OLIGOMERIZATION OF HIGHER OLEFINS

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Abstract

A series of new substituted cyclopentadienyl ligands and their chromium complexes were successfully synthesised and characterised using a wide range of analytical and spectroscopic techniques such as NMR, mass spectrometry, elemental analysis and melting points.

The ligands were then tested for the oligomerization of ethylene and 1-hexene. The chromium complexes were tested for the oligomerization of 1-hexene.

The synthesis of the alkyl-tetraphenylcyclopentadienes, 5-^{n}Butyl-1,2,3,4-tetraphenyl-1,3-cyclopentadiene (**1**) and 5-^{t}Butyl-1,2,3,4-tetraphenyl-1,3-cyclopentadiene (**2**) was carried out successfully. Both ligands were obtained in moderate yields. The aryl-substituted tetraphenylcyclopentadiene ligands, 1-butyl-4-(2,3,4,5-tetraphenylcyclopentadien-1-yl)benzene (**3**) and 1-hexyl-4-(2,3,4,5-teraphenylcyclopentadien-1-yl)benzene (**4**) were also synthesised and obtained in good yields. This was then followed by the synthesis of the alkyl-substituted pentaphenylcyclopentadiene, 1,2,3,4,5-penta-(3,5-dimethyl phenyl) cyclopenta-1,3-diene (**5**) and 1,2,3,4,5-penta-(3,5-di-t-butyl phenyl) cyclopenta-1,3-diene (**6**).

The cyclopentadiene ligands were used for the synthesis of the dinuclear chromium complexes. Mass spectrometry was used to characterise these complexes. Due to the paramagnetic nature of the complexes, NMR spectroscopy could not be used to characterise the complexes. Further characterisation of these complexes was not possible due to their unstable nature.

Ethylene trimerization reaction was tested with the cyclopentadienyl ligands using a four component system. All ligands were found to be active towards ethylene oligomerization and selective towards ethylene trimerization with the exception of ligand 5-^{t}Butyl-1,2,3,4-

tetraphenyl-1,3-cyclopentadiene (**2**), which only gave polymers. The same ligands were also found to be active towards oligomerization of 1-hexene and selective towards higher olefins. Chromium complexes were also tested for oligomerization of 1-hexene. They were all active and selective towards higher olefins.

All the catalytic products were characterised by gas chromatography.

Abbreviations

L	: Ligand
Cp	: Cyclopentadienyl
Cp*	: Pentamethylcyclopentadienyl
MAO	: Methyl Aluminoxane
MMAO	: Modified Methyl Aluminoxane
TEA	: Triethylaluminium
TMA	: Trimethylaluminium
MOGD	: Mobil Olefins towards Gasoline and Distillate
GPC	: Gel-permeation chromatography
GC	: Gas Chromatography
MS	: Mass Spectrometry
THF	: Tetrahydrofuran
Ph	: Phenyl
n-BuLi	: *n*-butyllithium
DMF	: Dimethylformamide
$Cr(acac)_3$	: Chromium(III) tris(acetylacetanoate)
PE	: Polyethylene
$Cr(2\text{-}EH)_3$	: Chromium(III) tris(2-ethylhexanoate)
HCE	: Hexachloroethane
HCl	: Hydrochloric acid
DCM	: Dichloromethane
Et_2O	: Diethyl ether
NMR	: Nuclear Magnetic Resonance

s : Singlet

d : Doublet

t : Triplet

m : Multiplet

ppm : parts per million

J : constant coupling

Hz : Hertz

mp : Melting point

ºC : degrees Celsius

min : minutes

g : grams

mmol : millimoles

ml : millilitres

h : hours

M^+ : parent molecular ion

m/z : mass to charge ratio

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CHAPTER 1

INTRODUCTION AND REVIEW ON OLIGOMERIZATION OF α-OLEFINS USING CHROMIUM AND OTHER METALS -BASED CATALYSTS

1.1 Introduction

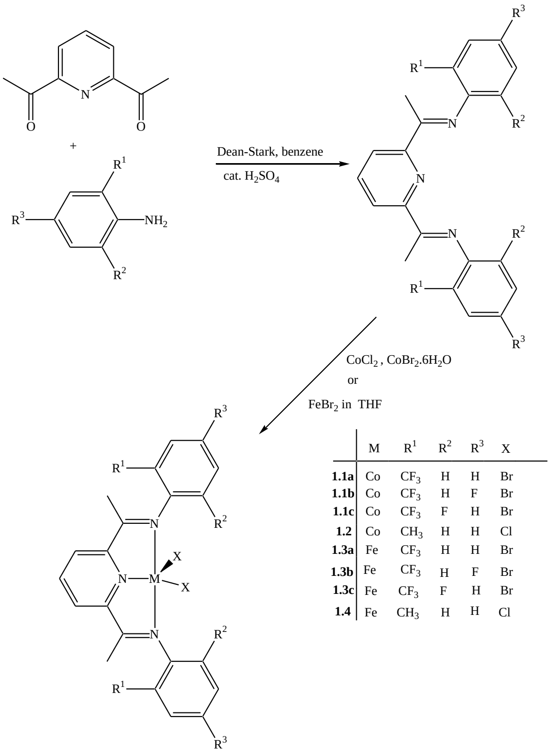
Linear α-olefins are of importance in many chemical industries as they are versatile intermediates and building blocks for a variety of downstream processes.[1] These olefins are mainly produced by ethylene oligomerization because of the high product quality and the ready availability of ethylene.[1] Other routes used in the production of α-olefins involve paraffin-wax cracking, paraffin dehydrogenation and alcohol dehydration.[2] Oligomerization of propylene can also be used to produce α-olefins however, branched olefins are mainly produced.[3] In South Africa, α-olefins are also a product of the petrochemical industry SASOL. The main applications of α-olefins are as co-monomers for polyethylene (C_4-C_8) in polymer production, feedstocks for surfactants (C_{12}-C_{20}), plasticizers and lubricants (C_6-C_{10}). There are many different catalytic systems which are used for the oligomerization of olefins using ethylene as a feedstock.

This chapter reviews the oligomerization of α-olefins using transition metal catalysts, focusing on chromium catalyst systems.

The mechanistic aspects of the oligomerization system are briefly outlined. A short summary of the use of acid catalysts for the oligomerization of higher olefins is also given as it is valuable for the production of pollutant-free lubricant. The last part of this review includes the synthesis of cyclopentadienyl ligands and their chromium complexes.

1.2 Iron and cobalt based-oligomerization catalysts

"Highly-active" iron and cobalt-based olefin polymerization catalysts precursors were discovered in the late 1990s. This led to much interest in the chemistry of transition-metal complexes bearing terdentate bis(imino)pyridine ligands prepared by Schiff-base condensation procedures.[26] Complexation of these ligands with cobaltous and ferrous bromides gave the complexes (Scheme 1.1) which were obtained in high yields.[29]



	M	R^1	R^2	R^3	X
1.1a	Co	CF_3	H	H	Br
1.1b	Co	CF_3	H	F	Br
1.1c	Co	CF_3	F	H	Br
1.2	Co	CH_3	H	H	Cl
1.3a	Fe	CF_3	H	H	Br
1.3b	Fe	CF_3	H	F	Br
1.3c	Fe	CF_3	F	H	Br
1.4	Fe	CH_3	H	H	Cl

Scheme 1.1

The complexes were tested for their oligomerization catalytic activity towards ethylene upon activation with MAO or modified-MAO. All of the fluorinated catalyst precursors (**1.1a – 1.1c** and **1.3a – 1.3c**) gave higher activities when compared to the non-fluorinated catalyst precursors (**1.2** and **1.4**).[29]

The catalyst precursors which were activated with modified-MAO, gave a higher activity than those activated with MAO. The cobalt complexes (**1.1a – 1.1c**) were found to be more active than the iron complexes (**1.3a -1.3c**).[29] It was observed that substitution on the *ortho*-position of the *N*-aryl group exerted a steric effect, which affected the rate of chain termination relative to chain propagation, thereby, giving short chain oligomers. Cobalt complexes (**1.1a – 1.1c)** with O-CF_3 substituents, gave products with increased molecular weights while complex **1.2**, with substituted O-CH_3, gave small molecular weight oligomers.

1.2.1 Oligomerization of propene using both iron and cobalt complexes

The oligomerization of propene was performed complexes **1.1-1.4**, Scheme 1.1, at 0°C and 1bar with MAO. None of the iron complexes studied yielded any products, while oligomers were formed with the cobalt complexes. Cobalt complex **1.1c** showed a higher activity when compared to other cobalt complexes due to the *ortho*-substituted electron releasing aryl substituent exerting a steric effect, as previously mentioned.

1.2.2 Oligomerization of 1-butene and 1-hexene using cobalt complex 1.1c

Based on the higher activity in propene oligomerization, complex **1.1c** was used for the oligomerization of 1-butene and 1-hexene. The activity of this complex was found to be between 19000g and 8310g per g of Co h^{-1}over 30 min runs at -20°C.[29] The main products for 1-butene were linear dimers consisting of 2 and 3-octenes, while branched trimers were formed from 1-butene and 1-hexene and partly from propene.

When complex **1.1c** was activated with MAO, it oligomerized 1-hexene with an activity of 1090g per g of Co h^{-1} at 0°C, while at -20°C, the activity increased to 8310g per g of Co h^{-1}. The dimers obtained from oligomerization of 1-hexene were all internal olefins.[30]

1.2.3 The mechanism of α-olefin oligomerization

The suggested mechanism for the oligomerization process using the above cobalt catalysts is shown in Fig. 1.1. As an example, oligomerization of 1-propene, 1-butene and 1-hexene is presented.

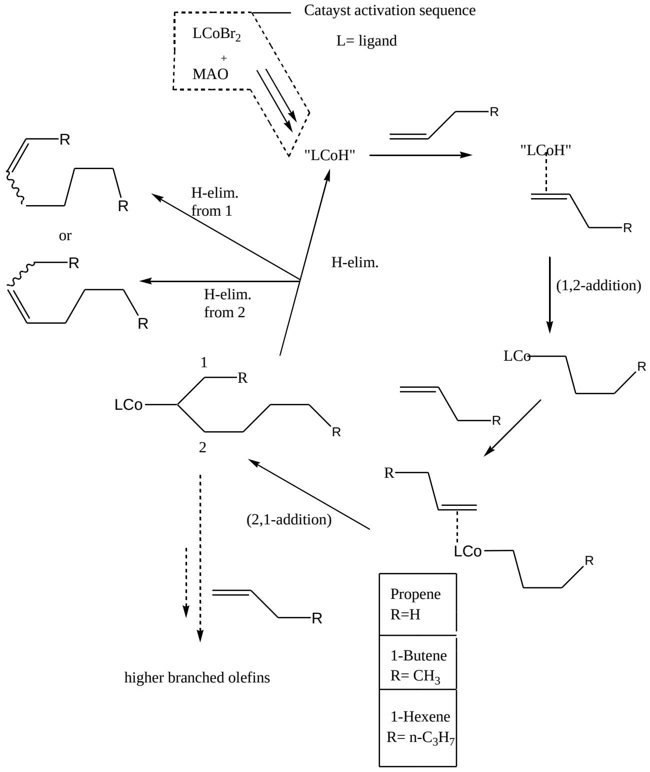


Figure 1.1: Proposed mechanism for the dimerization of α-olefins using cobalt complexes as catalysts

29

The mechanism involves the activation of the cobalt dihalide with MAO to form an active catalyst. This active species goes through a cycle to form a cobalt hydride-like species denoted as “LCoH”. This hydride species undergoes two consecutive addition reactions, 1,2-

addition and 2,1-addition. Chain termination via β-H elimination then follows.[31, 32] A third addition to form a branched cobalt alkyl species is possible, but this process occurs slowly to generate branched trimers. It is therefore impossible to form linear propene trimers and tetramers by successive addition. However, a linear propene trimer can form via co-dimerization of propene and 1-hexene, while linear tetramers are possible by dimerization of 1-hexene. From this study, no isomerization of terminal olefins to internal olefins was observed.[32]

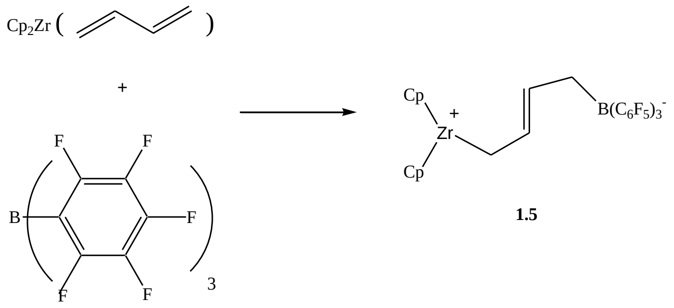
In summary, all the dimers were linear. In addition, the 1-butene and 1-hexene dimers formed from complex **1.1a** (Scheme 1.1) were all internal olefins, while oligomerization of propene showed a mixture of branched and linear olefins. The product distribution for the oligomerization reactions does not follow a standard mathematical distribution meaning that it does not follow a Schulz-Flory distribution.

1.3 Olefin polymerisation by metallocene catalysts

Metallocene are complexes which helped in the understanding the factors that are important for stabilizing active metal centres for the polymerization and control of their activity and selectivity. Once activated with MAO, the complex result in active and long-lived catalyst systems.[27]

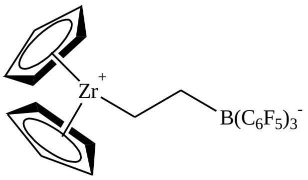
There has been an increase in the application of metallocene complexes as α-olefin polymerization catalysts. It is known that the catalytically active species in olefin polymerization is a coordinatively unsaturated cationic alkyl complex that is stabilised by several ligands e.g. $[L_nMR]^+$.[33] Erker *et al.* introduced a strategy to generate the catalytically active species, which involved the treatment of the metal complex$[Cp_2Zr(butadiene)]$ with $B(C_6F_5)_3$. This resulted in a metallocene-borate-betaine system as a zwitterionic metallocene

(Scheme 1.2). This system was found to be highly active for the polymerization of olefins.[27,34]



Scheme 1.2

Another example was reported by Piers and Zhivers, where alkene coordination to the complex, followed by reaction with $B(C_6F_5)_3$ formed a zwitterionic metallocene (Fig. 1.2: **1.6**) capable of initiating olefin polymerization.[28]



1.6

Figure 1.2: An example of a zwitterionic metallocene

Group IV metallocene and related catalysts have been at the forefront in the development of highly active and long lived catalyst systems. These catalytic systems showed high polymerization reaction activity towards ethylene and other olefins.[36,38,39]

1.4 Group IV metal complexes for oligomerization of α-olefins

Group-IV transition metals, such as titanium, zirconium and hafnium containing the Cp-ligands are known as “metallocene catalysts” [35]. Titanocene is however, unstable under conventional polymerization temperatures and hafnium systems are too expensive, making zirconocene the centre of academic and industrial attention. Since the 1990s, the bis(cyclopentadienyl)group-IV metal complexes were introduced as a new generation of Ziegler-Natta catalysts for the polymerization of olefins.[36,37] It was reported that more metallocene catalysts can be used effectively in the oligomerization of α-olefins and other monomers.[38, 39]

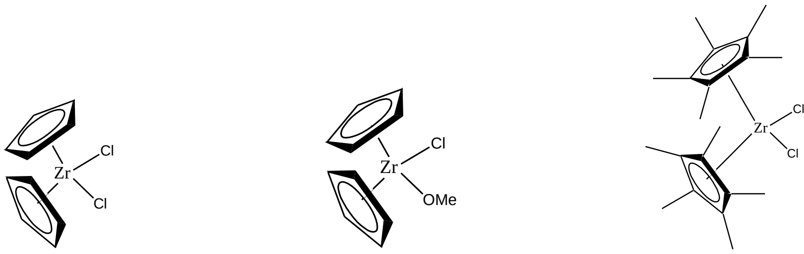
The metallocene catalyst $(\eta^5\text{-}C_5H_5)_2ZrCl_2$/MAO appeared to be one of the most popular systems for the oligomerization of propene, leading to vinylidene-terminated oligopropenes.[40-42]

It was also found that members of the methyl substituted series, $(\eta^5\text{-}C_5H_{5-n}Me_n)_2ZrCl_2$, as well as mixed methyl substituted metallocenes, gave atactic propene oligomers in combination with MAO.[43]

Christoffers and Bergman found that $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, when activated with MAO, selectively and catalytically dimerizes 1-butene to 2-ethyl-1-hexene without formation of any higher oligomeric species. [39] These metallocene catalysts were then tested with higher olefins such as 1-pentene, 1-hexene, 1-heptene and 1-octene.

The olefin reactivity was investigated by Hoffmann and his co-workers. The reactivity in their systems decreased in the following order: ethylene > propylene > 1-butene > 1-hexene > 1-octene > 1-decene.[44] It was observed that longer chains undergo a more difficult oligomerization reaction than ethylene and propylene and that the selectivity in higher olefins is lower. It was suggested that higher α-olefins can form a greater number of isomers than ethylene and propylene in the oligomerization cycle. Most of the complexes used for ethylene were also active toward higher olefins.[44]

The oligomerization of 1-pentene was studied using metallocene catalyst such as $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, $(\eta^5\text{-}C_5H_5)_2HfCl_2$, $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$, $(\eta^5\text{-}C_5H_5)_2ZrCl\{O(Me)CW(CO)_5\}$ and $(\eta^5\text{-}C_5H_5)_2ZrCl(OMe)$. All catalysts were activated with MAO (Fig. **1.3**). Depending on the metallocene used, the oligomers obtained ranged from the dimer of 1-pentene to polymers with molecular weights M_w = 149,000g mol^{-1}.[45]



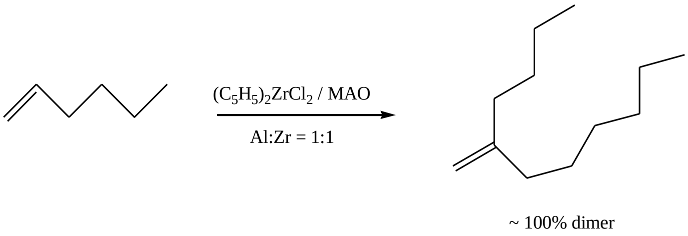
1.7 **1.8** **1.9**

Figure 1.3 Zirconium complexes used for oligomerization/polymerization of higher olefins

$(\eta^5\text{-}C_5H_5)_2ZrCl\{O(Me)CW(CO)_5\}$/MAO was found to be highly active for 1-pentene to afford a low-molecular weight product, while $(\eta^5\text{-}C_5H_5)_2ZrCl_2$/MAO gave a low molar mass oligomer containing 25% of dimers, 18% trimers and 14% tetramers. Its analogue, the $(\eta^5\text{-}C_5H_5)_2HfCl_2$ complex yielded an atactic oligomer, while the sterically hindered $(C_5Me_5)_2ZrCl_2$ complex gave a viscous oil with the vinylidene groups.

Christoffers and Bergman reported that $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (**1.7**), when activated with MAO, selectively and catalytically dimerizes 1-pentene to 2-propyl-1-heptene without the formation of other oligomeric species.[39]

(η^5-$C_5H_4{}^tBu)_2ZrCl_2$/ MAO (**1.9**) was reported by Suzuki and his co-workers to oligomerize 1-hexene with a high activity of 8 x 10^5g per g of Zr h^{-1} and was selectively active towards forming 1-hexene dimers. It was suggested that the (η^5-$C_5H_5)_2Zr(H)Cl$ complex is the actual active species for the oligomerization of 1-hexene (Scheme 1.3).[46]

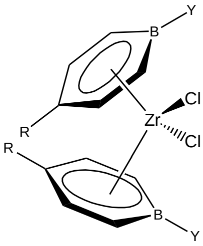


Scheme 1.3

Christoffers and Bergman also reported the oligomerization of 1-heptene using the (η^5-$C_5H_5)_2ZrCl_2$ complex (**1.7**), activated with MAO.[39] In this case it was observed that the complex was highly selective towards forming the dimer as 2-pentyl-1-nonene. No higher oligomers were formed. In comparison with 1-octene oligomerization, it was observed that the co-oligomerization of ethylene/1-octene using the same catalytic system was selective towards dimers as well.

$[Zr(CH_2C_6H_5)_4]$ and $[Ti(CH_2C_6H_5)_4]$ complexes were reported to have moderate activities when activated with Lewis acids, such as MAO, $[(Ph_3C)]^-[B(C_6F_5)_4]^+$or $B(C_6F_5)_3$, and were found to be active as polymerization catalysts.

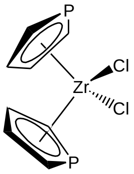
Other reported complexes of zirconium contained boratabenzene ligands (**1.10**) (Fig. 1.4) and showed high polymerization activity when activated with MAO.[47, 48]



[$(C_5B)^-$, $(C_5B)^-$]

Y = diisopropylamine, phenyl or ethoxide
R = H or Me

1.10



[$(C_4P)^-$, $(C_4P)^-$]

1.11

Figure 1.4: Zirconium complexes used for polymerization of olefins

Changing the Y-substituent on the boron from diisopropylamine to phenyl or ethoxide, resulted in an increase in the β-H-elimination of the coordinated alkene, favouring the formation of lower molecular weight oligomers instead of polymers .[49]

Other zirconium complexes (**1.11**) with Cp analogue containing P-atom (phosphacyclopentadienyl ligands) were also found to be very active polymerization catalysts.[50]

1.5 Liquid phase oligomerization of 1-hexene

Oligomerization of olefins over an acid catalyst is an important industrial method for the production of high molecular weight compounds useful as fuels and lubricants.

The “Ipatieff catalysts”, which consists of phosphoric acid impregnated kieselguhr silica, was used successfully to oligomerize propylene and butylenes.[51] Mobil researchers have found a most remarkable oligomerization process for converting light olefins into higher molecular weight products. The process is called Mobil Olefins towards Gasoline and Distillate (MOGD), and was found to be selective towards gasoline (C_5-C_{12}) or diesel (C_{13}-C_{22}) by tuning the reaction conditions.[52]

A 10-membered ring HZSM-5 zeolite is the main catalyst in the MOGD process. Owing to its steric hindrance towards the formation of bulky coke species inside the pore, HZSM-5 was found to exhibit a slow deactivation rate when compared to other zeolites.[53]

The liquid-phase oligomerization of alkenes towards gasoline and diesel is a subject of growing interest. The advantage of such oligomerization is that the gasoline octane number can be enhanced with the formation of a more valuable hydrocarbon fraction, free from pollutant precursors (fuels without nitrogen and sulphur). Moreover, there is also a significant economic incentive for the production of lubrication oil by solid acid catalysts as it is the cheapest way to catalysis.[55]

The liquid phase oligomerization of 1-hexene was studied over two solid acid catalysts, acid beidellite and ultra stable Y-zeolite. It was reported that, using n-octane and dodecane as solvents, the catalyst deactivation rate was decreased resulting in an increase in catalyst life time.[54]

Oligomerization with the reactants in the liquid phase is preferred from an activity, selectivity and stability point of view.[54]

Oligomerization of 1-hexene and 1-octene were tested over amorphous silica-alumina, sulphated zirconia, MCM-41 and the zeolite ZSM-5, zeolite H-Y and zeolite Omega in an attempt to identify the catalyst properties required for higher olefin oligomerization. All the tests were done with the reactants at low temperatures.[55] Rapid deactivation of the solid acid catalyst was observed with zeolites H-ZSM-5 and H-Y, while SO_4^{2-}/ZrO_2 displayed better stability but also deactivated visibly during the test period.

At the reaction temperature of 100˚C, zeolite H-MCM-41 was not active during the oligomerization because it lacked stronger acid sites when compared to other catalysts. The sulphated zeolite catalyst was used to study product selectivity with time due to its stability at that temperature. It was observed that there was a gradual shift to lighter products. Chromium salt was then added to all the catalysts and a noticeable influence was observed on the zeolite H-MCM-41, which produced a large oil fraction. However, no improvement in the life-time of the catalyst was observed.

With 1-octene, oligomerization was carried out in the temperature range of 100ºC to 200ºC in an attempt to improve conversion, but the catalysts still deactivated at those conditions. With the SO_4^{2-}/ZrO_2 catalysts, dimers were mostly formed with no other oligomers. It was observed that at temperatures exceeding 200◦C, cracking increased rapidly. However, an increase in the stability of the complexes was observed with a threshold where the rate of deactivation levelled off.

Oligomerization of 1-pentene [56] and 1-hexene[57] over solid-solid acid catalysts showed that cracking only became significant at temperatures above 270ºC to 300ºC. In the temperature range 100-300ºC, 1-hexene oligomerization was susceptible to cracking, while 1-octene was susceptible irrespective of the temperature range. It was observed that both oligomerization and cracking required strong acid sites for isomerization of olefins. In addition, branched olefins formed tertiary carbocations which are more stable and preferred. It was also observed that the oligomerization of the branched products was much faster than that of the linear olefins.[55]

The selectivity towards dimers and trimers was observed at temperatures below 200ºC for 1-hexene, where cracking was not significant, while 1-octene had more than 90% selectivity towards dimer formation.

The strength and the nature of the acid-site catalyst played a major role in the selectivity of the oligomers formed. When using H-Y zeolites, heavy oligomers were the main products while the sulphated zirconia catalysts were only selective towards C_{20}. It was expected that the zirconia catalyst, with a larger pore size would produce heavy oligomers when compared to the narrow pore catalyst, H-Y zeolite. This was however, not the case as the narrow pore catalyst, H-Y zeolite, produced the heavy oligomers. This could mean that the interaction between the catalyst and the olefin is stronger, allowing successive oligomerization steps to occur before desorption.

The introduction of chromium into the pores restricted the environment of the catalyst and the formation and mobility of heavy products. The products formed from Cr/H-ZSM-5 were heavier while those formed from Cr/H-Y were large. A great impact was seen when chromium was introduced into the zeolite H-MCM-41 catalysts, where it showed significant oligomerization activity, but too weak on its own to show any activity.[57]

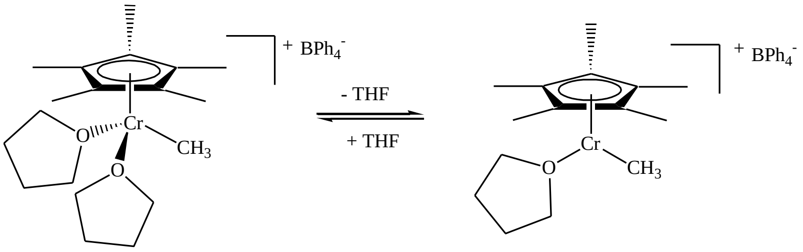
Since the catalyst life-time was found to be shorter at lower temperatures, the operating conditions were chosen to ensure that both the oligomerization and cracking extended the catalyst life-time. At low temperature, catalyst deactivation occurs mainly due to the heavy oligomers trapped in the catalyst, while at higher temperatures (>230°C), heavy oligomers can be cracked and the deactivation of the catalyst reduced.[62]

It was concluded that using catalysts with larger pores is beneficial because it allows heavy oligomers to leave the pores once they are formed. In addition, the chromium-catalysed oligomerization isomerized products to a lesser extend and yielded heavy oligomers when compared to acid catalysts, which only yielded lighter products (the dimers).

1.6 Homogeneous chromium catalysts for olefin polymerization

The first homogeneous catalysts, for α-olefin oligomerization based on chromium as the metal, were discovered by Hogan and Banks at Phillips Petroleum Co. In the 1950s, not much was known about the mechanism and the active site of this chromium catalyst.[7]

The synthesis and reactivity of chromium alkyls in +3 oxidation state were explored due to their solubility and stability.[8] The first complex that was synthesized and characterized was the [Cp*Cr(THF)$_2$Me]BPh$_4$ where Cp*= η^5-C_5Me_5. It was found that this paramagnetic 15-electron cationic complex exists in equilibrium with the unsaturated [Cp*Cr(THF)Me]$^+$ by dissociation of a THF ligand as shown in Scheme 1.4. [8]



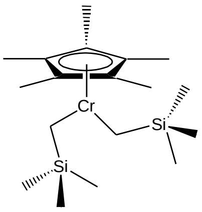
1.12 **1.13**

Scheme 1.4: Chromium complexes used for polymerization of olefins

[Cp*Cr(THF)Me]BPh$_4$ (**1.13**) was found to catalyse the polymerization of ethylene at ambient temperature and pressure in dichloromethane without the use of a co-catalyst. However, addition of THF inhibited the rate of polymerization by shifting the equilibrium to the unreactive [Cp*Cr(THF)$_2$Me]BPh$_4$ (**1.12**).

The polymers obtained were identified as high density polyethylene by infrared spectroscopy and their melting points (135-140˚C) were determined. Gel-permeation chromatography (GPC) was used to obtain the molecular weights of the polymers. These polymers were also found to be linear and no side branches were detected by ^{13}C NMR spectroscopy.[8]

Theopold *et al.* reported a neutral dialkyl Cp*Cr(CH$_2$SiMe$_3$)$_2$ complex (**1.14**), Fig 1.5, whose magnetic moment was found to be temperature independent. This complex was found to polymerize ethylene in good yield. Hydrocarbon solutions of the complex precipitated polyethylene at lower reaction temperatures ranging from 0 to -42˚C, while at room temperature, decomposition of the complex was observed.[8]



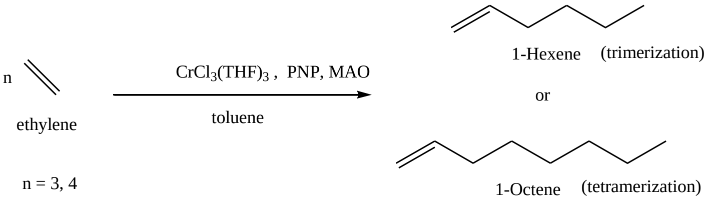
1.14

Figure 1.5: A chromium complex used as a catalyst for the polymerization of olefins

Complex **1.14** showed some activity at 0˚C for polymerization of propene and 1-hexene. ^{1}H NMR and GC-MS were used to characterise the oily residues obtained, which were mainly the dimers and trimers.[8]

1.6.1 Ethylene oligomerization using a chromium source with PNP ligands

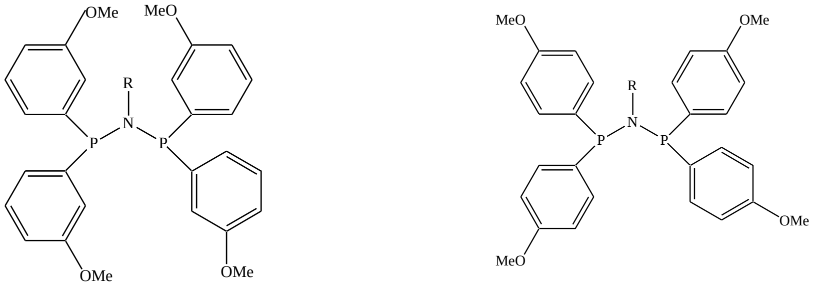
Catalytic systems that give specific oligomers of alkenes are of great interest. In this regard, ethylene trimerization and tetramerization have been extensively studied for the production of 1-hexene and 1-octene using a chromium-based catalyst with $(Ph_2P)_2N$-R (PNP) ligands and methylaluminoxane (MAO) as the activator (Scheme 1.5).[4,5]



Scheme 1.5: Ethylene trimerization and tetramerization using a PNP ligand system.

Using the PNP ligand system, it has been shown that the *ortho*-substituted diphosphinoamine ligands ,$Ar_2PN(R)PAr_2$,with non-coordinating groups (Ar = *ortho*- substituted-aryl) resulted in a highly selective trimerization system to give 1-hexene in high yield, while using Ar = Ph promoted the tetramerization of ethylene to 1-octene with a selectivity of 70%.[4] This study showed that the catalytic activity is affected by the position and nature of the substituents on the aryl groups of the PNP ligands.

It was also shown that changing the position of the aryl substitution group (Fig. 1.6) from *meta* **1.15** to *para* **1.16** and **1.17** changes the selectivity of the catalyst from trimerization to tetramerization. In addition, the replacement of the N-methyl group of ligand **16** with an isopropyl group to give **1.17**, improved both catalytic activity and selectivity to C_6 and C_8 alkenes. Ligand **1.16** was also found to be selective towards tetramer, C_8.[4]



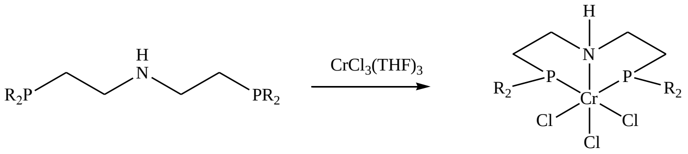
1.15: R = Me

1.16: R = Me
1.17: R = ^{i}Pr

Figure 1.6: Examples of PNP ligands

It was also observed that changing the temperature and pressure of the chromium-based catalyst system affected the activity and selectivity of the oligomerization.

Chromium(III) complexes with tridentate PNP ligands, Scheme 1.6, have also been prepared and evaluated as catalysts for ethylene trimerization reactions.[5b] These complexes in combination with MAO, selectively convert ethylene to 1-hexene with turn-over frequencies of up to 70 000 h^{-1}.[5b]



1.18 : R= Phenyl
1.19 : R= Cyclohexyl
1.20 : R= Ethyl

Scheme 1.6

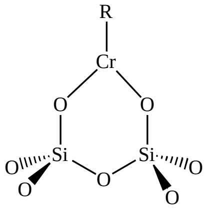
Complex **1.18** was found to give reasonable activity when activated with 120 equivalents of MAO and was highly selective towards producing 1-hexene. Using sterically demanding dicyclohexylphosphino substituents, complex **1.19**, led to a dramatic decrease in activity and produced mainly polymers. Complex **1.20**, however, led to a large increase in activity and selectivity for 1-hexene.[5]

Increasing MAO to 680 equivalents resulted in an increase in activity for complex **1.18**, but a higher proportion of polymers and 6% of 1-butene were obtained. Complex **1.19** also showed an increase in activity but the selectivity was maintained. A further increase in the amount of MAO did not significantly increase the activity of the complexes.

Furthermore, the ethylene uptake during the catalytic reaction at 100ºC, dramatically decreased towards the end of the run for complex **1.20**, suggesting catalyst deactivation. At 50ºC, the activity dropped significantly and a high proportion of polymer was formed, while at 80ºC, the selectivity and activity were restored. At higher temperatures it was noticed that all the catalysts were deactivated after 15 min with the formation of higher olefins with decreased selectivity.

1.6.2 Higher olefin oligomerization with other chromium complexes

The Phillips catalyst system (Fig. 1.7) was the first example of an ethylene trimerization catalyst to yield 1-hexene in greater than 90% overall selectivity.[21] Chromium pyrrolyl complexes were also found to be catalytically active towards ethylene oligomerization upon activation with triethylaluminium (TEA). It was also discovered that these complexes were catalytically active when supported on $AlPO_4$, SiO_2 or Al_2O_3. [22]



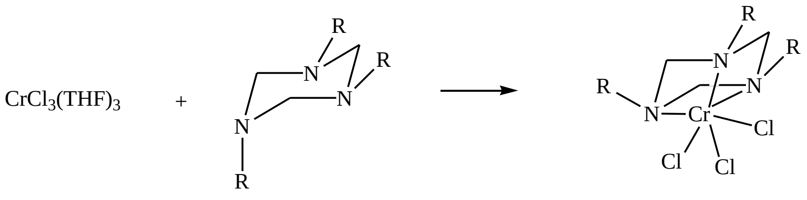
1.21

Figure 1.7: A model system for Phillips catalyst

A more active ethylene trimerization catalyst system was discovered by Reagen and his co-workers,[21] where chromium alkanoate was used with 2,5-dimethylpyrrole (DMP), triethylaluminium (TEA) and toluene as the solvent . Their study was extended to higher olefins such as 1-heptene and 1-decene to produce oligomers. Reaction selectivity and conversion rate were increased when the reactions were conducted in ionic liquids.[21]

1.6.3 Chromium catalysts used for higher olefins oligomerization reactions

Many complexes having triazacyclohexane and larger macrocyclic amines as ligands are known catalysts for olefin oligomerization/polymerization reactions.[23-25,67] The trimerization system of α-olefins was reported with triazacyclohexane complexes of chromium as catalyst, consisting of $CrCl_3(THF)_3$ with 1,3,5-triazacyclohexane as a ligand (Scheme 1.7, where R is either n-octyl or n-dodecyl) and an activator.[23]



R= n-Octyl, n-Dodecyl

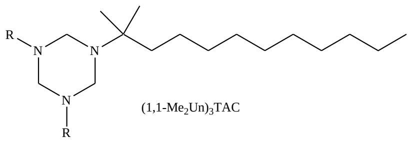
1.22

Scheme 1.7

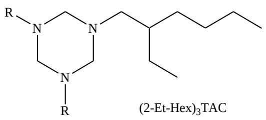
The above system was found to be highly selective for the trimerization of 1-hexene with dimers and tetramers found at less than 1% selectivity. Small traces of methane and 2-methyl-1-hexene were detected by ^{1}H NMR spectroscopy and GC. The kinetic consumption of 1-hexene was monitored by ^{1}H NMR spectroscopy and described by a rate law equation.[23]

The chromium complexes showed high trimerization activity. The activity ceased after a few hours at room temperature obtaining 80% conversion. However, at 0˚C the trimerization activity continued for several days with up to 90% conversion. The system was found to be highly selective for α-olefins, while the donor-functionalized olefins and solvents deactivated the system. ^{1}H NMR spectroscopy could not be used due to the paramagnetic nature of chromium. However, the deuterated complex is observable by ^{2}H NMR spectroscopy.

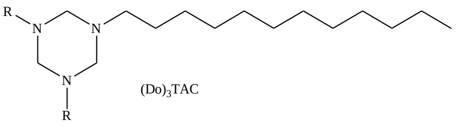
The same system was also found to be highly selective for the trimerization of 1-decene and 1-dodecene to form C_{30} and C_{36} alkenes. The catalytic activity and trimerisation/isomerisation ratio depended on the R-group substituent of the ligand. In addition, a higher degree of branching of the alkyl R-group in the α-position, such as in ligand **1.23** (Fig 1.8), enhanced the undesired isomerisation reaction. Conversely, ligands **1.24** and **1.25** showed a higher selectivity towards C_{36} alkene formation with a high turnover number .[24]



1.23



1.24

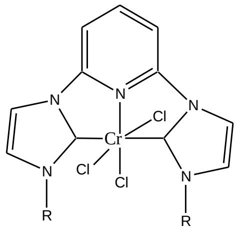


1.25

Figure 1.8: Examples of *N,N,N*"-trialkyltriazacyclohexane (TAC) ligands

Even though trimerization of 1-dodecene showed high selectivity towards C_{36}, small amounts of unconverted 1-dodecene were still present after the reaction. C_{12} products as well as higher oligomer C_{48+} were found in small traces.[24] The catalytic system was very sensitive at elevated temperatures. The optimum conditions for oligomerization reactions involved performing the reaction in an aromatic or aliphatic hydrocarbon solvent at 0ºC for less than 5 hours. Longer reaction time resulted in reaction slow-down.[24]

Chromium complexes that oligomerize and polymerize olefins via metallacycle mechanism represent possible models for the commercially important Phillips catalyst. The oligomerization and polymerization of ethylene via a metallacyclic mechanism has received much attention lately due to their selectivity towards 1-hexene and 1-octene.[22, 66] In contrast to ethylene, very few studies have investigated the effect of α-olefins on the metallacyclic mechanism. The only known system capable of homo-oligomerization of higher α-olefins via a metallacyclic mechanism is the chromium–triazacyclohexane system of Kohn and Wasserscheid.[24,25] McGuinness and his co-workers recently reported that the bis(carbene)pyridine complexes of chromium, Figure 1.9, are highly active ethylene oligomerization catalysts via an extended metallacyclic mechanism. [64]



1.26: R= Me
1.27: R= ^{i}Pr
1.28: R= 2,6-$^iPr_2C_6H_3$

Figure 1.9: Bis(carbene)pyridine chromium complexes

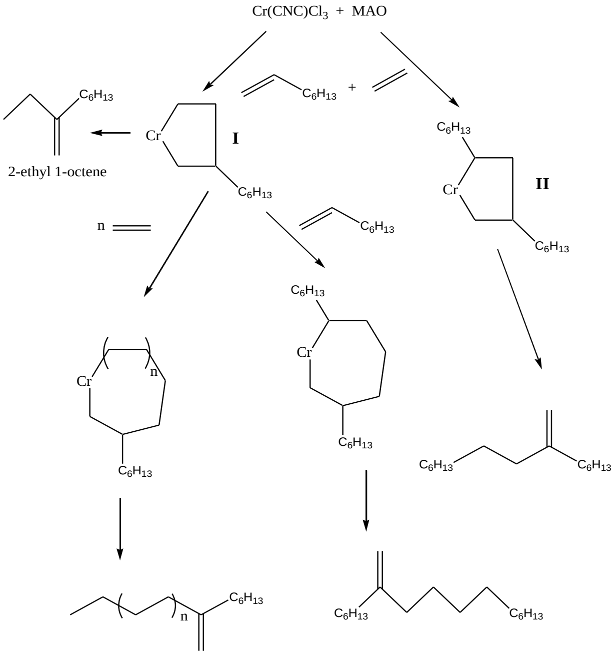
1.6.4 Mechanism for the oligomerization of higher olefins using bis(carbene)pyridine chromium complexes

The catalysts shown in Figure 1.9 were also investigated in the oligomerization of α-olefins, focusing on product selectivity and reaction kinetics in order to gain further insight into metallacycle formation, growth and decomposition, Scheme 1.8.[64]

1.6.4.1 Mechanism for the Co-oligomerization of ethylene with 1-Octene

Oligomerization of ethylene with complex **1.27** and MAO was carried out in 1-octene as a solvent and at a pressure of 1bar of ethylene. Homo-oligomerization of ethylene resulted in linear α-olefins and a secondary major product distribution of vinylidene olefins. 2-ethyl-1-octene, which resulted from a coupling of ethylene and 1-octene via metallacycle **I** (Scheme 1.8) was one of the major products formed.[64] C_{12} and C_{14} products were also detected as a result of further insertion of ethylene into metallacycle **I**. It was noted that the amount of C_{16}

was higher than that expected. It was therefore suggested that it could have been produced by the insertion of three ethylene molecules into metallacycle **I** and from oxidative coupling of two 1-octene units to afford metallacycle **II**. The C_{18} product resulted from a further insertion of 1-octene into metallacycle **I**.[64]



Scheme 1.8

1.6.4.2 α-Olefin Oligomerization

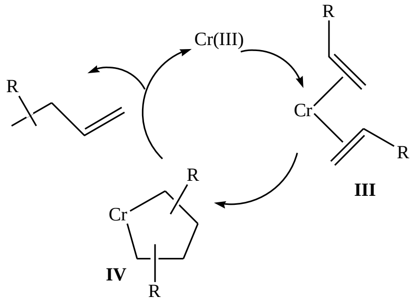
The oligomerization of 1-octene catalyzed by chromium carbene complexes **1.26-1.28** with MAO was reported by McGuinness.[64] It was shown that these complexes deactivated after 3 hours. Dimers, internal olefins and traces of trimers were formed. Complex **1.26** (Fig. 1.9) gave a lower conversion but the distribution of the products was similar to that of complex **1.27**. Complex **1.28** was found to be the most active catalyst for 1-octene conversion, where an increased amount of linear internal olefin dimers and trimers were formed.

For further oligomerization reactions, complex **1.28** was used as it was the most active catalyst when activated with MAO. It was found to have a high turnover number over a prolonged period and low catalyst loading. The oligomerization of 1-pentene proceeded at twice the rate of 1-octene, in which oligomerization selectivity shifted with a 1% formation of tetramers. An increase in the amount of tetramers and trimers were observed with 1-butene and 1-propene.

1.6.4.3 The kinetics of 1-octene oligomerization

Theoretical modelling studies of ethylene trimerization catalysts generally suggest that metallacyclopentane formation is fast, while the metallacycle growth is the rate-determining step.[27,28] It is known that with higher olefins, insertion into the metallacyclopentane is not favoured. This provided an opportunity to investigate the kinetics of metallacycle formation and decomposition. The rate of formation of the major 1-octene dimerization was investigated using complex **1.28** and MAO as an activator.

At a given chromium concentration, the rate of formation of both the vinylidene and internal olefin dimer was found to be constant, which showed that the reaction is zero-order in 1-octene. This is surprising given that there are two molecules of 1-octene involved in the reaction. Dimerization was found to be first-order in chromium. The rate of vinylidene formation was found to be 0.16 s^{-1}, while that for internal olefins was 0.042 s^{-1}. There were two possible explanations for these findings. Firstly, the formation of the bis-olefin complex (**III**) occurs fast, followed by a rate-determining step of oxidative coupling to form the metallacycle (**IV**), Scheme 1.9. The second possibility was that the metallacycle formation (**IV**) occurs fast, followed by a rate-determining β-hydrogen shift and product release.



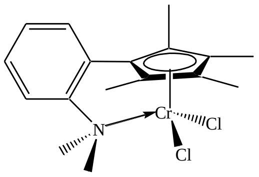
Scheme 1.9

The difficulty in differentiating between the two possibilities prompted further investigations. The metallacycle was hydrolysed with hydrochloric acid at a very high catalyst loading during 1-octene dimerization, 30s into the catalytic run. It was expected that the hydrolysis of the chromium metallacycle would generate the corresponding paraffins, while the hydrolysis of the bis-olefin complex would release the olefin. Despite the dimers formed, there were no paraffins, suggesting that the metallacycle was not present. The evidence accumulated was by no means conclusive but it favoured a rate-determining oxidative coupling and a bis-olefin catalyst resting state.[27, 28]

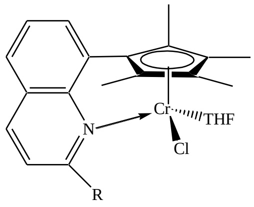
1.7 Chromium complexes containing cyclopentadienyl ligands used in the catalytic oligomerization of olefins

After the discovery of α-olefin polymerization[7], numerous metallocene and monocyclopentadienyl derivatives, with different steric and electronic properties, were synthesised and employed as catalysts in the polymerization reaction.[7-11] The monocyclopentadiene derivatives entailed a cyclopentadienyl ring with a heteroatom functionalised side chain.[9]

Some significant advances in cyclopentadienyl-based chromium catalysts have been made with the ones that bear an additional neutral nitrogen donor (Fig. 1.10: **1.29**), either bridged or unbridged, to the cyclopentadiene unit .[10]



1.29

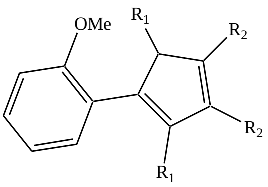


1.30

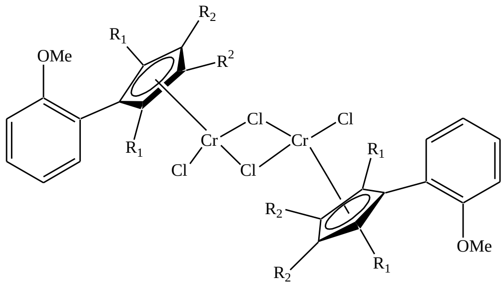
Figure 1.10: Chromium cyclopentadienyl complexes used in the oligomerization of olefins

Half-sandwich-type chromium complexes have been reported and showed good activity for the polymerization of ethylene to give polyethylene. Enders *et al.* [11] described cyclopentadienyl chromium(III) complexes (Fig. 1.10: **1.30**), functionalised by a quinolinyl group, to exhibit high catalytic activity. Most recently, Huang *et al.* [12] reported bridged cyclopentadienyl chromium complexes to be effective ethylene polymerization catalysts.

The synthesis and characterisation of the methoxy substituted Cp ligands **1.31** and **1.32** and their chromium complexes **1.33** and **1.34** (Fig 1.11)**,** as well as their catalytic performance for the polymerization of ethylene, have been reported.[13]



1.31: R_1 = H, R_2 = Ph
1.32: R_1= R_2= Me



1.33: R_1= H, R_2= Ph
1.34: R_1= R_2= Me

Figure 1.11: Cyclopentadienyl ligands and their chromium complexes[13]

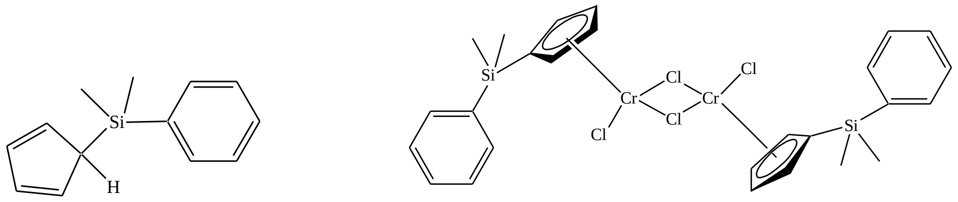
Ligands **1.31** and **1.32** were characterised by ^1H, ^{13}C NMR spectroscopy and elemental analysis. The ^1H NMR spectra showed that **1.32** exists as three regio-isomers with respect to the position of the two double bonds relative to the phenyl substituents. Similar behaviour has been reported before for the *N*,*N*-dimethylaminophenyl-tetramethylcyclopentadiene ligand system[14] as well as the tetramethylcyclopentadienylphenol ligand system.[15] However, this was not observed for ligand **1.31**, which exists as one isomer.

Complexes **1.33** and **1.34** were found to be air and moisture-sensitive in solution, whereas in the solid state, the complexes could be exposed to air for several days without decomposition.[13] Owing to the paramagnetic nature of the complexes, an NMR study was not feasible. The elemental analysis of both complexes was found to fit the respective structures. Crystal structures were obtained for further characterisation of the complexes.

Upon activation with $Al(^iBu)_3$ or $Ph_3C^+[B(C_6F_5)_4]^-$, complex **1.33** and **1.34** were then tested as catalysts for ethylene polymerization. Complex **1.33** showed reasonable activity, while **1.34** showed high activity, producing polyethylene with moderate molecular weights and melting points. No oligomers were obtained. [13]

It is known that the coordination of the oxygen atom to the chromium atom would increase the stability of the chromium cation centre and weaken the interaction between the cationic chromium center and the anionic co-catalyst,[13] thereby increasing the activity of the catalyst. It was expected that complex **1.34** would show higher catalytic activity than **1.33** by electron donation of the methyl groups on the Cp ring of **1.34**, but that was not the case. However, the activity of both complexes were found to be low at room temperature and only increased at elevated temperatures. The activity also increased with an increase in Al/Cr ratio with the highest ratio being 300. A further increase in the ratio resulted in a decrease in the activity of the complexes.

Ligand modification is an effective means of optimizing both catalyst activity as well as polymer properties such as molecular weight, stereoregularities and molecular structures in the polymerization reactions. Zirconocene complexes have shown evidence for the coordination of a phenyl group to the zirconium centre via anagostic C-H-M interaction.[16] In addition, most of the active centres in the homogenous catalyst systems are cationic. Chromium also showed a simple coordination to a phenyl ring.[17]



1.35 **1.36**

Figure 1.12: A silyl cyclopentadiene ligand and its dimeric chromium complex

A chromium-based paramagnetic homogeneous catalyst bearing a phenyl ring bound to a cyclopentadienyl group via a silicon bridge, has also been synthesised following a straight forward procedure.[18] Ligand **1.35** and its complex **1.36** (Fig. 1.12) were synthesised and were obtained in high yields. [18] The ^{1}H NMR spectra of the ligand showed two broad Cp resonances due to the rapid sigmatropic shift of the silyl group. Sigmatropic rearrangements are well known in related silyl-substituted cyclopentadienyl systems.[19] The chromium complex was characterised by X-ray diffraction from the crystals obtained (Fig. 1.13). The X-ray structure showed that each Cr-atom is bonded to one Cp^{Si} ligand, one terminal chlorine atom and two chlorine bridging atoms giving a pseudooctahedral coordination of a three legged piano stool (Fig. 1.13). The ^{1}H NMR spectrum could not be obtained due to the paramagnetic nature of the complex.

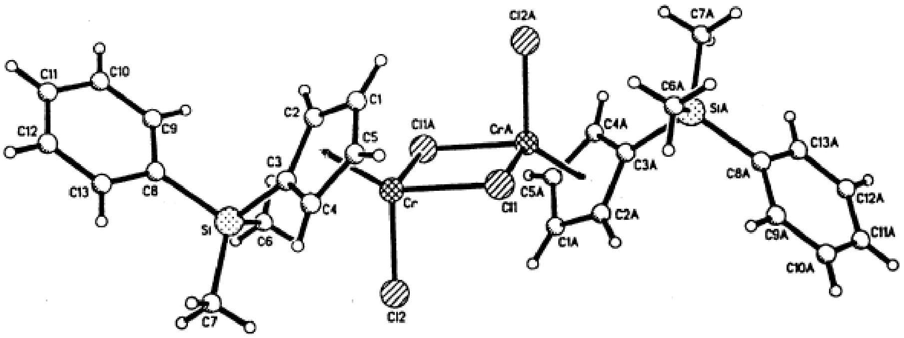


Figure 1.13: Molecular structure of complex **1.36**

Complex **1.36** showed moderate activity for ethylene polymerization when activated with MAO. It was concluded that a low Al/Cr ratio (500/1) was needed to obtain high activity and that the activity did not decrease much when the Al/Cr ratios were changed from 500 to 1000. The catalytic activity and the molecular weights of the polyethylene were much higher than the reported chromium-based cationic half-sandwich catalysts. [20] This observed feature was explained by a phenyl chromium interaction, which weakens the interaction between the cationic chromium centre and the anionic co-catalyst, thereby preventing the active catalyst from bimolecular deactivation. It was also observed that a small amount of MAO is required to keep the catalyst in an active state to form relatively long polyethylene chains.[20]

1.7.1 Ethylene trimerization using a four-component system

The selective trimerization and tetramerisation of ethylene was demonstrated successfully using a four-component system comprising of $Cr(acac)_3$ as a chromium source, a bis(diphenylphosphino)amine ligand $(Ph_2P)_2N$-R), hexachloroethane as chlorine source and the activator MAO.[68] The mechanism shown in figure 1.14 explains the selective formation of 1-hexene and 1-octene.[68]

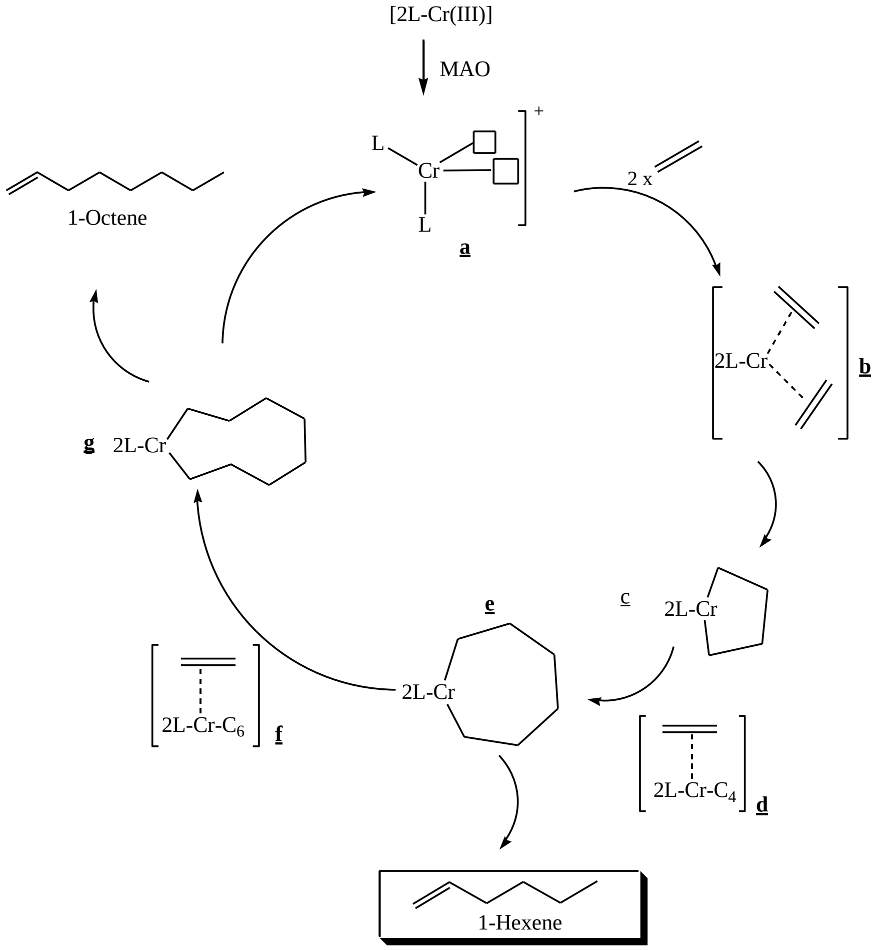


Figure 1.14: The proposed metallacyclic mechanism for the selectivity of ethylene trimerizaion and tetramerization using chromium complexes[68]

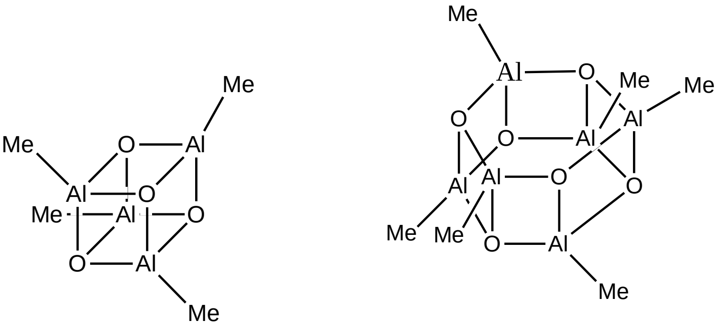
The activated catalyst (Fig. 1.14: **a**) coordinates to two ethylene molecules to form the chromocyclopentane intermediate (**c)** via (**b**), which is followed by further insertion of an ethylene molecule (via intermediate **d**) to form the chromocycloheptane (**e**). The chromocycloheptane can now undergo several transformations. The first is the reductive elimination of 1-hexene with formation of the chromium active species, while the second route is the further insertion of an ethylene molecule via intermediate **f** to form chromocyclononane (**g)**, which also undergoes reductive elimination to form 1-octene and the regeneration of the active species.[68]

1.8 The role of MAO in the chromium catalyzed ethylene tri- and tetramerization

Most of the transition metal complexes used for oligomerization catalysis generally do not operate alone and are activated by suitable co-catalysts such as perfluoroaryl boranes, fluoroarylalanes, trityl- and ammonium borates and aluminate salts. Aluminium alkyls and methylaluminoxane (MAO) are believed to facilitate alkyl abstraction from the catalyst precursor to yield an anionic co-catalyst fragment $[RX]^-$ and a cationic metal fragment $[L_nM]^+$ as the active catalyst system $[L_nM]^+[RX]^-$.[65]

The study of the effect of MAO in catalysis requires an accurate model of MAO, which is a challenge as its structure is not fully resolved. Different structures have been proposed based on the possible combination of methylaluminoxane $(\text{-Al (Me)-O-})_n$ units, which include linear chains, rings, two-dimensional structures, and three-dimensional structure clusters.[58]

Barron et al.[60] suggested that the MAO composition $(AlOMe)_n$ has a three-dimensional cage structure in which four-coordinate Al atoms are bridged by three-coordinate oxygen atoms. These results were confirmed by Al NMR data. It was also discovered that *n* in $(AlOMe)_n$ ranges between 9 and 14 at high temperatures.[61] Examples of some cage structures are shown in Figure 1.15.



1.37: $(AlOMe)_4$ **1.38**: $(AlOMe)_6$

Figure 1.15: Examples of the cage structures for $(AlOMe)_n$ with n = 4 and 6

Zurek and Zeigler[62] concluded that MAO consist of three-coordinate oxygen and four-coordinate aluminium in three-dimensional cage structures. These are the most stable structures when compared to linear, ring, or fused rings. This was in agreement with experiments carried out by Barron.[60]

It is known that trimethylaluminium (TMA) in MAO is often necessary for this species to be catalytically active.[63] It is believed that the TMA in solution participates in the equilibria involving interconvertion of various MAO oligomers.

It has been observed that the presence of free TMA in MAO plays a dual role. Firstly, in the methylation of the catalyst precursor chromium complex and secondly, in the activation of MAO itself for the interaction with methylated chromium species and subsequent ion-pair formation. The formation of the dissociated ion-pair complex and the more active cationic chromium complex have been demonstrated to be the prerequisite for catalysis to proceed.[58] This provided direction for computational studies on the fundamentals of the chromium-catalyzed α-olefin tetramerization mechanism.

1.9 Conclusions

The review has revealed the use of chromium complexes for oligomerization reactions despite their paramagnetic nature, and that these catalysts are active and selective towards certain monomers. It has been observed that various ligands have an effect on the selectivity and activity of these complexes. Changing the substituents on the ligand or the position of the substituents greatly influences the performance of the complex. Steric and electronic effects of the ligand also play a major role in the oligomerization reactions.

Other transition-metal catalysts, such as cobalt and iron, also showed activity towards higher olefins. The formation of olefins was explained by the dimerization mechanism of olefins.

The role of the activator, MAO, in the oligomerization reactions was also reviewed in order to understand the active species in the catalytic reactions of the chromium catalysed reactions. It showed that the use of MAO has a great impact on the oligomerization reaction and it is very important for the formation of the active species.

Liquid phase oligomerization using acid catalysts with different supports is advantageous towards the formation of valuable hydrocarbons, which are free from pollutants, and also significant in the economic production of lubricants.

1.10 Aims and objectives of this project

The aim of this project was to develop new chromium catalysts for the oligomerization of 1-hexene with MAO as the activator, focusing mainly on the cyclopentadienyl-chromium complexes.

Ethylene polymerization reactions using cyclopentadienyl chromium complexes have been reported to show good activity. The only drawback about these complexes was their solubilities, which restricted further studies towards this system.

The objectives of this project were:

- To synthesize new substituted cyclopentadiene ligands and their chromium complexes in an attempt to increase the solubility of these complexes, isolate the complexes and characterize their molecular structure.

- To gain further insight into the oligomerization process using such ligands in the cyclopentadiene/chromium system focusing on the factors affecting the selectivity and activity of the olefin production.
- To develop an understanding of the steric and electronic effects of the ligands in the oligomerization process.

1.11 References

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CHAPTER 2

SYNTHESIS OF CYCLOPENTADIENYL LIGANDS AND THEIR CHROMIUM COMPLEXES

1 Cyclopentadienyl Ligand Synthesis

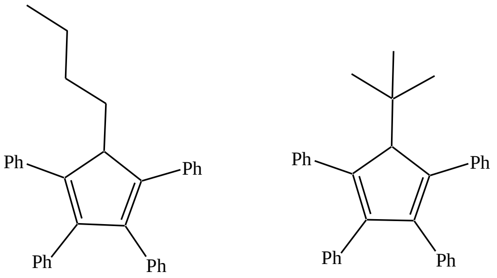
The cyclopentadienyl ligand has occupied a central role in the development of organometallic chemistry.[1] Owing to increased steric bulk, solubility, stability and electron donor properties, pentamethylcyclopentadienyl (Cp*) derivatives have been used in place of cyclopentadienyl (Cp) ligands.[2]

Complexes containing Cp* ligands have been reported since 1960s.[3-5] However, the first catalysis reported using these type of ligands showed that they greatly enhance stereoselectivity in asymmetric synthesis,[6] and that the bulkiness of the ligand increases activity and selectivity in chromium-catalysed ethylene oligomerization.[7]

This chapter describes the synthesis and the characterisation of relevant cyclopentadienyl ligands and their chromium complexes.

2.1.1 The synthesis of tetraphenylcyclopentadienyl ligands

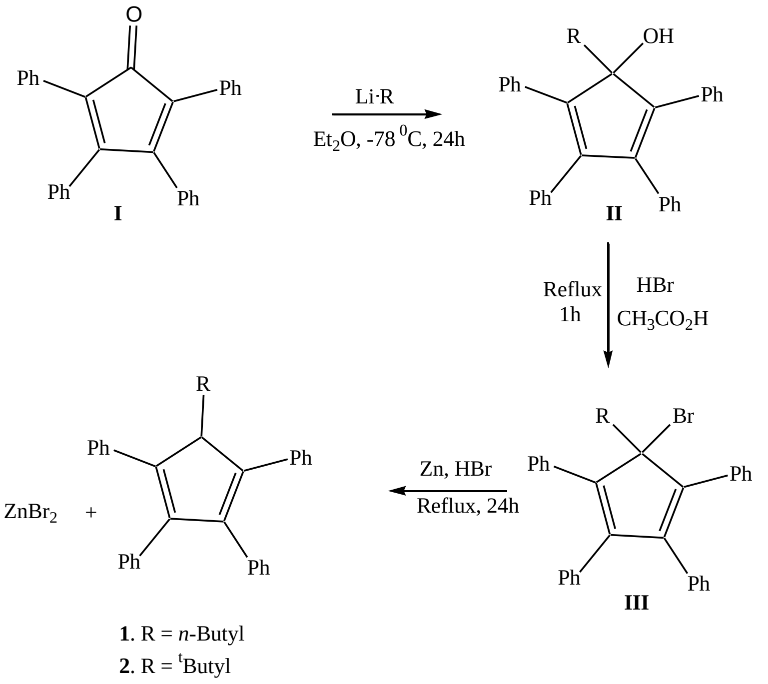
Alkyl-substituted tetraphenylcyclopentadiene ligands **1** and **2** (Fig. 2.1) were synthesized as precursors to chromium complexes for the oligomerization of 1-hexene. Various alkyl substituents were introduced onto the ligands in order to increase ligand solubility and stability.



1 **2**

Figure 2.1: Alkyl-substituted tetraphenylcyclopentadiene ligands

A known literature procedure[8] was followed for the synthesis of ligands **1** and **2** (Scheme 2.1, below). The first step involved reaction of the appropriate alkyllithium with tetraphenylcyclopentadienone (**I**) in diethyl ether to form the substituted cyclopentadienol (**II**). This was followed by nucleophilic substitution of the hydroxyl group by bromine using hydrogen bromide and acetic acid. Zinc dust was then added to reduce the bromo derivative (**III**) to the target compound. This route was also followed for the synthesis of new ligands.



Scheme 2.1: The synthesis of alkyl-substituted tetraphenylcyclopentadiene ligands

When the commercially available alkyllithium was added to a solution of tetraphenylcyclopentadienone (**I**) in dry diethyl ether, the colour change from purple to yellow due to the abstraction of the proton. The final products were obtained as solid with a yield of 51% for ligands **1** and **2**.

The reaction times and temperatures were chosen according to the literature procedure. All the ligands were recrystallised to constant melting point using a mixture of diethyl ether and hexane, which gave a yield of 51% for ligand **1** and 50% for **2** as yellow solids. The ligands were structurally characterised by ^{1}H and ^{13}C NMR spectroscopy, mass spectroscopy, elemental analysis and melting point determination.

*^{1}H and ^{13}C NMR spectra of alkyl- substituted tetraphenylcyclopentadienes **1** and **2***

5-Butyl-1,2,3,4-tetraphenyl-1,3-cyclopentadiene **1** is a known ligand and the characterisation data obtained for this compound were in agreement with the literature data.[8] The characteristic feature in the ^{1}H NMR spectra of this class of ligands is the presence of a Cp-*H* proton resonating at around 4 – 5 ppm, depending on the alkyl-chain substituent of the ligand. The Cp-*H* proton of ligand **1** was observed as a triplet at 4.29 ppm (Fig. 2.2) as a result of coupling to the two adjacent methylene alkyl protons with a coupling constant of $J = 4.7$ Hz.

In the upfield region of the ^{1}H NMR spectrum, three alkyl signals were observed, one for the terminal methyl protons (triplet) integrating for three protons, one for the two internal methylene protons (multiplet) integrating for four protons and the homoallylic protons (multiplet) integrating for two protons. The downfield region showed the phenyl protons as a multiplet integrating for twenty protons.

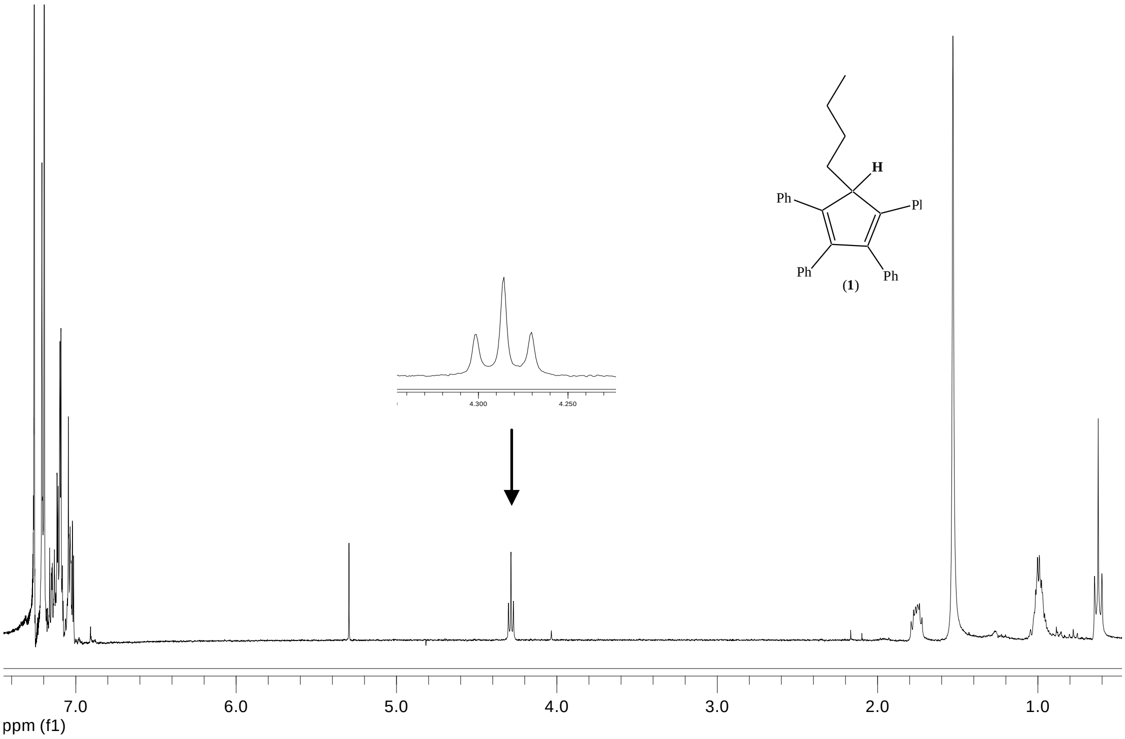


Figure 2.2: The ^{1}H NMR of 5-Butyl-1,2,3,4-tetraphenyl-1,3-cyclopentadiene **1**

In the ^{13}C NMR for ligand **1**, the sp^3 *Cp-C* was observed at 54.7. The alkyl carbons were observed as four singlets in the upfield region at 22.7 ppm, 24.8 ppm, 28.2 ppm and 28.6 ppm ($CDCl_3$). The aromatic and vinyl carbon signals appeared downfield between 126.4 ppm and 137.4 ppm

Ligand **2** (Fig. 2.1) is a new compound. Its ^{1}H NMR spectrum showed similarities to compound **1**, but the Cp-*H* proton of compound **2** appeared as a singlet at 4.48 ppm (Fig. 2.3). This was expected as there are no coupling protons adjacent to it. The methyl (homotopic) protons appeared as a broad singlet at 1.27 ppm due to restricted rotation with averaging of the conformations. The phenyl region appeared as a multiplet between 6.68 ppm and 7.49 ppm and integrating for twenty protons relative to the Cp-*H* proton. Solvent signals due to water and residual acetone from the NMR tube were also observed.

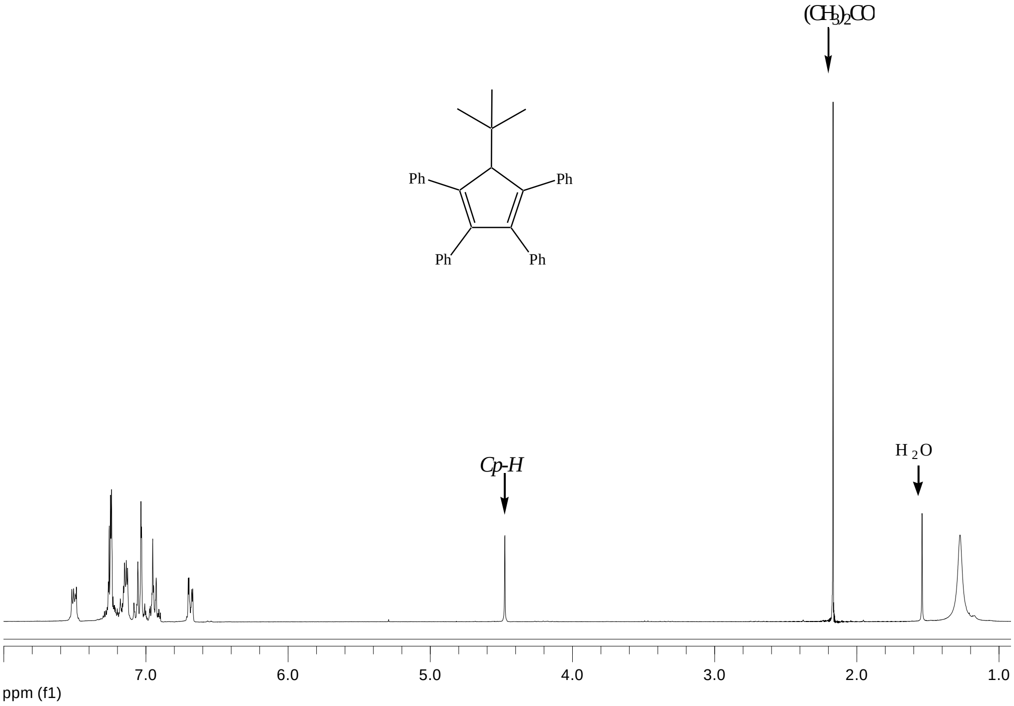


Figure 2.3: The ^{1}H NMR spectrum for 5-^{tert}butyl-1,2,3,4-tetraphenyl-1,3-cyclopentadiene (**2)**

The ^{13}C NMR spectrum of **2** (Fig. 2.4) gave further support for structure **2**. Eight aromatic, two vinyl as (C-4,5), one benzylic methine (C-3) and two *t*-butyl (C-1,2) carbon singlets were observed in accordance with symmetry considerations. This strongly supported the idea that the bulky *t*-butyl group prefers to lie out of the plane of the Cp-ring. Isomerisation of the benzylic hydrogen via a prototropic shift would have placed the *t*-butyl group at an sp^2 centre and in plane with the *Cp*-ring as a higher energy isomeric form. Such a structure would have been less symmetrical, with more ^{13}C resonances for the phenyl carbons.

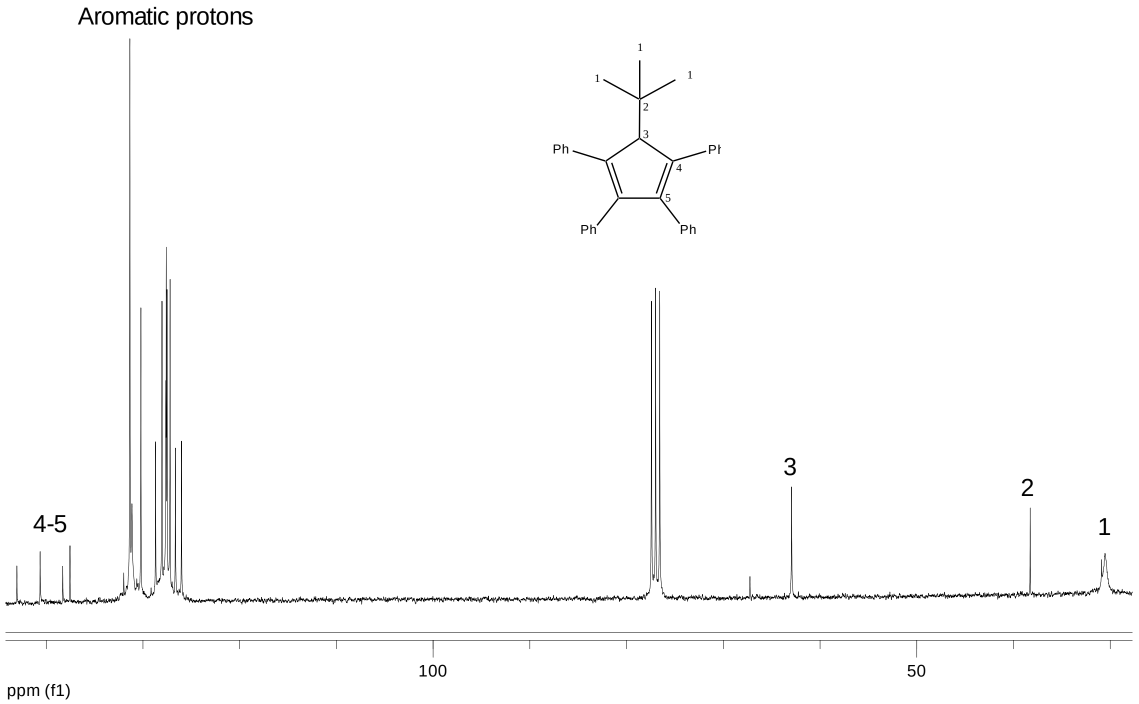


Figure 2.4: The ^{13}C NMR spectrum for5-^{tert}butyl-1,2,3,4-tetraphenyl-1,3-cyclopentadiene (**2)**

Mass spectrometry, melting points and elemental analysis for tetraphenylcyclopentadiene ligands

The ligands proved to be thermally stable after recrystallization as observed from melting point determinations, which were established at 158 - 160°C for ligand **1** and 188 - 191°C for ligand **2**. The ligands were soluble in most polar non-protic organic solvents like chloroform, ethyl acetate and tetrahydrofuran, while insoluble in hexane and partially soluble in less polar solvents such as toluene.

The elemental analysis and mass spectra were also determined. From elemental analysis data, the carbon content for ligand **1** was out by 0.94%, which was likely due to occlusion of the solvent, in spite of extensive vacuum drying at room temperature (Table 2.1). The low-resolution mass spectrum of ligand **1** showed a molecular-ion peak of M^+ = 426 m/z (Fig. 2.5), in agreement with the molecular formula $C_{33}H_{30}$ with a calculated M+ = 426 m/z.

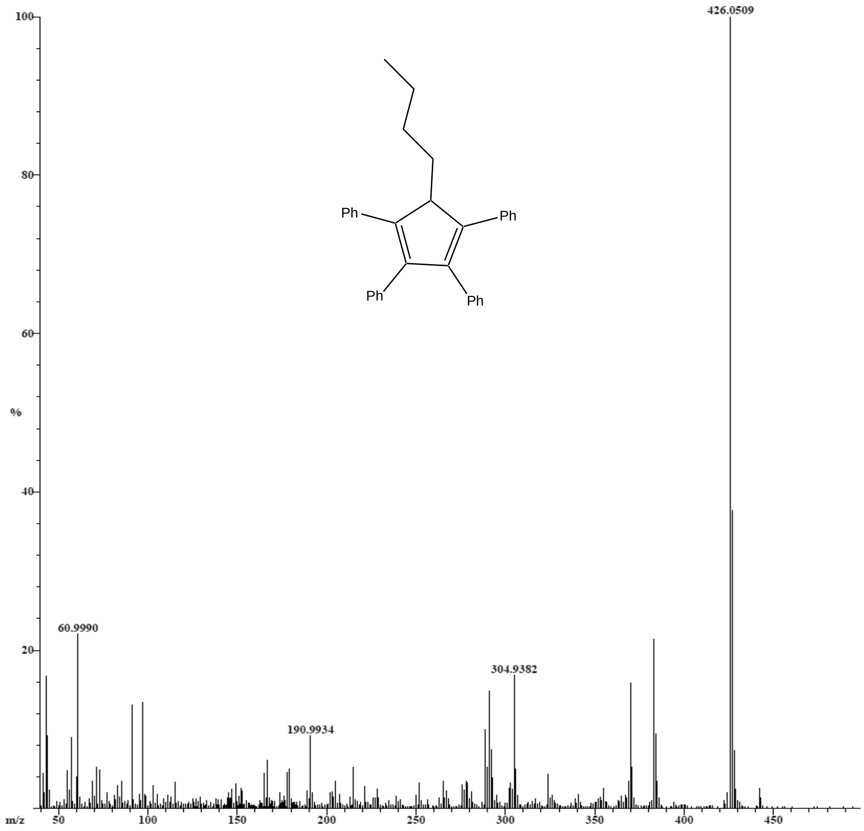


Figure 2.5: Mass spectrum of ligand **1** showing the parent ion with the molecular formula $C_{33}H_{30}$

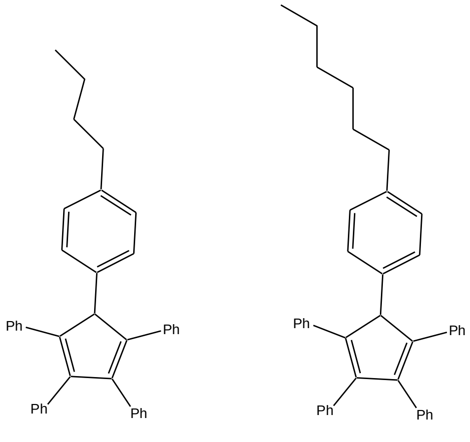
The elemental analysis data obtained for ligand **2** was not in agreement with the theoretical value but did agree to within 0.5% with the molecular formula for $C_{33}H_{30}.H_2O$ (Table 2.1). These ligands were dried under vacuum prior to submission for elemental analysis, which presumably removed acetone that was observed in the ^{1}H NMR spectrum (Table 2.1) but not the water.

Table 2.1: The melting points, Cp-*H* chemical shifts, molecular ion and elemental analysis for ligands **1** and **2**

Ligand	Melting Point (ºC)	Cp-*H* protons (ppm)	Molecular Formula	Elemental Analysis [found] (calculated)	
				C%	H%
1	158-160	4.29	$C_{33}H_{30}$	[91.97 (92.91	7.09] 7.09)
2	188-191	4.46	$C_{33}H_{30}.H_2O$	[88.62 (89.15	6.91] 7.25)

2.1.2 The synthesis of aryl-substituted tetraphenylcyclopentadiene ligands

The same procedure as for the alkyl-tetraphenylcyclopentadiene ligands was followed for the synthesis of the aryl-substituted tetraphenylcyclopentadienes, whose structures are shown in Fig. 2.6. These ligands were obtained as yellow powders. Yields of 60% and 40% were obtained for ligand **3** and **4** respectively after recrystallization.

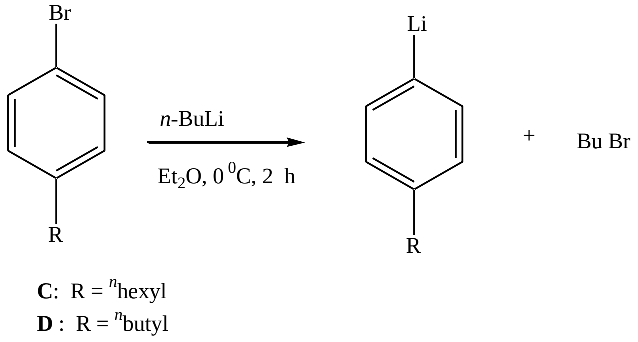


3

4

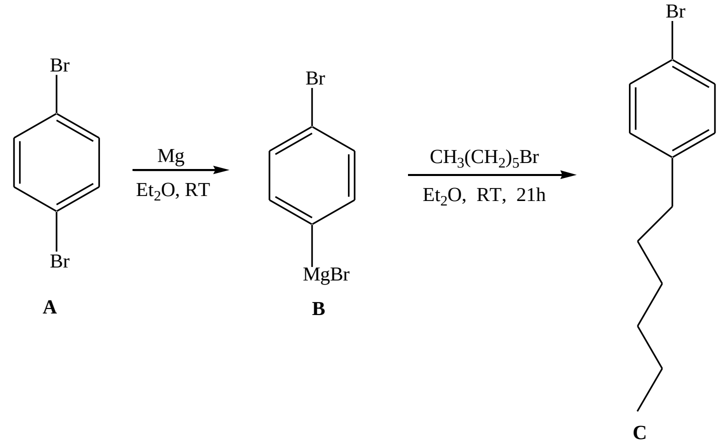
Figure 2.6: Aryl-substituted tetraphenylcyclopentadiene ligands

The aryllithium (Scheme 2.2) starting materials for both were first prepared from the bromides via a known meatal-halogen exchange procedure,[8] as they were not commercially available.



Scheme 2.2

The bromo precursor for **3** was commercially available. For ligand **4**, access to the *para*-substituted bromobenzene **C**, required for the metal-halogen exchange reaction, was provided via substitution of 1-bromohexane with the mono-Grignard derived from 1,4-dibromobenzene (Scheme 2.3).



Scheme 2.3

The Grignard reagent **B** was prepared by reacting magnesium turnings with 1,4-dibromobenzene **A** in a ratio of 1:2 in diethyl ether (Scheme 2.3). The reaction involves the oxidative addition of magnesium into a carbon-halogen bond. This was followed by the substitution of 1-bromohexane with the Grignard reagent in diethyl ether to form the *para*-substituted bromobenzene **C**.

1-Hexyl-4-bromobenzene **C** was obtained as a yellow oil after work-up and used in subsequent steps without further purification. It was considered pure enough by ^{1}H NMR and ^{13}C NMR spectroscopy. The upfield region of the ^{1}H NMR (Fig. 2.7) showed all of the alkyl protons for the terminal methyl group as a triplet (**1**: 0.93 ppm) integrating for three protons, followed by a multiplet (**2**: between 1.33 and 1.48 ppm) integrating for six protons. In addition, two multiplets (**3**: 1.86 ppm and **4**: 3.41 ppm) were observed, integrating for two protons each (Fig. 2.7), **4** being the benzylic protons (triplet). The downfield region revealed a multiplet (**5-6**) integrating for four aromatic protons, where long range coupling was observed with the alkyl protons (Fig. 2.7). The structure was further confirmed with ^{13}C NMR spectroscopy, where the alkyl region showed six upfield singlets while the aromatic carbons were observed downfield as four singlets.

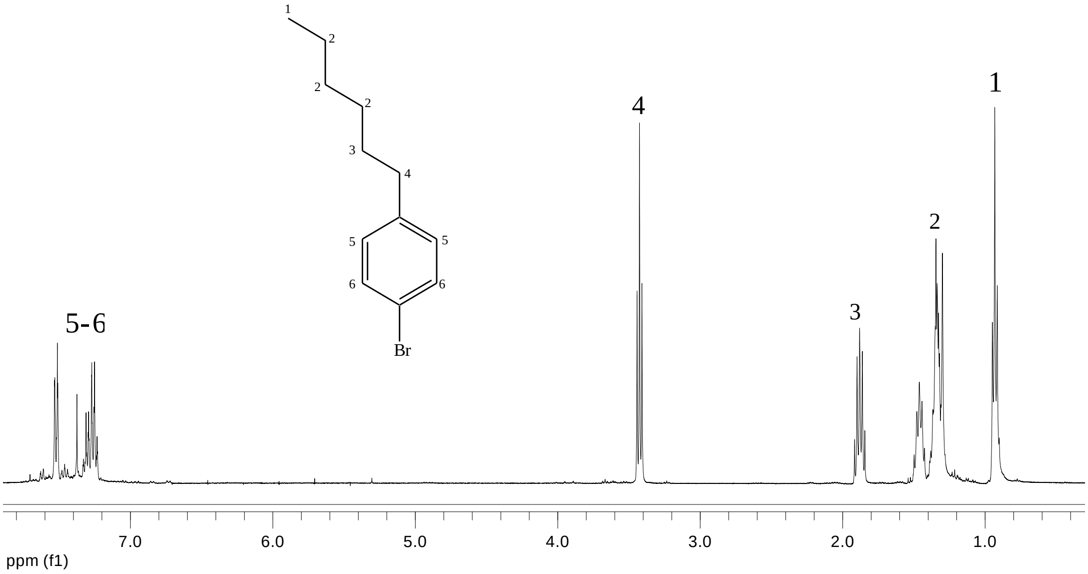


Figure 2.7: The ^{1}H NMR spectrum for crude 1-bromo-4-hexylbenzen (**II**)

The starting materials for ligands **3** and **4**, 1-hexyl-4-bromobenzene **C** and 1-butyl-4-bromobenzene **D** respectively, were then converted into their lithium alkyls in situ (Scheme 2.2). The lithium alkyls were prepared via a metal-halogen exchange reaction, which involves the direct nucleophilic attack on the bromine by *n*-butyllithium. The resultant aryllithium reagents were then used as described previously (Scheme 2.1) to access ligands **3** and **4**.

^{1}H NMR and ^{13}C NMR spectra of the aryl-substituted tetraphenylcyclopentadiene ligands

Ligands **3** and **4** are new ligands according to Scifinder, and were characterised using NMR spectroscopy to confirm their structures. The Cp-*H* protons were observed in the ^{1}H NMR spectra at 5.06 ppm for ligand **3** and 5.08 ppm for ligand **4**. This was approximately 0.5 ppm downfield compared to the equivalent protons in ligands **1** and **2** due to the deshielding influence of the aryl group. Both ligands showed downfield aromatic signals integrating for 24 protons. For ligand **3,** the ^{1}H NMR spectrum showed the existence of two isomers (Fig. 2.8). Two triplet signals were observed at 2.42 and 2.54 ppm (d) due to the benzylic protons in the two different isomers, in an approximate ratio of 2:1. The *Cp-H* protons appeared as a singlet, suggesting the overlap of signals from each of the isomers.

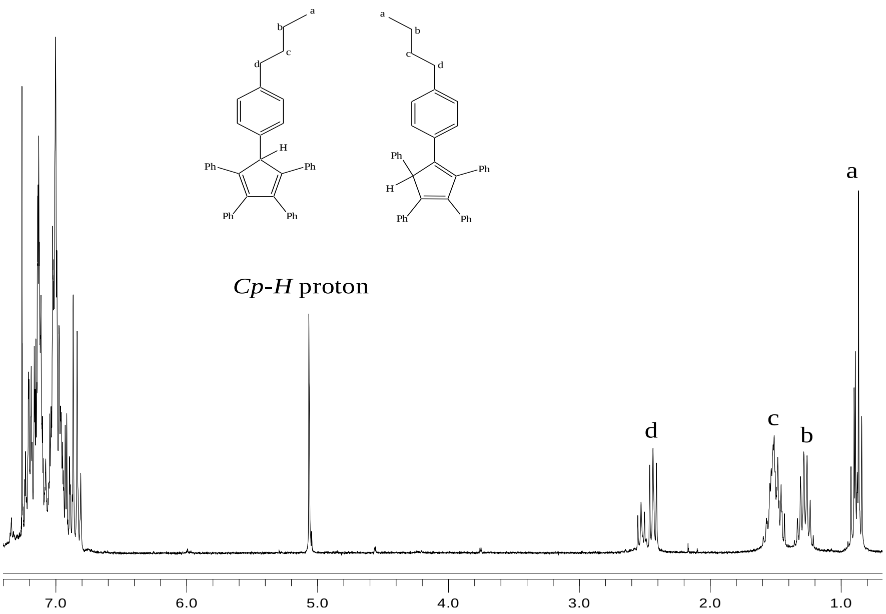
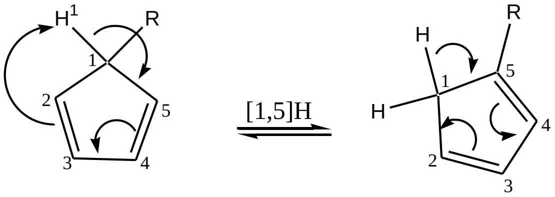


Figure 2.8: The ^{1}H NMR spectrum for 5-(4'-n-butylphenyl)-1,2,3,4-tetraphenyl-1,3-cyclopentadiene **3**

Scheme 2.4 shows a mechanism for the formation of the isomers of **3**. It is known that a hydrogen may slide across the face of the planar cyclopentadiene ring.[9]



Scheme 2.4: [1,5] Sigmatropic rearrangement for the cyclopentadiene ligands[8]

The formation of the isomers presumably results from a symmetry-allowed (Woodward and Hoffmann) [1, 5] sigmatropic hydrogen shift, which is known for most cyclopentadiene ligands (Scheme 2.4). It is called 1,5 because the C-H δ-bond has migrated in a 1,5 manner. The driving force behind the sigmatropic (prototropic) shift for **3** reflects a subtle balance of steric and hyperconjugative resonance effects.

The ^{13}C NMR spectrum for ligand **3** (Fig. 2.9) showed five signals upfield whereas the phenyl and cyclopentadienyl signals appeared downfield. The four upfield carbons (C1-C4) are due to the butyl chain of the ligand. The cyclopentadienyl carbon (C5) was observed at around 62.4 ppm as two overlapping signals, due to the different isomers. It is slightly deshielded due to its benzylic character when compared to that of ligand **2** (38.7 ppm). The aromatic and vinyl carbon signals were observed downfield between 125-135 ppm.

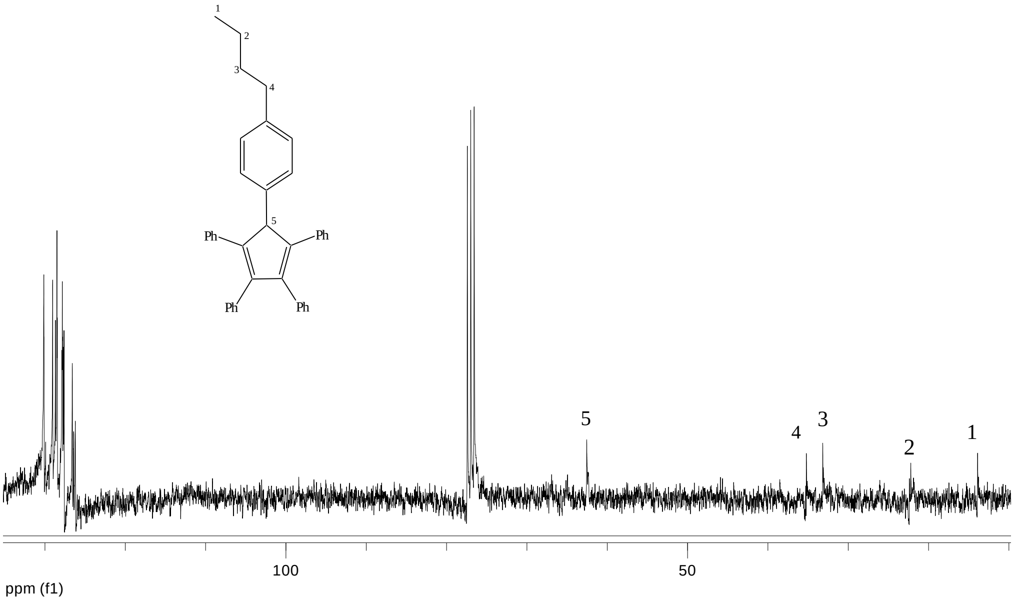


Figure 2.9: The ^{13}C NMR spectrum for 5-(4'-n-butylphenyl)-1,2,3,4-tetraphenyl-1,3-cyclopentadiene **3**

In the ^{1}H NMR spectrum for ligand **4** the alkyl region signals appeared upfield, due to the hexyl chain and the aromatic region further downfield, integrating for 24 protons. The ^{13}C NMR spectrum showed a similar trend with six upfield alkyl singlets and a cyclopentadienyl carbon signal at 62.5 ppm.

Mass spectrometry, melting points and elemental analysis for ligand ***3*** *and* ***4***

The ligands were further characterised by mass spectrometry, elemental analysis and melting point. The ligands were recrystallised to constant melting points. From the elemental analysis, it was observed that the carbon content of ligand **3** was out by two percent units, which might have been due to the incorporation of the solvent (Table 2.2).

Table 2.2: The molecular formulae, elemental analysis, the Cp-*H* chemical shifts and melting points for ligand **3** and **4**.

Ligand	Melting Point (°C)	Cp-*H* shift (ppm)	Molecular Formula	Elemental Analysis [found], (calculated)	
				C %	H%
3	102-104	5.06	$C_{39}H_{34}$	[91.27; (93.18;	6.76] 6.82)
4	98-101	5.08	$C_{41}H_{38}$	[92.24; (92.78;	6.71] 7.22)

In the mass spectrum of **3**, the parent ion observed at M^+ = 501 m/z corresponded to the calculated molecular weight of the ligand (Fig. 2.10). The melting points after recrystallization of ligand **3** were found to be in the range of 102-104°C.

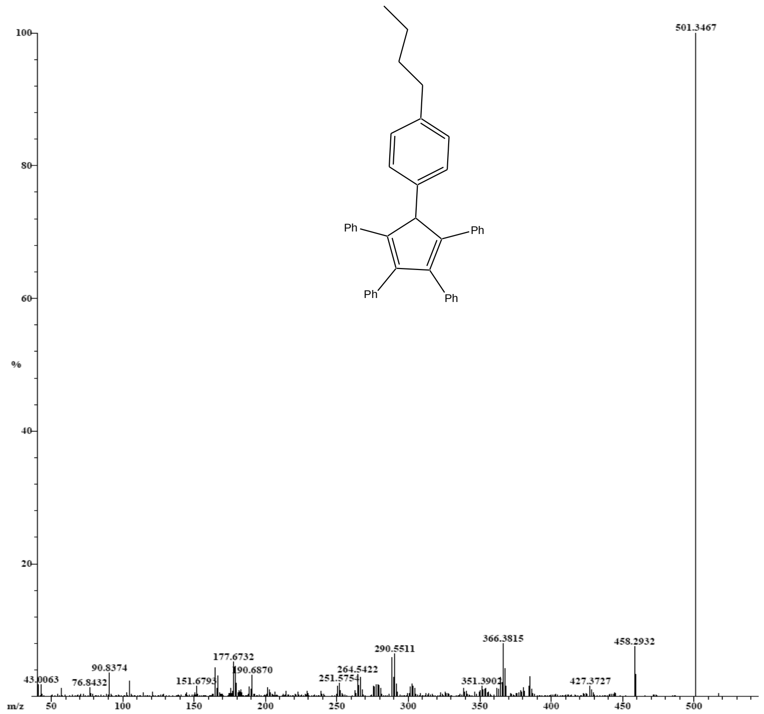


Figure 2.10: The mass spectrum of ligand **3**, showing the parent ion.

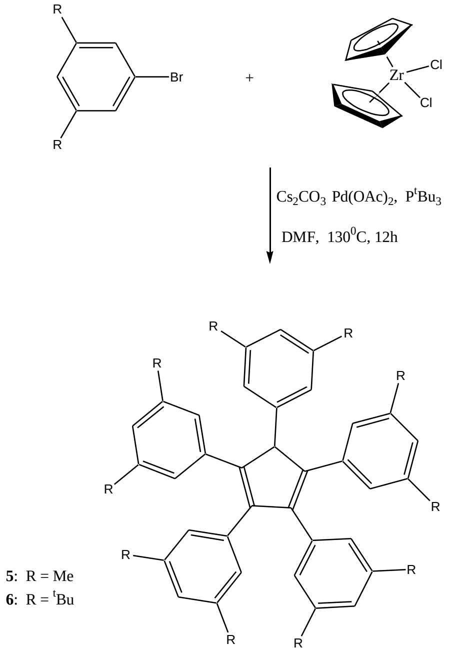
In comparison, the elemental analysis of ligand **4** was in good agreement with that of the calculated structure (Table 2.2), while the low resolution mass spectrum showed a parent ion peak at M^+ = 501 m/z, due to a loss of $[CH_3CH_2]^+$ fragment.

The melting points after recrystallization for ligand **4** were found to be in the range of 98-101°C.

2.1.3 Synthesis of alkyl-substituted pentaphenylcyclopentadienyl ligands

Ligands **5**, 1,2,3,4,5-penta-(3,5-dimethylphenyl)cyclopenta-1,3-diene, and **6**, 1,2,3,4,5-penta-(3,5-di-*t*-butylphenyl)cyclopenta-1,3-diene, with bulky phenyl substituents were synthesized by a known procedure,[10] which involved the multiple arylation of a metallocene with an aryl bromide via a palladium(II)-catalysed substitution, using $(\eta^5 C_5H_5)_2ZrCl_2$ as the source of cyclopentadiene. The reaction was conducted by refluxing in dimethylformamide (DMF) for

12h under inert conditions, followed by a work-up and purification by column chromatography (Scheme 2.5).



Scheme 2.5

The target ligands **5** and **6** were successfully synthesized. Yellow-orange crystals in yields of 60-62% were obtained after recrystallisation from toluene. The melting points were determined to be 213-215°C for ligand **5** and 270-273°C for ligand **6**. NMR spectroscopy, elemental analysis and mass spectroscopy were used to characterize the ligands.

*The ^{1}H and ^{13}C NMR spectra of ligands **5** and **6***

Ligands **5** and **6** are symmetrical cyclopentadienes, which was confirmed by their ^{1}H NMR spectra. The ^{1}H NMR spectrum for ligand **5** showed the methyl protons as three singlets in a ratio of 6:12:12 at 1.97 ppm (a), 2.04 ppm (b) and 2.11 ppm (c), respectively (Fig. 2.11). The

Cp-*H* proton appeared as a singlet at 4.89 ppm. The 15 aromatic protons were expected to appear downfield in a ratio of 1:2:2:4:2:4 for the three rings, but four singlets were observed, in an intensity ratio of 2:2:9:2 (Fig. 2.11).

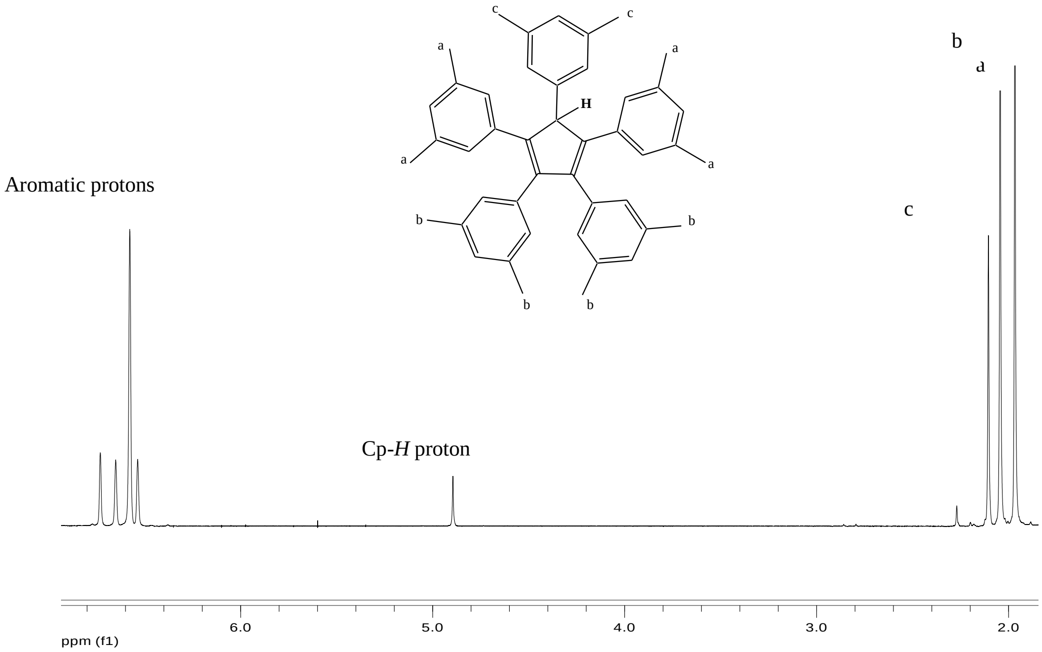


Figure 2.11: The ^{1}H NMR for 1,2,3,4,5-penta-(3,5-dimethylphenyl)cyclopenta-1,3-diene **5**

The ^{13}C NMR spectrum (Fig. 2.12) for ligand **5** showed a similar trend to the ^{1}H NMR spectrum (Fig. 2.11), with three distinct singlets for the methyl groups in a ratio of 2:2:1 (C1:C2:C3). The cyclopentadiene carbon, C4, appeared slightly upfield (61.6 ppm) when compared to ligand **3** (62.9 ppm), while the aromatic and vinyl carbon signals were observed downfield (Fig. 2.12). In the aromatic region, the 15 C-H carbons were observed as 6 singlets in a ratio of 1:2:2:4:2:4, as expected. The quaternary carbons showed the same six singlets in a ratio of 1:2:2:4:2:4 for the 15 carbons, while the vinyl carbon signals showed two singlets for the 4 carbons.

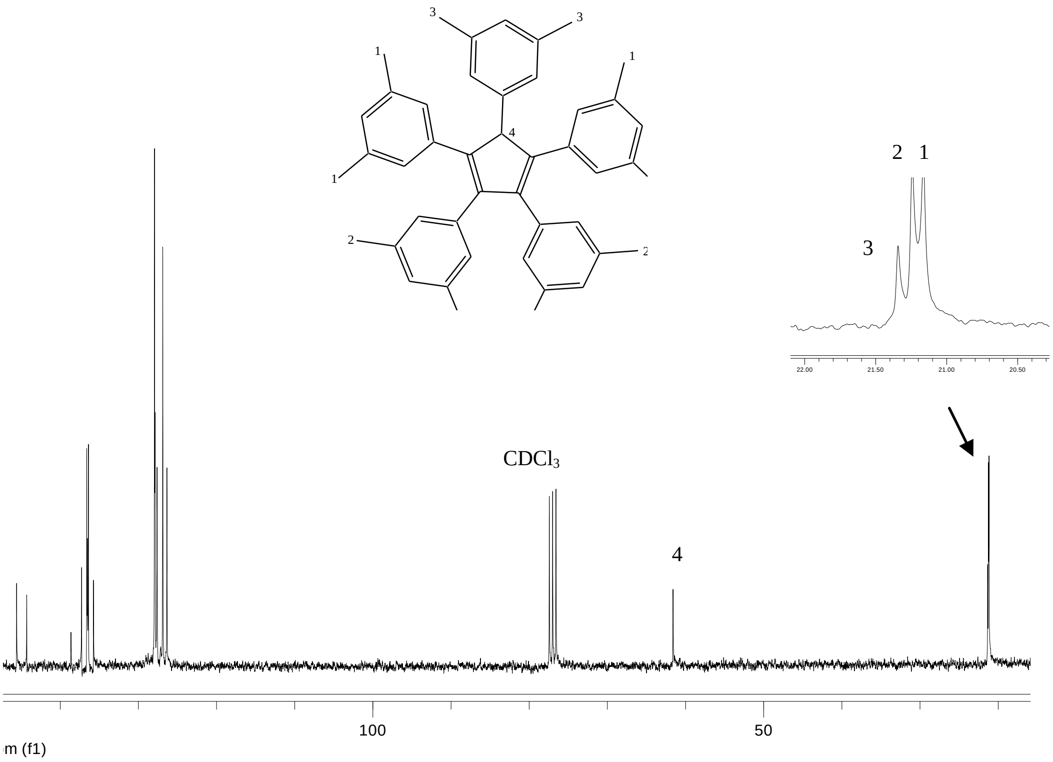


Figure 2.12: The ^{13}C NMR spectrum for 1,2,3,4,5-penta-(3,5-dimethyl phenyl) cyclopenta-1,3-diene **5**

The ^{1}H NMR for ligand **6** showed a similar trend to that of **5,** with three distinct *t*-butyl singlets appearing upfield in a ratio of 18:36:36 integrating for 90 protons in total (Fig. 2.13). The Cp-*H* proton was observed at 3.97 ppm (Fig. 2.13), which was upfield compared to ligand **6** (4.89 ppm). This could be due to the shielding effect by the tertiary butyl groups. The aromatic protons appeared as six signals, where the first three signals appeared in a ratio of 1:2:2 and the last three signals in a ratio of 2:4:4. Ligand 6 was further characterised by ^{13}C NMR spectroscopy to confirm its structure.

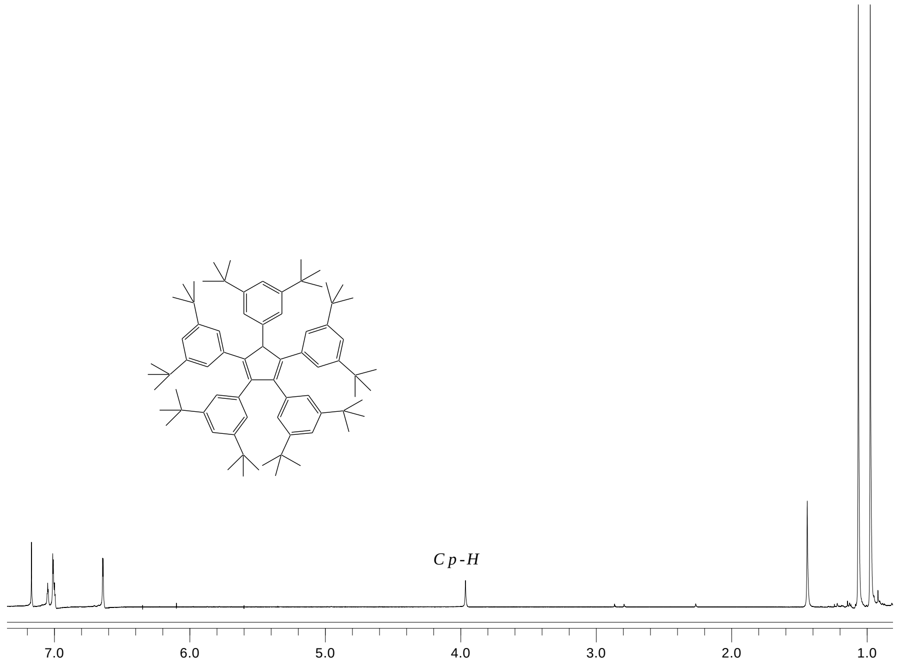


Figure 2.13: The ^{1}H NMR for 1,2,3,4,5-penta-(3, ,5-di-*t*-butyl phenyl)cyclopenta-1,3-diene **6**

The ^{13}C NMR spectrum for ligand **6** (Fig. 2.14) showed three signals upfield. The first signal C1 (31.2 ppm) was due to all of the *t*-butyl methyl carbons while the second signal C2 (34.3 ppm), was due to the quaternary *t*-butyl carbons. The Cp-carbon (C-3) appeared downfield from the alkyl group at 45.2 ppm, The aromatic and vinyl carbons were observed between 119.4 and 149.9 ppm (Fig. 2.14). A total of 14 resonances was expected as 2 vinyl, 6 quaternary, but only 9 were observed, indicating significant overlap (Fig. 2.14).

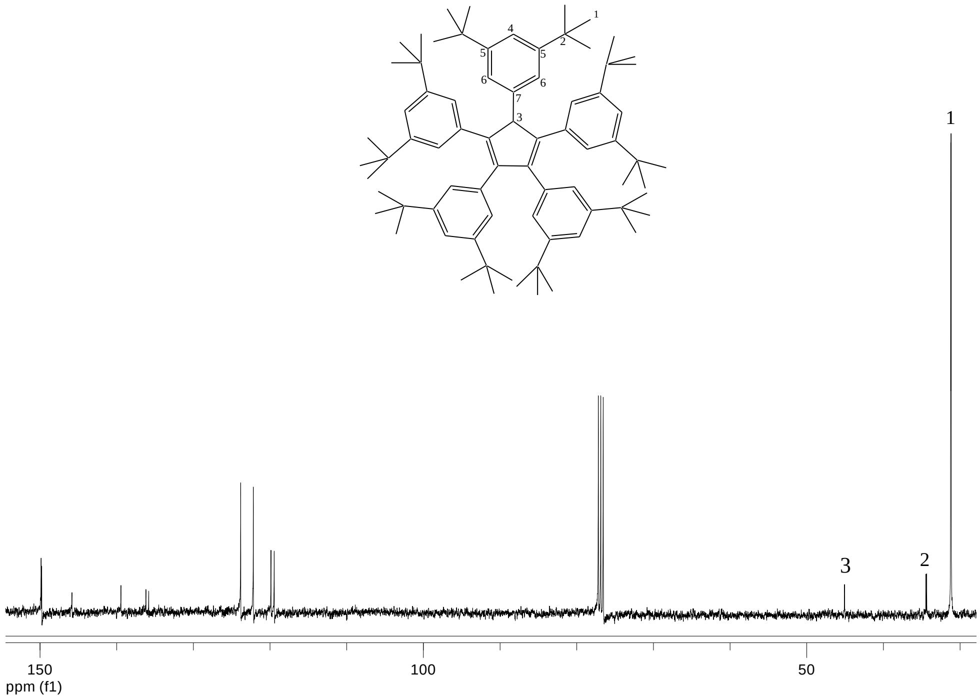


Figure 2.14: The ^{13}C NMR for ligand **6**

Elemental analysis and mass spectrometry for ligand ***5*** *and* ***6***

The ligands were further characterised by elemental analysis and mass spectroscopy for structural identification. The elemental analysis of **5** was out by 1% on carbon (Table 2.3) which could also have been due to the incorporation of water or solvent.

Table 2.3: The molecular formula, elemental analysis, the Cp-*H* chemical shifts and melting points for ligand **5** and **6**

Ligand	Melting Point (°C)	Cp-*H* shift (ppm)	Molecular Formula	Elemental Analysis [found] (calculated)	
				C%	H%
5	213-215	4.89	$C_{45}H_{46}$	[91.10 (92.10	7.43] 7.90)
6	270-273	3.97	$C_{75}H_{106}$	[88.75 (89.40	9.55] 10.60)

The low resolution mass spectrum of ligand **5** showed a molecular ion at M^+ = 585 m/z (Fig. 2.15), in agreement with the molecular weight of the structure of $C_{45}H_{46}$. In addition, fragments were observed corresponding to demethylated structures, as shown in Figure 2.15.

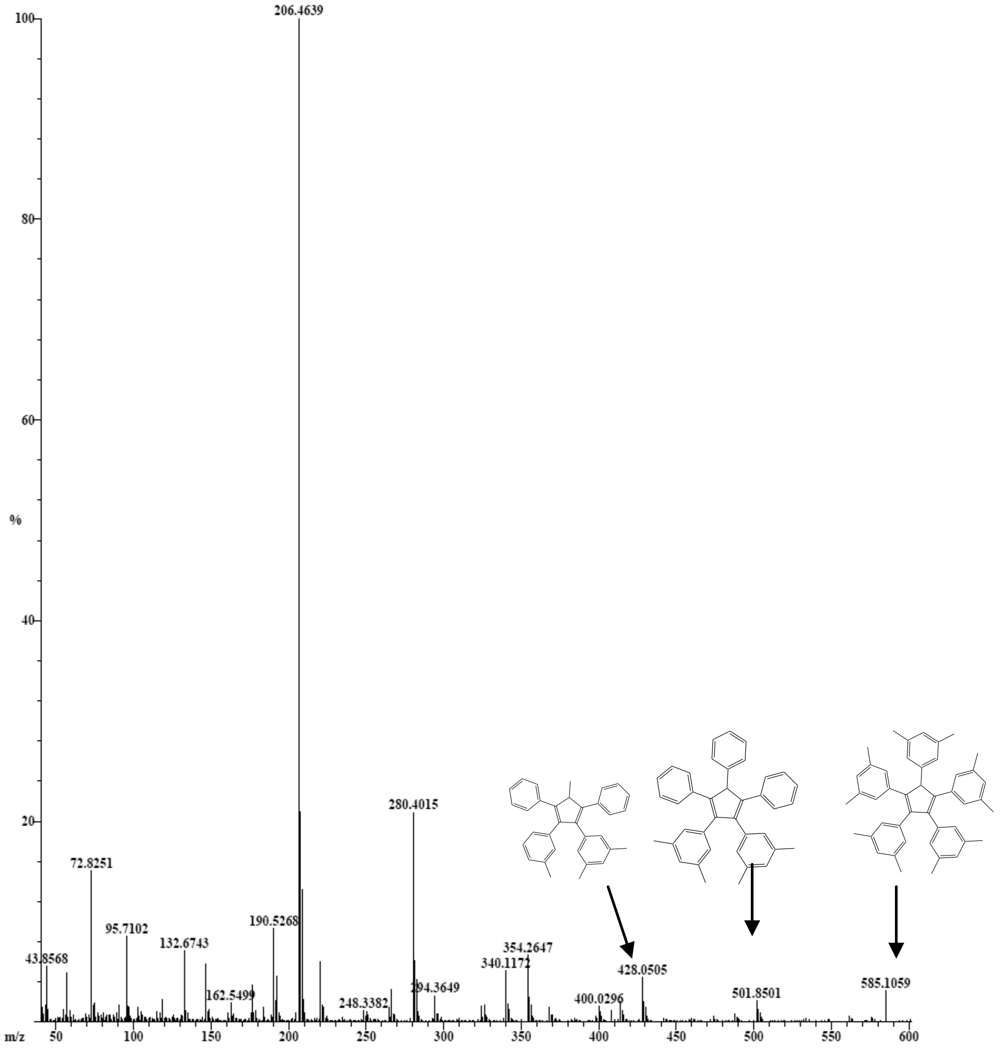


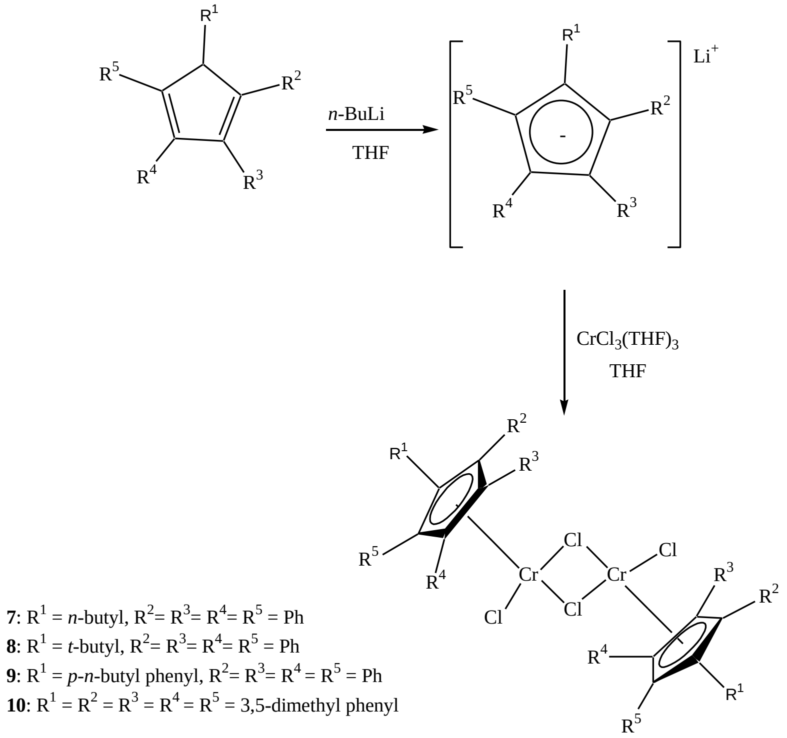
Figure 2.15: The mass spectrum for ligand **5** showing the fragmentations

In comparison, ligand **6** showed a dominant ion for M^+ at 817.06 m/z due to the loss of one phenyl ring. The elemental analysis of **6** was in agreement with the molecular formula (Table 2.3) to within 0.65% on carbon, although the hydrogen percent was out.

3.2 The Synthesis of the Chromium Complexes

The study of paramagnetic organometallic complexes has in recent years expanded greatly. Some of the complexes are believed to be highly reactive reaction intermediates.[11] Chromium catalysts have played a key role in the development of heterogeneous catalysts for the oligomerization or polymerization of olefins. Recently, most of the Cp-based chromium catalyst systems have been reported as catalyst precursor for the oligomerization of olefins as mentioned in chapter 1, section 1.6.[12-14]

Herein, the synthesis of dimeric Cp-based chromium complexes (Fig. 2.16) is reported. These complexes were synthesised using a known procedure[1] and were obtained as green solids in yields of 50-60%. The cyclopentadienyl ligands were used for the synthesis of such chromium complexes **7-10** (Fig. 2.16), based on ligands **1**, **2**, **3** and **5**. Ligands **4** and **6** were not converted. With these ligands, the reaction mixture turned brown after the addition of $CrCl_3(THF)_3$, showing decomposition.



7: R^1 = *n*-butyl, R^2= R^3= R^4= R^5 = Ph
8: R^1 = *t*-butyl, R^2= R^3= R^4= R^5 = Ph
9: R^1 = *p*-*n*-butyl phenyl, R^2= R^3= R^4 = R^5 = Ph
10: R^1 = R^2 = R^3 = R^4 = R^5 = 3,5-dimethyl phenyl

Figure 2.16: The general procedure used for the synthesis of chromium complexes **7-10**

The Scheme shown in Fig. 2.16 was followed for the synthesis of the complexes (**7-10**). The lithium salts of the cyclopentadienyl ligands were first prepared by dissolving the corresponding ligand in THF followed by the addition of *n*-BuLi at -78°C for deprotonation. The reaction was left to stir overnight at room temperature. This was followed by the removal of the solvent and washing of the salt with hexane. The remaining solid was then dried under vacuum. The generated lithium salt was then dissolved in THF, followed by the addition of $CrCl_3(THF)_3$, where the solution changed from purple to green due to the formation of the dinuclear complex. The mixture was left to stir overnight at room temperature. The resulting green solution was filtered and the volume of the solvent reduced. This resulted in crystallisation. The green solid obtained was dried under vacuum.

The complexes were then characterised by elemental analysis, mass spectroscopy and melting point.

Elemental analysis, mass spectroscopy and melting point

^{1}H and ^{13}C NMR spectroscopy could not be used for analysis of these complexes due to the paramagnetic nature of the complexes and would therefore result in broad peaks in the spectrum.

The elemental analysis obtained did not agree with the proposed structures as it was mostly out by 10% for the carbon content. This could have been due to decomposition of the complexes when exposed to air during the analysis. This is known for most of the complexes as they are sensitive to air and unstable in solution.[15]

Mass spectrometry was used to further analyse the complexes. The spectra showed no parent peak ion for the complexes, but rather a loss of a fragment as either a chlorine atom or the ligand or both. The other fragments that were observed were based on Cp^+, which varied depending on the ligand used. This kind of behaviour was also observed with a literature complex $[(C_5Ph_5)_2Cr(\mu\text{-}Cl)Cl]_2$, where the mass spectrum also did not display the parent ion peak.[16] In this case the mass spectrum of this literature complex exhibited a high mass peak, which was inconsistent with $[(C_5Ph_5)Cr_2Cl_3]^+$, but due to a loss of a terminal chloride followed by structural rearrangement to give $[(C_5Ph_5)Cr(\mu\text{-}Cl)_3Cr(C_5Ph_5)]^+$.[17]

The mass spectrum for complex **7** showed a dominant peak at M^+ = 676.1 m/z due to $[(^n\text{Bu}(Ph)_4Cp)Cl_2Cr_2\text{-}\mu\text{-}Cl_2]^+$. The other fragment obtained was due to the Cp^+, which was observed at M^+ (-H) = 425 m/z. Complex **8** showed a similar trend in the spectrum, with a peak observed due to loss of the ligand. $[(^t\text{Bu}(Ph)_4Cp)Cl_2Cr_2\text{-}\mu\text{-}Cl_2]^+$ appeared at M^+ = 663.47 m/z. A substituted Cp^+ fragment was also observed at (M^+ +H) = 427 m/z.

Complex **9** and **10** showed a different trend. Both were analysed using Maldi-TOF, which involved mixing with two matrices, alpha-cyno-4-hydroxycinnamic acid and 2,5-

dihydroxybenzoic acid . Both the linear and reflector mode were used. The mass spectrum of **9** revealed a peak due to the loss of both terminal chlorine atoms, $[(^{n}Bu(Ph)_4Cp)Cr_2\text{-}\mu\text{-}Cl_2]^+$ fragment, at M^+ =1178.19 m/z. The Cp^+ fragment was also observed at M^+ = 502.28 m/z. For complex **10,** a parent peak was observed at M^+ = 1413 m/z. In addition, a secondary fragment due to the loss of one Cp ligand $[(3,5\text{-}(Me)_2(Ph)_5Cp)Cl_2Cr_2\text{-}\mu\text{-}Cl_2]^+$, M^+ = 837.4841 m/z. was observed. The Cp^+ fragment was also observed at M^+ = 585.4 m/z.

The melting points of all complexes were determined and found to be in the range of 300-333 °C (Table 2.3). Complexes **7** and **8** started to melt at 311-313°C and 300-304°C respectively, while the melting points for complex **9** and **10** were found to be higher than complex **7** and **8** and obtained to be 330-333°C and 325-328° respectively.

2.3 Conclusions

A number of ligands were synthesized and fully characterised using ^{1}H and ^{13}C NMR, mass spectrometry, elemental analysis and melting point. They were obtained in good yields. The chromium complexes were also prepared and characterised by mass spectrometry, elemental analysis and melting point but due to their paramagnetic nature, NMR spectroscopy could not be used.

2.4 References

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CHAPTER 3

RESULTS AND DISCUSSION

CATALYTIC OLIGOMERIZATION OF ETHYLENE AND 1-HEXENE

3.1 Introduction

1-Hexene is one of the most important co-monomer components for low density polyethylene.[17] The linear ethylene trimerization reaction has been studied for the future commercial production of 1-hexene. In 1977, Manyik *et al.* reported the first selective formation of 1-hexene by trimerization of ethylene using chromium-based catalysts.[2] Chromium cyclopentadienyl catalyst systems for ethylene trimerization are nowadays extensively studied in many industries.[4] Recently, few systems have been reported that selectively trimerize ethylene with higher selectivity.[5,16]

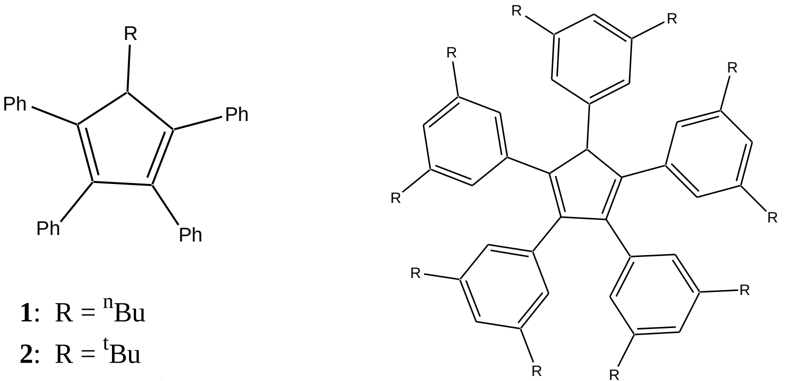
Oligomerization of 1-hexene with transition metals such as Ni, Co, Fe and Zr have been extensively studied.[6-8] These systems form mainly the dimers. Isomerization of 1-hexene was observed when the β-diketiminato Ni(II) bromide complexes were used.[6] The chromium-based system by Kohn and Wasserscheid was the only system that was reported capable of oligomerizing higher olefins via a metallacycle.[9] This led to the development of many chromium systems for the oligomerization of higher olefins with high activity and selectivity .[10, 11]

This chapter evaluates chromium-cyclopentadienyl-based catalyst systems for the oligomerization of ethylene and 1-hexene to higher olefins using various substituted cyclopentadienyl ligands, which were mixed together with a chromium source and a co-catalyst.

3.2 Ethylene trimerization using a four-component system

H. Mahomed *et al.* reported the use of chromium-cyclopentadiene-based catalysts system that selectively trimerize ethylene to 1-hexene. The catalyst of the system comprised of chromium(III) tris(2-ethylhexanoate), a phenyl-substituted cyclopenta-1,3-diene, hexachloroethane and trimethylaluminium.[13] In their work a number of substituted cyclopentadiene ligands were evaluated in an effort to increase the selectivity. 1-Hexene in up to 77.6 mass % was produced at an activity of 57700 g of product/(gCrh). Internal olefins, 2-hexene and 3-hexene, C-10's and polyethylene were also produced in small quantities.[13]

Since the Cp-ligands are widely used for this system and show good selectivity towards 1-hexene, new substituted cyclopentadiene ligands (Fig. 3.1) were investigated in this project in an effort to improve 1-C6 selectivity.



1: R = ^{n}Bu
2: R = ^{t}Bu
3: R = Ph-(^{n}Bu)

5: R = Me
6: R = ^{t}Bu

Figure 3.1: Different substituted cyclopentadiene ligands

3.2.1 Results and discussion

All ligands were found to be active towards ethylene oligomerization and were highly selective towards ethylene trimerization with the exception of ligand **2**, which formed only polymers. Chromium complexes were also found to be active towards 1-hexene oligomerization to selectively give C-12 and C-18 products. When the co-catalyst molar concentration was decreased, the selectivity shifted towards C-24. All the oligomeric products were analysed by gas chromatography using an internal standard.

The ligands were tested under various conditions for trimerization of ethylene. The results are summarised in Table 3.1.

Table 3.1: Trimerization of ethylene with chromium based cyclopentadienyl system

Ligand L	Molar ratio $Cr(2EH)_3$:L:HCE:TEA	Activity [(g/(g Cr h))]	PE (wt%)	Liquid product (g)	1-Hexene selectivity[a] %	Liquid product distribution (wt%)	
						C_6	(C_4,C_8,C_{10}^+)
1	1:3:5:45	4926	15.83	2.07	81.7	70.6	29.4
2	1:3:5:45	37640	100	-	-	-	-
3	1:3:5:45	87088	0.90	43.15	84.9	88.2	11.8
5	1:3:5:45	56060	2.53	27.32	87.8	86.3	13.7
6	1:3:5:45	7929	35.31	2.56	65.2	63.0	37.0
Blank[b]	1:0:5:45	3800	2.00	4.2	75.4	80.0	20.0

General conditions: 20 µmol catalyst, 60 µmol ligand, 100 µmol HCE, 50 bar ethylene pressure, reaction time 30 min, stirrer speed of 1100 rpm and reaction temperature, 70 ºC in 95 ml cyclohexane.

L- ligand, HCE- hexachloroethane , $Cr(2\text{-}EH)_3$ – chromium(III) tris (2-ethylhexanoate), TEA- triethylaluminium, PE - polyethylene

[a] Selectivity to 1-hexene in C_6 fraction.

A [b] Blank does not contain a ligand.

It was observed that ligand **3** was the most active ligand with an activity of 87088 (g /g Cr h) and a selectivity towards 1-hexene of 84.9 % (Table 3.1). The improvement in the selectivity to the pentaphenylcyclopentadiene ligand (1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene), could be due to the alkyl chain in the structure of ligand **3**. An analogous ligand reported in the literature, 5-(4'-t-butylphenyl)-tetraphenyl-1,2,3,4-cyclopentadiene, was reported to have an activity of 93500 [(g/(g Cr h))] and a selectivity of 85.2% towards 1-hexene under the same conditions.[5] Mahomed *et al.* 2003 reported, pentaphenylcyclopentadiene ligand (1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene) which gave the selectivity of 80.7% torwards 1-hexene**.** The selectivity of the highly substituted pentaphenyl-cyclopentadiene, ligand **5**, towards 1-hexene was 87.8% (Table 3.1).

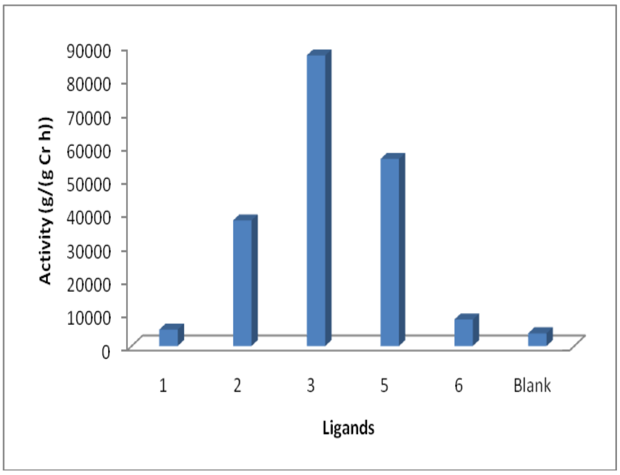


Figure 3.2: The effect on activity using different substituted cyclopentadiene ligands on ethylene trimerization

Even though ligand **5** showed the highest selectivity (87.8%) towards 1-hexene, the activity was lower when compared to that of ligand **3** (Table 3.1). The pentaphenyl-substituted ligands (**3** and **5**, Fig. 3.2) showed in general, higher activity and selectivity when compared to the tetraphenyl substituted ligands (**1** and **2,** Fig. 3.2). The exception however, was observed with sterically crowded ligand **6** with electron-donating, bulky, tertiary butyl substituents. These effects counteracted the electron withdrawing nature of the phenyl-group on the cyclopentadiene ligands.

5'-t-butyltetraphenyl-1,2,3,4-cyclopentadiene (**2**) only produced polymers and no liquid products were observed. This could be due to the combination of electron donation capacity together with the bulky ^{t}Bu hindering metallacycle formation. Polymer formation is thus preferred.

Another factor that might have played a role in the activity and the selectivity of the system, is the solubility of the ligands. Ligand **2** showed low solubility during catalytic activation, which could possibly explain why only polymers were obtained. Other ligands however, upon activation, showed good solubility in cyclohexane.

The role of having a chlorine compound in the system was investigated by Yang and his co-workers.[1] It was found that the presence of a germinal chloro-group improves the catalytic activity and selectivity in ethylene trimerization towards 1-hexene formation. It is believed that an increase in the number of chloro-substituents improves the conversion rate and the selectivity towards 1-hexene.[1] It was also postulated that a weak coordination exist between chlorine and chromium in the active species, which improves the catalytic activity. In the Sasol system, hexachloroethane (HCE) was used to improve the selectivity and the activity of ethylene trimerization, as compared to other chloro-compounds, such as chloroform, carbontetrachloride and 1,3-dichloroethane, used in literature**.**[1]

The kinetic data of the ethylene oligomerization system provides important information as it allows the understanding of the catalyst behaviour and necessary optimisation conditions.[14]

Walsh *et al*. reported the first kinetic study on an ethylene tetramerization catalyst system using bis(diphenylphosphino)isopropylamine/Cr(acac)$_3$/MAO.[15] In this work, the reaction rates were also performed on the ethylene oligomerization catalyst system using chromium(III) tris (2-ethylhexanoate) as a chromium source, together with substituted cyclopentadienyl ligands, hexachloroethane and triethylaluminium as the co-catalysts.

Ethylene uptake measurements can be used to deduce the most active system for the trimerization reactions. The ethylene uptake curves for various ligand systems used at constant temperature and pressure are illustrated in Fig. 3.3. Ligand **2** was not included in the data as it only formed polymers and in less than 10 mins.

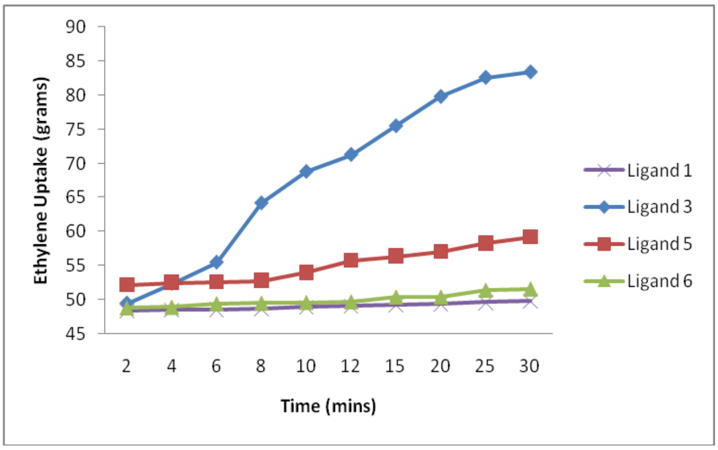


Figure 3.3: Effect of various substituted ligands on ethylene uptake at 70˚C and 50 bar

From the graph it was observed that the most active catalytic system (ligand **3)** showed an increase of ethylene uptake with time, while ligand **5** showed an increase which was then followed by a constant uptake of ethylene. The systems where ligands **1** and **6** were used, had the lowest activity as only a constant uptake of ethylene was observed with time.

3.3 Oligomerization of 1-hexene using a Cyclopentadienyl-Chromium Complex Catalysed System

The same ligands (Fig. 3.1) were then tested for the oligomerization of 1-hexene. The four-component system was used. The active catalysts were comprised of the chromium(III)tri(2-acetylacetanoate), substituted cyclopentadienyl ligand, carbon tetrachloride and ethylaluminium dichloride. All the catalytic reactions evaluated in this system, were performed looking at different factors such as the effect of having a different ligand, Cr : Al ratio and different co-catalysts.

The active catalyst was prepared using a Schlenk-line technique. The ligand, the chromium source and carbon tetrachloride were dissolved in toluene under argon atmosphere followed by the addition of the activator and 1-hexene. The resulting mixture was then stirred for an hour at room temperature. The reaction was terminated by the addition of 10% HCl, where the organic product was analysed by GC. The results obtained from the catalytic reactions are shown in Table 3.2 below.

Table 3.2: Oligomerization of 1-hexene with chromium based cyclopentadienyl system

Ligand L	Molar ratio $Cr(acac)_3:L:CCl_4:EtAlCl_2$	Activity (g/(g Cr h))	Liquid product (g)	Liquid product distribution (wt %) C_{12}	C_{18}
1	1:3:5:45	4245	4.24	63.4	36.6
2	1:3:5:45	5674	5.67	72.8	27.2
3	1:3:5:45	3751	3.75	53.8	21.9
5	1:3:5:45	3780	3.78	74.6	25.4
6[a]	1:3:5:45	3074	3.07	22.1	11.1
Blank	1:0:5:45	2076	2.01	50.9	26.0
2	1:3:5:**90**	8296	8.20	62.1	31.0
5	1:3:5:**90**	21249	21.15	48.6	35.5

[a]Only 33.2% conversion of 1-hexene

General conditions: 22.77 μmol catalyst, 68.31 μmol ligand, 20 μl CCl_4, 3 ml 1-hexene, reaction time 2 h and reaction temperature, 25 ºC in 5 ml toluene.

Effect of different ligands

All ligands were found to be active towards oligomerization of 1-hexene with 100% conversions, with the exception of ligand **6** (Table 3.2). In order to investigate the role of the ligand towards improving the activity of the system, a blank was conducted in the absence of the ligand. The activity was found to be 2076 (g/(g Cr h)), which was lower than all the individual ligands tested (Table 3.2). Therefore, the ligands play a key role in enhancing the activity of the catalyst system. This trend was also observed by Mahomed and his co-workers for ethylene trimerization.[5]

When different substituted ligands were used in the oligomerization of 1-hexene system, a different trend was observed compared to the ethylene oligomerization system. The tetraphenyl-substituted ligands **1** and **2** (Fig. 3.4) gave higher activity when compared to the pentaphenyl-substituents **3**, **5** and **6**, (Fig. 3.4). This could be due to steric interaction of the longer chains produced with the bulky ligands. As it was observed with ethylene, ligand **6** gave the lowest activity (Fig. 3.4) for the oligomerization of 1-hexene.

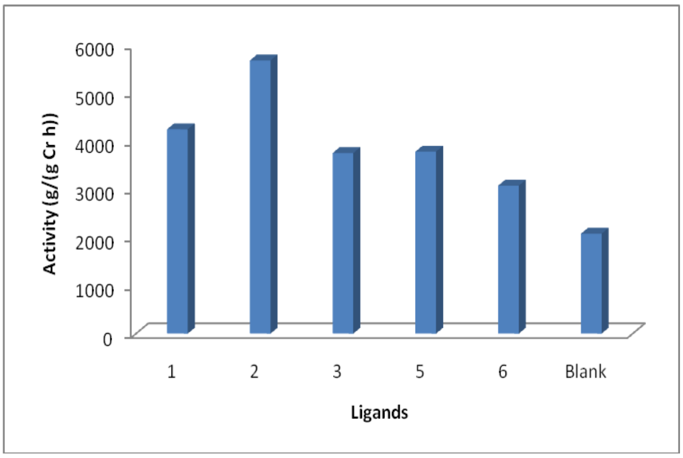


Figure 3.4: The effect of substituted cyclopentadiene ligands on the oligomerization of 1-hexene

The oligomeric products formed were analysed by GC, using known standards and the internal standard method. From the known standard, it was observed that the catalytic reaction is selective toward C-12 and C-18 fractions (Table 3.2). Small traces of 1-C-12 were detected when ligand **1**, **2** and **6** were used. The rest of the products were internal olefins, while branched C-12 isomers were also detected when ligands **3** and **6** were used. The C-18 fractions were a mixture of linear products, branched and internal olefins for all ligands (Table 3.2).

The liquid product distribution for oligomerization of 1-hexene is illustrated in Fig 3.5 below.

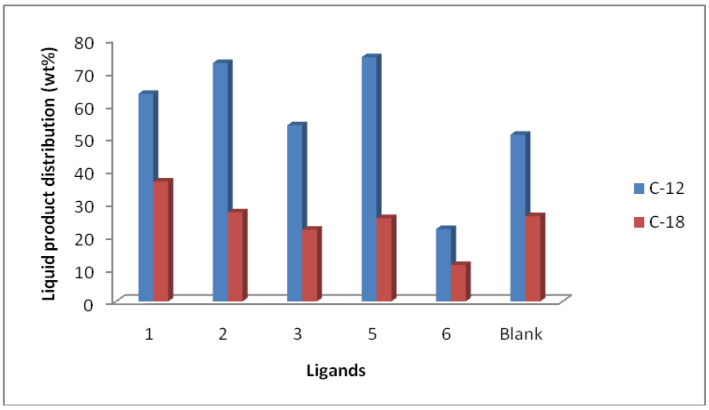


Figure 3.5: Liquid product distribution for oligomerization of 1-hexene

All ligands were observed to be highly selective towards C-12 (Fig. 3.5), with ligands **2** and **5** showing the highest selectivity (72.8% and 74.6% respectively). Substituted-tetraphenyl ligands (**1**, **2**) were highly selective towards C-18, while the pentaphenyl-substituted ligands (**3**, **5**, and **6**) showed low selectivity towards C-18 (Fig. 3.5). The observed trend could be due to the steric interaction of the active catalyst with the longer chain, which resulted in the β-hydrogen elimination to yield a low weight percentage of C-18. The blank was observed to be selective towards C-12 when compared to longer chains.

Effects of Cr/Al ratio

Ligands **2** and **5**, which gave the highest selectivity towards C-12, were further investigated for the change in the molar Cr/Al ratio. The results are tabulated in Table 3.2. An increase in the Cr/Al ratio from 45 to 90 (Table 3.2), increased the activity but decreased the selectivity of the system. A decrease of C-12 oligomers from 72.8% to 62.1% was observed with ligand **2,** while ligand **5** showed a decrease from 74.6% to 48.6%. However, an increase was observed in the formation C-18 oligomers, from 27.2% to 31.0% for ligand **2** and from 25.4% to 35.5% for ligand **5** (Table 3.2).

Effect of the Modified MethylAluminoxane (MMAO)

MMAO was used to see its effect on the system. There was < 10% conversion of 1-hexene when MMAO was used as the co-catalyst. This implied that the best activator for oligomerization of 1-hexene is $EtAlCl_2$. Its strong Lewis acidity, when compared to the MMAO, improves the activity of the catalytic systems.[12]

3.4 Conclusions

The cyclopentadienyl ligands (**1, 2, 3, 5 and 6**), with a chromium source and the activator proved to be active ethylene oligomerization catalytic systems, with **3** showing the highest activity of 87088 (g /g Cr h) and **1** the lowest activity of 4926 (g /g Cr h). The 1-hexene selectivity was improved with ligand **6**, which showed the highest selectivity of 87.8% compared to the reported literature values. The alkyl substituted pentaphenyl-cyclopentadiene ligands showed an increase in activity and selectivity of ethylene oligomerization.

The same system was investigated for the oligomerization of 1-hexene with $EtAlCl_2$ as the co-catalyst. The tetraphenyl-substituted ligands (**1**, **2**) showed the highest activity when compared to the sterically hindered pentaphenyl-substituted ligands (**3**, **5** and **6**).

The system used showed selectivity towards C-12 and C-18. It was also observed that increasing the molar ratio of the $Cr/EtAlCl_2$ resulted in an increase in the activity. Oligomerization of 1-hexene was achieved using this system.

3.5 References

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CHAPTER 4

EXPERIMENTAL

4.1 General remarks

All reactions (unless otherwise stated) were carried out under argon using a dual vacuum/argon line in a Schlenk-line technique. A glove-box under nitrogen at a positive pressure of 200 mbar was used to prepare air-sensitive materials for sample analysis and for the preparation of reactions.

4.2 Solvents and materials

All solvents were distilled prior to use and stored in Teflon-sealed glass storage vessels. The following solvents were purified using the drying agents shown in Table 4.1.

Table 4.1: Solvents used and their dying agents

Solvent	Drying Agent
Diethylether	Sodium/ benzophenone
Tetrahydrofuran	Sodium/ benzophenone
Hexane	Sodium/ benzophenone
Toluene	Sodium/ benzophenone
Dimethylformamide	Zn powder (molecular sieves were used 36 mins prior to distillation)

Other solvents such as dichloromethane and chloroform, were dried using molecular sieves and stored in a glass container with a Teflon cap.

Tetraphenylcyclopentadienone; *n*-butyllithium; *tert*-butyllithium; sec-butyllithium; 1,4-dibromobenzene; bromohexane; 3.5-di-*tert*-butyl-1-bromobenzene; 3.5-dimethyl-1-bromobenzene; palladium acetate; caesium carbonate; tri-*tert*-butyl phosphine and *p*-toluenesulfonic acid were obtained from Aldrich and used as received.

All the deuterated solvents were purchased from Aldrich and used without further purification. Anhydrous magnesium sulphate was used to dry products. All air- sensitive materials were stored in a glove box. Column chromatography was carried out with silica-gel (70-230 mesh ASTM).

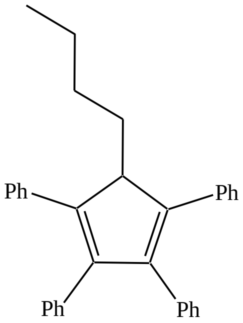
4.3 Instrumentation

Melting points were determined on a Kofler hot stage microscope (Reichert Thermovar). Elemental analysis was carried out on a Fisons EA1108 CHNS elemental analyser in the microanalysis laboratory at the University of Cape Town. IR-spectra were recorded on a Perkin-Elmer 1000 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity-XR400 MHz, XR300 MHz or XR400 MHz spectrometer. ^{1}H spectra were referenced internally using residual $CHCl_3$ and reported relative to the internal standard tetramethylsilane (TMS). GC analysis were carried out using a Varian 3900 gas chromatograph equipped with an FID and a 30 m x 0.32 mm CP-Wax 52 CB column (0.25 μm film thickness). The carrier gas was Helium at 5.0 psi. A JOEL GC mate II double focusing magnetic sector mass spectrometer operating in electron ionization mode (EI) was used for ligand analysis at University of Cape Town. Water API Q-TOF Ultima operating in LCMS with high sensitivity and resolution was used for chromium complex analysis at the Stellenbosch University, while for other complexes, a matrix-Assisted Laser Desorption

Ionization Time-of-Flight (MALDI-TOF) system for high quality data was used (Stellenbosch University).

4.4 Ligand Synthesis

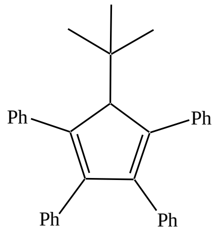
4.4.1 Synthesis of 5-^{n}butyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene (1)



To a solution of tetraphenylcyclopentadienone (5.00 g, 13.01 mmol) in diethyl ether (30 ml), *n*-butyl lithium (2.5 M, 19.52 mmol) was added dropwise at -78ºC. The reaction was stirred at this temperature for 2h followed by stirring at room temperature for 5h. The solvent was then removed from the mixture. Acetic acid (30 ml) and HBr (10 ml) were added to the remaining yellow-brown residues. The resulting mixture was refluxed for an hour, followed by the addition of zinc dust (3.5 g, 53.34 mmol). The mixture was left to reflux for 16h. It was then left to cool to room temperature followed by the dilution of the mixture with chloroform and the separation of the organic product. The organic layer was washed with $NaHCO_3$, brine and then water, and then dried over $MgSO_4$ for 2 hours. After filtration of the drying agent the solvent was removed to give a powder, which was recrystallised from hexane/DCM to afford a pure yellow solid powder. (2.58 g, 51%), mp (158-160 ºC)[Lit[8] : mp 168 ºC], ^{1}H NMR ($CDCl_3$): δ_H 0.62 (t, 3H, ^{3}J = 6.9 Hz, CH_3), 0.99-1.01 (m, 4H, $CpCH_2CH_2CH_2CH_3$), 1.75 (m, 2H, $CpCH_2$), 4.29 (t, 1H, ^{3}J = 4.7 Hz, Cp*H*), 7.01-7.27 (m, 20H, Ar-*H*); ^{13}C NMR ($CDCl_3$): δ_C 136.6-145.2 (5C, Cp-*C*) 126.4-130.3 (Ar-*C*) 54.7, 28.6, 24.7, 22.7, 13.8 ; Anal. Calc. for $C_{33}H_{30}$: C, 92.91; H, 7.09%. Found: C, 91.97; H, 7.09%; MS

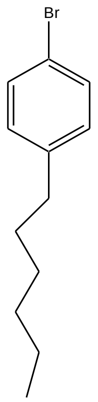
(EI): m/z 426.0509 (M^+), 383 $[C_5Ph_4CH]^+$, 370 $[C_5Ph_4H]^+$, 305 $[C_5Ph_3CH_2]^+$, 291 $[Ph_3C_5]^+$, 216, 190, 167, 97, 91 $[PhCH_2]^+$

4.4.2 Synthesis of 5-^{t}butyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene (2)



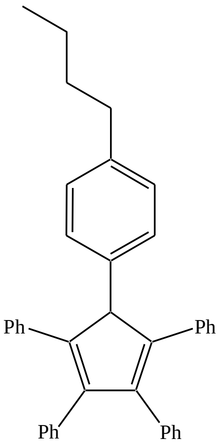
To a solution of tetraphenylcyclopentadienone (1.00 g, 2.60 mmol) in diethyl ether (10 ml), *tert*-butyllithium (1.7M ,3.25 mmol) was added dropwise at -78 ºC, The reaction was stirred at this temperature for 2h followed by stirring at room temperature for 5h. The solvent was then removed from the mixture followed by the addition of acetic acid (15 ml) and HBr (1.67 ml) to the remaining yellow-brown residues. The resulting mixture was refluxed for an hour, followed by the addition of zinc dust (0.70 g, 10.66 mmol). The mixture was left to reflux for 16 hours, after which it was left to cool to room temperature. Chloroform was then used (2 x 5 ml) to extract the organic product. The organic layer was then washed with aqueous $NaHCO_3$, brine and then water, and dried over $MgSO_4$ for 2 hours. After filtration, the solvent was removed resulting in a powder which was recrystallised from hexane/DCM to afford a solid powder, (0.51 g, 51%), mp (205-208 ºC). ^{1}H NMR ($CDCl_3$): δ_H 1.27 (br s, 9H, CH_3) 4.48 (s, 1H, Cp-*H*) 6.67-7.26 (m, 20H, Ar-*H*); ^{13}C NMR ($CDCl_3$): δ_C 138.3-143.0 (5C, Cp-*C*), 126.0-131.4 (Ar-*C*) 62.9 (Cp-*C*H), 38.2 ($C(CH_3)_3$), 30.2 ($C(CH_3)_3$); Anal. Calc. for $C_{33}H_{30}.H_2O$: C, 89.11; H, 7.10%. Found: C, 88.62; H, 6.91%; MS (EI) : m/z 443.6639 $[M + H_2O]^+$.

4.4.3 Synthesis of 1-bromo-4-hexylbenzene (C)



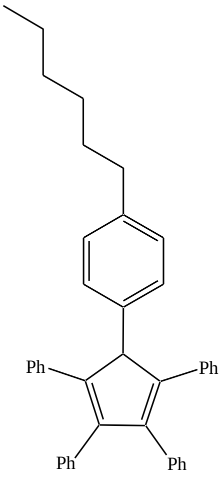
To a solution of Mg (0.62 g, 25.43 mmol) in Et_2O (20 ml) was added, 1,4-dibromobenzene (5 g, 21.19 mmol) at 0 ºC. The reaction was then refluxed for 5 hours, followed by stirring at room temperature for 21h. Hexyl bromide (3.75 ml, 25.43 mmol) was then added into the reaction mixture and left to stir over night. The reaction was then quenched with aqueous NH_4Cl (3 x5 ml) followed by extraction of the organic product with DCM. The organic layer was then dried over $MgSO_4$, the salt filtered to give a yellow-brown oil. The product was judged to be pure enough by ^{1}H NMR to carry out the next step. ^{1}H NMR ($CDCl_3$): δ_H 0.92 (t, 3H, ^3J = 6.9 Hz, CH_3) 1.31-1.54 (m, 6H, $CH_3(CH_2)_3$) 1.84-1.91 (m, 2H, CH_2) 3.43 (t, 2H, ^3J = 6.9 Hz, ArCH_2), 7.23-7.53 (m, 4H, Ar-*H*); ^{13}C NMR ($CDCl_3$): δ_C 133.1 (*C*-C), 131.6 (*C*H), 130.0 (*C*H), 126.9(*C*-Br), 33.9 (*C*H_2), 32.9 (*C*H_2), 30.9 (*C*H_2), 29.7 (*C*H_2), 22.5 (*C*H_2), 13.9 (*C*H_3)

4.4.4 Synthesis of 1-butyl-4-(2,3,4,5-tetraphenylcyclopentadien-1-yl)benzene (3)



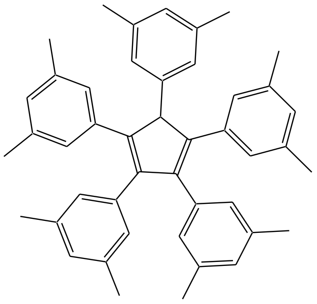
To a solution of 1-bromo-4-*n*-butylbenzene (1.00 g, 4.69 mmol) in Et_2O (10 ml), *n*-BuLi (2.25 ml, 5.63 mmol) was added dropwise at 0 ºC. The mixture was stirred at room temperature for 21h. The solvent was then removed and tetraphenylcyclopentadienone (2.71 g, 7.04 mmol) was added in Et_2O (5 ml). The reaction was left to stir overnight at room temperature followed by the removal of the solvent where upon acetic acid (15 ml) and HBr (1.67 ml) were added. The resulting mixture was refluxed for an hour followed by the addition of Zn (1 g, 15.29 mmol). The mixture was then left to reflux overnight. The reaction was quenched with $NaHCO_3$, brine and water, and then extracted with chloroform (3 x 5 ml). The organic extracts were dried from $MgSO_4$ for 2 hours. After drying, the solvent was removed resulting in a yellow solid residue. Recrystallization of the residue from DCM and hexane gave a product (0.612g, 60%), mp (102-104 ºC). ^1H NMR ($CDCl_3$): δ_H 0.87 (m, 3H, CH_3); 1.29 (m, 2H, CH_2), 1.51 (m, 2H, CH_2); 2.50 (m, 2H, CH_2); 5.06 (s, 1H, Cp-*H*), 6.81-7.26 (m, 24H, Ar-*H*); ^{13}C NMR ($CDCl_3$): δ_C 13.1 (*C*H_3); 22.2 (*C*H_2); 33.2 (*C*H_2); 35.7 (*C*H_2); 62.5 (Cp-*C*H); 126.2; 126.4; 126.5; 127.6; 127.7; 127.8; 128.5; 128.7; 129.0; 129.4; 129.9; 130.1 (Ar-*C*); Anal. Calc. for $C_{39}H_{34}$: C, 93.18; H, 6.82%. Found: C, 91.27; H, 6.76%, MS (EI) : m/z 501.35 [(nBuPh)Ph_4(M^+)].

4.4.5 Synthesis of 1-hexyl-4-(2,3,4,5-teraphenylcyclopentadien-1-yl)benzene (4)



In a Schlenk flask, **3** (1 g, 4.15 mmol) was added to Et_2O (10 ml) followed by the dropwise addition of *n*-BuLi (5.63 mmol, 2.25 ml) at -78 ºC, where the reaction was stirred at room temperature for 21h. The solvent was then removed and tetraphenycyclopentadienone (7. 04 mmol, 2.71 g) added in Et_2O (5 ml). The reaction was left to stir overnight at room temperature followed by the removal of the solvent where upon acetic acid (15 ml) and HBr (1.67 ml) were then added. The resulting mixture was refluxed for an hour followed by the addition of Zn (1.00 g, 15.29 mmol). The mixture was left to reflux overnight. The reaction was quenched with $NaHCO_3$, brine and water, then extracted with chloroform (2 x 10 ml) to afford a yellow residue after drying and evaporating the solvent. Recrystallisation from DCM and hexane gave a product, (0.34 g, 40%) . mp (98-101 ºC). ^{1}H NMR ($CDCl_3$): δ_H 0.87-0.94 (m, 3H, C*H*$_3$); 1.27-1.35 (m, 4H, C*H*$_2$), 1.46-1.59 (m, 2H, C*H*$_2$); 2.46 (t, 2H, C*H*$_2$); 2.55 (t, 2H, C*H*$_2$); 5.09 (s, 1H, Cp-*H*), 6.84-7.36 (m, 24H, Ar-*H*). ^{13}C NMR ($CDCl_3$): δ_C 12.8 (*C*H$_3$); 13.6 (*C*H$_2$); 22.0 (*C*H$_2$); 22.1 (*C*H$_2$); 32.9 (*C*H$_2$); 35.0 (*C*H$_2$); 62.3 (Cp-*C*H); 126.0; 126.6; 127.1; 127.6; 127.8; 128.0; 128.3; 128.7; 129.0; 130.1; 135.8; 136.2 (Ar-*C*) Anal. Calc. for $C_{41}H_{38}$: C, 92.78; H, 7.22%. Found: C, 92.24; H, 6.71%, MS (EI): m/z 501.09 [M - (CH_3CH_2)]$^+$.

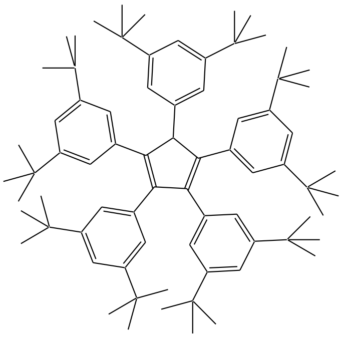
4.4.6 Synthesis of 1,2,3,4,5-penta-(3,5-dimethylphenyl)cyclopenta-1,3-diene (5)



The literature procedure reported by Giesbrecht *et al.* was followed. In a glove box Cp_2ZrCl_2 (0.58 g, 2.00 mmol), 3,5-dimethyl-1-bromobenzene (4.44 g, 24.00 mmol), caesium carbonate (7.82 g, 24.00 mmol), tri-t-butyl phosphine (0.40 g, 2.00 mmol) and palladium acetate (0.11 g, 0.50 mmol) were added in a Schlenk tube. DMF (50 ml) was added to the mixture, which was stirred at 130ºC for 24h, forming a creamy brown slurry. The mixture was then cooled to room temperature and exposed to air. DCM (150 ml) was added followed by the addition of p-toluenesulfonic acid (9.12 g, 49 mmol). The mixture was left to stir at room temperature for 15 min, then passed through a column of silica gel yielding a brown solution. The column was rinsed with DCM and DMF till the washing were colourless. The solvent was removed under vacuum to give a brown solid as a crude product. The solid was dissolved in chloroform (150 ml) and extracted with aqueous $NaHCO_3$ (3 x 150 ml) solution and saturated NaCl (3 x 150 ml). The organic layer was then added over $MgSO_4$ and passed through a column of silica gel to give a brown solution. The solvent was removed under vacuum to give an oil which was washed with hexane to yield a yellow-orange solid. (60% yield), mp (213-215 ºC). ^{1}H NMR ($CDCl_3$): δ_H 2.06 (s, 12H, C*H*$_3$); 2.14 (s, 12H, C*H*$_3$); 2.20 (s, 6H, C*H*$_3$); 4.99 (s, 1H, Cp-*H*); 6.63-6.83 (m, 15H, Ar-*H*); ^{13}C NMR ($CDCl_3$): δ_C 21.1 (*C*H$_3$); 21.2 (*C*H$_3$); 21.3 (*C*H$_3$); 61.5 (Cp-*C*); 126.3 (Ar-*C*);126.5 (Ar-C); 126.9 (Ar-*C*); 127.6 (Ar-*C*); 127.8 (Cp-*C*); 127.9 **(Cp-*C*);** 135.7 (Ar-*C*); 136.4 (Ar-*C*); 136.6 (Ar-*C*); 137.2 (Ar-*C*); 138.1(Ar-*C*);

139.0 (Ar-*C*); 145.3 (Cp-C); 146.1 (Cp-C); Anal. Calc. for $C_{45}H_{46}$: C, 92.10; H, 7.90%. Found: C, 91.10; H, 7.43%; MS (EI): m/z 585.11 (M^+ -H).

4.4.7 Synthesis of 1,2,3,4,5-penta-(3,5-di-*t*-butylphenyl)cyclopenta-1,3-diene (6)

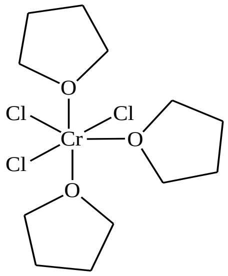


In a glove box, Cp_2ZrCl_2 (0.58 g, 2.00 mmol), 3,5-di-t-butyl-1-bromobenzene (4.44 g, 24.00 mmol), caesium carbonate (7.82 g, 24.00 mmol), tri-*t*-butylphosphine (0.40 g, 2.00 mmol) and palladium acetate (0.11 g, 0.50 mmol) were added in a Schenk tube. DMF (50 ml) was added to the mixture, which was stirred at 130ºC for 24 h, forming a creamy brown slurry. The mixture was then cooled to room temperature and exposed to air. DCM (150 ml) was added followed by the addition of p-toluenesulfonic acid (9.12 g, 49 mmol). The mixture was left to stir at room temperature for 15 min, then passed through a column of silica gel yielding a brown solution. The column was rinsed with DCM and DMF till the washing were colourless. The solvent was removed under vacuum to give a brown solid as a crude product. The solid was dissolved in chloroform (150 ml) and extracted with aqueous $NaHCO_3$ (3 x 150 ml) solution and saturated NaCl (3 x 150 ml). The organic layer was then dried over $MgSO_4$ and passed through a column of silica gel to give a brown solution. The solvent was removed under vacuum to give an oil which was washed with hexane to yield a yellow-orange solid (62% yield), mp (270-273ºC). ^{1}H NMR ($CDCl_3$): 1.07 (s, 36H, C*H*$_3$); 1.16 (s, 36H, C*H*$_3$); 1.31 (s, 18H, C*H*$_3$); 4.06 (s, 1H, Cp-*H*);); ^{13}C NMR

($CDCl_3$): δ_C 31.1 (C(*C*H_3)$_3$); 31.2 (C(*C*H_3)$_3$); 34.3 (*C*(CH_3)$_3$); 34.4 (*C*(CH_3)$_3$); 45.0 (Cp-*C*); 119.4 (Ar-*C*); 119.8 (Ar-*C*); 122.1 (Ar-*C*); 123.8 (Cp-*C*); 135.8 (Cp-*C*); 136.1 (Ar-*C*); 139.4 (Ar-*C*); 145.8 (Ar-*C*); 149.8 (Ar-*C*)**;** Anal. Calc. for $C_{75}H_{106}$: C, 89.40; H, 10.60%. Found: C, 88.75; H, 9.55%; MS (EI): m/z 817.07 (M^+ -Ph).

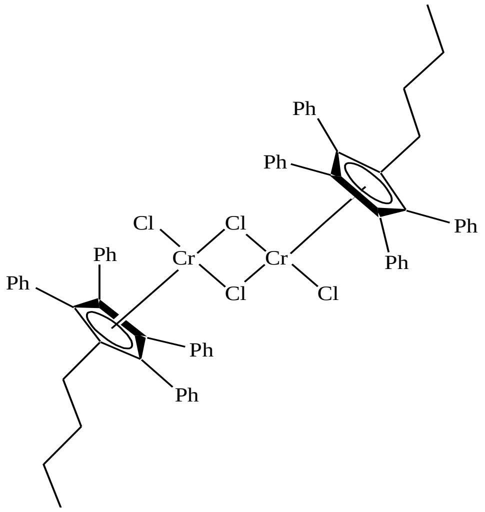
4.5 Synthesis of chromium complexes

4.5.1 Synthesis of $CrCl_3(THF)_3$ (E)



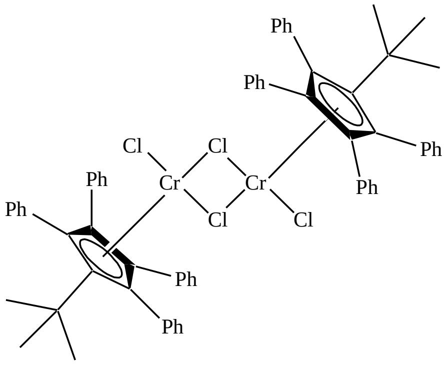
A literature procedure was followed for the synthesis of **E**. Into a 250 ml flask fitted with a condenser and a stirrer bar, $CrCl_3(H_2O)_6$ (10.00 g, 37.47 mmol) and $SOCl_2$ (65 ml, 0.86 mmol) were introduced. The solution mixture was refluxed for 5 hrs, where a colour change from green to grey was observed. An excess of dry THF (55.00 ml, 178.75 mmol) was then added to the reaction through the top of the condenser. There was an immediate colour change observed from grey to bright purple and the reaction was left to stir for an hour. After cooling, the solid was filtered off and washed four times with hexane to yield a purple powder (13.54 g, 90%), mp 250- 251°C. Anal. Calc. for $C_{12}H_{24}O_3Cl_3Cr$: C, 38.45; H, 6.45% found C, 38.39; H, 6.20%.

4.5.2 Synthesis of $[(\eta^5\text{-}C_5(^{n}B(Ph)_4))CrCl_2]_2$ (7)



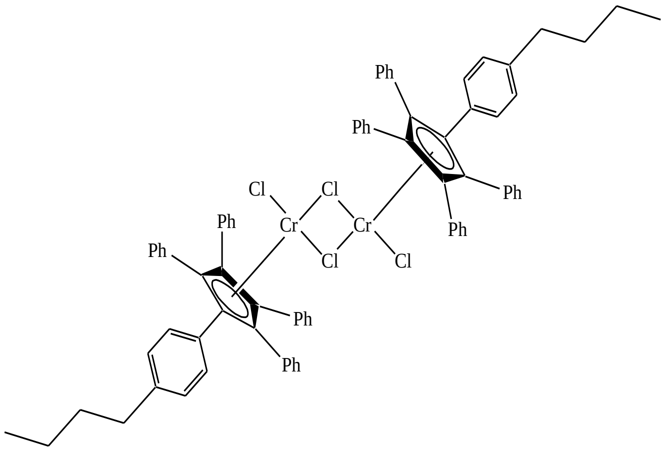
A known literature procedure was used. Ligand **1** (0.10 g, 0.23 mmol) was dissolved in THF (5 ml) followed by the addition of *n*-BuLi (1.6 M, 0.35 mmol, 0.22 ml) at -78 °C under inert conditions. The reaction was left to stir at room temperature for 12 hours, where there was colour change observed from yellow to orange. This was followed by the removal of the solvent and washing the generated salt three times with hexane, each time removing the supernatant. The remaining solid was then dried under vacuum. $CrCl_3(THF)_3$ (0.30 g, 0.11 mmol) was then added to a solution of the lithium salt in THF (5 ml), where the solution changed from purple to green. The mixture was left to stir overnight at room temperature. The resulting green solution was filtered and the solvent reduced. Upon recrystallisation with Et_2O and C_6H_{14}, the solid formed was dried under vacuum to afford an olive-green solid (0.15 g, 50%), mp 332-333°C. $[C_{66}H_{58}Cl_4Cr_2]$ MS (MALDI-TOF): m/z 676.1 $[M - (^{n}Bu(Ph)_4Cp)]^+$.

4.5.3 Synthesis of [(η^5-C_5(^{t}B(Ph)$_4$))$CrCl_2$]$_2$ (8)



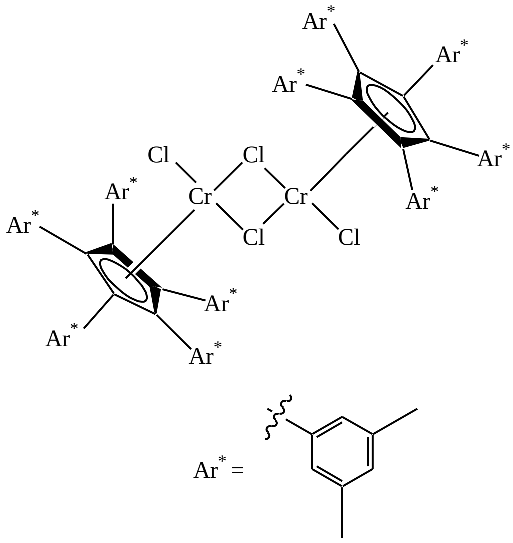
The same procedure used for **8** was followed. To a solution of **2** (0.10 g, 0.23 mmol) in 5 ml of THF, n-BuLi (1.6 M, 0.35 mmol, 0.22 ml) was added at -78 °C under inert conditions. The reaction was left to stir at room temperature for 12 hours, where a colour change was observed from a white solution to orange. The solvent was then removed and the generated salt was washed three times with hexane each time removing the supernatant. The remaining solid was then dried under vacuum. $CrCl_3(THF)_3$ (0.30 g, 0.11 mmol) was then added to a solution of the lithium salt in THF (5 ml), where the solution changed from purple to green. The mixture was left to stir overnight at room temperature. The resulting green solution was filtered and the solvent reduced. Upon recrystallisation with Et_2O and C_6H_{14} the solid formed was dried under vacuum to afford an olive green solid. (0.17 g, 57%) mp 352-355°C. [$C_{66}H_{58}Cl_4Cr_2$] MS (MALDI-TOF): m/z 663.47 [M - (^{t}Bu(Ph)$_4$Cp)]$^+$.

4.5.4 Synthesis of $[(\eta^5\text{-}C_5(^nB(Ph)_5))CrCl_2]_2$ (9)



Ligand **4** (0.10 g, 0.20 mmol) was dissolved in 5 ml of THF. This was followed by the addition of *n*-BuLi (1.6 M, 0.30 mmol, 0.19 ml) in hexane at -78°C. The resulting mixture was left to stir at room temperature for 12 hours. The solution changed from yellow to dark orange. The solvent was then removed and the generated salt washed with hexane. The remaining solid was then dried under vacuum. To a solution of the lithium salt in THF (5 ml), $CrCl_3(THF)_3$ (0.09 g, 0.25 mmol) was added. The solution changed from purple to green and was left to stir overnight at room temperature. The resulting green solution was filtered and the solvent reduced. Upon recrystallisation with Et_2O and toluene the solid formed was dried under vacuum to afford an olive green solid. (0.05 g, 56%) mp 322-327°C. $[C_{78}H_{66}Cl_4Cr_2]$ MS (MALDI-TOF): m/z 1178.19 $[M - (^nBu(Ph)_4Cp)]^+$.

4.5.5 Synthesis of [(η^5-C_5Ar_5*)$CrCl_2$]$_2$, Ar*= $C_6H_4Me_2$ (10)



A lithium salt of **6** was first prepared by dissolving the ligand (0.10 g, 0.099 mmol) in 5 ml of THF, followed by the addition of *n*-BuLi (1.6 M, 0.15 mmol, 0.09 ml) at -78 °C. The solution was left to stir overnight at room temperature. The generated white lithium salt was then washed three times with hexane, each time removing the supernatant. The lithium salt was then dried in vacuum and used in the next step. $CrCl_3(THF)_3$ (0.053 g, 0.14 mmol) was added to a solution of the lithium salt in THF (5 ml), where the solution changed from purple to green. The mixture was left to stir overnight at room temperature. The resulting green solution was filtered and the solvent reduced. Upon recrystallisation with toluene, the solid formed was dried under vacuum to afford a green solid. (0.03 g, 60%) mp 365-368°C. [$C_{90}H_{90}Cl_4Cr_2$] MS (MALDI-TOF): m/z 1413 [M^+].

4.6 Catalytic Reactions Condition

4.6.1 Ethylene Oligomerization

The catalyst was first prepared by adding the ligand (60 μmol), a solution of Cr-(2-EH)$_3$ (20 μmol) in cyclohexane and HCE (100 μmol) solution together in a glove box. The reaction mixture was left to stir at room temperature for 30 mins, which was followed by the addition of the triethylaluminium (900 μmol). The reaction was then stirred for a further 1-2 min to furnish the activated catalyst.

The reactor was heated at 120 ºC for an hour, followed by cooling to 70 ºC. It was then charged with cyclohexane (95.11 ml) and the activated catalyst while stirring. The content was then heated to 70 ºC, and charged with ethylene at a pressure of 50 bar. The stirring speed was 1100 rpm and the temperature was held at 70 ºC through water cooling for 30 mins. The internal standard was introduced after cooling and depressurising the reactor. The polymers formed were filtered and dried in an oven. The liquid products were analysed by GC.

4.6.2 Oligomerization of 1-Hexene

In situ catalytic system of four components

In a Schlenk tube charged with the ligand (68.31 μmol), Cr(acac)$_3$ (22.77 μmol) and CCl$_4$ (20 μl), 5 ml of toluene was added followed by the addition of EtAlCl$_2$ and 1-hexene. A colour change was observed from purple to green. The reaction was left to stir for 2 h at room temperature, which was then terminated by the addition of 10% HCl. The organic contents were then analysed by GC and ^{1}H and ^{13}C NMR.

CHAPTER 5

GENERAL CONCLUSIONS AND FUTURE WORK

5.1 General conclusions

In this project, a series of substituted cyclopetantadeinyl ligands have been synthesised and characterised by NMR spectroscopy, elemental analysis and mass spectrometry and their melting points. Other cyclopentadienyl ligands are new compounds.

A new series of dinuclear chromium complexes were prepared and characterised. These complexes showed a high solubility in polar solvents and proved to be very unstable as elemental analysis could not be obtained. They were purely isolated and characterised. Mass spectroscopy and the melting points of these complexes were determined. The molecular structure could not be determined as they could not crystalise.

Catalytic polymerization of ethylene and oligomerization of 1-hexene to higher olefins was evaluated. The oligomerization and polymerization included the use of various substituted cyclopentadienyl ligands which were mixed together with a chromium source and a co-catalyst.

The substituted ligands showed higher activities for ethylene polymerization and were very selective towards trimers. Higher olefins were obtained from the oligomerization of 1-hexene with high activity and selectivity.

From the results obtained, oligomerization and polymerization of ethylene and 1-hexene are dependent on factors such as the activator, the Cr/Al ratio used and the steric effect of the ligands.

The oligomerization of ethylene showed the lowest activity for the less steric ligands, **1** and **2**, while the activity increased with the more steric ligands **3** and **5**. This means that the steric effect improves the insertion of the ethylene towards the active site. The exception was seen with ligand **6** which too sterically hindered.

The oligomerization of 1-hexene showed a different trend where the sterically hindered showed the lowest activity, ligand **3**, **5** and **6**. Ligand **1** and **2** showed the highest activity as 1-hexene molecule can still insert into the active site for further consumption.

All the catalytic products were analysed by GC and showed that chromium complexes can oligomerize 1-hexene to higher olefins with high selectivity.

5.2 Future work

- New substituted cyclopentadienyl ligands should be designed, focusing specifically on the electronic properties of the ligand.
- The dimeric complexes should be characterized fully, using new analytical methods that could provide information that is more useful.
- The crystal structures of new chromium complexes should be determined to fully characterize the complexes.
- The rate of the oligomerization of 1-hexene using the chromium catalyst should be studied in order to obtain a new effective system.