HETEROGENISATION OF SELECTIVE ETHYLENE TETRAMERISATION CATALYSTS

By

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As the candidate's supervisor I have approved this dissertation for submission.

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ABSTRACT

The aim of the study was to heterogenise existing tetramerisation catalysts by supporting the bis(diphenylphosphino)amine ligands on polymer. The polymer of choice was Merrifield's resin which was functionalized to enable attachment of the ligands. These supported ligands were characterized via ATR, solid-state NMR, SEM and TGA-DSC. In order to compare activity of the supported and unsupported ligands, homogeneous bis(diphenylphosphino)amine ligands were synthesized and characterized via NMR, elemental Analysis, ATR and GC-MS. Tetramerisation reactions were carried out in a Parr pressure reactor using $Cr(acac)_3$ as the precursor and MMAO-3A as the activator. The homogeneous ligands proved active in the tetramerisation of ethylene, with the selectivity of 1-octene in the C8 fraction being comparable with that mentioned in literature (> 98 wt%). When comparing the homogeneous ligands with their heterogeneous counterparts, the heterogeneous ligands performed poorly due to steric effects caused by the polymer chain. The activity dropped by more than four times that of their homogeneous counterparts and the selectivity towards the main product, 1-octene, was very low (< 10 wt%). These ligands seemed to create a system that favoured the formation of the C6 products more than any other product, with the C6 cyclics being the most dominant.

PREFACE

The experimental work described in this dissertation was carried out in the School of Chemistry, University of KwaZulu-Natal, Durban, from May 2008 to August 2010, under the supervision of Professor Holger B. Friedrich.

These studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others, it is duly acknowledged in the text.

DECLARATION - PLAGIARISM

I, Mzamo Shozi, declare that

1. The research reported in this thesis, except where otherwise indicated, is my original research.
2. This thesis has not been submitted for any degree or examination at any other university.
3. This thesis does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.
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- My friends and family for encouraging and motivating me.

DEDICATIONS

This thesis is dedicated to my mother Ntombizodwa Mlotha.

ABBREVIATIONS

Ar	Aryl
ATR	Attenuated total reflectance
Cm	Centimeter
DRIFTS	Diffuse reflectance infrared fourier transform spectroscopy
PNP	Diphosphinoamines
Et	Ethyl
EAO	Ethylaluminoxane
GC-FID	Gas chromatography-flame ionisation detector
GC-MS	Gas chromatography-mass spectrometry
g	Gram
Hr	Hour
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
IR	Infrared
IBAO	Isobutylaluminoxane
iPr	Isopropyl
LAO	Linear alpha olefins
MAS-NMR	Magic-angle spinning-nuclear magnetic resonance
OMe	Methoxy
Me	Methyl
MAO	Methylaluminoxane
mL	Milliliter
Mmol	Millimole
MMAO	Modified methylaluminoxane
Mol	Mole
NMR	Nuclear magnetic resonance

Ppm	Parts per million
Ph	Phenyl
C6	Products from oligomerization containing 6 carbons
C8	Products from oligomerization containing 8 carbons
C10 – C14	Products from oligomerization containing 10 to 14 carbons
C16+	Products from oligomerization containing 16 or more carbons
SEM	Scanning electron microscopy
SS-NMR	Solid state-nuclear magnetic resonance
TGA-DSC	Thermogravimetric analysis-differential scanning calorimetry
TAC	Triazacyclohexane
TEA	Triethylaluminium
TIBA	Triisobutylaluminium
TMA	Trimethylaluminium
UV	Ultraviolet
Wt	Weight

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF SCHEMES

LIST OF TABLES

Chapter 1

Introduction and Literature review

1.1. An introduction to catalysis

Catalysis is an important technology in the modern world. The majority of chemicals and materials are produced using catalysis at one stage or another. Catalysis is defined as a process whereby a reaction occurs faster than an uncatalysed reaction, the reaction being accelerated by the presence of a catalyst [1]. It is not a new phenomenon and a systematic study of it began early in the 19th century when Davy began experiments in 1815 on catalytic combustion with platimum gauzes; platinum having then been only recently discovered and extracted. A catalyst is a substance that makes a reaction proceed faster without being used up in the process. In a process, the catalyst can take part in many cycles, so only a small amount is required relative to the substrate [1,2].

Activity, conversion and selectivity are important quantities used in catalysis to compare the efficiency of a catalyst. The activity of a catalyst is the rate of consumption of reactant and should be accurately measured since the profit of an industrial plant can be affected by as little as a 1 % change in activity. Conversion is the amount of reactant that has reacted to form the product. The higher the conversion, the more product is formed. Conversion cannot be related to the main product of interest, since side reactions can occur with the reactant, resulting in by-products. Selectivity is the fraction of the total products which a particular substance represents [1].

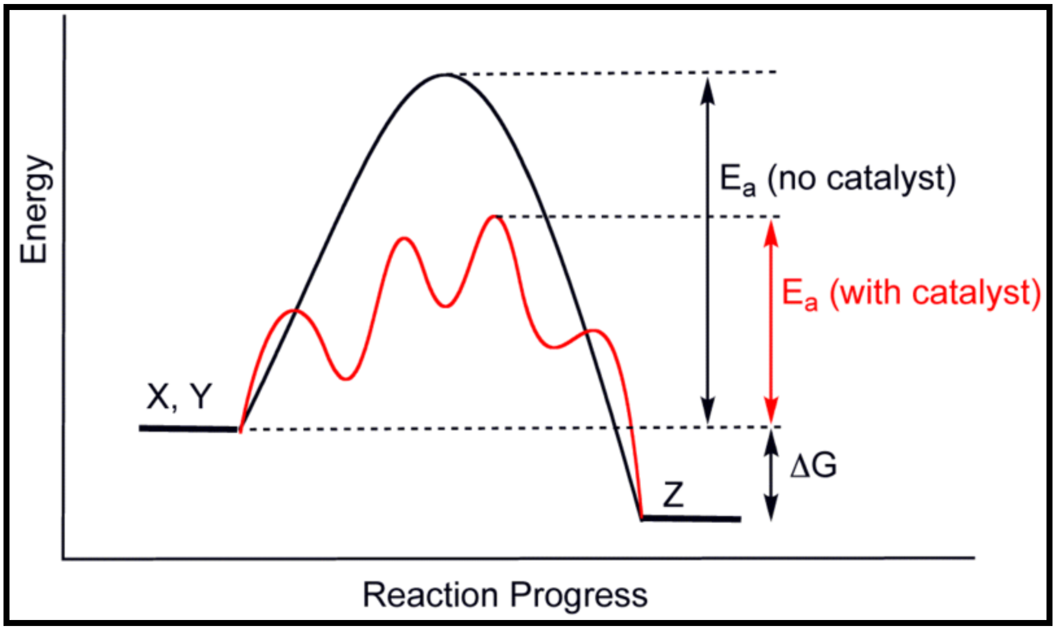


Figure 1.1. Energy diagram showing the effect of a catalyst in a hypothetical exothermic chemical reaction [3].

Figure 1.1 shows the effect of the addition of a catalyst in an exothermic reaction, where X and Y react to form Z. It shows a different pathway and lower activation energy; however the final result is still the same. Catalysts range from organometallic complexes, organic and inorganic polymers, through Lewis acids, all the way to enzymes. Catalysis is divided into three categories: heterogeneous catalysis, homogeneous catalysis and biocatalysis [2].

In heterogeneous catalysis, the catalyst and the reactant are in different phases, where the catalyst is usually a solid and the reactants gases or liquids. An important advantage of heterogeneous catalysis is that the product and the catalyst can be easily separated, mostly by simple filtration. In homogeneous catalysis, the catalyst and the reactants and products are in the same phase. The catalyst and the reactant are usually reacted in a solvent. Most of the time, the catalyst is based on a metal atom, usually a transition metal, that is complexed with a ligand. The ligand is usually organic and by changing this ligand, the catalyst properties can change. Biocatalysis is said to exist somewhere between homogeneous and heterogeneous catalysis. A biocatalyst is usually an enzyme, which is a protein that catalyses the reactions in living cells. It can complete a thousand catalytic cycles in one second, which is extremely fast when compared to conventional homogeneous and heterogeneous catalysts which complete approximately 100 – 10 000 cycles per hour. Further advantages of biocatalysis are the shorter synthesis routes and milder reaction conditions.

1.2. Trimerisation and tetramerisation of ethylene using chromium-based catalysts

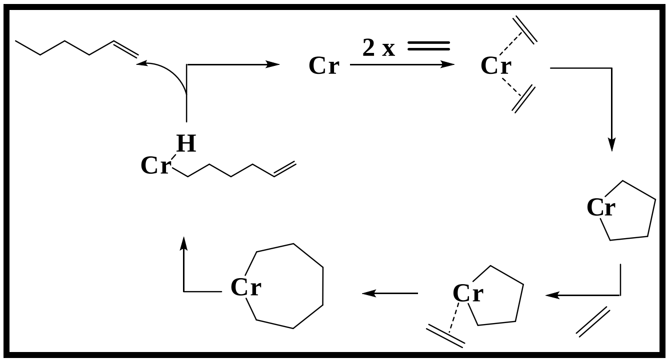
1.2.1. Introduction

Olefins are the basic building block of the petrochemical industry. They are easily available, cheap, reactive and readily transferable into a range of useful products [4-8]. Alpha olefins are usually obtained via the following processes: thermal and catalytic cracking of paraffins, oligomerisation of ethylene, dehydrogenation of paraffins, dimerisation and metathesis of olefins, dehydration of alcohols and electrolysis of C3-C30 straight chain carboxylic acids [9,10]. Full range linear alpha olefin (LAO) production is based on non-selective oligomerisation catalysts and more selective systems are desireable [11]. The oligomerisation of ethylene to LAOs is an important process because the products are useful intermediates in the synthesis of polymers, lubricants and detergents. The catalysts for ethylene oligomerisation and or polymerisation most mentioned in literature are complexes of chromium, titanium, nickel, and zirconium. These have been studied extensively and are very active. There have been reports on copper and palladium catalysts but these are not common. Other metals that have been investigated in olefin oligomerisation are iron, cobalt [12-20] and tantalum [21,22].

A broad Schultz-Flory distribution of olefins is obtained by non-selective catalytic oligomerisation of ethylene [17,23-34]. Only some of these are commercially useful, 1-hexene and 1-octene being two of the most important required for synthesis of linear low-density polyethylene [21,35,36]. Over the years, the market demand for 1-hexene and 1-octene has increased at a fast rate and the selective oligomeriation of ethylene to these two products has become highly attractive [11,36,37]. The most direct routes to 1-hexene and 1-octene are the trimerisation and tetramerisation of ethylene respectively.

1.2.2. Trimerisation of ethylene

Trimerisation of ethylene to give 1-hexene as the main product is achieved primarily by the use of chromium-based catalysts [36]. Diphosphine/Cr/MAO catalysts show strong ligand effects on catalyst activity and selectivity [26,35,38,39]. The most successful of the Cr based catalysts in the trimerisation of ethylene are the pyrrolyl-Cr complexes [40] as well as complexes of neutral phosphorus containing ligands [36,38,41-43].



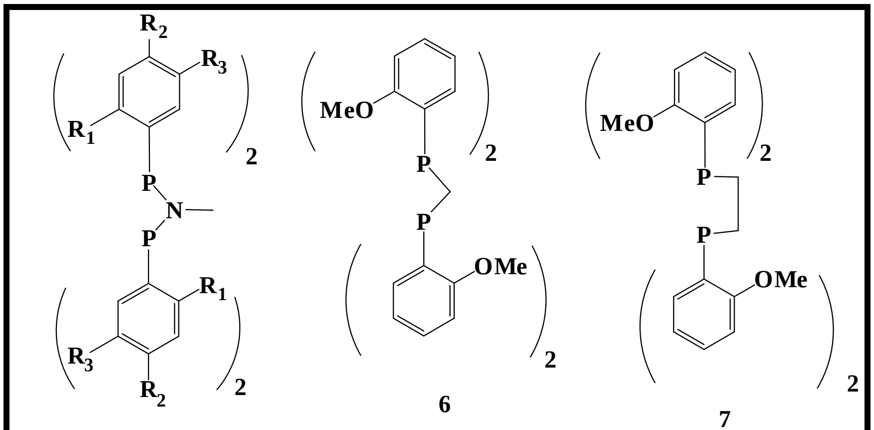
Scheme 1.1. Proposed catalytic cycle for ethylene trimerisation [29,30,35,36,44-46].

The catalytic cycle for ethylene trimerisation (Scheme 1.1) occurs as follows: It begins with the oxidative coupling of two ethylene molecules with the metal, resulting in a metallocyclopentane intermediate. The elimination of 1-butene is prevented due to the limited interaction of the β-hydrogens with the metal. Another ethylene molecule coordinates resulting in the metallocycloheptane intermediate which is flexible enough to allow for β-hydride transfer and the reductive elimination of 1-hexene [22,29,30,35,36,44-47].

1.2.2.1. Homogeneous systems

1.2.2.1.1. Catalysts based on diphosphinoamine ligands

Palladium complexes containing the ligand $Ar_2PN(Me)PAr_2$ (Ar = *ortho*-substituted aryl group), as well nickel complexes of the same ligand, have been shown to be efficient in ethylene/CO copolymerisation and ethylene polymerization, respectively, by the British Petroleum [48]. These same ligands containing *ortho*-methoxy-substituted aryl groups together with a chromium source and an alkyl aluminoxane (MAO) activator have been shown to be highly active and selective ethylene trimerisation catalysts [38,49]. These are shown in Figure 1.2 below.



6

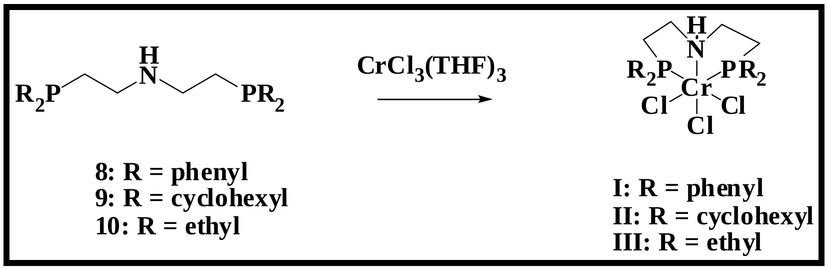
7

1: R_1 = MeO, R_2 = R_3 = H
2: R_1 = Et, R_2 = R_3 = H
3: R_1 = R_3 = H, R_2 = MeO
4: R_1 = R_3 = MeO, R_2 = H
5: R_1 = MeO, R_2 = H, R_3 = F

Figure 1.2. The various ligands used by D.F. Wass *et al.* in the selective trimerisation of ethylene using $CrCl_3(THF)_3$ and $CrCl_2$(*p*-tolyl)$(THF)_3$ as the chromium source [38].

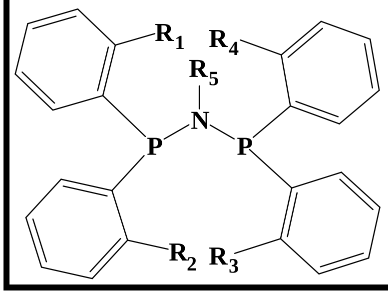
When the ethylene pressure was increased from 1 to 20 bar at a temperature of 80 °C using ligand **1**, there was an increase in catalyst activity and selectivity of 1-hexene (in excess of 99 wt%) in the C6 fraction. At 20 bar, the activity was over 1 million g/g Cr hr. This activity exceeded that reported for the Phillips catalyst at 37.4 bar and 80 °C [50]. The performance of ligand **1** led to a further investigation of other related ligand systems. An initial postulation was made that the steric bulk of the *ortho* substituents plays a critical role in the performance of the catalyst, however, ligand **2** containing *ortho*-ethyl substituents was completely inactive at a pressure of 1 bar and room temperature. Ligand **3** containing *para*-methoxy substituents was also inactive under the same conditions. Ligands **4** and **5**, containing variations to *para* and *meta* substituents but maintaining the *ortho*-methoxy substituents were active, yielding a selectivity of 99.4 wt% 1-hexene in the C6 fraction. This led to a hypothesis that the potential for *ortho*-methoxy substituents to act as pendant donors and increase the coordinative saturation of the chromium centre is an important factor. Following this hypothesis, ligands **6** and **7**, containing the same aryl substituents as ligand **1** but different chelate backbones, were tested but both proved to be inactive. It was clear that the ligand backbone also played an important role [38].

McGuinness *et al*. [43,51] investigated complexes of Cr(III) containing novel tridentate PNP ligands (Scheme 1.2) for the trimerisation of ethylene. Ligands **8** – **10** were synthesized and reacted with $CrCl_3(THF)_3$ to form complexes **I** – **III**.



Scheme 1.2. Preparation of chromium PNP complexes using $CrCl_3(THF)_3$ as the chromium source [43].

Complex **I** was the first to be prepared and gave reasonable activity and excellent selectivity towards 1-hexene (99.2 wt% in the C6 fraction) at an ethylene pressure of 40 bar, a temperature of 100 °C and 120 equivalents of MAO. Attempts were made to improve the system by modifying the substitution on the phosphorus. Complex **II**, containing highly basic but sterically demanding cyclohexyl substituents led to a decrease in activity, with polymer being the predominant product. This was under the same conditions as those for complex **I**. Complex **III**, also under the same conditions as the previous two complexes, gave a large increase in activity with excellent selectivity towards 1-hexene (99.2 wt% in the C6 fraction). Increasing the amount of MAO to 680 equivalents at the same temperature and pressure caused the activity of complex **I** to double, with an increase in polymer production. For complex **III**, higher MAO loadings of 340 and 680 equivalents led to an increase in activity, while the selectivity towards 1-hexene was maintained. At 850 equivalents of MAO, the highest activity was achieved with complex **III** but a decrease in 1-hexene selectivity was observed. An increase in MAO above this led to no further significant increase in activity of the complexes. It was noted that at 50 °C, the activity decreases significantly and a high polymer production is observed. At 80 °C, the high activity and selectivity is restored. At 120 °C, a lower activity relative to 80 – 100 °C was observed and the hexenes selectivity was reduced from 98 wt% to 93 wt% [43].



11: $R_1 = R_2 = R_3 = R_4 = R_5$ = Me
12: $R_1 = R_2 = R_3 = R_4$ = Et, R_5 = Me
13: $R_1 = R_2 = R_3 = R_4$ = iPr, R_5 = Me
14: R_1 = H, $R_2 = R_3 = R_4$ = Me, R_5 = Me
15: $R_1 = R_2$ = H, $R_3 = R_4$ = Me, R_5 = Me
16: R_1 = H, R_2 = Me, R_3 = H, R_4 = Me, R_5 = Me
17: R_1 = H, R_2 = Et, R_3 = H, R_4 = Et, R_5 = Me
18: R_1 = H, R_2 = Et, R_3 = H, R_4 = Et, R_5 = iPr
19: $R_1 = R_2 = R_3$ = H, R_4 = Et, R_5 = iPr

Figure 1.3. Bulky diphosphinoamines ligands for ethylene trimerisation [42].

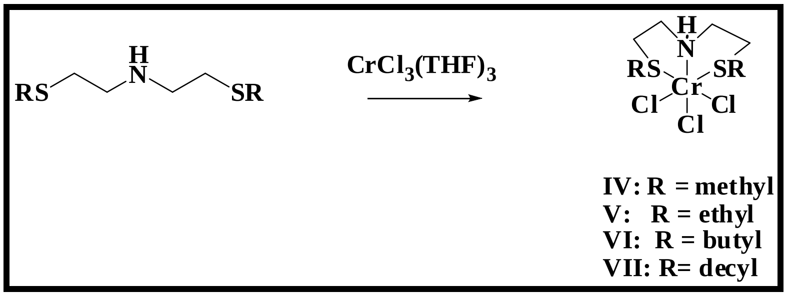
The use of bulky diphosphinoamine ligands for ethylene trimerisation has also been investigated [42]. The first account of the use of diphosphinoamines ligands with ortho-methoxy substituents, R_1 to R_4 = OMe and R_5 = Me (see Figure 1.3), and Cr as catalysts for trimerisation was published by Carter *et al*. [38].

Attention was then drawn towards the ligands **11 – 19** (Figure 1.3) for chromium-based oligomerisation catalysts. A number of these catalysts proved to be highly active and selective towards ethylene trimerisation. Results from ligand **11** showed selectivity of 90 wt% towards the C6 fraction of which 99.5 % was 1-hexene. There was also a lower selectivity to the C10 fraction (0.5 wt%) compared to that reported by British Petroleum (BP) with the ortho-methoxy equivalent (7-29 wt%) [52]. Increasing the ethylene pressure from 30 to 45 bar and reducing the temperature from 65 to 45 °C using ligand **11**, showed improvement in activity of the catalyst and an increase in 1-octene selectivity at the expense of 1-hexene [42]. It is assumed that the steric bulk around the metal centre caused by the ortho-methyl substituents is responsible for increased selectivity towards 1-hexene, since the unsubstituted diphosphinoamines derived catalyst yielded predominantly 1-octene [38]. Upon evaluation of ligands **12** and **13** at an ethylene pressure of 45 bar and a temperature of 45 °C, the catalyst containing ligand **12** produced 93 wt% 1-hexene while there was no improvement in moving to bulkier ligand **13**. The best trimerisation result was obtained using ligand **12** with a selectivity towards 1-hexene of 93 wt% and the total quantity of useful products (1-hexene and 1-octene) was 96.6 wt%.

Ligands **14 – 19** were synthesized in order to observe the effect of changing the number of ortho-substituents on the aromatic rings. Removal of only one ortho-methyl group (ligand **14**) caused an increase in the C8 selectivity to 42 wt%. The selectivity to 1-hexene in the C6 fraction was also reduced to 82 wt%. Unsymmetrical ligand **15** and its symmetrical counterpart **16** favoured the formation of 1-octene. Ligand **17** was the ortho-ethyl analogue and acted similarly. When ligand **18** was used, a change in selectivity towards 1-hexene was apparent. This is caused by the increase in the steric effect caused by the bulkier isopropyl group. The 1-hexene selectivity in the C6 fraction was also significantly improved. Ligand **19** gave a catalyst that was selective towards C8, in line with its reduced steric demand [42].

1.2.2.1.2. Catalysts based on bis(sulphanyl)amine ligands

McGuinness et al. [53] have reported the first Cr(III)-SNS complexes (Scheme 1.3) and their use as highly efficient catalysts for the trimerisation of ethylene to 1-hexene. Using MAO as a cocatalyst, complexes **IV – VII** were highly active and selective in the trimerisation of ethylene to 1-hexene. At 80 °C and an ethylene pressure of 40 bar, selectivity to 1-hexene in the C6 fraction was found to be > 99 wt%. When complexes **IV – VI** were tested, complex **VI** was found to be the most active as it was more soluble in the reaction solvent (toluene) than the other complexes.



Scheme 1.3. Trimerisation complexes that display Cr(III)-SNS bonding [53].

Complexes **V** and **VII** were then investigated further using a temperature close to 85 °C for complex **V** and 90 °C for complex **VII**. Using low concentrations of **V** and 280 equivalents of MAO resulted in high activity and a selectivity of 99.7 wt % of 1-hexene in the C6 fraction. Activity was found to be optimum at an ethylene pressure of 30 – 50 bar. Increasing the pressure to 70 bar resulted in no increase in activity and an increase in polymer formed. For complex **VII**, using similar chromium concentrations and ethylene pressures resulted in high activity being obtained with low amounts of MAO (30 – 100 equivalents. This was due to the high solubility of **VII** in toluene.

Jabri *et al.* [54] have also reported the use of the catalyst $[CySCH_2CH_2N(H)CH_2CH_2SCy]CrCl_3$ in the trimerisation of ethylene using three different alkyl aluminium activators. The activators that were used were isobutylaluminoxane

(IBAO) and trimethylaluminium (TMA) which were complexed with the catalyst before use and MAO. Catalytic testing was performed using a temperature of 50 °C and an ethylene pressure of 35 bar. When the TMA complex was used, a decrease in MAO from 2000 to 500 equivalents resulted in an increase in catalyst activity as well as an increase in 1-hexene selectivity to greater than 98 mol%. The catalyst which was not complexed with an activator also afforded a 1-hexene selectivity greater than 98 mol%, as did the catalyst complexed with IBAO at 300 MAO equivalents.

Further investigation was done where the catalyst was complexed with 2, 10 and greater than 10 equivalents of $AlCl_3$. When 2 and 10 equivalents of $AlCl_3$ were used, trimerisation of ethylene was successful and afforded a 1-hexene selectivity greater than 98 mol%. When excess $AlCl_3$ was used, the complex could not be isolated and therefore no further investigation was carried out. The ligand $CySCH_2CH_2N(H)CH_2CH_2SCy$ was also complexed with $CrCl_2(THF)_2$ to investigate the effect of the oxidation state of chromium. With the catalyst $[CySCH_2CH_2N(H)CH_2CH_2SCy]CrCl_2$, a 1-hexene selectivity greater than 98 mol% was achieved using 1000 equivalents of MAO. It was concluded that the Cr(III) species is a precursor to the Cr(II) species, which in turn is a precursor to the catalytically active species, which is in line with other systems analyzed previously [54-56].

Temple *et al*. [57] have further investigated Cr(III) and Cr(II) complexes containing SNS ligands. The ligands investigated were $[2,6\text{-}(CySCH_2)_2\text{-py}]$ and $[2,6\text{-}(PhSCH_2)_2\text{-py}]$ and complexes were prepared using both $CrCl_3(THF)_3$ and $CrCl_2(THF)_2$. Catalyst testing was carried out using 35 bar of ethylene, a temperature of 50 °C and MAO as the activator.

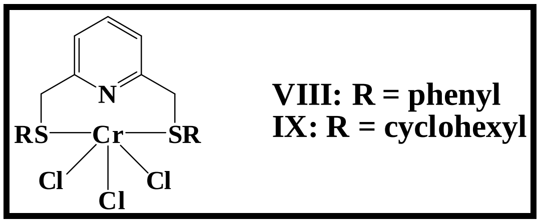
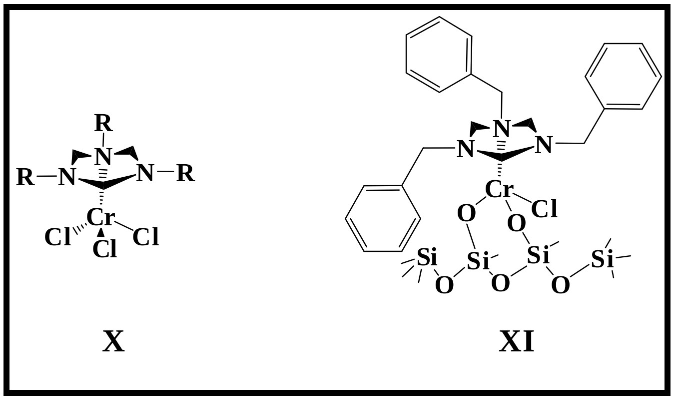


Figure 1.4. SNS complexes investigated by Temple et al. for the trimerisation of ethylene [57].

Complexes in Figure 1.4 are those prepared using Cr(III) and were the ones that were used for catalysis. When Cr(II) complexes were tested, there was a complete loss of activity, so no further investigation was carried out. Complexes **VIII** and **IX** were found to be very selective towards the production of 1-hexene (> 99 wt%). When the MAO concentration was increased from 50 to 500 equivalents, complex **IX** yielded an increase in polymer formation and activity. At 1000 equivalents of MAO, the activity dropped but there was no change in 1-hexene selectivity. When the ethylene pressure was reduced to 10 bar, again the activity decreased but there was no change in 1-hexene selectivity.

1.2.2.2. Heterogeneous systems

Nenu and Weckhuysen [58] have reported the use of a heterogeneous chromium-based catalyst for selective ethylene trimerisation. It involved the use of a catalyst containing a chromium centre attached via two silanol groups to an amorphous silica carrier and surrounded by three nitrogen atoms of a 1,3,5-tribenzylhexahydro 1,3,5-triazine ligand (Figure 1.5). This ligand has also formed active trimerisation complexes with other metals [59,60].



X **XI**

Figure 1.5. Structure of the homogeneous Cr-TAC complex X and the proposed structure of the heterogeneous anchored complex XI [58].

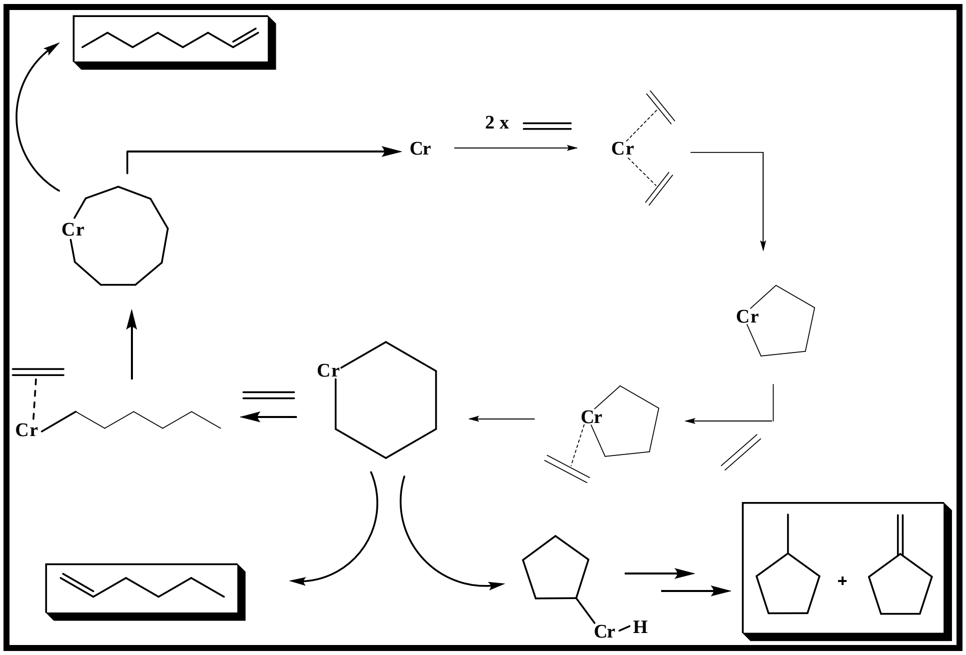
The heterogeneous system **XI** is said to be more active than its homogeneous counterpart **X** [61]. Both catalysts were tested in the trimerisation of ethylene using N,N-dimethylanaliniumtetra(pentafluorophenyl) borate (0.04 mmol) and triisobutyl-aluminium (20 equivalents) as activators. System **XI** was found to be three times more active towards ethylene trimerisation than complex **X** at 25 and 90 °C. The high activity is believed to be due to the distortion of the Cr coordination induced by the support oxide. A disadvantage of system **XI**, however, is that it forms up to three times more solid product than **X**. An increase in temperature from 25 to 90 °C causes a decrease in 1-hexene selectivity by almost 40 wt%. An increase in pressure from 1 to 30 bar causes an increase in solids, although 1-hexene is still produced in small amounts. It was concluded that system **XI** is a highly selective and active trimerisation catalyst at low pressure and low temperature, with its activity maintained for longer than 3.5 hours [58].

Another heterogeneous system has been patented [62-64] and published [65] by Monoi *et al*. It involved the use of a catalyst prepared by supporting $Cr[N(SiMe_3)_2]_3$ and isobutylalumoxane on silica and calcined at 600 °C, in the trimerisation of ethylene. The main by-products were decenes and high molecular weight polyethylene. When trimerisation was performed without using the silica support, the activity decreased, which showed that the active site was formed on the silica support. When the silica was calcined at 300 °C and 780 °C, the activity decreased, but the selectivity towards 1-hexene was greatest when the calcination temperature was 780 °C. The selectivity towards 1-hexene was also found to increase with reaction time, with the rate gradually decreasing. The selectivity towards the decenes increased with time, implying that they were formed from 1-hexene and two equivalents of ethylene.

The introduction of 1,2-dimethoxyethane favoured the formation of 1-hexene, with an increase in its concentration resulting in an increase in 1-hexene selectivity in excess of 80 wt%. This ether compound is said to co-ordinate to the Cr active site and increase the selectivity towards 1-hexene by suppressing the production of the decenes. Introduction of diethyl ether, dimethoxymethane and 1,4-dioxane yielded a decrease in 1-hexene selectivity and steric factors were concluded to be the main reason to explain the difference.

1.2.3. Tetramerisation of ethylene

Tetramerisation of ethylene to 1-octene was thought to be unlikely due to the belief that if it were to proceed via a similar mechanism to that for trimerisation [29,30,45], it would mean formation of a nine-membered metallacycle (metallocyclononane) intermediate instead of a seven-membered (metallocycloheptane) intermediate (Scheme 1.4). It has been argued that this is unlikely to occur [22,47] because the nine-membered ring is the least favoured medium sized ring [47]. Tetramerisation, however, does occur, probably as a result of both the relative stability of the metallocycloheptane intermediate and the instability of the metallocyclononane intermediate which rapidly eliminates 1-octene [31,44].



Scheme 1.4. Postulated mechanism for the tetramerisation of ethylene, with the main products in boxes [44].

1.2.3.1. Homogeneous systems

1.2.3.1.1. Catalysts based on diphosphinoamine ligands

Ethylene tetramerisation reactions that produce 1-octene in good selectivity using diphosphinoamine ligands have been reported [35,66]. They were first reported by Bollmann *et al*. [35] in 2004. The catalyst system involved MAO and chromium/$((R_2)_2P)_2NR_1$, with $CrCl_3(THF)_3$ and $Cr(acac)_3$ being the two sources of chromium.

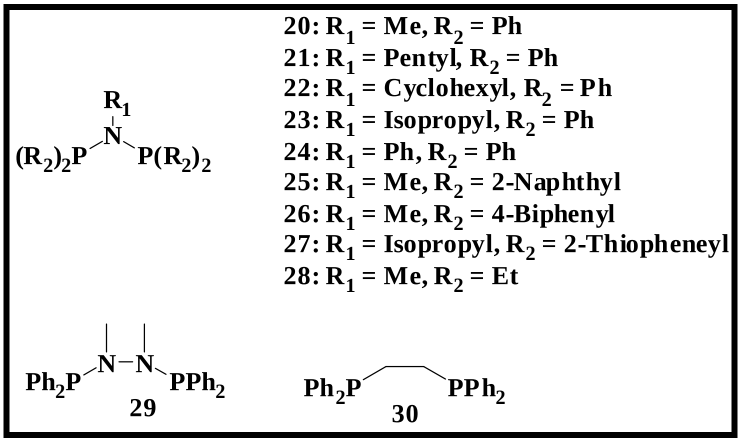


Figure 1.6. Ligands used for ethylene tetramerisation [35].

Ligands **20 – 30** (Figure 1.6) were evaluated under two different conditions; the first condition being an ethylene pressure of 30 bar and a temperature of 65 °C and the second condition being an ethylene pressure of 45 bar and a temperature of 45 °C. All these ligands produced active catalysts, with selectivities greater than 93 wt% towards 1-octene in the C8 fraction being obtained. Although the substituent on the nitrogen had a minor effect on the 1-octene selectivity, it affected the catalyst activity and 1-hexene selectivity. The highest selectivity towards 1-hexene was observed for ligands **22** and **23**. Ligands with variations on the phosphorus also produced 1-octene in good selectivity. Ligands with bulkier aromatic substituents, ligands **25** and **26**, gave selectivity of 54 and 56 wt% respectively towards C8 products under the first conditions; and ligand **27**, containing heteroatomic substituents gave a selectivity of 60 wt% towards C8 products under the second conditions. It was also found that ligands **29** and **30** were active for ethylene tetramerisation, giving selectivities of 39 and 62 wt%, respectively, towards C8 products [35].

Ligand **23** was further investigated using different activators and it was discovered that modified methylaluminoxane (MMAO-3A), ethylaluminoxane (EAO) and silica-supported MAO in combination with trimethylaluminium were suitable co-catalysts for this system, with selectivity towards C8 products being greater than 67 wt% at condition 1. It was also discovered that the use of paraffinic solvents such as cyclohexane more than doubles the activity of the catalyst [35].

An alternative source of chromium, $Cr(CO)_6$, for ethylene tetramerisation has been reported by Rucklidge *et al*. [67]. $Cr(CO)_6$ was complexed with ligand **23** above to create the $[Cr(CO)_4(PNP^{iPr})]$ catalyst. Tetramerisation runs were performed using triethylaluminium (TEA) and triisobutylaluminium (TIBA) as activators, a temperature of 60 °C and an ethylene pressure of 40 bar. Tetramerisation using TEA as the activator (50 – 400 equivalents) yielded C6 and C8 products and 1-octene in C8 selectivities which were close to those obtained when using a Cr(III)/MAO system. Activity of the catalyst was found to increase with increase in TEA equivalents; a maximum activity being obtained with 200 equivalents. When TIBA was used as the activator, the activity dropped although the C6 and C8 products and 1-octene in C8 selectivities were retained.

Kuhlmann *et al*. [31] have reported the application of PNP ligands containing N-cycloalkyl moieties for the selective tetramerisation of ethylene. A range of N-cycloalkyl PNP ligands with varying ring sizes (Figure 1.7) were synthesised to gain information on the substitution pattern that would be necessary for improved selectivity.

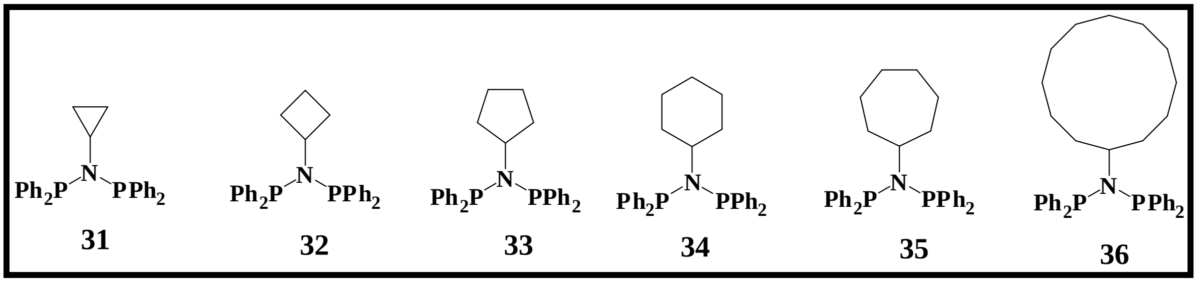
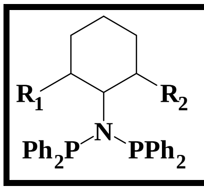


Figure 1.7. N-cycloalkyl PNP ligands [31].

Ligands **31** and **32** formed relatively unselective catalyst systems, with the overall alpha selectivity (1-hexene and 1-octene) being low. Increasing the ring size from 3 to 12 carbons (ligands **31 – 36**) led to an increase in overall alpha selectivity, mainly due to an increase in

1-hexene selectivity in the C6 products. Also an increase in ring size from 4 to 7 carbons (ligands **32** – **35**) led to an increase in 1-octene selectivity, however, increase to 12 carbons (ligand **36**) led to a decrease in the 1-octene selectivity. Catalyst activity also increased with ring size due to an increase in catalyst solubility.



34: $R_1 = R_2 = H$
37: $R_1 = H; R_2 = Me$
38: $R_1 = H; R_2 = Et$
39: $R_1 = H; R_2 = iPr$
40: $R_1 = Me; R_2 = Me$

Figure 1.8. 2- and 2,6-alkylcyclohexyl PNP ligands [31].

Based on the above results, a further investigation was carried out with the ligand **34**. The effect of substituents that are in close proximity to the N-atom on the cyclohexyl ring, ligands **37** – **40** (Figure 1.8), was investigated. It was observed that substitution with increasingly bulkier groups led to an increase in overall alpha selectivity. Ligands **37** – **39** favoured the formation of 1-hexene over 1-octene. The activities achieved were among the highest reported thus far. When the bulk of the ligand was further increased (ligand **40**), an even higher 1-hexene selectivity in the C6 products was obtained.

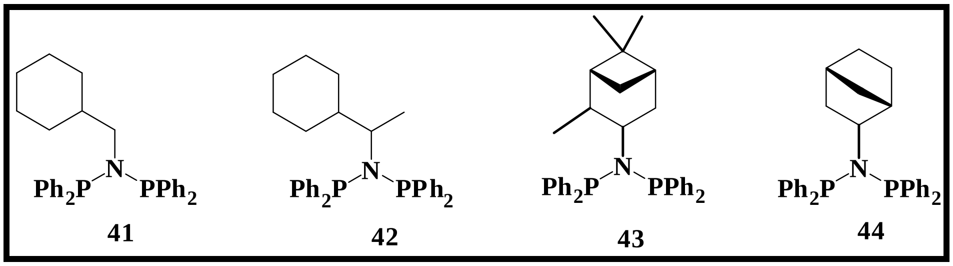


Figure 1.9. Various N-substituted cyclohexyl PNP ligands [31].

It was decided to broaden the research and explore ligands with structurally related cycloalkyl patterns (Figure 1.9). Introduction of a methylene spacer on ligand **34** to give **41** led to a decrease in overall alpha selectivity due to an increase in the formation of cyclic C6 products. When the H atom on the methylene bridge on **41** was substituted with another methyl group to give **42**, this led to an increase in overall alpha selectivity. The selectivity obtained with this ligand compares with that obtained with ligand **37** since they are structurally similar. Ligand **43** also gave similar results to that of ligand **37** and removal of the 2-methyl substituent (ligand **44**) gave selectivities that were comparable to ligand **34**.

Killan *et al.* [32] have also reported the application of PNP ligands containing N-aryl moieties for the selective trimerisation and tetramerisation of ethylene. Initially they investigated the addition of ortho-substituents onto the N-phenyl ring of $Ph_2PN(Ph)PPh_2$ (Figure 1.10).

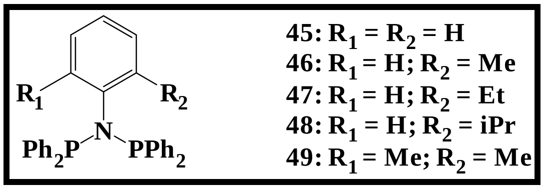
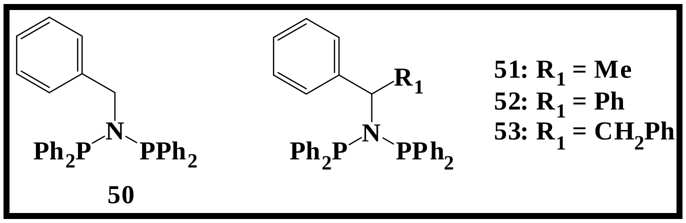


Figure 1.10. The ortho-substituents used on the N-phenyl PNP [32].

An increase in substituent size from an H-atom to an isopropyl group (ligands **45 – 48**) led to an increase in the selectivity of C6 products at the expense of the C8 products, although the selectivity towards the C8 products was still greater. The selectivity of 1-octene in the C8 products increased from 97 to 99 % when using ligands **45** to **48**, which led to an overall alpha selectivity increase of 12%. The bulkiest of these ligands (ligand **48**) showed the least activity and yielded the most polymer. Ligand **49** led to an increase in the overall alpha selectivity compared to **48**.

The second investigation involved the use of ligands containing a single spacer carbon between the N-atom and the phenyl group (Figure 1.11). Bollmann *et al.* [35] had previously reported that in the presence of an N-alkyl group, α-branching on this alkyl moiety leads to an increase in the overall alpha selectivity. Introduction of a methylene spacer in ligand **45** to yield ligand **50**, released some steric strain and had little effect on product composition, but an increase in activity by 30 % was observed. Steric strain was re-introduced by replacing the H-atom on the methylene spacer with a methyl group to yield ligand **51**. This led to an increase in overall alpha selectivity compared to **50**. This ligand also yielded the highest C8 selectivity and the highest overall alpha selectivity, when comparing ligands **45 – 51**. It also showed high activity and low polymer formation.

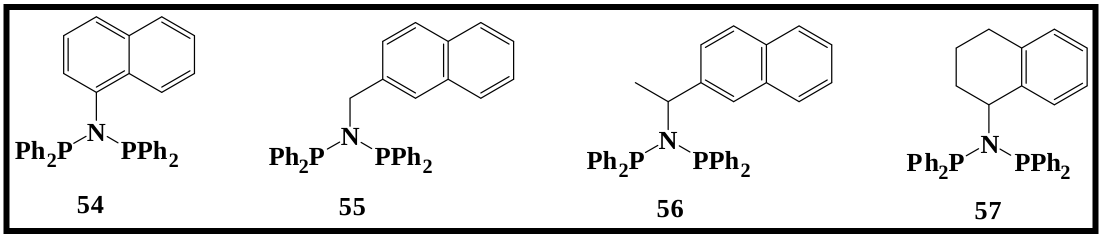


50

51: R_1 = Me
52: R_1 = Ph
53: R_1 = CH_2Ph

Figure 1.11. PNP ligands with a single carbon spacer between the N-atom and the phenyl group [32].

Steric strain was further increased by replacing the methyl group on **51** by a phenyl group to yield **52**. Ligand **52** did not give a further increase in overall alpha selectivity but yielded high quantities of polymer. The activity was also more than 40 % lower than that of **51**. Ligand **53**, obtained by introducing a phenyl group on the methylene spacer of **50**, gave similar selectivities to those of **51**. This is due to their structural similarities.



54 **55** **56** **57**

Figure 1.12. N-naphthyl PNP analogues [32].

The third investigation involved the use of naphthyl-PNP analogues of ligands **45**, **50** and **51** (Figure 1.12). Using ligand **54** resulted in an increase in overall alpha selectivity from 69 to 72.6 %. When ligand **55** was used, the C6 and 1-hexene selectivities remained constant while the C8 products increased. The activity also increased. Introduction of a methyl branch on ligand **55** to give ligand **56** resulted in an increase in 1-hexene and overall alpha selectivity. Ligand **57**, the 1,2,3,4-tetrahydronaphthyl analogue of **54**, gave the best overall selectivity in the study. It was concluded that PNP ligands with an N-aryl functionality give catalysts which are less selective than their N-cyclohexyl analogues in terms of both 1-octene formation and overall alpha selectivity [31].

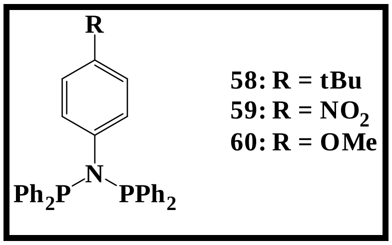
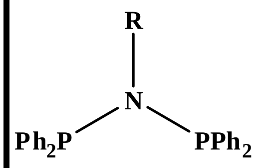


Figure 1.13. Different electronic substituents on the N-phenyl PNP [32].

Ligands **58**, **59** and **60** (Figure 1.13) were synthesised to study electronic influences, since the ligands that had been studied previously focused mainly on steric influence. Ligand **58**, containing an electronic rich tertiary butyl group, led to an increase in activity and a decrease in polymer formation. Ligand **59**, containing an electron withdrawing nitro substituent, led to a decrease in overall alpha selectivity, due to a significant increase in polymer formation. Ligand **60**, containing an electron donating methoxy group, led to a decrease in catalyst activity and a decrease in overall alpha selectivity due to a decrease in 1-hexene selectivity. It was concluded that the electronic property of the N-phenyl group does affect reaction selectivities but to a limited extent.

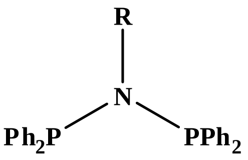


61: R = H
62: R = Methyl
63: R = Propylene
64: R = Propyl morpholine
65: R = Propyltrimethoxysilane
66: R = Pentyl
67: R = Decyl
68: R = Phenyl
69: R = Ethylhexyl
70: R = Isopropyl
71: R = Methylheptyl

Figure 1.14. Diphosphinoamine ligands evaluated for selective ethylene tetramerisation [68].

Blann *et al*. [68] have investigated the effect of steric bulk and basicity of various N-substituted PNP ligands in the tetramerisation of ethylene. Ligands investigated can be seen in Figures 1.14 – 1.16. Evaluation of ligand **61** involved the use of MAO as the activator and Cr(EH)$_3$ (chromium 2-ethylhexanoate) as the chromium source. A temperature of 65 °C and an ethylene pressure of 30 bar were also used. There was no clear selectivity towards C6 and C8, but a broad distribution of alpha olefins. When ligand **62** was used under the same conditions and using CrCl$_3$(THF)$_3$, there was an increase in C6 and C8 selectivity. There was also a decrease in the selectivity of 1-hexene in the C6 fraction and 1-octene in the C8 fraction. It was also noted that methylcyclopentane and methylenecyclopentane were the dominant products in the C6 fraction (more than 50 wt%). It was decided to introduce an olefin (**63**), an alkyl morpholine (**64**) and an alkoxy silyl (**65**) moiety on the N atom on the PNP ligand. With ligand **63**, Cr(EH)$_3$ was used and with ligands **64** and **65**, Cr(acac)$_3$ was used. All three systems produced comparable results with similar selectivities towards 1-hexene and 1-octene. For ligands **63** and **64** there was an increase in solids formation, however the selectivity was not affected.

Comparing ligands with an alkyl substituent (**62, 63** and **67**) yielded an increase in activity and overall alpha selectivity on increasing the alkyl chain length. The C6 and C8 products remained constant while the C6 cyclics decreased. Using ligands **68** and **69** yielded an increases in the selectivity of 1-hexene. The 1-hexene and 1-octene selectivity also increased (66 wt%) relative to that of **62** (39 wt%). To investigate branching on the alkyl chain of the N-substituent, ligands **70** and **71** were synthesized. Ligand **70** yielded an increase in 1-hexene to >86 wt% and an overall alpha selectivity of 88 wt%. No improvement was observed when using ligand **71**.



72: R = Ethyl
73: R = Cyclohexyl
74: R = Adamantylmethyl
75: R = Dimethylpropyl
76: R = Cyclohexylethyl
77: R = tert-Butyl
78: R = Adamantyl
79: R = *S*-Dimethylbutyl
80: R = *R*-Dimethylbutyl
81: R = *R*,*S*-Dimethylbutyl
82: R = Trimethylsilyl

Figure 1.15. Diphosphinoamine ligands evaluated for selective ethylene tetramerisation [68].

Blann *et al*. [68] then decided to investigate the use of an aliphatic solvent such as methylcyclohexane. Ligands **61 – 71** were investigated using toluene as the reaction medium and for ligands **68 – 70** (re-investigated) and **72 – 82** (Figure 1.15), methylcyclohexane was used. The activator was also changed to MMAO-3A. The temperature was 60 °C and the ethylene pressure was 45 bar. $Cr(acac)_3$ was used as the chromium source.

There was a 40-fold increase in the activity compared to when toluene was used as the solvent. There was also a 14 % increase in the overall alpha selectivity. Ligands **70** and **73** yielded comparable results. Ligands **74 – 81** were synthesized to investigate steric bulk. Selectivity towards 1-hexene was found to increase with increase in steric bulk. The overall alpha selectivity (1-hexene and 1-octene) also increased to 88 wt% with a concurrent decrease in the C8 products and an increase in the C6 products. When ligand **82** was used, the activity was low and there was a decrease in the overall alpha selectivity to 53 wt% and an increase in solids. When ligand **82** was precomplexed before testing, there was an increase in activity and the overall alpha selectivity increased to 75 wt%.

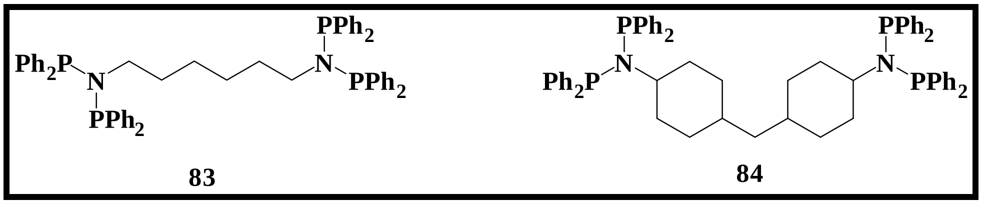


Figure 1.16. Multi-site ligands evaluated for selective ethylene tetramerisation [68].

To investigate multi-site catalysis, bifunctional ligands **83** and **84** (Figure 1.16) were synthesized. These gave results that were comparable to their respective single site analogues.

1.2.3.1.2. Catalysts based on diphosphine ligands

Overett *et al*. [69] had reported the use of carbon-bridged diphosphine for the oligomerisation of ethylene. Complexes of ligands **85 – 91** (Figure 1.17), complexed with $CrCl_3(THF)_3$, were activated with MMAO-3A and tested in ethylene trimerisation and tetramerisation reactions. Complexes of ligands **85** and **86** were found to be unselective catalysts. The other complexes with the 2- or 3-carbon spacer ligands (ligands **87 – 91**) were active for selective oligomerisation. Ligands **87 – 89** were found to produce more 1-hexene than 1-octene, while ligand **90** gave the lowest 1-octene:1-hexene ratio. Ligand **91** was found to produce more 1-hexene than 1-octene. A very high catalyst activity was observed with the complex of ligand **89**. However, its selectivity was still inferior to that of the complexes of PNP ligands, since there was an increase in C6 cyclic products (methylcyclopentane and methylenecyclopentane).

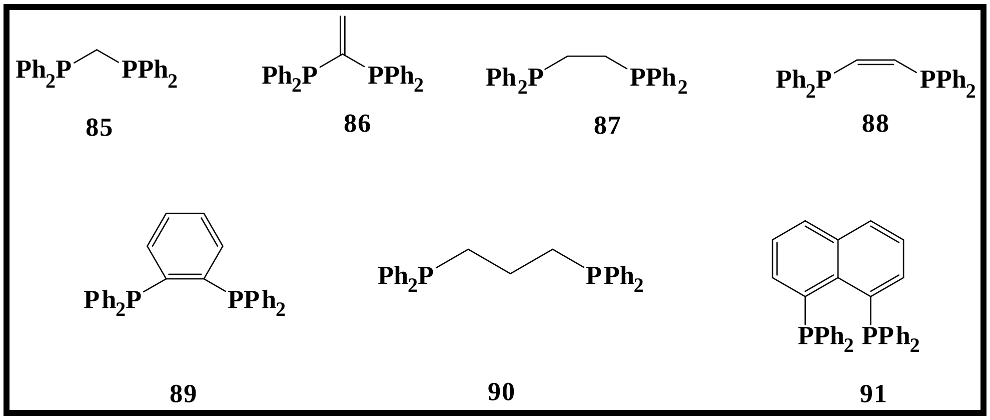


Figure 1.17. Carbon-bridged diphosphine ligands evaluated in selective oligomerisation reactions [69].

The Cr complex of ligand **89** was further studied and it was found that an increase in temperature from 60 to 80 °C at 50 bar of ethylene led to a decrease in the C6 cyclic products. The activity also increased. When the temperature was increased from 60 to 100 °C at 70 bar of ethylene, there was a decrease in the C6 cyclic products and there was an increase in 1-hexene at the expense of 1-octene. When $Cr(acac)_3$ was used as the chromium source instead of $CrCl_3(THF)_3$ at 60 °C and 50 bar of ethylene, the activity decreased dramatically, however, there was a slight increase in overall alpha selectivity. There was also a significant increase in the polymeric product.

In another investigation by Overett *et al*. [69], ligand **92** (Figure 1.18) was synthesized to decrease the acidity of the methylene hydrogens to prevent ligand deprotonation. Tetramerisation was accomplished using the Cr complex of this ligand, with selectivity to 1-octene being the highest out of all the ligands investigated. However, compared to other carbon-bridged ligands, the selectivity to 1-hexene was low due to the steric effect of the isopropyl groups.

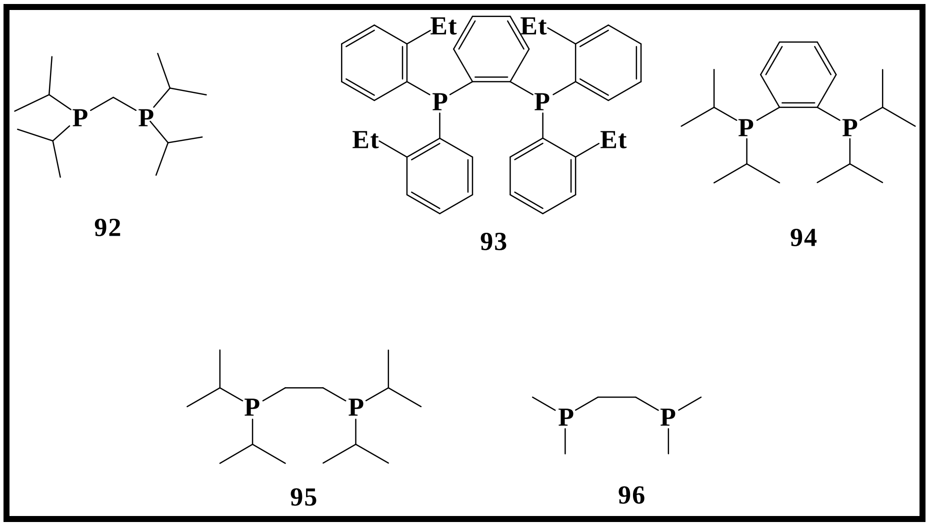
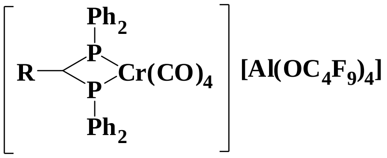


Figure 1.18. Carbon-bridged diphosphine ligands with varying phosphine substituents [69].

Ligands **93** and **94** (Figure 1.18) were synthesized as a further investigation of variations to ligand **89**. The change in phosphine substitution caused a change from a tetramerisation catalyst (ligand **89**) to a trimerisation catalyst (ligands **93** and **94**). This was noted by the dramatic increase in 1-hexene selectivity and decrease in 1-octene selectivity. Ligands **95** and **96** (Figure 1.18) were used to further investigate the relationship between steric and electronic factors for carbon-bridged ligands. These too also yielded trimerisation catalyst with the selectivity towards 1-hexene for ligands **95** and **96** being 90 and 86 wt% respectively. The activity was also much lower than that obtained using ligands **92 – 94**. There was also a considerable decrease in 1-octene selectivity.

It was concluded that bite angle, rigidity, phosphine basicity and bridge unsaturation play a role in catalyst selectivity. Changing of substituents on the phosphines, by increasing or decreasing basicity, can also result in change of the catalyst from a trimerisation to a tetramerisation catalyst and vice versa.



XII: R = CH_3
XII: R = n-C_6H_{13}
XIV: R= benzyl

$Ph_2PCH_2PPh_2$

97

$Ph_2PCH(Me)PPh_2$

98

$[Cr(Ph_2PN(i\text{-pentyl})PPh_2)(CO)_4][Al(OC_4F_9)_4]$

XV

Figure 1.19. Ligands and complexes investigated by Dulai *et al*. in the oligomerisation of ethylene [33].

Dulai *et al*. [33] have reported the use of C-substituted diphosphine ligands for ethylene oligomerisation reactions using $[Cr(CO)_4(dppm)]$ (chromium tetracarbonyl diphenylphosphinomethane) as the chromium source and triethyaluminium as the activator. The temperature was 60 °C and the ethylene pressure was 55 bar. Complexes **XII – XV** (Figure 1.19) yielded selectivities to C6 and C8 products above that expected for the Schulz-Flory distribution. There was also a significant amount of polymer produced. Moving from the methyl (**XII**) to the hexyl (**XIV**) substituent doubled the activity and reduced the amount of polymer produced. There was also an increase in 1-octene at the expense of 1-hexene. Using the benzyl substituent retained most of the activity with a slight increase and decrease in the selectivities of 1-hexene and 1-octene respectively.

To compare, complex **XV** was synthesized and tested and the selectivity towards tetramerisation was as expected, with a selectivity of 99.4 wt% towards 1-octene in the C8 fraction. There was also very low polymer formation. Testing of ligand **98** with $Cr(acac)_3$ and MMAO gave an increase in activity compared to complexes **XII – XIV** and a decrease in polymer formation. Comparing these ligands with dppm revealed that backbone substitution leads to increased activity. Selectivity is also influenced with dppm, giving a Schulz-Flory distribution [69].

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Chapter 2

Polymer-supported phosphine ligands

2.1. Introduction

There are a number of problems associated with homogeneous catalysts and these include corrosion, difficulty in recovery of the catalyst from reaction products and deposition of the catalyst on the wall of the reactor [1-3]. One solution in overcoming these problems is to anchor the catalysts on polymers or other supports and, in a way, heterogenizing them, which is becoming a diverse interest [2,4]. This forms chemically homogeneous but physically heterogeneous catalysts [5,6]. The advantages of these heterogenized catalysts are the ease of recovery and thermal stability. They are also less sensitive to oxidation and moisture and their toxicity is reduced [3,4,7-10]. However, there is a disadvantage in that there is often metal leaching during a reaction [8].

The use of organic supports such as polymers has been widely studied and the polymers must be macroporous to provide a highly reachable internal surface area. Macroporous polymers are rigid and sponge-like, and their rigidity allows them to be used in several solvents. Important criteria for a polymer to be a useful support is that it must be swellable, it must not react with the reagents as well as the products formed, it must be stable at moderate temperatures and pressures and the active site of the polymer must dissolve in the reaction medium and not cause steric hinderance such that no reaction takes place [11-13].

2.2. Synthesis of polymer-supported phosphine ligands

The most common polymers that are used as supports for phosphine ligands are polyvinyl chloride and polystyrene [14]. Polystyrene has been used widely due to its ease of synthesis, low cost, availability and relative inertness [14]. The type of polystyrene preferred is usually chlorinated polystyrene, normally Merrifield's resin, although brominated polystyrene has also been used [2,12]. This is because they contain the halogen ion, which is a good leaving group and is also susceptible to nucleophilic attack by the phosphorus on the phosphine. Although these polymers are insensitive to moisture and air, the reactions are still carried out under inert atmosphere using dried solvents due to the sensitive nature of the phosphines.

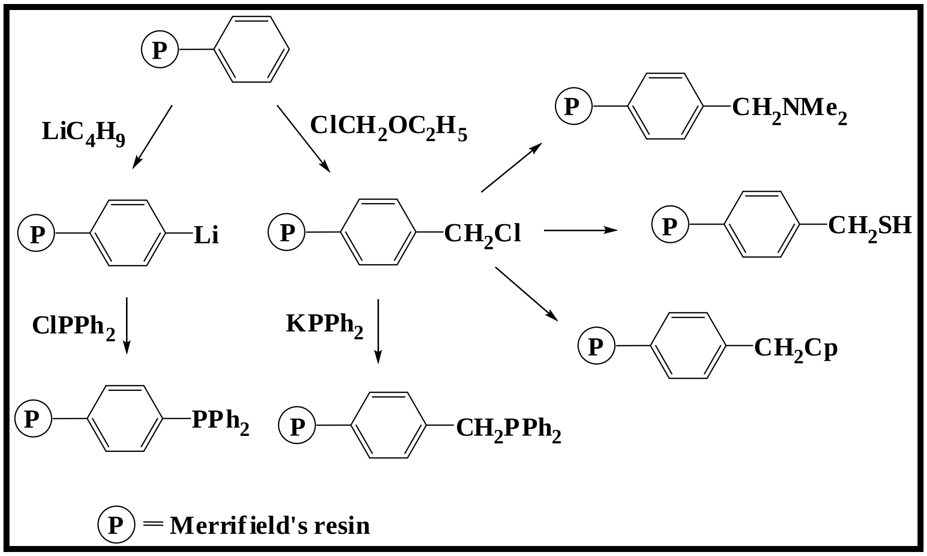

Figure 2.1. The multiplicity of ways in which to functionalize Merrifield's resin [12,15].

Some polymer-bound phosphines are commercially available but due to their high cost and sometimes undesired chemical 'make-up', synthesis of these seems more cost effective and obtaining the desired supported ligand is assured. Most reactions are done at room temperature and may involve long periods (24 – 72 hours) of stirring the solution containing the polymer and phosphine. This is referred to as wet impregnation. There are two types of impregnation techniques; incipient wet impregnation, which involves wetting the support with a quantity of solution containing the metal compound corresponding to the pore volume of the particular support, and dipping impregnation which involves immersing the support in a solution of the metal compound. It also involves functionalizing a polymer and incorporating the metal compound onto the functionalized support [16-18].

2.3. Characterization of polymer-supported phosphine ligands

2.3.1. Nuclear Magnetic Resonance spectroscopy

Nuclear Magnetic Resonance (NMR) is a spectroscopic technique that is widely used for the determination of molecular structures of compounds in solution and pure liquids. It also gives information about the rate and nature of the interchange of ligands and can be used to follow reactions and providing mechanistic detail. Its sensitivity depends on many parameters such as the abundance of the isotope and the size of its nuclear magnetic moment [19]. Solid-State Nuclear Magnetic Resonance (SS-NMR) spectroscopy is a powerful and versatile technique in the characterization of polymer-supported compounds and other insoluble compounds [20,21]. High resolution is obtained by the combination of $^{1}H/^{13}C$ cross-polarization, high power proton decoupling, and magic-angle spinning nuclear magnetic resonance (MAS-NMR) which, over the years, have had numerous applications to solid polymers. A disadvantage of this technique is the appearance of spinning side bands which can be mistaken as sample signals [20,22,23].

2.3.2. Infrared spectroscopy

Infrared (IR) spectroscopy is one of the main optical techniques used to characterize polymers. Another technique that can be used is Ultraviolet (UV) spectroscopy, but this is limited to soluble polymers. IR spectroscopy has the advantage of being both qualitative and quantitative. Not only can it be used in the determination of functional groups on the polymer, but also for structural investigations such as branching.

Common techniques in polymer analysis include Attenuated Total Reflection (ATR) and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) [21,24]. Diffuse reflectance, where the diffusely scattered radiation is collected by an ellipsoidal mirror and focused on the detector, is used for strongly scattering or absorbing particles [24].

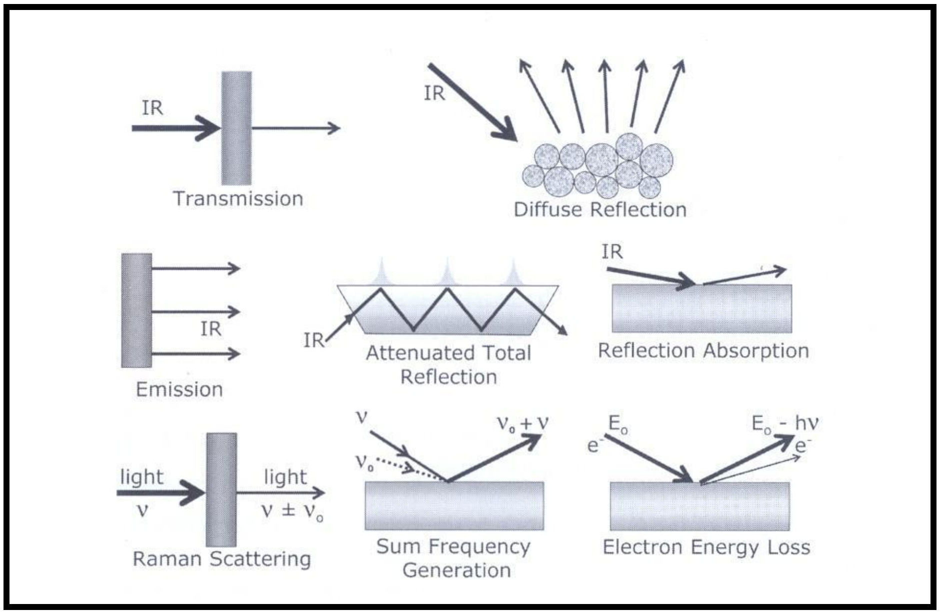

Figure 2.2. The various techniques encountered in vibrational spectroscopy [24].

Figure 2.2 shows eight forms of IR spectroscopy currently in general use; the most common being transmission IR. As mentioned above, reflectance infrared spectroscopy is commonly used for polymeric substances and in this study, ATR will be used. An ATR accessory operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample. An infrared beam is directed onto an optically dense crystal with a high refractive index at a certain angle. This internal reflectance creates a momentary wave that extends beyond the surface of the crystal into the sample held in contact with the crystal. There must be good contact between the sample and the crystal surface. In regions of the infrared spectrum where the sample absorbs energy, the momentary wave will be attenuated or altered. The attenuated energy from each momentary wave is passed back to the IR beam, which then exits the opposite end of the crystal and is passed to the detector in the IR spectrometer. The system then generates an infrared spectrum [24,25]. The operation of an ATR accessory can be seen in Figure 2.3.

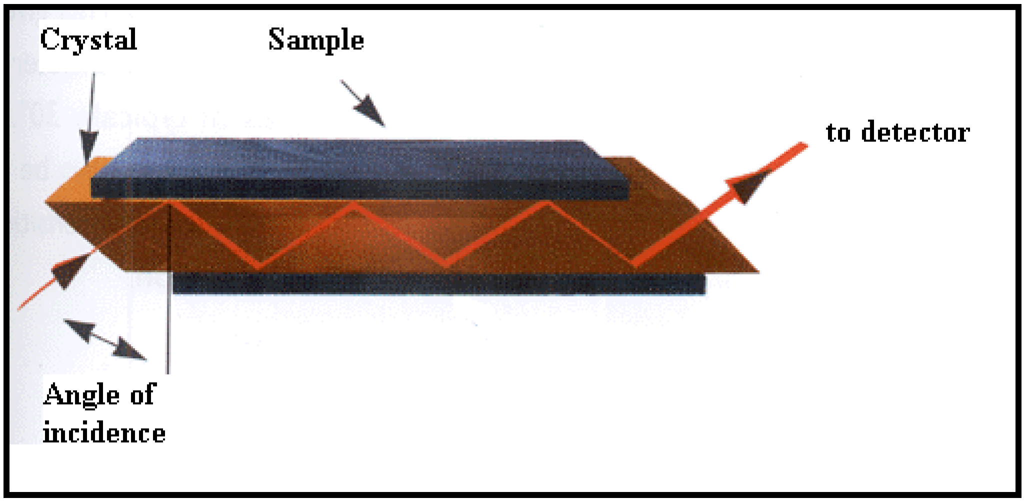

Figure 2.3. Operation of an ATR accessory showing the sample in contact with the crystal and the infrared beam forming a momentary wave on the crystal [25].

2.3.3. Scanning electron microscopy

Scanning electron microscopy (SEM) is used to study the surface morphology of a sample by viewing its magnified image. SEM operates by casting a narrow electron beam over the surface of a sample and detecting the yield of either secondary or backscattered electrons as a function of the position of the primary beam. The images produced from this technique can be approximately 15 – 30 000 times magnified and the images produced are of a high resolution. SEM images have a characteristic three-dimensional appearance and information that about the shape and size of the particles that constitute the sample as well as the chemical composition on the surface of the sample can be obtained. Charging of samples under the electron beam may occur and is a common problem in SEM, but this may be overcome by coating the sample with a thin film of gold or carbon [24]. This technique can assist in determination of the distribution of supported particles over the surface of the polymer. It can also be used be used to quantify how many of the particles of interest have been supported.

2.3.4. Thermal analysis

The thermal behaviour of polymers is usually studied using Thermogravimetric Analysis – Differential Scanning Calorimetry (TGA-DSC). Polymeric substances behave differently to low molecular weight compounds when it comes to thermal behaviour. They do not have sharp meting points and melt over a wide temperature range. The glass transition temperature is an important characteristic quantity of polymeric substances. Below a certain temperature, a polymeric substance behaves as a hard glass. When heated above this temperature, the polymer becomes soft and the temperature at which this change occurs is known as the glass transition temperature T_g. it depends on the chemical nature of the polymer, the degree of crystallinity and the degree of branching [21,26]. The T_g of normal polystyrene is 100 °C [27]. Other thermal quantities of polymers that can be determined are the crystallization temperature (T_c), melting temperature (T_m) and decomposition temperature (T_d). Figure 2.4 shows where one would expect to find these thermal quantities on a typical Differential Scanning Calorimetry (DSC) plot.

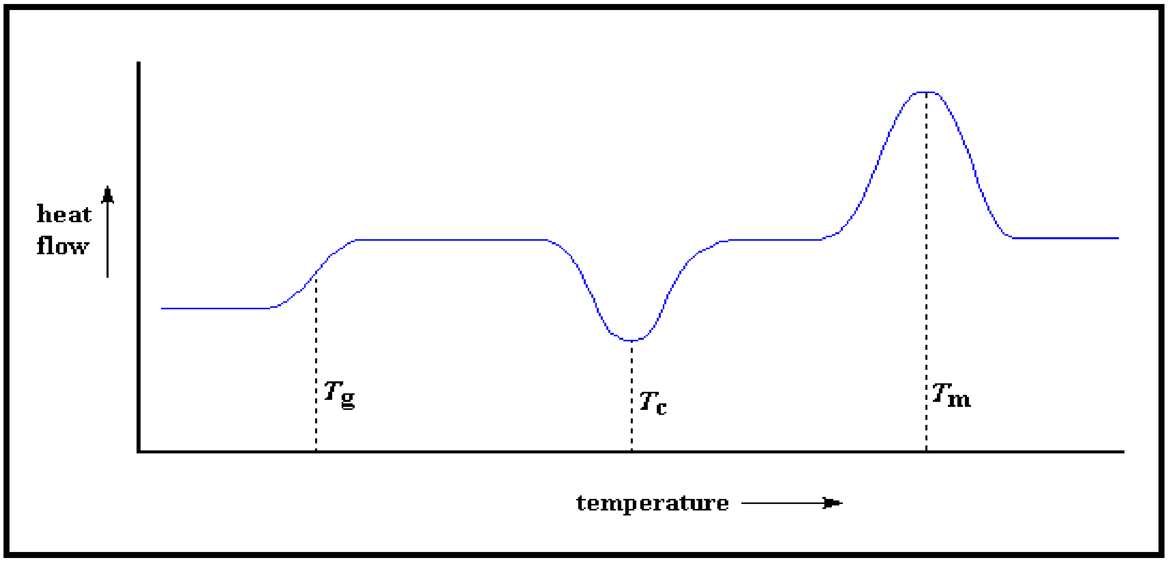

Figure 2.4. A typical DSC plot for a polymeric substance showing the glass transition temperature, crystallization temperature and melting temperature [28].

2.4. Polymer-supported phosphine ligands and catalysis

Polymer-supported phosphines have had many applications in the field of catalysis. They have been used in the conversion of alcohols to alkyl chlorides [29] and in Wittig reactions [30-32] in order to assist in separation of the products from phosphine oxides at the end of the reaction. Diphenylphosphino polystyrene resins have also been used to form supported complexes of iridium [33,34], nickel [35-37], rhodium [38-40] and ruthenium [41], and these catalysts have been used in hydrogenation [33,34,38], alkene dimerization [35] and hydroformylation reactions [39-41]. Diphenylphosphinomethyl polystyrene resins have been complexed with palladium [42-44] and rhodium [38] to form recyclable catalysts for use in Suzuki [42] and hydrogenation reactions [33,34,42] respectively. Although there is a lot of literature covering the use polymer-supported phosphine ligands in catalysis, very little or none exists for oligomerisation reactions of current interest, i.e. trimerisation and tetramerisation of ethylene, which leads to the aims of the study below.

2.5. Project Aims

The selective oligomerisation of ethylene to targeted comonomers, such as 1-hexene and 1-octene, is an area of strategic and commercial importance. The only commercial process converting ethylene to 1-hexene (Chevron-Philips) is based on a homogeneous Cr catalyst using a pyrrole ligand and TEA as an activator [45]. In addition to this, the only known catalyst system selectively converting ethylene to 1-octene is also based on a homogeneous Cr catalyst system [46,47].

To date there have been very few examples of heterogeneous selective oligomerisation catalysts in the open and patent literature [48-52]. Since the catalyst cost represents a significant portion of the total cost of a selective oligomerisation process, the successful heterogenisation of these catalyst systems could present significant cost savings for the process since this could result in a recyclable catalyst which can also be easily separated from the product mixture. It would therefore be prudent to pay attention to this, up to now, somewhat neglected area of research. Since trimerisation is already a well established commercial process, this study focuses on tetramerisation.

Therefore the aim of this project is to synthesize various PNP ligands and support them using a polymer based support, in this case functionalized polystyrene, Merrifield's resin. PNP ligands will be synthesized by varying the substituents on the N. Substituents to be used are a methyl, isopropyl, pentyl, cyclohexyl and phenyl group. Characterization of these ligands will be done by ^{1}H, ^{13}C, and ^{31}P NMR (nuclear magnetic resonance), Elemental Analysis, ATR (Attenuated Total Reflectance) and GC-MS (Gas chromatography – Mass spectrometry). After supporting on polymer, the ligands will be characterized by ATR, solid-state NMR, SEM (Scanning electron microscopy) and TGA-DSC (Thermogravimetric analysis-Differential Scanning Calorimetry). Tetramerisation reactions will be carried out in a Parr pressure reactor using $Cr(acac)_3$ as the precursor and MMAO-3A (Modified methylaluminoxane) as the activator. This study hopes to develop a re-usable catalyst for the tetramerisation of ethylene.

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Chapter 3

Experimental

3.1. Materials and Instrumentation

All synthetic work was carried out under nitrogen using standard Schlenk techniques. The nitrogen gas (HP) used was obtained from Afrox. Dichloromethane (Sigma-Aldrich, 99.8 %) was dried over P_2O_5 (Saarchem, 99 %) prior to use. Diethyl ether (Merck, 99 %) and hexane (Merck, 99 %) were dried over sodium wire prior to use. Tetrahydrofuran (Merck, 98 %) was dried over sodium wire and benzophenone (Sigma-Aldrich, 99 %) prior to use. Methylcyclohexane (Merck, 99 %) was filtered through alumina (Sigma-Aldrich) in an inert nitrogen atmosphere and stored in an inert atmosphere prior to use. The chlorodiphenylphosphine (Merck, 97 %), dichlorophenylphosphine (Alfa-Aesar, 97 %), methylamine (Merck, 40 %), isopropylamine (Fluka, 99.5 %), pentylamine (Merck, 98 %), cyclohexylamine (Merck, 99 %), benzylamine (Merck, 99 %), triethylamine (Fluka, 99.5 %), tert-butylamine (Merck, 99 %), potassium iodide (Saarchem, 99.8 %), absolute ethanol (Merck, 99.5 %), chromium acetylacetonate (Merck, 98 %) and Merrifields resin (Sigma-Aldrich, 1% cross-linked) were used without further purification. Ethylene was supplied by Air Liquide and used as received. MMAO-3A (Akzo Nobel) was supplied by SASOL and used as received. The GC standards 1-hexene (Aldrich, 97 %), 1-octene (Sigma-Aldrich, 98 %), nonane (Sigma-Aldrich, 99 %) and methylcyclopentane (Fluka, 95 %) were used as received.

NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer fitted with a 5 mm BBOz probe and equipped with an autosampler; and a Bruker Avance III 600 MHz solid-state MAS spectrometer fitted with a 4 mm MAS BB/1H probe. Elemental analyses were performed using a LECO Elemental Analyser. Infrared spectra were recorded on a Perkin Elmer Attenuated Total Reflectance spectrophotometer (4000 – 400 cm^{-1}). SEM images were obtained using a Jeol JSM-6100 Scanning Microscope. TGA-DSC was performed from room temperature to 1000 °C at a rate of 10 °C/min under static air using an SDT Q 600 TGA-DSC instrument. Catalytic testing was carried out using a 450 mL stainless steel Parr 4843 high pressure reactor and the ethylene flow rate was monitored using a Siemens Sitrans Massflo flowmeter. GC-FID analyses were carried out on a Perkin Elmer Clarus 500 chromatograph using a PONA 50 m x 0.32 mm column, oven programme: Initial temperature = 40 °C, hold for 20 minutes, ramp at 4 °C/minute to 300 °C and hold for 5 minutes, carrier gas: Nitrogen. GC-MS spectra were recorded on a Perkin Elmer Clarus 500 chromatograph equipped with an autosampler using a PONA SGE 50 m x 0.15 mm column, carrier gas: Helium.

3.2. Synthesis of bis(diphenylphosphino)amine ligands (PNP ligands)

The bis(diphenylphosphino)amine ligands were synthesized according to literature [1,2]. At room temperature, chlorodiphenylphosphine (2.01 mL, 11.2 mmol) was added to a solution containing dichloromethane (50 mL), the corresponding amine (11.2 mmol) and triethylamine (15 mL). The mixture was stirred for 30 minutes after which a second aliquot of chlorodiphenylphosphine (2.01 mL, 11.2 mmol) was added. The reaction mixture was stirred overnight at room temperature. The mixture was filtered to remove the triethylammonium hydrochloride salt formed and the product was isolated by removal of the solvent under vacuum.

Bis(diphenylphosphino)methylamine (1):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.80 (s, 3 H, CH_3), 7.20 – 7.48 (m, 20 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 32.5 (t, CH_3), 128.9 (3 CH), 132.4 (t, 2 CH), 138.4 (t, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 73.0 (s). IR (ATR) ν_{max}/cm^{-1}: 3052, 2927, 1585, 1478, 1433, 1277, 858, 741, 694. MS (EI, 70 eV): *m/z* (%) = 400 (13, $[M + H]^+$), 399 (51, $[M]^+$), 384 (15, $[M – CH_3]^+$), 214 (15, $[M – PPh_2]^+$), 185 (6, $[PPh_2]^+$). Anal. Calc. for $C_{25}H_{23}NP_2$: C, 75.18; H, 5.80; N, 3.51; P, 15.51. Found: C, 74.94; H, 5.89; N, 3.31; P, 15.86. Yield: 65 %. Mp: 114 – 116 °C.

Bis(diphenylphosphino)isopropylamine (2):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20 (d, 1 H, CH), 3.75 (m, 6 H, 2 CH_3), 7.25 – 7.47 (m, 20 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 24.7 (2 CH_3), 51.9 (t, CH), 128.5 (3 CH), 132.8 (t, 2 CH), 139.2 (t, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 48.7 (br s). IR (ATR) ν_{max}/cm^{-1}: 3050, 2965, 1585, 1478, 1431, 1376, 871, 738, 692. MS (EI, 70 eV): *m/z* (%) = 428 (2, $[M + H]^+$), 427 (12, $[M]^+$), 384 (100, $[M – i\mathrm{Pr}]^+$), 242 (10, $[M – PPh_2]^+$), 185 (25, $[PPh_2]^+$). Anal. Calc. for $C_{27}H_{27}NP_2$: C, 75.86; H, 6.37; N, 3.28; P, 14.49. Found: C, 75.67; H, 6.15; N, 3.42; P, 14.76. Yield: 77 %. Mp: 133 – 135 °C.

Bis(diphenylphosphino)pentylamine (3):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.40 (t, 2 H, CH_2), 0.85 (m, 5 H, CH_2 + CH_3), 1.10 (q, 4 H, 2 CH_2), 3.25 (t, 2H, CH_2), 7.35 – 7.50 (m, 20 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.3 (CH_3), 22.4 (CH_2), 29.3 (CH_2), 31.3 (CH_2), 53.1 (t, CH_2), 128.5 (3 CH), 132.7 (t, 2 CH), 139.7 (t, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 62.2 (s). IR (ATR) ν_{max}/cm^{-1}: 3051, 2935, 2857, 1584, 1454, 1431, 1280, 878, 740, 693. MS (EI, 70 eV): *m/z* (%) = 456 (2, $[M + H]^+$), 455 (16, $[M]^+$), 384 (32, $[M – C_5H_{11}]^+$), 270 (2, $[M – PPh_2]^+$), 185 (25, $[PPh_2]^+$), 71 (1, $[C_5H_{11}]^+$). Anal. Calc. for $C_{29}H_{31}NP_2$: C, 76.47; H, 6.86; N, 3.07; P, 13.60. Found: C, 76.12; H, 6.93; N, 2.90; P, 14.05. Yield: 83 %. Mp: 78 – 79 °C.

Bis(diphenylphosphino)cyclohexylamine (4):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.50 (m, 4 H, 2 CH_2), 1.65 (m, 4 H, 2 CH_2), 1.80 (m, 3 H, CH_2 + CH), 2.80 (q, 4 H, 2 CH_2), 7.25 – 7.40 (m, 20 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$):

δ = 25.4 (CH_2), 25.8 (2 CH_2), 37.0 (2 CH_2), 56.0 (t, CH), 128.5 (3 CH), 131.0 (t, 2 CH), 143.2 (t, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 50.8 (br s). IR (ATR) ν_{max}/cm^{-1}: 3052, 2927, 2852, 1584, 1477, 1433, 859, 741, 691. MS (EI, 70 eV): *m/z* (%) = 469 (2.4, $[M + H]^+$), 468 (1.5, $[M]^+$), 385 (0.6, $[M – C_6H_{11}]^+$), 283 (48, $[M – PPh_2]^+$), 185 (13, $[PPh_2]^+$), 83 (2, $[C_6H_{11}]^+$). Anal. Calc. for $C_{30}H_{31}NP_2$: C, 77.07; H, 6.68; N, 3.00; P, 13.25. Found: C, 77.26; H, 6.38; N, 3.27; P, 13.09. Yield: 88 %. Mp: 170 – 171 °C.

Bis(diphenylphosphino)benzylamine (5):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.70 (d, 2 H, 2 CH), 6.80 (unresolved coupling, CH), 7.00 (m, 2 H, 2 CH), 7.35 – 7.50 (m, 20 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 115.9 (CH), 119.4 (CH), 128.0 (CH), 129.1 (CH), 131.2 (t, CH), 139.2 (t, CH), 146.6 (t, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 73.0 (s). IR (ATR) ν_{max}/cm^{-1}: 3055, 1594, 1480, 1432, 871, 738, 690. MS (EI, 70 eV): *m/z* (%) = 462 (0.5, $[M + H]^+$), 461 (1, $[M]^+$), 312 (0.5, $[M – C_6H_5]^+$), 276 (0.5, $[M – PPh_2]^+$), 185 (11, $[PPh_2]^+$), 149 (2, $[C_6H_5]^+$). Anal. Calc. for $C_{30}H_{25}NP_2$: C, 78.08; H, 5.46; N, 3.04; P, 13.42. Found: C, 77.98; H, 5.52; N, 3.14; P, 13.36. Yield: 80 %. Mp: 160 – 163 °C.

3.3. Synthesis of functionalized PNP ligands

3.3.1. Synthesis of diphenylphosphinoamines

The diphenylphosphinoamines $RN(H)PPh_2$ (R = *i*Pr [3], cyclohexyl [4], Ph [5]) were prepared according to the literature procedures or modifications thereof. To a stirring ice-cold solution of the corresponding amine (20 mmol) in dichloromethane (50 mL) and triethylamine (2.8 mL, 20 mmol) was added dropwise chlorodiphenylphosphine (3.6 mL, 20 mmol) and the reaction mixture was stirred at room temperature overnight. Amine hydrochloride was removed by filtration, and the product was isolated from the solvent under vacuum.

(Diphenylphosphino)isopropylamine (6):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (d, 1 H, CH), 1.80 (s, 1 H, NH), 3.30 (m, 6 H, 2 CH_3), 7.26 – 7.42 (m, 10 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 26.2 (2 CH_3), 48.6 (d, CH), 128.2 (3 CH), 132.2 (d, 2 CH), 143.1 (d, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 34.1 (s). IR (ATR) ν_{max}/cm^{-1}: 3058, 2962, 1591, 1471, 1438, 1382, 892, 721, 691. MS (EI, 70 eV): *m/z* (%) = 244 (1, $[M + H]^+$), 243 (1, $[M]^+$), 200 (54, [M – *i*Pr]$^+$), 185 (22, $[PPh_2]^+$), 59 (3, $[M - PPh_2]^+$), 44 (79, [*i*Pr]$^+$). Anal. Calc. for $C_{15}H_{18}NP$: C, 74.05; H, 7.46; N, 5.76; P, 12.73. Found: C, 74.02; H, 7.42; N, 5.74; P, 12.82. Yield: 85 %. Mp: 98 – 100 °C.

(Diphenylphosphino)cyclohexylamine (7):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (m, 4 H, 2 CH_2), 1.57 (m, 4 H, 2 CH_2), 1.90 (m, 3 H, CH_2 + CH), 2.92 (q, 4 H, 2 CH_2), 7.30 – 7.49 (m, 20 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 24.9 (CH_2), 25.4 (2 CH_2), 36.8 (2 CH_2), 56.1 (d, CH), 128.5 (3 CH), 130.8 (d, 2 CH), 143.2 (d, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 34.4 (s). IR (ATR) ν_{max}/cm^{-1}: 3059, 2926, 2851, 1548, 1435, 887, 740, 693. MS (EI, 70 eV): *m/z* (%) = 284 (10, $[M + H]^+$), 283 (24, $[M]^+$), 200 (26, $[M - C_6H_{11}]^+$), 185 (10, $[PPh_2]^+$), 98 (17, $[M - PPh_2]^+$), 83 (4, $[C_6H_{11}]^+$). Anal. Calc. for $C_{18}H_{22}NP$: C, 76.30; H, 7.83; N, 4.94; P, 10.93. Found: C, 76.35; H, 7.79; N, 4.97; P, 10.89. Yield: 94 %. Mp: 48 – 50 °C.

(Diphenylphosphino)benzylamine (8):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.63 (s, 1 H, NH), 6.68 (d, 2 H, 2 CH), 6.90 (d, 1 H, CH), 7.02 (m, 2 H, 2 CH), 7.28 – 7.33 (m, 20 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 115.9 (CH), 119.4 (CH), 128.5 (CH), 129.3 (CH), 131.2 (d, CH), 139.3 (d, CH), 147.5 (d, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 28.0 (s). IR (ATR) ν_{max}/cm^{-1}: 3055, 1598, 1480, 1433, 871, 738, 689. MS (EI, 70 eV): *m/z* (%) = 278 (12, $[M + H]^+$), 277 (39, $[M]^+$), 200 (5, $[M - C_6H_5]^+$), 185 (22, $[PPh_2]^+$), 149 (62, $[C_6H_5]^+$), 92 (99, $[M - PPh_2]^+$). Anal. Calc. for

$C_{18}H_{16}NP$: C, 77.96; H, 5.82; N, 5.05; P, 11.17. Found: C, 77.93; H, 5.86; N, 5.08; P, 11.13. Yield: 72 %. Mp: 68 – 70 °C.

3.3.2. Synthesis of (chlorophenylphosphino)(diphenylphosphino)N-amines (chlorinated PNP ligands)

Triethylamine (2.8 mL, 10 mmol) was added to a solution of the corresponding diphenylphosphinoamine (10 mmol) in dichloromethane (30 mL). After 30 minutes this solution was added to a stirred solution of dichlorophenylphosphine (1.4 mL, 10 mmol) in dichloromethane (20 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature. Amine hydrochloride was removed by filtration, and the product was isolated by column chromatography.

(Chlorophenylphosphino)(diphenylphosphino)N-isopropylamine (9):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46 (d, 1 H, CH), 3.12 (m, 6 H, 2 CH_3), 7.31 – 7.51 (m, 20 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 22.0 (2 CH_3), 45.9 (t, CH), 129.1 (3 CH), 131.5 (t, 2 CH), 133.8 (t, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 43.0 (br s), 135.1 (br s). IR (ATR) ν_{max}/cm^{-1}: 3056, 2969, 1586, 1479, 1434, 1382, 875, 741, 692. MS (EI, 70 eV): *m/z* (%) = 385 (11, $[M + H]^+$), 384 (100, $[M]^+$), 349 (8, $[M – Cl]^+$), 343 (2, [M – *i*Pr]$^+$), 199 (6, $[M – PPh_2]^+$), 185 (17, $[PPh_2]^+$). Yield: 56 %.

(Chlorophenylphosphino)(diphenylphosphino)N-cyclohexylamine (10):

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.52 (m, 4 H, 2 CH_2), 1.41 (m, 4 H, 2 CH_2), 1.82 (m, 3 H, CH_2 + CH), 3.12 (q, 4 H, 2 CH_2), 7.31 – 7.43 (m, 20 H, CH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 25.3 (CH_2), 25.9 (2 CH_2), 45.9 (2 CH_2), 59.9 (t, CH), 128.9 (3 CH), 131.7 (t, 2 CH), 139.8 (t, CH). ^{31}P NMR (400 MHz, $CDCl_3$): δ = 47.4 (br s), 134.9 (br s). IR (ATR) ν_{max}/cm^{-1}: 3054, 2930, 2853, 1587, 1478, 1434, 868, 742, 692. MS (EI, 70 eV): *m/z* (%) = 426 (7, $[M + H]^+$), 425 (5, $[M]^+$), 342 (7, $[M – C_6H_{11}]^+$), 240 (3, $[M – PPh_2]^+$), 185 (4, $[PPh_2]^+$), 83 (1, $[C_6H_{11}]^+$). Yield: 64 %.

(Chlorophenylphosphino)(diphenylphosphino)N-benzylamine (11):

^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 6.50$ (d, 2 H, 2 CH), 7.00 (unresolved coupling, CH), 7.20 (m, 2 H, 2 CH), 7.36 – 7.92 (m, 20 H, CH). ^{13}C NMR (400 MHz, CDCl$_3$): $\delta = 123.8$ (CH), 127.7 (CH), 128.6 (CH), 129.7 (CH), 131.2 (t, CH), 140.4 (t, CH), 146.6 (t, CH). ^{31}P NMR (400 MHz, CDCl$_3$): $\delta = 44.6$ (d), 124.7 (d). IR (ATR) ν_{max}/cm^{-1}: 3024, 1602, 1494, 1452, 824, 740, 697. MS (EI, 70 eV): *m/z* (%) = 421 (2, $[M + H]^+$), 420 (6, $[M]^+$), 385 (0.5, $[M - Cl]^+$), 271 (3, $[M - C_6H_5]^+$), 235 (0.5, $[M - PPh_2]^+$), 185 (4, $[PPh_2]^+$), 149 (15, $[C_6H_5]^+$). Yield: 51 %.

3.4. Functionalizing of Merrifield's resin

Merrifield's resin was functionalized according to literature procedure [6]. A solution of tert-butylamine (21 mmol) and potassium iodide (0.3 mmol) in 50 mL of tetrahydrofuran was treated with Merrified resin (2.5 mmol/g, 1 mmol) while stirring at room temperature for 30 minutes. The suspension was then refluxed for 48 hours before the solution was filtered off. The resulting resin was washed with water (3 x 15 mL), tetrahydrofuran (3 x 10 mL) and hexane (3 x 12 mL). The resin was then dried overnight under vacuum. ^{13}C MAS SS-NMR (600 MHz): $\delta = 28.2$, 41.0, 46.7, 128.6, 145.8. IR (ATR) ν_{max}/cm^{-1}: 3025, 2923, 1602, 1493, 1452, 1360, 868, 757, 697.

3.5. Supporting of (chlorophenylphosphino)(diphenylphosphino) N-amine on functionalized resin

The (chlorophenylphosphino)(diphenylphosphino)N-amines were supported on functionalized Merrifield's resin by modification of the reported literature procedure [6]. A solution of the corresponding (chlorophenylphosphino)(diphenylphosphino)N-amine (0.5 mmol) in tetrahydrofuran (20 mL) was treated slowly with functionalized Merrifield's resin (2.5 mmol/g, 0.1 mmol) while stirring at room temperature for a period of 30 minutes before triethylamine (0.4 mmol) was added. The resulting suspension was stirred at room temperature overnight before the solution was filtered off. The resin was washed with dichloromethane (5 x 8 mL), and hexane (5 x 5 mL). The resulting resin was dried overnight under vacuum.

The NMR data below for each supported ligand does not contain information from ^{1}H NMR as conclusive spectra could not be obtained.

Supported isopropyl PNP (12):

^{13}C MAS SS-NMR (600 MHz): δ = 28.0, 41.3, 46.9, 62.1, 128.6, 145.9. ^{31}P MAS SS-NMR (600 MHz): δ = 9.02 (s), 16.5 (s). IR (ATR) ν_{max}/cm^{-1}: 3044, 2915, 1601, 1493, 1437, 747, 694.

Supported cyclohexyl PNP (13):

^{13}C MAS SS-NMR (600 MHz): δ = 22.5, 25.2, 32.4, 40.5, 45.9, 62.1, 127.9, 145.0. ^{31}P MAS SS-NMR (600 MHz): δ = 9.00 (s), 21.0 (s). IR (ATR) ν_{max}/cm^{-1}: 3059, 2944, 2854, 1636, 1541, 1438, 1434, 924, 739, 697.

Supported benzyl PNP (14):

^{13}C MAS SS-NMR (600 MHz): δ = 22.4, 29.9, 40.6, 47.9, 62.1, 128.6, 139.6, 146.5. ^{31}P MAS SS-NMR (600 MHz): δ = 8.37 (s), 21.4 (s). IR (ATR) ν_{max}/cm^{-1}: 3024, 1601, 1494, 1451, 824, 740, 697.

3.6. Tetramerization of ethylene

3.6.1. Homogeneous runs

These were done using ligands **1 – 5**. A solution of ligand (0.005 mmol) in methylcyclohexane (2 mL) was added to a solution of $Cr(acac)_3$ (0.005 mmol) in methylcyclohexane (2 mL). The mixture was stirred for 5 minutes at room temperature after which MMAO (9.6 mmol, 2.50 mL) was added. The mixture was then transferred to a pressure reactor containing methylcyclohexane (93.5 mL) at the required temperature. The pressure reactor was charged with ethylene at 45 bar and the temperature was controlled. The reaction was terminated after 30 minutes by discontinuing the ethylene feed and quenching with ethanol (10 mL). The liquid phase was analysed by GC-FID using nonane as the internal standard.

3.6.2. Heterogeneous runs

These were done using supported ligands **12 – 14**. The loading of the ligand on the polymer was determined by ICP-OES and reported as mmol P/gram of supported ligand (Table 3.1). From this information, the appropriate amount of supported ligand could be weighed out using the same mole quantities as those of the homogeneous runs.

Table 3.1. Loadings of the supported ligands as determined by ICP-OES.

Ligand	**Loading / mmol P per gram**
12	**0.77**
13	**2.74**
14	**0.30**

A solution of supported ligand (0.005 mmol) in methylcyclohexane (2 mL) was added to a solution of $Cr(acac)_3$ (0.005 mmol) in methylcyclohexane (2 mL). The mixture was stirred for 5 minutes at room temperature after which MMAO (9.6 mmol, 2.50 mL) was added. The mixture was then transferred to a pressure reactor containing methylcyclohexane (93.5 mL) at the required temperature. The pressure reactor was charged with ethylene at 45 bar and the temperature was controlled. The reaction was terminated after 30 minutes by discontinuing the ethylene feed and quenching with ethanol (10 mL). The liquid phase was analysed by GC-FID using nonane as the internal standard.

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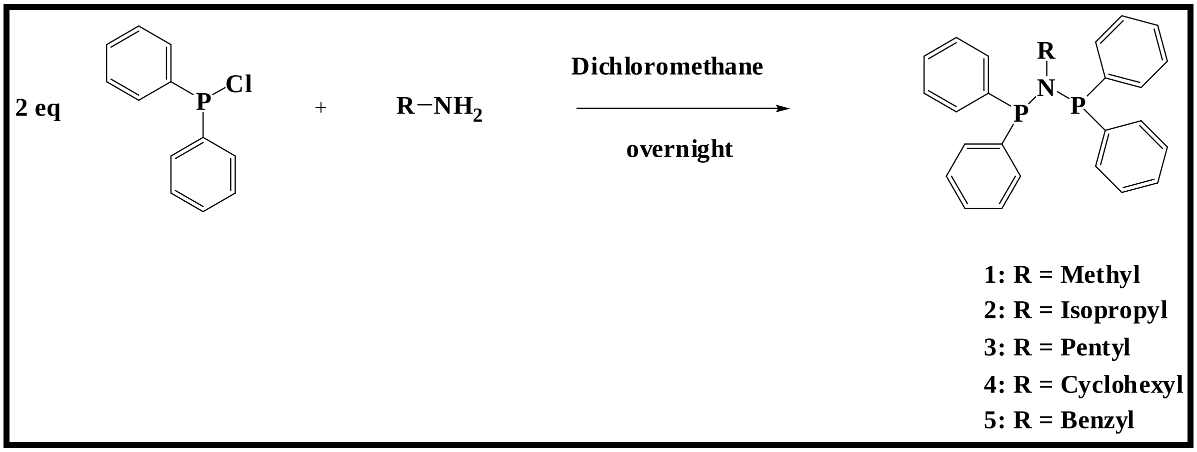
Chapter 4

Results and Discussion: Synthesis and Characterization of Ligands

4.1. Synthesis and characterization of homogenous PNP ligands

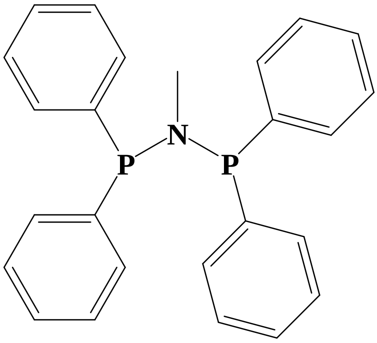
The bis(diphenylphosphino)amine ligands **1 – 5** were synthesized according to literature methods [1-3]. Reactions of two equivalents of chlorodiphenylphosphine with one equivalent of the respective amine gave the required compound as a white solid in moderate to high yield after it was isolated by filtration through a column of neutral alumina using diethyl ether as the mobile phase and monitored by ^{31}P NMR.



Scheme 4.1. Synthesis of the homogeneous PNP ligands.

For the above synthesis (Scheme 4.1), triethylamine was used in order to react with the HCl on the chlorodiphenylphosphine and precipitate out as the ammonium chloride salt. All the above ligands were characterized using ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry, elemental analysis and infrared spectroscopy. The solvent used for NMR spectroscopy was $CDCl_3$. For all five compounds, similar shifts were obtained in the ^1H and ^{13}C NMR spectra for the phenyl rings bonded to the two phosphorus atoms, as they are in the same environment and the compound is symmetrical. In the ^1H NMR spectra a multiplet was observed at 7.20 – 7.50 ppm for the protons on the phenyl rings. In the ^{13}C NMR spectra of **1 – 3**, peaks in the region 128 – 139 ppm were observed for the carbons of the phenyl rings. A singlet at 128 ppm was due to the carbon *para* to the phosphorus atoms. A triplet was observed at 133 ppm due to splitting by the phosphorus atoms two and three bonds away. This multiplet was due to the carbons on the *ortho* and *meta* positions. Another triplet was observed at 139 ppm and this was due to the carbons bonded directly to the phosphorus atoms.

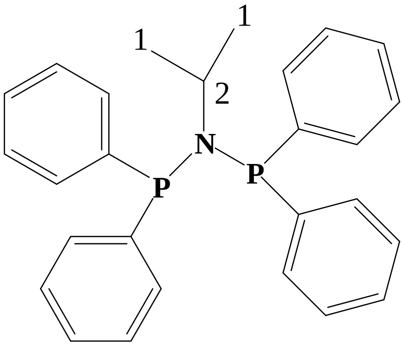
In the ^{13}C NMR spectrum of **4**, a peak was observed at 128 ppm due to the carbon *para* to the phosphorus atoms. A triplet was observed at 131 ppm, due to splitting by the phosphorus atoms, for the carbons on the *ortho* and *meta* positions. Another triplet was observed at 143 ppm for the carbons directly bonded to the phosphorus atoms. In the ^{13}C NMR spectrum of **5**, observations similar to those on the ^{13}C NMR spectrum of **4** were observed and the shifts were at 129, 131 and 139 ppm respectively. The other distinct peaks for each compound on the ^1H and ^{13}C NMR spectra are discussed below. These were due to the different substituents on the N of each compound.



1

Figure 4.1. The structure of the synthesized bis(diphenylphosphino)methylamine ligand.

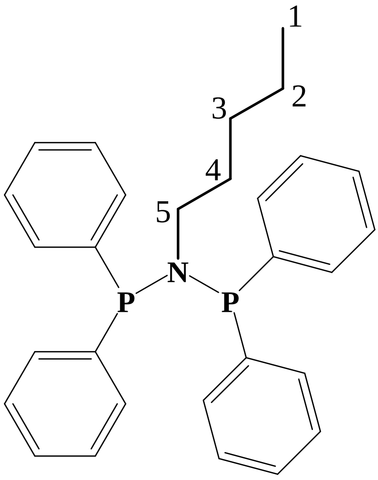
Figure 4.1 shows the structure of the synthesized bis(diphenylphosphino)methylamine ligand. In the ^{1}H NMR spectrum of the bis(diphenylphosphino)methylamine ligand, a singlet was observed at 2.80 ppm due to the three protons of the CH_3 substituent. The ^{13}C NMR spectrum showed a triplet at 32.5 ppm due to the carbon atom of CH_3 being split by the phosphorus atoms.



2

Figure 4.2. The structure of the synthesized bis(diphenylphosphino)isopropylamine ligand.

Figure 4.2 shows the structure of the synthesized bis(diphenylphosphino)isopropylamine ligand. The ^{1}H NMR spectrum of bis(diphenylphosphino)isopropylamine showed a heptet at 1.20 ppm for the proton at C_2. A doublet was observed at 3.75 ppm for the six protons from the two CH_3 groups (C_1). The ^{13}C NMR spectrum showed a singlet at 24.7 ppm due to the carbons C_1. Only one peak was observed since the two carbons are equivalent. A triplet was observed at 51.9 ppm due to C_2 being split by the phosphorus atoms.

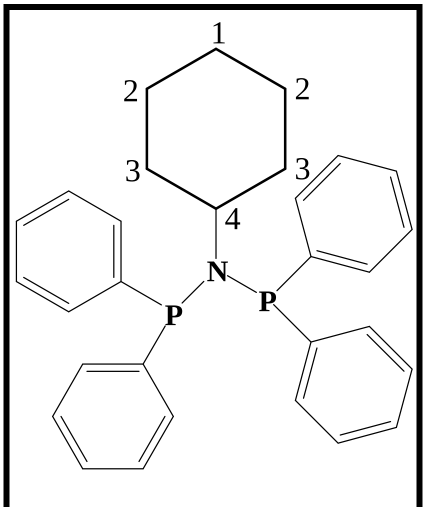


3

Figure 4.3. The structure of the synthesized bis(diphenylphosphino)pentylamine ligand.

Figure 4.3 shows the structure of the synthesized bis(diphenylphosphino)pentylamine ligand. In the ^{1}H NMR spectrum of bis(diphenylphosphino)pentylamine, a triplet was observed at 0.40 ppm for the protons on C_1, which couple with those on C_2. A multiplet for the C_2 protons was observed at 0.85 ppm. This was due a combination of a quartet due to the protons on C_1 coupling with those on C_2 as well as a triplet due to the protons on C_3 coupling with those on C_2. A quintet was observed at 1.10 ppm for the C_4 protons and this was due to four protons coupling with those on C_4; two on C_3 and two on C_5. A triplet was observed at 3.25 ppm due to the two protons on C_4 coupling with those on C_5. In the ^{13}C

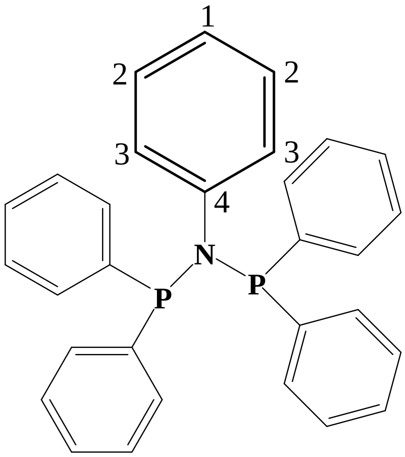
NMR spectrum, the following shifts for singlets were observed: 14.3 ppm due to C_1, 22.4 ppm for C_2, 29.3 ppm for C_3 and 31.3 ppm for C_4. A triplet was observed at 53.1 ppm due to the signal for C_5 being split by the phosphorus atoms.



4

Figure 4.4. The structure of the synthesized bis(diphenylphosphino)cyclohexylamine ligand.

Figure 4.4 shows the synthesized bis(diphenylphosphino)cyclohexylamine ligand. In the ^{1}H NMR spectrum of bis(diphenylphosphino)cyclohexylamine, multiplets were observed at 0.50, 1.65, 1.80 and 2.80 ppm due to the protons on C_2, C_1, C_3 and C_4 respectively, instead of quartets or triplets. This led to a belief that the structure of the cyclohexyl ring in Figure 4.4 was not as depicted, but instead is in a chair conformation. The multiplets would then result due to protons on adjacent carbons as well as interaction of protons that are axial and equatorial on carbons that are even three bonds away from each other. The proton on C4 gives a multiplet which is further downfield than the other mutiplets as it is deshield by N bonded to C_4. In the ^{13}C NMR spectrum, peaks were observed at 25.4 ppm due to C_1, at 25.8 ppm due to carbons C_2 and at 37.0 ppm due carbons C_3. A triplet was observed at 56.0 ppm due to C_4 being split by the phosphorus atoms.



5

Figure 4.5. The structure of the synthesized bis(diphenylphosphino)benzylamine ligand.

Figure 4.5 shows the structure of the synthesized bis(diphenylphosphino)benzylamine ligand. The ^{1}H NMR spectrum of bis(diphenylphosphino)benzylamine showed a doublet at 6.70 ppm due to the protons on carbons C_3. At 6.80 ppm, there was unresolved coupling due to the proton on C_1 coupling with those on carbons C_2. At 7.00 ppm there was a multiplet due to the protons on carbons C_2 coupling with those on carbons C_1 and C_3. In the ^{13}C NMR spectrum, a peak was observed at 116 ppm due to carbons C_3 and another at 119 ppm due to carbon C_1. For carbons C_2, a peak at 128 ppm was observed. A triplet was observed at 146 ppm due to C_4 being split by the phosphorus atoms.

The ^{31}P NMR spectra for each ligand showed singlet peaks and the results have been tabulated below (Table 4.1). The literature values are those reported by Blann *et al*. [3].

Table 4.1. ^{31}P NMR shifts of the synthesized PNP ligands.

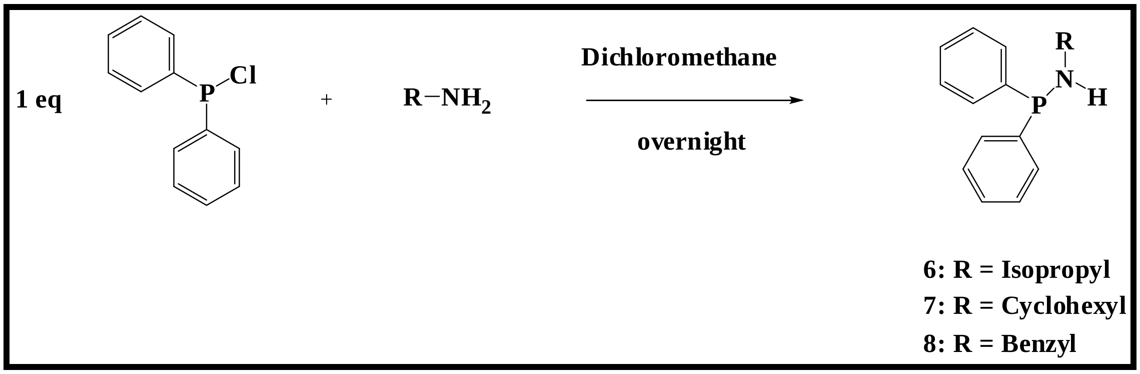
Ligand	Actual / ppm	Literature / ppm [3]
1	73.0 (s)	74.2 (s)
2	48.9 (br s)	50.1 (br s)
3	62.2 (s)	62.3 (s)
4	50.8 (br s)	50.7 (s)
5	62.3 (s)	62.3 (s)

4.2. Synthesis and characterization of chlorinated PNP ligands

Only the PNP ligands containing isopropyl, cyclohexyl and phenyl as a substituent were chlorinated in preparation to be supported on the functionalized Merrifield's resin and the reason behind this is discussed further in Chapter 5.

4.2.1. Synthesis of diphenylphosphinoamines

The diphenylphosphinoamines **6 – 8** were synthesized according to literature procedures or modifications thereof in high yield [4-6]. This involved the reaction of one equivalent of chlorodiphenylphosphine with one equivalent of the corresponding amine. The reaction scheme can be seen below (Scheme 4.2.)



Scheme 4.2. Synthesis of the diphenylphosphinoamines.

Table 4.2 shows the IR data for the synthesized bis(diphenylphosphino)amine ligands.

Table 4.2. Infrared data for the synthesized bis(diphenylphosphino)amine ligands.

Ligand	Functional group	Wavenumber (cm^{-1})
1	C-H on phenyl	694, 741
	CH_3	1277
	Phenyl	1478, 1585
	Amine	3052
	C-H on CH_3	2927
2	C-H on phenyl	692, 738
	CH_3	1376
	Phenyl	1478, 1585
	Amine	3050
	C-H on CH_3	2965
3	C-H on phenyl	693, 740
	Phenyl	1454, 1584
	Amine	3051
	C-H's on alkyl chain	2857, 2935
4	C-H on phenyl	691, 741
	C-N on aliphatic amine	1091
	CH_2	1449
	CH_3	1280
	Phenyl	1477, 1584
	Amine	3052
5	C-H on phenyl	690, 738
	Phenyl	1480, 1594
	Amine	3055

The diphenylphosphinoamines were characterized using ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry, elemental analysis and infrared spectroscopy. The solvent used for NMR spectroscopy was $CDCl_3$. For all three compounds, similar shifts were obtained in the ^{1}H and ^{13}C NMR spectra for the phenyl rings bonded to the phosphorus atoms. In the ^{1}H NMR spectra a multiplet was observed at 7.26 – 7.49 ppm for the protons on the phenyl rings bonded to the phosphorus. In the ^{13}C NMR spectra of, peaks in the region 128 – 143 ppm were observed for the carbons of the phenyl rings. A singlet at 128 ppm was due to the carbon *para* to the phosphorus atoms. A doublet was observed at 133 ppm due to splitting by the phosphorus atom two and three bonds away. This multiplet was due to the carbons on the *ortho* and *meta* positions. Another doublet was observed at 139 ppm and this was due to the carbons bonded directly to the phosphorus atom. The first carbon bonded to N on the substituent was also split into a doublet by the phosphorus atom and the signals obtained for each compound can be found in Table 4.3.

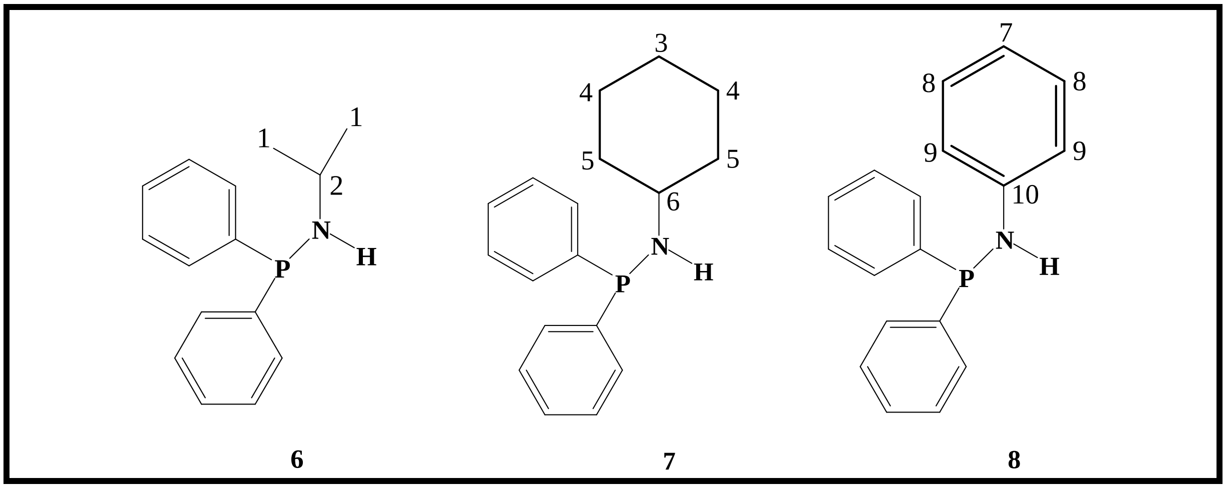


Figure 4.6. Structures of the synthesized diphenylphosphinoamines with labeled atoms.

The structures containing labeled atoms are shown in Figure 4.6 and the summarized NMR data can be found in Table 4.3. The ^{1}H and ^{13}C NMR data obtained for the substituents on

N for the diphenylphosphinoamines were found to be similar to that obtained for the bis(diphenylphosphino)amine ligands **2**, **4** and **5** and therefore the data has been summarized.

Table 4.3. ^{1}H and ^{13}C NMR data for the synthesized diphenylphosphinoamines.

Compound	Atom	δ ^{1}H / ppm (multiplicity)	δ ^{13}C / ppm (multiplicity)
6	1	3.30 (m)	26.2
	2	1.14 (d)	48.6 (d)
	N-H	1.80	-
7	3	1.17 (m)	24.9
	4	1.57 (m)	25.4
	5	1.90 (m)	36.8
	N-H	unresolved	-
	6	2.92 (q)	56.1 (d)
8	7	6.68 (d)	115.9
	8	6.90 (d)	119.4
	9	7.02 (m)	128.5
	10	-	147.5 (d)
	N-H	1.63	-

The ^{31}P NMR spectra for each compound showed singlet peaks and the results have been tabulated below (Table 4.4). The literature values were obtained from the following sources: $RN(H)PPh_2$ (R = *i*Pr [4], Cyclohexyl [5], Ph [6,7]. Although the shifts obtained could easily be mistaken for oxidized compounds, it has been reported that diphenylphosphinoamines generally give rise to singlet resonances between 25 and 35 ppm [6,8-10].

Table 4.4. ^{31}P NMR shifts of the synthesized diphenylphosphinoamines.

Compound	Actual / ppm	Literature / ppm
6	34.1 (s)	35.8 (s)
7	34.4 (s)	36.1 (s)
8	28.0 (s)	25.9 (s)

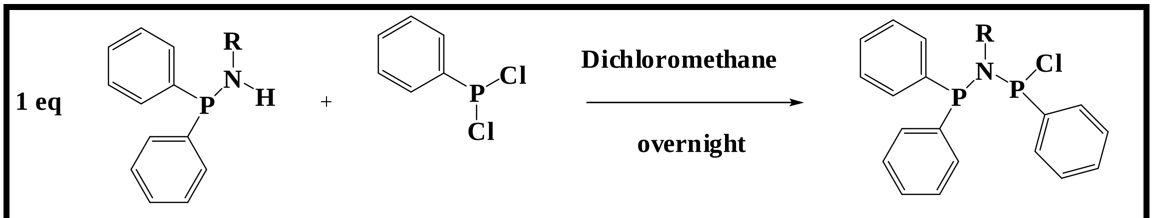
The infrared spectroscopy data obtained are summarized in Table 4.5.

Table 4.5. Infrared data for the synthesized diphenylphosphinoamines.

Ligand	Functional group	Wavenumber (cm^{-1})
9	C-H on phenyl	691, 721
	CH_3	1382
	Phenyl	1471, 1591
	Amine	3058
	C-H on CH_3	2962
10	C-H on phenyl	693, 740
	C-N on aliphatic amine	1091
	CH_2	1435
	Phenyl	1548
	Amine	3059
11	C-H on phenyl	689, 738
	Phenyl	1480, 1598
	Amine	3055

4.2.2. Synthesis of (chlorophenylphosphino)(diphenylphosphino)N-amines (chlorinated PNP ligands)

The chlorinated PNP ligands were synthesized by reacting one equivalent of the respective diphenylphosphinoamine with one equivalent of dichlorophenylphosphine. The target ligands were similar to the bis(diphenylphosphino)amine ligands, except that one phenyl group attached to the one of the phosphorus atoms was replaced by a chlorine atom. The yield was low due to the sensitivity of these ligands to air and they can easily be oxidized and a lot of product was lost during purification. The reaction scheme is shown in Scheme 4.3.



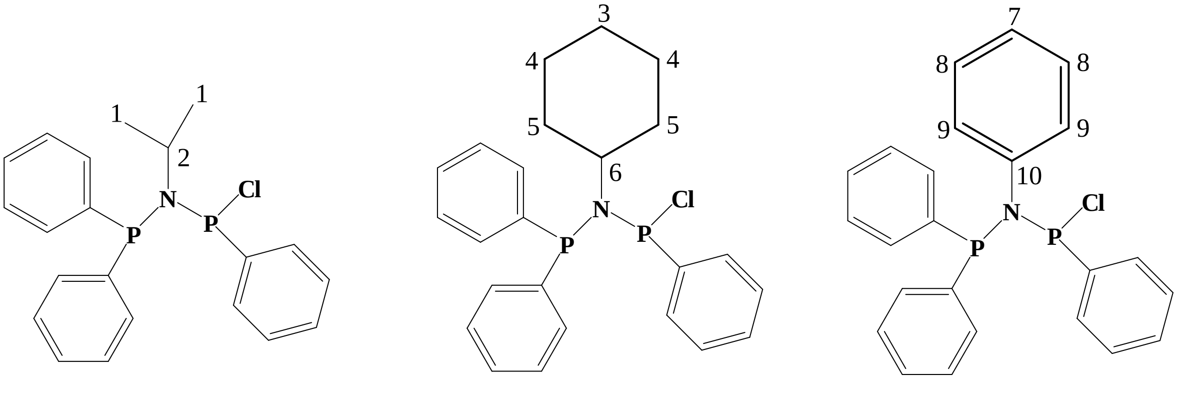
9: R = Isopropyl
10: R = Cyclohexyl
11: R = Benzyl

Scheme 4.3. Synthesis of the chlorinated PNP ligands.

The chlorinated PNP ligands were characterized using ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry and infrared spectroscopy. The solvent used for NMR spectroscopy was $CDCl_3$. For all three ligands, similar shifts were obtained in the ^{1}H and ^{13}C NMR spectra for the phenyl rings bonded to the two phosphorus atoms, as they are in the same environment and the compound is symmetrical. In the ^{1}H NMR spectra a multiplet was observed at 7.20 – 7.50 ppm for the protons on the phenyl rings. In the ^{13}C NMR spectra, peaks in the region 128 – 139 ppm were observed for the carbons of the phenyl rings. A singlet at 128 ppm was due to the carbon *para* to the phosphorus atoms. A triplet was observed at 133 ppm due to splitting by the phosphorus atoms two and three bonds away.

This multiplet was due to the carbons on the *ortho* and *meta* positions. Another triplet was observed at 139 ppm and this was due to the carbons bonded directly to the phosphorus atoms.

The ^{1}H and ^{13}C NMR data obtained for the substituents on N for the diphosphinoamines were found to be similar to these obtained for the bis(diphenylphosphino)amine ligands **2**, **4** and **5** and therefore the data has been summarized. The structures containing labeled atoms are shown in Figure 4.7 and the summarized NMR data can be found in Table 4.6.



9 **10** **11**

Figure 4.7. Structures of the synthesized chlorinated PNP ligands with labeled atoms.

Table 4.6. ^{1}H and ^{13}C NMR data for the synthesized chlorinated PNP ligands.

Compound	Atom	δ ^{1}H / ppm (multiplicity)	δ ^{13}C / ppm (multiplicity)
9	1	3.12 (m)	22.0
	2	1.46 (d)	45.9 (t)
10	3	0.52 (m)	25.3
	4	1.41 (m)	25.9
	5	1.82 (m)	45.9
	6	3.12 (q)	59.9 (t)
11	7	6.50 (d)	123.8
	8	7.00 (unresolved)	127.7
	9	7.20 (m)	129.7
	10	-	146.6 (t)

The ^{31}P NMR data for each ligand has been tabulated in Table 4.7. Only the literature values for the isopropyl ligand could be obtained since the synthesis procedure for these ligands was based on the synthesis procedure of the isopropyl ligand [11]. The literature values for ligands **10** and **11** have not previously been reported.

Table 4.7. ^{31}P NMR shifts of the synthesized chlorinated PNP ligands.

Ligand	Actual / ppm	Literature / ppm
9	43.0 (s), 135.1 (s)	42.1 (s), 132.0 (s)
10	47.4 (s), 134.9 (s)	-
11	44.6 (s), 124.7 (s)	-

Two doublets were expected in the ^{31}P NMR spectra of the chlorinated PNP ligands due to the two phosphorus atoms being in different environments and therefore slitting each other's signal. However two broad peaks were observed, which led to the belief that these resulted from the overlapping of each pair of doublets. The infrared spectroscopy data obtained are summarized in Table 4.8 below.

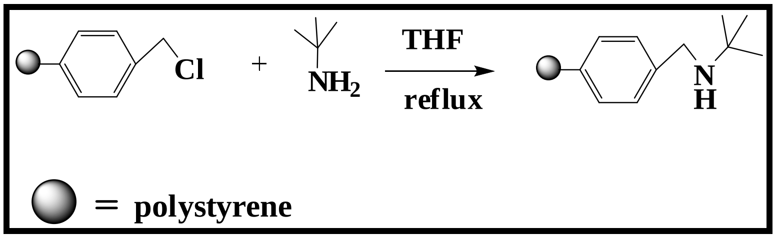
Table 4.8. Infrared data for the synthesized chlorinated PNP ligands.

Ligand	Functional group	Wavenumber (cm^{-1})
9	C-H on phenyl	692, 741
	CH_3	1382
	Phenyl	1479, 1586
	Amine	3056
	C-H on CH_3	2969
10	C-H on phenyl	692, 742
	C-N on aliphatic amine	1056
	CH_2	1434
	Phenyl	1478, 1587
	Amine	3054
11	C-H on phenyl	697, 740
	Phenyl	1493, 1602
	Amine	3024

4.3. Synthesis and characterization of supported PNP ligands

4.3.1. Functionalizing of Merrifield's resin

Merrifield's resin was functionalized by reacting it with excess *tert*-butylamine under reflux for two days. The functionalized resin was characterized via infrared, solid-state NMR, thermogravimetric analysis and scanning electron microscopy. The reaction scheme can be seen below (Scheme 4.4).



Scheme 4.4. Functionalization of Merrified's resin with *tert*-butylamine.

The infrared spectrum of functionalized Merrifield's resin contained similar stretching absorbances to those of Merrifield's resin such as at 1602 and 1493 cm^{-1} due to the aromatic rings, at 1452 cm^{-1} due to the methylene carbons on the polymer backbone and at 757 and 697 cm^{-1} due to C-H stretching on the monosubstituted aromatic rings. The exception was the appearance of secondary amine stretching at 3025 cm^{-1} and a band at 2923 cm^{-1} for the methyl groups on the *tert*-butyl moiety. In the ^{13}C NMR spectrum of Merrifield's resin, peaks were observed at 28.2 ppm due to the carbons on the CH_3 groups on *tert*-butyl, at 41.0 ppm due to the tertiary carbon on *tert*-butyl, at 46.7 ppm due to the methylene carbons on the polystyrene backbone and at 128.6 and 145.8 ppm due to the carbons on the aromatic rings [12,13]. The peak at 145.8 ppm was also characteristic of an isotactic polymer [13], which means that the CH_2 groups on the backbone are located on the same side [14]. Spinning sidebands observed at ~195 and ~212 ppm [15,16].

Table 4.9. Thermogravimetric analysis data for the polymers showing the glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m).

Polymer	T_g / °C	T_c / °C	T_m / °C
Merrifield's resin	91	300	377
Functionalized Merrifield's resin	94	258	326

Table 4.9 shows the data obtained from thermogravimetric analysis of Merrifield's resin and functionalized Merrifield's resin. There is an increase in the glass transition temperature data from Merrifield's resin to when it is functionalized. This is probably due to the introduction of the *tert*-butylamine group which causes the polymer to become more stable and more resistant to the temperature changes. The decrease in crystallization temperature could be due to the *tert*-butylamine group causing the polymer to crystallize faster. The TGA curves showed complete combustion of polymer, i.e. a 100 % weight loss.

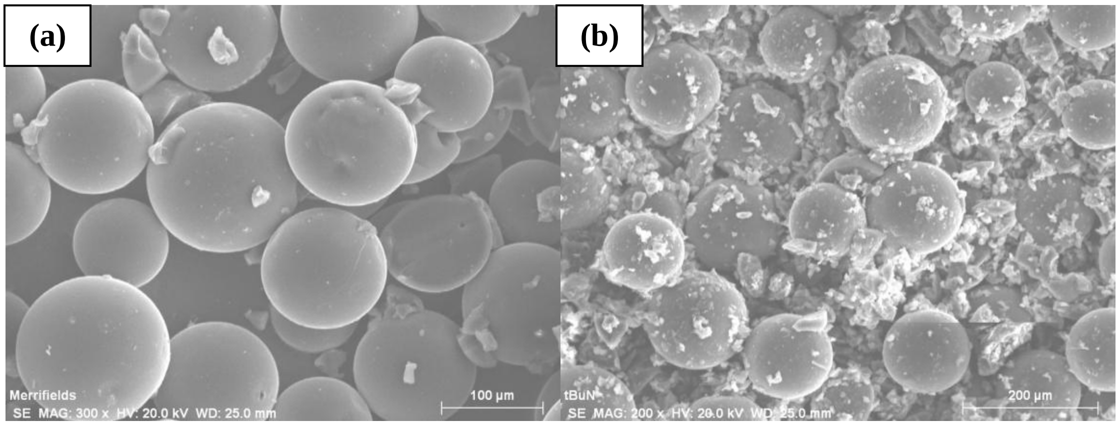
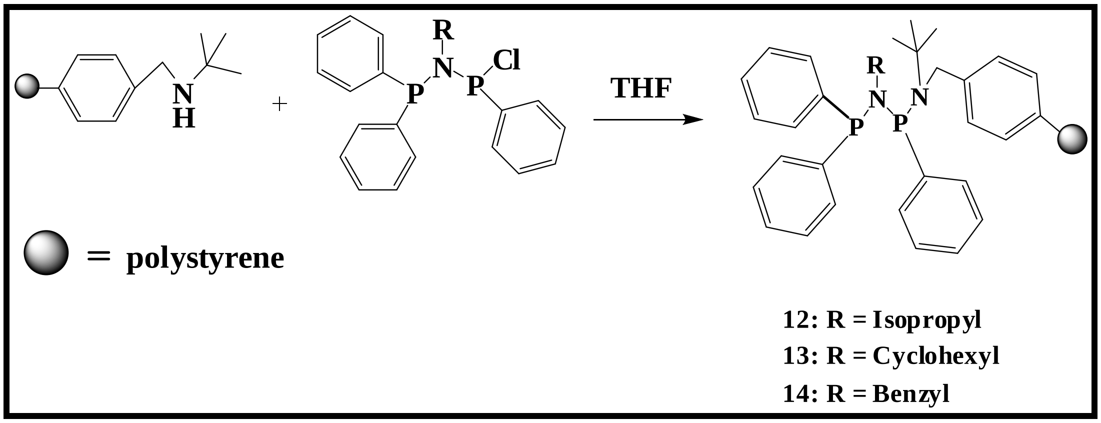


Figure 4.8. SEM images of (a) Merrifield's resin and (b) functionalized Merrifield's resin.

Figure 4.8 shows the SEM images for Merrifield's resin and functionalized Merrifield's resin. Both images consist of polystyrene spheres, with image (b) containing broken particles of the spheres due to stirring during functionalization. The spheres are not uniformly covered by the particles which gives one the impression that not all the chlorine atoms from Merrifield's resin reacted with *tert*-butylamine. The bright particles are due to charging of atoms by the electron beam from the microscope.

4.3.2. Supporting of (chlorophenylphosphino)(diphenylphosphino) N-amine on functionalized resin

The chlorinated PNP ligands were supported on polymer by reacting the polymer with excess ligand. The supported ligands were characterized via Infrared, ^{13}C and ^{31}P solid-state NMR, Thermogravimetric analysis and Scanning electron microscopy. The reaction scheme can be seen below.



Scheme 4.5. Supporting of chlorinated PNP ligands on functionalized Merrifield's resin.

Similarly to functionalized Merrifield's resin, the infrared spectra of ligands **12 – 14** contained stretching absorbances at ~1600 and ~1490 cm^{-1} due to the aromatic rings, at 1430 - 1450 cm^{-1} due to the methylene carbons on the polymer backbone, at 760 and 700 cm^{-1} due to C-H stretching on the monosubstituted aromatic rings, secondary amine stretching at 3020 - 3050 cm^{-1} and bands at 2920 - 2960 cm^{-1} for the methyl groups on *tert*-butyl. There P-Cl stretching bands at ~520 – 540 cm^{-1} observed for the chlorinated PNP ligands were no longer observed and the P-N stretching bands in the range ~780 – 1100 cm^{-1} [17] were more intense. Characteristic peaks for the ligands were as follows: For ligand **12**, a stretch at 1378 cm^{-1} due to the methyl groups on the isopropyl group; for ligand **13**, at 1051 cm^{-1} due to C-N on the aliphatic amine and at 1438 cm^{-1} due to CH_2 on the cyclohexyl ring; for ligand **14**, the stretch for the aromatic ring on N overlapped with those for the other aromatic rings on the ligand at 1601 and 1494 cm^{-1}.

In the ^{13}C NMR spectra of ligands **12 – 14**, peaks were observed at ~22 ppm due to the carbons on the CH_3 groups on the *tert*-butyl group, at ~41 ppm due to the tertiary carbon on the *tert*-butyl group, at ~47 ppm due to the methylene carbons on the polystyrene backbone and at ~128 and ~145 ppm due to the carbons on the aromatic rings. Spinning sidebands were also observed at ~195 and ~212 ppm. Table 4.10 below shows the characteristic peaks observed for the substituent on the N for each of the supported ligands. Please note that the atom numbering is identical to that used in Figures 4.6 and 4.7. Also note that all peaks were broad singlets. Where the shift is identical to that described above for the polystyrene, it indicates signal overlap.

Table 4.10. ^{13}C NMR data for the supported PNP ligands.

Compound	Atom	δ ^{13}C / ppm
12	1	28.0
	2	41.3
13	3	25.2
	4	32.4
	5	40.5
	6	62.1
14	7 and 8	128.6
	9	139.6
	10	146.5

In the ^{31}P NMR spectra of ligands **12 – 14** two signals were observed, each due to the two phosphorus atoms present in a different environment. The shifts can be seen on Table 4.11. No literature values are known.

Table 4.11. ^{31}P NMR shifts of the supported PNP ligands.

Ligand	δ / ppm
12	9.02 (s), 16.5 (s)
13	9.00 (s), 21.0 (s)
14	8.37 (s), 21.4 (s)

The data for the Thermogravimetric analysis was also obtained and is recorded on Table 4.12 below. The TGA curves showed complete combustion of supported ligand, i.e. a 100 % weight loss. No real trend can be observed between the different temperatures for the supported ligands, but they also possessed the different temperature characteristics typical of polymeric substances, i.e. glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m).

Table 4.12. Thermogravimetric analysis data for the supported ligands showing the glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m).

Supported ligand	T_g / °C	T_c / °C	T_m / °C
12	93	269	318
13	95	283	315
14	95	276	313

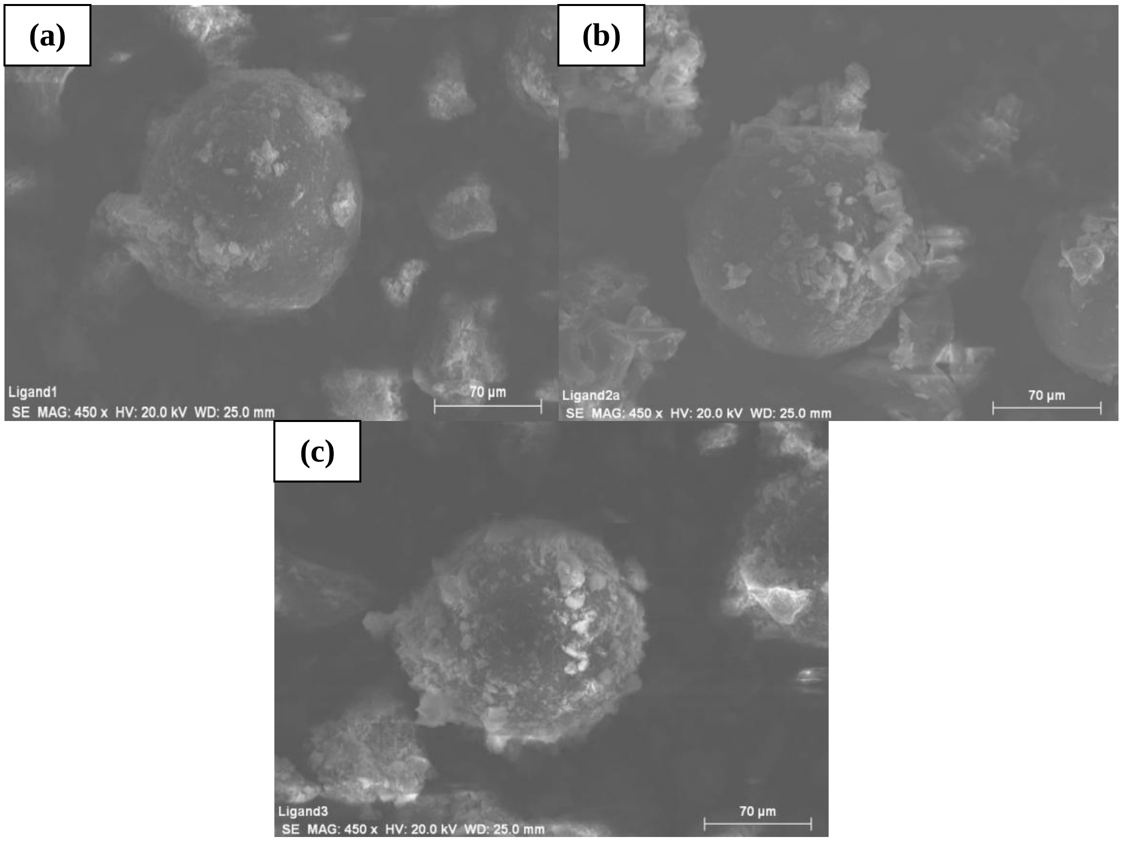


Figure 4.9. SEM images of the supported (a) isopropyl, (b) cyclohexyl and (c) benzyl PNP ligands.

The SEM images for the supported ligands can be seen in Figure 4.9. The images show polystyrene balls with some particles on the surface. By the balls are also some fragments of polymer which are broken down polystyrene balls caused by stirring during supporting. The bright particles are due to charging of atoms by the electron beam from the microscope. Mapping the images for phosphorus (Figure 4.10) using scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) showed that the particles on the surface of the polystyrene balls contained phosphorus, which led to the conclusion that the PNP ligands were on the surface of the support.

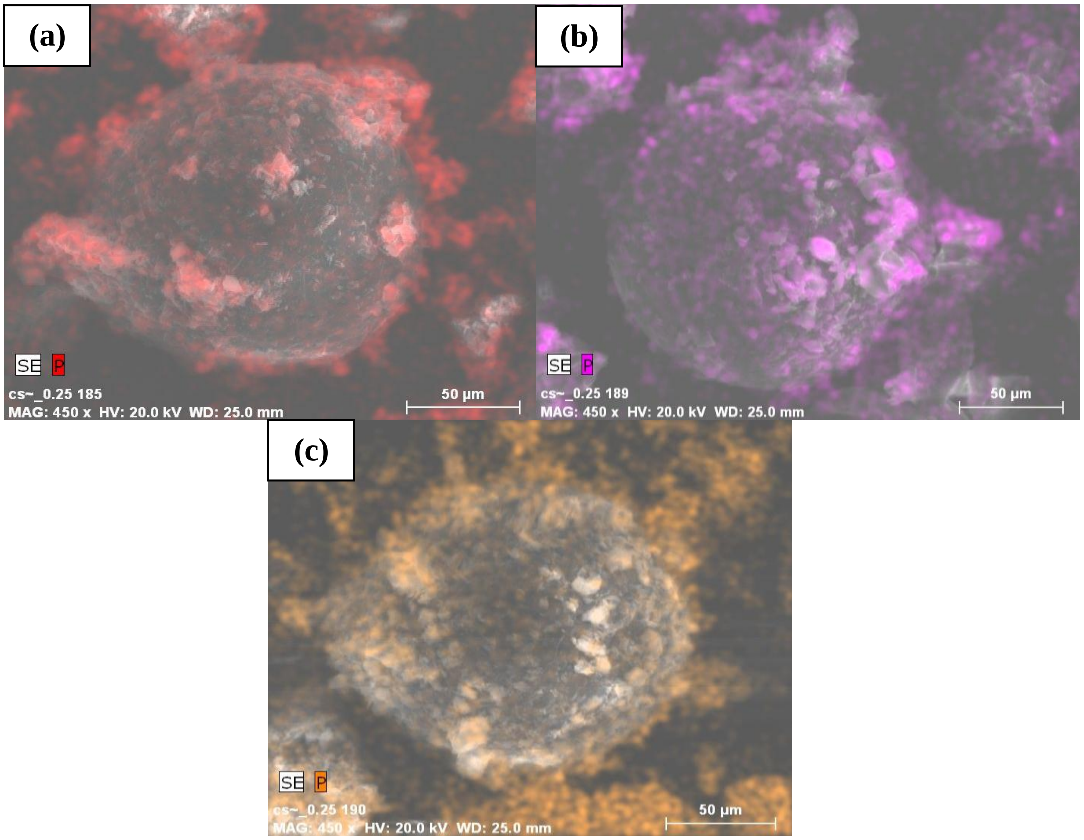


Figure 4.10. Electron mapping images shown in Figure 4.9 of the supported (a) isopropyl, (b) cyclohexyl and (c) benzyl PNP ligands.

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Chapter 5

Results and Discussion: Catalytic Testing

5.1. General comments

The bis(diphenylphosphino)amine ligands discussed in Chapter 4 were evaluated in the tetramerisation of ethylene using a high pressure Parr reactor. The source of chromium was $Cr(acac)_3$ (chromium acetylacetonate) and the activator was modified methylaluminoxane (MMAO-3A). The reaction solvent of choice was methylcyclohexane instead of toluene because it has been reported that reactions in this solvent show improved catalytic activity [1]. Evaluation was done at temperatures of 60 and 80 °C and an ethylene pressure of 45 bar. A summary of the results has been tabulated in Table B1 in Appendix B. The temperature range was chosen because at temperatures below 60 °C, activity and overall alpha selectivities are not at optimum and at temperatures above 100 °C, the system becomes one which promotes polymerization over oligomerisation. A temperature study investigation was carried out. A catalytic run was performed at 45 °C using isopropyl PNP as the ligand and it yielded low selectivities towards the main products. The selectivity of 1-hexene in the C6 fraction was 5.4 wt% and the selectivity towards 1-octene in the C8 fraction was 66 wt%. The activity was only 3400 g product/g Cr h^{-1}. A catalytic run was also performed at 90 °C and the reaction resulted in the formation of more polyethylene than at lower temperatures. At 100 °C the reactor product contained almost exclusively polyethylene.

As is discussed later in this Chapter, it is important to mention that the isopropyl, cyclohexyl and benzyl analogues of the bis(diphenylphosphino)amine ligands, yielded the highest catalyst activity (see Figure 5.10) and only these analogues of the homogeneous ligands were supported on the polymer and characterized (Chapter 4).

5.2. Homogeneous catalytic testing

5.2.1. The light fraction

5.2.1.1. The C6 fraction selectivity profile

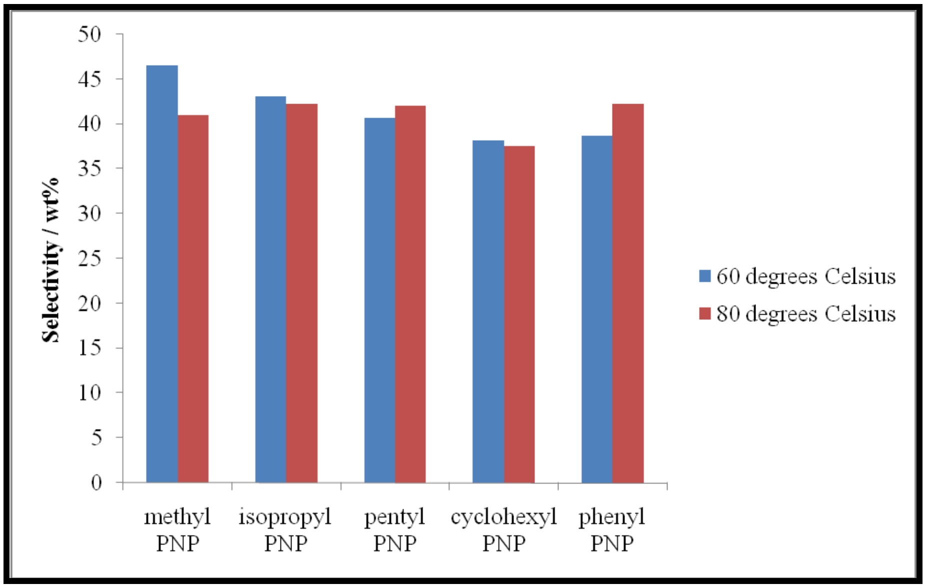
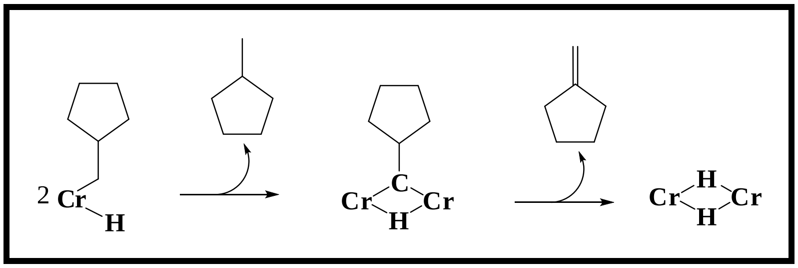


Figure 5.1. Selectivity of the C6 products for each catalyst system at different temperatures.

Figure 5.1 shows the selectivity of the C6 products that was obtained at temperatures of 60 and 80 °C. The C6 products consist of hexanes, 1-hexene, internal hexenes and the cyclic C6 products, methylenecyclopentane and methylcyclopentane. The selectivity values of the C6 products are higher than those obtained in literature (18 – 44 wt%) for the same catalyst systems under similar condtions [2], but are still within that range. Methylenecyclopentane and methylcyclopentane are believed to be formed by disproportionation of a cyclopentyl hydride species and are usually formed at a ratio of almost 1:1 [3,4]. This equimolar formation suggests that these two compounds are formed via a disproportionation step. An increase in these two cyclic products results in a decrease in the selectivity towards 1-hexene and 1-octene.



Scheme 5.1. Postulated mechanism for the formation of methylcyclopentane and methylenecyclopentane [2].

Sheldon and Kochi [5] and Jenkins and Kochi [6] have reported the formation of methylcyclopentane and methylenecyclopentane from cyclopentylmethyl or 5-hexen-1-yl free radicals. Findings by Theopold and co-workers [7] allowed Overett *et al*. [4] to postulate a mechanism which accounts for the equimolar formation of these cyclic compounds (Scheme 5.1). The overall selectivity towards these cyclic compounds can be seen in Figure 5.2. An increase in steric bulk of the substituent on the ligand led to a decrease in the formation of these compounds, which corresponds with what is also observed in literature [2,8].

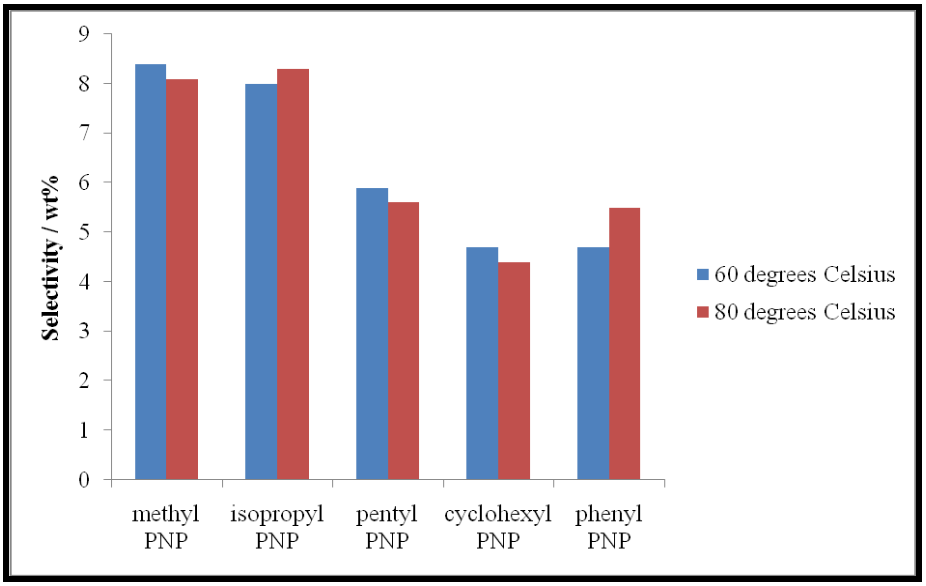


Figure 5.2. Selectivity of the C6 cyclics for each catalyst system at different temperatures.

5.2.1.2. 1-hexene in the C6 fraction selectivity profile

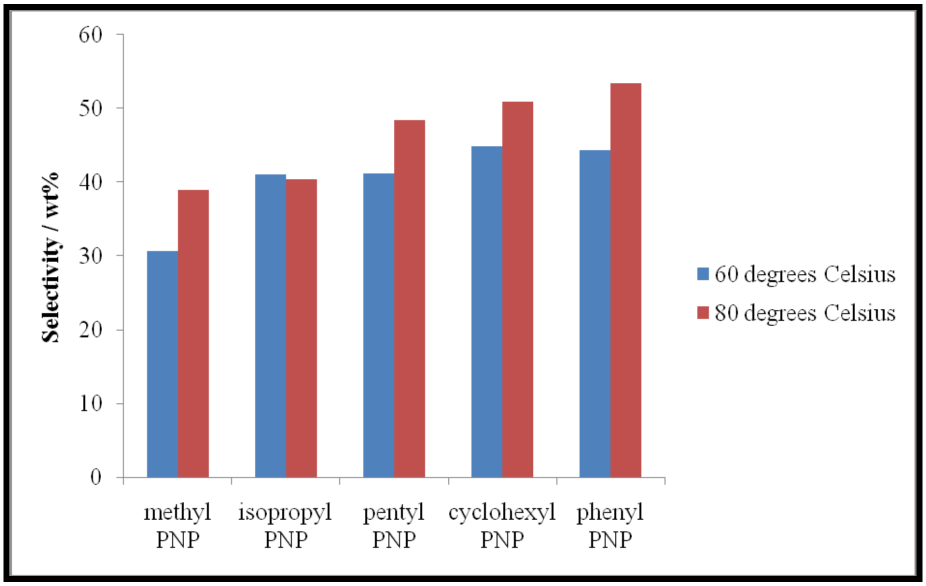


Figure 5.3. Selectivity of 1-hexene in the C6 products for each catalyst system at different temperatures.

Figure 5.3 shows the selectivity of 1-hexene in the C6 products for each catalyst system at different temperatures. 1-Hexene is formed by the reductive elimination of the chromacycloheptane species in the tetramerisation catalytic cycle [3]. The graph shows that as the temperature increases, so too does the selectivity towards 1-hexene. This also corresponds to what is observed in literature [9,10]. This occurs at the expense of 1-octene and the C6 cyclics. This is evident in Figure 5.2, where there is a decrease in the selectivity towards the C6 cyclics for the same systems that produced the highest selectivity of 1-hexene in the C6 products (pentyl, cyclohexyl and phenyl). The cyclohexyl and phenyl systems yielded higher selectivities due to their steric nature. It has been reported that ligands having the bulkiest moieties on the N-atom yield the best alpha olefin selectivity [2].

5.2.1.3. The C8 fraction selectivity profile

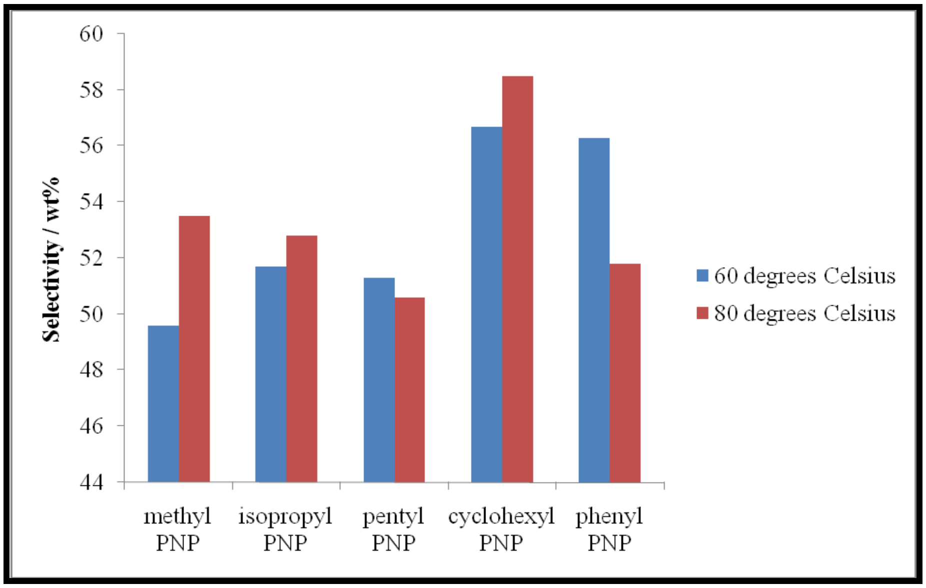


Figure 5.4. Selectivity of the C8 products for each catalyst system at different temperatures.

Figure 5.4 shows the selectivity of the C8 products for each catalyst system at different temperatures. These had the highest selectivity out of all the products due to the formation of a large amount of 1-octene (Figure 5.5) within the C8 fraction, since these catalysts were tetramerisation catalysts. The C8 products consist of octane, 1-octene and internal octenes. An increase in temperature generally showed an increase in selectivity to the C8 products with the exception of the pentyl and phenyl systems. A decrease in selectivity with an increase in temperature was expected as reported in literature [2,3,9]. The cyclohexyl system yielded the highest selectivity.

5.2.1.4. 1-octene in the C8 fraction selectivity profile

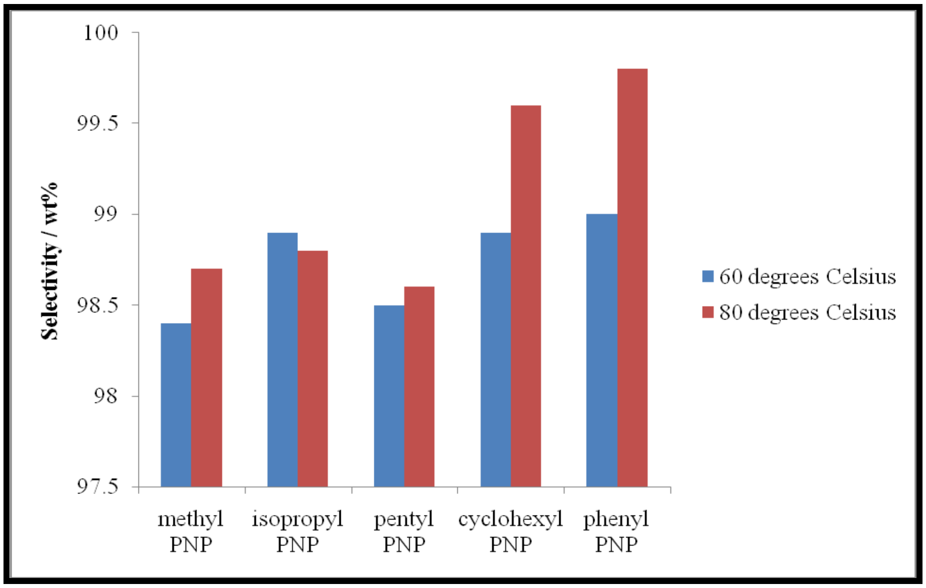


Figure 5.5. Selectivity of 1-octene in the C8 products for each catalyst system at different temperatures.

Figure 5.5 shows the selectivity of 1-octene in the C8 products for each catalyst system at different temperatures. Selectivities greater than 98 wt% were obtained and these are comparable with those obtained in literature [2,3,8]. 1-octene is formed when an ethylene molecule is inserted into the chromacycloheptane to form chromacyclononane, which then undergoes reductive elimination [3]. Chromacyclononane is an unstable intermediate and the reductive process is rapid. As the temperature increases, so too does the selectivity towards 1-octene for each catalyst system. This is unusual since Kuhlmann *et al.* [9] reported that an increase in temperature results in a decrease in the selectivity towards 1-octene while the selectivity towards 1-hexene increases. Reasons for the discrepancies could be the difference in the reaction conditions as opposed to those used in literature; the purity of the ethylene fed into the reactor, the reaction solvent and its purity and the lack of a completely inert reaction atmosphere. The bulky ligands (isopropyl, cyclohexyl and phenyl) yielded the highest selectivity towards 1-octene.

5.2.1.5. The C10-C14 fraction selectivity profile

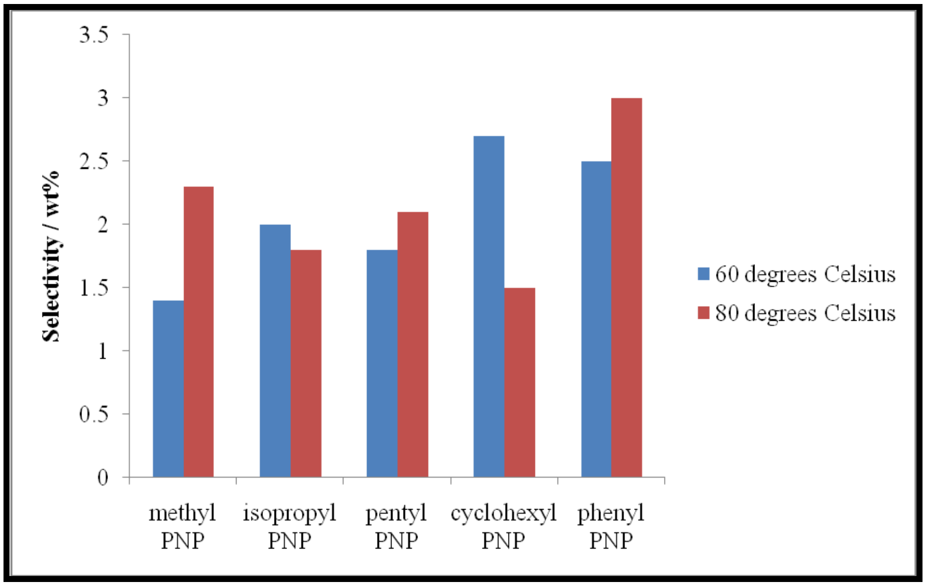


Figure 5.6. Selectivity of the C10 – C14 products for each catalyst system at different temperatures.

The selectivity towards the C10 – C14 products for each catalyst system at different temperatures can be seen in Figure 5.6 above. These products are formed due to further insertions of ethylene molecules on the chromacyclononane intermediate, as well as the co-trimerisation and co-tetramerisation of ethylene with 1-hexene and 1-octene [4]. Confirmation that these products are not formed directly from ethylene was obtained when a tetramerisation reaction was spiked with 1-pentene and C9 co-trimerisation and C11 co-tetramerisation products were formed [4]. As the temperature increases, so too does the selectivity towards the C10 – C14 products with exception of the isopropyl and cyclohexyl systems which showed a decrease. Both these ligands behaved similarly due to the similarity in their structure (bulky alkyl substituent on N). An increase in steric bulk of the ligand results in a decrease in the selectivity towards the C10 – C14 products as the temperature increases.

5.2.2. The heavy fraction

5.2.2.1. The C16+ fraction selectivity profile

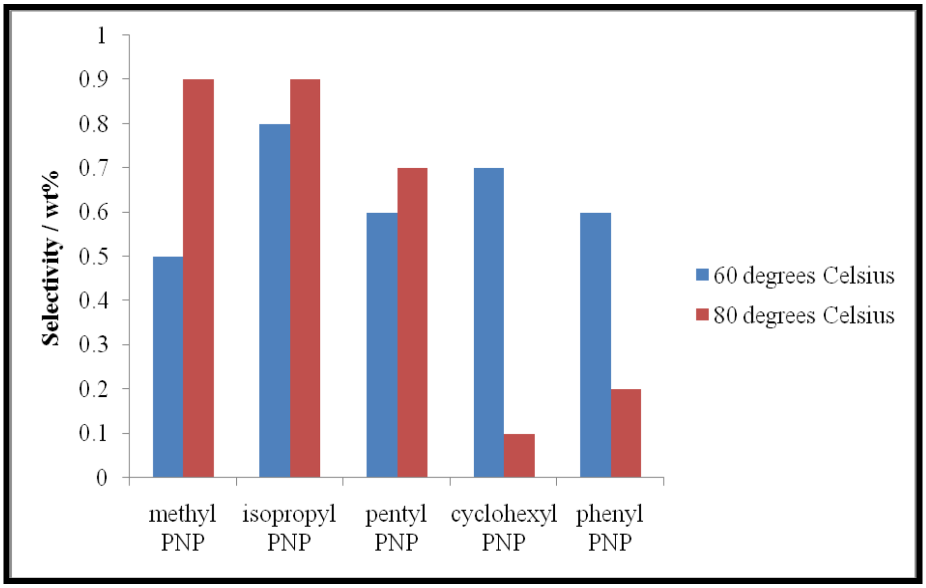


Figure 5.7. Selectivity of the C16+ products for each catalyst system at different temperatures.

The selectivity towards the C16+ products for each catalyst system at different temperatures can be seen in Figure 5.7 above. These products are formed by a linear chain growth mechanism [4]. It can be seen that as the temperature increases, so too does the selectivity towards the C16+ products except for the cyclohexyl and phenyl systems. Similarly as observed with the C10 – C14 products, an increase in steric bulk of the ligand (cyclohexyl and phenyl), results in a decrease in the selectivity towards the C16+ products.

5.2.2.2. The solid fraction selectivity profile

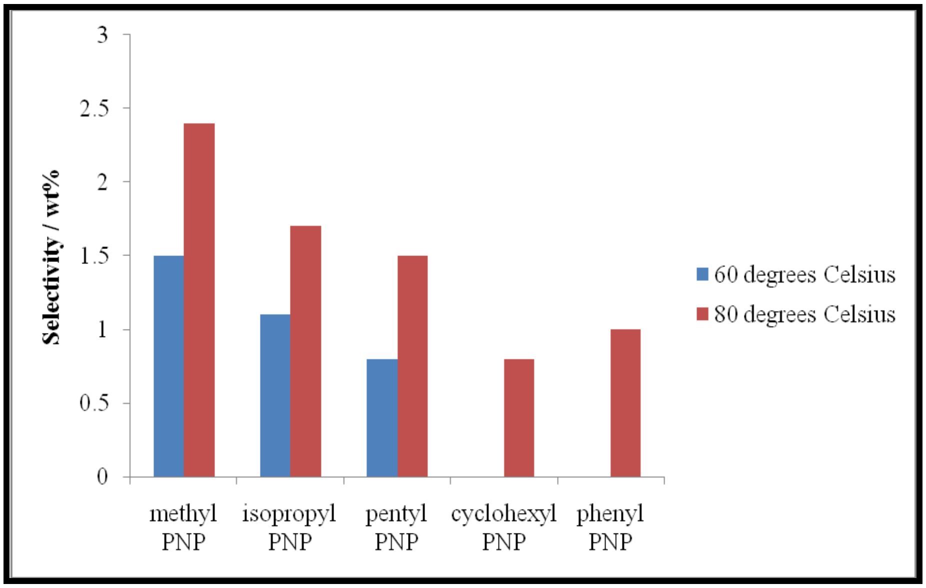


Figure 5.8. Yield of the solids for each catalyst system at different temperatures.

The solids referred to in Figure 5.8 were a powder that remained after the liquid from the reactor was removed *in vacuo*. The selectivity obtained is calculated as the mass of this powder per total mass of liquid product. As the temperature increased, there was an increase in the solids yield for the catalyst systems; with the methyl system yielding the most solids. The cyclohexyl and phenyl systems had the lowest yield, with no yield at 60 °C and this is due to most of the ethylene being used in the formation of 1-hexene and 1-octene. These two systems had the highest yield of these two products (Figures 5.3 and

5.5). The major component of these solids was suspected to be polyethylene, which is one of the major by-products in these types of reactions. Infrared spectra of the solid by-product and commercial polyethylene were obtained and compared and it was concluded that the solid was polyethylene. These infrared spectra can be seen in Figure 5.9.

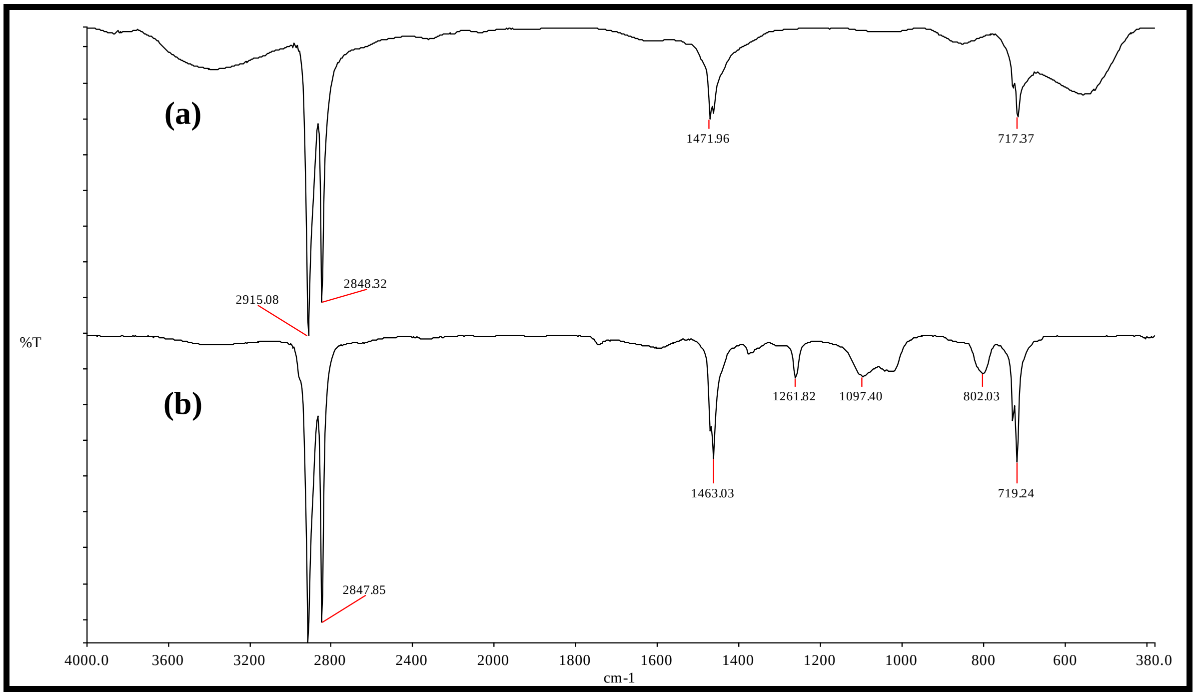


Figure 5.9. Infrared spectrum of (a) commercial polyethylene and (b) solid by-product from tetramerisation runs.

Both spectra look similar, with the solid by-product from tetramerisation having additional peaks, probably due to other products formed which were incorporated in the solids. These are insoluble aluminium-containing compounds from the activator MMAO-3A.

5.2.3. The activity profile

An increase in temperature yielded a slight increase in the activity of the systems as seen in Figure 5.10, with the cyclohexyl and phenyl systems yielding the highest activity. The activity was in the 10^4 – 10^5 g/g Cr h^{-1} range, whereas in literature it is in the 10^6 g/g Cr h^{-1}

range [2]. This could have resulted from air getting into the activator (MMAO-3A) during transfer into the reactor. This could have been avoided if a glove box was available. Also the ethylene used was from South Africa and contained some impurities. In literature, the ethylene used was imported and extensively purified.

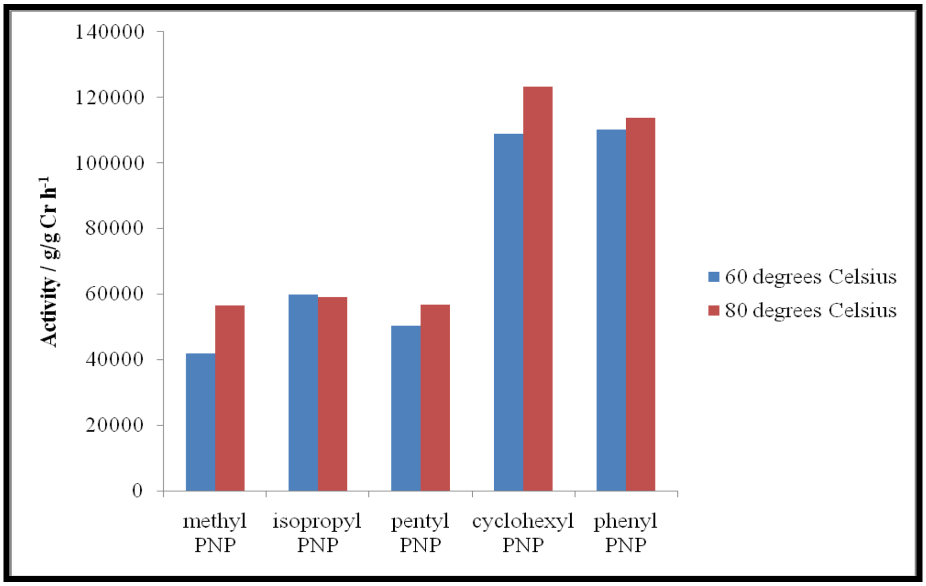


Figure 5.10. Activity for each catalyst system at different temperatures.

5.3. Testing of heterogeneous catalyst systems

As mentioned above, testing of the heterogeneous catalysts was carried out using the supported ligands (isopropyl, cyclohexyl and phenyl) using the same conditions as those for the homogeneous catalytic testing. These systems proved unfavourable for the tetramerisation of ethylene, yielding a high selectivity towards the C6 products (Figure 5.11) and a poor selectivity towards 1-hexene in the C6 products (Figure 5.12). The systems also yielded a poor selectivity towards the C8+ products and 1-octene in the C8 products (Figure 5.13). In fact, the selectivity towards the C10+ products was less than 0.5 wt%, at times 0 wt%, which can be regarded as negligible.

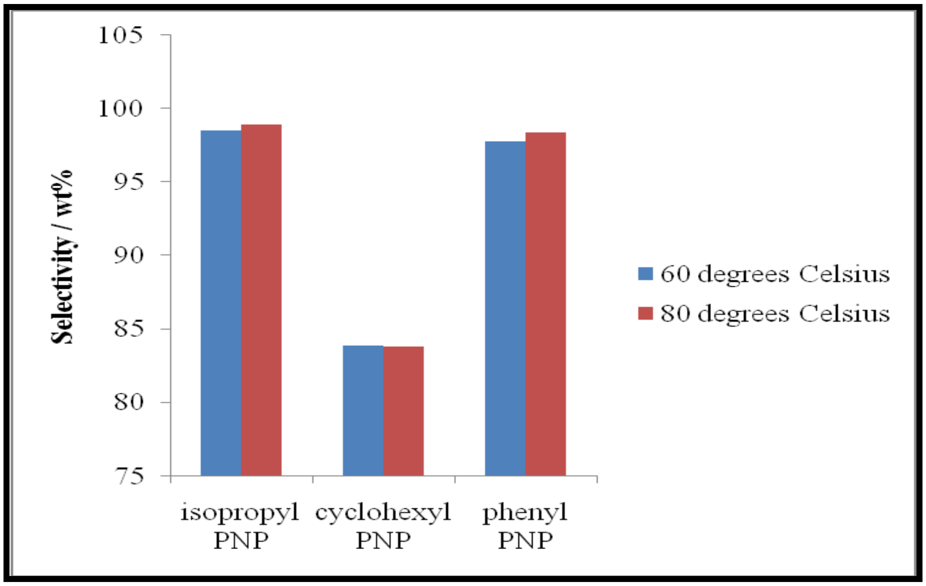


Figure 5.11. Selectivity of the C6 products for each heterogeneous catalyst system at different temperatures.

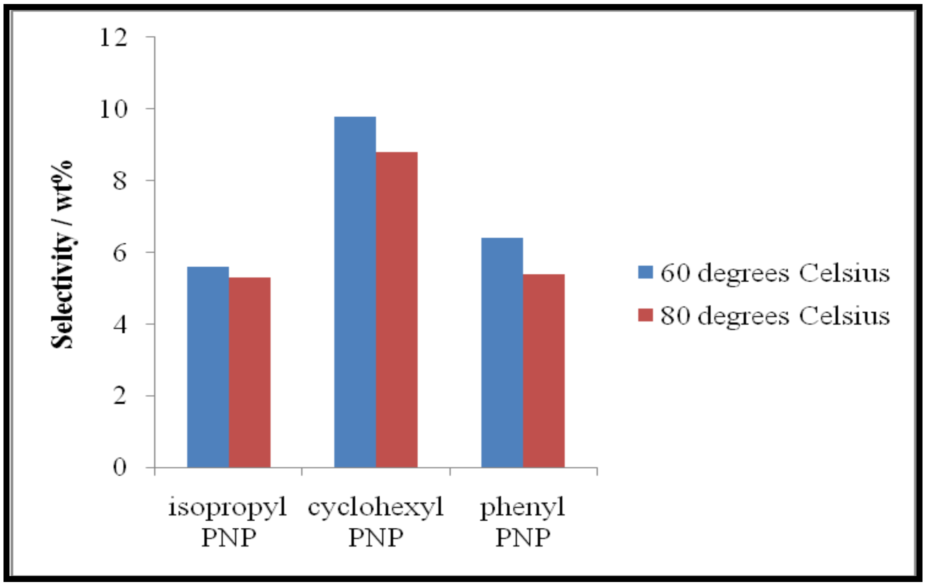


Figure 5.12. Selectivity of 1-hexene in the C6 products for each heterogeneous catalyst system at different temperatures.

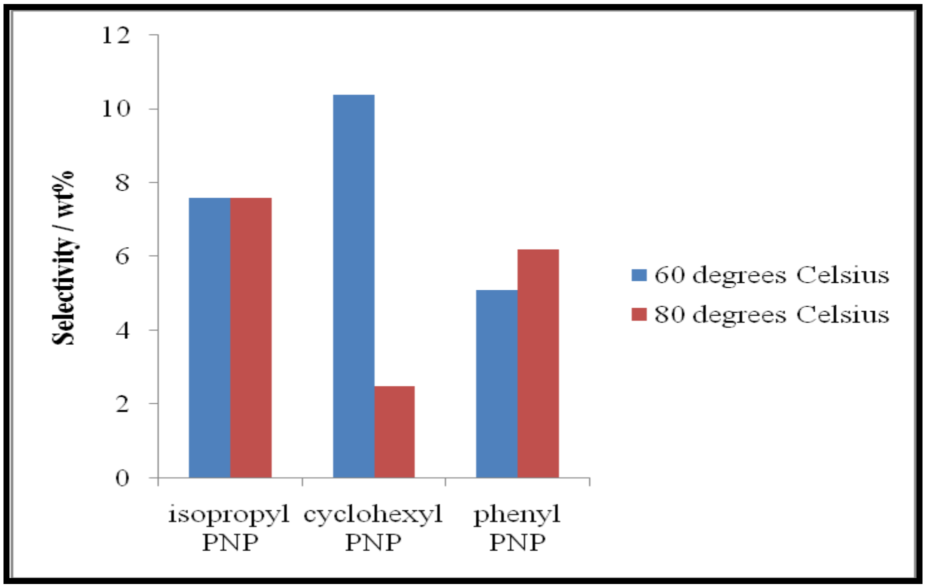


Figure 5.13. Selectivity of 1-octene in the C8 products for each heterogeneous catalyst system at different temperatures.

In the C6 fraction, the majority of the products were the cyclics, i.e. methylcyclopentane and methylenecyclopentane. The selectivity towards these two products was found to be greater than 60 wt% (Figure 5.14). This leads to the belief that the catalytic cycle is favoured up until the insertion of three ethylene molecules to form the chromacycloheptane intermediate, after which the disproportionation step to form the cyclic products is favoured over the reductive elimination step to form 1-hexene.

Similar observations were observed by Wang *et al*. [11] whose catalyst system gave predominantly cyclic products. They investigated the oligomerisation of ethylene using Cp_2ZrCl_2 as the catalyst and ethylaluminoxane and triethylaluminium as the activators. Scheme 5.2 is a proposed catalytic cycle for the catalyst system reported in this thesis and is adapted from that proposed by Wang *et al*. It shows how the two C6 products are predominantly formed over the other products.

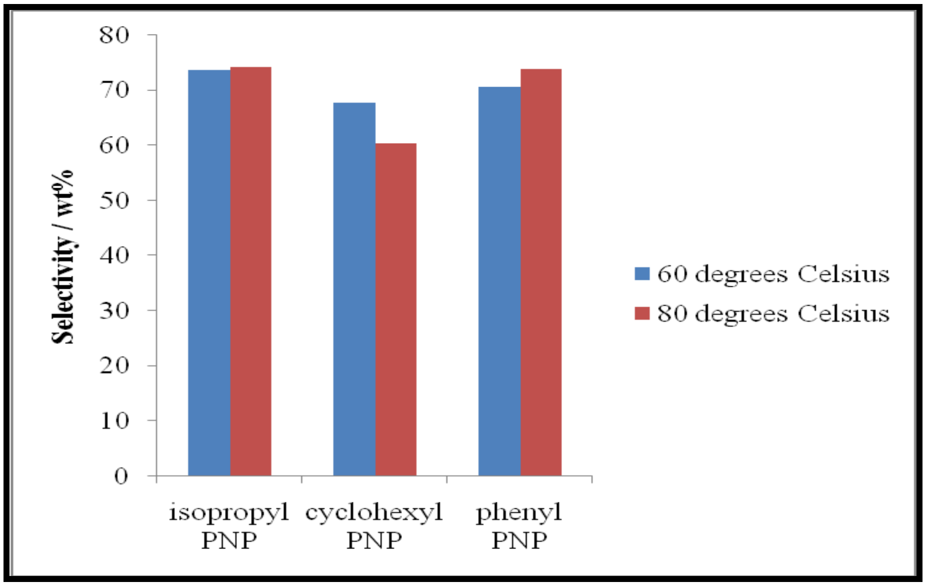
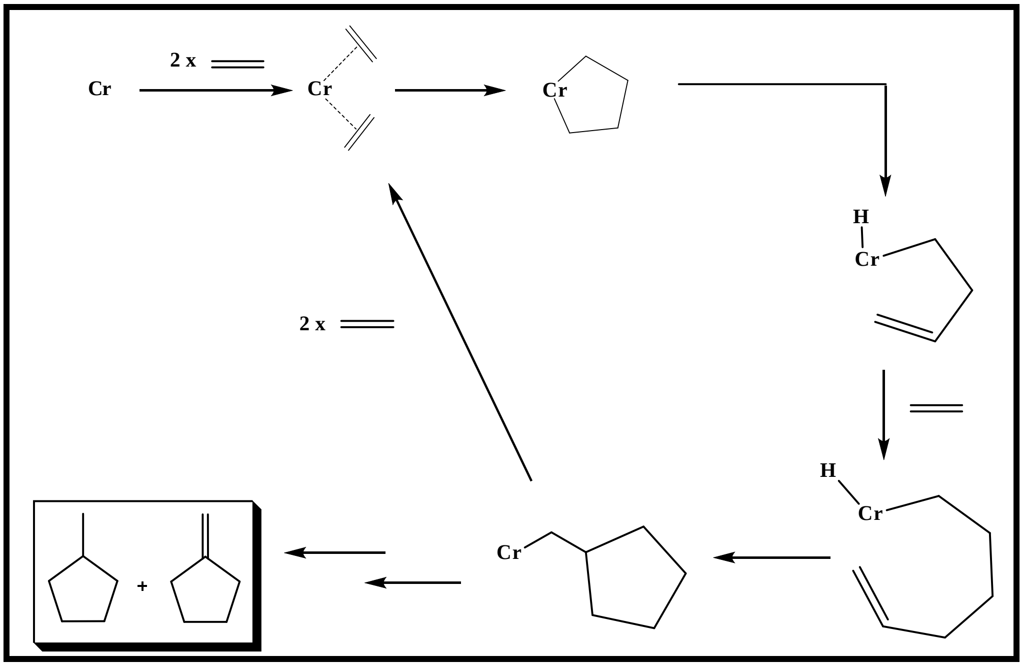


Figure 5.14. Selectivity of the C6 cyclics in the C6 fraction for each heterogeneous catalyst system at different temperatures.



Scheme 5.2. Proposed catalytic cycle for the oligomerisation of ethylene using the polymer-supported PNP ligands. Adapted from Wang *et al*. [11].

The poor selectivity towards 1-octene and C8+ could be a result of steric hinderance, since as mentioned earlier, the bulkier ligands favour the formation of the C6 products over the C8 products. Also the steric hinderance could result in the blocking of the possible active sites of the intermediate. Perhaps toluene, which is another solvent used for these types of reactions, would have been a better solvent for these systems because it swells polymers and allows them to be more soluble [12-14]. The poor selectivity towards 1-octene and 1-hexene has also affected the co-trimerisation and co-tetramerisation steps, which explains the low selectivity towards C10+ products. It is believed that the complex that forms *in situ* during catalysis between the chromium precursor and the supported ligand does not contain active sites to fully complete the catalytic cycle in good yield. This could also be due to the polymer which blocks access to sites on chromium required for catalysis. This would also explain the decrease in the activity compared to the homogeneous counterparts due to the low availability of chromium as seen in Figure 5.15.

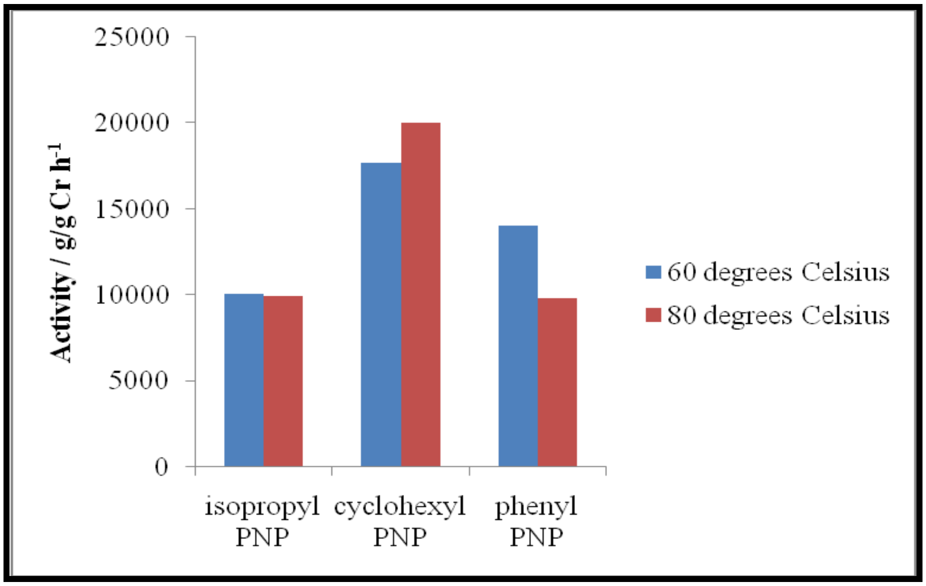


Figure 5.15. Activity for each heterogeneous catalyst system at different temperatures.

The yield of solids has not been taken into account since no observable polymer was formed and the solid remainder after removal of solvent was believed to contain a mixture of the supported catalyst as well as product from the catalytic testing.

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Chapter 6

Summary and conclusions

The heterogenisation of some selective tetramerisation ligands has been achieved. This involved the supporting of highly active homogeneous ligands on functionalized polystyrene. The homogeneous ligands that were supported were the isopropyl, cyclohexyl and phenyl bis(diphenylphosphino)amine analogues. Successful synthesis of these compounds was confirmed by ATR, solid-state NMR, TGA-DSC and SEM. The homogeneous analogues of these three supported ligands as well as a methyl and pentyl analogue were synthesized. Successful synthesis of these five homogeneous ligands was confirmed by a variety of techniques including NMR, ATR, elemental analysis and GC-MS. The homogeneous ligands were synthesized in order to compare their catalytic activity with their heterogeneous counterparts. Catalytic testing involved the oligomerisation of ethylene using a high pressure Parr reactor after which product identification and quantification was achieved by GC-FID and GC-MS.

The homogeneous ligands proved active in the tetramerisation of ethylene, with the selectivity of 1-octene in the C8 fraction being comparable with that mentioned in literature (> 98 wt%) [1-3] although the same cannot be said about the activity. When comparing the homogeneous ligands, an increase in the alkyl chain length (methyl and pentyl PNP), there was an increase in activity as well the selectivity towards the alpha olefins (1-hexene and 1-octene). Addition of a branch on the alkyl chain (isopropyl PNP) yielded a further increase in activity and an increase in alpha olefins. Increase of steric bulk (cyclohexyl and phenyl PNP) yielded similar results to isopropyl PNP with a considerable increase in activity. An increase in temperature, irrespective of the substituent size also yielded an increase in alpha olefin selectivity and activity.

When comparing the homogeneous ligands with their heterogeneous counterparts, the heterogeneous ligands performed poorly. The activity dropped by more than four times that of their homogeneous counterparts and the selectivity towards the main product, 1-octene, was very low (< 10 wt%). These ligands seemed to create a system that favoured the formation of the C6 products more than any other product, with the C6 cyclics being the most dominant. There was little or no selectivity towards the C10+ products due to little or no further co-trimerisation and co-tetramerisation steps. Although these ligands were successfully synthesized, they do not favour tetramerisation due to steric effects caused by the polymer chain. Since they are novel, further investigations, perhaps into other types of oligomerisation reactions (trimerisation and dimerisation) can be done to see their catalytic behavior in these reactions. Toluene could be the solvent of choice since it has the ability to swell the polymer and overcome the steric effects.

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APPENDIX A

REACTOR SETUP

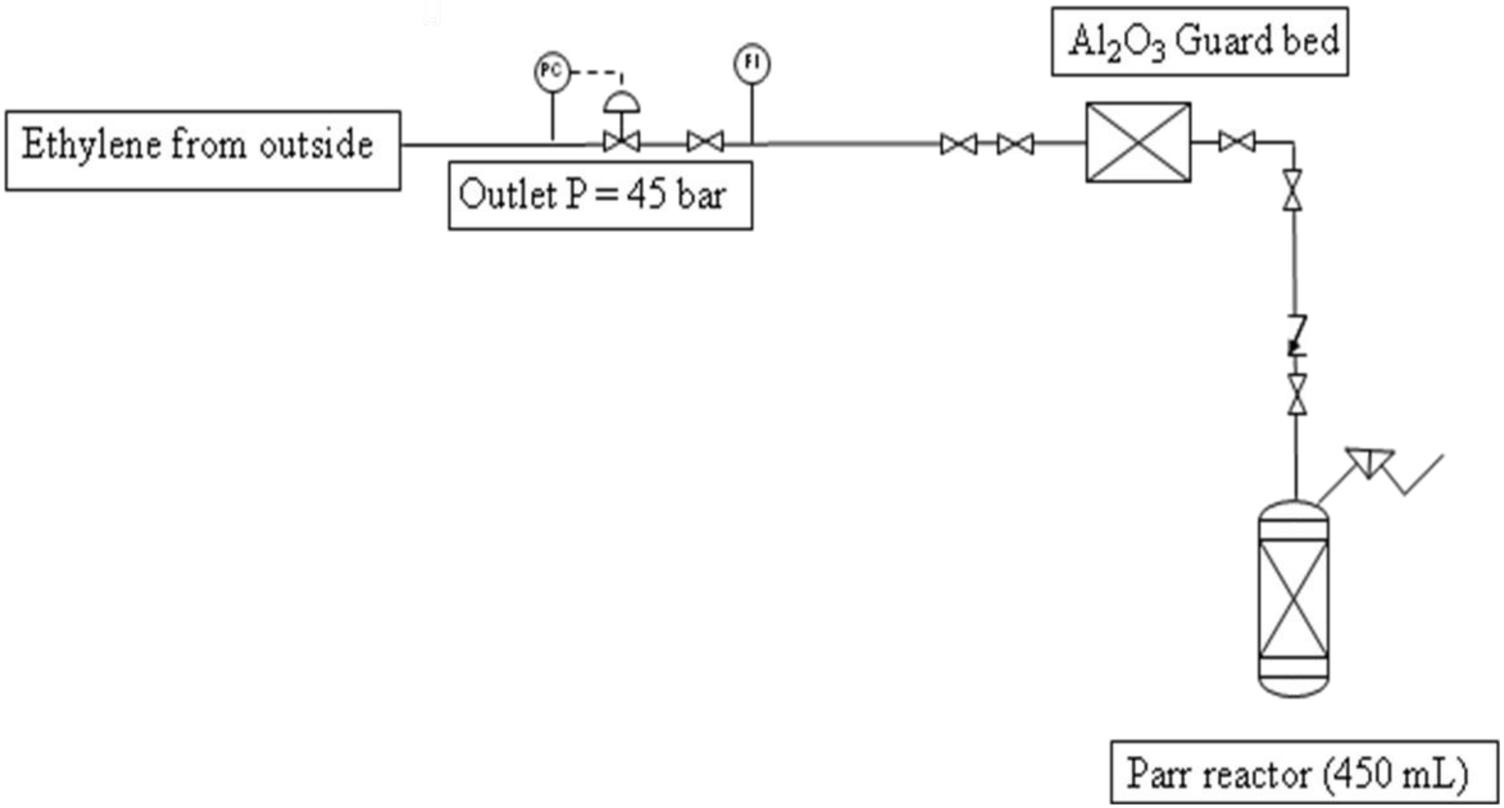

Figure A1. Reactor setup for the tetramerisation reactions.

APPENDIX B

PRODUCT QUANTIFICATION

All the tetramerisation reactions were monitored by GC-FID with the use of an internal standard to quantify the products. The internal standard used was nonane.

Equations used for results discussed in Chapter 5:

Assigning a Relative response factor (RRF) of 1 to nonane:

$$\text{RRF of component} = \frac{\text{moles of nonane} \times \text{peak area of component}}{\text{moles of component} \times \text{peak area of nonane}}$$

Corrected area of component = Area of component x RRF

$$\text{Mass \% component} = \frac{\text{Corrected area of component}}{\text{Total area}} \times 100$$

Selectivity calculations for the products discussed in Chapter 5:

$$\text{Selectivity to 1-hexene} = \frac{\text{Mass\% of } 1-\text{hexene}}{\text{Sum of mass\% of all products}} \times 100$$

A similar calculation was performed for selectivity to the other products.

$$\text{Selectivity of 1-hexene in C6 products} = \frac{\text{Mass\% of } 1-\text{hexene}}{\sum \text{Mass\% of all C6 products}} \times 100$$

A similar calculation was performed using 1-octene and C8 products.

$$\text{Activity} = \frac{\text{Mass of liquid product}}{\text{Mass of Cr used / hour}}$$

Table B1. Ethylene tetramerisation using the homogeneous ligands under different temperatures.

Ligand	Temperature / °C	Activity / g/g Cr h^{-1} [a]	C6 cyclics / wt% [c]	C6 / wt% [b]	1-hexene in C6 / wt% [c]	C8 / wt% [b]	1-octene in C8 / wt% [c]	C10 – C14 / wt% [b]	C16+ / wt% [b]	Solids / wt% [d]
Methyl	60	41800	8.4	46.5	30.7	49.6	98.4	1.4	0.5	1.5
	80	56370	8.1	41.0	39.0	53.5	98.7	2.3	0.9	2.4
Isopropyl	60	59760	8.0	43.1	41.1	51.7	98.9	2.0	0.8	1.1
	80	59130	8.3	42.3	40.4	52.8	98.8	1.8	0.9	1.7
Pentyl	60	50360	5.9	40.7	41.2	51.3	98.5	1.8	0.6	0.8
	80	56830	5.6	42.1	48.4	50.6	98.6	2.1	0.7	1.5
Cyclohexyl	60	108810	4.7	38.2	44.9	56.7	98.9	2.7	0.7	0
	80	123420	4.4	37.5	50.9	58.5	99.6	1.5	0.1	0.8
Phenyl	60	110080	4.7	38.7	44.3	56.3	99.0	2.5	0.6	0
	80	113730	5.5	42.3	53.4	51.8	99.8	3.0	0.2	1.0

Conditions: 100 mL methylcyclohexane, 45 bar ethylene, 5 µmol Cr(acac)$_3$, 5 µmol ligand and 960 equivalents of MMAO-3A.

Reaction time: 30 minutes

[a] Mass of product per mass of Cr used per hour

[b] Identified by GC-MS

[c] Identified by GC-FID by injection of standards

[d] Mass of weighed solids/mass of total product

APPENDIX C

GAS CHROMATOGRAMS

Table C1. The peak number and corresponding component for the chromatograms from a typical tetramerisation reaction.

	Peak number	**Identified Component**
Light fraction	1	Ethanol
	2	1-hexene
	3	Internal hexenes
	4	Methylcyclopentane
	5	Methylenecyclopentane
	6	Methylcyclohexane
	7	1-octene
	8	Nonane
	9	1-decene
	10	Other C10 products
	11	C12 products
	12	C14 products
Heavy fraction	13 – 17	C16+ products

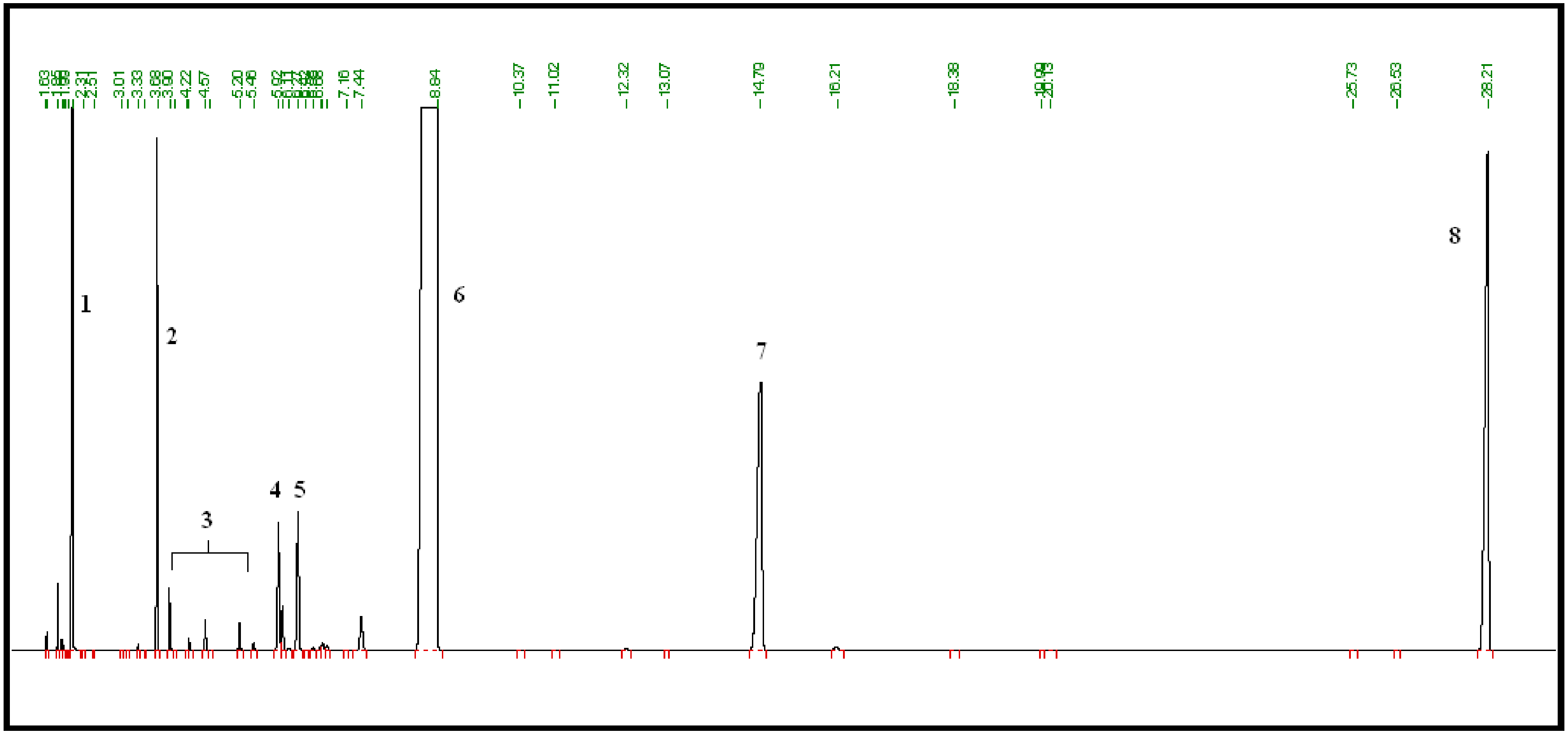

Figure C1. The light fraction (C2 – C9) chromatogram for a typical tetramerisation reaction. The green numbers are the retention times.

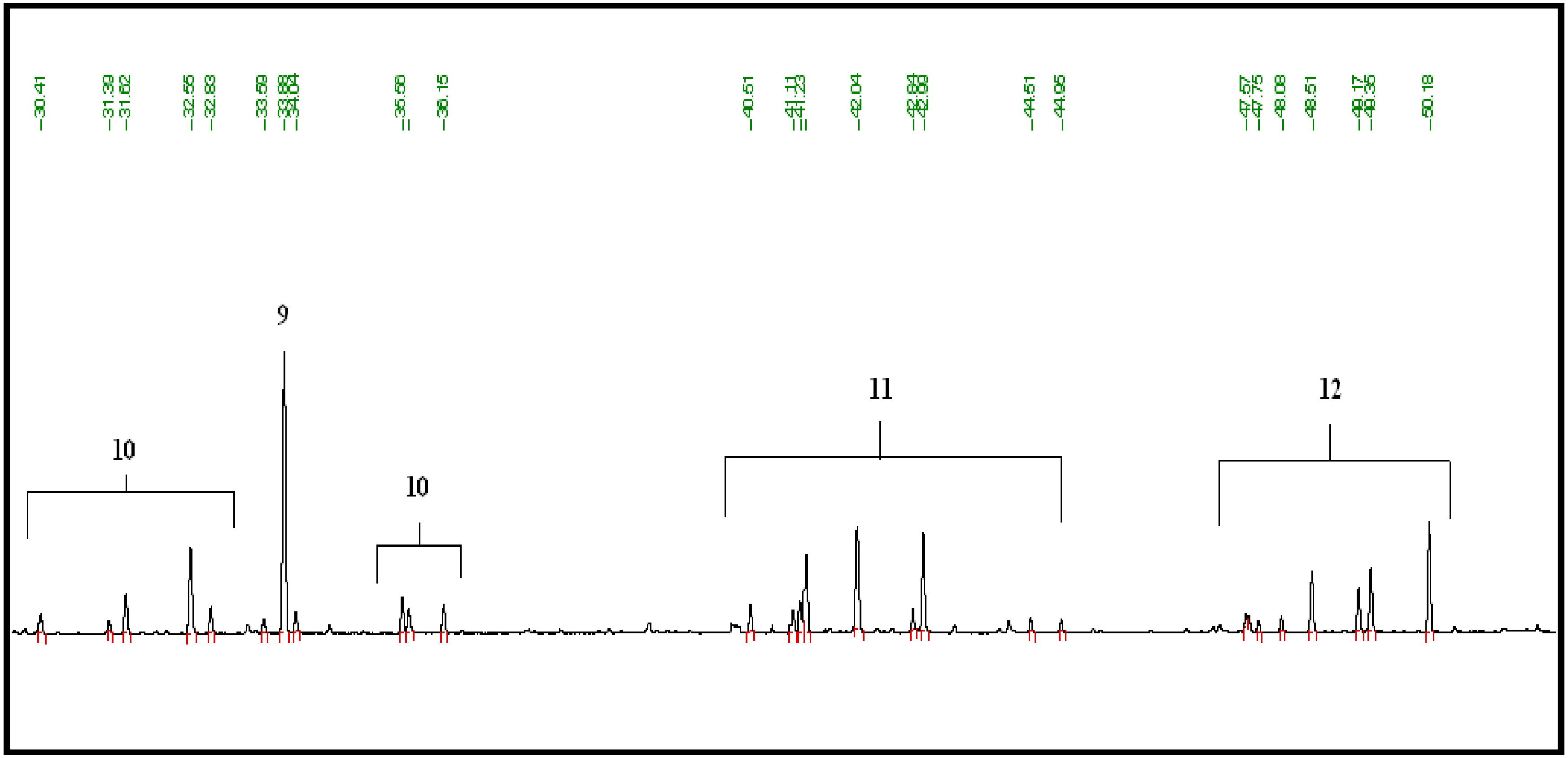

Figure C2. The C10 – C14 products chromatogram for a typical tetramerisation reaction. The green numbers are the retention times.

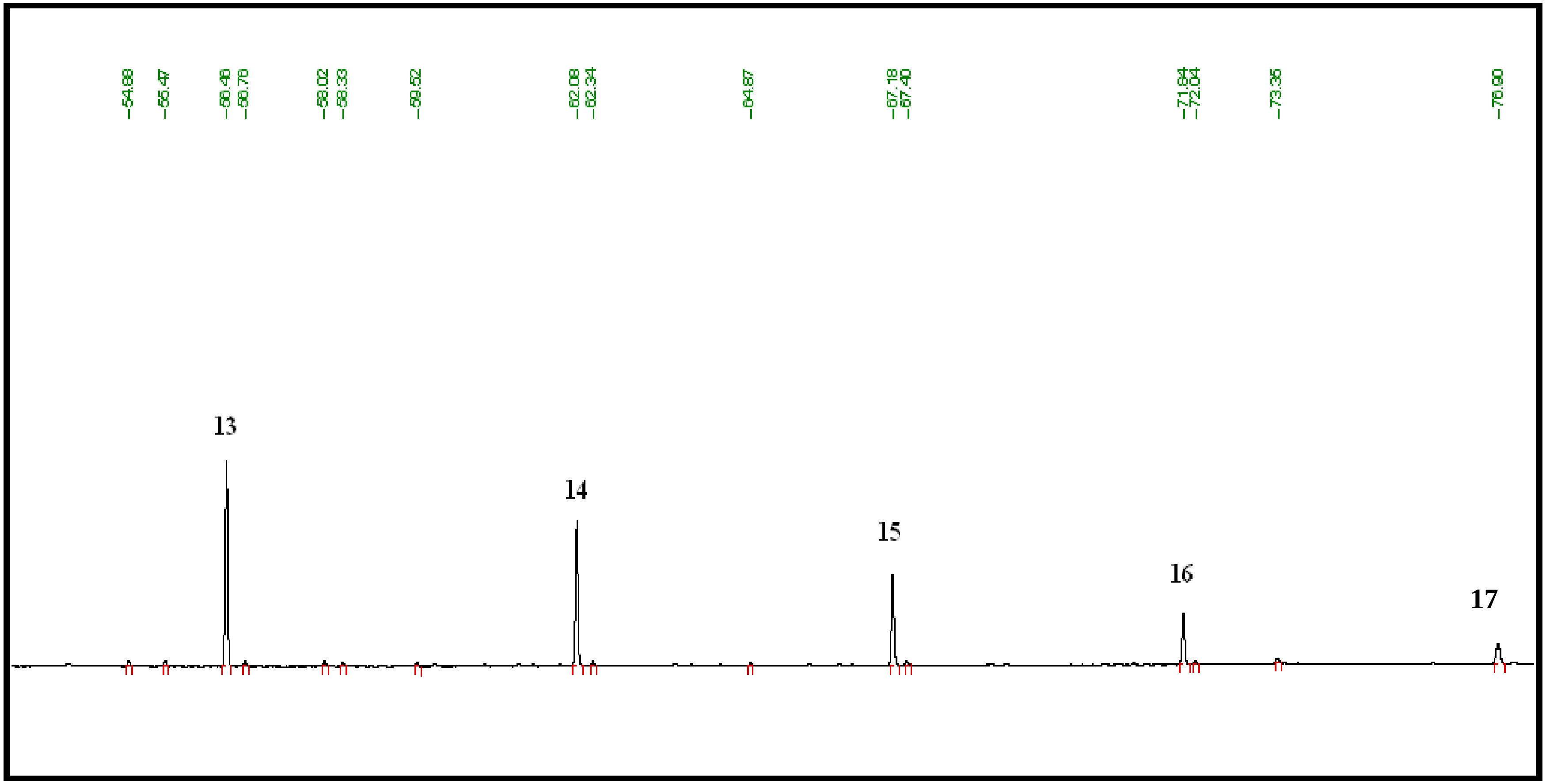

Figure C3. The C16+ products chromatogram for a typical tetramerisation reaction. The green numbers are the retention times.