62}\)MgO\(_4\): C, 81.69; H, 8.62. Found: C, 81.53; H, 8.46.

7.6.6. Lactide Polymerization

Dichloromethane/toluene solution of 10 μmol catalyst was mixed with a solution containing 100 equivalents (144 mg) of lactide in dichloromethane/toluene (total volume of the reaction was 10 mL, [LA] = 0.1 M). Reaction was stirred in room temperature for a given time (Table S1), after which it was stopped by adding 2-5 mL of methanol. PLA was precipitated in methanol and washed with excess methanol to remove all the impurities. For further purification, the polymer was dissolved using minimal amount of DCM and then added to 20 mL of methanol to precipitate pure PLA. Excess methanol was decanted, and the polymer was dried for 1 hour under vacuum. The reaction with 200 and 300 equivalents of lactide (0.2 M and 0.3 M, respectively) in dichloromethane and toluene solutions was carried out in a similar fashion (Table
S1). The resulting polymer was characterized by $^1$H NMR spectroscopy, to determine the nature of the end groups and polymerization degree. The methine region was also analyzed by homonuclear decoupled $^1$H NMR, to determine the tacticity of the polymer.

7.6.7. Copolymerization of Epoxides with Cyclic Anhydrides

In a Braun Labmaster glovebox, a magnetically stirred reactor vessel (10 mL) was charged with the anhydride. Subsequently, a solution of catalyst, cocatalyst and epoxide in 1 mL of toluene was added. The reaction mixture was stirred at 110 °C. At desired times, small aliquots of the reaction mixture were sampled, dissolved in CDCl$_3$ and analyzed by $^1$H NMR spectroscopy. At the end of the polymerization, the product was dissolved in CH$_2$Cl$_2$, precipitated in wet hexane and dried under vacuum oven. All analyses were performed on crude samples.
8.1. Introduction

As discussed in the Introduction to this thesis (Chapter 1), the properties of a polymer depend on its tacticity, a relative stereochemistry of the nearby stereocenters. Typically, polymers with ordered tacticity (isotactic or syndiotactic) exhibit better properties compared with polymers featuring random tacticity (atactic). Synthesis of polymers featuring ordered tacticity require mechanism of a chiral recognition (or enchainment) of an incoming monomer. There are two chiral recognition mechanisms: (1) enantiomorphic site control, and (2) chain-end control mechanism.\(^{137}\) In the chain-end control mechanism, the stereochemistry of the incoming monomer will be determined by the last inserted monomer unit. Chiral catalyst environment determines the stereochemistry of the incoming monomer in the enantiomorphic site control mechanism.\(^{137}\) Enantiomorphic site-control mechanism in polymerization is similar to the asymmetric induction mechanism in stereoselective catalysis and is the more common and the well-defined method to design stereoselective polymerization catalyst. Gao and coworkers reported series of chiral aluminum catalysts for stereoselective polymerization of a racemic lactide.\(^{138}\) Hayes and coworkers introduced zinc complexes with chiral phosphinimine scaffold for stereoselective polymerization of racemic lactide.\(^{139}\) Aiming to introduce a new type of stereoselective, efficient, and sustainable polymerization catalysts, we have designed new magnesium alkoxide complexes bearing simple chiral alkoxide ligands.

In this chapter, we describe the synthesis of series of new chiral alkoxide ligands towards asymmetric catalysis. The synthesis, coordination chemistry, and reactivity of the respective chiral magnesium complexes with selected ligands are also explored. Specifically, catalytic
polymerization studies of lactide, caprolactone and two macrolactones, \(\omega\)-pentadecalactone (PDL) and \(\omega\)-hexadecenlactone (HDL) (Scheme 8.1) by a chiral magnesium complex are reported, and its reactivity is compared with an achiral \(\text{Mg(OC}^\text{tBu}_2\text{Ph)}_2(\text{THF})_2\) complex described in Chapter 7. Lactone polymerization was done in collaboration with the Mazzeo group in the Department of Chemistry and Biology at the University of Salerno.

\[ \text{PDL} \]

\[ \text{6HDL} \]

**Scheme 8.1.** Structures of macrolactones

### 8.2. Synthesis of Chiral Alkoxide Ligands

To design well-defined mononuclear chiral magnesium alkoxide complexes, a bulky and asymmetric alkoxide ligand environment is needed. An alkoxide ligand \([\text{OCR}_3]\) has three substituents at the central carbon. An alkoxide with three different substituents is a chiral molecule. It is anticipated that these substituents need be sufficiently sterically different to create an
asymmetric environment ("steric gradient") at the metal. Overall, our design included one very large aliphatic (1-adamantyl) substituent, a smaller aliphatic substituent (‘Bu or Me), and an aromatic (phenyl/aryl) group with varying substitution in the meta positions. The adamantyl group was used to maintain the overall bulkiness of the ligand, and to create steric gradient. The phenyl/aryl group was used to maintain the crystallinity of the ligand. While the methyl group is much smaller than adamantyl, even the larger ‘Bu group is sufficiently different from the adamantyl group (Figure 8.1) to maintain the overall steric gradient within the [OCR\textsuperscript{1}R\textsuperscript{2}R\textsuperscript{3}] ligand. Overall, 8 different chiral alkoxide ligands (Figure 8.2) were designed, synthesized, and fully characterized. The synthetic strategy towards all ligands involved initial synthesis of the Ad(R)C=O (1-adamantyl tert-butyl ketone or 1-adamantyl methyl ketone), followed by a nucleophilic attack of the appropriate aryl lithium reagent. 1-Adamantyl tert-butyl ketone and 1-adamantyl methyl ketone were synthesized by the reaction between 1-adamantyl carboxylic acid and tert-butyl lithium, using a modification of a previously published procedure.\textsuperscript{140} The synthesis of specific ligands is discussed in details below.
Figure 8.2. Chiral alkoxide ligands

Ligand 20 (Scheme 8.2) and 21 (Scheme 8.3) were synthesized by the addition of phenyl lithium to 1-adamantyl tert-butyl ketone or 1-adamantyl methyl ketone, followed by the extraction with hexane and water.

Scheme 8.2. Synthesis of chiral ligand 20
Scheme 8.3. Synthesis of chiral ligand 21

Ligands 22-24 (Scheme 8.4) were synthesized by treatment of ArBr precursors with two equivalents of t-butyllithium followed by its subsequent in-situ addition to 1-adamantyl tert-butyl ketone to form lithium salt of the ligand. Ligands 25-27 (Scheme 8.5) were synthesized by treatment of ArBr precursors with two equivalents of t-butyllithium followed by its addition to 1-adamantyl methyl ketone to form the lithium salt of the ligand. Subsequent extraction with hexane and water gives protonated ligands 22-27 as yellowish white color residues. The products were purified via column chromatography using 1% ethyl acetate/hexane as eluent. The ligands were characterized using ¹H and ¹³C NMR spectroscopy, and HRMS. Ligands 20, 24, 25, and 27 were also characterized by X-ray crystallography (Figure 8.3 and Figure 8.4) which confirmed their overall connectivity. As all ligands were obtained as racemic mixtures, all crystall structures were centrosymmetric.
**Figure 8.3.** ORTEP diagram of the X-ray structure of 20 (left) and 24 (right). H atoms were omitted for clarity.

**Scheme 8.5.** Synthesis of ligand 25-27
Figure 8.4. ORTEP diagrams of the X-ray structure of 25 (left) and 27 (right). H atoms were omitted for clarity.
### Table 8.1. Experimental crystallographic parameters for 20, 24, 25 and 27

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8.3. Synthesis of the Magnesium Complexes

The synthesis of \( \text{Mg} (\text{OCAd}'\text{BuPh})_2(\text{THF})_2 \) (complex 28) was performed via the treatment of \( \text{n-butyl-sec-butylmagnesium} \) (0.7 M solution in hexane) with two equivalents of the racemic mixture of \( \text{HOCA}d'\text{BuPh} \) (Figure 8.5).

Figure 8.5. The synthesis and the structure (side view and top view) of complex 28. Only one enantiomer of the structure is shown. Selected bond distances (Å) and angles (º) for 28: Mg O1 1.842(4), Mg O2 1.831(4), O1 Mg O2 131.21(15), O3 Mg1 O4 90.53(14).

Complex 28 was characterized by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy, X-ray crystallography, and elemental analysis. The spectroscopic and analytical characterization are consistent with the \( \text{Mg} (\text{OCAd}'\text{BuPh})_2(\text{THF})_2 \) composition. \(^1\text{H}\) NMR spectrum of complex 28 demonstrates five aromatic signals for the ligand phenyl group, consistent with its restricted rotation, as previously described for \( \text{Mg}(\text{OC}'\text{Bu}_2\text{Ph})_2(\text{THF})_2 \) (see Chapter 7). Two \('\text{Bu}\) groups give rise to one singlet. The presence of one signal for both \('\text{Bu}\) groups and five signals for the two phenyl groups suggest the presence of a single diastereomer in solution. In general, the combination of a racemic mixture of the ligand can lead to two different diastereomers in the resulting \( \text{Mg} (\text{OCAd}'\text{BuPh})_2(\text{THF})_2 \)
product, a homochiral isomer of an approximate $C_2$ symmetry (mixture of $\text{Mg(OC}^\text{R} \text{Ad'}BuPh)}_2(\text{THF})_2$ and $\text{Mg(OC}^\text{S} \text{Ad'}BuPh)}_2(\text{THF})_2$ enantiomers) and a $\text{meso}$ isomer of an approximate $C_5$ symmetry ($\text{Mg(OC}^\text{R} \text{Ad'}BuPh)}(\text{OC}^\text{S} \text{Ad'}BuPh)(\text{THF})_2$). Due to their different physical properties, different diastereomers should give rise to different NMR spectra. The presence of a single species in solution indicates some sort of chiral resolution of the ligands to create a single diastereomer.

The solid-state structure of 28 clearly demonstrate the formation of a single homochiral diastereomer of $C_2$ symmetry, consistent with the spectroscopic data. The structure is given in Figure 8.5 and selected bond distances and angles are provided in the figure caption. Overall, the structure of 28 is in line with all previous structures of $\text{M(OR)}_2(\text{THF})_2$ complexes, including a closely related magnesium complex $\text{Mg(OC}^\text{t} \text{Bu}_2 \text{Ph)}_2(\text{THF})_2$ (17) in Chapter 7. Similarly to $\text{Mg(OC}^\text{t} \text{Bu}_2 \text{Ph)}_2(\text{THF})_2$, complex 28 exhibit distorted tetrahedral geometry, with a narrow THF-Mg-THF angle of 90.53 °, and a broader RO-Mg-OR/RO-Mg-C angle of 131.21 °. Complex 28 exhibits crystallographic $C_2$ symmetry; the $C_2$-symmetric structure of 28 is similar to the $C_2$-symmetric $\text{Mg(OC}^\text{t} \text{Bu}_2 \text{Ph)}_2(\text{THF})_2$ complex reported in Chapter 7. However, $\text{Mg(OC}^\text{t} \text{Bu}_2 \text{Ph)}_2(\text{THF})_2$ was achiral. In contrast, the $C_2$ symmetry of $\text{Mg(OCAd'}BuPh)}_2(\text{THF})_2$ implies the presence of the homochiral diastereomer. We postulate that the structure of $\text{Mg(OCAd'}BuPh)}_2(\text{THF})_2$ contains $C_2$-symmetric diastereomerically pure complexes ($RR$ and $SS$) with the same chirality on one metal center as a result of the steric gradient of the ligand, that pushes large adamantyl groups away from each other. One of the enantiomers ($RR$) is shown in Figure 8.5; the presence of the other enantiomer is implied by the centrosymmetric nature of the space group ($P-1$).
In contrast, ligand [OCAdMePh] ligand did not exhibit clean separation of the enantiomers at the magnesium center, likely due to a drastic decrease of the size of one of substituents from 'Bu to Me. While the overall steric gradient between the R groups is improved, the overall steric bulk of the alkoxide is decreased significantly, which likely leads to a less tight binding. The $^1$H NMR spectrum of Mg(OCAdMePh)$_2$(THF)$_2$ shows the presence of several species in the mixture, consistent with the presence of different diastereomers. Our attempt to separate the mixture of products led to the isolation of a dimeric species Mg$_2$(OCAdMePh)$_2$(sec-Bu)$_2$(THF)$_2$, (29) which was obtained in a very low yield and therefore characterized only by X-ray crystallography. The X-ray structure of Mg$_2$(OCAdMePh)$_2$(sec-Bu)$_2$(THF)$_2$ (29) reveals mixed chirality on the nearby magnesium center (RS).

Figure 8.6. ORTEP diagram of the X-ray structure of Mg$_2$(OCAdMePh)$_2$(sec-Bu)$_2$(THF)$_2$ 29. H atoms were omitted for clarity.
Table 8.2. Experimental crystallographic parameters for 28 and 29.

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</tr>
<tr>
<td>$2θ$, deg</td>
<td>51.112</td>
<td>51.016</td>
</tr>
<tr>
<td>$R_1^a$ (all data)</td>
<td>0.1295</td>
<td>0.2148</td>
</tr>
<tr>
<td>$wR_2^b$ (all data)</td>
<td>0.2400</td>
<td>0.3109</td>
</tr>
<tr>
<td>$R_1^a$ [(I&gt;2σ)]</td>
<td>0.0830</td>
<td>0.0959</td>
</tr>
<tr>
<td>$wR_2^b$ [(I&gt;2σ)]</td>
<td>0.2068</td>
<td>0.2430</td>
</tr>
<tr>
<td>GOF (F$^2$)</td>
<td>1.045</td>
<td>0.982</td>
</tr>
</tbody>
</table>
8.4. Polymerization of Cyclic Esters

Following the synthesis of the chiral compound Mg(OCAd'BuPh)₂(THF)₂, its reactivity in the polymerization of cyclic esters was studied. For reactivity comparison, we have also explored the reactivity of the achiral counterpart Mg(OC'Bu₂Ph)₂(THF)₂. Aliphatic polyesters possessing long methylene sequences between ester functionalities are highly hydrophobic materials. As the tensile properties of these materials are akin to those of the linear low-density poly(ethylene), these materials are commonly referred to as “polyethylene-like”. Thus, these materials may potentially represent a biodegradable alternative to the linear low-density poly(ethylene).141-143 These polyesters can be prepared utilizing several synthetic approaches, among them polycondensation of fatty acids and ring-opening polymerization (ROP) of macrolactones promoted by metal-based or organic catalysts, or enzymes.144-149 As described in Chapter 1, the chain-growth ROP of macrolactones offers the advantages of very good control over macromolecular parameters such as molecular weights and their dispersity, end-group fidelity, regio- and stereoregularity. As a result, sophisticated architectures may be obtained.146,150-152 Recently, the synthesis of block copolyesters were reported by a chemoselective switch catalysis between ROP of macrolactones and the ring opening copolymerization of epoxides and anhydrides.153 However, macrolactones are relatively unreactive monomers, in a large part because they are sufficiently large to not exhibit strain. Therefore, they are usually hard to polymerize using traditional ROP catalysts.154,155 A common industrial catalyst for ROP of lactides, tin octanoate, is barely reactive toward the ROP of macrolactones. Since the ROP of macrolactones is an entropy-driven reaction, the polymerizations are favored by high temperature, but these drastic reaction conditions frequently promote side detrimental transesterification reactions that compromise the control over molecular masses. Relatively few metal-based catalysts active in the ROP of macrolides have been reported.
Some of these catalysts relied on early transition metals, while others contained main group metals (Zn, Al, Ca, Mg). Generally, catalysts for the ROP of cyclic esters contain heteroleptic complexes in which the metal center is coordinated by electronically and sterically tailored ancillary ligand. In addition, these complexes feature labile ligand/s that serve as initiating groups. While these catalysts are typically well-behaved, the presence of an unreactive ancillary ligand is detrimental to the overall sustainability of the catalytic system. Recent studies have demonstrated that simple inexpensive “homoleptic” metal alkyl/alkoxide compounds, often used as metal precursors in organometallic and coordination chemistry, may exhibit significantly higher reactivity due to the presence of several reactive positions. Furthermore, these catalysts are more cost-effective due to the absence of (often costly) ancillary ligands. In 2014, Chen and Cui reported a simple binary catalyst Mg\textsuperscript{a}Bu\textsubscript{2}/Ph\textsubscript{2}CHOH that showed unprecedentedly high activity, also in the presence of a large excess amount of benzyl alcohol. Zn(HMDS)\textsubscript{2} was recently described as an efficient ligand-free metal catalyst for polyesters synthesis and their degradation by alcoholysis. The ‘immortal’ ring-opening polymerization (ROP) of pentadecalactone (PDL), catalyzed by magnesium 2,6-di-tert-butyl-4-methylphenoxide (Mg(BHT)\textsubscript{2}(THF)\textsubscript{2}) was reported by Dove.

![Scheme 8.6](image)

**Scheme 8.6.** The catalysts used in the polymerization of cyclic esters

The polymerization of complex 28 (Scheme 8.6) towards racemic lactide was investigated as described in Tables 8.3 – Table 8.5. In addition, we studied the reactivity of complex 28 toward
\(\varepsilon\)-caprolactone (\(\varepsilon\)-CL). 28 showed very high activity in the ROP of cyclic esters \(\varepsilon\)-caprolactone (\(\varepsilon\)-CL) and racemic lactide (\(rac\)-LA). Some results showed a turnover frequency (TOF) up to 18000 h\(^{-1}\) in the ROP of \(rac\)-LA performed at room temperature and in methylene chloride solution. Similar high activity was achieved in the ROP of \(\varepsilon\)-CL (Table 8.3) Complex 28 was able to convert 10000 equivalents of \(rac\)-LA to PLA within 15 minutes (Table 8.4). Furthermore, complex 28 showed fast solvent-free polymerization in the presence of 10 equivalents of benzyl alcohol as co-catalyst. This study was done for both purified and unpurified \(rac\)-LA (Table 8.5). Conversion was a little higher for unpurified \(rac\)-LA than purified \(rac\)-LA.

**Table 8.3.** TOF of ROP of cyclic esters \(\varepsilon\)-caprolactone (\(\varepsilon\)-CL) and racemic lactide (\(rac\)-LA) with 28

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>Lactone (eq)</th>
<th>T (°C)</th>
<th>time</th>
<th>Conversion (%)</th>
<th>TOF (h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28</td>
<td>(rac)-LA (200)</td>
<td>25</td>
<td>2 min</td>
<td>&gt;99</td>
<td>6,0*10(^3)</td>
</tr>
<tr>
<td>2</td>
<td>28</td>
<td>(rac)-LA (200)</td>
<td>25</td>
<td>30 sec</td>
<td>70</td>
<td>1,8*10(^4)</td>
</tr>
<tr>
<td>3</td>
<td>28</td>
<td>(\omega)-CL (200)</td>
<td>25</td>
<td>30 sec</td>
<td>78</td>
<td>1,9*10(^4)</td>
</tr>
</tbody>
</table>

**Table 8.4.** Reactivity of complex 28 in ROP of \(rac\)-LA, and the resulting tacticity of the PLA.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amount of catalyst ((\mu)mol)</th>
<th>Equivalent of lactide</th>
<th>Temperature/°C</th>
<th>Time/min</th>
<th>Conversion %</th>
<th>(P_m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>100</td>
<td>25</td>
<td>2 min</td>
<td>&gt;99</td>
<td>0.491</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>200</td>
<td>25</td>
<td>2 min</td>
<td>&gt;99</td>
<td>0.554</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>300</td>
<td>25</td>
<td>2 min</td>
<td>&gt;99</td>
<td>0.539</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>600</td>
<td>25</td>
<td>10 min</td>
<td>&gt;99</td>
<td>0.529</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>1000</td>
<td>25</td>
<td>15 min</td>
<td>&gt;99</td>
<td>0.532</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>5000</td>
<td>25</td>
<td>15 min</td>
<td>&gt;99</td>
<td>0.548</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>10000</td>
<td>25</td>
<td>15 min</td>
<td>&gt;97</td>
<td>0.533</td>
</tr>
</tbody>
</table>
Table 8.5. Solvent free polymerization of rac-LA with complex 28

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cocat (equiv)</th>
<th>Eq of lactide</th>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Conversion %</th>
<th>$P_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^a$</td>
<td>BnOH(10)</td>
<td>10000</td>
<td>1</td>
<td>150</td>
<td>65</td>
<td>0.564</td>
</tr>
<tr>
<td>2$^b$</td>
<td>BnOH(10)</td>
<td>10000</td>
<td>1</td>
<td>150</td>
<td>77</td>
<td>0.559</td>
</tr>
</tbody>
</table>

$a = \text{purified racemic lactide, } b = \text{raw racemic lactide}$

The tacticity of the resulting polymer was explored using homonuclear decoupled $^1$H NMR. The methine region of the polimer was irradiated to analyze the pattern of the NMR peaks at 5.12 ppm – 5.25 ppm (see Figure H.8 in Appendix H). Examination of the NMR spectra demonstrated that catalyst 28 does not show any stereoselectivity for ROP of rac-LA (Table 8.4) by giving atactic polymers which $P_m$ values are close to 0.5. For rac-lactide, $P_m = 0.50$ describes a completely atactic PLA. In contrast, $Pr = 1.00$ ($P_m = 0.00$) and $Pm = 1.00$ ($Pr = 0.00$) describe perfect heterotactic and isotactic polymers, respectively. The obtained $P_m$ values are similar to those observed for the achiral pre-catalyst ($\text{Mg(OC'Bu}_2\text{Ph)}_2(\text{THF})_2$. The lack of tacticity in the polymer demonstrates that the polymerization is likely preceded by the exchange of the chiral alkoxide by other initiating groups (such as benzyl alcohol). While the lack of chiral “ancillary” ligands leads to a highly reactive system, it appears to have a negative effect on the tacticity.

Based on the high activities obtained in the ROP of these monomers, we decided to extend the application of these systems to the less reactive substrates including $\omega$-pentadecalactone (PDL), and $\omega$-hexadecenlactone (HDL). Polymerization data are summarized in Table 8.6. The polymers produced were all characterized by $^1$H NMR and MALDI-ToF-MS analyses. The ROP reactions were generally done in toluene solution in the presence of benzyl alcohol (BnOH) as an initiator. Monomer conversions were evaluated during the polymerization using $^1$H NMR spectroscopy, by comparing the intensity of the signal at $\delta$ 4.14 ppm, related to methylene protons.
adjacent to the ester group of the monomer, and the signal of the same protons within the polymer (at δ 4.05 ppm).

**Table 8.6. Polymerizations of macrolactones promoted by 28 and 17.**

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>Lactone (eq)</th>
<th>T (°C)</th>
<th>Time</th>
<th>Conversion (%)</th>
<th>TOF (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17</td>
<td>ω-6-HDL (200)</td>
<td>110</td>
<td>10min</td>
<td>54</td>
<td>680</td>
</tr>
<tr>
<td>2</td>
<td>17</td>
<td>ω-6-HDL (200)</td>
<td>110</td>
<td>30min</td>
<td>&gt;99</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>17</td>
<td>ω-6-HDL (200)</td>
<td>25</td>
<td>24h</td>
<td>60</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>28</td>
<td>ω-6-HDL (200)</td>
<td>110</td>
<td>10min</td>
<td>50</td>
<td>620</td>
</tr>
<tr>
<td>5</td>
<td>17</td>
<td>ω-PDL (200)</td>
<td>110</td>
<td>10min</td>
<td>48</td>
<td>600</td>
</tr>
<tr>
<td>6</td>
<td>28</td>
<td>ω-PDL (200)</td>
<td>110</td>
<td>10min</td>
<td>74</td>
<td>920</td>
</tr>
</tbody>
</table>

*Reaction conditions: [monomer]/[catalyst]=200; 10 μmol of Mg; 10 μmol of benzyl alcohol, 0.5 mL of toluene.

The magnesium complex 28 and its achiral counterpart 17 both showed high activity in the polymerization of HDL, allowing the conversion of approximately 100 equivalents of the monomer after 10 minutes (runs 1 and 4, **Table 8.6**). Remarkably high turnover frequencies (TOF) of 680 and 620 h⁻¹ were obtained for these complexes, respectively. The quantitative conversion of HDL was achieved until 30 min (run 2, **Table 8.6**). Quite surprisingly, complex 17 was able to promote the polymerization of HDL also at room temperature. These very mild reaction conditions are unusual for ROP of macrolactones. Similar activities were achieved for both catalysts 28 and 17 toward PDL, a significantly less reactive macrolactone. The ¹H NMR spectra of the polymers obtained are reported in **Figures 8.7 and 8.8**. The observed activities were much higher than those obtained with (Mg(BHT)₂(THF))₂ that, under analogous reaction conditions, was able to convert only 50 equivalents of PDL after 5 hours.²⁴ This finding suggests that the steric bulk of the alkoxide ligands has an important role in the catalytic activity, likely in the initiation step.
Figure 8.7. $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum of poly(ω-PDL).

Figure 8.8. $^1$H NMR (300 MHz, CDCl$_3$, 298 K) spectrum of poly(ω-6-HDL).

The end-group analysis through MALDI-TOF mass spectrometry of a low molecular weight sample of poly(ω-6-HDL) prepared using a low monomer/ Mg ratio =20 showed a single distribution of OBn end-capped chains (Figure 8.9) In the range of the observed masses (3500 - 8500 m/z) no cyclic polymers were detected in the spectrum.
8.5. Summary and Conclusions

Overall, 8 new chiral ligands were designed, synthesized, and fully characterized. Magnesium complex \((\text{Mg} (\text{OC}_{\text{Ad'BuPh}})(\text{THF})_2)\) of \(\text{HOCA}_{\text{Ad'BuPh}}\) was synthesized and fully characterized. The combination of a racemic mixture of the ligand leads to a homochiral isomer of \(\text{Mg}(\text{OC}^\text{R}_{\text{Ad'BuPh}})(\text{THF})_2\) and \(\text{Mg}(\text{OC}^\text{S}_{\text{Ad'BuPh}})(\text{THF})_2\) enantiomers. (\(\text{Mg}(\text{OC}_{\text{Ad'BuPh}})(\text{THF})_2\)) was a very fast catalyst for polymerization of cyclic esters but it did not show selectivity over polymerization.

8.6. Experimental Section

8.6.1. General

All reactions involving air-sensitive materials were carried out in a nitrogen-filled glovebox. \(\text{n-Butyl-sec-butylmagnesium (0.7 M solution in hexane)}\) was purchased from Sigma and used as received. All non-deuterated solvents were purchased from Aldrich and were of HPLC...
grade. The non-deuterated solvents were purified using an MBraun solvent purification system. C₆D₆ and CDCl₃ were purchased from Cambridge Isotope Laboratories. Deuterated solvents were dried over molecular sieves. rac-Lactide was obtained from Sigma Aldrich and purified by recrystallization from toluene, following by drying over P₂O₅ for 72 h, as previously described. Toluene and hexane (Sigma-Aldrich) were distilled under nitrogen over sodium. Benzyl alcohol was purified by distillation over sodium. All solvents were stored over 3 Å molecular sieves. Complexes were characterized by ¹H and ¹³C NMR, X-ray crystallography, and elemental analysis. NMR spectra for metal complexes were recorded at the Lumigen Instrument Centre (Wayne State University) on an Agilent 400 and 600 MHz spectrometers in C₆D₆ at room temperature. Chemical shifts and coupling constants (J) were reported in parts per million (δ) and Hertz respectively. Elemental analysis was performed under ambient air-free conditions by Midwest Microlab LLC.

Mass spectra were acquired using a Bruker solariX XR Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 T refrigerated actively-shielded superconducting magnet (Bruker Biospin, Wissebourg, France). The polymer samples were ionized in positive ion mode using the MALDI ion source. The mass range was set to m/z 200 – 5000. The laser power was 12% and 18 laser shots were used for each scan. Mass spectra were calibrated externally using a mix of peptide clusters in MALDI ionization positive ion mode. A linear calibration was applied. The polymer samples were dissolved in THF at a concentration of 1 mg/mL. The cationization agent used was potassium trifluoroacetate (Fluka, > 99 %) dissolved in THF at a concentration of 5 mg/mL. The matrix used was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (Fluka) and was dissolved in THF at a concentration of 40 mg/mL. Solutions of matrix, salt and polymer were mixed in a volume ratio of 4:1:4, respectively. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry.
8.6.2. X-ray Crystallographic Details

The structures of HOCAd'BuPh (20), HOCAd'Bu(3,5Ph₂Ph) (24), HOCAdMe(3,5Me₂Ph) (25), HOCAdMe(3,5Ph₂Ph) (27), Mg(OAdMePh)₂(THF)₂ (28) and Mg₂(OAdMePh)₂(sec-Bu)₂(THF)₂ (29) and were determined by X-ray crystallography. A Bruker APEXIIE/Kappa three circle goniometer platform diffractometer with an APEX-2 detector was used for data collection. A graphic monochromator was employed for the wavelength selection (MoKα radiation, λ = 0.71073 Å). The data were processed, and the structure was solved using the APEX-2 software. The structure was refined by standard difference Fourier techniques with SHELXL (6.10 v., Sheldrick G. M., and Siemens Industrial Automation, 2000). Hydrogen atoms were placed in calculated positions using a standard riding model and refined isotropically; all other atoms were refined anisotropically.

8.6.3. Ring-Opening Polymerization of Rac-Lactide

Dichloromethane/toluene solution of 10 μmol catalyst was mixed with a solution containing 100 equivalents (144 mg) of lactide in dichloromethane/toluene (total volume of the reaction was 10 mL, [LA] = 0.1 M). Reaction was stirred in room temperature for a given time after which it was stopped by adding 2-5 mL of methanol. PLA was precipitated in methanol and washed with excess methanol to remove all the impurities. For further purification, the polymer was dissolved using minimal amount of DCM and then added to 20 mL of methanol to precipitate pure PLA. Excess methanol was decanted, and the polymer was dried for 1 hour under vacuum. The reaction with 200, 300, 600, 1000, 5000, 10000, equivalents of lactide (0.2 M, 0.3 M, 0.6 M, 1 M, 5 M, and 10 M respectively) in dichloromethane and 200, 300, 600, (0.2 M, 0.3 M, 0.6 M) toluene solutions was carried out in a similar fashion. The resulting polymer was characterized by ¹H NMR spectroscopy, to determine degree of the polymerization. The methine region was also
analyzed by homonuclear decoupled $^1$H NMR, to determine the tacticity of the polymer.

**8.6.4. Solvent-Free Polymerization**

10 µmol catalyst was mixed with 10000 equivalents (14.4 g) of lactide and 10 equivalent of benzyl alcohol in a pressure vessel. Reaction was heated at 150 °C for one hour.

**8.6.5. Synthesis of 1-Adamantyl tert-butyl Ketone**

To a cold (-35 °C) solution of 1-adamantanecarboxylic acid (0.50 g; mmol) and dry pentane (3 ml), tert-butyllithium (1.7M in pentane; 3.3 ml; 5.5mmol) was added slowly while stirring under nitrogen atmosphere with controlling temperature at -35 °C during 30 min. The reaction was warmed to room temperature and stirred for another 2 hours. Then the reaction was quenched by water and extraction was done using ether. Combined organic layers were dried over anhydrous magnesium sulfate, filtered, and solvents were evaporated in vacuo to give ketone. White color solid (71% yield) $^1$H NMR (CDCl$_3$, 600 MHz) δ 2.01 (m, 9H), 1.72 (bs, 6H), 1.24 (s, 9H); $^{13}$C{1H} NMR (CDCl$_3$, 150 MHz) δ 218.33, 48.92, 46.29, 39.72, 36.86, 28.58, 28.50; HR-MS m/z calcd for C$_{15}$H$_{25}$O [M+H]+: 221.1901, found: 221.1900, IR (cm$^{-1}$): 2901 (s), 1674(s), 1473 (w), 1134 (m), 995 (m).

**8.6.6. Synthesis of 1-Adamantyl Methyl Ketone**

To a cold (-35 °C) solution of 1-adamantanecarboxylic acid (0.50 g; mmol) and dry pentane (3 ml), methyllithium (1.6M in pentane; 3.5 ml; 5.5mmol) was added slowly while stirring under nitrogen atmosphere with controlling temperature at -35 °C during 30 min. The reaction was warmed to room temperature and stirred for another 2 hours. Then the reaction was quenched by water and extraction was done using ether. Combined organic layers were dried over anhydrous magnesium sulfate, filtered, and solvents were evaporated in vacuo to give ketone. White color solid (62 % yield). $^1$H NMR (C$_6$D$_6$, 600 MHz) δ 1.80 (bs, 3H), 1.76 (s, 3H), 1.62 (d, $J = 2.30$, 6H),
1.54 (m, 3H), 1.48 (m, 3H); 13C{1H} NMR (C6D6, 150 MHz) δ 211.41, 46.76, 38.81, 37.14, 28.71, 24.18 HR-MS m/z calcd for C12H19O [M+H]+: 179.1429, found: 179.1430.

8.6.7. Synthesis of HOCAd'BuPh (HOR1 (20))

To a cold (-35 °C) solution of 1-Adamantyl tert-butyl ketone (0.52 g; 2.4 mmol) in ether, phenyl lithium (1.9 M; 1.24 ml; 2.4 mmol) was added dropwise. The reaction was stirred for 24 hours at room temperature under nitrogen environment. After the reaction solvents were removed in vacuo and extracted with hexane. Combined organic layers were dried over anhydrous magnesium sulfate, filtered, and solvents were evaporated in vacuo to give transparent crystals at room temperature (63% yield) ¹H NMR (C₆D₆, 600 MHz) δ 7.78 (d, J = 8.2 Hz, 1H), 7.46 (d, J = 7.0 Hz, 1H), 7.26 (m, 1H), 7.11 (m, 2H), 1.9 (d, J = 12 Hz, 3H), 1.84 (bs, 3H) 1.72 (d, J = 12 Hz, 3H), 1.63 (s, 1H), 1.54 (d, J = 12 Hz, 3H), 1.49 (d, J = 12 Hz, 3H), 1.05 (s, 9H); 13C{1H} NMR (C₆D₆, 150 MHz) δ 145.54, 128.77, 126.59, 126.22, 83.65, 44.59, 42.57, 39.67, 37.61, 30.66, 29.90; HR-MS m/z calcd for C₂₁H₃₀O [M+H]+: 298.2243, found: 298.2305.

8.6.8. Synthesis of HOCAdMePh (HOR² (21))

To a cold (-35 °C) solution of 1-adamantyl methyl ketone (0.55 g; 3.1 mmol mmol) in ether, phenyl lithium (1.9 M; 1.64 ml; 3.1 mmol) was added dropwise. The reaction was stirred for 24 hours at room temperature under a nitrogen environment. After the reaction solvents were removed in vacuo and extracted with hexane. Combined organic layers were dried over anhydrous magnesium sulfate, filtered, and solvents were evaporated in vacuo to give transparent crystals at room temperature (74 % yield). ¹H NMR (C₆D₆, 600 MHz) δ 7.38 (d, J = 7.6 Hz, 2H), 7.20 (t, J = 7.9 Hz, 2H), 7.11 (m, 1H), 1.87 (bs, 3H), 1.66 (m, 3H), 1.54 (m, 6H), 1.46 (m, 3H), 1.28 (s, 3H), 1.05 (s, 1H); 13C{1H} NMR (C₆D₆, 150 MHz) δ 146.50, 128.14, 127.52, 126.83, 83.65, 44.59, 42.57, 39.67, 37.61, 30.66, 29.90, 24.33; HR-MS m/z calcd for C₁₈H₂₅ [M-H₂O+H]+: 239.1795, found:
239.1794, IR (cm⁻¹): 3518 (br), 2893 (s), 1690 (w), 1489 (w), 1435 (w), 10856 (m), 709 (s)

8.6.9. **Synthesis of HOCAđBu(3,5-Me₂Ph) (HOR₃⁺ (22))**

To a solution of 1-bromo-3,5-dimethylbenzene (0.330 g, 1.78 mmol) in 3 ml ether and 1 ml THF, solution of tBuLi in pentane (2.1 ml, 1.7 M) was added dropwise at −35 °C within 15 minutes. The solution changed color from clear to light yellow. This reaction stirred for one hour and slowly warm to room temperature, upon which it was cooled again to −35 °C and added to a cold ether solution of 1-Adamantyl tert-butyl ketone (0.392 g, 1.78 mmol). The reaction was stirred for 24 hours, upon which all solvents were removed in vacuo to yield yellowish-white residue. The residue was dissolved in hexanes and extracted with water and hexanes (3 × 25 mL). After the extraction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using 1% ethyl acetate/hexane as eluent. HOR₃⁺ was isolated in 63% yield (0.366 g). ^1^H NMR (C₆D₆, 600 MHz) δ 7.53 (s, 1H), 7.26 (s, 1H), 6.78 (s, 1H), 2.26 (s, 3H), 2.23 (s, 3H), 2.0 (d, J = 12 Hz, 3H), 1.87 (bs, 3H), 1.81 (d, J = 12 Hz, 3H), 1.65 (s, 1H), 1.54 (m, 6H), 1.13 (s, 9H) 13C{1H} NMR (C₆D₆, 150 MHz) δ 145.61, 137.10, 135.20, 128.30, 128.30, 126.89, 126.58, 83.68, 44.59, 42.63, 39.73, 37.65, 30.78, 29.94, 22.33, 22.29; HR-MS m/z calcd for C₂₃H₃₃O [M+H]^⁺: 325.2528, found: 325.2526.

8.6.10. **Synthesis of HOCAđBu(3,5-tBu₂Ph) HOR₄⁺ (23)**

To a solution of 1-bromo-3,5-tert-butylbenzene (0.431 g, 1.60 mmol) in 3 ml ether and 1 ml THF, solution of tBuLi in pentane (1.88 ml, 1.7 M) was added dropwise at −35 °C within 15 minutes. The solution changed color from clear to light yellow. This reaction stirred for one hour and slowly warm to room temperature, upon which it was cooled again to −35 °C and added to a cold ether solution of 1-Adamantyl tert-butyl ketone (0.351 g, 1.59 mmol). The reaction was stirred for 24 hours, upon which all solvents were removed in vacuo to yield a yellowish-white residue. The residue was dissolved in hexanes and extracted with water and hexanes (3 × 25 mL).
After the extraction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using 1% ethyl acetate/hexane as eluent. HOR$_4^+$ was isolated in 59% yield (0.387 g). $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta$ 7.85 (s, 1H), 7.55 (s, 1H), 7.44 (s, 1H), 2.04 (d, $J = 12$ Hz, 3H), 1.89 (bs, 3H), 1.86 (d, $J = 12.3$ Hz, 3H), 1.74 (s, 1H), 1.56 (bs, 6H), 1.39 (s, 9H), 1.37 (s, 9H), 1.15 (bs, 9H) $^{13}$C{$_1$H} NMR (C$_6$D$_6$, 150 MHz) $\delta$ 149.96, 147.89, 144.68, 123.92, 123.03, 119.64, 84.11, 44.83, 42.65, 39.92, 37.72, 35.53, 35.26, 32.24, 32.14, 30.71, 30.03; HR-MS m/z calcd for C$_{29}$H$_{45}$O [M+H]$^+$: 409.3456, found: 409.3465.

8.6.11. Synthesis of HOCAd′Bu(3,5-Ph$_2$Ph) HOR$_5^+$ (24)

To a solution of 1-bromo-3,5-phenylbenzene (0.387 g, 1.25 mmol) in 3 ml ether and 1 ml THF, solution of $^t$BuLi in pentane (1.47 ml, 1.7 M) was added dropwise at $-35$ °C within 15 minutes. The solution changed color from clear to light yellow. This reaction stirred for one hour and slowly warm to room temperature, upon which it was cooled again to $-35$ °C and added to a cold ether solution of 1-Adamantyl tert-butyl ketone (0.275 g, 1.25 mmol). The reaction was stirred for 24 hours, upon which all solvents were removed in vacuo to yield a yellowish-white residue. The residue was dissolved in hexanes and extracted with water and hexanes (3 x 25 mL). After the extraction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using 1% ethyl acetate/hexane as eluent. HOR$_3^+$ was isolated in 67% yield (0.378 g). $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta$ 8.24 (s, 1H), 7.97 (s, 1H), 7.78 (s, 1H), 7.70-7.68 (m, 4H), 7.27 (m, 4H), 7.17 (m, 2H), 2.01 (d, $J = 11.2$ Hz, 3H), 1.83 (bs, 6H), 1.50 (m, 6H), 1.14 (s, 9H); $^{13}$C{$_1$H} NMR (C$_6$D$_6$, 150 MHz) $\delta$ 146.78, 142.88, 142.83, 141.88, 140.10, 129.59, 129.40, 128.01, 127.89, 127.70, 127.03, 126.96, 124.91, 83.99, 44.66, 42.67, 39.74, 37.53, 30.81, 29.83; HR-MS m/z calcd for C$_{33}$H$_{37}$O [M+H]$^+$: 449.2846, found: 449.2850.
8.6.12. Synthesis of HOCAdMe(3,5-Me_2Ph) HOR^{6*} (25)

To a solution of 1-bromo-3,5-dimethylbenzene (0.453 g, 2.45 mmol) in 3 ml ether and 1 ml THF, solution of 'BuLi in pentane (2.9 ml, 1.7 M) was added dropwise at -35 °C within 15 minutes. The solution changed color from clear to light yellow. This reaction stirred for one hour and slowly warm to room temperature, upon which it was cooled again to -35 °C and added to a cold ether solution of 1-Adamantyl methyl ketone (0.436 g, 2.24 mmol). The reaction was stirred for 24 hours, upon which all solvents were removed in vacuo to yield a yellowish white residue. The residue was dissolved in hexanes and extracted with water and hexanes (3 x 25 mL). After the extraction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using 1% ethyl acetate/hexane as eluent. HOR_3^{*} was isolated in 78% yield (0.543 g). ^1H NMR (C_6D_6, 600 MHz) δ 7.12 (s, 2H), 6.77 (s, 1H), 2.22 (s, 6H), 1.90 (bs, 3H), 1.75 (d, J = 12 Hz, 3H), 1.62 (d, J = 12 Hz, 3H), 1.57 (d, J = 12 Hz, 3H), 1.50 (d, J = 12 Hz, 3H), 1.37 (s, 6H), 1.17 (s, 1H); ^13C{^1H} NMR (C_6D_6, 150 MHz) δ 146.59, 136.56, 126.13, 78.54, 39.72, 37.66, 37.21, 29.49, 24.60, 22.10; HR-MS m/z calcd for C_{20}H_{27}O [M+H]^+: 283.2067, found: 283.2067, IR (cm⁻¹): 3456 (br), 2978 (m), 2901 (s), 1697 (m), 1605 (w), 1450 (w), 1358 (w), 1096 (m), 849 (m), 723 (m).

8.6.13. Synthesis of HOCAdMe(3,5-^1Bu_2Ph) (HOR^{7*} (26))

To a solution of 1-bromo-3,5-tert-butylbenzene (0.489 g, 1.82 mmol) in 3 ml ether and 1 ml THF, solution of 'BuLi in pentane (2.14 ml, 1.7 M) was added dropwise at -35 °C within 15 minutes. The solution changed color from clear to light yellow. This reaction stirred for one hour and slowly warm to room temperature, upon which it was cooled again to -35 °C and added to a cold ether solution of 1-Adamantyl methyl ketone (0.324 g, 1.82 mmol). The reaction was stirred for 24 hours, upon which all solvents were removed in vacuo to yield a yellowish white residue. The residue was dissolved in hexanes and extracted with water and hexanes (3 x 25 mL). After the
extraction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using 1% ethyl acetate/hexane as eluent. HOR\textsubscript{4}* was isolated in 71% yield (0.476 g). \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 600 MHz) \(\delta\) 7.45 (s, 2H), 7.15 (s, 1H), 1.92 (bs, 3H), 1.77 (d, \(J = 13.8\) Hz, 3H), 1.64 (d, \(J = 15\) Hz, 3H), 1.57 (m, 3H), 1.50 (m, 3H), 1.40 (s, 3H), 1.37 (s, 9H), 1.19 (s, 1H); \textsuperscript{13}C{\textsuperscript{1}H} NMR (C\textsubscript{6}D\textsubscript{6}, 150 MHz) \(\delta\) 149.44, 145.69, 122.64, 120.28, 78.95, 39.80, 37.65, 37.18, 35.37, 32.17, 29.51, 24.57; HR-MS m/z calcd for C\textsubscript{25}H\textsubscript{39}O [M+H]\textsuperscript{+}: 367.3002, found: 367.3006, IR (cm\textsuperscript{-1}): 3572 (br), 2963 (m), 2901 (s), 1597 (m), 1479 (w), 1425 (w), 1211 (w), 1095 (s), 880 (s), 725 (s).

8.6.14. Synthesis of HOCAdMe(3,5-Ph\textsubscript{2}Ph) (HOR\textsubscript{8}* (27))

To a solution of 1-bromo-3,5-phenylbenzene (0.503 g, 1.63 mmol) in 3 ml ether and 1 ml THF, solution of ‘BuLi in pentane (1.91 ml, 1.7 M) was added dropwise at \(-35\) °C within 15 minutes. The solution changed color from clear to light yellow. This reaction stirred for one hour and slowly warm to room temperature, upon which it was cooled again to \(-35\) °C and added to a cold ether solution of 1-Adamantyl methyl ketone (0.290 g, 1.63 mmol). The reaction was stirred for 24 hours, upon which all solvents were removed in vacuo to yield a yellowish-white residue. The residue was dissolved in hexanes and extracted with water and hexanes (3 \(\times\) 25 mL). After the extraction, the volatiles were removed in vacuo, and the product was purified by column chromatography (silica gel), using 1% ethyl acetate/hexane as eluent. HOR\textsubscript{3}* was isolated in 75% yield (0.499 g). \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 600 MHz) \(\delta\) 7.79 (bs, 2H), 7.76 (s, 1H), 7.66 (d, \(J = 7.30\) Hz, 4H), (t, \(J = 7.6\) Hz, 4H), 7.17 (m, 2H), 1.87 (bs, 3H), 1.75 (d, \(J = 12\) Hz, 3H), 1.61 (d, \(J = 12\) Hz, 3H), 1.54 (d, \(J = 11.2\) Hz, 3H), 1.45 (d, \(J = 11.2\) Hz, 3H); \textsuperscript{13}C{\textsuperscript{1}H} NMR (C\textsubscript{6}D\textsubscript{6}, 150 MHz) \(\delta\) 147.77, 142.59, 141.39, 129.49, 128.13, 127.90, 126.29, 125.12, 78.77, 39.77, 37.50, 37.09, 29.38, 24.49; HR-MS m/z calcd for C\textsubscript{30}H\textsubscript{31}O [M+H]\textsuperscript{+}: 407.2380, found: 407.2380, IR (cm\textsuperscript{-1}): 3542 (br), 2930
8.6.15. Synthesis of Mg(OAd'BuPh)$_2$(THF)$_2$ (28)

A 1 mL solution of HOR$^{1*}$ (92 mg, 0.31 mmol, 2.0 equiv.) in diethyl ether and a 1 mL solution of Mg(n-butyl)(sec-butyl) (21 mg, 0.15 mmol, 1 equiv.) in hexane were prepared. The solution of HOR was then added dropwise to a stirring solution of Mg(n-butyl)(sec-butyl). 0.5 ml of THF was then added to the reaction mixture. The reaction mixture was stirred for 2 hours, upon which the volatiles were removed in vacuo. The resulting oily solid was extracted to diethyl ether, filtered and concentrated in vacuo to get white solid. Crystallization was done in concentrated solution of dichloromethane of Mg(OR$^{1*}$)$_2$(THF)$_2$ kept at −35 °C (97 mg, 0.13 mmol, 84%). $^1$H NMR (C$_6$D$_6$, 600 MHz) δ 8.09 (d, $J_{HH} = 7.9$ Hz, 2H), 7.93 (d, $J_{HH} = 7.9$ Hz, 2H), 7.36 (m, 2H), 7.27 (m, 2H), 7.22 (t, 3 $J_{HH} = 6.9$ Hz, 2H), 3.84 (m, 8H), 2.23 (m, 6H), 2.13 (d, $J_{HH} = 10.6$ Hz, 6H), 2.07 (s, 6H), 1.75(s, 12H) 1.38 (s, 18H) 1.27 (m, 8H) ; $^{13}$C{$_{^1}$H} NMR (C$_6$D$_6$, 150 MHz) δ 153.27, 130.50, 129.69, 126.68, 125.58, 125.17, 84.71, 70.65, 45.73, 43.70, 40.86, 38.52, 32.39, 30.75, 25.32. Anal. calcd for: C$_{50}$H$_{74}$MgO$_4$ C, 78.72; H, 9.77 Found: C, 78.72 ; H, 9.94, IR (cm$^{-1}$): 2963 (s), 2901 (m), 2832 (w), 1589 (w), 1474 (w), 1389 (w), 1358 (s), 1242 (m), 1204 (w), 1126 (m), 1096 (m), 1042 (m), 872 (s), 787 (m), 741 (m).
CHAPTER 9: CONCLUSIONS AND OUTLOOK

The first part of my work addressed the problem of synthesis of symmetric and asymmetric azoarenes catalytically, which are very commonly used in the chemical industry. Azoarenes are synthesized stoichiometrically using different synthetic pathways which include toxic co-reactants and produce toxic by-products. I have explored the reactivity of sustainable iron-alkoxide catalysts for catalytic nitrene coupling to produce aroazenes. I have demonstrated nitrene homocoupling to produce azoarenes catalytically using two different iron (II) alkoxide complexes, Fe(OC'Bu₂(3,5-Ph₂Ph)₂(THF)₂ and Fe[OO]₁(THF)₂. Our previous iron bis(alkoxide) catalysts Fe(OC'Bu₂Ph)₂(THF)₂ exhibited efficient transformation of bulky aryl azides ArN₃ (Ar = 2,4,6-Me₃Ph or 2,6-Et₂Ph) to the corresponding azoarenes. However, no azoarene formation was observed for smaller aryl azides (Ar = 2-MePh, 3,5-Me₂Ph, 4-MePh). Instead, formation of bridging imido mono(alkoxide) complexes Fe₂(μ₂-NAr)₂(OC'Bu₂Ph)₂(THF)₂ was observed, along with tris(alkoxide) Fe(OC'Bu₂Ph)₃ by-product. We postulated that favorable alkoxide disproportionation was responsible for the lack of catalysis with smaller aryl azides. To prevent this disproportionation, we have designed new Fe(OC'Bu₂(3,5-Ph₂Ph)₂(THF)₂ complex with bulkier HOC'Bu₂(3,5-Ph₂Ph) ligand. Due to the increased steric bulk of the ligand, this complex exhibited selectivity for the bis(alkoxide) ligation; no tris(alkoxide) complexes were observed. As a result, both bulky and non-bulky aryl nitrenes are coupled with Fe(OC'Bu₂(3,5-Ph₂Ph)₂(THF)₂, albeit the coupling of the less bulky substrates requires higher temperatures and longer reaction times. Stoichiometric reactions of Fe(OC'Bu₂(3,5-Ph₂Ph)₂(THF)₂ with non-bulky aryl azides led to the observation of the iron(III) tetrazene radical anion complexes, that can produce azoarene products after heating. Tetrazene complexes likely serve as a “masked form” of the reactive nitrene complex based on these observations and the QM/MM modeling of the reaction mechanism. These
calculations suggest that the tetrazene complex is more stable than nitrene, which may explain the sluggish reactivity of the less bulky aryl azides.

To further improve the stability of our iron(II) bis(alkoxide) catalytic system, our group has designed a new chelating bis(alkoxide) ligand H$_2$[OO]$^{Ph}$ and its corresponding iron(II) chelating complex. Fe[OO]$^{Ph}$(THF)$_2$ is selective for coupling aryl nitrenes lacking ortho substituents; no reactivity with ortho-substituted (i.e. mesityl) azide took place. The difference in the reactivity is hypothesized to be due to the sterically congested active site of Fe[OO]$^{Ph}$, which interferes with the reactivity of putative “Fe[OO]$^{Ph}$ (=NMes)” species.

Furthermore, I have investigated heterocoupling reactivity of different nitrenes to produce asymmetric azoarenes, using iron(II) alkoxide pre-catalysts. We have explored the heterocoupling reactivity of Fe(OC$^t$Bu$_2$(3,5-Ph$_2$C$_6$H$_3$)$_2$(THF)$_2$ (which previously exhibited wide substrate scope) by itself, as well as the combination of Fe(OC$^t$Bu$_2$(3,5-Ph$_2$C$_6$H$_3$)$_2$(THF)$_2$ and Fe[OO]$^{Ph}$(THF)$_2$ catalysts. As Fe(OC$^t$Bu$_2$(3,5-Ph$_2$C$_6$H$_3$)$_2$(THF)$_2$ was able to couple preferentially bulky nitrenes, and Fe[OO]$^{Ph}$(THF)$_2$ coupled preferentially non-bulky substrates, we postulated that the combination of these catalysts may be able to produce hetero-coupled azoarene combining bulky and non-bulky aryl groups. Fe(OC$^t$Bu$_2$(3,5-Ph$_2$C$_6$H$_3$)$_2$(THF)$_2$ has demonstrated efficient heterocoupling reactivity for a combination of mono-ortho-substituted aryl azides with di-ortho substituted aryl azides. In contrast, any combination involving less bulky metal/para substituted aryl azide did not lead to the efficient production of the heterocoupled product in a good yield due to stable tetrazene complexes with para/meta substituted azides. Mixed catalyst reactivity of Fe(OC$^t$Bu$_2$(3,5-Ph$_2$C$_6$H$_3$)$_2$(THF)$_2$ and Fe[OO]$^{Ph}$(THF)$_2$ was not successful again likely due to the stable tetrazene formation of Fe(OC$^t$Bu$_2$(3,5-Ph$_2$C$_6$H$_3$)$_2$(ArNNNNAr). I have synthesized and isolated six new ortho substituted azarenes: MesN=N(2-iPrC$_6$H$_4$), MesN=N(2-MeC$_6$H$_4$),
MesN=N(2-EtC₆H₄), (2-iPrC₆H₄)N=N(2,6-Et₂C₆H₃), (2,6-Et₂C₆H₃)N=N(2-MeC₆H₄) and MesN=N(2,6-Et₂C₆H₃) and their cis-trans isomerism was investigated. All azoarenes were shown to demonstrate the presence of both isomers in solution at room temperature, with the trans isomer being the predominant one. Thermal conditions lead to the full conversion of the mixture to the trans isomer only in all cases, while the irradiation of the mixture with the UV light leads to the predominant formation of the cis isomer. Cis isomer stability is higher in these asymmetric azoarenes which showed longer t₁/₂ values (9-10 days).

In the future we hope to study di-azide polymerization using our iron(II) alkoxide pre-catalyst due to attractive optical properties of azopolymers. Furthermore we have recently synthesized Fe(OC'Bu₂(3,5-Me₂C₆H₃))₂(THF)₂ catalyst; we hope to study both homo and hetero-coupled nitrene transfer reactivity with this pre-catalyst.

In a second major part of my dissertation, addressed problem of development of efficient and sustainable catalysts for the polymerization of polar monomers to produce biodegradable and biorenewable alternatives to polyolefins. I have studied polyester synthesis via ring opening-polymerization of cyclic esters and ring opening copolymerization of epoxide and anhydride using achiral magnesium bis(alkoxide) complex. We have reported synthesis, ROP, and ROCOP with a new well-defined mononuclear magnesium complex Mg(OC'Bu₂Ph)(THF)₂. The complex led to active albeit not well controlled ROP of lactide precursor. Utilization of coordinating solvent (THF) or benzyl alcohol as a co-catalyst leads to better control of polymerization. In contrast, well-behaved ROCOP was obtained with a variety of different monomers. While the use of PPNCl as a nucleophilic initiator leads to an efficient copolymerization of cyclohexene oxide (CHO) with phtalic anhydride (PA) or succinic anhydride (SA), the structure of the resulting copolymers was found to be only moderately alternating, demonstrating a small amount of ether linkages. In
contrast, the use of BnOH as an initiator forms a perfectly alternating copolymer of PA with CHO. More challenging biorenewable monomer limonene oxide (LO) was also co-polymerized with PA. The combination of PA with both CHO and LO leads to the formation of terpolymer. Finally, the combination of two biorenewable precursors, LO, and dihydrocumarin, formed a fully biorenewable novel copolymer. Due to the lack of an ancillary ligand system to support the metal center, our Mg(OC\textsubscript{t}Bu\textsubscript{2}Ph\textsubscript{2}(THF)\textsubscript{2} catalyst was extremely reactive towards ROP and ROCOP. Magnesium is a non-toxic metal and Mg(OC\textsubscript{t}Bu\textsubscript{2}Ph\textsubscript{2}(THF)\textsubscript{2} is a colorless catalyst. Therefore, we do not need to remove the catalyst after polymerization. Due to extreme reactivity, achiral nature of the catalyst, and transesterification, Mg(OC\textsubscript{t}Bu\textsubscript{2}Ph\textsubscript{2}(THF)\textsubscript{2} did not show stereoselectivity for polymerization.

Furthermore, I have designed several chiral ligands and a chiral magnesium complex to investigate the stereoselective polymerization of polar monomers for the synthesis of polyesters. Bulky HOCAd\textsubscript{t}BuPh ligand led to the formation of diasteriomerically pure magnesium complex (Mg(OCAd\textsubscript{t}BuPh\textsubscript{2}(THF)\textsubscript{2}) which was isolated as homochiral diastereomer of Mg(OCA\textsuperscript{R}Ad\textsubscript{t}BuPh\textsubscript{2}(THF)\textsubscript{2} and Mg(OCA\textsuperscript{S}Ad\textsubscript{t}BuPh\textsubscript{2}(THF)\textsubscript{2} enantiomers. (Mg(OCAd\textsubscript{t}BuPh\textsubscript{2}(THF)\textsubscript{2}) was a very fast catalyst for polymerization of cyclic esters but it was not able to produce tactic polymers, likely due to the loss of the chiral alkoxides. (Mg(OCAd\textsubscript{t}BuPh\textsubscript{2}(THF)\textsubscript{2}) was able to show very high reactivity for lactide, ε-caprolactone also showed reactivity for less reactive substrates including ω-pentadecalactone (PDL), and ω-hexadecenlactone (HDL). HOCAdMePh was unable to make diasteriomerically pure Mg complex due to drastic decrease of bulkiness of the ligand.

In the future we are planning to separate chiral isomers of chiral alkoxide ligands to synthesize homochiral magnesium complexes for stereoselective polymerization and to synthesize
transition metal alkoxide complexes for catalysis. Due to the drastic decrease of steric gradient of HOCAdMePh we were unable to get diastereomERICALLY pure magnesium complex. Therefore we have synthesized a series of ligands with different meta substitution to the phenyl ring. We hope to synthesize series of magnesium, zinc and calcium complexes as polymerization catalysts with new chiral ligands. These complexes will be used to study ring opening co-polymerization of CO₂ and epoxide for polycarbonate synthesis.
APPENDIX A: PERSONAL/LICENSE AGREEMENTS FOR COPYRIGHTED MATERIAL


Title: Group-transfer chemistry at transition metal centers in bulky alkoxide ligand environments
Author: Amanda Grass, Duleeka Wannipurage, Richard L. Lord, Stanislav Groysman
Publication: Coordination Chemistry Reviews
Publisher: Elsevier
Date: 1 December 2019
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Title: Synthesis of a mononuclear magnesium bis(alkoxide) complex and its reactivity in the ring-opening copolymerization of cyclic anhydrides with epoxides
Author: D. Wannipurage, T. S. Hollingsworth, F. Santulli, M. Cozzolino, M. Lamberti, S. Groysman and M. Mazzeo
Publication: Dalton Transactions
Publisher: RSC publication
Date: 04 Feb 2020

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Title: Catalytic Nitrene Homocoupling by an Iron(II) Bis(alkoxide) Complex: Bulking Up the Alkoxide Enables a Wider Range of Substrates and Provides Insight into the Reaction Mechanism

Author: Maryam Yousif, Duleeka Wannipurage, Caleb D. Huizenga, et al

Publication: Inorganic Chemistry

Publisher: American Chemical Society

Date: Aug 1, 2018

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Title: Tying the alkoxides together: an iron complex of a new chelating bulky bis(alkoxide) demonstrates selectivity for coupling of non-bulky aryl nitrenes
Author: S. S. Kurup, D. Wannipurage, R. L. Lord and S. Groysman
Publication: Chemical Communications
Publisher: RSC publication
Date: 14 Aug 2019

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**Title:** Synthesis, characterization, and alkoxide transfer reactivity of dimeric Tl$_2$(OR)$_2$ complexes  
**Author:** Grass, A.†; Kulathungage, L. W.†; Wannipurage, D.†; Ward, C. L.; Groysman. S.  
**Publication:** Dalton Transactions  
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**Date:** 20 Jan 2021

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**Title:** Synthesis of a mononuclear magnesium bis(alkoxide) complex and its reactivity in the ring-opening copolymerization of cyclic anhydrides with epoxides  
**Author:** D. Wannipurage, T. S. Hollingsworth, F. Santulli, M. Cozzolino, M. Lamberti, S. Groysman and M. Mazzeo  
**Publication:** Dalton Transactions  
**Publisher:** RSC publication  
**Date:** 04 Feb 2020

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1 NMR spectra demonstrating the catalytic formation of azoarene compounds
Figure B.1. $^1$H NMR spectrum demonstrating catalytic formation of MesN=NMes in C$_6$D$_6$. 
Figure B.2. $^1$H NMR spectrum demonstrating formation of (2,6-Et$_2$Ph)N=N(2,6-Et$_2$Ph) in C$_6$D$_6$. 
Figure B.3. $^1$H NMR spectrum demonstrating formation of (3,5-Me$_2$C$_6$H$_3$)N=N(3,5-Me$_2$C$_6$H$_3$) in C$_6$D$_6$ (8 hours, 60 °C).
Figure B.4. $^1$H NMR spectrum demonstrating formation of (3,5-\text{Me}_2\text{C}_6\text{H}_3)\text{N}=\text{N}(3,5-\text{Me}_2\text{C}_6\text{H}_3) \text{ in C}_6\text{D}_6 \text{ (24 hours, 60 °C).}
Figure B.5. $^1$H NMR spectrum demonstrating formation of (2-iPrC$_6$H$_4$)N=N(2-iPrC$_6$H$_4$) in C$_6$D$_6$. 
Figure B.6. $^1$H NMR spectrum demonstrating formation of (4-iplrC$_6$H$_4$)N=N(4-iplrC$_6$H$_4$) in C$_6$D$_6$. 
Figure B.7. $^1$H NMR spectrum demonstrating catalytic formation of (2-MeC$_6$H$_4$)N=N(2-MeC$_6$H$_4$) in C$_6$D$_6$. 
Figure B.8. $^1$H NMR spectrum demonstrating formation of (4-CH$_3$C$_6$H$_4$)N=N(4-CH$_3$C$_6$H$_4$) in C$_6$D$_6$. 
Figure B.9. $^1$H NMR spectrum demonstrating catalytic formation of (2-EtPh)N=N(2-EtPh) (4 hours, 60 °C) in C$_6$D$_6$. 
Figure B.10. $^1$H NMR spectrum demonstrating catalytic formation of (2-EtPh)N=N(2-EtPh) (8 hours, 60 °C) in C₆D₆
Figure B.11. $^1$H NMR spectrum demonstrating formation of (4-CF$_3$C$_6$H$_4$)N=N(4-CF$_3$C$_6$H$_4$) in C$_6$D$_6$. 
Figure B.12. $^1$H NMR spectrum demonstrating catalytic formation of (2-phC$_6$H$_4$)N=N(2-phC$_6$H$_4$) in C$_6$D$_6$. 
Figure B.13. $^1$H NMR spectrum demonstrating formation of (2-OMeC$_6$H$_4$)N=N(2-OMeC$_6$H$_4$) in C$_6$D$_6$. 
2. GCMS Method, formula, procedure and Spectra

Quantitative analysis of azoarene formation was done by Gas chromatography–mass spectrometry using Agilent 6890N spectrometer, Thermo TG5MS 30m × 0.32mm × 0.25μm column, 7683 series injector and Agilent 5973 detector. Standard Azobenzene 2mg/ml was used as a GCMS standard. We note that while GCMS yields are overall similar to NMR yields, some differ (generally lower) by few percent. This difference is ascribed to the fact that while NMR yields were taken directly from the reaction mixture, GCMS yields were determined following separation of the azoarene by extraction with hexane and filtration.

**General procedure:** Determination of the percent concentration of desired analyte within a crude product mixture.

All the solvents were removed by vacuum after the reaction. Product of azoarene was purified by silica plug using hexane as solvent. Final weight of the product was determined by removing hexane. Weight of 1-5 mg of product (according to concentration of the product) of each azoarene was measured carefully and dissolved in 1000 μl of dichloromethane (HPLC) to make sample stock solution. Volume of 20 μl or 40 μl (depending on the concentration of the product) of stock solution and 5μl of standard solution (azobenzene) were added to standard GCMS vials and dichloromethane was added to dilute to a total volume of 1000 μl (sample working solution). GCMS was taken and desired peak and internal standard were integrated to calculate GCMS yield. General procedure was followed for each azoarenes and product yields were calculated using following equations.

**Equations**

**Stock Solution:**

\[
[sample]_{stock\ solution} = \frac{mass_{sample}}{volume_{stock\ solution}}
\]  

1.1

**Working Solution:**

\[
[sample]_{working\ solution} = \frac{volume_{sample}}{volume_{working\ solution}} [sample]_{stock\ solution}
\]  

2.1

\[
[internal\ standard]_{working\ solution} = \frac{volume_{internal\ standard}}{volume_{working\ solution}} [internal\ standard]_{stock\ solution}
\]  

2.2

**Determine the concentration of analyte in the GCMS sample:**

\[
[analyte]_{working\ solution} = \frac{Area_{analyte}}{Area_{internal\ Standard}} [internal\ Standard]_{working\ sample}
\]  

3.1

**Determine the percent composition of the unknown:**

\[
w/w\ composition_{crude\ product} = \frac{[analyte]_{GCMS\ sample}}{[sample]_{GCMS\ sample}}
\]  

4.1
Table B.1. GCMS yields.

<table>
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<th>Entry</th>
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<th>Time (H)</th>
<th>Temperature (°C)</th>
<th>GCMS Yield (%)</th>
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</tr>
<tr>
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<tr>
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Figure B.14. GCMS spectrum demonstrating formation of MesN=NMes.
Figure B.15. GCMS spectrum demonstrating formation of (2,6-Et$_2$Ph)N=N(2,6-Et$_2$Ph)
Figure B.16. GCMS spectrum demonstrating formation of \((3,5\text{-Me}_2\text{C}_6\text{H}_3)\text{N} = \text{N}(3,5\text{-Me}_2\text{C}_6\text{H}_3)\) in \(\text{C}_6\text{D}_6\) (8 hours, 60 °C).
Figure B.17. GCMS spectrum demonstrating formation of $(3,5\text{-Me}_2\text{C}_6\text{H}_3)\text{N}=\text{N}(3,5\text{-Me}_2\text{C}_6\text{H}_3)$ in $\text{C}_6\text{D}_6$ (24 hours, 60 °C).
Figure B.18. GCMS spectrum demonstrating formation of (2-\text{iprC}_6\text{H}_4)N=N(2-\text{iprC}_6\text{H}_4) in C_6D_6 (8 hours, 60 °C).
Figure B.19. GCMS spectrum demonstrating formation of (4-iPrC₆H₄)N=N(4-iPrC₆H₄) in C₆D₆ (8 hours, 60 °C).
Figure B.20. GCMS spectrum demonstrating formation of $(2\text{-MeC}_6\text{H}_4)N=N(2\text{-MeC}_6\text{H}_4)$ in $C_6D_6$ (24 hours, 60 °C)
Figure B.21. GCMS spectrum demonstrating formation of (4-MeC₆H₄)N=N(4-MeC₆H₄) in C₆D₆ (8 hours, 60 °C)
Figure B.22. GCMS spectrum demonstrating catalytic formation of \((2\text{-EtPh})\text{N=N}(2\text{-EtPh})\) (4 hours, 60 °C) in \(\text{C}_6\text{D}_6\).
Figure B.23. GCMS spectrum demonstrating catalytic formation of \((2\text{-EtPh})\text{N=N(2-EtPh)}\) (8 hours, 60 °C) in C₆D₆.
Figure B.24. GCMS spectrum demonstrating formation of (4-CF₃C₆H₄)N=N(4-CF₃C₆H₄) in C₆D₆.
1. NMR spectra for the catalytic formation of azoarene

Figure C.1. $^1$H NMR spectrum demonstrating catalytic formation of (PhN=NPh) in C₆D₆ after 24 h at 60 °C.
Figure C.2. $^1$H NMR spectrum demonstrating catalytic formation of (4-CH$_3$Ph)N=N(4-CH$_3$Ph) in C$_6$D$_6$ after 24 h at 60 °C.
Figure C.3. $^1$H NMR spectrum demonstrating the catalytic formation of (4-EtPh)N=N(4-EtPh) in C$_6$D$_6$ after 24 h at 60 °C.
Figure C.4. $^1$H NMR spectrum demonstrating the catalytic formation of (4-$^i$PrPh)N=N(4-$^i$PrPh) in C$_6$D$_6$ after 24 h at 60 °C.
Figure C.5. $^1$H NMR spectrum demonstrating formation of (4-CF$_3$Ph)N=N(4-CF$_3$Ph) in C$_6$D$_6$ after 24 h at 60 °C.
Figure C.6. $^1$H NMR spectrum demonstrating formation of (4-CH$_3$COPh)N=N(4-CH$_3$COPh) in C$_6$D$_6$ after 24 h at 60 °C.
Figure C.7. $^1$H NMR spectrum demonstrating formation of (4-NO$_2$Ph)N=N(4-NO$_2$Ph) in C$_6$D$_6$ after 24 h at 60 °C.
Figure C.8. $^1$H NMR spectrum demonstrating formation of (4-CH$_3$OPh)N=N(4-CH$_3$OPh) in C$_6$D$_6$ after 24 h at 60 °C.
Figure C.9. $^{19}$F NMR spectrum demonstrating formation of $(4$-FPh)$N=N(4$-FPh) in C$_6$D$_6$ after 24 hours at 60$^\circ$C.
Figure C.10. $^1$H NMR spectrum demonstrating formation of (4-ClPh)N=N(4-ClPh) after 24 hours at 60 °C. The reaction was performed in C$_6$D$_6$, however, since the peak of the solvent interfered with the spectrum, it was recollected in CD$_2$Cl$_2$. 
Figure C.11. $^1$H NMR spectrum demonstrating formation of (4-BrPh)N=N(4-BrPh) in C$_6$D$_6$ after 24 h at 60°C
Figure C.12. $^1$H NMR spectrum demonstrating formation of (3,5-Me$_2$Ph)N=N(3,5-Me$_2$Ph) in C$_6$D$_6$ (24 hours, 60 °C).
Figure C.13. $^{19}$F NMR spectrum demonstrating formation of (3-CF$_3$C$_6$H$_4$)N=N(3-CF$_3$C$_6$H$_4$) in C$_6$D$_6$ (24 h, 60 °C).
2. NMR spectra for isolated azoarens

Figure C.14. $^1H$ NMR spectrum of isolated (4-CH$_3$Ph)N=N(4-CH$_3$Ph).
Figure C.15. $^{13}$C NMR spectrum of isolated (4-CH$_3$Ph)N=N(4-CH$_3$Ph).
Figure C.16. $^1$H NMR spectrum of isolated (4-FPh)N=N(4-FPh).
Figure C.17. $^{13}$C NMR spectrum of isolated (4-FPh)N=N(4-FPh).
Figure C.18. $^1$H NMR spectrum of isolated (4-$^i$PrPh)N=N(4-$^i$PrPh).
Figure C.19. $^{13}$C NMR spectrum of (4-iPrPh)N=N(4-iPrPh).
Figure C.20. $^1$H NMR spectrum of isolated (3,5-Me$_2$Ph)N=N(3,5-Me$_2$Ph).
Figure C.21. $^{13}$C NMR spectrum of isolated $(3,5$-$\text{Me}_2\text{Ph})\text{N}=$N$(3,5$-$\text{Me}_2\text{Ph})$. 
3. GC-MS Spectra

Figure C.22. GC-MS spectrum demonstrating the formation of (PhN=NPh) in C₆D₆ after 24 h at 60°C
Figure C.23. GC-MS spectrum demonstrating formation of (4-CH₃Ph)N=N(4-CH₃Ph) in C₆D₆ after 24 h at 60 °C.
Figure C.24. GC-MS spectrum demonstrating formation of (4-EtPh)N=N(4-EtPh) in C₆D₆ after 24 h at 60 °C.
Figure C.25. GC-MS spectrum demonstrating formation of (4-iPrPh)N=N(4-iPrPh) in C₆D₆ after 24 h at 60 ºC.
Figure C.26. GC-MS spectrum demonstrating formation of (4-CF₃Ph)N=N(4-CF₃Ph) in C₆D₆ after 24 h at 60 °C.
Figure C.27. GC-MS spectrum demonstrating formation of (4-CH$_3$COPh)N=N(4-CH$_3$COPh) in C$_6$D$_6$ after 24 h at 60 °C.
Figure C.28. $^1$H NMR spectrum demonstrating formation of (4-NO$_2$Ph)N=N(4-NO$_2$Ph) in C$_6$D$_6$ after 24 h at 60 $^\circ$C.
Figure C.29. GC-MS spectrum demonstrating formation of (4-CH₃COPh)N=N(4-CH₃COPh) in C₆D₆ after 24 h at 60 °C.
Figure C.30. GC-MS spectrum demonstrating formation of (4-FPh)N=N(4-FPh) in C₆D₆ after 24 h at 60 °C.
Figure C.31. GC-MS spectrum demonstrating formation of (4-ClPh)N=N(4-ClPh) in C₆D₆ after 24 h at 60 °C.
Figure C.32. GC-MS spectrum demonstrating formation of (4-BrPh)N=N(4-BrPh) in C₆D₆ after 24 h at 60 °C.
Figure C.33. GC-MS spectrum demonstrating formation of (3,5-Me₂Ph)N=N(3,5-Me₂Ph) in C₆D₆ after 24 h at 60 °C.
Figure C.34. GC-MS spectrum demonstrating formation of (3-CF$_3$Ph)N=N(3-CF$_3$Ph) in C$_6$D$_6$ after 24 h at 60 $^\circ$C.
4. Mass Spectra

Figure C.35. HRMS of isolated (4-MePh)N=N(4-MePh).
Figure C.36. HRMS of isolated (4-iPrPh)N=N(4-iPrPh).
Figure C.37. HRMS of (3,5-MePh)N=N(3,5-MePh).
Figure C.38. HRMS of \((4\text{-FPh})\text{N=N(F-Ph)}\).
Figure D.1. $^1$H NMR spectrum demonstrating catalytic formation of (MesN=NMes), (2-iprC$_6$H$_4$)N=N(2-iprC$_6$H$_4$) and (MesN=N(2-iprC$_6$H$_4$)) in C$_6$D$_6$ after 24 h at 60 ºC for Fe(OR')$_2$(THF)$_2$. 
**Figure D.2.** $^1$H NMR spectrum demonstrating catalytic formation of (MesN=NMes), (2-MePh)N=N(2-MePh) and (MesN=N(2-MePh)) in C$_6$D$_6$ after 24 h at 60 °C for Fe(OR')$_2$(THF)$_2$. 
Figure D.3. $^1$H NMR spectrum demonstrating catalytic formation of (MesN=NMes), (2-EtC$_6$H$_4$)N=N(2-EtC$_6$H$_4$) and (MesN=N(2-EtC$_6$H$_4$)) in C$_6$D$_6$ after 24 h at 60 °C for Fe(OR')$_2$(THF)$_2$. 
Figure D.4. $^1$H NMR spectrum demonstrating catalytic formation of (MesN=NMes), (2,6-Et$_2$Ph)N=N(2,6-Et$_2$Ph) and (MesN=N(2,6-Et$_2$Ph)) in C$_6$D$_6$ after 24 h at 60 °C for Fe(OR')$_2$(THF)$_2$. 
Figure D.5. $^1$H NMR spectrum demonstrating catalytic formation of (2,6-Et$_2$Ph)N=N(2,6-Et$_2$Ph), (2-iprPh)N=N(2-iprPh) and (2-iprPh)N=N(2,6-Et$_2$Ph) in C$_6$D$_6$ after 24 h at 60 °C for Fe(OR')$_2$(THF)$_2$.
Figure D.6. $^1$H NMR spectrum demonstrating catalytic formation of (2,6-Et$_2$Ph)N=N(2,6-Et$_2$Ph), (2-CH$_3$Ph)N=N(2-CH$_3$Ph) and (2,6-Et$_2$Ph)N=N(2-CH$_3$Ph) in C$_6$D$_6$ after 24 h at 60 °C for Fe(OR’)$_2$(THF)$_2$. 
**Figure D.7.** $^1$H NMR spectrum demonstrating catalytic formation of (3,5-Me$_2$Ph)N=N(3,5-Me$_2$Ph), (4-MePh)N=N(4-MePh) and (3,5-Me$_2$Ph)N=N(4-MePh), in C$_6$D$_6$ after 24 h at 60 ºC for Fe(OR')$_2$(THF)$_2$. 
Figure D.8. $^1$H NMR spectrum demonstrating catalytic formation of (2-EtPh)N=N(2-EtPh), (2-iPrPh)N=N(2-iPrPh) and (2-iPrPh)N=N(2-EtPh) in C$_6$D$_6$ after 24 h at 60 °C for Fe(OR')$_2$(THF)$_2$. 
Figure D.9. $^1$H NMR spectrum demonstrating catalytic formation of (MesN=NMes), (3,5-Me$_2$Ph)N=N(3,5-Me$_2$Ph) and (MesN=N(3,5-Me$_2$Ph) in C$_6$D$_6$ after 24 h at 60 °C for Fe(OR')$_2$(THF)$_2$. 
Figure D.10. $^1$H NMR spectrum demonstrating catalytic formation of $^1$H NMR spectrum demonstrating catalytic formation of (MesN=NMes), (4-MePh)N=N(4-MePh) and (MesN=N(4-MePh)) in C$_6$D$_6$ after 24 h at 60 ºC for Fe(OR')$_2$(THF)$_2$ and Fe[OO]$_{ph}$(THF)$_2$
Figure D.11. $^1$H NMR spectrum demonstrating catalytic formation of (MesN=NMes), (4-ClPh)N=N(4-ClPh) and (MesN=N(4-ClPh)) in C$_6$D$_6$ after 24 h at 60 ºC for Fe(OR’)$_2$(THF)$_2$ and
Figure D.12. $^1\text{H}$ NMR spectrum demonstrating catalytic formation of (MesN=NMes), (4-BrPh)N=N(4-BrPh) and (MesN=N(4-BrPh)) in C$_6$D$_6$ after 24 h at 60 ºC for Fe(OR')$_2$(THF)$_2$ and Fe[OO]$_{ph}$(THF)$_2$.
Figure D.13. $^1$H NMR spectrum demonstrating catalytic formation of (MesN=NMes), (4-CF$_3$Ph)N=N(4-CF$_3$Ph) and (MesN=N(4-CF$_3$Ph)) in C$_6$D$_6$ after 24 h at 60 °C for Fe(OR')$_2$(THF)$_2$ and Fe[OO]$_2$^{th}(THF)$_2$
**Figure D.14.** $^{19}$F NMR spectrum demonstrating catalytic formation of (MesN=NMes), (4-CF$_3$Ph)N=N(4-CF$_3$Ph) and (MesN=N(4-CF$_3$Ph)) in C$_6$D$_6$ after 24 h at 60 ºC for Fe(OR’)$_2$(THF)$_2$ and Fe[OØ]$_{th}$(THF)$_2$
Figure D.15. $^1$H NMR spectrum of isolated (MesN=N(2-iPrC$_6$H$_4$))
Figure D.16. $^{13}$C NMR spectrum of isolated (MesN=N(2-iprC$_6$H$_4$))
Figure D.17. $^1$H NMR spectrum demonstrating changes of *cis-trans* isomerization of isolated (MesN=N(2-iprC$_6$H$_4$)) after exposure to the UV light for 2 hours.
Figure D.18. $^1$H NMR spectrum of MesN=N(2-iprPh) after exposure to the UV (365nm) light for 4 hours.
Figure D.19. $^{13}$C NMR Spectrum of MesN=N(2-iprPh) after exposure to the UV (365nm) light for 4 hours.
Figure D.20. $^1$H NMR Spectrum of *trans* isomer of MesN=N(2-iPrPh)
Figure D.21. $^{13}$C NMR Spectrum of *trans* isomer of MesN=N(2-iPrPh)
Figure D.22. $^1$H NMR Spectrums of MesN=N(2-iPrPh): A = after exposure to the UV (365nm) light for 4 hours, B = at room temperature, C = heating after 2h at 60 °C
Figure D.23. Cosy spectrum of (MesN=N(2-iPrC₆H₄))
Figure D.24. Aromatic region of cosy spectrum of (MesN=N(2-iPrC₆H₄)) demonstrating one H of cis (MesN=N(2-iPrC₆H₄)) underneath of solvent C₆D₆
Figure D.25. HSQC spectrum of (MesN=N(2-iPrC₆H₄))
Figure D.26. HMQC spectrum of (MesN=N(2-іprC₆H₄))
Figure D.27. HMBC spectrum of (MesN=N(2-iPrC₆H₄))
Figure D.28. $^1$H NMR spectrum of isolated (MesN=N(2-CH$_3$C$_6$H$_4$))
Figure D.29. $^{13}$C NMR spectrum of isolated (MesN=N(2-CH$_3$C$_6$H$_4$))
Figure D.30. $^1$H NMR spectrum demonstrating changes of cis-trans isomerization of (MesN=N(2-CH$_3$C$_6$H$_4$)) after exposure to the UV light for 2 hours
Figure D.31. $^1$H NMR Spectrum of (MesN=N(2-CH$_3$C$_6$H$_4$)) after exposure to the UV (365nm) light for 4 hours.
Figure D.32. $^1$H NMR Spectrum of trans isomer of (MesN=N(2-CH$_3$C$_6$H$_4$))
Figure D.33. $^{13}$C NMR Spectrum of trans isomer of (MesN=N(2-CH$_3$C$_6$H$_4$))
Figure D.34. $^1$H NMR Spectrums of (MesN=N(2-CH$_3$C$_6$H$_4$)) : A = after exposure to the UV (365nm) light for 4 hours, B = at room temperature, C = heating for 2 h at 60 ºC.
Figure D.35. Cosy spectrum of (MesN=N(2-CH$_3$C$_6$H$_4$)).
Figure D.36. HSQC spectrum of (MesN=N(2-CH$_3$C$_6$H$_4$)).
Figure D.37. HMQC spectrum of (MesN=N(2-CH₃C₆H₄)).
Figure D.38. HMBC spectrum of (MesN=N(2-CH$_3$C$_6$H$_4$)).
Figure D.39. $^1$H NMR spectrum of isolated (MesN=N(2-EtC₆H₄))
Figure D.40. $^{13}$C NMR spectrum of isolated (MesN=N(2-EtC₆H₄))
**Figure D.41.** $^1$H NMR spectrum demonstrating changes of *cis-trans* isomerization of (MesN=N(2-EtC$_6$H$_4$)) after exposure to the UV light for 2 hours
Figure D.42. $^1$H NMR Spectrum of (MesN=N(2-EtC$_6$H$_4$)) after exposure to the UV (365nm) light for 4 hours.
Figure D.43. $^1$H NMR spectrum of trans isomer of (MesN=N(2-EtC$_6$H$_4$))
**Figure D.44.** $^{13}$C Spectrum of trans isomer of (MesN=N(2-EtC$_6$H$_4$))
Figure D.45. $^1$H NMR Spectrums of (MesN=N(2-EtC₆H₄)) : A = after exposure to the UV (365nm) light for 4 hours, B = at room temperature, C = heating after 2h at 60 °C
Figure D.46. COSY spectrum of (MesN=N(2-EtC₆H₄))
Figure D.47. Aromatic region of the COSY spectrum of (MesN=N(2-EtC₆H₄)) demonstrating 2H of *trans* isomer underneath the solvent C₆D₆.
Figure D.48. HSQC spectrum of (MesN=N(2-EtC₆H₄))
Figure D.49. HMQC spectrum of (MesN=N(2-EtC₆H₄))
Figure D.50. HMBC spectrum of (MesN=N(2-EtC₆H₄))
Figure D.51. $^1$H NMR spectrum of isolated (MesN=N(2,6-Et$_2$Ph))
Figure D.52. $^{13}$C NMR spectrum of isolated (MesN=N(2,6-Et$_2$Ph))
Figure D.53. $^1$H NMR spectrum demonstrating changes of cis-trans isomerization of (MesN=N(2,6-Et$_2$Ph)) after exposure to the UV light for 2 hours.
Figure D.54. $^1$H NMR spectrum of (MesN=N(2,6-Et$_2$Ph)) after exposure to the UV (365nm) light for 4 hours.
Figure D.55. $^{13}$C NMR spectrum of ($\text{MesN=N}(2,6\text{-Et}_2\text{Ph})$) after exposure to the UV (365nm) light for 4 hours.
Figure D.56. $^1$H NMR spectrum of trans isomer of (MesN=N(2,6-Et$_2$Ph)).
Figure D.57. $^{13}$C NMR spectrum of *trans* isomer of (MesN=N(2,6-Et$_2$Ph)).
Figure D.58. $^1$H NMR spectrums of (MesN=N(2,6-Et$_2$Ph)) : A = after exposure to the UV (365nm) light for 4 hours, B = at room temperature, C = heating after 2h at 60 °C.
Figure D.59. Cosy spectrum of (MesN=N(2,6-Et2Ph)).
Figure D.60. HSQC spectrum of (MesN=N(2,6-Et2Ph)).
Figure D.61. HMQC spectrum of \((\text{MesN}=\text{N}(2,6-\text{Et}_2\text{Ph}))\).
Figure D.62. HMBC spectrum of (MesN=N(2,6-Et2Ph))
Figure D.63. $^1$H NMR spectrum of isolated (2-iprPh)N=N(2,6-Et$_2$Ph)
Figure D.64. $^1$H NMR spectrum of isolated (2-iPrPh)N=N(2,6-Et$_2$Ph)
Figure D.65. $^1$H NMR spectrum demonstrating changes of cis-trans isomerization of (2-iprPh)N=N(2,6-Et$_2$Ph) after exposure to the UV light for 2 hours
Figure D.66. $^1$H NMR spectrum of (2- iprPh)N=N(2,6-Et$_2$Ph) after exposure to the UV (365nm) light for 4 hours.
Figure D.67. $^1$H NMR spectrum of trans isomer of (2-{	extit{i}}prPh)N=N(2,6-{	extit{Et}}$_2$Ph)
Figure D.68. $^{13}$C NMR spectrum of trans isomer of (2-iprPh)N=N(2,6-Et$_2$Ph)
Figure D.69. $^1$H NMR spectrum of $(2$-$i$prPh)$N=N$(2,6$-Et_2$Ph): A = after exposure to the UV (365nm) light for 4 hours, B = at room temperature, C = heating after 2h at 60 °C
Figure D.70. $^1$H NMR spectrum of isolated (2,6-Et$_2$Ph)N=N(2-CH$_3$Ph)
Figure D.71. $^{13}$C NMR spectrum of isolated (2,6-Et$_2$Ph)N=N(2-CH$_3$Ph)
Figure D.72. $^1$H NMR spectrum demonstrating changes of cis-trans isomerization of (2,6-Et$_2$Ph)N=N(2-CH$_3$Ph) after exposure to the UV light for 2 hours
Figure D.73. $^1$H NMR spectrum of (2,6-Et$_2$Ph)N=N(2-CH$_3$Ph) after exposure to the UV (365nm) light for 4 hours.
Figure D.74. $^1$H NMR spectrum of *trans* isomer of (2,6-Et$_2$Ph)N=N(2-CH$_3$Ph)
Figure D.75. $^{13}$C NMR spectrum of trans isomer of (2,6-Et$_2$Ph)N=N(2-CH$_3$Ph)
Figure D.76. $^1$H NMR spectra of (2,6-Et$_2$Ph)N=N(2-CH$_3$Ph): A = after exposure to the UV (365nm) light for 4 hours, B = at room temperature, C = heating after 2h at 60 ºC
Figure D.77. Cosy spectrum of isolated (2,6-Et$_2$Ph)N=N(2-CH$_3$Ph)
2. HRMS

Figure D.78. HRMS demonstrating formation of (MesN=NMes), (2-\textit{i}prC_6H_4)N=N(2-\textit{i}prC_6H_4) and (MesN=N(2-\textit{i}prC_6H_4))
Figure D.79. HRMS demonstrating formation of (MesN=NMes), (2-MePh)N=N(2-MePh) and (MesN=N(2-MePh))
Figure D.80. HRMS demonstrating formation of (MesN=NMes), (2-EtC₆H₄)N=N(2-EtC₆H₄) and (MesN=N(2-EtC₆H₄)).
**Figure D.81.** HRMS demonstrating formation of (MesN=NMes), (2,6-Et₂Ph)N=N(2,6-Et₂Ph) and (MesN=N(2,6-Et₂Ph))
Figure D.82. HRMS demonstrating formation of (2,6-Et$_2$Ph)N=N(2,6-Et$_2$Ph), (2-i-prPh)N=N(2-i-prPh) and (2-i-prPh)N=N(2,6-Et$_2$Ph)
Figure D.83. HRMS demonstrating formation of (2,6-Et₂Ph)N=N(2,6-Et₂Ph), (2-CH₃Ph)N=N(2-CH₃Ph) and (2,6-Et₂Ph)N=N(2-CH₃Ph)
Figure D.84. HRMS of isolated of (MesN=N(2-tprC₆H₄)).
Figure D.85. HRMS of isolated of (MesN=N(2-MePh))
**Figure D.86.** HRMS of isolated of (MesN=N(2-EtC₆H₄))
**Figure D.87.** HRMS of isolated of (MesN=N(2,6-Et₂Ph))
Figure D.88. HRMS of isolated of (2-iPrPh)N=N(2,6-Et₂Ph)
**Figure D.89.** HRMS of isolated of \((2,6\text{-Et}_2\text{Ph})\text{N}=\text{N}(2\text{-CH}_3\text{Ph})\)
3. GC-MS spectra

Figure D.90. GCMS demonstrating formation of (MesN=NMes), (2-iPrC₆H₄)N=N(2-iPrC₆H₄) and (MesN=N(2-iPrC₆H₄))
Figure D.91. GCMS demonstrating formation of (MesN=NMes), (2-MePh)N=N(2-MePh) and (MesN=N(2-MePh))
Figure D.92. GCMS demonstrating formation of (MesN=NMes), (2-EtC₆H₄)N=N(2-EtC₆H₄) and (MesN=N(2-EtC₆H₄))
Figure D.93. GCMS demonstrating formation of (MesN=NMes), (2,6-Et$_2$Ph)N=N(2,6-Et$_2$Ph) and (MesN=N(2,6-Et$_2$Ph))
Figure D.94. GCMS demonstrating formation of (2,6-Et₂Ph)N=N(2,6-Et₂Ph), (2- iprPh)N=N(2-iprPh) and (2-iprPh)N=N(2,6-Et₂Ph)
Figure D.95. GCMS demonstrating the formation of (2,6-Et₂Ph)N=N(2,6-Et₂Ph), (2-Ch₃Ph)N=N(2-Ch₃Ph), and (2,6-Et₂Ph)N=N(2-Ch₃Ph)
Figure D.96. GCMS demonstrating formation of (3,5-Me₂Ph)N=N(3,5-Me₂Ph), (4-MePh)N=N(4-MePh) and (3,5-Me₂Ph)N=N(4-MePh)
Figure D.97. GCMS demonstrating formation of (2-EtPh)N=N(2-EtPh), (2-iPrPh)N=N(2-iPrPh) and (2-iPrPh)N=N(2-EtPh)
Figure D.98. GCMS demonstrating formation of (MesN=NMes), (3,5-Me₂Ph)N=N(3,5-Me₂Ph) and (MesN=N(3,5-Me₂Ph)
Figure D.99. GCMS demonstrating formation of (MesN=NMes), (4-MePh)N=N(4-MePh) and (MesN=N(4-MePh))
Figure D.100. GCMS demonstrating formation of (MesN=NMes), (4-ClPh)N=N(4-ClPh) and (MesN=N(4-ClPh))
Figure D.101. GCMS demonstrating formation of (MesN=NMes), (4-BrPh)N=N(4-BrPh) and (MesN=N(4-BrPh))
Figure D.102. GCMS demonstrating formation of (MesN=NMes), (4-CF$_3$Ph)N=N(4-CF$_3$Ph) and (MesN=N(4-CF$_3$Ph))
Figure D.103. GCMS of isolated of (MesN=N(2-iptC₆H₄))
Figure D.104. GCMS of isolated of (MesN=NN(2-MePh))
Figure D.105. GCMS of isolated of (MesN=N(2-EtC₆H₄))
Figure D.106. GCMS of isolated of (MesN=N(2,6-Et₂Ph))
Figure D.107. GCMS of isolated of (2-iPrPh)N=N(2,6-Et₂Ph)
Figure D.108. GCMS of isolated of (2,6-Et₂Ph)N=N(2-CH₃Ph)
Figure D.109. UV-Vis spectrum for (MesN=N(2,6-Et2Ph) at five different concentrations. $\lambda_{\text{max}}$, nm ($\varepsilon_{\text{M}}, \text{Lmol}^{-1}\text{cm}^{-1}$): 237 (sh, 1347), 255 (1445), 299 (1530), 466 (172).
Figure D.110. UV-Vis spectrum for (MesN=N(2-MePh)) at five different concentrations. $\lambda_{\text{max}}$, nm ($\varepsilon_M$, Lmol$^{-1}$cm$^{-1}$): 236 (sh, 935), 243 (sh, 1046), 250 (sh, 953), 330 (1679), 465 (101)
Figure D.111. UV-Vis spectrum for (MesN=N(2-¡prC\text{6}H\text{4})) at five different concentrations. $\lambda_{\text{max}}, \text{nm} (\varepsilon_M, \text{Lmol}^{-1}\text{cm}^{-1}): 237 \text{ (sh, 1584), 242 (sh, 1523), 330 (2147), 463 (143).}$
Figure D.112. UV-Vis spectrum for (MesN=N(2-EtC₆H₄)) at five different concentrations. $\lambda_{\text{max}}, \text{nm} (\varepsilon_M, \text{Lmol}^{-1}\text{cm}^{-1}): 236 \text{ (sh, 4808), 331 (7320), 465 (370)}$
Figure D.113. UV-Vis spectrum for (2-îprPh)N=N(2,6-Et2Ph) at four different concentrations.  
$\lambda_{\text{max}}$, nm ($\varepsilon_M$, Lmol$^{-1}$cm$^{-1}$): 226 (sh, 1170), 240 (sh, 1272), 280 (sh, 1166), 316 (1421) 465 (102).
Figure D.114. UV-Vis spectrum for (2,6-Et₂Ph)N=N(2-CH₃Ph) at five different concentrations. 
$\lambda_{\text{max}}$, nm ($\varepsilon_{\text{M, Lmol}^{-1}\text{cm}^{-1}}$): 251 (sh, 3290) 320 (2580), 460 (170).
Figure E.1. Field-dependent Mössbauer spectra recorded at 4.35 K for 12.
Figure E.2. Temperature-dependent Mössbauer spectra recorded at 8 T for 12.
Figure E.3. Left: Spin expectation values as function of the applied field; Right: Thermally-averaged spin expectation values as function of temperature obtained for an applied field of 8 T. These plots were obtained using the spin-Hamiltonian of equation 1a using a $D = -14 \text{ cm}^{-1}$, $E/D = 0.1$, $g_x = g_y = g_z = 2.0$. 
1. NMR spectra

Figure F.1. $^1$H NMR of LiOC'Bu$_2$(3,5-Me$_2$C$_6$H$_3$) (C$_6$D$_6$, 600 MHz).
Figure F.2. $^{13}$C NMR of LiOC'Bu$_2$(3,5-Me$_2$C$_6$H$_3$) (C$_6$D$_6$, 150 MHz). *Carbons a and b appear under C$_6$D$_6$ peaks, and were detected by HSQCAD, HMBC and HMQC.
Figure F.3. $^1$H-$^1$H COSY NMR of LiOCBu$_2$(3,5-Me$_2$C$_6$H$_3$) (C$_6$D$_6$, 600 MHz).
Figure F.4. $^1$H-$^{13}$C HSQCAD NMR of LiOC'Bu$_2$(3,5-Me$_2$C$_6$H$_3$) (C$_6$D$_6$, 600 MHz).
Figure F.5. $^{1}$H-$^{13}$C HMBCAD NMR of LiOC'Bu$_2$(3,5-Me$_2$C$_6$H$_3$) (C$_6$D$_6$, 600 MHz).
Figure F.6. $^1$H-$^{13}$C HMQC NMR of LiOCBu₂(3,5-Me₂C₆H₃) (C₆D₆, 600 MHz).
Figure F.7. $^1$H NMR of TiOC'Bu$_2$(3,5-Me$_2$C$_6$H$_3$) (C$_6$D$_6$, 600 MHz) (single isomer, obtained after prolonged storage at -35 °C).
Figure F.8. $^{13}$C NMR of TIOC'Bu$_2$(3,5-Me$_2$C$_6$H$_3$) (C$_6$D$_6$, 150 MHz).
Figure F.9. $^1\text{H}-^1\text{H}$ COSY NMR of TIOC'Bu$_2$(3,5-Me$_2$C$_6$H$_3$) (C$_6$D$_6$, 600 MHz).
Figure F.10. $^1$H NMR of freshly prepared $\text{Tl}_2(\text{OC}^\prime\text{Bu}_2(3,5-\text{Me}_2\text{C}_6\text{H}_3))_2$ ($\text{C}_6\text{D}_6$, 600 MHz, room temperature) demonstrating two isomers.
Figure F.11. \(^1\)H NMR of Ru(cymene)(\(κ^2\)-OC\(^7\)Bu\(_2\)(3,5-Me\(_2\)C\(_6\)H\(_3\))) (C\(_6\)D\(_6\), 600 MHz).
Figure F.12. $^{13}$C NMR of Ru(cymene)($\kappa^2$-OC'Bu$_2$(3,5-Me$_2$C$_6$H$_3$)) ($C_6D_6$, 150 MHz).
Figure F.13. $^1$H-$^1$H COSY NMR of Ru(cymene)(κ²-OC'Bu₂(3,5-Me₂C₆H₃)) (CD₆, 600 MHz).
Figure F.14. $^1$H-$^{13}$C HSQCAD NMR of Ru(cymene)(κ²-OC $^{t}$Bu₂(3,5-Me₂C₆H₃)) (C₆D₆, 600 MHz).
Figure F.15. $^1$H-$^{13}$C HMBCAD NMR of Ru(cymene)(κ²-OC'Bu₂(3,5-Me₂C₆H₃)) (C₆D₆, 600 MHz).
Figure F.16. $^1$H-$^{13}$C HMQC NMR of Ru(cymene)(κ²-OC'O'Bu₂(3,5-Me₂C₆H₃)) (C₆D₆, 600 MHz).
2. UV-Vis Spectra

Figure F.17. UV-Vis spectrum for Tl₂(OC⁶Bu₂(3,5-Me₂C₆H₃))₂ at four different concentrations. \( \lambda_{\text{max}} \), nm \((\varepsilon_M, \text{Lmol}^{-1}\text{cm}^{-1})\): 316 (900), 297 (1200).
Figure F.18. UV-Vis spectra for Ru(cymene)(κ²-OC'Bu₃(3,5-Me₂C₆H₃)) at six different concentrations. λₘₚ, nm (εₘ, Lmol⁻¹cm⁻¹): 545 (5200), 361 (15400), 263 (30000).
Figure F.19. UV-Vis spectrum of Fe(OCBC2tBu2(3,5-Me2C6H3))2(THF)2 at five different concentrations. λ_max, nm (ε_M, Lmol⁻¹cm⁻¹): 407 (Sh, 250).
3. IR Spectra

Figure F.20. IR spectra of LiOCiBu2(3,5-Me2C6H3) in the 3400-600 cm⁻¹ range.
Figure F.21. IR spectra of Fe(OC'Bu₂(3,5-Me₂C₆H₃))₂(THF)₂ in the 3400-600 cm⁻¹ range.
APPENDIX G: SUPPLEMENTARY MATERIAL FOR CHAPTER 7

1. $^1$H and $^{13}$C NMR Spectra of complexes 1, 2 and 3

Figure G.1. $^1$H NMR of Mg(OR)$_2$(THF)$_2$ ($C_6D_6$, 600 MHz).
Figure G.2. $^{13}$C NMR of Mg(OR)$_2$(THF)$_2$ (C$_6$D$_6$, 150 MHz).
Figure G.3. $^1$H NMR of Mg(OR)(sec-butyl)(THF)$_2$ ($C_6D_6$, 600 MHz).
Figure G.4. $^{13}$C NMR of Mg(OR)(sec-butyl)(THF)$_2$ (C$_6$D$_6$, 150 MHz).
Figure G.5. $^1$H NMR of Mg(OR')$_2$(THF)$_2$ (CD$_2$Cl$_2$, 400 MHz).
Figure G.6. $^{13}$C NMR of Mg(OR')$_2$(THF)$_2$ (CD$_2$Cl$_2$, 100 MHz).
2. Selected Characterization Data for PLA

Figure G.7. Typical $^1$H NMR spectrum demonstrating the conversion of lactide to PLA.
Figure G.8. Typical HHDEC NMR spectrum of PLA, indicating the atactic nature of the resulting polymer.
Figure G.9. $^1$H NMR spectrum demonstrating end group analysis of PLA synthesized by Mg(OR)$_2$(THF)$_2$. 
Figure G.10. GPC trace of polymer obtained in run 7 of Table 7.1.
Figure G.11. GPC trace of polymer obtained in run 2 of Table 7.1.
5. Characterization Data for the DHC/LO copolymers

Figure G.12. MALDI-ToF-MS spectrum of DCH/LO copolymer synthesized by 17.
Figure G.13. Regioisomers for DCH/LO sequences

Figure G.14. $^{13}$C NMR spectrum of DCH/LO copolymer synthesized by 17.
Figure G.15. $^1$H NMR spectrum of CHO/PA copolymer obtained in the absence of alcohol
Figure G.16. TGA analysis of the of DCH/LO copolymer.
Figure H.1. $^1$H NMR of 1-Adamantyl tert-butyl Ketone
Figure H.2. $^{13}$C NMR of 1-Adamantyl tert-butyl Ketone
Figure H.3. $^1$H NMR of 1-Adamantyl methyl Ketone
Figure H.4. $^{13}$C NMR of 1-Adamantyl methyl Ketone
Figure H.5. COSY NMR of 1-Adamantyl methyl Ketone
Figure H.6. HSQC NMR of 1-Adamantyl methyl Ketone
**Figure H.7.** HMBC NMR of 1-Adamantyl methyl Ketone
Figure H.8. HMQC NMR of 1-Adamantyl methyl Ketone
Figure H.9. $^1$H NMR of HOR$^+$
Figure H.10. $^{13}$C NMR of HOR$^{1*}$
Figure H.11. COSY NMR of HOR$^{1n}$
Figure H.12. $^1$H NMR of HOR$^{2*}$
**Figure H.13.** $^{13}$C NMR of HOR$^{2e}$
Figure H.14. $^1$H NMR of HOR$^{3+}$
Figure H.15. $^{13}$C NMR of HOR$^{3*}$
Figure H.16. COSY NMR of HOR$_3^*$
Figure H.17. HMBC NMR of HOR$^3$
Figure H.18. HMQC NMR of HOR$^{39}$
Figure H.19. HSQC NMR of HOR$^{3}$
Figure H.20. $^1$H NMR of HOR$^4$
Figure H.21. $^{13}$C NMR of HOR$^4$
Figure H.22. COSY NMR of HOR$^4$
Figure H.23. HSQC NMR of HOR4*
Figure H.24. HMQC NMR of HOR$^{19}$
Figure H.25. HMBC NMR of HOR$^4$
Figure H.26. $^1$H NMR of HOR$^5$
Figure H.27. $^{13}$C NMR of HOR$^5$
Figure H.28. $^1$H NMR of HOR$^6$
Figure H.29. $^{13}$C NMR of HOR$^6$
Figure H.30. $^1$H NMR of HOR$^7$
Figure H.31. $^{13}$C NMR of HOR$^7$
Figure H.32. $^1$H NMR of HOR$^8$
Figure H.33. $^{13}$C NMR of HOR$_8^*$
Figure H.34. $^1$H NMR of Mg(OAd'BuPh)$_2$(THF)$_2$
Figure H.35. $^{13}$C NMR of Mg(OAd' BuPh)$_2$(THF)$_2$
Figure H.36. $^1$H NMR of Mg(OMePh)$_2$(THF)$_2$
Figure H.37. HRMS of 1-Adamantyl tert-butyl Ketone
Figure H.38. HRMS of 1-Adamantyl methyl ketone
Figure H.39. HRMS of HOR$^1$
Figure H.40. HRMS of HOR$^{2+}$
Figure H.41. HRMS of HOR$^{3+}$
Figure H.42. HRMS of HOR$^{4+}$
Figure H.43. HRMS of HOR$^3^+$
Figure H.44. HRMS of HOR^6+
Figure H.45. HRMS of HOR$^{2*}$
**Figure H.46.** HRMS of HOR$^8^+$
Figure H.47. IR spectra of 1-Adamantyl tert-butyl Ketone
Figure H.48. IR spectra of HOR$^{2+}$
Figure H.49. IR spectra of HOR$^6$
Figure H.50. IR spectra of HOR$^*$
Figure H.51. IR spectra of HOR$^8$
Figure H.52. IR spectra of Mg(OAd'BuPh)$_2$(THF)$_2$
REFERENCES


27. Polymer Properties Database. Polyarylates.


ABSTRACT

SYNTHESIS AND REACTIVITY OF METAL BIS(ALKOXIDE) COMPLEXES IN NITRENE COUPLING AND POLYMERIZATION OF POLAR MONOMERS

by

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Major: Chemistry (Inorganic)
Degree: Doctor of Philosophy

The nitrene homocoupling to produce azoarenes was done using two different iron (II) alkoxide complexes, Fe(OC′Bu₂(3,5-Ph₂C₆H₃)₂(THF)₂ and Fe[OO]Ph(THF)₂. Due to the steric bulkiness of HOC′Bu₂(3,5-Ph₂C₆H₃ ligand, this complex exhibited selectivity for the bis(alkoxide) ligation; no tris(alkoxide) complexes were observed. As a result, both bulky and non-bulky aryl nitrenes are coupled with Fe(OC′Bu₂(3,5-Ph₂Ph)₂(THF)₂, albeit the coupling of the less bulky substrates requires higher temperatures and longer reaction times. Stoichiometric reactions of Fe(OC′Bu₂(3,5-Ph₂C₆H₃)₂(THF)₂ with non-bulky aryl azides led to the observation of the iron(III) tetrazene radical anion complexes, that can produce azoarene products after heating. Tetrazene complexes likely serve as a “masked form” of the reactive nitrene complex based on these observations and the QM/MM modeling of the reaction mechanism. These calculations suggest that the tetrazene complex is more stable than nitrene.

Fe[OO]Ph(THF)₂ is selective for coupling aryl nitrenes lacking ortho substituents; no reactivity with ortho-substituted (i.e. mesityl) azide took place. The difference in the reactivity is hypothesized to be due to the sterically congested active site of Fe[OO]Ph, which interferes with the reactivity of putative “Fe[OO]Ph(=NMes)” species.
Furthermore, heterocoupling reactivity of different nitrenes was investigated to produce asymmetric azoarenes, using iron(II) alkoxide pre-catalysts. We have explored the heterocoupling reactivity of Fe(OC\textsc{\textprime}Bu\textsubscript{2}(3,5-Ph\textsubscript{2}C\textsubscript{6}H\textsubscript{3}))\textsubscript{2}(THF)\textsubscript{2} (which previously exhibited wide substrate scope) by itself, as well as the combination of Fe(OC\textsc{\textprime}Bu\textsubscript{2}(3,5-Ph\textsubscript{2}C\textsubscript{6}H\textsubscript{3}))\textsubscript{2}(THF)\textsubscript{2} and Fe[OO]\textsuperscript{Ph}(THF)\textsubscript{2} catalysts. Fe(OC\textsc{\textprime}Bu\textsubscript{2}(3,5-Ph\textsubscript{2}C\textsubscript{6}H\textsubscript{3}))\textsubscript{2}(THF)\textsubscript{2} has demonstrated efficient heterocoupling reactivity for a combination of mono-ortho-substituted aryl azides with di-ortho substituted aryl azides. In contrast, any combination involving less bulky meta/para substituted aryl azide did not lead to the efficient production of the heterocoupled product in a good yield due to stable tetrazene complexes with para/meta substituted azides. Mixed catalyst reactivity of Fe(OC\textsc{\textprime}Bu\textsubscript{2}(3,5-Ph\textsubscript{2}C\textsubscript{6}H\textsubscript{3}))\textsubscript{2}(THF)\textsubscript{2} and Fe[OO]\textsuperscript{Ph}(THF)\textsubscript{2} was not successful again likely due to the stable tetrazene formation of Fe(OC\textsc{\textprime}Bu\textsubscript{2}(3,5-Ph\textsubscript{2}C\textsubscript{6}H\textsubscript{3}))\textsubscript{2}(ArNNNNAr). A variety of new asymmetric azoarenes were isolated and their cis-trans isomerism was investigated. All azoarenes were shown to demonstrate the presence of both isomers in solution at room temperature, with the trans isomer being the predominant one. Thermal conditions lead to the full conversion of the mixture to the trans isomer only in all cases, while the irradiation of the mixture with the UV light leads to the predominant formation of the cis isomer.

In a second major part of my dissertation, I have reported synthesis, ROP, and ROCOP with a new well-defined mononuclear magnesium complex Mg(OC\textsc{\textprime}Bu\textsubscript{2}Ph)\textsubscript{2}(THF)\textsubscript{2}. The complex led to active albeit not well controlled ROP of lactide precursor. Utilization of coordinating solvent (THF) or benzyl alcohol as a co-catalyst leads to better control of polymerization. In contrast, well-behaved ROCOP was obtained with a variety of different monomers. While the use of PPNCl as a nucleophilic initiator leads to an efficient copolymerization of cyclohexene oxide (CHO) with phtalic anhydride (PA) or succinic anhydride (SA), the structure of the resulting copolymers was
found to be only moderately alternating, demonstrating small amount of ether linkages. In contrast, the use of BnOH as an initiator forms perfectly alternating copolymer of PA with CHO. More challenging biorenewable monomer limonene oxide (LO) was also co-polymerized with PA. The combination of PA with both CHO and LO leads to the formation of terpolymer. Finally, the combination of two biorenewable precursors, LO and dihydrocumarin, formed a fully biorenewable novel copolymer. No stereoselectivity was observed in all the above reactions, likely due to the achiral nature of the catalyst.

Furthermore, several chiral ligands and a chiral magnesium complex were synthesized to investigate stereoselective polymerization of polar monomers for polyester synthesis. Bulky HOCAAd'BuPh ligand led to the formation of diasteriomerically pure magnesium complex (Mg(OCAAd'BuPh)2(THF)2) which was isolated as homochiral diastereomer of Mg(OC'RAd'BuPh)2(THF)2 and Mg(OC'SAd'BuPh)2(THF)2 enantiomers. (Mg(OCAAd'BuPh)2(THF)2) was a very fast catalyst for polymerization of cyclic esters but it was not able to produce tactic polymers, likely due to the loss of the chiral alkoxides. (Mg(OCAAd'BuPh)2(THF)2) was able to show very high reactivity for lactide, ε-caprolactone also showed reactivity for less reactive substrates including ω-pentadecalactone (PDL), and ω-hexadecenlactone (HDL). HOCAdMePh was unable to make diasteriomerically pure Mg complex due to drastic decrease of bulkiness of the ligand.
AUTOBIOGRAPHICAL STATEMENT

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2. Kurup, S. S.; Wannipurage, D.; Stoian, S. A.; Lord, R. L.; Groysman, S. Chem. Commun. 2019, 55, 10780-10783. †Authors have contributed equally to this work


5. Grass, A.; Kulathungage, L. W.; Wannipurage, D.; Ward, C. L.; Groysman. S. Dalton Trans. 2021, 50, 2501-2509. †Authors have contributed equally to this work


Conference Presentations


• D. Wannipurage, S. Groysman. Reactivity of Iron Alkoxide Complexes Towards Catalytic Azoarene Synthesis. Ohio Inorganic Weekend, University of Toledo, November 2019, Talk