

**The Synthesis of a New Aryl Phosphine-Imidazolium Ligand as a  
Catalyst for Ring Opening Olefin Metathesis Polymerization**

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**2006/2008**

**Declaration**

**DECLARATION**

I hereby declare that this project was conducted by me at the Cardiff University, UK under the supervision of Prof. Peter G. Edwards as a partial fulfilment of the MSc in Polymer Science and Technology and the contents of this thesis is true and correct to the best of my knowledge.



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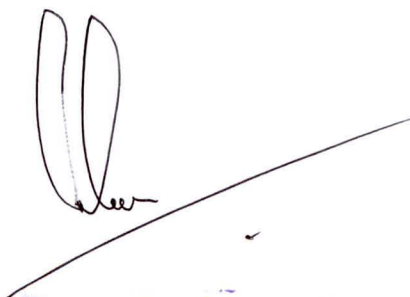
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## Abstract

Homogeneous catalysis has been responsible for many major recent developments in synthetic organic chemistry. The combined use of Coordination and Organometallic Chemistry has produced a number of new and powerful synthetic methods for important classes of compounds in general.

A major requirement for homogeneous catalysis is the presence of available reaction sites commonly provided by labile spectator ligands. Phosphine ligands as well as N-heterocyclic carbene ligands have been successfully used in these systems for past decades. Recently scientists also have more interested on the mixed donor ligands, which are mostly a combination of phosphine ligands with N-heterocyclic carbene ligands.

Mechanistic and synthetic studies in organometallic chemistry have provided considerable insight into olefin metathesis, which has received tremendous attention as a powerful technology for the formation of carbon-carbon bonds and has found numerous applications in polymer chemistry.

New homogeneous olefin metathesis catalysts based on high oxidation state transition metals have opened new opportunities in polymer synthesis by providing unprecedented control in ring-opening polymerization of cyclic alkenes.

As a study of the Chemistry of the mixed donor ligands, we have been interested in carbene-phosphines with rigid back bone functions and their complexes. As a result, a chelating phosphine-imidazolium salt has been synthesized and the reaction has been analyzed by altering the reaction path, changing the solvent and purifying the starting materials, in order to make proper 1,3-bis(o-diisopropylbenzene) imidazolium chloride.

The aryl linker ligand, forms two 6-membered chelate rings (Figure i) with a metal, which can be used as a catalyst for the ring-opening olefin metathesis polymerization. The more rigid aryl rings may impart more stability by limiting the amount of movement of the linker around the metal centre. Attaching two aryl rings directly to the imidazole ring would form two 6-membered chelate rings upon coordination to a metal centre. This should prevent any squeezing of the ligand and so stop or slow down any reductive elimination.

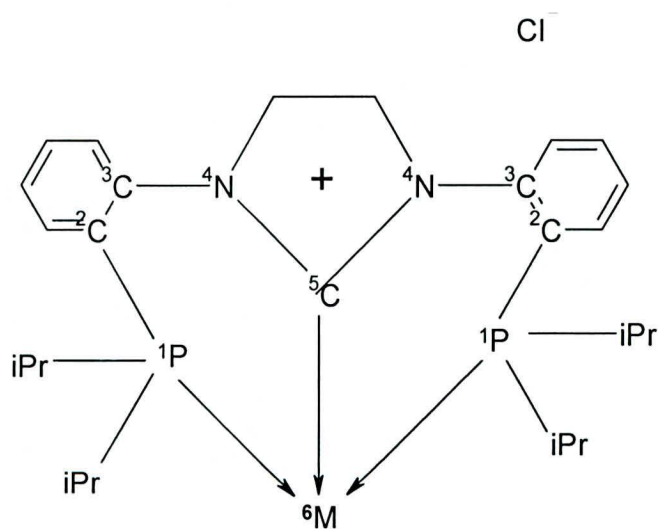


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Thank you all very much

## Glossary

NHC	- N-Heterocyclic carbene
Me <sub>3</sub> P	- Trimethyl Phosphine
PPh <sub>3</sub>	- Triphenyl Phosphine
t-BuP <sub>3</sub>	- Tertiarybutyl Triphosphine
THF	- Tetrahydrofuran
DCM	- Dichloromethane
CCl <sub>4</sub>	- Carbon Tetrachloride
Et <sub>2</sub> O	- Diethyl Ether
DMSO	- Dimethylsifoxide
NH <sub>4</sub> OAc	- Ammonium Acetate
NaOH	- Sodium Hydroxide
NaHCO <sub>3</sub>	- Sodium Bicarbonate
HCl	- Hydrochloric acid
CH <sub>3</sub> COOH	- Acetic acid
BuLi	- Butyl Lithium
Pr <sub>2</sub> PCl	- Diisopropyl Chloride
Pr <sub>2</sub> PH	- Diisopropyl Phosphine
Ar	- Aromatic
X	- Halogens

**CHAPTER 1**  
**INTRODUCTION**

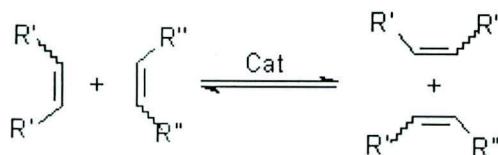
## CHAPTER 1

### INTRODUCTION

#### 1.1: Introduction

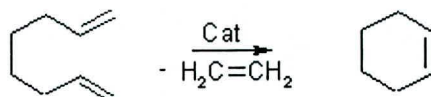
Over the past 50 years, the development of organometallic chemistry has had a major impact on the growth of homogeneous catalysis, much of which has been justified on the basis of the insight it gives in to catalytic reactions. Homogeneous catalysis is an elegant method of chemical synthesis and can provide new products and processes as well as efficient and clean solutions to many current problems in the petrochemical, pharmaceutical and agrochemical industries. In recent years, olefin metathesis catalysis has received tremendous attention as a powerful technology for the formation of carbon carbon-bonds and has found numerous applications in organic synthesis and polymer chemistry.

Olefin metathesis is a popular and useful reaction, which is an organic reaction that entails redistribution of alkylene fragments by the scission of carbon - carbon double bonds in olefins in a number of different ways, including cross metathesis<sup>1</sup>, ring closing metathesis<sup>2</sup>, ring opening metathesis polymerization<sup>3</sup> and acyclic diene metathesis<sup>4</sup> as seen in the Figure 1.1 below. Since its discovery, olefin metathesis has gained widespread use in research and industry for making products ranging from medicines and polymers to enhanced fuels.

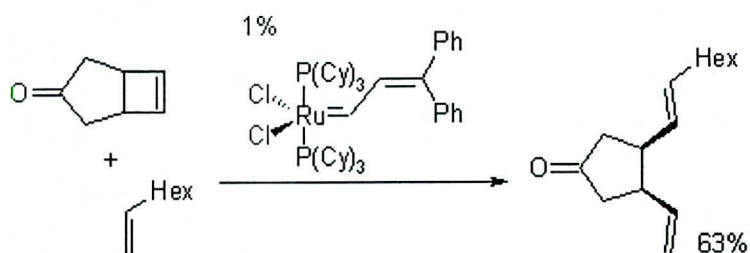


Cross Metathesis

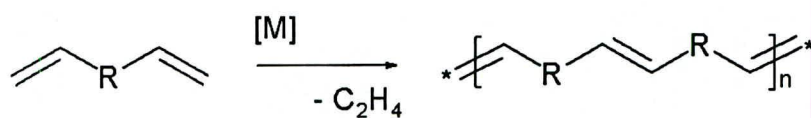
The cross metathesis reaction was first used in petroleum reformation for the synthesis of higher olefins (Shell higher olefin process - SHOP), with nickel catalysts under high pressure and high temperatures.



Ring closing metathesis



Ring opening metathesis (Polymerization) - ROM(P)



Acyclic diene metathesis (ADMET)

Figure 1.1: Examples of Metathesis reactions

A major requirement for homogeneous catalysis is the presence of available reaction sites, ideally *cis*, and this is commonly provided by labile spectator ligands. Our strategy is to address the control of liability by use of carefully designed ligands to provide free reaction sites by dissociation but only to a well-defined extent. A very robustly coordinating ligand is required, which occupies several of the coordination sites rigidly, but allows remaining sites to be free for other spectator ligands and reactant species to coordinate reversibly.

The virtues of phosphine ligands have long been known in the above-mentioned properties, and recently, a second generation of catalyst incorporating N-heterocyclic carbene ligands as well as the phosphines has been developed. The incorporation of the carbene functionality into ligands systems containing other donor groups such as phosphines offers exciting opportunities for ligand design, which promises the discovery of new efficient catalysts.

## 1.2: Historical Notes on Phosphine and Carbene Ligands

Both phosphines and carbenes have found useful applications as ligands in organometallic reactions for many years. Varying the substituents can control the electronic and steric properties of these ligands. This can increase reaction rates and gives a much greater control of the types of products formed.

Carbenes are both reactive intermediates and ligands in catalysis, also they are neutral divalent carbon species ( $\text{:CH}_2$ ), featuring two non bonding unpaired electrons. As intermediates, they carry carbon and hydrogen substituents and belong therefore to the class of Schrock carbenes (Fig. 1.2c)<sup>5</sup>. As ligands they contain nitrogen substituents and are clearly Fischer carbenes (Fig.1.2b)<sup>5</sup>. A free carbene such as  $\text{CH}_2$  has two spin states, singlet ( $\uparrow\downarrow$ ) and triplet ( $\uparrow\uparrow$ ). These are distinct isomers, not resonance forms.

In the singlet, the electrons are paired up in the  $sp^2$  lone pair but in the triplet there is one electron in each of the  $sp^2$  and  $p$ -orbitals (Fig.1.2a)<sup>[5]</sup>. Carbenes are rarely stable in the free state. Methylene,  $:CH_2$  for example, is a transient intermediate which reacts rapidly with a wide variety of species. This instability (both thermodynamic and kinetic) contributes to the very strong bonding of carbenes to metal atoms by disfavoring dissociation. They have received a great deal of attention in the last decade as ligands in catalytic metal complexes, but the structural motive was already explored in the early seventies.

