
**AN INVESTIGATION INTO THE SYNTHESIS,
CHARACTERISATION AND SOME APPLICATIONS OF
NOVEL METAL-CONTAINING POLYMERS AND
DENDRIMERS OF TRANSITION METALS**

by

Gregory Stuart Smith

A dissertation submitted in partial fulfilment of the
requirements for the degree of
UNIVERSITY of the
WESTERN CAPE
Doctor of Philosophy
in the Department of Chemistry,
University of the Western Cape,
Cape Town, Western Cape, South Africa



Supervisor: Prof. S.F. Mapolie

October 2003

DECLARATION

I declare that **AN INVESTIGATION INTO THE SYNTHESIS, CHARACTERISATION AND SOME APPLICATIONS OF NOVEL METAL-CONTAINING POLYMERS AND DENDRIMERS OF TRANSITION METALS** is my own work and that all the sources I have used or quoted have been indicated and acknowledged by means of complete references.



.....
Gregory S. Smith

ACKNOWLEDGEMENTS

My life as a postgraduate student was significantly enhanced by the following people, to whom I wish to extend my sincere thanks and appreciation:

Prof. S.F. Mapolie, for his constant guidance, advice and friendship during this project, and for bearing with me, despite all my “peripheral” activities.

Prof. J.R. Moss (UCT), for the proof-reading of this thesis, and for his willingness to provide support, advice and encouragement toward the completion of this dissertation.

Profs. J. Darkwa and Prof. I.R. Green, for the useful advice and insight throughout the duration of this project.

Mr G.P. Benin-Casa (UCT) and Mr T. Lesch (UWC) for microanalyses and recording the mass spectra. Mr W. Mhlongo for recording the TGA and DSC traces. Dr V. Grümel (US) and Mr R. Khan (SOMCHEM) for performing the GPC analyses. Prof. F. Ayorinde (Howard) for allowing me to study the samples using MALDI-TOF mass spectrometry. Mrs R. Rossouw (US) for the ICP analyses.

My colleagues in the department (UWC) for keeping me (in)sane:

Mrs D. Dooling-Mopp, Mrs F. Waggie, Ms N. Makaluza, Ms N. Maithufi, Mr J. Cloete, Ms F. Zigxashi, Ms R. Pearce, Ms N. October.

The National Research Foundation, The Canon Collins Educational Trust For Southern Africa and the University of the Western Cape for financial assistance.

My family and friends, especially my parents The Rev. I. Smith and Mrs M. Smith, for their continuous support, guidance and encouragement throughout my academic studies.

ABSTRACT

Development in the field of materials science is propagated by the synthesis of polynuclear metal-containing complexes, that exhibit enhanced chemical and physical properties. This thesis describes the synthesis of new metal-containing linear polymers and dendritic molecules.

Chapter 1 presents an overview of the field of metal-containing polymers, with particular attention to the synthesis of polymers via condensation polymerisation. This review includes the various types of metal-containing condensation polymers and the applications of these materials, where available. This discussion is followed by a brief summary of metal-containing dendrimers, which includes a concise description of their structure and applications in general.

There are two routes to preparing metal-containing polymers. Chapter 2 describes the synthesis of three bifunctional organometallic monomers, of the general type $[M]-O-\{2,6-(CH_2OH)_2-4-CH_3-C_6H_2\}$, where $[M]$ represents the various metal-containing moieties, $(\eta^5-C_5H_5)(CO)_2 Fe(CH_2)_3$ (**25**), $(\eta^5-C_5H_4-CH_2CH_2CH_2-)Re(CO)_3$ (**26**) and *Fp-dendr* (**27**). These monomers were prepared using 2,6-bis(hydroxymethyl)-*p*-cresol as the key reagent. The monomers were used in classical polycondensation reactions with terephthaloyl chloride using ambient temperature solution techniques. This yielded new low molecular weight oligomeric polyesters, that were characterised using FTIR and 1H -NMR spectroscopy, differential scanning calorimetry, thermogravimetric analysis and size-exclusion chromatography.

In Chapter 3, an alternate route to metal-containing polymers is described. In this case, bifunctional organic monomers were polymerised to give preformed organic polymers. Two types of organic polymers were prepared, viz. polyesters (with pendant vinyl moieties) and polyimines (with α -diimine units along the polymer backbone). Functionalisation of these preformed organic polymers with various metal sources was attempted. Hydrozirconation reactions of the vinyl polyesters with Schwartz's reagent, $Cp_2Zr(H)Cl$, were attempted and were largely unsuccessful. Competing reactions with the

ester functionality prevailed, preventing the desired reaction. Reaction of the polyimines with PdCl₂(COD) yielded insoluble, intractable metal-containing oligomers. Partial characterisation of the complexes is described.

The synthesis of new poly(propylene imine) iminopyridyl metallodendrimers is described in Chapter 4. Schiff-base condensation reaction of the commercially available DAB dendrimers with 2-pyridinecarboxaldehyde, gave the dendrimers **51**, **52**, and **53**, with four, eight and sixteen pyridylimine functionalities respectively on the periphery. Successful complexation reactions with PdCl₂(COD), PtCl₂(COD) and CuCl₂ produced the corresponding metal-containing dendrimers, with either PdCl₂ (**54**, **55**, **56**), PtCl₂ (**57**) or CuCl₂ (**58**) moieties bound on the periphery. The metallodendrimers were insoluble in the more common organic solvents, and were characterised by IR and ¹H-NMR spectroscopy and microanalysis where possible. Dendrimers with salicylaldimino ligands on the periphery were prepared by reacting the DAB dendrimers with salicylaldehyde. These ligands were reacted with various metal acetates in an attempt to prepare new metal-containing salicylaldimine dendrimers. This work yielded either paramagnetic metal complexes or insoluble, intractable compounds.

Chapter 5 describes the applications of the catalyst precursors (**54**, **55**, **56**, **57**, **58**), discussed in Chapter 4, in the polymerisation of ethylene and the use of complexes **54** and **55** as Heck cross-coupling catalyst precursors. The complexes all showed catalytic activity toward ethylene polymerisation. A discussion of their activity, the polyethylene molecular weight and microstructure is presented in this chapter. The precursors **54** and **55** are also effective catalysts in the Heck reactions, coupling iodobenzene with methyl acrylate, styrene and 1-octene in high conversions.

General conclusions are given in Chapter 6.

ABBREVIATIONS

Ar	=	aryl
Bu	=	butyl
Cp	=	cyclopentadienyl ($\eta^5\text{-C}_5\text{H}_5$)
d	=	days
dec.	=	decomposition
DRIFTS	=	diffuse reflectance infrared transmission spectroscopy
DSC	=	differential scanning calorimetry
E.I.	=	electron impact
Et	=	ethyl
Fp	=	CpFe(CO)_2
G	=	generation
FTIR	=	fourier transform infrared
L	=	ligand
L_n	=	associated ligands
M	=	transition metal
MAO	=	methylaluminoxane
M^+	=	molecular ion
Me	=	methyl
M.p.	=	melting point
m/z	=	mass to charge ratio
NMR	=	nuclear magnetic resonance
Ph	=	phenyl
Pr	=	propyl
R	=	alkyl
r.t.	=	room temperature
<i>tert</i>	=	tertiary
TGA	=	thermogravimetric analysis
THF	=	tetrahydrofuran
t.l.c.	=	thin layer chromatography
X	=	halogen atom

PUBLICATIONS

JOURNAL ARTICLES :

Selwyn F. Mapolie, John R. Moss and Gregory S. Smith

The Polymerisation of Metal-Containing Vinylic Monomers of Iron and Tungsten with Metal-Carbon Sigma Bonds

JOURNAL OF INORGANIC AND ORGANOMETALLIC POLYMERS, Vol.7(4), 233-250 (1997)

Selwyn F. Mapolie, John R. Moss and Gregory S. Smith

The Synthesis and Characterisation of Metal-Containing Vinylic Monomers of Iron and Tungsten

APPLIED ORGANOMETALLIC CHEMISTRY, Vol. 12, 1-7 (1998)

Selwyn F. Mapolie, Ipe J. Mavunkal, John R. Moss and Gregory S. Smith

The Synthesis, Characterisation and Polycondensation of Metal-Containing Diols. Crystal Structure of $[(\eta^5-C_5H_5)(CO)_2Fe(CH_2)_3O-\{2,6(CH_2OH)_2-4-CH_3-C_6H_2\}]$

APPLIED ORGANOMETALLIC CHEMISTRY, Vol. 16, 307-314 (2002)

Gregory S. Smith, Rui Chen and Selwyn F. Mapolie

The Synthesis and Catalytic Activity of a First-Generation Poly(Propyleneimine) Pyridylimine Palladium Metallodendrimer

JOURNAL OF ORGANOMETALLIC CHEMISTRY, Vol. 673(1-2), 111-115 (2003)

CONFERENCE CONTRIBUTIONS :

Selwyn F. Mapolie, and Gregory S. Smith

2000

The Synthesis and Characterisation of New Metal-Containing Polyesters

34TH INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY

EDINBURGH, SCOTLAND

Selwyn F. Mapolie, Gregory S. Smith and Fazlin Waggie

2000

Synthetic Approaches to New Polynuclear Hydrocarbyl Complexes of Transition Metals Containing M-C σ Bonds

34TH INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY
EDINBURGH, SCOTLAND

Selwyn F. Mapolie and Gregory S. Smith **2000**
The Synthesis and Characterisation of New Polyesters With Metal-Containing Moieties

35TH CONVENTION OF THE SOUTH AFRICAN CHEMICAL INSTITUTE
POTCHEFSTROOM, SOUTH AFRICA

Selwyn F. Mapolie and Gregory S. Smith **2001**
Inorganic Condensation Polymers Containing Late Transition Metals
INORGANIC / CATALYSIS SYMPOSIUM
PILANESBURG, SOUTH AFRICA

Selwyn F. Mapolie and Gregory S. Smith **2002**
Design of Multinuclear Polyesters, Polyimines, Polyurethanes and Calixarenes Containing Late Transition Metals and Their Potential Applications
36TH CONVENTION OF THE SOUTH AFRICAN CHEMICAL INSTITUTE
PORT ELIZABETH, SOUTH AFRICA

Selwyn F. Mapolie and Gregory S. Smith **2002**
The Synthesis and Catalytic Activity of a First-Generation Poly(propyleneimine) Palladium Metallodendrimer
CATSA CATALYSIS CONFERENCE
CAPE TOWN, SOUTH AFRICA

Gregory S. Smith and Selwyn F. Mapolie **2003**
Poly(propyleneimine) Pyridylimine Metallodendrimers : Catalytic Activity Toward Ethylene Polymerisation.
INORGANIC CONFERENCE
PRETORIA, SOUTH AFRICA

TABLE OF CONTENTS

TITLE	i
DECLARATION	ii
ACKNOWLEDGEMENTS	iii
ABSTRACT	iv
ABBREVIATIONS	vi
PUBLICATIONS	vii
TABLE OF CONTENTS	ix

CHAPTER 1 : GENERAL INTRODUCTION

1.1	Introduction to Organometallic Polymers	1
1.2	A Review of Condensation Organometallic Polymers	2
1.3	Functionalisation of preformed organic polymers	19
1.4	Metal-containing Dendrimers / Metallodendrimers	23
1.5	Summary / Conclusions	25
1.6	Scope and Objectives of the Thesis	25
1.7	Organisation of the Thesis	26
1.8	References	28

CHAPTER 2 : THE SYNTHESIS AND CHARACTERISATION OF METAL-CONTAINING POLYESTERS AND POLYURETHANES

2.1	Introduction	32
2.2	Results and Discussion	34
2.2.1	Monomer Syntheses	34
2.2.2	Characterisation of the Bifunctional Monomers	37
2.2.3	Synthesis of Metal-Containing Polyesters	46
2.2.4	Synthesis of Metal-Containing Polyurethanes	55
2.2.5	Characterisation of the Metal-Containing Polyurethanes	58
2.3	Conclusions	59
2.4	Experimental	60
2.5	References	65

CHAPTER 3 : THE SYNTHESIS AND ATTEMPTED COMPLEXATION OF FUNCTIONALISED ORGANIC CONDENSATION POLYMERS

3.1 Introduction	67
3.2 Results and Discussion	69
3.2.1 Polyesters with terminal vinyl groups in the side chains	69
3.2.2 Attempted Hydrozirconation Reactions	71
3.2.3 Linear Polyimine Synthesis	74
3.2.4 Functionalisation reactions with PdCl ₂ (COD)	80
3.3 Conclusions	82
3.4 Experimental	83
3.5 References	86

CHAPTER 4 : THE SYNTHESIS AND CHARACTERISATION OF POLY(PROPYLENEIMINE)PYRIDYLIMINE AND POLY(PROPYLENEIMINE)SALICYLALDIMINE METALLODENDRIMERS

4.1 Introduction	88
4.2 A Concise Notation for the Dendrimers in this Chapter	92
4.3 Results and Discussion	93
4.3.1 Synthesis of Pyridylimine-functionalised DAB dendrimers	93
4.3.2 Complexation reactions with PdCl ₂ (COD)	98
4.3.3 Complexation reactions with PtCl ₂ (COD)	102
4.3.4 Complexation reactions with anhydrous CuCl ₂	103
4.3.5 Synthesis of Salicylaldimine-functionalised DAB dendrimers	104
4.3.6 Reactions of DAB-G1(Salicyl) ₄ with M(OAc) ₂ .xH ₂ O (M = Cu, Ni) and FeCl ₂ .4H ₂ O	111
4.4 Conclusions	116
4.5 Experimental	117
4.6 References	123

CHAPTER 5 :	CATALYTIC REACTIONS USING METALLODENDRIMERS	
5.1	Introduction	126
5.2	Late Transition Metal Catalysts For Ethylene Polymerisation	129
5.2.1	Mechanistic Considerations	129
5.2.2	Catalytic Evaluation of DAB-G1(Impyr-PdCl ₂) ₄ at 3 atm	131
5.2.3	Catalytic Evaluation of DAB-G1(Impyr-PdCl ₂) ₄ and DAB-G2(Impyr-PdCl ₂) ₈ at 5 atm	136
5.2.4	Catalytic Evaluation of DAB-G1(Impyr-PtCl ₂) ₂ and DAB-G1(Impyr-CuCl ₂) ₄ at 5 atm	139
5.3	Heck reactions using metallodendrimer, DAB-G1(Impyr-PdCl ₂) ₄	141
5.3.1	Catalytic reactions with Methyl Acrylate	144
5.3.2	Catalytic reactions with Styrene	147
5.3.3	Catalytic reactions with 1-Octene	149
5.4	Conclusions	151
5.5	Experimental	152
5.6	References	154
CHAPTER 6 :	GENERAL CONCLUSIONS	157



CHAPTER 1

General Introduction

1.1 Introduction to Organometallic Polymers

The growing importance of organometallic polymer chemistry has been underscored by the demand for new materials with unique and unusual chemical and physical properties.¹⁻⁴ Examples of these include materials with magnetic, electrical and liquid crystalline properties.⁵⁻⁷ The applications of organometallic polymeric materials have already been implicated in fields such as non-linear optics and catalysis, and continue to break new ground.⁸⁻¹²

An organometallic polymer can be defined as a polymer that contains either a direct metal-carbon σ or π bond.^{1,3,13,14} The different properties of organometallic polymers in part depend on the chemical structure of the organometallic complexes contained in the polymer framework. For example, polymers that have metals interspersed in the main chain (Figure 1.1) may display electrical conductivity whereas polymers pendant to the main chain (Figure 1.2) may show non-linear optical properties.

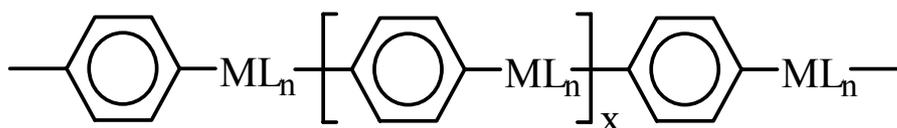
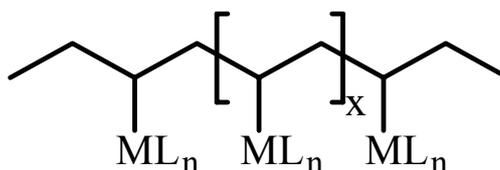


Figure 1.1 Organometallic polymers with metals in a polymer main chain

Figure 1.2 Organometallic polymers with metals pendant to the polymer main chain

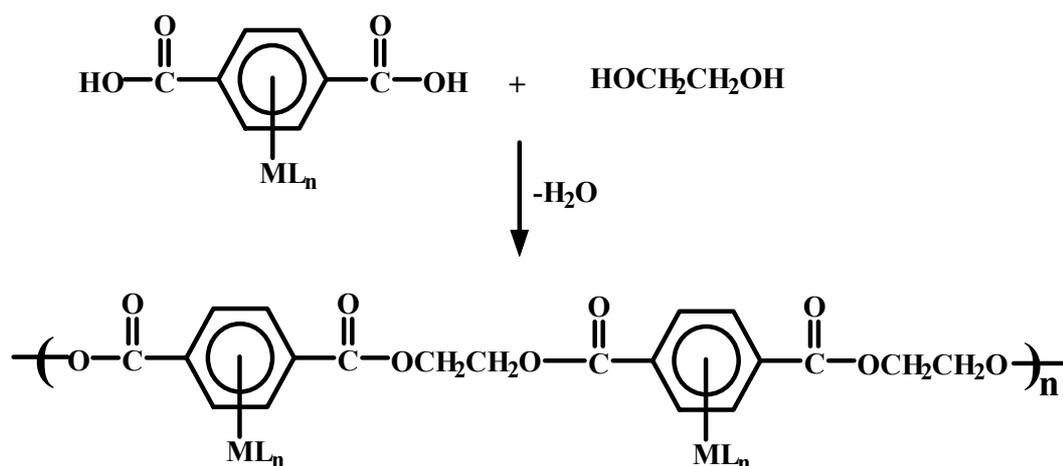


Synthetic routes to organometallic polymers often use classical organic methods of polymerisation, such as addition¹⁵⁻¹⁹, condensation (step)²⁰⁻²² and ring-opening polymerisation.^{23,24} Other techniques also commonly used, such as coordination polymerisation^{25,26} and derivatising a preformed organic polymer^{27,28}, have been well-established in the preparation of metal-containing polymers.

This chapter describes the research that has been covered in the field of condensation (step) organometallic polymer chemistry. The organometallic polymers are discussed as products of various polycondensation reactions, with emphasis on the method employed to incorporate the metal-containing moiety into the polymer chain.

1.2 A Review of Condensation (Step) Organometallic Polymers

Of the two major types of polymerisation methods used to convert monomers to polymers, namely addition and step polymerisation, the latter method has been extensively researched and cited as a means of preparing polymers of metal-containing organic derivatives. Organometallic step polymerisation, which is an extension of classical organic step reactions, employs two difunctional monomers (Scheme 1.1), with one of the monomers containing an organometallic moiety. For example, a metal-containing di-acid can react with a diol to afford a polyester.



Scheme 1.1

As in organic polymerisations, two different polycondensation processes can also be identified as providing a route to polymer production. The first process is solution polycondensation, in which two monomers are reacted in a liquid medium and any acidic by-products are removed by the presence of some basic additives. The second process called interfacial polycondensation, entails the polymerisation of two monomers at the interface between two immiscible liquid phases, each one containing one of the reactants. The reactants normally diffuse to and undergo polymerisation at the interface. The polymer precipitates and is continuously withdrawn as a film or filament.

1.2.1 Main-chain polymers

Polyesters, Polyamides and Polyureas : A large amount of initial work in this area has shown that ferrocene has been included in a considerable number of step polymers.^{1,3} The earliest reports of these types of organometallic polymers generally gave little characterisation data and the polymers produced were of low molecular weight. One of the first reports in the 1960's by Knobloch and Rauscher described the synthesis of polyamides and polyureas containing the ferrocene nucleus in the main polymer chain²⁹. These were prepared via interfacial polycondensation at room temperature, by the reaction of 1,1'-ferrocenyldicarbonyl chloride (Figure 1.3) with several diamines and diols to give low molecular weight polymers.

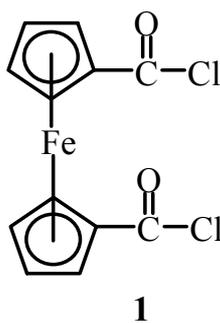


Figure 1.3 1,1'-ferrocenyldicarbonyl chloride

In 1968, Pittman synthesised a series of ferrocene-containing polyesters and polyamides³⁰. These were based on reacting the organometallic monomer, shown in the Figure 1.3 above, at high temperatures (70EC), with various diols and primary amines in a xylene-pyridine solvent mixture. Generally, low molecular weight (below 4000) polyamides and polyesters

were obtained, which are possibly due to the insolubility of the polymers.

This work was extended to include polyesters containing other metals, such as cobalt.³¹ These compounds were formed by the reaction of the 1,1'-diacidchloride of cobalticinium hexafluorophosphate **2** with various diols (Figure 1.4). The organometallic polymers (**3**) showed promise as heat resistant materials due to the stability of the cobalticinium nucleus, which is also resistant to oxidation.

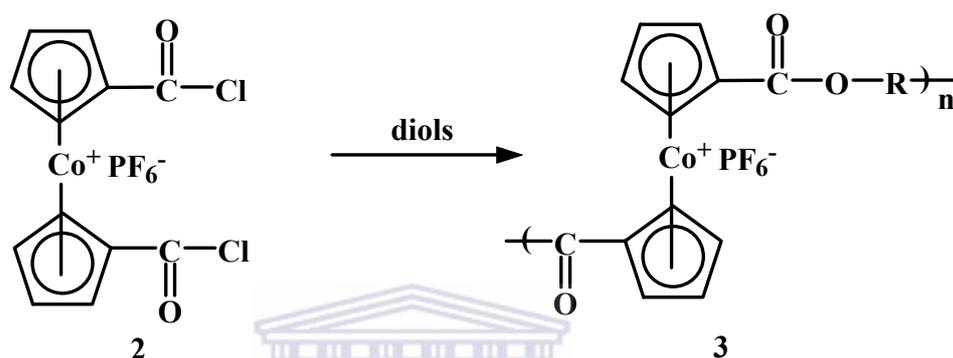


Figure 1.4 Organometallic polyesters containing a cobalticinium nucleus

Sheats³² and Neuse³³ also reported studies on similar cobalticinium polymers, based on structures that are isoelectronic with analogous ferrocene derivatives. Apart from step polymers based on ferrocene-type metallocene complexes, a large variety of polyethers, polythioethers, polyesters and polyamines have been reported based on the Group 4 metallocenes, containing Ti, Zr and Hf. A thorough review by Carraher in 1977 describes the synthesis of these polymers and their characteristics.³⁴

The work of Gonsalves, Rausch and co-workers³⁵⁻³⁸ has also significantly augmented the field of organometallic-condensation polymerisation research. These researchers have carried out extensive work on ferrocene-containing step polymers, such as ferrocene-containing polyamides and polyureas³⁵ **4** and **5** (Figures 1.5 and 1.6).

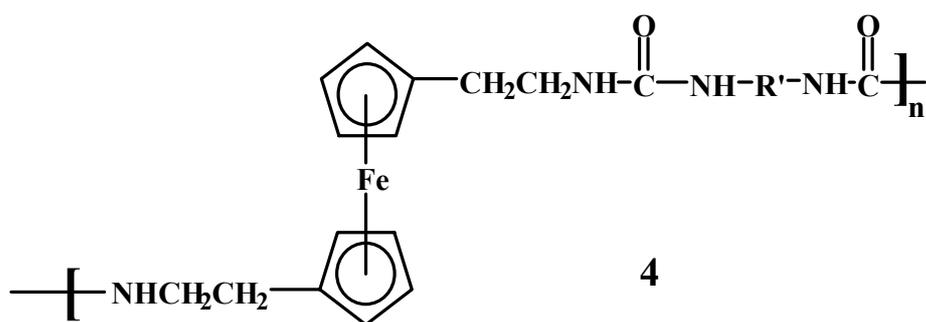


Figure 1.5 Ferrocene-containing polyurea

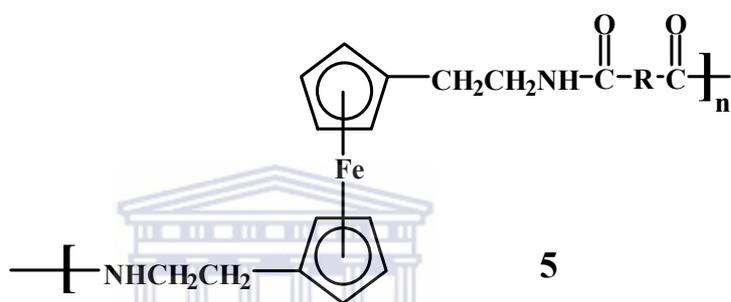


Figure 1.6 Ferrocene-containing polyamide

They used the monomer 1,1'-bis(β -aminoethyl)ferrocene with a variety of diacid chlorides and diisocyanates to produce the ferrocene-containing polyamides and polyureas shown above. This was achieved via interfacial polycondensation of the monomers at room temperature, in contrast to earlier step polymerisations (like those of Pittman) that were conducted at higher temperatures. Attempts to obtain the molecular weights of the polymers were unsuccessful due to the limited solubilities of the materials in various organic solvents.

While reports on synthesising organometallic polymers via step polymerisation are rather sparse, there have been a few recent articles which underscores the need for the construction of new condensation reaction systems and modification of existing systems. Organometallic polymers containing a cobalt bis(dicarbollide) anion³⁹ have been prepared. These materials are synthesised by the selective deprotonation of cobalt dicarbollide, forming a monomeric cobalt dicarbollide dicarboxylic acid, which is further reacted with

hexamethylenediamine in THF to afford oligomeric amide compounds. Characterisation of the resulting condensation product was done by FTIR and NMR (30EC) spectroscopy. Unfortunately, molecular weight determinations using SEC have been inconclusive. The presence of the cobalt dicarbollide in the polymer backbone is seen to have potential use as cation exchange materials for the removal of cesium-137 and strontium-90 from nuclear wastes.

Endo and co-workers⁴⁰ recently focussed on organocobalt polymers containing (η^4 -cyclobutadiene)cobalt moieties in the polymer backbone. A range of organocobalt polyethers and polyesters were prepared by polycondensation reactions of cobalt-containing bis-phenols **6** and **7** ($R_1 = \text{H}, \text{OC}_6\text{H}_{13-n}, \text{OC}_{10}\text{H}_{21-n}, \text{OC}_{14}\text{H}_{29-n}$) with aliphatic or aromatic comonomers. The products were soluble in most organic solvents and displayed low to moderate molecular weights.

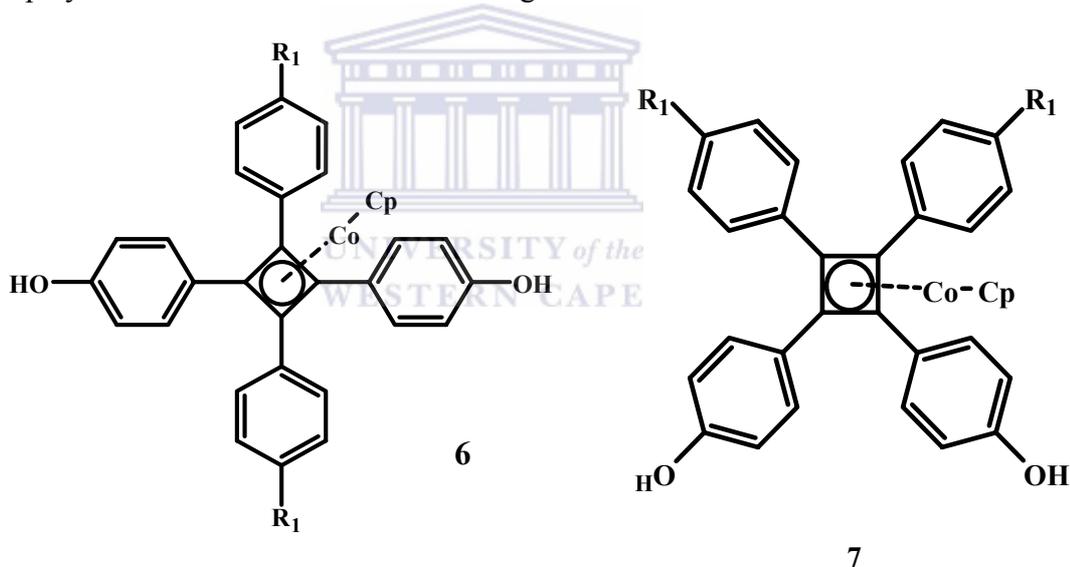
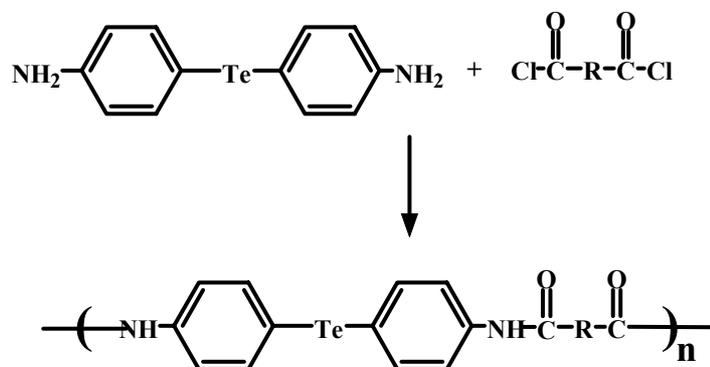


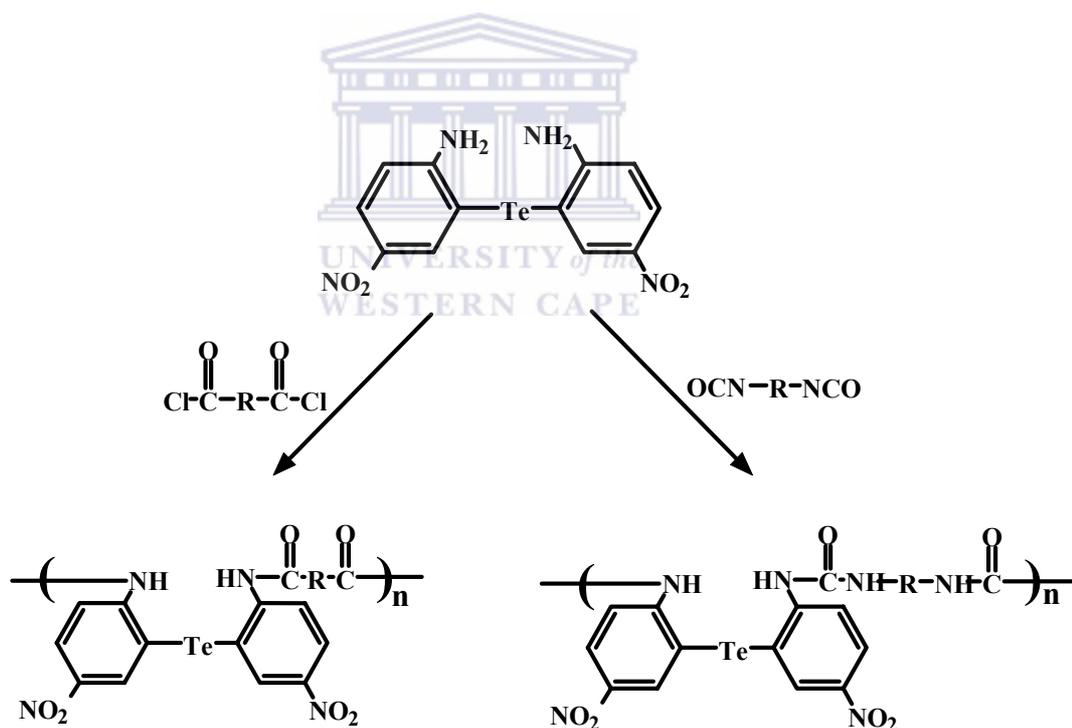
Figure 1.7 Cobalt-containing bis-phenols

Recent work on polycondensation reactions have also been extended to main group metals. Al-Rubaie and Al-Jadaan have prepared polyamides and polyureas containing tellurium.⁴¹ Their syntheses are based on the tellurium-containing diamino complexes shown in Schemes 1.2 and 1.3, which were polymerised in solution with either sebacoyl chloride or terephthaloyl chloride at ambient temperature. Low solubilities of these new products made molecular mass determinations impossible. IR and ¹H NMR data, however,

confirmed the presence of the polymeric compounds. The applicability of the new polyamide as a conducting polymer at room temperature was evaluated, and the results showed this compound to be an insulator.



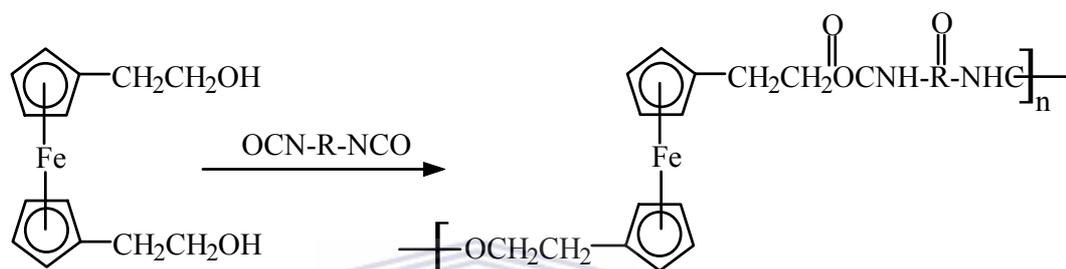
Scheme 1.2



Scheme 1.3



Polyurethanes : The preparation of ferrocene-containing polyurethanes at ambient temperatures was reported by Pittman and Rausch⁴² in 1986. This synthesis was accomplished by the reaction of 1,1'-bis(β -hydroxyethyl)ferrocene with various aliphatic and aromatic diisocyanates (Scheme 1.4). This gave rise to more stable ferrocene polymers, as opposed to those obtained from α -functional ferrocenes, since the reactive groups (NH_2 , OCN) are two methylene units removed from the ferrocene nucleus, steric effects are thus reduced, and the instability found in polymers of α -functional ferrocenes, due to α -ferrocenyl carbonium ion stability, is removed.



Scheme 1.4

The ferrocene-containing polymers mentioned thus far represent a group of compounds where the difunctional moiety is bonded to a Cp ring, which in turn is π -bonded to the metal centre. Similarly, half-sandwiched organometallic complexes have been prepared and using the Cp structure to their advantage owing to the known chemistry of these types of compounds. Tyler *et al.*⁴³ synthesised the metal-metal bonded diols **8-10** shown in Figure 1.9. These were polymerised via solution polycondensation reactions in THF with hexamethylene diisocyanate, in the presence of dibutyltin diacetate acting as a catalyst. These photochemically reactive polymers possessed Mo-Mo or Fe-Fe bonds along the polymer backbone and showed low molecular weights of the order 3500-6000.

For the oligomer produced from **8**, the low molecular weight was attributed to (1) the low reactivity of the OH group on the Cp ring due to steric effects, (2) the low reaction temperature (67°C), (3) the unbalanced reactant ratios resulting from errors in measuring small quantities, and (4) the dilute reaction mixture required to dissolve dimer **8**. Although Tyler and co-workers attempted to increase the reactivity by replacing the carbonyl group

adjacent to the ring in **8**, with a methylene group in compound **9**, and in so doing possibly increase the nucleophilicity on the OH group, the molecular weight did not increase significantly. Tyler and his coworkers have worked on various similar complexes over the years, which includes the recent production of a range of π -bonded photochemically reactive polymers.⁴⁴⁻⁴⁶

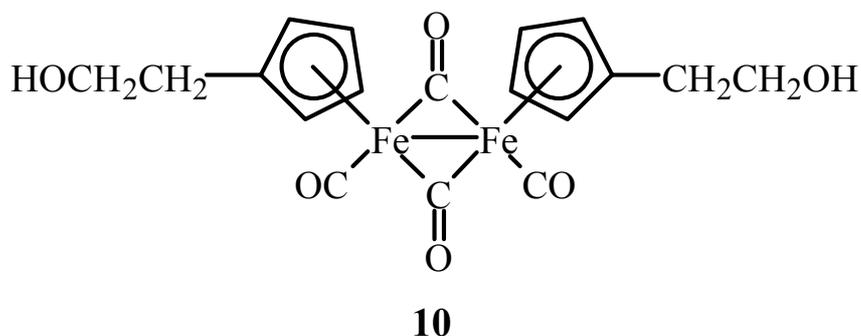
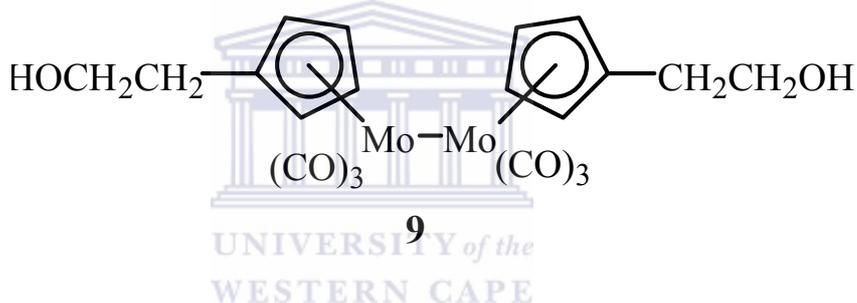
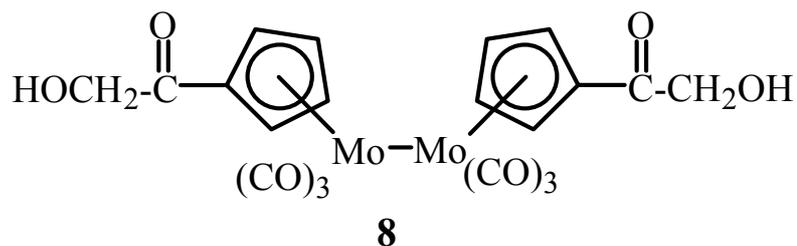


Figure 1.9 Metal-metal bonded diols

Other examples of main chain polymers : Pittman *et al.* synthesised and characterised a number of ferrocene-containing siloxane polymers.⁴⁷ The main objective here was to obtain higher molecular weight polymers by polymerising compound **11** with **12**, **13** and **14** at high temperatures (Figure 1.10). The reaction of **11** with **12** gave low molecular weight products (M_w , 7420) which was ascribed to an intramolecular cyclisation process. Reactions of **11** with **13** and **14** gave considerably higher molecular weight (M_w , 44000-51000) polymers.

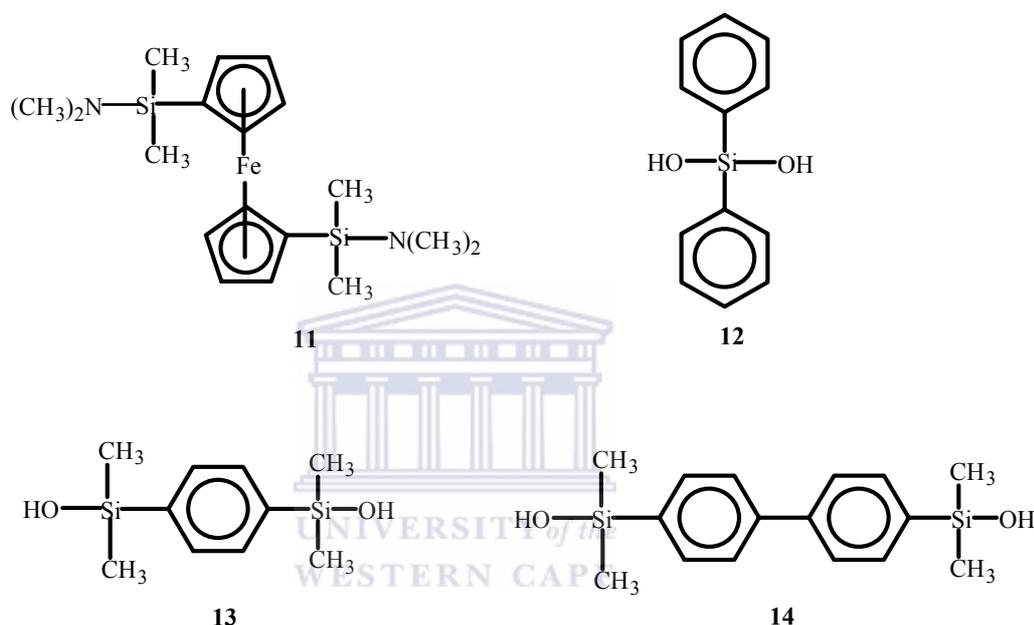


Figure 1.10 Monomers used to prepare ferrocene-containing siloxane polymers

Recent work by the Casado⁴⁸ group also focussed on the silicon-containing polymers **15** and **16** (Figures 1.11 and 1.12) having transition metals in the structure. Their studies centred on preparing systems containing ferrocenyl moieties with flexible methylsiloxane backbones. The polymerisation reactions were carried out using ambient or low temperature solution or interfacial techniques. The molecular weights ranged from 4800-12500.

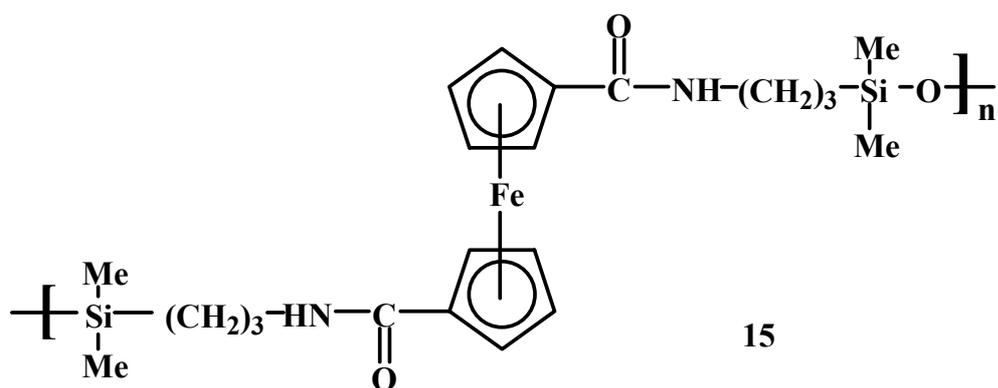


Figure 1.11 Ferrocene polymer with methylsiloxane backbone

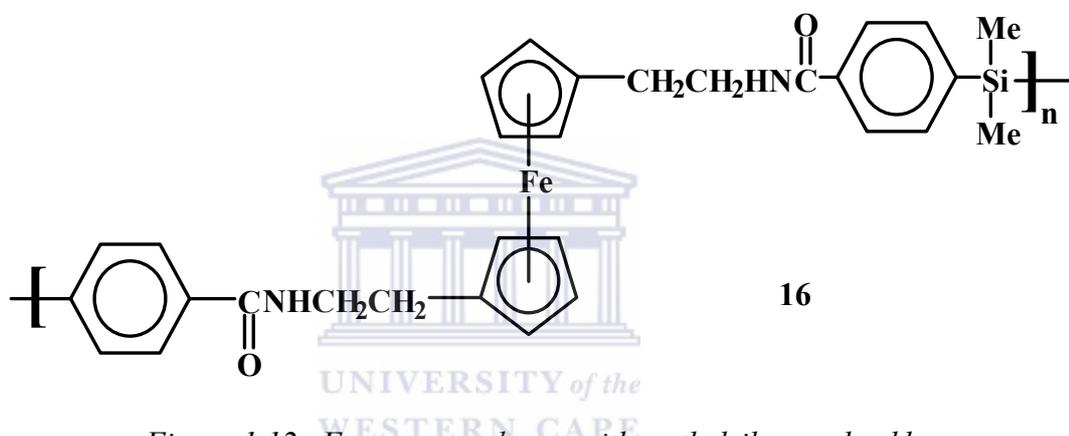


Figure 1.12 Ferrocene polymer with methylsiloxane backbone

Masuda⁴⁹ *et al.* prepared novel organometallic polymers containing Fischer-type amino carbene moieties in the main chain. The bifunctional monomer (Figure 1.13) was prepared following general routes for the preparation of alkoxy-carbenes.

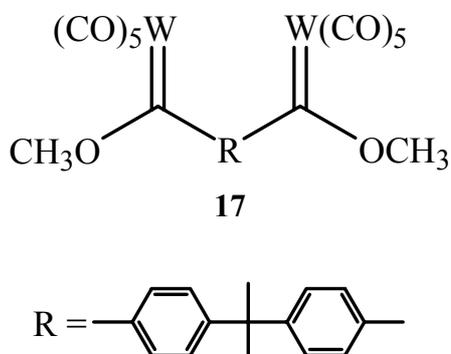


Figure 1.13 Fischer-type amino carbene organometallic complexes

Polymerisation reactions were then performed by reacting **17** with various diamines in dry THF at room temperature. The resulting polymers (Figure 1.14) were stable, soluble in common organic solvents, and had molecular weights ranging from 2200 - 8800, as determined by GPC measurements.

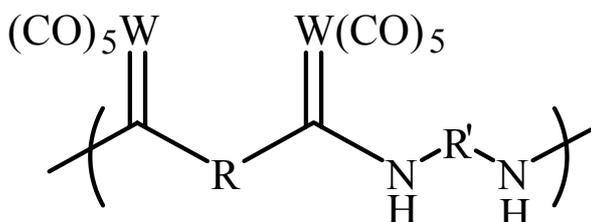


Figure 1.14 Masuda's organometallic carbene polymer

Xue and co-workers⁵⁰ have explored synthesising organometallic coordination polymers containing metal-metal bonds in the backbone. The reaction of the bimetallic monomer **18** (Figure 1.15) with 1,1'-bis(4-pyridylethynyl)-ferrocene **19** (Figure 1.15) in solution at room temperature, yielded an organometallic oligomer with repeat units of 3 (where R = CH₃) or ~14 (where R = CF₃). The new materials exhibited poor solubility in common organic solvents, such that further investigation of their potential electrochemical properties were thwarted.

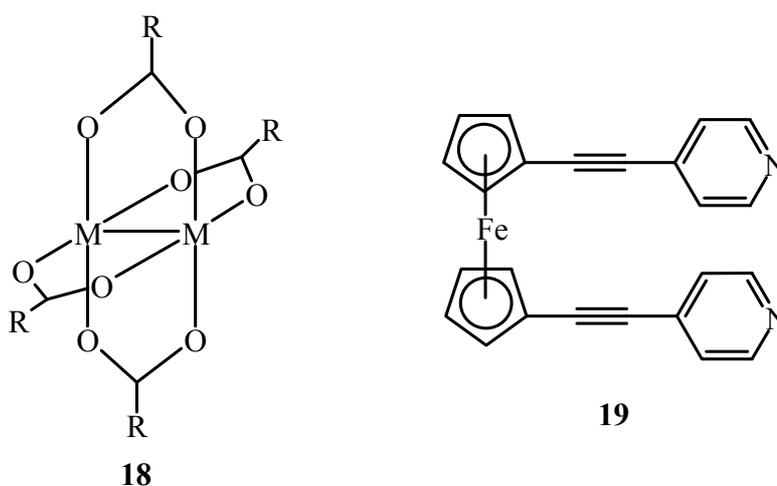
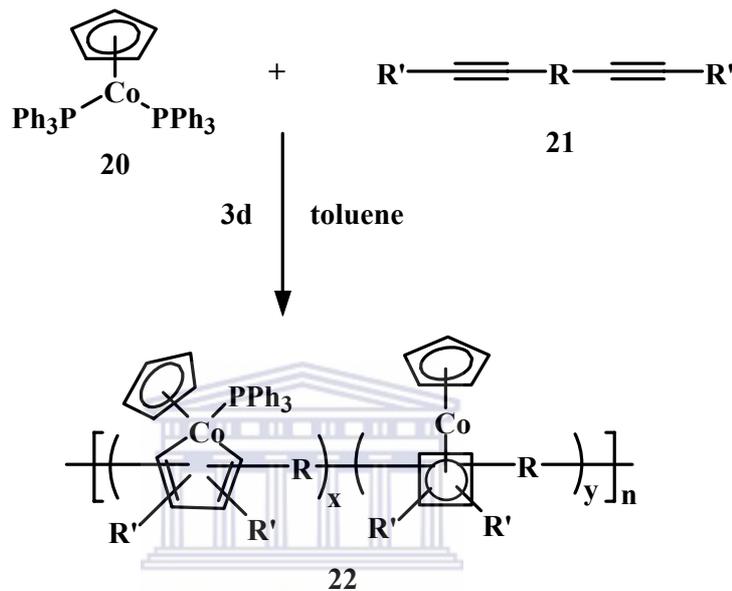


Figure 1.15 Bimetallic tetracarboxylate (**18**) and

1,1'-bis(4-pyridylethynyl)ferrocene (19)

Endo and co-workers⁵¹ have used a very elegant methodology to prepare organocobalt polymers containing cyclopentadienylcobalt moieties in the main chain (Scheme 1.5). Their approach entailed polymerising the cobalt compound shown in the scheme with various diene monomers in toluene for 3 days under nitrogen.



UNIVERSITY of the
WESTERN AUSTRALIA
Scheme 1.5

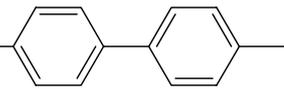
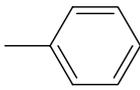
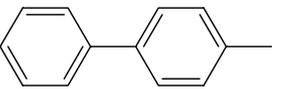
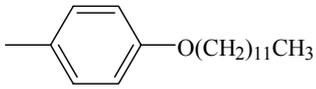
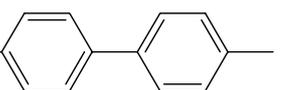
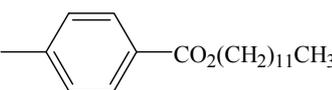
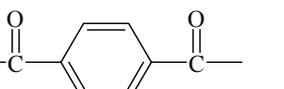
22A	R = 	R' = $-(\text{CH}_2)_n\text{CH}_3$
22B	R = $-(\text{CH}_2)_6-$	R' = 
22C	R = 	R' = 
22D	R = 	R' = 
22E	R = 	R' = $-(\text{CH}_2)_7\text{CH}_3$

Table 1.1 : Alkyl substituents for the various organocobalt polymers

The mechanism, as described in the literature, proposes that the sterically hindered substituent of the acetylene tends to locate in the 2,5-position of cyclopentadienylcobalt moieties. The molecular weights of the polymers are summarised in Table 1.2 below :

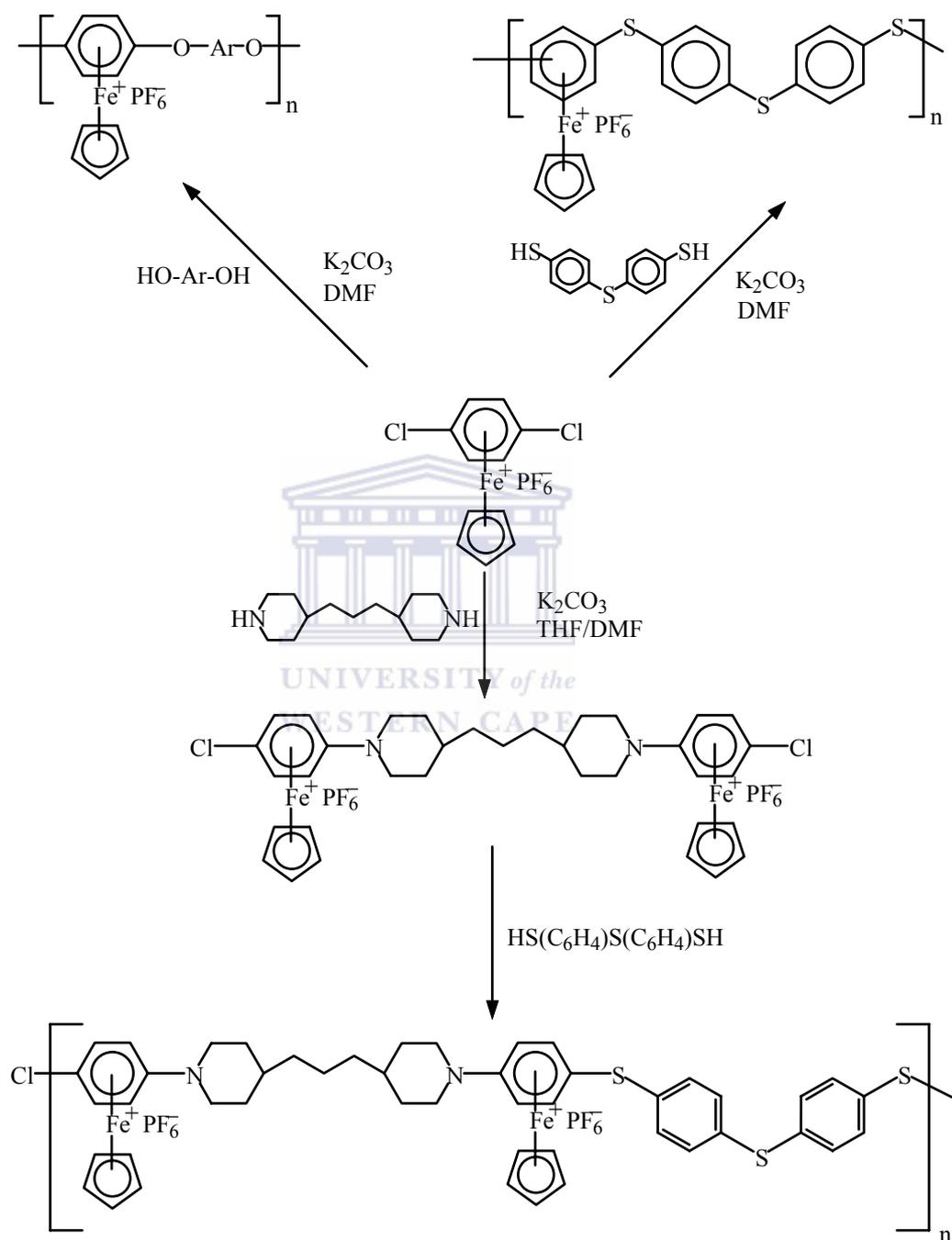
Table 1.2 : Results obtained from the polymerisation experiments

Run	Polymer	Temp. (EC)	Yield (%)	Ratio of x:y	M _n (M _w /M _n)
1	22A	rt	82	79:21	6800 (1.5)
2	22B	rt	89	100:0	2500 (2.3)
3	22C	40	98	82:18	22900 (1.6)
4	22D	60	85	82:18	9100 (1.3)
5	22E	40	81	100:0	8400 (2.0)

It was found that polymer **22A** formed from the diyne, 4,4'-bis(1-propynyl)biphenyl was insoluble in organic solvents. The authors decided to use 4,4'-bis(1-decynyl)biphenyl to improve the solubility of the polymers, and the reaction was found to take place quite successfully at room temperature, to produce organocobalt polymers in high yields (run 1, Table 1.2). Polymerisation runs of diynes bearing aromatic substituents on both sides of the acetylene moieties is seen to require reaction temperatures of 50EC. The only exception is 1,10-diphenyl-1,9-decadiyne, which is observed to polymerise at room temperature (run 2).

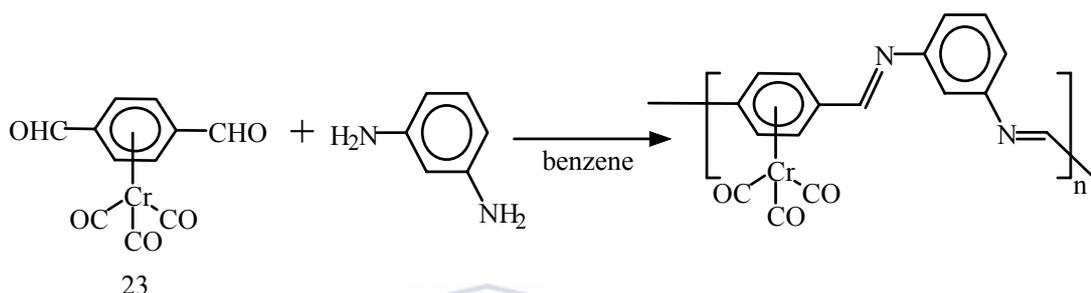
1.2.2 Polymers with metals in the side chain

Polyethers, Polyamines, Polyamides : Abd-El-Aziz and co-workers⁵² prepared organometallic polyethers, thioethers and amines with iron moieties pendant to the polymer backbone. Their strategies involved reacting cyclopentadienyliron complexes of dichloroarenes with various oxygen and sulphur dinucleophiles (Scheme 1.6). These produced soluble organoiron polymers with aliphatic or aromatic bridges. Demetallation studies of the organometallic polymers showed that the corresponding organic polymers have reduced solubility. Abd-El-Aziz has recently reviewed polymers containing arenes with pendent transition metal moieties.^{52(b)}



Scheme 1.6

Polyimines : The first example of an organometallic polyimine was reported by Wright and Lowe-Ma⁵³. These polymers contain chromium tricarbonyl units pendant to a conjugated organic polymer backbone (Scheme 1.7). Their synthetic methodology entailed the condensation of η^6 -terephthaldialdehyde chromium tricarbonyl (**23**) with 1,3-phenylenediamine in benzene for 4h at reflux. The resulting microcrystalline solid is insoluble in common organic solvents. Infrared spectroscopy shows a significant change in the carbonyl bands which is consistent with the formation of a polyimine.



Scheme 1.7

Polyether/imines bearing cyclopentadienyliron moieties have recently been reported by Abd-El-Aziz.⁵² Organometallic polymers of the type shown in Figure 1.16 were synthesised by the reaction of a dialdehyde complex of cyclopentadienyliron with various

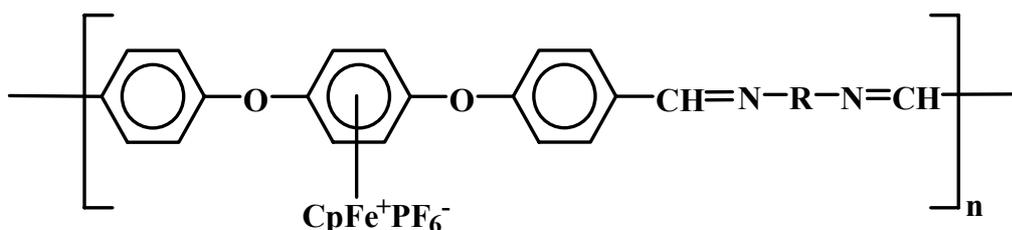
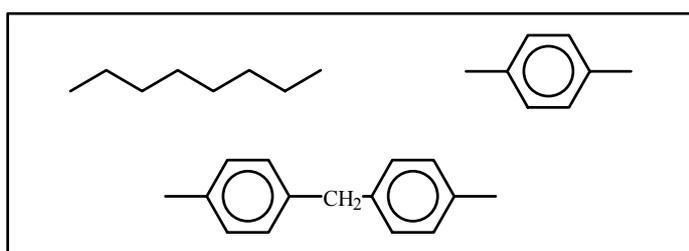


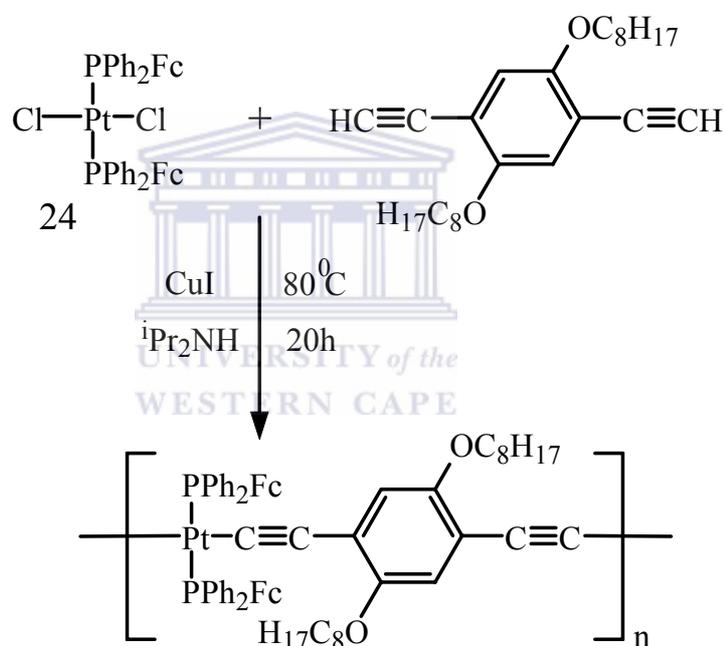
Figure 1.16 Organometallic polyether/imine

aliphatic and aromatic diamines.

R - represents the following:



Other examples of polymers with pendant metals : Long and co-workers⁵⁴ have recently communicated the synthesis of platinum ethynyl polymers with pendant ferrocenyl groups. Polycondensation reactions of **24** and a diethynyl xylene ligand (Scheme 1.8) afforded insoluble polymeric products, as confirmed by solid-state IR spectroscopy. The presence of a broad band ascribed to $\nu(-C/C)$ in the 2100 cm^{-1} region, and the disappearance of the band for $\nu(C/C-H)$ of the ethynyl ligand at 3301 cm^{-1} is diagnostic and alludes to the formation of a polymer chain. The lack of solubility of this compound precluded further spectroscopic characterisation. The authors are currently looking at introducing alkyl groups on the phosphine ligand, to improve the solubility of the polymeric materials.

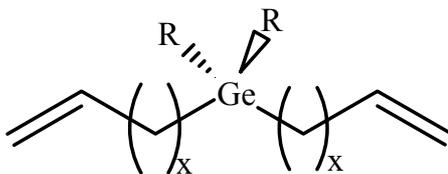


Scheme 1.8

1.2.3 Metal-catalysed polycondensations

New routes to organometallic polymers following condensation methods continue to spark interest in this field of chemistry. Metathesis polycondensation reactions have been used to attain high molecular weight unsaturated organometallic polymers, of the type shown in Figure 1.17. This main chain germanium-containing polymer was synthesized via the

acyclic diene metathesis (ADMET) polymerisation of germanadienes.⁵⁵



$$x = 2 \quad R = C_2H_5$$

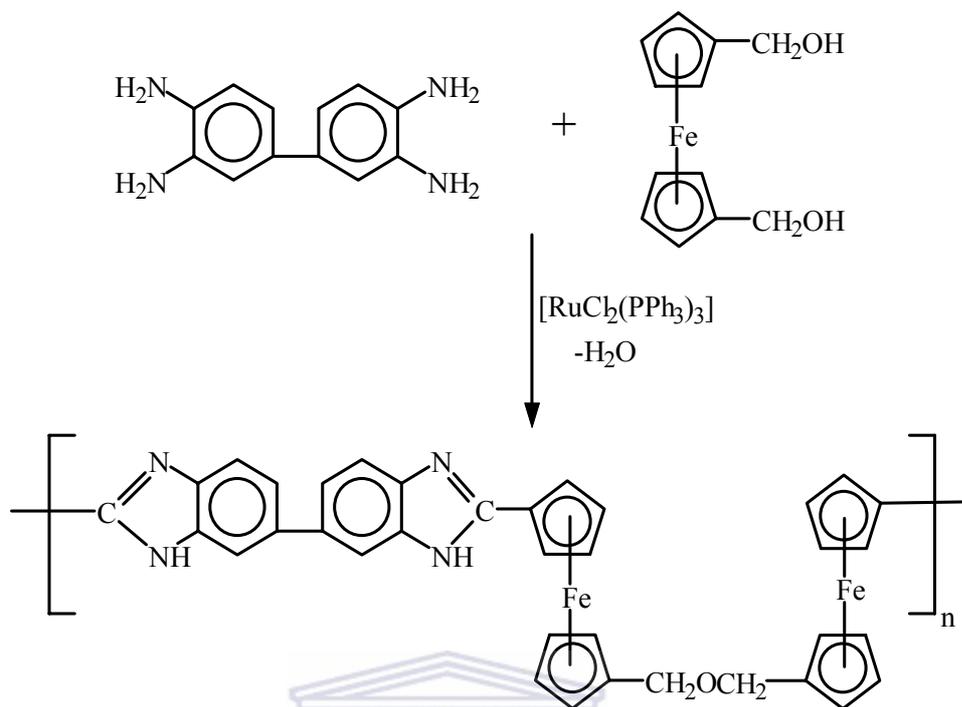
$$x = 3 \quad R = CH_3, C_2H_5$$

Figure 1.17 Germanadiene

This method of polymerisation is a transition metal-catalysed step polycondensation producing an unsaturated polymer from α, ω -dienes. The polycarbogermanes exhibit number average molecular weights (M_n) ranging from 5000 to 18000 g/mol. This method is breaking new ground, as it generates essentially linear structures and can be further functionalised, thorough derivatisation of the olefin moiety.

Ferrocene-containing polymers have formed an integral part of organometallic polymer chemistry over the years, owing to the stability of the ferrocenyl unit. Today, the ferrocene moiety still plays a vital role in polymer chemistry. Polybenzimidazoles containing ferrocenyl groups⁵⁶ were synthesized via the polycondensation reaction of 3,3',4,4'-biphenyltetramine and 1,1'-ferrocenedimethanol (Scheme 1.9). The reaction conducted in the presence of $[RuCl_2(PPh_3)_3]$ catalyst gives the polymer shown in Scheme 1.9, of molecular weight, $M_w = 4.5 \times 10^4$.

Transition metal phthalocyanine and porphyrin complexes play a role in transition metal polymer chemistry, through their utility as photorefractive materials. Photorefractive polymers allow reversible modulation of the refractive index. Wang *et al.*⁵⁷ synthesized photorefractive polymers containing neutral transition metal phthalocyanine and porphyrin complexes via Heck polycondensation reactions. These were shown to have high photorefractive performance, as a result of large photoconductivity.

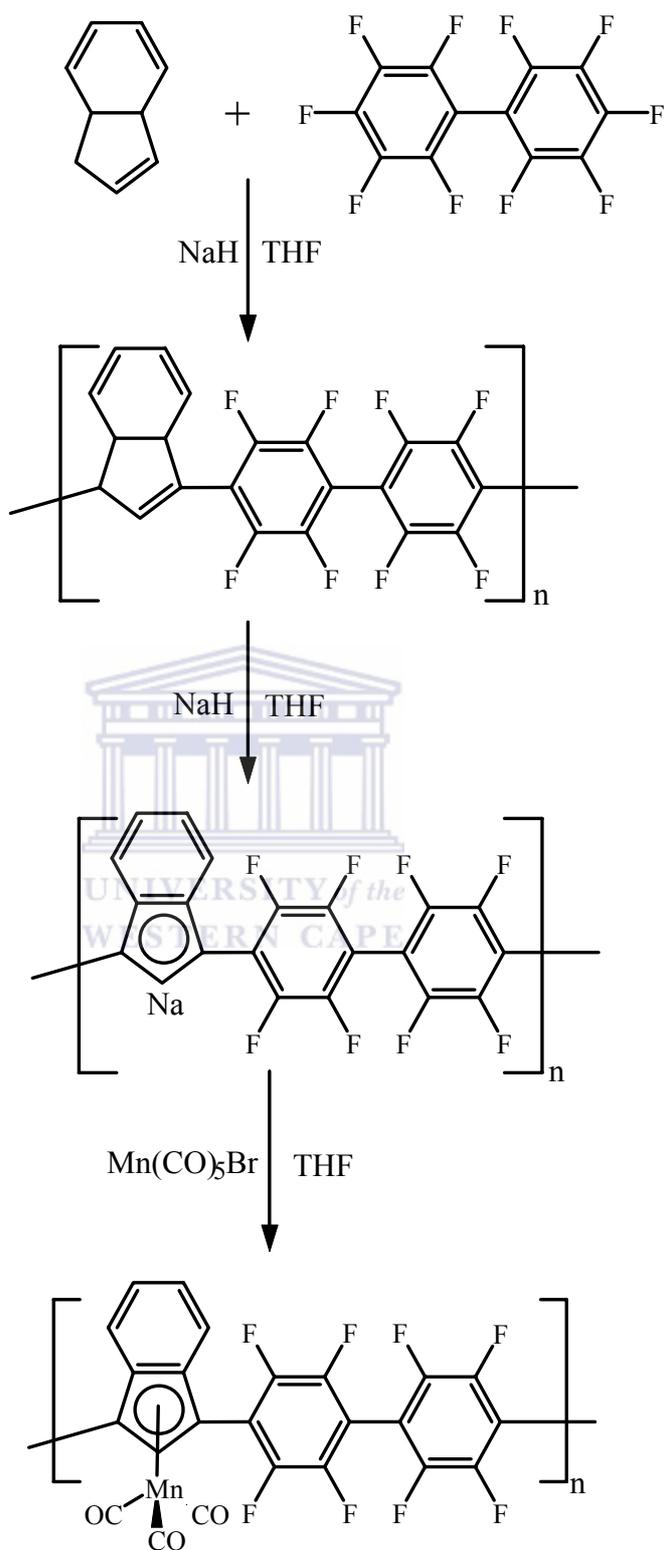


Scheme 1.9

UNIVERSITY of the
WESTERN CAPE

1.3 Functionalisation of preformed organic polymers

As mentioned earlier, the incorporation of metals into the side chain of polymers is often achieved by derivatising a preformed organic polymer. Condensation organometallic polymers formed via this route are very scarce and a few examples were cited previously in this chapter.^{27,28} A more recent article describes the formation of a linear, step-growth polymer by the reaction of indene with one equivalent of decafluorobiphenyl in the presence of excess sodium hydride.⁵⁸ Toluene fractionation of the crude material gave rise to toluene-soluble and toluene-insoluble fractions. Treatment of the toluene-soluble polymer with excess NaH gave the polysodiated polymer, which was further reacted with $\text{Mn}(\text{CO})_5\text{Br}$ to afford the $\text{Mn}(\text{CO})_3$ -functionalised polymer (Scheme 1.10). Supporting characterisation data such as IR and ^1H NMR spectroscopy and microanalysis confirm that most of the indenyl units are metallated.



Scheme 1.10

Bronstein and co-workers⁵⁹ have used polybutadiene and polystyrene-polybutadiene block copolymers as the basis for the synthesis of organometallic polymers. Various organometallic compounds were immobilised on these polymer matrices and their catalytic activities studied. An example of the work performed by these authors is the hydrozirconation of polybutadiene using Schwarz's reagent, $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]$. This gives rise to soluble Zr-C σ -bonded organometallic polymers (Figure 1.18), with zirconium moieties pendant to the polymers backbone.

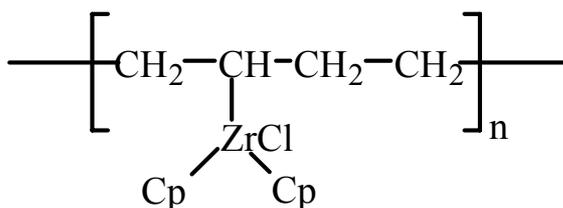
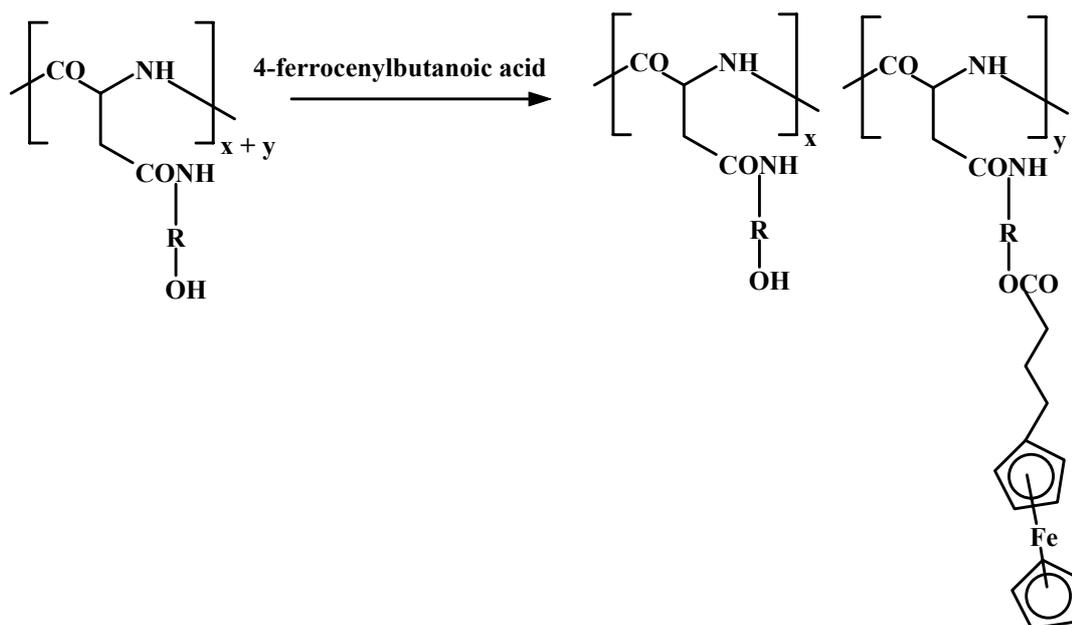


Figure 1.18 σ -bonded Zr polymer

Other metal-containing polymers have similarly been prepared by the interaction of the olefinic groups of the afore-mentioned polybutadiene polymers. The structures of the polymers prepared by this group are based on Fe, Pd, Pt and Rh. The films produced from iron-containing polymers can possibly be used as gas permeable membranes, and the catalytic properties of Pd- and Rh-containing polymers in hydrogenation has been described⁵⁹.

The use of preformed polyamides by Neuse and his group as carrier polymers for ferrocene anchoring was recently communicated.^{28(b)} These polymers were functionalised in their side chains using 4-ferrocenylbutanoic acid, by a simple esterification with the pendant hydroxyl groups (Scheme 1.11). NMR data, together with microanalysis, shows that 30-40% of the ferrocenylation agent was effectively incorporated in the polymer chain. These polymers are water-soluble and will now be implemented in a bioactivity screening program. It is hoped that the results obtained will shed some new light on the study surrounding drug conjugation to polymeric carriers and the effectiveness of drug dissipation in central circulation.



Scheme 1.11

Roviello and co-workers²⁶ used two parent polymers, namely polyvinylchloroacetate (PVCA) and polyvinylpyridine (PVP) to synthesise soluble organometallic polymers. This was achieved by reacting PVCA with a $[\text{Pt}(\text{N}-\text{N})(\text{olefin})]$ complex and by reacting PVP with an appropriate cationic platinum(II) complex, generating polymers of the type shown in Figure 1.19. The geometry around the metal centre is trigonal bipyramidal and the organometallic polymers show good stability, as a result of the coordinatively saturated platinum(II) fragment.

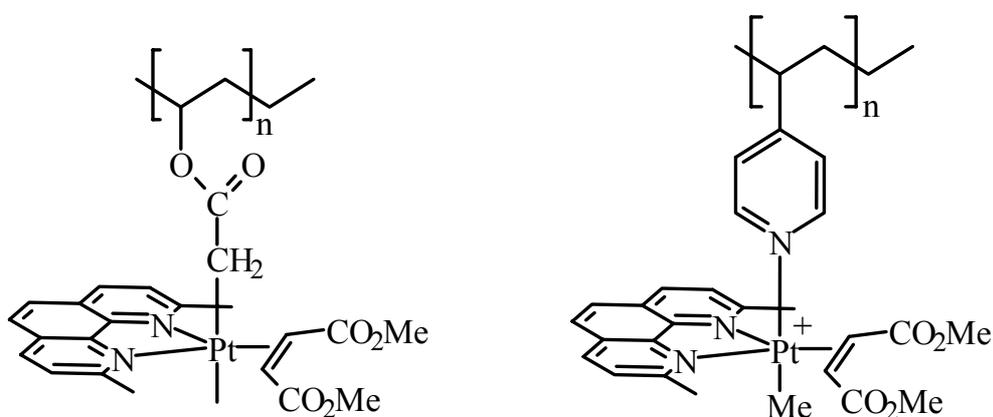


Figure 1.19 Organometallic polymers with pendant coordinatively saturated Pt(II) complexes

1.4 Metal-containing Dendrimers / Metallo dendrimers

The interest in synthesizing highly-branched polymers with well-defined three-dimensional structures has increased at a prolific rate recently. These tree-like polymers are also known by various names, such as dendrimer (Greek: *dendron* = tree), arborol (Latin: *arbor* = tree), cascade molecules or starburst polymers. A number of review articles have been published, that describe their synthesis, characterisation and properties.⁶⁰⁻⁶³

The reason for the interest in dendrimers stems from their molecular architecture, that consists of a rigid highly branched structure, with end groups that lie on the surface of the molecule. A schematic structure of a typical dendrimer is shown in Figure 1.20.

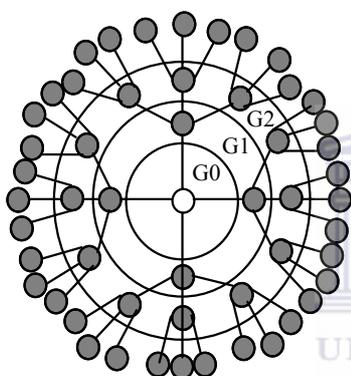


Figure 1.20

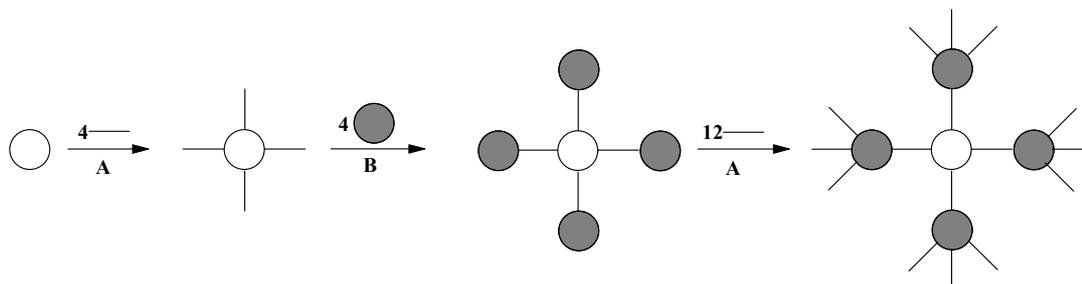
Structure of a typical dendrimer; hollow circle = central core, grey circles = branch point, black circles on the

periphery = end groups, G_n = generation number.

Four branches emanate from the initiator core and each branch contains three branch sites. Repetition of the branch growing process results in a highly branched molecule with an exponentially increasing number of end groups residing on the periphery of the molecule. Each reaction cycle generates a new “generation”.

Dendrimers are synthesized in a stepwise manner, employing either of the two step by step approaches, namely, the divergent method⁶⁴ or the convergent method.⁶⁵

Divergent Method : In this approach the dendrimer grows layer by layer in an outward fashion (Scheme 1.12). The branches are first attached to a polyfunctional core molecule. This is followed by functionalising the ends of the branches so that they can act as reactive

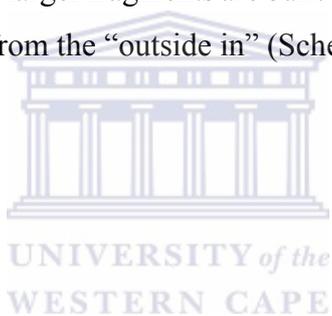


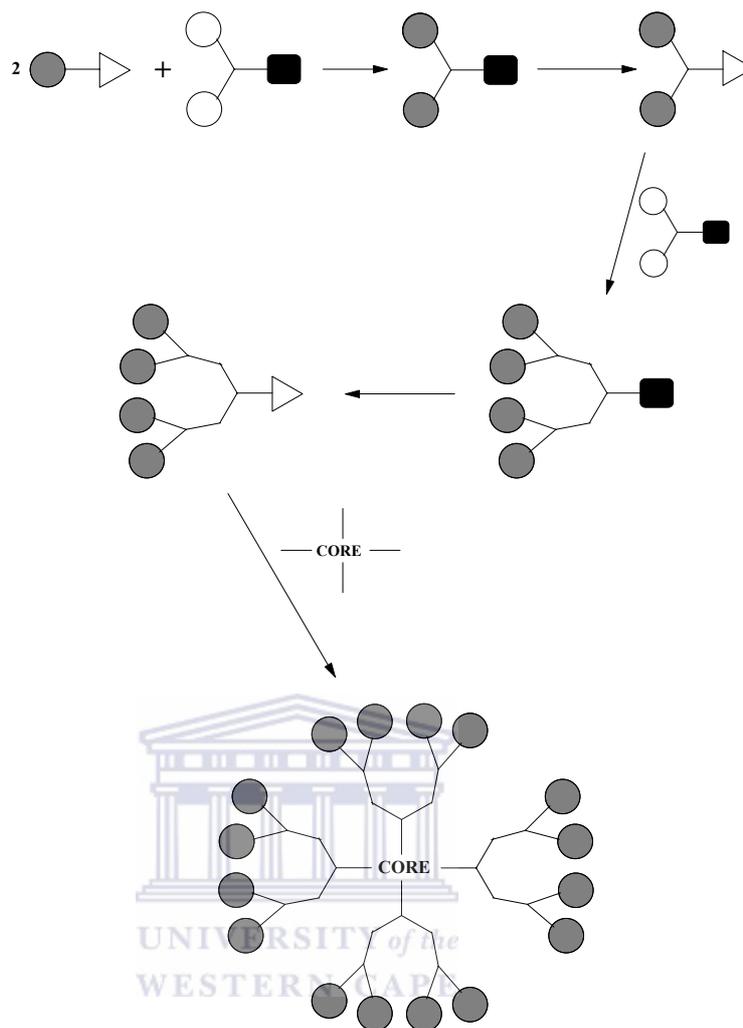
branch points from which new branches can emanate.

Scheme 1.12 Representation of the divergent dendrimer method

A = attachment of branches; B = introduction of new branch points

Convergent Method : The convergent method is basically the reverse of the divergent method. In this approach, larger fragments are built up first and then coupled to a core, that is, the dendrimer grows from the “outside in” (Scheme 1.13).





Scheme 1.13 Building of a dendrimer by the convergent method

The advent of dendrimers and metal-containing dendrimers has also brought with it a myriad of potential new applications.⁶⁶⁻⁶⁷ For example, polyamidoamine (PAMAM) dendrimers are used as carriers for DNA, peptide antigens and agrochemicals.⁶⁸ Metal-containing dendrimers have also been cited as active catalysts⁶⁹⁻⁷², such as their use in the addition reactions of polyhalogenalkanes to carbon-carbon double bonds.⁷³ In addition, metal-containing dendrimers also have potential applications in host-guest chemistry, liquid-crystals, ion exchange materials and many more.⁷⁴⁻⁷⁶

1.5 Summary / Conclusions

The preceding discussion serves to inform the reader of the field of research concerning

the incorporation of transition metal moieties into polymer structures by polycondensation and into metal-containing dendrimers. As can be seen from the review, the work done on the polycondensation of bifunctional organometallic monomers is rare and the materials isolated are often not very soluble or are not well characterised. There is a prolific interest in this field, since an increased development in the field of synthetic organometallic chemistry, is coupled to the application of the new materials in various fields ranging from catalysis to optical applications. This has prompted us to conduct further research into the synthesis of metal-containing polymers produced through polycondensation methods. We have also extended our research to the synthesis of metal-containing dendrimers or 3-D polymer networks and have further studied their potential utility as ethylene polymerisation and Heck cross-coupling catalyst precursors. This is discussed in detail in the ensuing chapters.

1.6 Scope and Objectives of the Thesis

There is a prolific development in the use of organometallic and inorganic compounds. These compounds are increasingly being used as precursors to new materials, rather than as materials in their own right. The fields of applications are commonly catalysis and as reagents for organic synthesis. The objectives of the research described in this thesis are to synthesize multi-nuclear metal-containing polymers (linear) and dendrimers (star-shaped), and study their potential utility in the field of catalysis.

Metal-containing polymers : The focus of this research deals with a series of projects under the umbrella of condensation organometallic polymer chemistry. There are two basic routes to the formation of metal-containing polymers. One approach has been to develop bifunctional organometallic monomers capable of undergoing copolymerisation reactions with organic monomers. A second approach involves derivatizing preformed organic polymers with organometallic or inorganic complexes.

Metal-containing dendrimers : A number of dendrimers containing metals have been reported. Our approach centred on functionalising the periphery of commercially available dendrimers. The goal of this work was to form terminal diimine ligands on the periphery of the dendrimer, in order to perform subsequent complexation reactions with transition metals. This would give rise to new metallodendrimers, which would be fully characterized. Their applicability as ethylene polymerisation and Heck cross-coupling

catalyst precursors would then be studied and the properties of the resulting products analyzed. Three generations of DAB dendrimers were also prepared with salicylaldimine ligands on the periphery. The rationale behind this study was to functionalise the new dendrimers with various metals, using different metal acetates as the source.

1.7 Organisation of the Thesis

This thesis is divided into two sections. Section **I**, which encompasses chapters **2** and **3** deals with the synthesis and characterisation of metal-containing polymers employing polycondensation routes. Section **II** comprises chapters **4** and **5**, and deals with the synthesis of metal-containing dendrimers and their application in catalysis.

Chapter **1** provides an overall introduction and describes the scope of the thesis. In this chapter, the synthesis of metal-containing polymers through various condensation methodologies is described. These refer mainly to linear metal-containing compounds. A brief introduction to dendrimers is also given, emphasizing the shift from linear to more star-shaped or branched metal-containing polymers.

Chapter **2** describes the synthesis and characterisation of new organometallic diols of the type $[ML_n(CH_2)_3O-\{2,6(CH_2OH)_2-4-CH_3-C_6H_2\}]$, where $M = Fe, Re$. These compounds were prepared using 2,6-bis(hydroxymethyl)-*p*-cresol as the key reagent, to incorporate a bifunctional moiety. The diols were used in solution polycondensation reactions with organic comonomers to produce metal-containing polyesters and polyurethanes.

Chapter **3** reports the alternative approach to preparing metal-containing polymers. Here the synthesis of organic polyesters bearing terminal vinyl groups in pendant side chains are described. Hydrozirconation reactions with these polymers were attempted and the results are discussed in this chapter. In addition, organic polyimines were prepared following conventional condensation polymerisation techniques. The subsequent complexation reactions with $PdCl_2(COD)$ are described.

Chapter **4** describes the synthesis and characterisation of three new metallodendrimers. This was achieved by first functionalizing the periphery of commercial samples of the

DAB dendrimer with pyridylimino groups. The metallodendrimers were synthesized by reacting the functionalized DAB dendrimer with PdCl₂(COD). In addition, three salicylaldimine DAB dendrimers were prepared by reacting the DAB dendrimer with salicylaldehyde. The salicylaldimine ligands were further reacted with various metal acetates of the general formula, M(OAc)₂.4H₂O (M = Ni, Cu) and FeCl₂.4H₂O.

In Chapter 5, catalytic polymerisation reactions, using the pyridylimine metallodendrimers discussed in Chapter 4, are described. Their usefulness as ethylene polymerisation catalysts and the characterisation of the polymerisation products is also discussed in this chapter. The application of the first-generation palladium metallodendrimer as a Heck cross-coupling catalyst precursor is also described.

Chapter 6 gives an overview of the work and lists the conclusions.



1.8 References

1. C.U. Pittman, Jr., C.E. Carraher, Jr., J.E. Sheats, M.D. Timken and M. Zeldin, *Inorganic and Metal-Containing Polymeric Materials*, 1990, 1.
2. J.E. Sheats, C.U. Pittman, Jr. and C.E. Carraher, Jr, *Chem. Br.*, 1984, **20**, 709.
3. C.E. Carraher, Jr., *J. Chem. Ed.*, 1981, **58**, 921.
4. R.L. Rawls, *C&EN*, 1987, **65**, 29.
5. R. Deschenaux, V. Izvolenski, F. Turpin, D. Guillon and B. Heinrich, *Chem Commun.*, 1996, 439.
6. H.J. Coles, S. Meyer, P. Lehmann, R. Deschenaux and I. Jauslin, *J. Mater. Chem.*, 1999, **9**, 1085.
7. L. Oriol and J.L. Serrano, *Adv. Mater.*, 1995, **7**, 348.
8. T. Yamamoto and N. Hayashida, *Reactive and Functional Polymers*, 1998, **37**, 1.
9. R.H. Grubbs and S.H. Su, *Organometallic Polymers*, Academic Press, New York, 1978, 129.
10. K. Kaneda and T. Mizugaki, *Organometallics*, 1996, **15**, 3247.
11. M.J. Sundell and J.H. Nasman, *Chemtech*, 1993, 16.
12. I. Manners, *Chem. Br.*, 1996, **32**, 46.
13. J.E. Sheats, C.E. Carraher, Jr., C.U. Pittman, Jr. and M. Zeldin, *Macromol. Symp.*, 2000, **156**, 79.
14. M.L. Turner, *Annu. Rep. Prog. Chem., Sect. A*, 1999, **95**, 453.
15. J.C. Lai, T.D. Rounsefell and C.U. Pittman, Jr., *J. Polym. Sci.: Part A-1*, 1971, **9**, 651.
16. A.K. Saha and M.M. Hossain, *J. Organomet. Chem.*, 1993, **445**, 137.
17. S.S. Kher and T.A. Nile, *Transition Met. Chem.*, 1991, **16**, 28.
18. S. Achar, R.J. Puddephatt and J.D. Scott, *Can. J. Chem.*, 1996, **74**, 1983.
19. S.F. Mapolie, J.R. Moss and G.S. Smith, *J. Inorg. Organomet. Polym.*, 1997, **7**, 233.
20. C.E. Carraher, Jr., *Organometallic Polymers*, Academic Press, New York, 1978, 79.
21. K.E. Gonsalves and X. Chen (Eds. A. Togni and T. Hayashi), *Ferrocenes from Catalysis to Materials Science*, VCH Publishers, 1994, 497.
22. I. Manners, *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 1603.

23. I. Manners, *Can. J. Chem.*, 1998, **76**, 371.
24. P. Nguyen, P. Gómez-Elipé, and I. Manners, *Chem. Rev.*, 1999, **99**, 1515.
25. S. Kelch and M. Rehahn, *Macromolecules*, 1999, **32**, 5818.
26. B. Panunzi, A. Roviello, F. Ruffo and A. Vivo, *Inorg. Chim. Acta*, 1998, **281**, 141.
27. C.U. Pittman, Jr. and R.F. Felis, *J. Organomet. Chem.*, 1974, **72**, 389.
28. (a) L.B. Chen, J.X. Jin, J. Lin, H.S. Chen, and X.X. Lin, *Makromol. Chem., Rapid Commun.*, 1987, **8**, 187;
(b) E.W. Neuse, M.G. Meirim, D.D. N'Da and G. Caldwell, *J. Inorg. Organomet. Polym.*, 1999, **9**, 221;
(c) C. Huber, F. Bangerter, W.R. Caseri and C. Weder, *J. Am. Chem. Soc.*, 2001, **123**, 3857.
29. F.W. Knobloch and W.H. Rauscher, *J. Polym. Sci.*, 1961, **54**, 651.
30. C.U. Pittman, Jr., *J. Polym. Sci., Part A-1*, 1968, **6**, 1687.
31. C.U. Pittman, Jr., *ChemTech*, 1971, 416.
32. J.E. Sheats, *Organometallic Polymers*, Academic Press, New York, 1978, 87.
33. E.W. Neuse, *Organometallic Polymers*, Academic Press, New York, 1978, 95.
34. C. E. Carraher, Jr., *In Interfacial Synthesis*; F. Millich, C.E. Carraher, Jr., Eds., Marcel Dekker, Vol. II, 1977, 367.
35. K.E. Gonsalves and M.D. Rausch, *J. Polym. Sci., Part A : Polym. Chem.*, 1988, **26**, 2769.
36. K.E. Gonsalves, L. Zhan-ru and M.D. Rausch, *J. Am. Chem. Soc.*, 1984, **106**, 3862.
37. K.E. Gonsalves, R.W. Lenz and M.D. Rausch, *Appl. Organomet. Chem.*, 1987, **1**, 81.
38. K.E. Gonsalves and M.D. Rausch, *Inorganic and Organometallic Polymers*, ACS Symposium Series, 1988, 437.
39. S.A. Fino, K.A. Benwitz, K.M. Sullivan, D.L. LaMar, K.M. Stroup, S.M. Giles, G.J. Balaich, R.M. Chamberlin and K.D. Abney, *Inorg. Chem.*, 1997, **36**, 4604.
40. I.L. Rozhanskii, I. Tomita and T. Endo, *Polymer*, 1999, **40**, 1581.
41. A.Z. Al-Rubaie and S.A.N. Al-Jadaan, *Appl. Organomet. Chem.*, 1998, **12**, 79.
42. C.U. Pittman, Jr. and M.D. Rausch, *Pure & Appl. Chem.*, 1986, **58**, 617.
43. S.C. Tenhaeff and D.R. Tyler, *Organometallics*, 1991, **10**, 473.
44. S.C. Tenhaeff and D.R. Tyler, *Organometallics*, 1992, **11**, 1466.

45. G.F. Nieckarz and D.R. Tyler, *Inorg. Chim. Acta*, 1996, **242**, 303.
46. G.F. Nieckarz, J.J. Litty, D.R. Tyler, *J. Organomet. Chem.*, 1998, **554**, 19.
47. W.J. Patterson, S.P. McManus and C.U. Pittman, Jr, *J. Polym. Sci., Polym. Chem. Ed.*, 1974, **12**, 837.
48. C.M. Casado, M. Moran, J. Losada and I. Cuadrado, *Inorg. Chem.*, 1995, **34**, 1668.
49. (a) R. Nomura, K. Watanabe and T. Masuda, *Macromolecules*, 2000, **33**, 1936;
(b) R. Nomura, K. Watanabe and T. Masuda, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1999, **40**, 80.
50. (a) W.-M. Xue, F.E. Kühn, E. Herdtweck and Q. Li, *Eur. J. Inorg. Chem.*, 2001, 213;
(b) W.-M. Xue and F.E. Kühn, *Eur. J. Inorg. Chem.*, 2001, 2041;
(c) W.-M. Xue, F.E. Kühn and E. Herdtweck, *Polyhedron*, 2001, **20**, 791.
51. J.C. Lee, A. Nishio, I. Yomita and T. Endo, *Macromolecules*, 1997, **30**, 5205.
52. (a) A.S. Abd-El-Aziz, E.K. Todd and G.Z. Ma, *J. Polym. Sci.: Part A: Polym. Chem.*, 2001, **39**, 1216;
(b) A.S. Abd-El-Aziz, *Coord. Chem. Rev.*, 2002, **233-234**, 177.
53. M.E. Wright and C.K. Lowe-Ma, *Inorg. Chim. Acta*, 1995, **232**, 223.
54. N.J. Long, A.J.P. White, D.J. Williams and M. Younus, *J. Organomet. Chem.*, 2002, **649**, 94.
55. F.J. Gómez and K.B. Wagener, *J. Organomet. Chem.*, 1999, **592**, 271.
56. I. Yamaguchi, K. Osakada, T. Yamamoto and M. Katada, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 2557.
57. Q. Wang, L. Wang, J. Yu and L. Yu, *Adv. Mater.*, 2000, **12**, 974.
58. P.A. Deck and C.R. Maiorana, *Macromolecules*, 2001, **34**, 9.
59. (a) L.M. Bronstein and P.M. Valetskii, *Polym. Sci.*, 1993, **35**, 1585;
(b) L.M. Bronstein, M.V. Seregina, O.A. Platonova, Y.A. Kabachii, D.M. Chernyshov, M.G. Ezernitskaya, LV. Dubrovina, T.P. Bragina and P.M. Valetsky, *Macromol. Chem. Phys.*, 1998, **199**, 1357.
60. G.R. Newkome, C.N. Moorefield and F. Vögtle, *Dendritic Molecules : Concepts, Syntheses, Perspectives*, VCH Publishers, Inc., New York, 1996, 1.
61. G.R. Newkome, E. He and C.N. Moorefield, *Chem. Rev.*, 1999, **99**, 1689.
62. I. Cuadrado, M. Morán, C.M. Casado, B. Alonso and J. Losada, *Coord. Chem.*

- Rev., 1999, **193-195**, 395.
63. M.A. Hearshaw and J.R. Moss, *Chem. Commun.*, 1999, 1.
64. D.A. Tomalia, A.M. Naylor and W.A. Goddard,III, *Angew. Chem. Int. Ed. Engl.*, 1992, **31**, 1571.
65. C.J. Hawker and J.M.J. Fréchet, *J. Am. Chem. Soc.*, 1992, **114**, 8405.
66. R.M. Crooks, B.I. Lemon III, L.Sun, L.K. Yeung and M. Zhao, *Topics in Curr. Chem.*, 2001, **212**, 81.
67. D. Astruc and F. Chardac, *Chem. Rev.*, 2001, **101**, 2991.
68. R.F. Barth, D.M. Adams, A.H. Soloway, F. Alam and M.V. Darby, *Bioconjugate Chem.*, 1994, **5**, 58.
69. K. Vassilev, J. Kreider, P.D. Miller, W.T. Ford, *React. Funct. Polym.*, 1999, **41**, 205.
70. R.van Heerbeek, P.C.J. Kramer, P.W.N. van Leeuwen and J.N.H. Reek, *Chem. Rev.*, 2002, **102**, 3717.
71. L.J. Twyman, A.S.H. King and I.K. Martin, *Chem. Soc. Rev.*, 2002, **31**, 69.
72. I. Anggurell, G. Muller, M. Rocamora, O. Rossell and M. Seco, *J. Chem. Soc., Dalton Trans.*, 2003, 1194.
73. J.W.J. Knapen, A.W. van der Made, J.C. de Wilde, P.W.N.M. van Leeuwen, P.Wijkens, D.M. Grove and G. van Koten, *Nature*, 1994, **372**, 659.
74. J.F.G.A. Jansen, E.M.M. de Brabander-van Berg and E.W. Meijer, *Science*, 1994, **266**, 1226.
75. A. Cherestes and R. Engel, *Polymer*, 1994, **35**, 3343.
76. Y.H. Kim, *J. Am. Chem. Soc.*, 1992, **114**, 4947.

CHAPTER 2

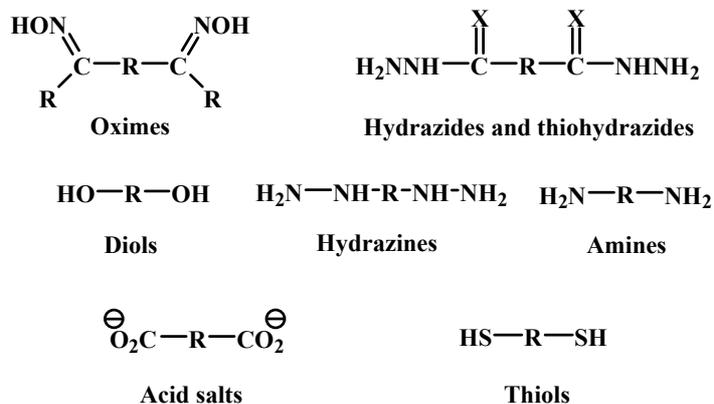
The Synthesis and Characterisation of Metal-containing Polyesters and Polyurethanes

2.1 Introduction

The field of condensation organometallic polymers is a relatively neglected area of research and little attention has been directed to the synthesis of these types of polymers. This highlights the need for the construction of new organometallic monomers and perhaps the modification of existing systems.

The previous chapter has provided a background to these types of polymers, where the metals and their associated ligands are either pendant to the polymer backbone¹⁻³ or in the main chain.⁴⁻⁷ Certain of their chemical and physical properties⁸⁻⁹ and potential applications¹⁰⁻¹³ have also been described. Synthetic routes for preparing bifunctional organometallic monomers are often not straightforward, and vary from compound to compound. Much endeavour is often required to prepare M-C σ - and π -bonded organometallic monomers for polymerisation. Organometallic monomers for condensation polymerisation often contain an organometallic halide, which reacts with bifunctional (or polyfunctional) Lewis bases. Reactants that have been typically used are shown in Chart 2.1.

Chart 2.1 *Lewis Bases Employed in the Synthesis of Condensation Organometallic Polymers*



This chapter reports the preparation of some new organometallic polyesters and polyurethanes. Firstly, the synthesis and characterisation of new organometallic monomers that contain polymerizable bifunctional groups is described. Our research efforts have focussed on using 2,6-bis(hydroxymethyl)-*p*-cresol as the key reagent to prepare some new transition metal-containing bifunctional monomers (Figure 2.1), for further polycondensation reactions. The syntheses of these monomers were based on the organic coupling reactions employed by Fréchet and co-workers.¹⁴⁻¹⁵ Secondly, polycondensation reactions were carried out in solution at room temperature to produce new organometallic polyesters and polyurethanes. We have published preliminary results of this work.¹⁶

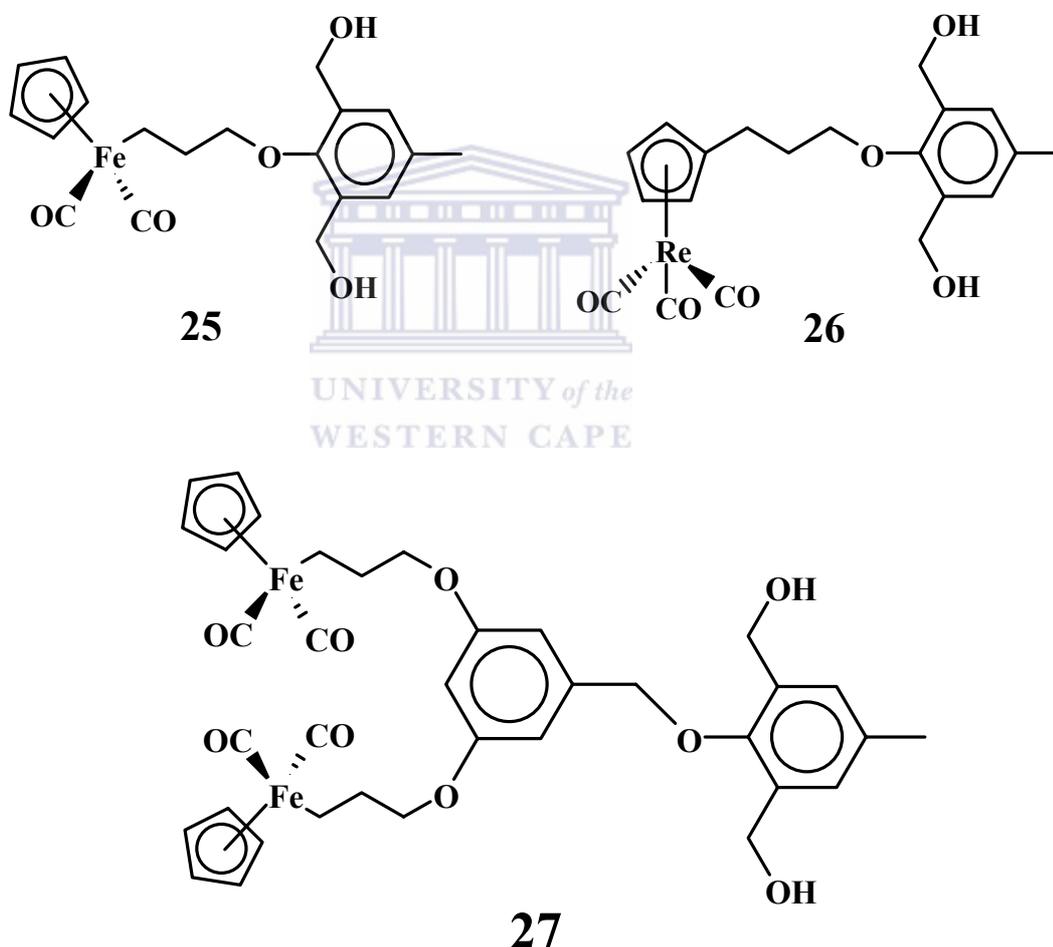


Figure 2.1 Organometallic Bifunctional Monomers

2.2 Results and Discussion

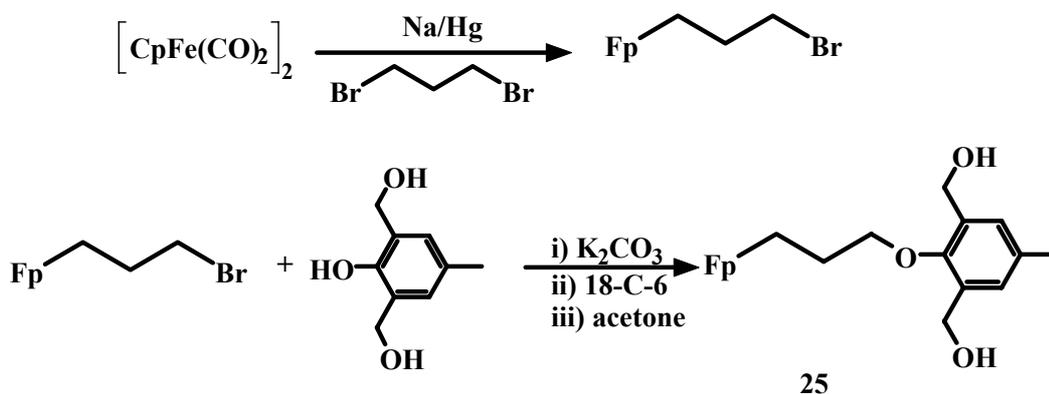
2.2.1 Monomer Syntheses

Preparation

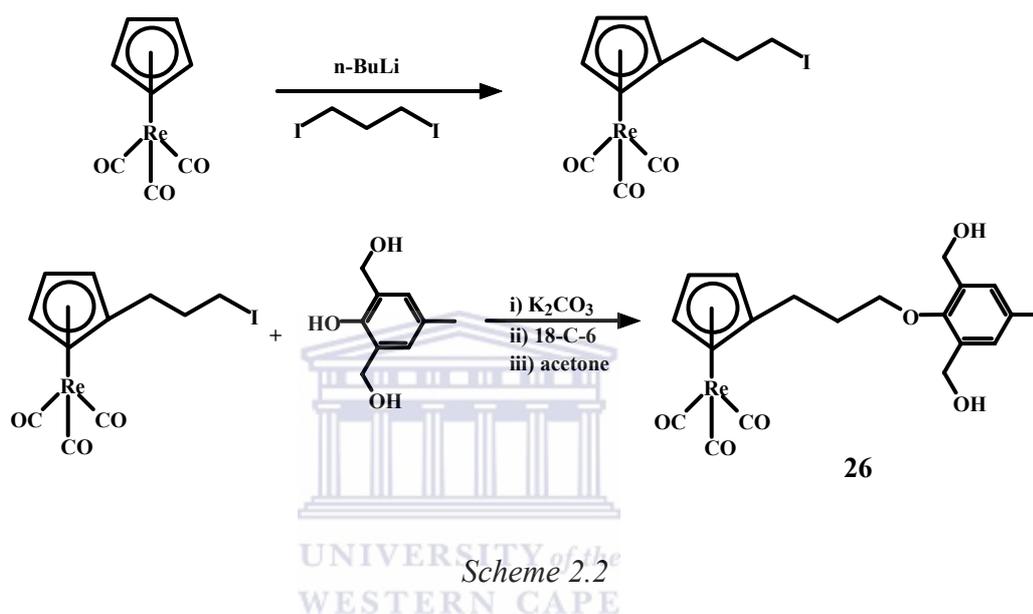
The organometallic monomers **25**, **26** and **27**, and the organic monomer **28** were synthesised using methods analogous to those reported previously by Fréchet and co-workers.¹⁴⁻¹⁵ Details of the synthetic routes for **25**, **26** and **27** are outlined in Schemes 2.1, 2.2 and 2.3 respectively. We used 2,6-bis(hydroxymethyl)-*p*-cresol as the key reagent to incorporate a bifunctional moiety into our organometallic monomers. These methods generally entailed reacting a transition metal haloalkyl complex with 2,6-bis(hydroxymethyl)-*p*-cresol in the presence of K_2CO_3 and 18-crown-6. In this way, we have prepared both M-C σ -bonded (**25**, **27**) and M-C π -bonded (**26**) organometallic monomers.

Monomer **25** represents the M-C σ -bonded compound in our studies. This was achieved by first preparing the precursor $Fp(CH_2)_3Br$. This compound, previously reported by Moss¹⁷, was synthesised by reacting the iron anion $Na[CpFe(CO)_2]$ *in situ* with 1,3-dibromopropane (Scheme 2.1). $Fp(CH_2)_3Br$ is then refluxed with 2,6-bis(hydroxymethyl)-*p*-cresol in acetone, in the presence of K_2CO_3 and 18-crown-6. Purification by column chromatography yielded a brown solid (37%). This solid is stable in air, but decomposes in solution, in the absence of nitrogen.

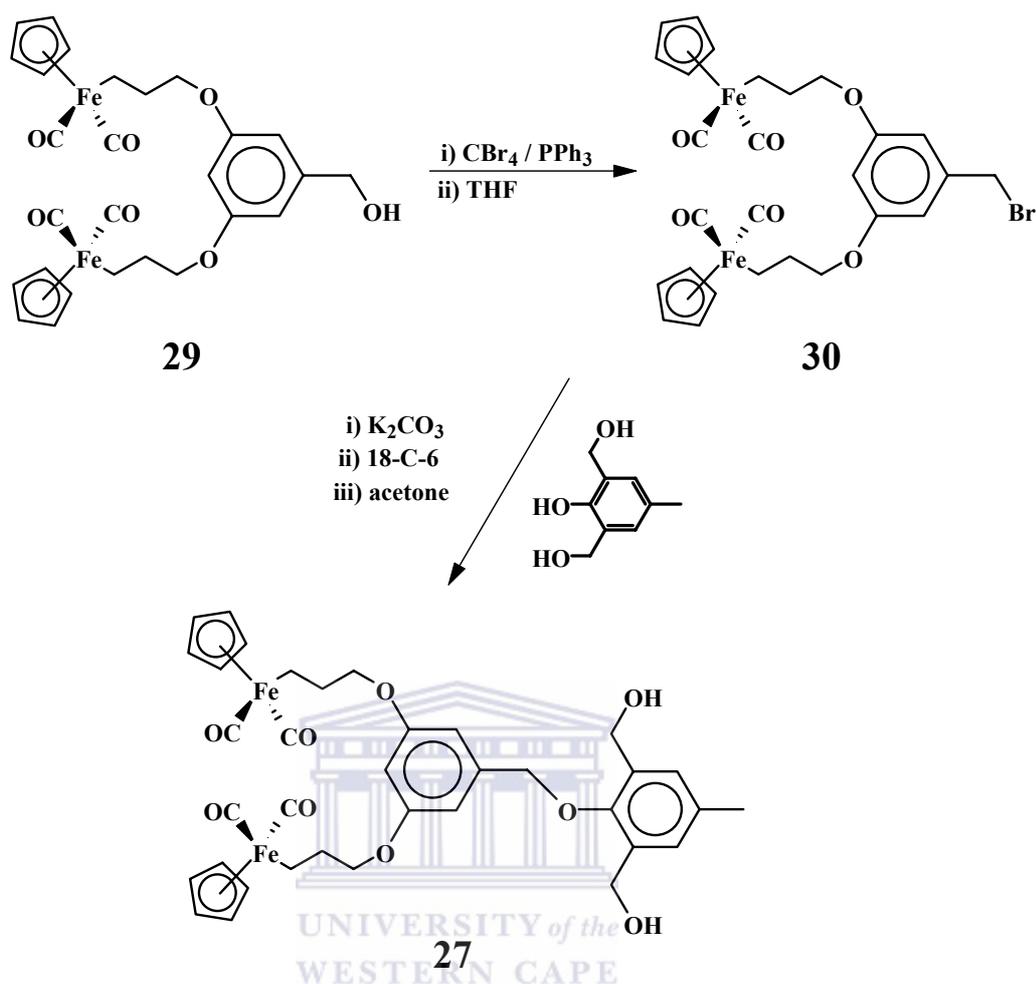
Scheme 2.1



The synthesis of monomer **26** followed a similar methodology to that of monomer **25**. Initially, the rhenium iodo-alkyl precursor was prepared, as per literature procedure.¹⁸ Starting from $\text{CpRe}(\text{CO})_3$, the Cp ring is lithiated with *n*-BuLi at -78°C and then 1,3-diiodopropane added (Scheme 2.2). The iodopropyl complex was then reacted with 2,6-bis(hydroxymethyl)-*p*-cresol in acetone, again in the presence of K_2CO_3 and 18-crown-6. This afforded monomer **26** as a stable, white solid in high yield (85%).



We explored reactions of the binuclear complex **30** (see Scheme 2.3) with the key reagent, 2,6-bis(hydroxymethyl)-*p*-cresol in acetone, to produce the binuclear, bifunctional organometallic monomer **27**. The organometallic benzyl bromide **30** and its precursor **29**, were synthesized by the method of Moss and co-workers¹⁹⁻²², and were used to build up organometallic dendritic wedges. The complex **27** was successfully synthesized (as determined by ^1H NMR analysis), with a small amount of impurities, that were difficult to remove. These impurities originate from the use of the unstable precursor **30**. Moss *et al* attributed this to the instability of the iron-alkyl bond of the benzyl bromide complex. Sigma-bonds between transition metals and carbon are, in general, kinetically unstable, and their stability depends largely on the kind of central metals, alkyl groups and other ancillary ligands bonded to the metal.²³



Scheme 2.3

Our interest in forming polynuclear organometallic compounds by polycondensation reactions, led us to study the effects of metal-containing moieties on the polycondensation process. Hence, it was decided to prepare the model organic monomer **28** (Figure 2.2). The reason for choosing this monomer was that the terminal $-\text{CH}_3$ group is isolobal with the organometallic moiety $\text{CpFe}(\text{CO})_2$. Thus, the organometallic and organic structures of **25** and **28** respectively can be jointly considered under conditions for polycondensation. Monomer **28** was easily prepared, albeit in low yields, by reacting 1-bromobutane with 2,6-bis(hydroxymethyl)-*p*-cresol, in the presence of K_2CO_3 and 18-crown-6.

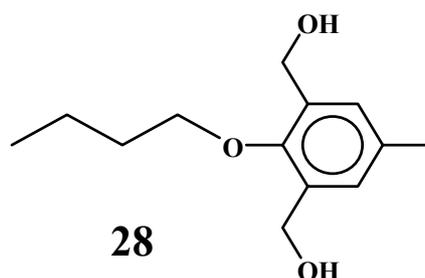


Figure 2.2 Model organic bifunctional monomer 28

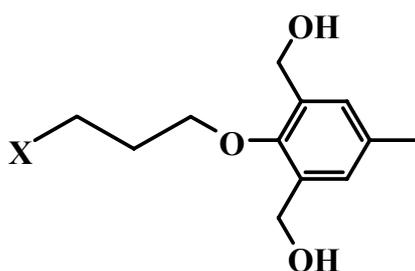
2.2.2 Characterisation of the Bifunctional Monomers

IR Spectra

The IR spectra of the iron monomers **25** and **27** show two strong $\nu(\text{CO})$ bands for the terminal carbonyl ligands at 2005 cm^{-1} and 1945 cm^{-1} . These frequencies are similar to those of other $\text{CpFe}(\text{CO})_2\text{R}$ compounds and are in good agreement with the proposed structure. The rhenium analogue **26** has two strong $\nu(\text{CO})$ bands, one a sharp peak at 2020 cm^{-1} and the other a broad one at 1923 cm^{-1} . These resemble frequencies for compounds of the general formula $[(\eta^5\text{-C}_5\text{H}_4\text{-R})\text{Re}(\text{CO})_3]$. Details and complete IR data have been summarised in the Experimental, Section 2.4.

^1H and ^{13}C NMR Spectroscopy

The ^1H and ^{13}C NMR data for the monomers (**25-28**) are given in Section 2.4. These compounds exhibit similar resonances, characteristic of the diol moiety (Figure 2.3) that is present in the structure.

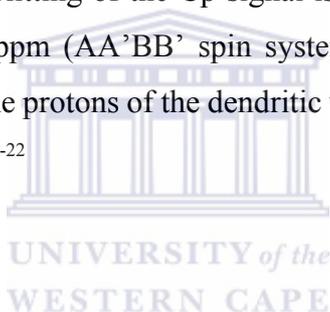


- $\text{X} = \text{CpFe}(\text{CO})_2$ (25)
 $(\text{Cp-R})\text{Re}(\text{CO})_3$ (26)
 Fp-dendr (27)
 CH_3 (28)

Figure 2.3 Bifunctional moiety

The peaks for the aliphatic $-\text{CH}_2-$ protons adjacent to the metal centre in monomer **25** is observed to be a triplet and is consistent with the proposed structure. The COSY spectrum shown in Figure 2.4 clearly indicates their interaction. The COSY spectrum also confirms the broad band at 2.2 ppm to be the proton of the hydroxyl group, and its coupling with the $-\text{CH}_2$ group next to the aromatic ring is clearly illustrated. Long-range coupling of this $-\text{CH}_2$ group and the methyl group with the aromatic protons is also clearly depicted.

The NMR spectrum of monomer **26** shows a similar spectrum to **25** except for the triplet due to the $-\text{CH}_2$ protons, which are now bonded to the Cp ring. These protons are now shifted greatly downfield, as a result of the overall deshielding effect of the $\text{CpRe}(\text{CO})_3$ moiety. The expected splitting of the Cp signal is observed, as two sets of resonances between 5.24 and 5.29 ppm (AA'BB' spin system) due to the cyclopentadienyl ring protons. The peaks for the protons of the dendritic wedge in monomer **27** resemble those reported by Moss *et al.*¹⁹⁻²²



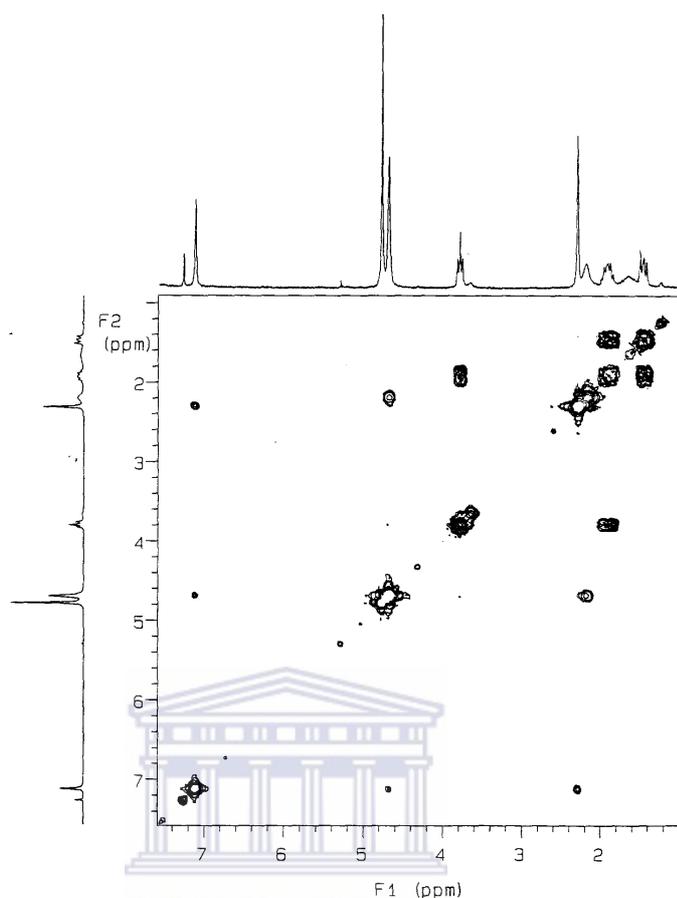


Figure 2.4 COSY spectrum of monomer **25**

Mass Spectra

The mass spectrum of the organometallic monomer **25** shows characteristic patterns in the fragmentation pathways. The iron-system (Figure 2.5) is consistent with metal-carbon σ -bonded compounds.

For the iron-monomer, the first fragmentation pathway involves the initial loss of the terminal CO ligands, followed by the extrusion of the organic ligand bonded directly to the metal. This gives rise to the CpFe^+ ion (m/e 121), which represents the base peak. The Cp ligand is then lost, to give the metal ion Fe^+ (m/e 56).

The second pathway involves the cleavage of the C-C bond adjacent to the ether-oxygen. This gives to rise to an iron-alkyl ion $\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_2^+$ (m/e 205), which most likely

rearranges to the-Fp-olefinic fragment $[\text{Cp}(\text{CO})_2\text{Fe}(\eta^2\text{-C}_2\text{H}_4)]^+$. The loss of the terminal CO ligands, followed by the extrusion of the remaining organic ligand gives the CpFe^+ ion (m/e 121). This ion is then again decomposed to the metal ion (m/e 56).

The third fragmentation scheme results from the cleavage and release of the organometallic moiety and the subsequent degradation of the aromatic ring, to generate the tropylium ion at m/e 91. This further breaks down via elimination of a neutral acetylene molecule to give the frequently observed peak at m/e 65. A breakdown of the various ions for monomer **25** is presented in Table 2.2.

Table 2.2 : Assignment of fragment ions from the mass spectrum of monomer **25**

m/e	Ion ^a	Relative Peak Intensities ^b
330	$\text{CpFe}(\text{CH}_2)_3\text{-O-C}_9\text{H}_{11}\text{O}_2^+$	53
205	$\text{CpFe}(\text{CO})_2\text{CH}_2\text{CH}_2^+$	84
150	$\text{C}_9\text{H}_{10}\text{O}_2^+$	20
149	$\text{CpFeCH}_2\text{CH}_2^+$	37
121	CpFe^+	100
91	C_7H_7^+	24
65	C_5H_5^+	16

^a ion refers to proposed assignment; Cp = $\eta^5\text{-C}_5\text{H}_5$; ^b Peak intensities relative to m/e 121

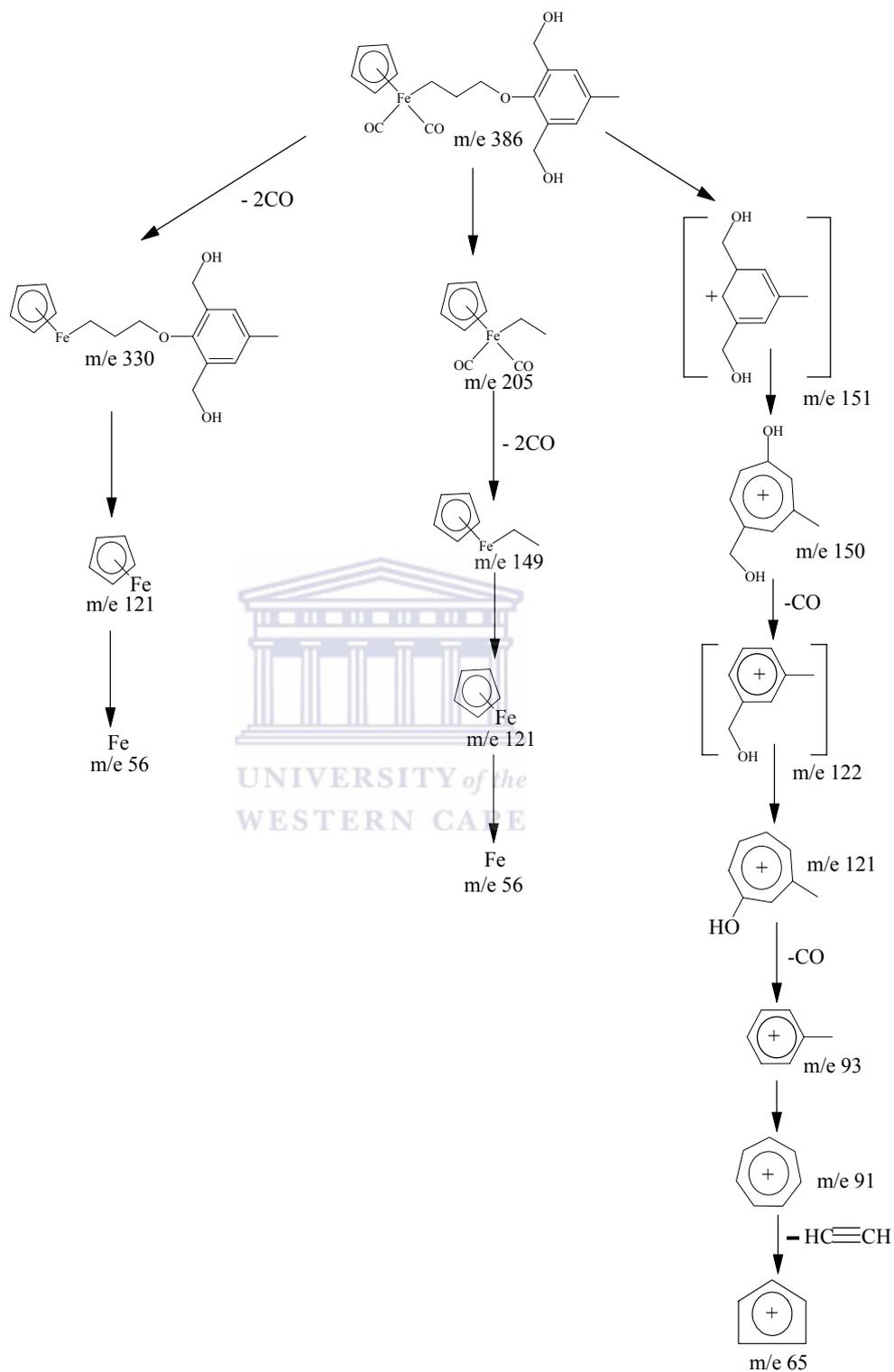


Figure 2.5 Fragmentation pathways of monomer 25

Structural Investigation

The characterisation of compound **25** has been confirmed by X-ray single crystal structure analysis. The molecular structure with the atomic-numbering scheme is shown in Figure 2.6. The crystallographic data are summarised in Table 2.3, atomic coordinates in Table 2.4, and selected bond lengths and angles in Table 2.5.

Crystals of monomer **25** were grown by slow infusion of hexane into a dichloromethane solution of the monomer at -5 EC. The data were collected at low temperature. This new compound crystallizes in the orthorhombic crystal system, space group *Pbca*, with $Z = 8$, and adopts a slightly distorted tetrahedral geometry around the metal centre. The ORTEP plot of compound **25** in Figure 2.6 clearly shows how the Cp rings are almost perpendicular to the plane of the aromatic ring. The Fe-CH₂ distance of 2.067(2) D compares well with similar Fe-C (alkyl) single-bond lengths²⁴, which normally occur around 2.091D. There is a slight shortening of the bond length (1.503 D) between C(9) and C(10). Known C_{sp³}-C_{sp³} bond lengths occur around 1.530 D.

Table 2.3 Crystallographic data and structure refinement for monomer **25**

Empirical formula	C ₁₉ H ₂₂ Fe O ₅	
Formula weight	386.22	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P bca	
Unit cell dimensions	a = 8.6803(3) Å	α = 90°.
	b = 14.6794(3) Å	β = 90°.
	c = 29.0830(10) Å	γ = 90°.
Volume	3705.8(2) Å ³	
Z	8	
Density (calculated)	1.384 Mg/m ³	
Absorption coefficient	0.839 mm ⁻¹	
F(000)	1616	
Crystal size	0.67 x 0.50 x 0.33 mm ³	

Theta range for data collection	2.81 to 25.34°.
Index ranges	-9<=h<=10, -16<=k<=16, -33<=l<=13
Reflections collected	7572
Independent reflections	3084 [R(int) = 0.0197]
Completeness to theta = 25.34°	90.9 %
Max. and min. transmission	0.7693 and 0.6034
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3084 / 0 / 260
Goodness-of-fit on F ²	1.050
Final R indices [I>2σ(I)]	R1 = 0.0327, wR2 = 0.0712
R indices (all data)	R1 = 0.0456, wR2 = 0.0763
Extinction coefficient	0.00000(19)
Largest diff. peak and hole	0.250 and -0.253 e.Å ⁻³



Table 2.4 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for monomer **25**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	2245(1)	3702(1)	4345(1)	25(1)
O(5)	1634(2)	3677(1)	2323(1)	31(1)
C(14)	3410(3)	6110(1)	1397(1)	28(1)
O(4)	4213(2)	7210(1)	2835(1)	27(1)
O(3)	4230(2)	4852(1)	2661(1)	24(1)
C(16)	3200(2)	4793(1)	1901(1)	20(1)
C(15)	2944(2)	5218(1)	1482(1)	25(1)
O(1)	5579(2)	3778(1)	4403(1)	53(1)
C(12)	4428(2)	6182(1)	2176(1)	21(1)
C(18)	2752(2)	3811(1)	1969(1)	26(1)
C(11)	3929(2)	5291(1)	2249(1)	19(1)
O(2)	1816(2)	5219(1)	4968(1)	59(1)
C(4)	-49(3)	3263(2)	4295(1)	38(1)
C(2)	1987(3)	4607(2)	4725(1)	37(1)
C(8)	2434(3)	4672(2)	3833(1)	29(1)
C(13)	4156(2)	6571(1)	1749(1)	25(1)
C(9)	3349(3)	4388(2)	3411(1)	28(1)
C(17)	5251(2)	6713(2)	2545(1)	29(1)
C(1)	4257(3)	3737(2)	4385(1)	35(1)
C(3)	736(3)	2997(2)	3900(1)	39(1)
C(5)	656(3)	2843(2)	4673(1)	44(1)
C(7)	1947(3)	2425(2)	4024(1)	47(1)
C(6)	1880(3)	2323(2)	4511(1)	52(1)
C(19)	3143(4)	6540(2)	934(1)	52(1)
C(10)	3220(3)	5097(2)	3040(1)	29(1)

Table 2.5 Selected bond lengths [\AA] and angles [$^\circ$] for monomer 25

Fe(1)-C(2)	1.743(3)
Fe(1)-C(1)	1.751(3)
Fe(1)-C(8)	2.067(2)
Fe(1)-C(4)	2.098(2)
Fe(1)-C(5)	2.099(2)
Fe(1)-C(6)	2.106(2)
Fe(1)-C(7)	2.109(2)
Fe(1)-C(3)	2.113(2)
O(1)-C(1)	1.151(3)
O(2)-C(2)	1.152(3)
C(4)-C(3)	1.392(3)
C(4)-C(5)	1.403(4)
C(8)-C(9)	1.519(3)
C(9)-C(10)	1.503(3)
C(3)-C(7)	1.393(4)
C(5)-C(6)	1.391(4)
C(7)-C(6)	1.425(4)
C(2)-Fe(1)-C(1)	93.67(12)
C(2)-Fe(1)-C(8)	86.73(11)
C(1)-Fe(1)-C(8)	87.05(10)
O(2)-C(2)-Fe(1)	178.4(2)
C(9)-C(8)-Fe(1)	115.78(15)
O(1)-C(1)-Fe(1)	178.3(2)

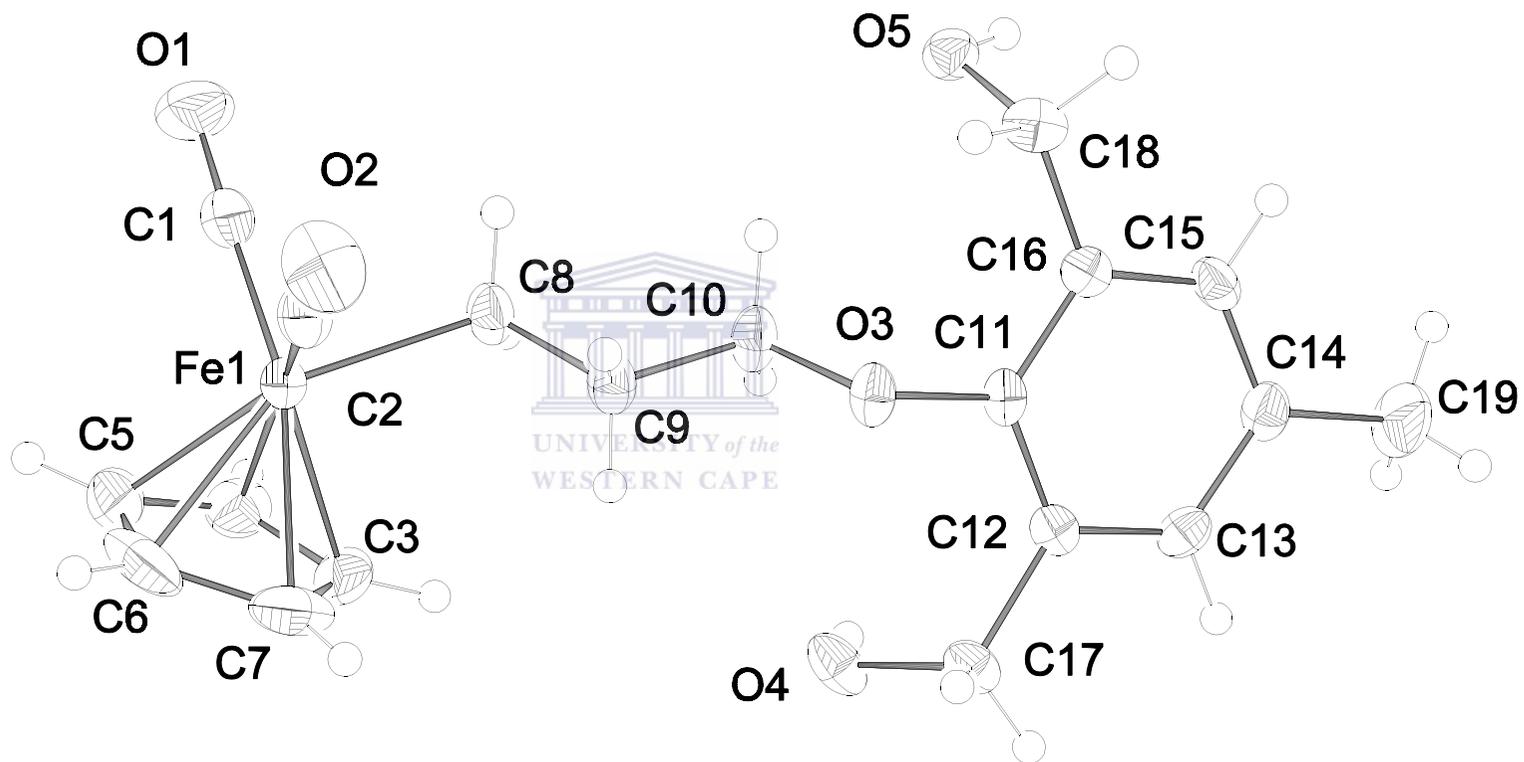
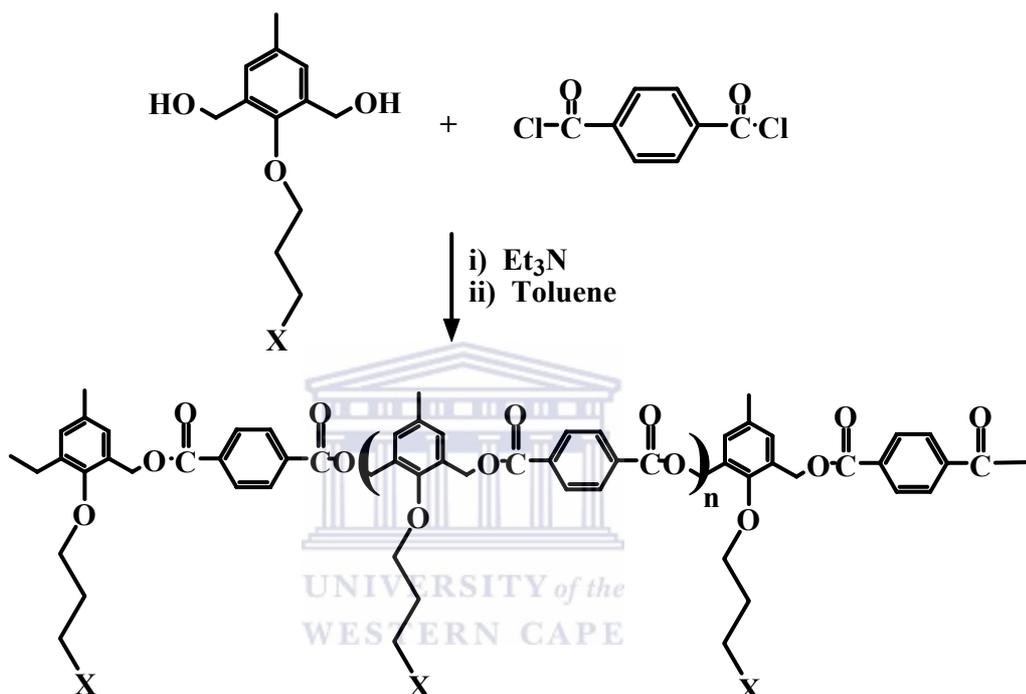


Figure 2.6 Molecular structure of monomer 25 showing the atom-numbering scheme

2.2.3 Synthesis of Metal-Containing Polyesters

Preparation

The organometallic polymers (**31-33**) and organic polymer (**34**) shown in Scheme 2.4 were prepared in high yields by reacting the organometallic monomers with terephthaloyl chloride in toluene solution at room temperature. Triethylamine was added to remove HCl.



Scheme 2.4

The newly-formed metal-containing polyesters (**31-33**) contain metal moieties in side chains pendant to the polymer backbone. The toluene-soluble fractions were dried under vacuum and all showed good solubilities in a range of common organic solvents. The toluene-insoluble fractions were also shown to be polymeric in nature, by comparison of the IR spectra of the toluene-soluble and toluene-insoluble fractions. The toluene-insoluble fraction is thought to be some higher molecular weight polyester.

Polymer Characterisation

The ^1H NMR data for the new toluene-soluble polyesters are given in the Experimental section. Most of the peaks in the NMR spectra of the polymeric material resemble those of their respective precursors, with the exception of the peak due to the aliphatic protons adjacent to the hydroxy groups. For example, in monomer **25**, this peak is found at 4.70 ppm, and was found to have shifted significantly to 5.44 ppm in compound **31** (Figure 2.7). This indicates that esterification has occurred at the aliphatic hydroxyl groups. However, for compound **31**, a peak is still observed at 4.70 ppm. This implies that the polymer chains have hydroxyl groups as their terminal endgroups, since all the starting organometallic monomer was consumed in the reaction. The same trends were observed in the ^1H NMR spectra of the polyesters formed from the rhenium and “dendritic-iron” monomers and the model organic monomer. Again, the aliphatic protons adjacent to the hydroxyl groups have shifted significantly downfield, confirming the formation of a polyester. For **32** and **34**, however, the small peak intensities for the aliphatic protons of the precursor, indicate that the chain ends in these compounds have predominantly acid chloride functionalities.

IR spectroscopy is also a useful diagnostic tool for confirming the formation of polyesters. The IR spectra for compounds **31** and **33** show strong, sharp absorption peaks at 2005 cm^{-1} and 1943 cm^{-1} , and those for the rhenium compound **32** occur at 2021 cm^{-1} and 1925 cm^{-1} respectively for the terminal carbonyl ligands (Figure 2.8). These absorptions are similar to those found in the monomeric precursors, and serve to confirm the integrity of the organometallic moieties in the polymer side-chains. The strong absorption band around 1720 cm^{-1} for all four compounds **31**, **32**, **33** and **34** is due to the acyl group found in the polyester backbone. This data serves to confirm the existence of the polyester linkage.

Molecular Weight Analysis

The average molecular weights of the polyesters (**31**, **32**, **34**) were determined by GPC using THF as the eluent (Table 2.6). The molecular weights of the toluene-insoluble fractions could not be obtained as a result of their low solubilities, but these fractions were confirmed by IR spectroscopy to contain polyester linkages. The molecular weights of the toluene-soluble fractions show that the new compounds are oligomeric, low-molecular weight esters, which generally correspond to a degree of polymerisation of about four. The

presence of organometallic moieties in comparison with model compound seems to indicate that the metal-containing moieties have a significant effect on the nature of the polymer formed. A study was conducted of the effect of time on the polymer yields. It was found that over a longer reaction period, the monomers bearing metal-containing moieties formed more toluene-insoluble fractions. These insoluble materials are also polymeric in nature, as was confirmed by comparison of its IR spectra with those of the toluene-soluble fractions. Polymerisations carried out with the purely organic monomer however gave largely soluble materials, which showed no significant decrease in yield irrespective of reaction time.

Table 2.6. GPC data for compounds 31, 32 and 34

Compound	Polymerisation Reaction Time (h) ^a	M_w ^b	M_n ^c	P.I. ^d
31	2	2724	1460	1.86
31	24	2482	1768	1.40
32	24	2612	1769	1.48
34	2	2327	1081	2.15
34	24	2604	1286	2.02

^a The polymerisation reactions were conducted in toluene

^b M_w = weight average molecular weight

^c M_n = number average molecular weight

^d P.I. = polydispersity index

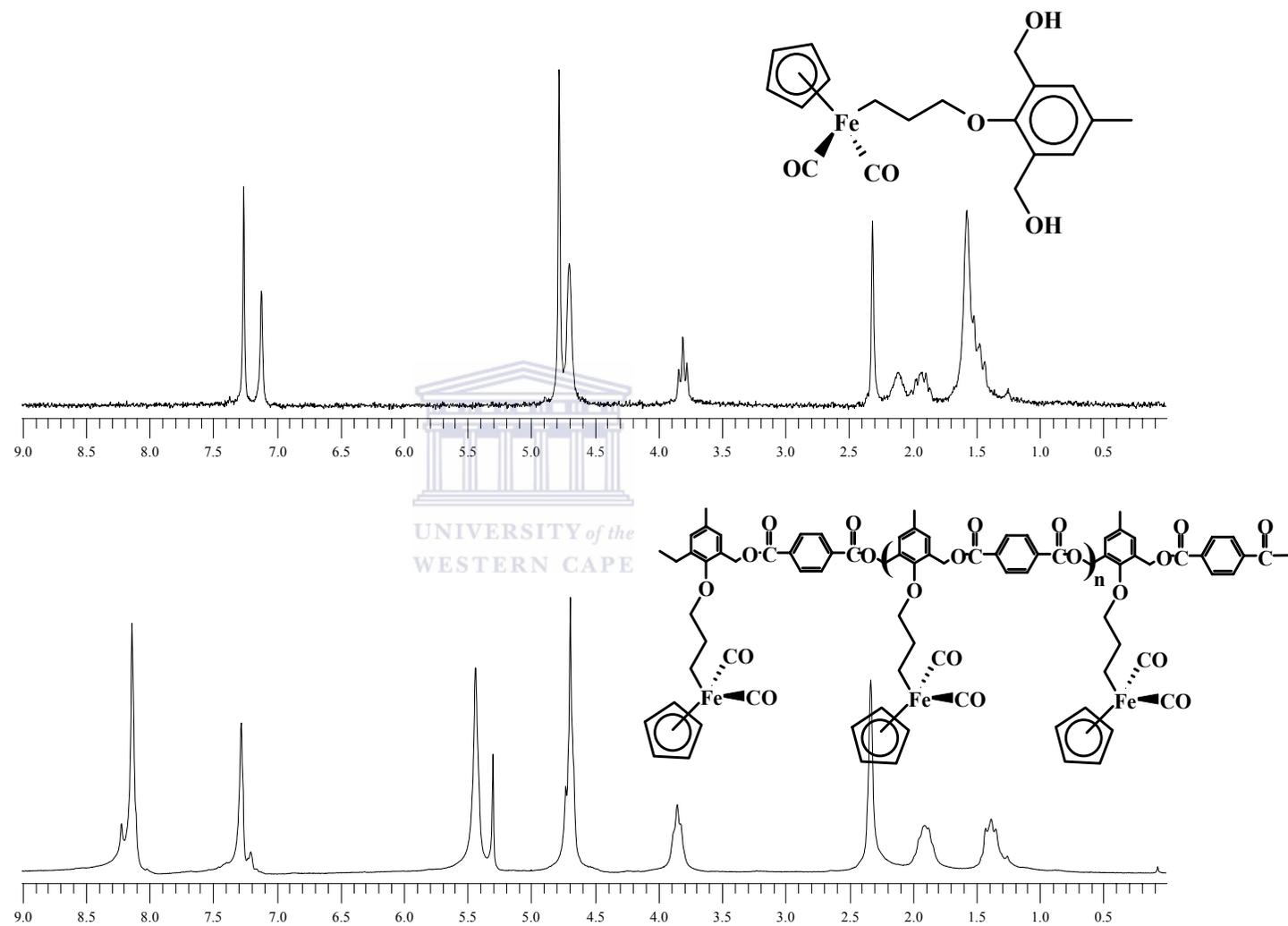


Figure 2.7 ¹H NMR spectra of the iron-bifunctional monomer (25) and iron-containing polyester in (31) CDCl₃

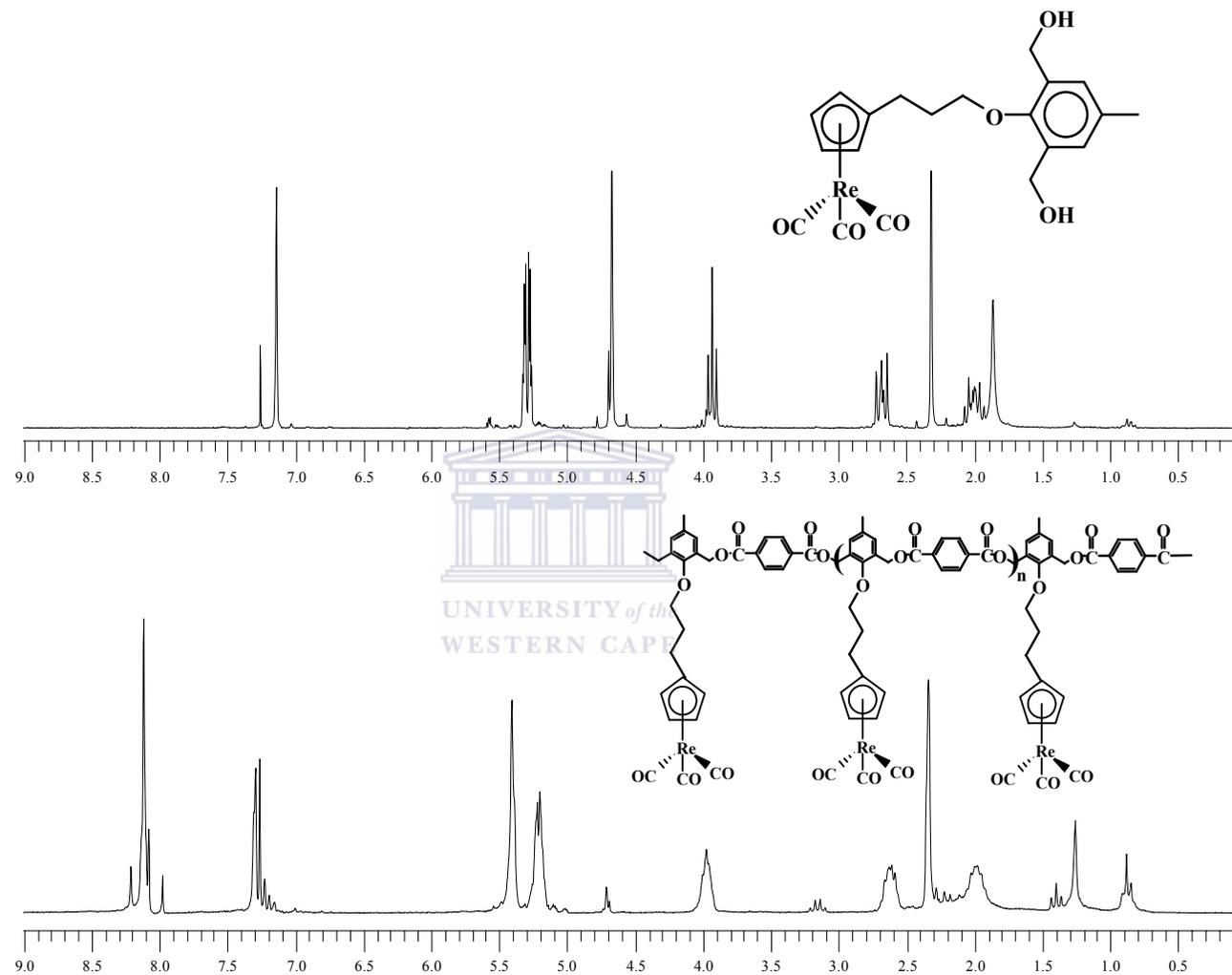


Figure 2.8 ¹H NMR spectra of the rhenium-bifunctional monomer (26) and rhenium-containing polyester in (32) CDCl₃

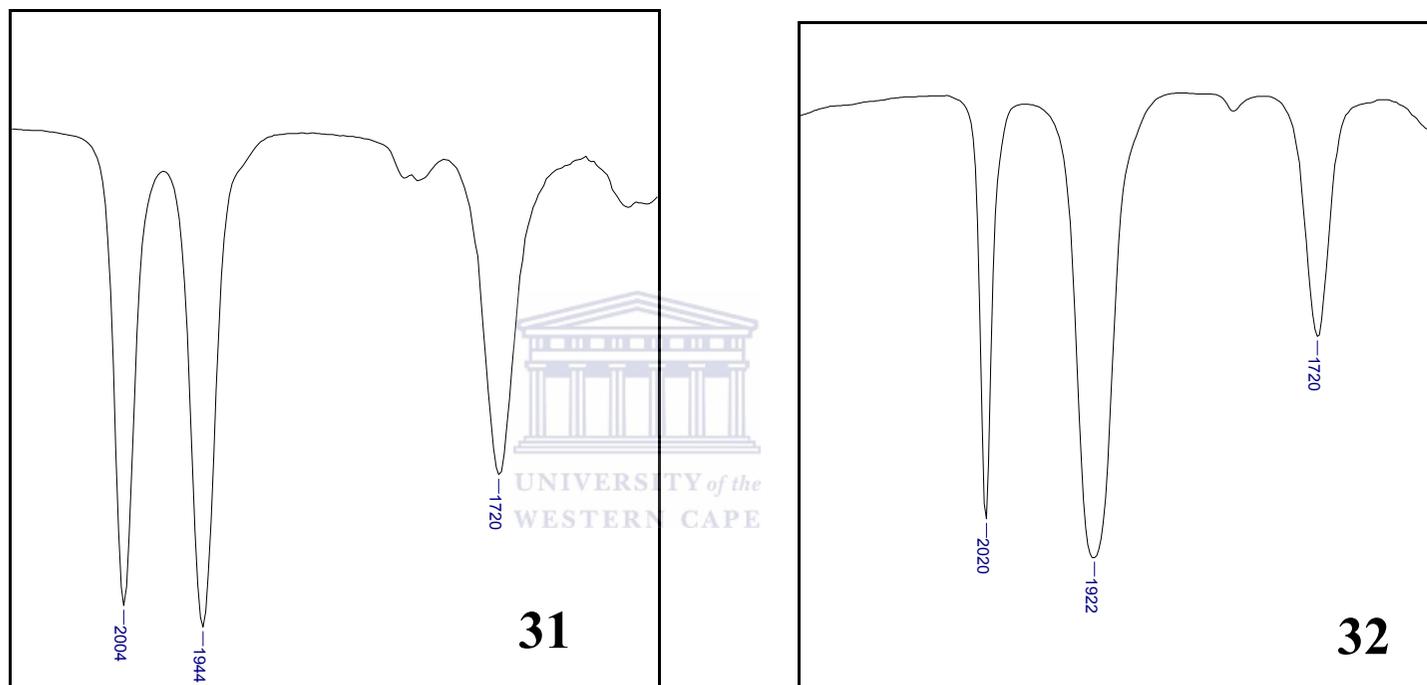


Figure 2.9 IR spectra of the iron (31)- and rhenium (32)- containing polyesters in CH_2Cl_2 in NaCl solution cells

Thermal Properties

The thermal behaviour of the organometallic polyesters were studied by DSC and TGA at a heating rate of 10.0 EC/min, under a nitrogen atmosphere. The organoiron compound **31** shows two exotherms, one small exotherm centred at 65 EC and a large, broad exotherm at 190 EC (Figure 2.10). The start of the broad exotherm corresponds with the onset of decomposition, without melting, which was observed using a Fischer-Johns hotstage microscope, and found to be in the range 170 - 175EC. A small endotherm was recorded at 75 EC. The TGA thermogram of **31** shows a two-step degradation, starting at 82 EC. The 8% weight loss which is observed to occur over the range 82 E to 155 EC, corresponds to the loss of the terminal carbonyl ligands of the iron-carbonyl moiety. This is followed by a mass loss at 250 EC associated with the decomposition of the complex.

The DSC trace for compound **32** shows two very small endothermic transitions, centred at 118 and 202 EC, and a small exothermic peak at 230 EC (Figure 2.11). The endothermic transition at 118 EC corresponds with the melting point of the solid at 115 EC, which was recorded on a Fischer-Johns hotstage apparatus. This solid was observed to soften at around 78 EC. The TGA thermogram did not show an appreciable mass loss up to 250 EC. A weight loss of approximately 0.6% is observed from 59 to 116 EC, and cannot be attributed to any fragment.

These data seem to indicate that the rhenium compound is more thermally stable than the iron analogue, as it shows very little thermal activity up to 250 EC. This is generally the case for most rhenium compounds with alkyl groups bonded through the cyclopentadienyl ring.

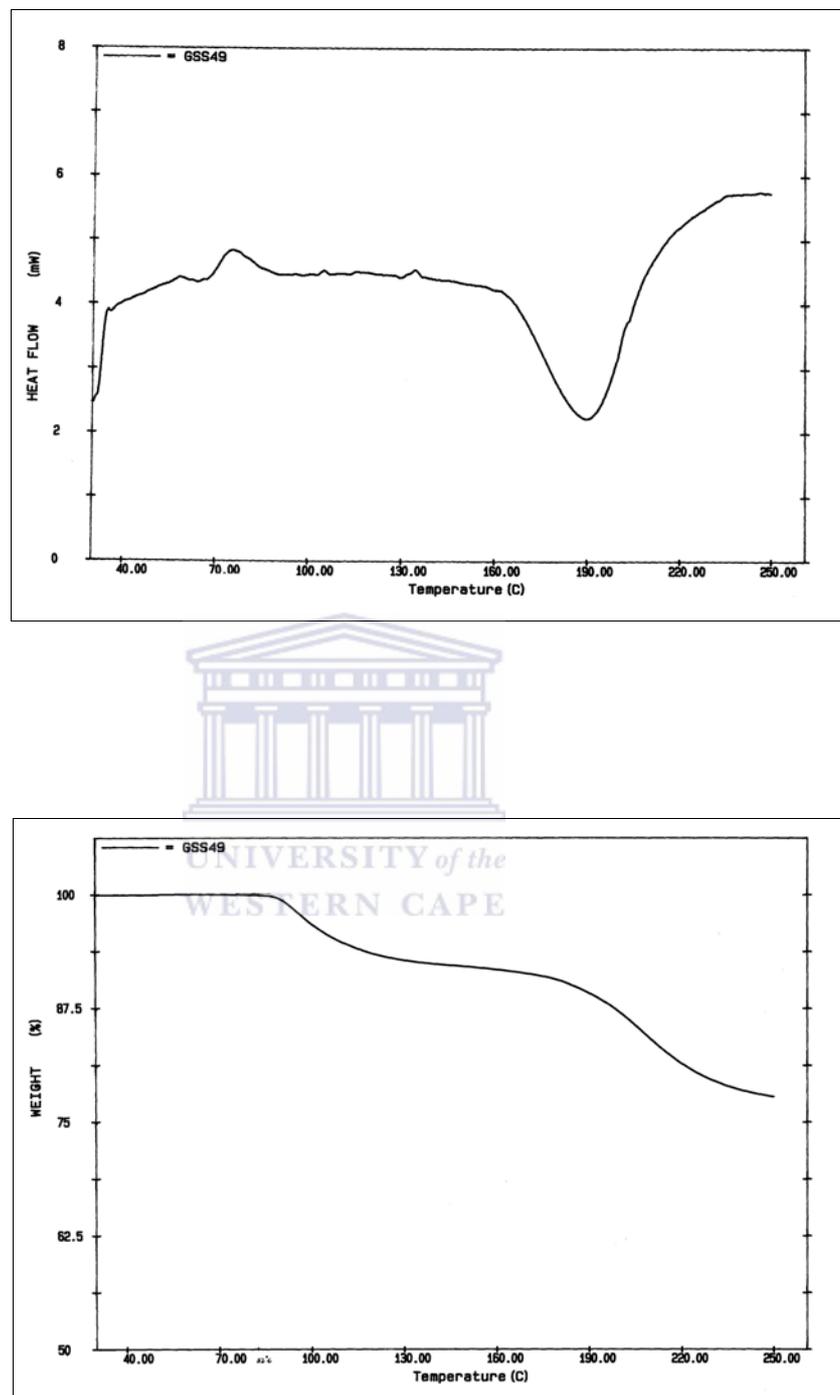


Figure 2.10 DSC trace (above) and TGA trace (below) for the iron polyester 31

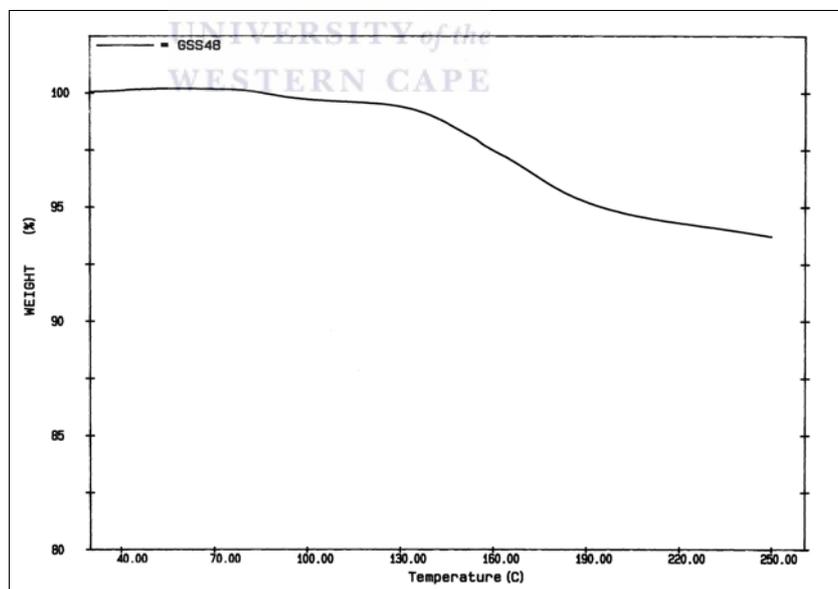
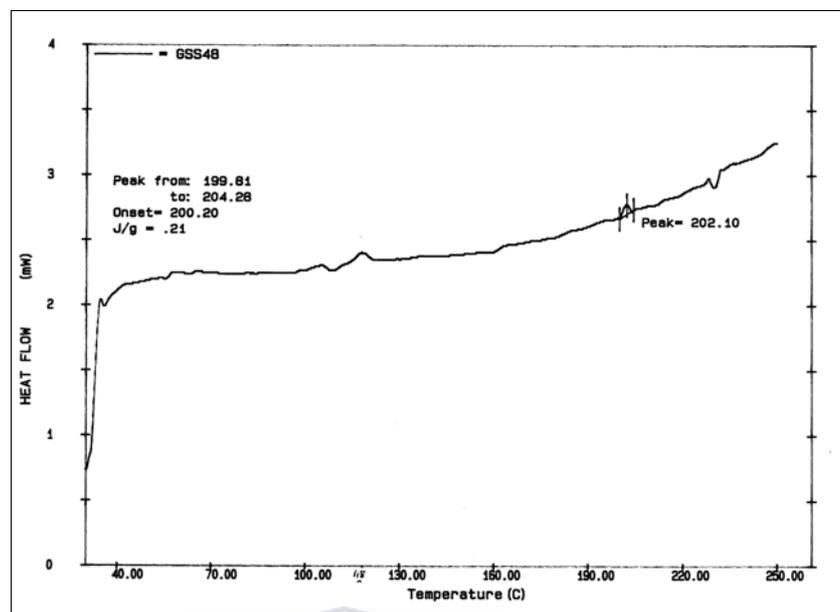
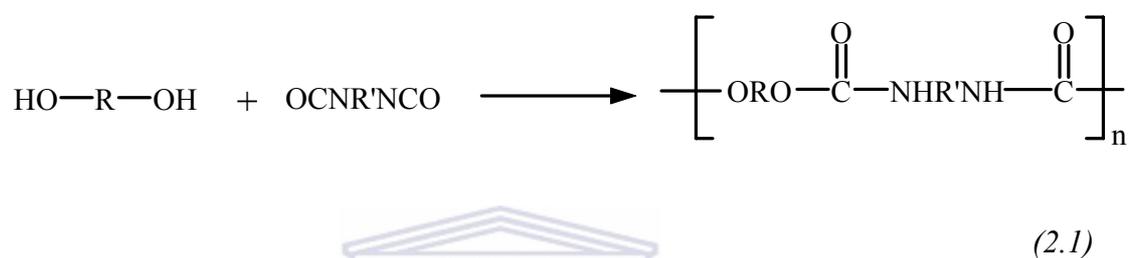


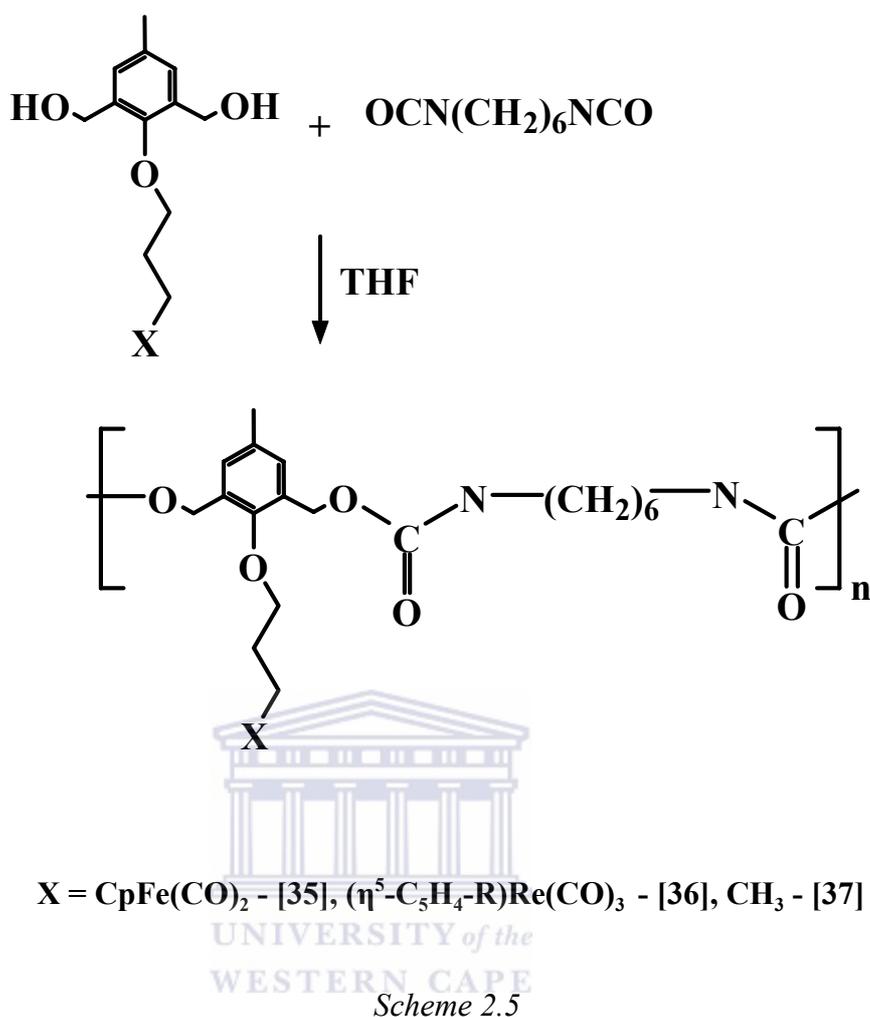
Figure 2.11 DSC trace (above) and TGA trace (below) for the rhenium polyester 32

2.2.4 Synthesis of Metal-Containing Polyurethanes

Urethane chemistry comprises the reactions that an isocyanate (NCO) group will undergo with compounds containing functionalities with active hydrogens^{25,26}, such as alcohols (to form urethanes, Equation 2.1), amines (to form ureas) or carboxylic acids (to form amides). Thus, if the reagents are bifunctional, polymer formation can take place. In these reactions, no by-products are produced that require removal as the polymers are built up. Therefore no Lewis bases or drying agents need to be added to the reaction mixture. Essentially linear products result if the reactants are bifunctional, but higher functionality leads to the formation of branched chain or cross-linked compounds.



In this research project, it was decided to study the susceptibility of the newly-prepared organometallic bifunctional monomers (**25**, **26**), described in the previous section, to undergo copolymerisation with diisocyanates. The rationale for this work was to attempt to prepare metal-containing polyurethanes (as outlined in Scheme 2.4), with metal centres in pendant side chains. Due to the insolubility of the obtained products, complete characterisation could not be carried out. Certain of the results obtained allude to the existence of an organometallic polyurethane, and these results are discussed in the following text.



Preparation

The synthesis of the metal-containing polyurethanes was attempted using solution polycondensation reactions. The organometallic bifunctional monomer **26** was stirred with 1,6-diisocyanatohexane in THF at room temperature for 16h. The reactions were carried out with a 1:1 ratio of diisocyanate and organometallic diol. After workup, a slightly viscous oil was obtained, which was found to contain some unreacted diisocyanate. This was observed as a strong broad absorption for the -NCO group at $\sim 2250\text{ cm}^{-1}$ in the IR spectrum. It was extremely difficult to remove the excess diisocyanate, despite trying various purification methods. Figure 2.12 shows the ^1H NMR spectrum of the crude material, which presents some evidence for the formation of a polyurethane. The most important distinguishing feature is the shift of the triplet at 3.94 ppm for the aliphatic protons adjacent to the diols in the rhenium monomer, to 3.80 ppm in the condensation

product. The appearance of this resonance presents some evidence for the formation of the polyurethane linkage. The reaction was repeated over a longer period (3 days) and the reaction then worked up in the same manner. An off-white solid was isolated and was thoroughly washed with CH_2Cl_2 , to remove any traces of the starting materials. This solid proved to be insoluble in all organic solvents.

The reaction was repeated with the iron monomer **25** for 16h at room temperature. The solution turned cloudy and an insoluble tan solid was collected after workup. Again, the resulting solid was thoroughly washed with CH_2Cl_2 to ensure that none of the reactants were present.

A possible explanation for the insolubility and intractability of the formed products is probably that extensive branching and cross-linking has occurred. In the preparation of polyurethanes, side reactions such as branching and cross-linking due to the formation of allophanate linkages are known to occur. This type of linkage arises from the additional side reaction of the isocyanate with the urethane already introduced during the initial polymer formation.

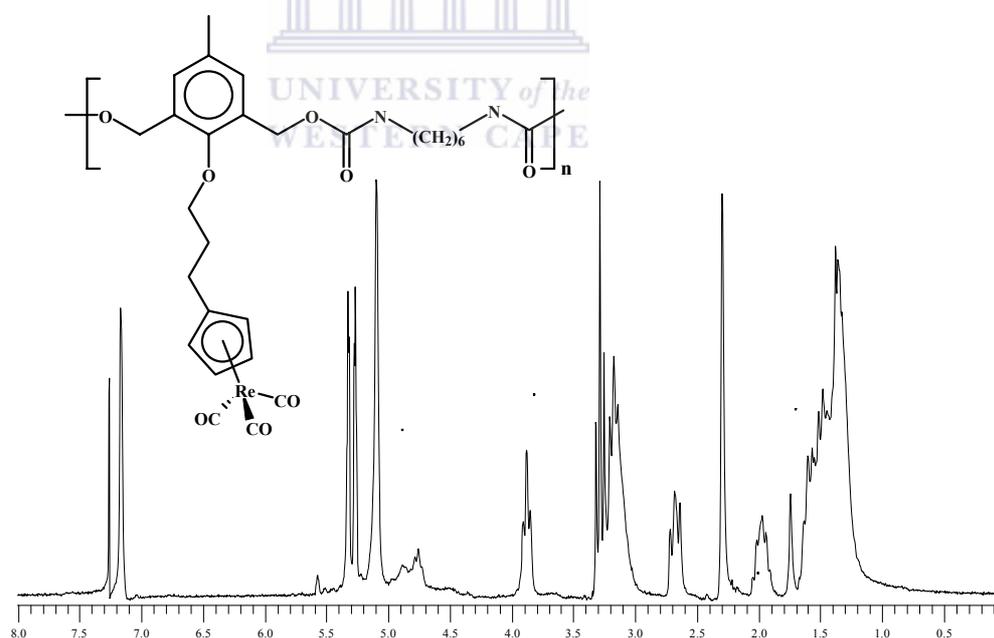


Figure 2.12 ^1H NMR spectrum of crude rhenium polyurethane **36**

2.2.5 Characterisation of the Metal-Containing Polyurethanes

IR spectroscopy

Due to the insoluble nature of the formed condensation products, solid-state infrared spectroscopy was used to provide further information as to the integrity of the organometallic moieties in the proposed structures. The samples were recorded using DRIFTS with the solid samples mixed in a KBr matrix. Both the iron and rhenium derivatives (**35**, **36**) exhibit similar IR spectra in the solid-state. The spectra showed characteristic peaks at $\sim 3320\text{ cm}^{-1}$ due to the N-H stretching and the C-H symmetrical and asymmetrical stretching due to the methylene groups can be observed between 2856 and 2932 cm^{-1} . Confirmation of the integrity of the organometallic moieties is found by the presence of two strong absorption bands due to the terminal carbonyl ligands of the respective metal centres. These occur at positions similar to those of the original monomers. The carbonyl group of the urethane shows a peak typically around 1720 cm^{-1} and appears as a strong broad absorption band.

Solubility

The solubility of the polyurethanes was tested in various polar and nonpolar solvents. The polyurethanes were insoluble in polar solvents such as DMSO and DMF, and were also insoluble in acetone, ethyl acetate, toluene, benzene, chloroform, carbon tetrachloride, *n*-hexane and tetrahydrofuran.

Thermal Analysis

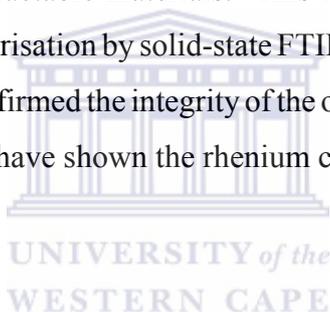
The thermal properties of the organometallic polyurethanes were studied by differential scanning calorimetry and thermogravimetric analysis at a heating rate of 10.0 EC/min , under a nitrogen atmosphere. The TGA curve of the rhenium polyurethane **36** shows an initial 5% weight loss at 193 EC , and a residual weight loss at 481 EC which corresponds to 75%, associated with the decomposition of the compound. The DSC thermogram shows a small exotherm centred at 129 EC and two small endotherms at 261 and 295 EC .

The iron polyurethane **35** shows a lower thermal stability than its rhenium counterpart. The TGA curve of the iron analogue shows a one-step decomposition with the onset occurring at 83 EC and ends at 465 E , a residual weight loss of 84%. The DSC trace shows a small endotherm centred at 258 EC .

2.3 Conclusions

In this study, new polyesters were synthesized containing organometallic and alkyl pendant side chains. Three new bifunctional monomers were prepared and polymerized with terephthaloyl chloride in toluene solution, using triethylamine as a base. This gave low molecular weight, oligomeric materials, which were soluble in most organic solvents. Toluene-insoluble fractions were also isolated from the reaction mixture and their IR spectra were found to be identical to the toluene-soluble fractions. The former are thought to be higher molecular weight polymers. It can be seen that the presence of the metal moieties retards the extent of polymerisation, compared with purely organic systems, and can be ascribed to the steric bulk of the metal centre and its ancillary ligands. The rhenium oligomers were found to be more thermally stable than their iron analogues.

Polymerisation reactions of the organometallic diols with 1,6-hexanediisocyanate produced mainly insoluble and intractable materials. This is thought to be an extensively cross-linked polymer. Characterisation by solid-state FTIR spectroscopy alluded to the formation of a polyurethane and confirmed the integrity of the organometallic moieties in the polymer chains. Thermal studies have shown the rhenium compound to be more thermally stable than the iron analogue.



2.4 Experimental

All reactions were carried out under nitrogen using standard Schlenk tube techniques, unless otherwise stated. Tetrahydrofuran (THF) and toluene were dried over sodium/benzophenone and distilled under nitrogen before use. Acetone was dried and distilled over CaCl_2 . $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$; 1,3-dibromopropane; 2,6-bis(hydroxymethyl)-*p*-cresol and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-Crown-6) were purchased from Sigma-Aldrich. Potassium carbonate, terephthaloyl chloride and triethylamine were obtained from SAARCHEM. Compounds **29**¹⁹, **30**¹⁹, $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_2)_3\text{Br}]^{17}$, and $[\{\eta^5\text{-(C}_5\text{H}_4\text{)CH}_2\text{CH}_2\text{CH}_2\text{I}\}\text{Re}(\text{CO})_3]^{18}$ were prepared according to literature procedures. All column chromatography was done on either deactivated alumina 90 (70-230 mesh) or silica gel (70-230 mesh), obtained from Merck. Infrared spectra were recorded on a Perkin Elmer Paragon 1000PC FT-IR spectrophotometer, using either solution cells with NaCl windows or DRIFTS (diffuse reflectance infrared transmission spectroscopy) in a KBr matrix. ^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Varian XR200 spectrometer, using tetramethylsilane as an internal standard. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. Mass spectra were obtained with a V.G. Micromass 16F spectrometer, operating at 70eV ionising voltage. Melting points were determined on a Fisher-Johns hotstage microscope, and are uncorrected. GPC analysis of the molecular weight distribution of the polymers was performed on a system equipped with a Spectra Physics RI detector, a Spectra Physics LC pump, and Spectra Physics Winner software. A series of four 300 X 7.8mm columns was packed with 10 μm packing material of phenogel (styrene-divinylbenzene). These had pore sizes of 100, 500, 10³, and 10⁴ D. The eluting solvent was THF at a flow rate of 1.25 ml/min. The system was calibrated against polystyrene standards, Mp 580, 1320, 5050, 7000, 11600, 66000 and 156000. DSC and TGA data were performed at the University of Cape Town on a Perkin-Elmer PC7 Series Thermal Analysis System, at a scanning rate of 10EC/min under N₂ gas-purge with a flow rate of 30 ml/min.

X-ray diffraction intensity data were collected at 173K on a Nonius Kappa CCD with 1.5 kW graphite monochromated Mo radiation. The strategy for the data collection was evaluated using the COLLECT software.²⁷ The data were scaled and reduced using DENZO-SMN.²⁸ Unit cell dimensions were refined on all data. The structure was solved and refined using SHELX97.²⁸ Hydrogen atoms belonging to Cp-ring and methyl carbons were placed

in calculated positions. All other hydrogens were located from difference electron density maps. The plot of the molecular structure for publication was obtained using the program PLATON.³⁰

2.4.1 Preparation of monomer **25**

2,6-Bis(hydroxymethyl)-*p*-cresol (0.566g, 3.36mmol), K₂CO₃ (1.40 g, 10.1 mmol) and 18-Crown-6 (0.179 g, 0.677 mmol) were transferred to a nitrogen-purged Schlenk tube and taken up in freshly-distilled acetone (10 ml), to give a dark orange/brown slurry. [(η⁵-C₅H₅)(CO)₂Fe(CH₂)₃Br] (1.01g, 3.36mmol) was dissolved in freshly distilled acetone(10 ml) and added dropwise to the stirred slurry. This mixture was heated to reflux and stirred vigorously for 48h. The reaction mixture was cooled to room temperature, the solvent removed using a rotary evaporator and the resulting oily residue extracted with CH₂Cl₂. After filtration by gravity and removal of the solvent, the residual oil was transferred to an alumina column, using hexane as eluent. The desired major product, i.e. monomer **25**, was contained in the second fraction that was eluted with a 70% CH₂Cl₂/hexane mixture. Removal of the solvent gave a light brown solid. Yield = 0.502 g (39%).

¹H NMR (200 MHz, CDCl₃, δ): 1.46(t, 2H, FeCH₂), 1.93(m, 2H, CH₂), 2.31(s, 3H, CH₃), 3.80(t, 2H, CH₂OAr), 4.70(s, 4H, CH₂OH), 4.78(s, 5H, Cp), 7.12(s, 2H, Ar). ¹³C NMR (50 MHz, CDCl₃, δ): 2.86(FeCH₂), 20.74(CH₂), 38.34(CH₃), 61.31(CH₂OAr), 85.42 (Cp), 77.97(CH₂OH), 129.40, 133.80, 134.07, 153.20(Ar), 217.48(CO).

IR (CH₂Cl₂), ν(CO) cm⁻¹: 2005(s), 1945(s). Mp: 102E-103EC

Analysis: Found for C₁₉H₂₂FeO₅: C, 59.04%; H, 5.70%. Calcd.: C, 59.10%; H, 5.70%.

E.I. Mass spectra (*m/e*): 330 [53%, (η⁵-C₅H₅) Fe(CH₂)₃O-{2,6-(CH₂OH)₂-4-CH₃-C₆H₂}], 205 [84%, (η⁵-C₅H₅)(CO)₂ Fe(CH₂CH₂-)], 121 [100%, (η⁵-C₅H₅)Fe].

2.4.2 Preparation of monomer **26**

A Schlenk tube was evacuated and filled with nitrogen.

2,6-Bis(hydroxymethyl)-*p*-cresol (0.215 g, 1.28 mmol), K₂CO₃ (0.270 g, 1.95 mmol) and 18-Crown-6 (0.0540 g, 0.204 mmol) were transferred to the Schlenk tube, together with [(η⁵-(C₅H₄)CH₂CH₂CH₂I]Re(CO)₃ (0.650g, 1.27mmol) and freshly distilled acetone(20 ml). The reaction mixture was refluxed for 48h under a nitrogen atmosphere. The solvent was then removed under reduced pressure, and the resulting residue dissolved in CH₂Cl₂. After

filtration by gravity, the solution was concentrated using a rotary evaporator, and transferred to a silica gel column. Purification was achieved by column chromatography, using a column made up with a slurry of silica gel in 5% ethyl acetate (in CH_2Cl_2). The polarity was slowly increased to 10% ethyl acetate/ CH_2Cl_2 , to elute the desired product. Monomer **26** was isolated as a white solid. Yield = 0.591 g (85%).

^1H NMR (200 MHz, CDCl_3 , δ): 1.98(m, 2H, CH_2), 2.31(s, 3H, CH_3), 2.67(t, 2H, $-\text{CH}_2\text{Cp}$), 3.88(t, 2H, $-\text{CH}_2\text{O}-$), 4.65(s, 4H, CH_2OH), 5.24-5.29(m, 4H, Cp), 7.13(s, 2H, Ar).

^{13}C NMR (50 MHz, CDCl_3 , δ): 20.78($-\text{CH}_2-$), 24.71($-\text{CH}_2\text{Cp}$), 32.27(CH_3), 60.85($-\text{CH}_2\text{OAr}$), 74.02(CH_2OH), 83.08, 83.67(Cp), 129.56, 133.58, 134.31, 152.67(Ar), 194.38(CO).

IR (CH_2Cl_2), $\nu(\text{CO}) \text{ cm}^{-1}$: 2020(s), 1923(s). Mp: 98E-99EC

Analysis: Found for $\text{C}_{20}\text{H}_{21}\text{ReO}_6$: C, 43.35%; H, 4.16%. Calcd.: C, 44.19%; H, 3.89%.

E.I. Mass Spectra (m/e): 544 [52%, molecular ion peak], 460 [6%, $\text{Re}(\eta^5\text{-C}_5\text{H}_4\text{-(CH}_2\text{)}_3\text{O-}\{2,6\text{-(CH}_2\text{OH)}_2\text{-4-CH}_3\text{-C}_6\text{H}_2\})$].

2.4.3 Preparation of monomer 27

2,6-Bis(hydroxymethyl)-*p*-cresol (0.139 g, 0.829 mmol), K_2CO_3 (0.332 g, 2.40 mmol) and 18-crown-6 (53.7 mg, 0.203 mmol) were transferred to a nitrogen-purged Schlenk tube and taken up in freshly-distilled acetone (10 ml), to give a dark orange/brown slurry. The benzyl bromide **30** (0.511 g, 0.800 mmol) was dissolved in freshly distilled acetone (10 ml) and added dropwise to the stirred slurry. This mixture was heated to reflux and stirred vigorously for 48h. The reaction mixture was cooled to room temperature, the solvent removed using a rotary evaporator and the resulting oily residue extracted with CH_2Cl_2 . After filtration by gravity and removal of the solvent, the residual oil was transferred to a silica gel column, using hexane initially as eluent. The polarity was gradually increased to a 60% hexane/ethyl acetate mixture, to elute monomer **27** as a dark yellow oil (main fraction), with unidentified minor impurities.

^1H NMR (200 MHz, CDCl_3 , δ): 1.44(t, 4H, FeCH_2), 1.92(br m, 4H, CH_2), 2.33(s, 3H, CH_3), 3.88(t, 4H, CH_2OAr), 4.69(s, 4H, CH_2OH), 4.77(s, 10H, Cp), 4.85(s, 2H, Ar-O- CH_2 Ar), 6.44(br s, 1H, Ar), 6.56(br s, 2H, Ar), 7.16(s, 2H, Ar).

IR (CH_2Cl_2), $\nu(\text{CO}) \text{ cm}^{-1}$: 2005(s), 1945(s).

2.4.4 Preparation of monomer **28**

2,6-Bis(hydroxymethyl)-*p*-cresol (2.00 g) was transferred to a 250 ml Erlenmeyer flask, together with K_2CO_3 (5.00 g). The mixture was taken up in acetone (100 ml) and 1-bromobutane (1.3 ml) added to the stirring dark orange/brown slurry. The mixture was refluxed under nitrogen for 3 days and then allowed to cool to room temperature. The solvent was removed using a rotary evaporator and the remaining residue extracted with CH_2Cl_2 . This was filtered by gravity and the solvent was removed from the filtrate using a rotary evaporator to yield an orange oil. The oil was dissolved in a small amount of CH_2Cl_2 and hexane added to precipitate a white solid. This was purified by further washing with hexane to give monomer **28** as a white solid. Yield = 0.406 g (18%).

1H NMR (200 MHz, $CDCl_3$, δ): 0.99(t, 2H, CH_3), 1.51(m, 2H, CH_2), 1.78(m, 2H, CH_2), 2.31(s, 3H, CH_3), 3.86(t, 2H, $-CH_2OAr$), 4.67(s, 4H, $-CH_2OH$), 7.12(s, 2H, Ar).

^{13}C NMR (50 MHz, $CDCl_3$, δ): 13.84(CH_3), 19.18(CH_2), 20.70(CH_2), 32.41(Ar- CH_3), 60.78(CH_2OAr), 74.85(CH_2OH), 129.19, 133.67, 133.96, 152.70(Ar). Mp: 62E-63EC

Analysis: Found for $C_{13}H_{20}O_3$: C, 69.87%; H, 8.22%. Calcd.: C, 69.61%; H, 8.99%.

E.I. Mass Spectra (m/e): 224[26%, molecular ion peak], 150[100%, $C_9H_{10}O_2$], 91[22%, C_7H_7], 65[11%, C_5H_5]



2.4.5 Preparation of Polyesters (General Procedure)

The organometallic diol was transferred to a N_2 -purged Schlenk tube and dissolved in a minimum amount of dry toluene. Four equivalents of triethylamine were syringed into the stirred solution. An equivalent amount of terephthaloyl chloride was dissolved in dry toluene (8 ml) and this solution was added dropwise to the above mixture. Reactions were performed for either 2h or 24h periods. During this time the reaction mixture was observed to turn cloudy. The mixture was then filtered by gravity into a round-bottomed flask containing hexane, when a solid product precipitated. The supernatant liquid was syringed off and the solid washed with hexane. The product was dried under vacuum.

All other polyesters were prepared using a similar procedure.

31. Yield = 0.177 g (76%). 1H NMR (200 MHz, $CDCl_3$, δ): 1.40(t, 2H, $FeCH_2$), 1.88(m, 2H, CH_2), 2.32(s, 3H, CH_3), 3.85(t, 2H, CH_2OAr), 4.66(s, 4H, CH_2OH), 4.69(s, 5H, Cp), 5.44(s, 4H, $PhCH_2OC(O)Ar$), 7.28(s, 2H, Ar), 8.11-8.21(m, 4H, Ar).

IR (CH_2Cl_2), $\nu(CO)$ cm^{-1} : 2005(s), 1943(s), 1724(m, acyl).

32. Yield = 0.157 g (73%). $^1\text{H NMR}$ (200 MHz, CDCl_3 , δ): 1.99(m, 2H, CH_2), 2.34(s, 3H, CH_3), 2.63(t, 2H, $-\text{CH}_2\text{Cp}$), 3.99(t, 2H, $-\text{CH}_2\text{OAr}$), 5.19-5.23(m, 4H, Cp), 5.41(s, 4H, $\text{PhCH}_2\text{OC(O)Ar}$), 7.29(s, 2H, Ar), 8.09-8.20(m, 4H, Ar).

IR (CH_2Cl_2), $\nu(\text{CO}) \text{ cm}^{-1}$: 2021(s), 1925(s), 1721(m, acyl).

33. $^1\text{H NMR}$ (200 MHz, CDCl_3 , δ): 1.38(br t, 4H, FeCH_2), 1.86(br m, 4H, CH_2), 2.36(s, 3H, CH_3), 3.80(br t, 4H, CH_2OAr), 4.72(br s, 10H, Cp), 4.93(br s, Ar-O- CH_2Ar), 5.44(br s, 4H, $\text{PhCH}_2\text{OC(O)Ar}$), 6.38(br s, 1H, Ar), 6.55(br s, 2H, Ar), 7.19(br s, 2H, Ar), 8.10(br s, 4H, Ar).

IR (CH_2Cl_2), $\nu(\text{CO}) \text{ cm}^{-1}$: 2004(s), 1944(s), 1720(m, acyl).

34. Yield = 0.159 g (82%). $^1\text{H NMR}$ (200 MHz, CDCl_3 , δ): 0.91(m, 2H, CH_3), 1.38-1.50(m, 2H, CH_2), 1.71-1.84(m, 2H, CH_2), 2.33(s, 3H, CH_3), 3.94(t, 2H, $-\text{CH}_2\text{OAr}$), 5.43(s, 4H, $\text{PhCH}_2\text{OC(O)Ar}$), 7.28(s, 2H, Ar), 8.15(s, 4H, Ar).

IR (KBr, DRIFTS), $\nu(\text{CO}) \text{ cm}^{-1}$: 1719(m, acyl).

2.4.6 Preparation of Polyurethanes (General Procedure)

A Schlenk tube was evacuated and filled with nitrogen. A sample of the organometallic bifunctional monomer was transferred to the Schlenk tube and dissolved in dry, degassed THF (20 ml). A slight excess of 1,6-hexanediisocyanate was syringed into the clear solution and the mixture stirred at room temperature for 2 days. The solvent was removed by rotary evaporation and then remaining solid was washed thoroughly with CH_2Cl_2 , to remove the unreacted starting materials. The products were dried under vacuum.

All other polyurethanes were prepared using a similar procedure.

35. IR (KBr, DRIFTS), $\nu(\text{NH}) \text{ cm}^{-1}$: 3320, $\nu(\text{CH}) \text{ cm}^{-1}$: 2932, 2858, $\nu(\text{CO}) \text{ cm}^{-1}$: 1999, 1947(s), $\nu(\text{CO}) \text{ cm}^{-1}$: 1718(m, acyl).

36. IR (KBr, DRIFTS), $\nu(\text{NH}) \text{ cm}^{-1}$: 3359, $\nu(\text{CH}) \text{ cm}^{-1}$: 2931, 2856, $\nu(\text{CO}) \text{ cm}^{-1}$: 2014, 1929(s), $\nu(\text{CO}) \text{ cm}^{-1}$: 1720(m, acyl).

37. IR (NaCl plates), $\nu(\text{NH}) \text{ cm}^{-1}$: 3320, $\nu(\text{CH}) \text{ cm}^{-1}$: 2931, 2859, $\nu(\text{CO}) \text{ cm}^{-1}$: 1697(s, acyl).

2.5 References

1. S.F. Mapolie, J.R. Moss and G.S. Smith, *J. Inorg. Organomet. Polym.*, 1997, **7**, 233.
2. B. Panunzi, A. Roviello, F. Ruffo and A. Vivo, *Inorg. Chim. Acta.*, 1998, **281**, 141.
3. A.S. Abd-El-Aziz, E.K. Todd and G.Z. Ma, *J. Polym.Sci.: Part A: Polym. Chem.*, 2001, **39**, 1216.
4. P. Nguyen, P. Gomez-Elipse and I. Manners, *Chem. Rev.*, 1999, **99**, 1515.
5. W.-M. Xue, F.E. Kühn, E. Herdtweck and Q. Li, *Eur. J. Inorg. Chem.*, 2001, 213.
6. F.J. Gomez and K.B. Wagener, *J. Organomet. Chem.*, 1999, **592**, 271.
7. R.J. Puddephatt, *Chem Commun.*, 1998, 1055.
8. J.E. Sheats, C.E. Carraher, Jr., C.U. Pittman, Jr. and M. Zeldin, *Macrol. Symp.*, 2000, **156**, 79.
9. M.L. Turner, *Annu. Rep. Prog. Chem. Sect. A*, 1999, **95**, 453.
10. U. Caruso, A. Di Matola, B. Panunzi, A. Roviello and A. Sirigu, *Polymer*, **42**, 2001, 3973.
11. C.U. Pittman, Jr., C.E. Carraher, Jr., J.E. Sheats, M.D. Timken and M. Zeldin, *Inorganic and Metal-Containing Polymeric Materials*. Plenum Press: New York, 1990, 1.
12. D.E. Bergbreiter, *ChemTech*, 1987, 686.
13. M.J. Sundell and J.H. Näsman, *ChemTech*, 1993, 16.
14. K.E. Uhrich, C.J. Hawker, J.M.J. Fréchet and S.R. Turner, *Macromolecules*, 1992, **25**, 4583.
15. I. Gitsov, K.L. Wooley and J.M.J Fréchet, *Angew. Chem. Int. Ed. Engl.*, 1992, **31**, 1200.
16. S.F. Mapolie, I.J. Mavunkal, J.R. Moss and G.S. Smith, *Appl. Organomet. Chem.*, 2002, **16**, 307.
17. J.R. Moss, *J. Organomet.Chem.*, 1982, **231**, 229.
18. I.J. Mavunkal, J.R. Moss and J. Bacsa, *J. Organomet. Chem.*, 2000, **593-594**, 361.
19. Y.H. Liao and J.R. Moss, *J. Chem. Soc., Chem. Commun.*, 1993, 1774.
20. Y.H. Liao and J.R. Moss, *Organometallics*, 1995, **14**, 2130.
21. Y.H. Liao and J.R. Moss, *Organometallics*, 1996, **15**, 4307.
22. M.A. Hearshaw and J.R. Moss, *Chem. Commun.*, 1999, 1.

23. M.L.H. Green, In *Organometallic Compounds*, Methuen: London, 1968, **2**, 203.
24. A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
25. J.H. Saunders and K.C. Frisch, In *Polyurethanes, Chemistry and Technology. Part I. Chemistry*, Interscience: New York, 1962, 174.
26. C. Hepburn, *Polyurethane Elastomers*, Applied Science Publishers: London, 1982, 1.
27. Nonius BV COLLECT Data Collection Software 1999.
28. Otwinowski Z, Minor W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. In *Methods in Enzymology*, Carter CW, Sweet RM (Eds); Academic Press: New York, 1997, **276**, 307.
29. Sheldrick GM SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany 1997.
30. Spek AL PLATON, A Program for Plotting Molecular and Crystal Structures, University of Utrecht, The Netherlands 1997.



CHAPTER 3

The Synthesis and Attempted Complexation Of Functionalised Organic Condensation Polymers

3.1 Introduction

Polycondensations of organometallic monomers represent a field of organometallic polymers, where organometallic compounds bearing suitable bifunctional moieties, can undergo classical organic or inorganic condensation polymerisation reactions.¹⁻²

These types of polymers have come to include a subclass of this field, where the organometallic moiety is either pendant to the polymer backbone or is in the main chain. The inception of organometallic polymers³⁻⁵ containing metals in the main chain came into being after the discovery of ferrocene. Polymerisable bifunctional groups were incorporated on the cyclopentadienyl rings of ferrocene and other similar metallocene-type complexes.⁶⁻⁸ Most of the work that started in the 1950s and 1960s focussed on poly(metallocenes).^{9,10} Probably the most substantial contribution directed toward the synthesis of linear metal-containing polymers was done by the research group lead by Manners. This group initiated projects using ring-opening polymerisation of strained ring-tilted metallocenophanes, producing a diverse array of poly(metallocenes).¹¹⁻¹⁴ Over the years, novel ways of introducing bifunctional ligands into organometallic complexes have been developed. These have ranged from the conventional metallocene-type systems, and have given rise to organometallic polymers with metal anchored to the polymer backbone.^{15,16} Recently, a novel route to organometallic polymers was developed, by synthesising metal-carbene systems, and polymerising the bifunctional alkoxy carbene with diamines.^{17,18}

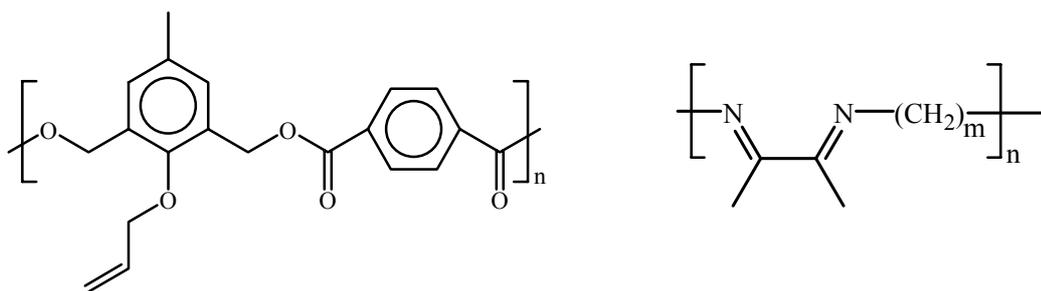
Although the construction of new systems for polymerisation varies from compound to compound, the methods for the synthesis of polymers are often similar. That is, polymers may be prepared by incorporating a polymerisable bifunctional group into the metal complex monomer, which is then followed by polymerisation. Alternatively, metal-containing polymers can be prepared by derivatising preformed organic polymers with metal-containing moieties, as was explained in the previous Chapters of this thesis. Both

these approaches have their own advantages and disadvantages, some of which are tabulated below.

Table 3.1 Comparison of routes to forming metal-containing polymers

Synthesis of metal-containing polymers by polymerisation of the metal-containing monomer	Synthesis of metal-containing polymers by derivatizing preformed organic polymers
<ul style="list-style-type: none"> ● Resultant polymers are fully metallated ● Molecular weight characteristics are governed by solubility factors and cannot be controlled ● Metal loadings cannot be varied 	<ul style="list-style-type: none"> ● Often results in partially metallated polymers ● Metal-containing polymers with specified molecular weight characteristics can be synthesized ● Metal-containing polymers with different metal loadings can be prepared

The prolific interest in organometallic and inorganic polymer chemistry has focussed on preparing new materials with special chemical and physical properties.¹⁹⁻²² We extended the latter methodology to attempt to prepare metal-containing polyesters and polyimines. In this chapter attention is focussed on the preparation of organic polymers of type **A** (polyester) and type **B** (polyimine).



Type A

Type B

Figure 3.1 Preformed organic polyester (Type A) and polyimine (Type B)

In principle, a number of metal-containing moieties can be coordinated to the terminal

vinyl moiety of polymer **A** or to the diimine moiety of polymer **B**. Thus, we have attempted hydrozirconation reactions with **A** and complexation reactions of PdCl₂(COD) with **B**.

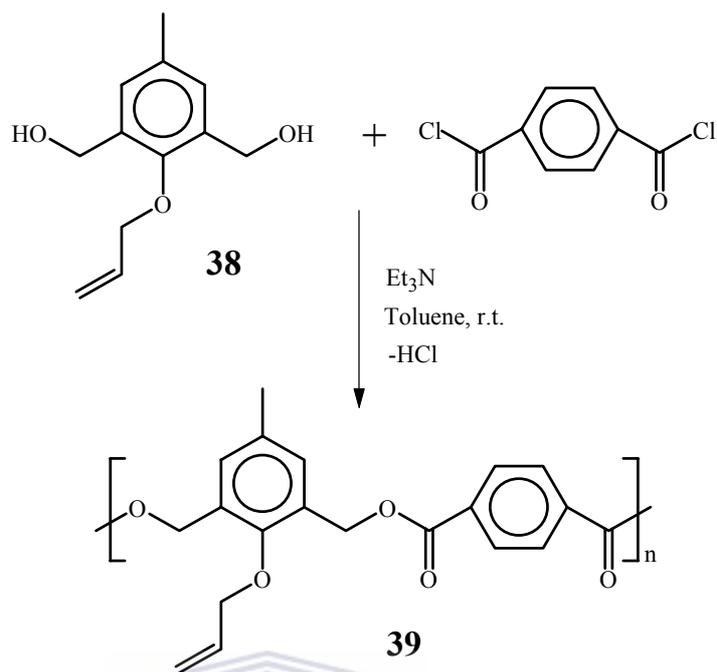
The rationale behind this study was to prepare metal-containing polymers that could serve as potential catalyst precursors. Anchoring a catalytic functionality to a polymer support offers the advantage of the ease with which one can physically separate a supported reagent from substrates and products.²³⁻²⁵ Polymer supported catalysts are fast becoming a prolific area of research, where metal complexes are supported on polymers.^{26,27} Probably the most popular example is Merrifield's resin,²⁸ which is a chloromethylated styrene/divinylbenzene copolymer. Many examples abound where metal complexes have been bonded to these polymers and their use in various applications described.²⁹⁻³¹

Our proposed polymer-supported metal systems could be specifically used in the polymerisation of ethylene. The results of this work are discussed in the following text.

3.2 Results and Discussion

3.2.1 Polyesters with terminal vinyl groups in the side chains

The parent organic polymer of type **A** (i.e. **39**) was synthesized by condensing the monomer **38** with terephthaloyl chloride, as shown in Scheme 3.1. Triethylamine is added as a base to remove HCl that is formed as a by-product of the reaction. This results in the formation of the salt, Et₃N.HCl, which is insoluble in the reaction medium, toluene, and is easily filtered from the reaction mixture. After removing the solvent from the filtrate by use of a rotary evaporator, the polyester **39** is taken up in CH₂Cl₂ and precipitated by addition of hexane. The choice of monomer **38** allows incorporation of a terminal vinyl moiety, which is pendant to the polymer main chain. This has the potential for further reaction with a host of suitable metal complexes.



Scheme 3.1

The polyester **39** was prepared previously via a different route by Bronstein and co-workers.³² The incorporation of the vinyl moiety was confirmed by NMR spectroscopy.

The ¹H NMR spectrum of the polymer **39** (Figure 3.2) shows a number of well-resolved signals, consistent with the formation of a polyester. The peaks corresponding to the aromatic rings are seen at δ 8.12 and 7.29 ppm. The presence of the vinyl moiety is noted by a splitting pattern, characteristic of AMX spin systems. These correspond to the vinylic protons (-CH=CH₂), and display two doublets (around 5.3 ppm) and a doublet of doublets (~6.1 ppm). This pattern arises from the coupling between the three magnetically non-equivalent protons. Furthermore, the appearance of a new signal at δ 5.43 ppm confirms the formation of an ester linkage. This is assigned to the -CH₂- protons of the newly-formed ester bond. The complete assignments are given in the experimental section.

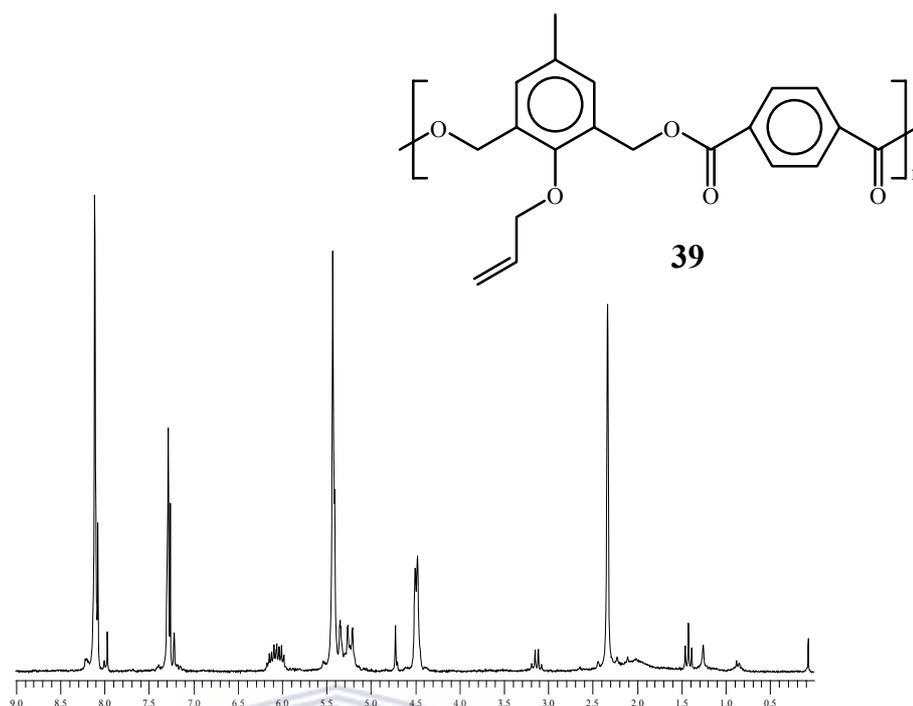
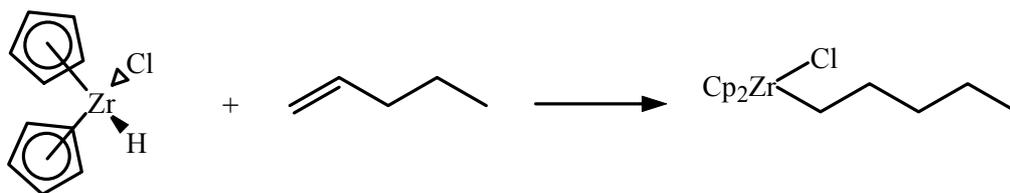


Figure 3.2 ^1H NMR spectrum of organic polyester **39**

In support of the above evidence, IR spectroscopy shows a strong, sharp band due to the carbonyl of the ester linkage [$\nu(\text{CO}) = 1724 \text{ cm}^{-1}$]. The molecular weight characteristics of **39**, as determined from gel permeation chromatography were, $M_n = 4914$; $M_w = 6140$; $M_w/M_n = 1.25$. This suggests a degree of polymerisation of about 13 and it is found to be a low molecular weight polymer. The polymer **39** was isolated as an off-white solid that is soluble in a range of common organic solvents, such as CH_2Cl_2 , acetone, diethyl ether and THF.

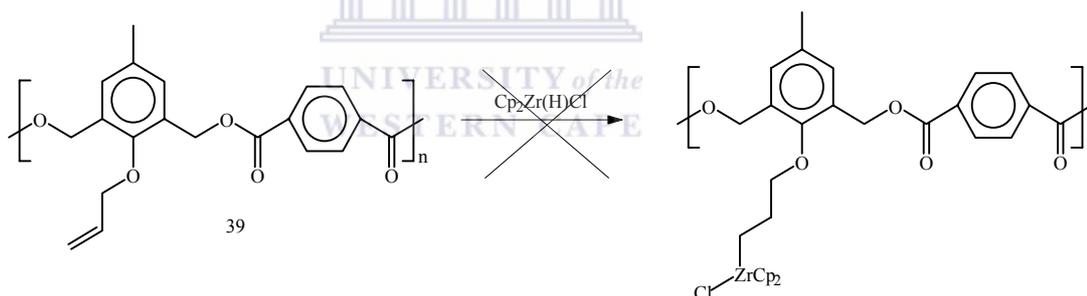
3.2.2 Attempted Hydrozirconation Reactions

A number of synthetic routes are available to functionalize the pendant allyl-terminated polyester **39**, using various metal complexes. Our interest in using zirconium led us to attempt hydrozirconation reactions using Schwartz's reagent, $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$.³³ Hydrozirconation reactions occur under mild conditions with a variety of olefins and give rise to alkylzirconium(IV) complexes, as is illustrated in Scheme 3.2. The zirconium moiety is usually bonded to the sterically least hindered position of the olefin.



Scheme 3.2

The attempted functionalization of polyester **39** and the idealized structure of the target product is shown in Scheme 3.3. The reaction was followed by ¹H NMR spectroscopy in deuterated CDCl₃. In our case, reaction of the hydride, Cp₂Zr(H)Cl, with the organic allyl-terminated polyester **39** was not successful. The reaction was attempted at room temperature on an NMR scale. The reactants were mixed in a sample vial in a glove-box and allowed to stand for a few minutes until a homogeneous solution was attained. The solution was then transferred to an NMR tube and monitored.

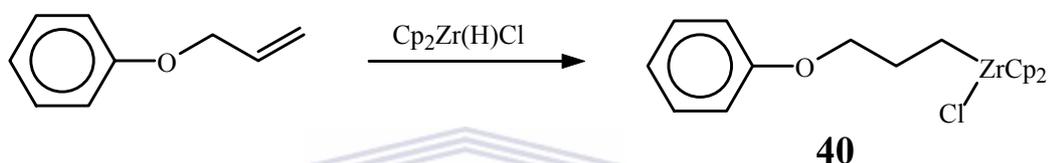


Scheme 3.3

No alkylzirconium formation was observed. The AMX spin pattern corresponding to the pendant vinyl groups of the polymer was still present, which is clear proof that hydrozirconation had not occurred. In addition, the presence of some other unknown zirconium species is present. This is noted by the presence of another signal due to the Cp protons, other than that due to the hydride. A slight shift of the peak due to the -CH₂- protons next to the ester linkage is observed. Reactions over a prolonged period again only showed the presence of the starting materials and the formation of another zirconium complex. Schwarz and

Labinger³⁴ found that the moiety, Cp_2ZrCl , is incompatible with a number of functional groups, and suggest that in most cases, the reaction with functional groups that are present take precedence over the reaction with olefins. It is thus feasible to propose that there may be some interaction between the ester functionality and the hydrozirconation reagent. It was decided to confirm this finding by a series of model reactions. These reactions were performed under the same conditions and were all carried out on an NMR scale in dry deuterated chloroform.

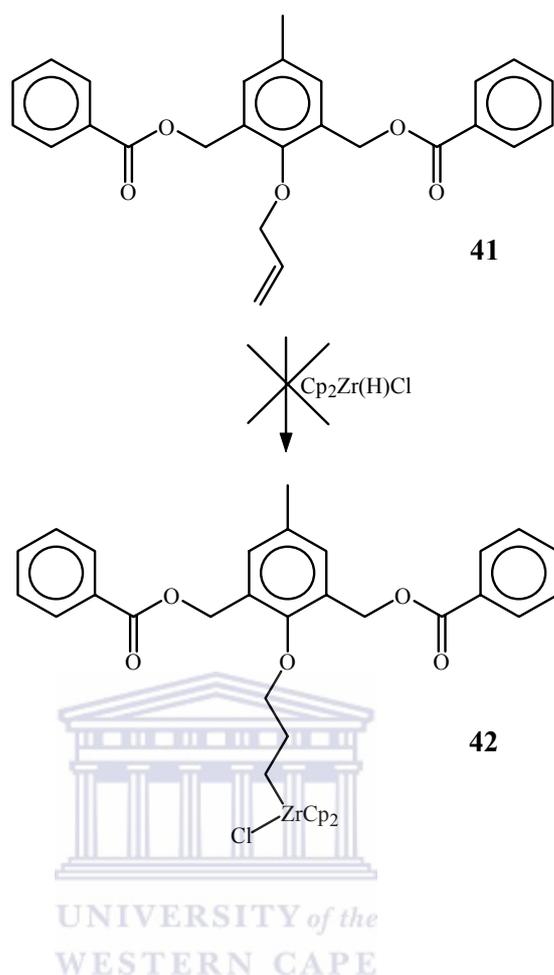
Initially, allyl phenyl ether was reacted with the hydride, $\text{Cp}_2\text{Zr(H)Cl}$ (Scheme 3.4).



Scheme 3.4

The ^1H NMR spectrum for the reaction shown in Scheme 3.4 indicated the formation of the desired alkylzirconium **40**. There were trace amounts of the allyl moiety noticeable in the spectrum. All the allyl groups can be converted by allowing the reaction to proceed for a longer period. This reaction has shown that there is no evidence of reaction at the ether linkage. Reaction rather occurs at the terminal end of the allyl group.

Reaction of the biphenyl ester **41** (Scheme 3.5) with the hydride was attempted. This reaction did not yield the desired alkylzirconium compound **42**, but rather showed the presence of some unknown zirconium species, by the appearance of a Cp signal different from that of the hydride. This observation is similar to that in the ^1H -NMR spectrum of the vinyl polyesters. The signals due to the allyl group are still present. A slight shift in the signal for the $-\text{CH}_2-$ protons of the ester linkage, clearly indicates interaction at the ester functionality. This clearly seems to show that some competing reaction of the zirconium complex with the carbonyl group is prevalent, when an ester functionality is present.



Scheme 3.5

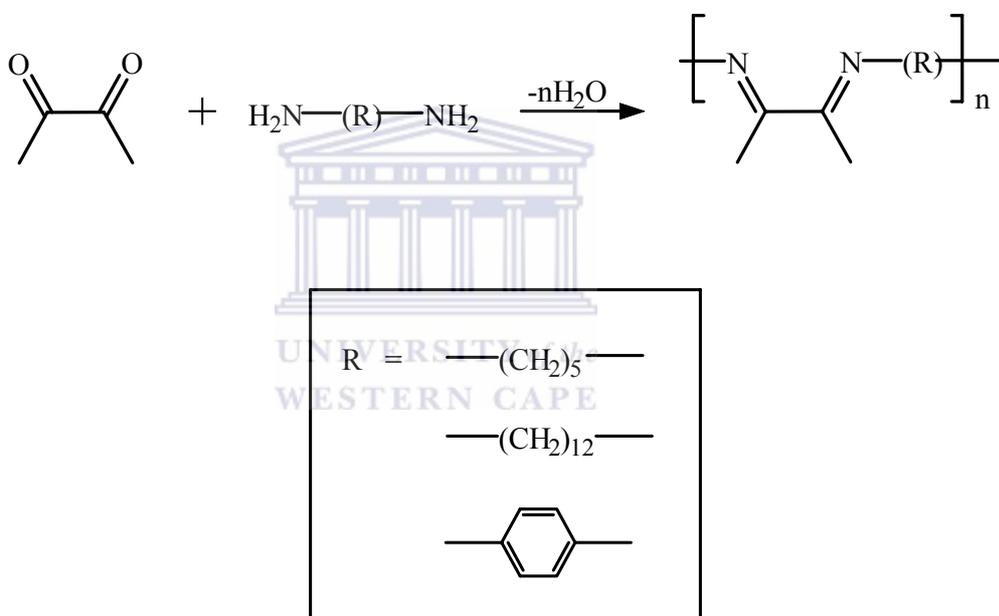
These model reactions have added weight to our proposal that there is indeed interaction with the ester functionality in our allyl-terminated organic polyester, suppressing the desired hydrozirconation reaction. We were not able to isolate and determine the exact nature of this undesired product.

3.2.3 Linear Polyimine Synthesis

As part of the continuing research studying the synthesis of metal-containing polymers, the strategy for functionalizing preformed organic polymers was used to prepare metal-containing polyimines. Imines are formed through the classical Schiff-base condensation

of an aldehyde or ketone with an amine. Thus, by employing two bifunctional monomers, for example, one containing a dione and the other a diamine, essentially linear polyimines could be formed.^{35,36}

It was desired to form short chain oligomers, thus studies using a concurrent addition of all reagents were performed. The alternate approach would be the slow addition of monomer to comonomer, which could conceivably lead to the preferential condensation of the monomer with the growing polymer chain. The polycondensations were also conducted in concentrated solutions, as lower concentrations of monomer units in the



reaction mixture should favour additions to existing oligomers, rather than new initiation processes. The polycondensations were achieved by reacting either 2,3-butanedione or 3,4-hexanedione in dry ether with various alkyl and aryl diamine monomers. These are illustrated in the general equation, equation 3.1. The oligomeric imines (**43**, **45**, **47**) prepared in this study are known compounds.³⁷⁻³⁹

(3.1)

The corresponding polymers (Table 3.2) were obtained as orange oils. The polymers are very soluble in common organic solvents and this allowed for characterisation using

conventional spectroscopic techniques.

The ^1H NMR spectra of these compounds revealed that condensation had indeed occurred between the carbonyl and amino functionalities, giving rise to polyimine compounds. This evidence was interpreted by comparison of the diamino monomers with that of the corresponding polymers. Two ^1H NMR spectra of the general structure for an aliphatic polyimine (**44**) and an aromatic polyimine (**45**) are shown in Figures 3.3 and 3.4 respectively. In Figure 3.3, the absence of CH_2 signals adjacent to the NH_2 of the starting aliphatic diamino monomer around 2.70 ppm, as well as by the appearance of a new signal downfield around 3.40 ppm of the CH_2 group adjacent to the imine moiety, presents proof that the polyimine has been formed. The backbone protons of the aliphatic polyimine resonate at 1.30 ppm and 1.65 ppm. The complete assignments are given in the experimental section.

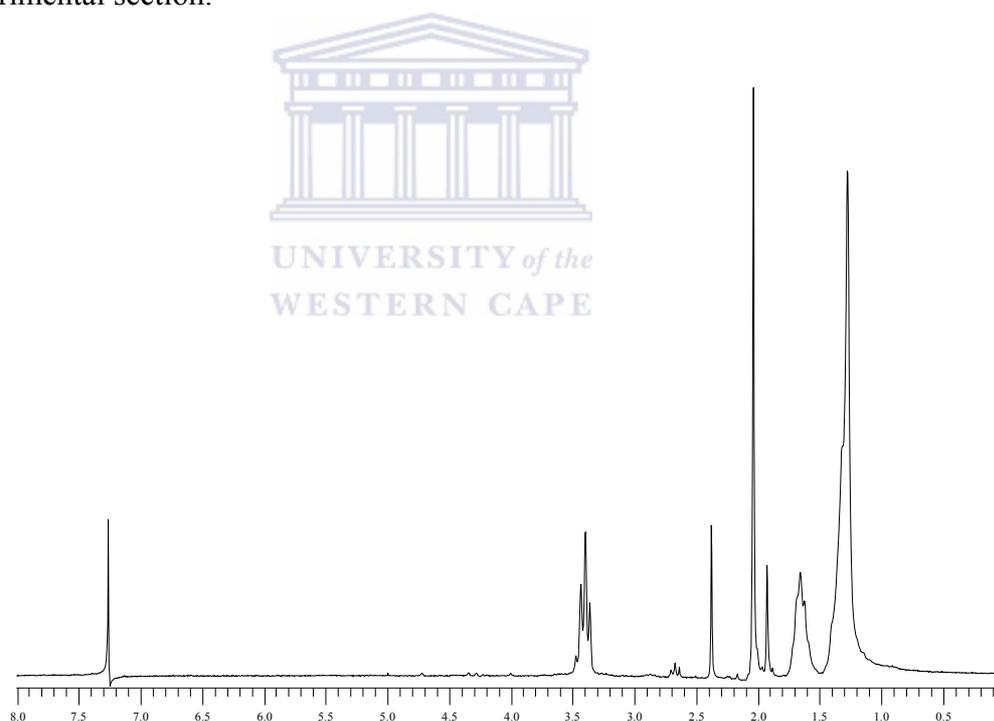


Figure 3.3 ^1H NMR spectrum of a linear aliphatic polyimine (CDCl_3)

Confirmation of the general structure of an aromatic polyimine is shown in Figure 3.4. This shows resonances characteristic of the various structural features of the short chain polyimine. Common to both spectra (Figures 3.3 and 3.4) are three different resonances

around 2ppm for the methyl protons. The centre, more intense peak, corresponds to the internal methyl groups in the linear polymer chain. This peak is flanked by two smaller peaks, that are ascribed to the methyl protons at the varying chain ends. For the preformed polyimines (**46**, **47**) where 3,4-hexanedione was used, more complex ^1H -NMR spectra with overlapping signals are obtained. In these oligomers, the methyl groups are now replaced by ethyl groups along the main chain.

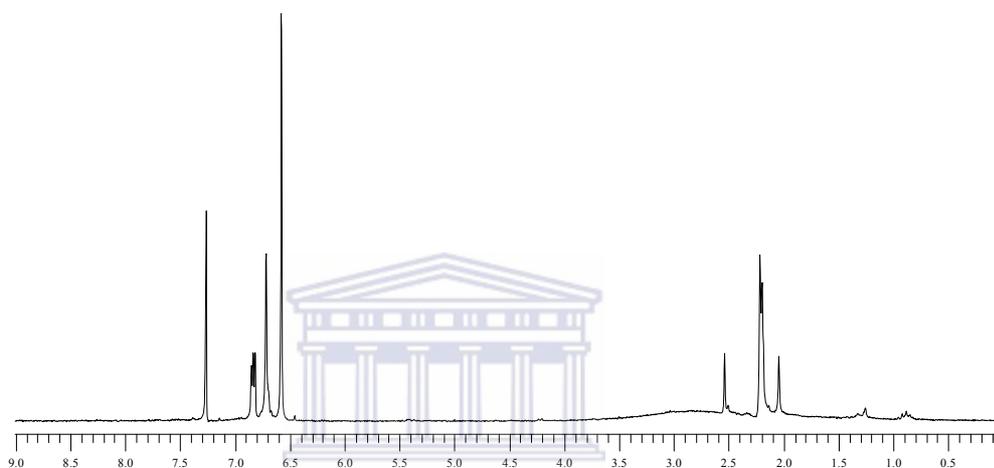


Figure 3.4 ^1H NMR spectrum of a linear aromatic polyimine (CDCl_3)

The presence of the imine moiety within the polymer chain was confirmed on the basis of infrared spectroscopy. The samples were recorded as neat oils between NaCl plates. In all the samples, a strong absorption band occurs around ca. 1654 cm^{-1} and a weaker band is apparent at 1580 cm^{-1} . These frequencies are assigned to the $\text{C}=\text{N}$ vibrations of the diimine moiety. For the aliphatic chain polyimines, characteristic peaks between 2856 and 2932 cm^{-1} are observed. These are ascribed to the $\text{C}-\text{H}$ symmetrical and asymmetrical stretching frequencies of the methylene groups of the polymer backbone.

The molecular weights of the polyimines as determined by size exclusion chromatography correlate with these compounds being short chain oligomers. The degree of polymerisation averages around five. The values are reported in Table 3.2.

Table 3.2 Monomers used for polyimine synthesis, their corresponding polymers and molecular weight data

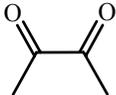
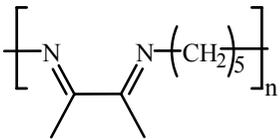
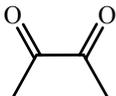
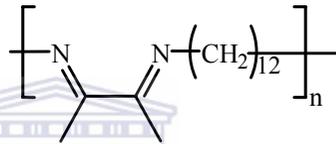
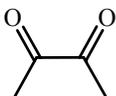
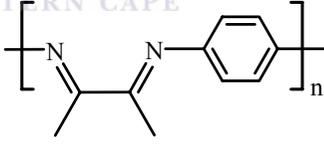
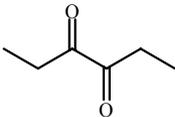
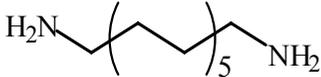
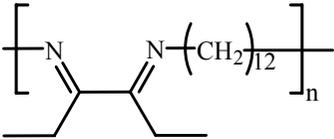
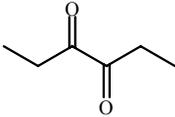
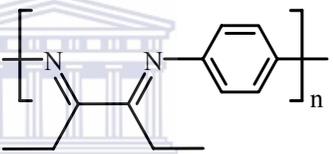
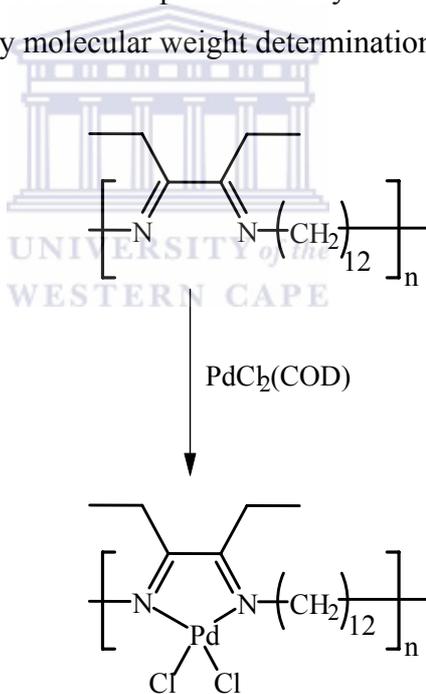
Monomer 1	Monomer 2	Polyimine	M_w	M_n	M_w/M_n
	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$	 43	856	719	1.19
	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$	 44	1002	864	1.16
		 45	759	627	1.21

Table 3.2 (cont.)

Monomer 1	Monomer 2	Polyimine	M_w	M_n	M_w/M_n
		 46	1058	917	1.15
		 47	902	729	1.24

3.2.4 Functionalisation reactions with PdCl₂(COD)

We attempted to prepare linear “Werner-type” coordination polymers, where the polymer main chain contains coordinate covalent bonds of palladium. The preformed linear polyimines contain essentially α -diimine moieties, which are well-known to stabilise organometallic complexes.⁴⁰ In addition, they show high reactivity toward highly electrophilic, cationic metal centres.^{41, 42} An attempt was made to synthesize metal-containing polyimines by complexation reactions of selected linear polyimines (**44**, **45**, **46**) with (1,5-cyclooctadiene)palladium(II) dichloride in dry dichloromethane at room temperature (Scheme 3.6). Precipitation was observed to occur during the initial 10 minutes after the addition. The reactions were generally allowed to proceed for 24 hours. Orange to dark orange solids were isolated for complexes **48**, **49**, and **50**, derived from the polyimine precursors **44**, **45**, and **46**, respectively. These oligomers are completely insoluble in all organic solvents. The poor solubility did not allow characterisation by ¹H NMR spectroscopy nor by molecular weight determination using GPC.



Scheme 3.6

The incorporation of palladium in the polyimine oligomers (**44**, **45**, **46**) was quantified by inductively coupled plasma (ICP) analysis. The palladium concentrations in 5% HCl aqueous solutions ranged from 23 to 25 wt%, and the values are given in Table 3.3. The results indicate that for **48** and **49**, complete metallation occurred. However, for **50**, 60%

of palladium incorporated. This implies that there are three palladium centres for every pentameric polyimine. The lower percentage of incorporation into the oligomer may be due to the increased steric nature of the ethyl groups adjacent to the imine moieties.

Table 3.3 ICP results of **48**, **49**, **50** of various Pd content

Oligome r	Estimated wt%	Measured wt%
48	24.88	23.54
49	31.72	30.48
50	23.35	16.85

The solid-state IR spectra (KBr DRIFTS) of the proposed palladium complexes show only a single absorption peak at $\sim 1588\text{ cm}^{-1}$, due to the coordinated imine moiety (C=N) and no absorption at 1654 cm^{-1} , which is a characteristic stretching frequency for the free uncomplexed imine system. Lavery and Nelson reported the disappearance of C=N absorptions in the IR spectra of metal complexes.⁴³ This is ascribed to be an infrared inactive C=N vibration in the Pd(II) complexes. This provides further proof of the incorporation of palladium in the polyimine oligomeric chain.

3.3 Conclusions

Linear polyesters of moderate molecular weight were prepared, containing terminal vinyl groups in side chains pendant to the polymer main chain. Attempts to hydrozirconate these vinyl polyesters using Schwarz's reagent proved unsuccessful, despite extended reaction times or increased reaction temperatures. It seems a competing reaction with the ester functionality is prevalent in these reactions.

Soluble, linear polyimines can be obtained by the reaction of aliphatic or aromatic diamine compounds with either 2,3-butanedione or 3,4-hexanedione. The concurrent addition of the monomers produced low molecular weight oligomers with degree of polymerisation of ~5. Functionalisation of the diimine moieties with PdCl₂(COD), yielded insoluble, intractable palladium-containing derivatives of the polyimines. This evidence was presented in part by ICP analysis and solid-state FTIR spectroscopy. However, the poor solubility limited the extent of characterisation.



3.4 Experimental

All polymerisation reactions were performed under nitrogen using standard Schlenk tube techniques, unless otherwise stated. Toluene, hexane and diethyl ether were dried over sodium/benzophenone and distilled under nitrogen before use. Dichloromethane was dried and distilled over P_2O_5 . 2,3-Butanedione; 3,4-hexanedione; 1,5-diaminopentane; 1,12-diaminododecane and 1,4-phenylenediamine were purchased from Sigma-Aldrich. Terephthaloyl chloride and triethylamine were obtained from SAARCHEM. $PdCl_2(COD)$ was prepared according to a published procedure.⁴⁴ Infrared spectra were recorded using DRIFTS (diffuse reflectance infrared transmission spectroscopy) in a KBr matrix (unless otherwise stated) on a Perkin Elmer Paragon 1000PC FT-IR spectrophotometer. 1H NMR spectra were recorded on a Varian XR200 spectrometer, using tetramethylsilane as an internal standard and $CDCl_3$ as solvent. Melting points were determined on a Fisher-Johns hotstage microscope, and are uncorrected. Inductively coupled plasma (ICP) analysis was carried out on a Varian Liberty II, radial ICP spectrometer, with a plasma gas flow of 15.0 L/min, a nebulizer pressure of 190kPa and an inner gas flow of 1.5 L/min. Readings were taken using a sample aspiration rate of 15 rpm.

3.4.1 General Procedure for the Preparation of Polyesters of Type A

The allyl-terminated bifunctional monomer³² (0.202 g, 0.971 mmol) was transferred to a N_2 -purged Schlenk tube and dissolved in a minimum amount of dry toluene (30 ml). Four equivalents of triethylamine were syringed into the stirred solution. An equivalent amount of terephthaloyl chloride (0.197 g, 0.971 mmol) was dissolved in dry toluene (10ml) and this solution was added dropwise to the above mixture. The reaction was performed for 24h at room temperature. During this time the reaction mixture was observed to turn cloudy. The mixture was then filtered by gravity into a round-bottomed flask and the solvent removed from the filtrate by rotary evaporation. The residual oil was dissolved in a little CH_2Cl_2 and hexane added to precipitate the product. The supernatant liquid was syringed off and the solid washed with hexane. The polyester **39** was dried under vacuum and isolated as an off-white solid. Yield = 0.308 g (76%).

1H NMR (200MHz, $CDCl_3$, δ): 2.34(s, 3H, \underline{CH}_3), 5.25(d, 1H, $=\underline{CH}_2$), 5.40 (d, 1H, $=\underline{CH}_2$), 5.43(s, 4H, $Ph\underline{CH}_2OC(O)Ar$), 6.00-6.15(dd, 1H, $\underline{CH}=\underline{CH}_2$), 7.29(s, 2H, Ar), 8.08-8.12(m, 4H, Ar). IR (CH_2Cl_2), $\nu(CO)cm^{-1}$: 1724(m, acyl). $M_n = 4914$; $M_w = 6140$; $M_w/M_n = 1.25$.

3.4.2 General Procedure for the Preparation of Polyimines of Type B

A solution of the dione in dry diethyl ether was added to nitrogen-purged Schlenk tube. Anhydrous MgSO_4 was added to the solution, together with a one-portion addition of the diamine compound in dry diethyl ether. The reaction mixture was stirred at r.t. overnight and then filtered by gravity. The solvent was removed from the filtrate by rotary evaporation to give the desired product.

43 : ^1H NMR (200MHz, CDCl_3 , δ): 1.40 - 1.57(m, $-\text{CH}_2-$), 1.69 - 1.82(m, $-\text{CH}_2-$), 1.93(s, CH_3), 2.04(s, CH_3), 2.36(s, CH_3), 3.46(t, $-\text{CH}_2-\text{N}=\text{C}$).
IR (neat oil), $\nu(\text{C}=\text{N})\text{cm}^{-1}$: 1697.54.

44 : ^1H NMR (200MHz, CDCl_3 , δ): 1.20 - 1.43(br m, $-\text{CH}_2-$), 1.58 - 1.75(br m, $-\text{CH}_2-$), 1.92(s, CH_3), 2.04(s, CH_3), 2.37(s, CH_3), 3.39(t, $-\text{CH}_2-\text{N}=\text{C}$).
IR (neat oil), $\nu(\text{C}=\text{N})\text{cm}^{-1}$: 1697.79.

45 : ^1H NMR (200MHz, CDCl_3 , δ): 2.04(s, CH_3), 2.12(s, CH_3), 2.54(s, CH_3), 6.57(s, Ar), 6.72(s, Ar), 6.82(m, Ar).
IR (neat oil), $\nu(\text{C}=\text{N})\text{cm}^{-1}$: 1697.28.

46 : ^1H NMR (200MHz, CDCl_3 , δ): 0.90 - 1.10(m, CH_3), 1.27(br m, CH_3), 1.64(br m, $-\text{CH}_2-$), 2.40 - 2.90(br m, $-\text{CH}_2\text{CH}_3$), 3.46(t, $-\text{CH}_2-\text{N}=\text{C}$).
IR (neat oil), $\nu(\text{C}=\text{N})\text{cm}^{-1}$: 1653.02.

47 : ^1H NMR (200MHz, CDCl_3 , δ): 0.96 - 1.10(m, CH_3), 2.70 - 3.05(m, $-\text{CH}_2\text{CH}_3$), 6.57(s, Ar), 6.58(s, Ar), 6.68(s, Ar).
IR (neat oil), $\nu(\text{C}=\text{N})\text{cm}^{-1}$: 1652.78.

3.4.3 General Procedure for the reaction of the Polyimines of Type B with PdCl₂(COD)

Reactions were attempted with the preformed polyimines, **44**, **45**, and **46**.

A Schlenk tube was evacuated and filled then with nitrogen. PdCl₂(COD) (4 equiv.) was transferred to the Schlenk tube. This was dissolved in dry CH₂Cl₂ (15 ml). The polyimine oligomer (0.200 g), was dissolved separately in dry CH₂Cl₂ (5 ml). This solution was added to the Schlenk tube and the mixture stirred at room temperature under nitrogen. After a few minutes, an orange precipitate formed. The reaction was allowed to proceed overnight, and the solid collected on a Hirsch funnel. The solid was washed with CH₂Cl₂ and dried under vacuum, yielding a dark orange solid. The solids were completely insoluble in all organic solvents. IR: **48**, **49**, **50** (DRIFTS, KBr matrix), $\nu(\text{C}=\text{N})\text{cm}^{-1}$: 1588.



3.5 References

1. C.E. Carraher, Jr., *Organometallic Polymers*, Academic Press, New York, 1978, 79.
2. I. Manners, *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 1063.
3. F.S. Arimoto and A.C. Haven, Jr., *J. Am. Chem. Soc.*, 1955, **77**, 6295.
4. C.U. Pittman, Jr. (Eds.: E. Becker and M. Tsutsui), *Organometallic Reactions*, Marcel Dekker, New York, 1977.
5. N. Hagihara, K. Sonogashira and S. Takahashi, *Adv. Polym. Sci.*, Springer-Verlag, 1981, 149.
6. A.D. Pomopailo (Ed.: J. Sheats), *Inorganic and Metal-Containing Polymeric Materials*, Plenum Press, New York, 1990, 29.
7. C.P. Gibson, D.S. Bem, S.B. Falloon and J.E. Cortopassi (Ed.: J. Sheats), *Inorganic and Metal-Containing Polymeric Materials*, Plenum Press, New York, 1990, 127.
8. A.K. Saha and M.M. Hossain, *J. Organomet. Chem.*, 1993, **445**, 137.
9. H.J. Rosenberg and E.W. Neuse, *J. Organomet. Chem.*, 1966, **6**, 76.
10. E.W. Neuse and H.J. Rosenberg, *J. Macromol. Sci.*, 1970, **C4**, 1.
11. F. Jäkle, Z. Wang and I. Manners, *Macromol. Rapid Commun.*, 2000, **21**, 1291.
12. I. Manners, *Can. J. Chem.*, 1998, **76**, 371.
13. P. Nguyen, P. Gómez-Elipe and I. Manners, *Chem. Rev.*, 1999, **99**, 1515.
14. I. Manners, *Science*, 2001, **294**, 1664.
15. C.U. Pittman, Jr., C.E. Carraher, Jr. J.E. Sheats, M.D. Timken and M. Zeldin, *Inorganic and Metal-Containing Polymeric Materials*, 1990, 1.
16. J.E. Sheats, C.E. Carraher, Jr., C.U. Pittman, Jr. and M. Zeldin, *Macromol. Symp.*, 2000, **156**, 79.
17. R. Nomura, K. Watanabe and T. Masuda, *Macromolecules*, 2000, **33**, 1936.
18. R. Nomura, K. Watanabe and T. Masuda, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1999, **40**, 80.
19. K. Kulbaba and I. Manners, *Macromol. Rapid Commun.*, 2001, **22**, 711.
20. C.U. Pittman, Jr., C.E. Carraher, Jr. J.E. Sheats, M.D. Timken and M. Zeldin, *Inorganic and Metal-Containing Polymeric Materials*, 1990, 1.
21. J.E. Sheats, C.U. Pittman, Jr. and C.E. Carraher, Jr, *Chem. Br.*, 1984, **20**, 709.
22. R.L. Rawls, *Chem. Eng. News*, 1987, **65**, 29.
23. M.J. Sundell and J.H. Nasman, *Chemtech*, 1993, 16.

24. B. Panunzi, A. Roviello, F. Ruffo and A. Vivo, *Inorg. Chim. Acta*, 1998, **281**, 141.
25. C. Huber, F. Bangerter, W.R. Caseri and C. Weder, *J. Am. Chem. Soc.*, 2001, **123**, 3857.
26. C.E. Carraher, Jr., *J. Chem. Ed.*, 1981, **58**, 921.
27. A. Kirschning, H. Monenschein and R. Wittenberg, *Angew. Chem. Int. Ed.*, 2001, **40**, 650.
28. R.B. Merrifield, *J. Am. Chem. Soc.*, 1963, **85**, 2149.
29. S.M. Baxter, W.E. Jones Jr., E. Danielson, L. Worl, G. Strouse, J. Younathan and T.J. Meyer, *Coord. Chem. Rev.*, 1991, **111**, 47.
30. S. Itsuno, G.D. Darling, H.D.H. Stöver and J.M.J. Fréchet, *J. Org. Chem.*, 1987, **52**, 4644.
31. B. Brix and T. Clark, *J. Org. Chem.*, 1988, **53**, 3365.
32. L.M. Bronstein and P.M. Valetskii, *Polym. Sci.*, 1993, **35**, 1585.
33. C.A. Bertelo and J. Schwartz, *J. Am. Chem. Soc.*, 1975, **97**, 228.
34. J. Schwartz and J.A. Labinger, *Angew. Chem. Int. Ed. Engl.*, 1976, **15**, 333.
35. K. Suematsu, K. Nakamura and J. Takeda, *Polymer Journal*, 1983, **15**, 71.
36. A. Natansohn, H. Yang and C. Clark, *Macromolecules*, 1991, **24**, 5489.
37. A.F. Shelikh, B.I. Tikhomirov and I.A. Nemchinov, *Vysokomol. Soedin., Ser. B*, 1982, **24**, 124.
38. X. Li, C. Li and S. Li, *Synth. Met.*, 1993, **60**, 285.
39. C. Li, X. Li and S. Li, *Gaofenzi Xuebao*, 1994, 418.
40. S.D. Ittel, L.K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169.
41. S.A. Svejda and M. Brookhart, *Organometallics*, 1999, **18**, 65.
42. G.J.P. Britovsek, V.C. Gibson and D.F. Wass, *Angew. Chem. Int. Ed.*, 1999, **38**, 428.
43. A. Lavery and S.M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1984, 615.
44. L. Chatt, L.M. Vallarino and L.M. Venanzi, *J. Chem. Soc.*, 1957, 3413.

CHAPTER 4

The Synthesis and Characterisation of Poly(propyleneimine) Pyridylimine and Poly(propyleneimine) Salicylaldimine Metallodendrimers

4.1 Introduction

The synthesis of metallodendrimers has in recent years, like the more linear metal-containing polymers, developed at a prolific rate and a number of reviews concerning their structure, synthesis and properties have been published.¹⁻⁵ These materials show potential in a number of applications and are thought to possess interesting electronic, magnetic and catalytic properties.⁶⁻⁸ These potential uses are ascribed to the incorporation of metal centres into the dendrimer. Essentially, the dendrimers consist of a central core and emanating from this are several branches leading to a number of successive, well-defined generations. As far as metallodendrimers are concerned, the introduction of metal centres may occur at various branching points within the dendrimer or they may be found on the periphery of the dendritic molecule (Figure 4.1).

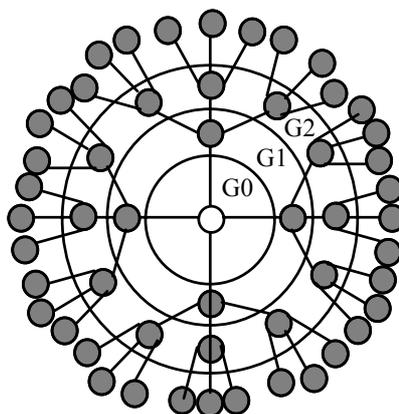


Figure 4.1 Structure of a typical dendrimer; hollow circle = central core, grey circles = branch point, black circles on the periphery = end groups, G_n = generation number.

In the case of terminal-functionalized dendrimers, a number of examples of

metallodendrimers have been reported in recent times.⁹⁻¹⁰ In addition several metallodendrimers have found application as catalysts or catalyst precursors.¹¹⁻¹⁵ Our interest in preparing catalytically active palladium metallodendrimers, prompted us to modify the end groups at the periphery of the commercially available poly(propyleneimine) dendrimer (DAB) (Figure 4.2). The DAB dendrimer has a diaminobutane core and amino groups as termini. This compound was first synthesized by Meijer *et al.* in 1993¹⁶ and can be built up to successive generations (G1, G2,.....,G6) containing up to 128 NH₂ termini. These dendrimers are now commercially available from the polymer company DSM[©].

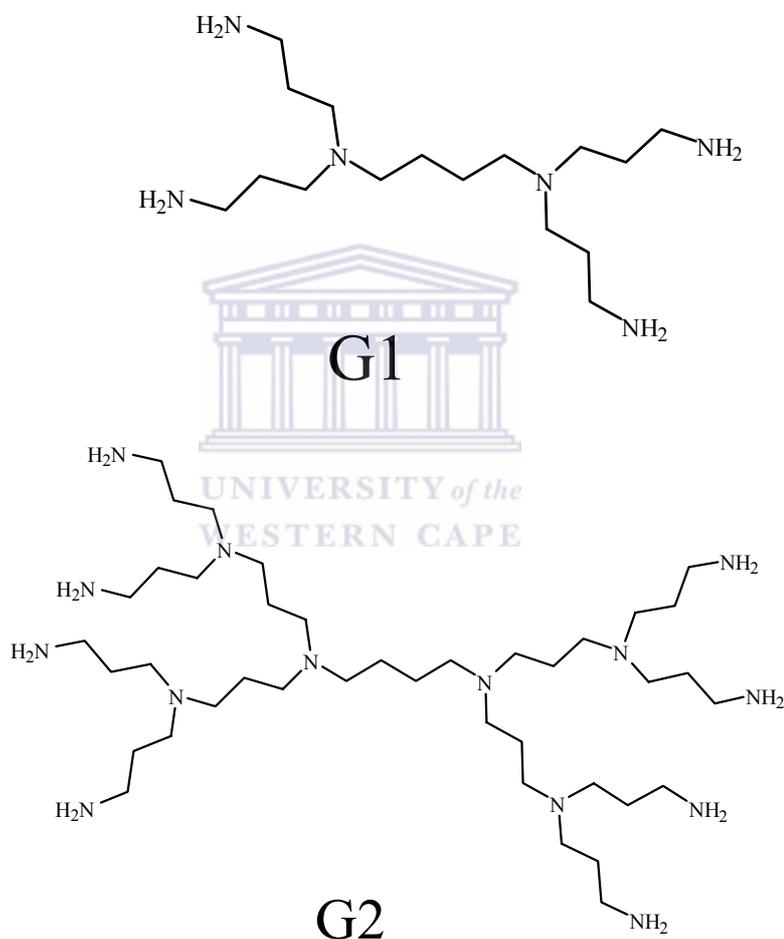
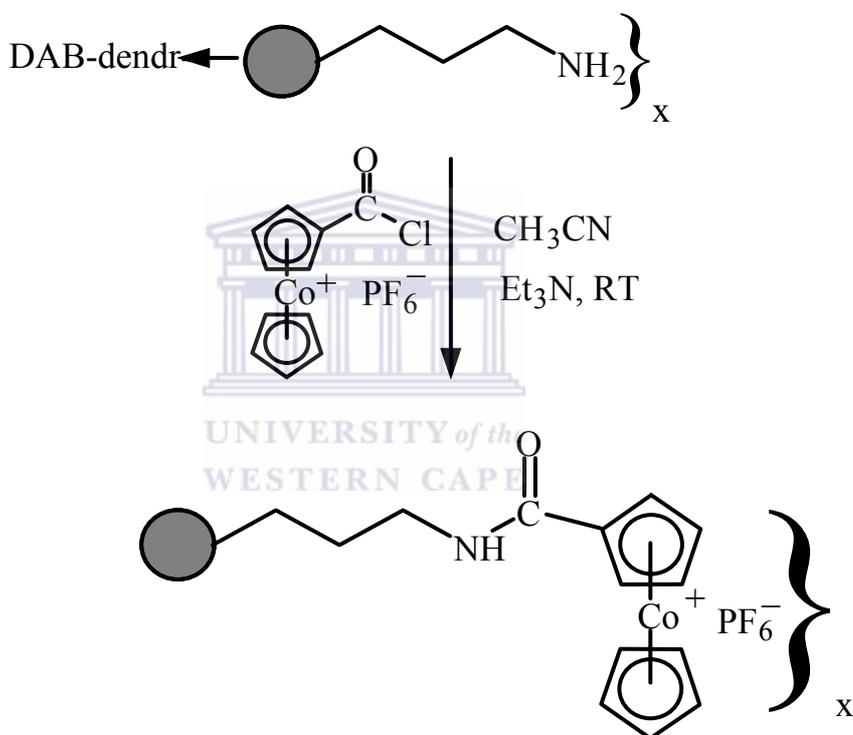


Figure 4.2 First (G1) and second (G2) generation DAB dendrimers

The DAB structure can serve as a strongly complexing tridentate coordination site for

various transition metals. Thus, by the addition of metal(II) chlorides (MCl_2 , with $M = Cu, Zn$ and Ni) in methanol to DAB, a number of metal ions have been incorporated onto the surface of the dendritic structure.¹⁷

Recently, Cuadrado and co-workers¹⁸ functionalized the periphery of the DAB with cobalticinium moieties. This was achieved through the reaction of the first four generations of DAB with an excess of the PF_6^- salt of 1-(chlorocarbonyl)cobalticinium in acetonitrile solution (Scheme 4.1).



Scheme 4.1

The metal-containing dendrimers were fully characterized by 1H NMR, ^{13}C NMR and IR spectroscopy and elemental microanalysis.¹⁸ Electrochemical studies were performed by cyclic voltammetry and these showed reversible redox chemistry. Prior to this work, Cuadrado and co-workers¹⁹ had also managed to functionalize the same poly(propyleneimine) dendrimer in good yields, up to the fifth generation with ferrocenyl moieties (Figure 4.3). These metallodendrimers were derived from the condensation

reaction of 1-(chlorocarbonyl)ferrocene with the terminal NH_2 groups of the respective DAB generations. They possess amide-linked ferrocenyl groups and their integrity on the periphery of the dendritic surface has been confirmed through ^1H NMR, ^{13}C NMR and IR spectroscopy, mass spectrometry and elemental microanalyses.

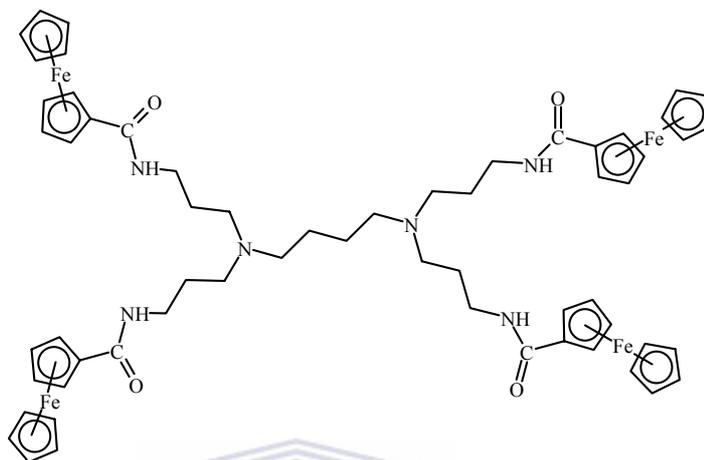


Figure 4.3 Ferrocenyl-functionalized poly(propyleneimine) dendrimer

Modification of the periphery with ferrocenyl groups was also achieved by Salmon and Jutzi.²⁰ Unlike Cuadrado, their strategy entailed starting from ferrocenecarboxaldehyde and condensing this with the amino groups of the DAB dendrimer, forming the corresponding imines. This method was employed up to the fifth generation, resulting in the introduction of 64 redox centres on the periphery. Reduction of these imino groups gives rise to the ferrocenyl dendrimers (Figure 4.4).

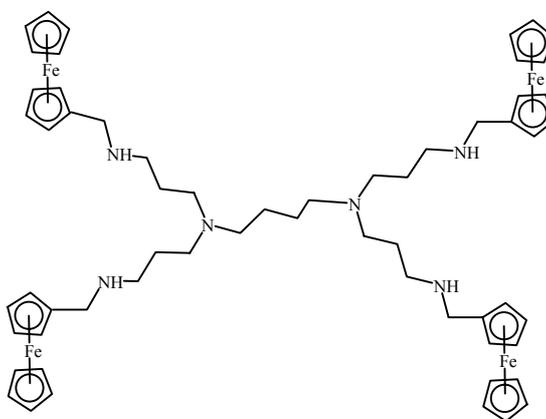


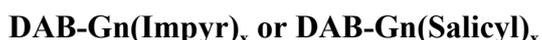
Figure 4.4 Salmon and Jutzi's ferrocenyl dendrimers

The work by Reetz and co-workers²¹ presents one of the few examples where a peripheral-functionalized DAB dendrimer was used as a catalyst. Their efforts focused on modifying the end-groups of DAB through phosphinomethylation of the primary amino groups. Metallodendrimers were then formed through the reaction of terminal diphosphane ligands with $[\text{PdCl}_2(\text{PhCN})_2]$, $[\text{Pd}(\text{CH}_3)_2(\text{tmeda})]$, $[\text{Ir}(\text{cod})_2\text{BF}_4]$ or $[\text{Rh}(\text{cod})_2\text{BF}_4]$. The use of the resulting complexes as catalysts in the Heck reaction was investigated and proved successful for the reaction of bromobenzene with styrene to produce stilbene.

In this chapter, we report the synthesis and characterisation of an pyridylimine end group functionalized poly(propyleneimine) dendrimer (DAB), by modifying the commercial DAB dendrimer up to the third generation on the periphery with 2-pyridinecarboxaldehyde. The subsequent complexation reactions of the resulting pyridylimine ligands with palladium, platinum and copper is also reported. The synthesis and characterisation of peripheral-functionalized salicylaldimine DAB dendrimers and their corresponding metallated complexes is also described. The preliminary results of this work have been published.²²

4.2 A Concise Notation for the Dendrimers in this Chapter

For clarity of presentation, the following concise notation for the dendrimers prepared in this chapter will be used. This notation is generally in the form :



where

- DAB: the diaminobutane core and poly(propyleneimine) network
G: represents the generation
n: the generation number of the dendrimer
Impyr: the iminopyridine end-group on the periphery of the dendrimer
Salicyl: the salicylaldimine end-group on the periphery of the dendrimer
x: the number of end-groups

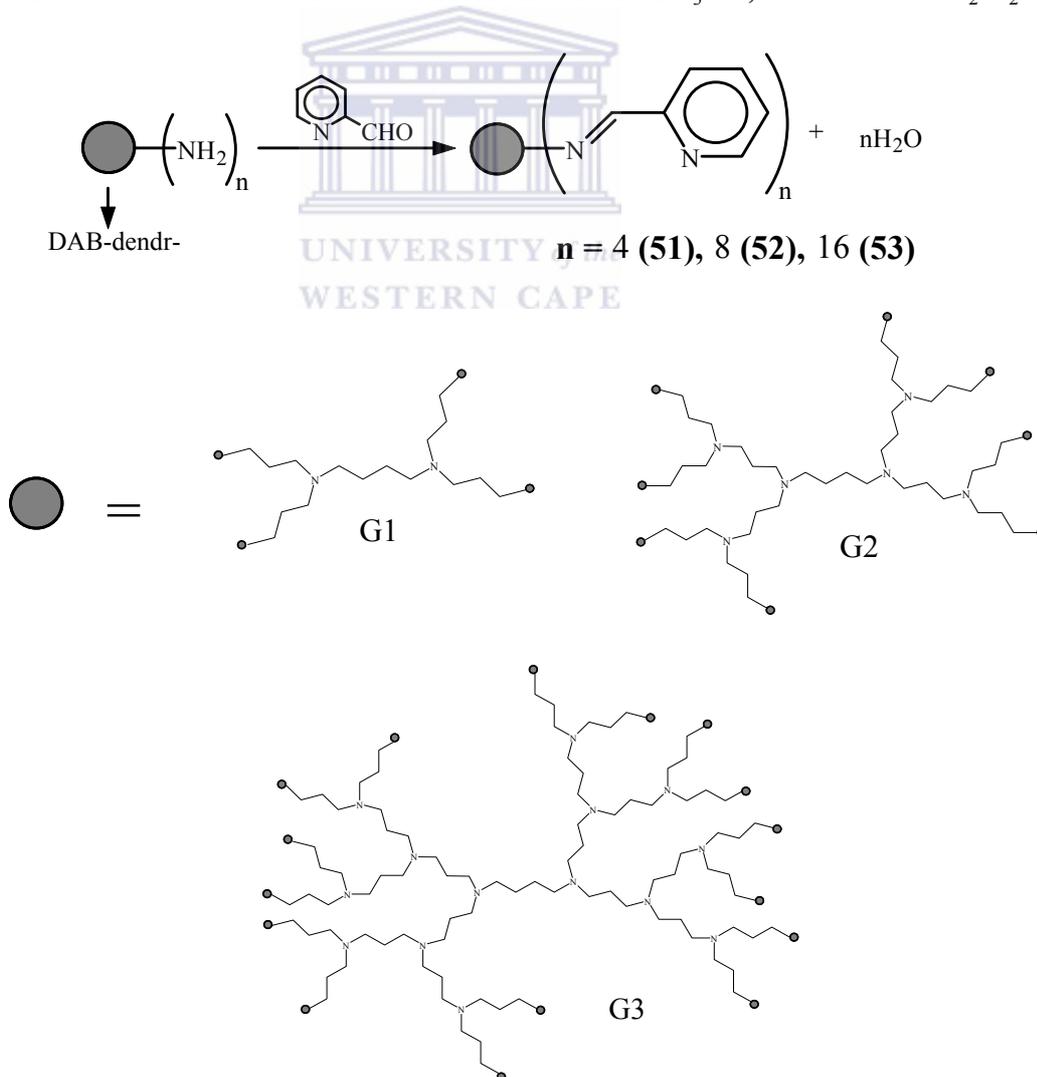
For example, DAB-G2(Impyr)_8 stands for the second generation DAB dendrimer with eight pyridylimine end-groups on the periphery. Also, the notation $\text{DAB-Gn(Impyr-ML}_n)_x$ suggests the corresponding metallodendrimer formed by the coordination of a metal (M)

and its ancillary ligands (L_n) to the diimine moiety.

4.3 Results and Discussion

4.3.1 Synthesis of Pyridylimine-functionalised DAB dendrimers

The first step towards the synthesis of the metallodendrimers employs conventional Schiff-base condensation (Scheme 4.2) of the commercially available 2-pyridinecarboxaldehyde with DAB-Gn(NH_2)_n ($n = 4, 8, 16$ for **51**, **52**, **53**, respectively). Anhydrous magnesium sulphate is used to remove the water formed as a by-product. The condensation reaction produced the pyridylimine-functionalized dendrimers, abbreviated in terms of the first-, second-, and third-generation respectively, as DAB-G1(Impyr)₄, DAB-G2(Impyr)₈ and DAB-G3(Impyr)₁₆. Copious washing with water is required to remove traces of excess 2-pyridinecarboxaldehyde. The dendrimers were isolated as stable orange oils in typical yields of 40-76% and are soluble in solvents such as CH_3CN , acetone and CH_2Cl_2 .



Scheme 4.2

¹H and ¹³C NMR spectroscopy

The three pyridylimine-functionalized dendrimers (**51** {n=4}, **52** {n=8}, **53** {n=16}) were characterized by ¹H and ¹³C NMR spectroscopy. Evidence of the condensation reaction is clearly seen in the ¹H NMR (Figure 4.5) of the DAB-G1(Impyr)₄ dendrimer (**51**) by the absence of CH₂ signals adjacent to the NH₂ of the starting dendritic polyamine around 2.70 ppm, as well as by the appearance of a new signal downfield around 3.70 ppm due to the CH₂ group adjacent to the imine moiety. In addition, the newly formed imine bond CH proton gives a singlet in the spectrum at δ = 8.35. This value for the imine proton stays constant and shows no significant shift with increasing generation. It has been noted that there is often an interaction of the imine proton with the protons in the position alpha to the nitrogen, when there is an increase in endgroup density. This development in dendritic character is, in certain cases, associated with hydrogen bond interactions, which results in a significant shift of the imine proton.

All three generations were characterized using 1D-NMR techniques. Upon increasing the dendrimer generation, the ¹H NMR spectra became slightly more complex. The reason for this is that the DAB network has a unique set of -CH₂-CH₂-CH₂- segments for each generation, that is separated from each other by trivalent nitrogen atoms. Thus 2D-COSY experiments (Figure 4.7) were used to provide further details and confirm the structure of the higher generation dendrimers.

The ¹³C NMR spectra (Figure 4.6) of the three generations are essentially very similar and show characteristic signals of the poly(propyleneimine) dendritic framework. The absorptions of the aliphatic -CH₂- protons are found in the region δ = 25 - 55, and the aromatic and imine carbons are typically found between 120 and 165 ppm.

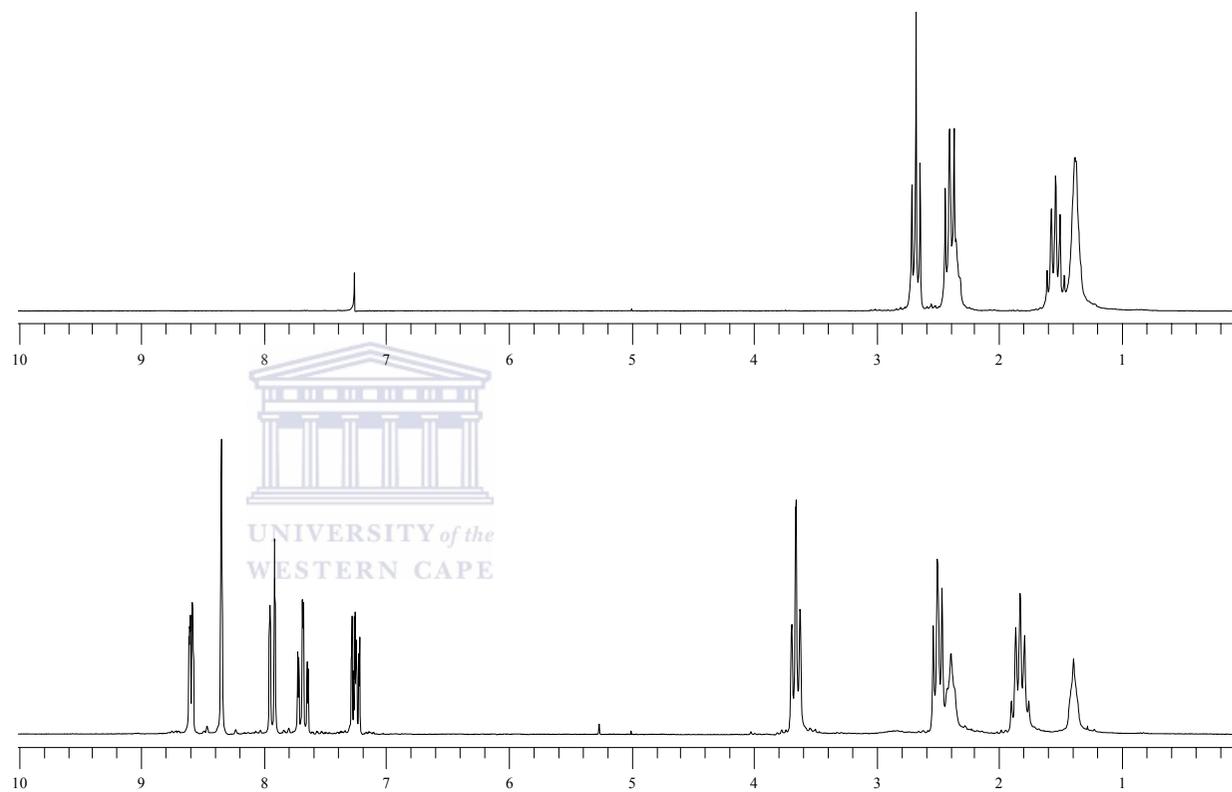


Figure 4.5 ^1H NMR spectra of $\text{DAB-G1}(\text{NH}_2)_4$ (above) and $\text{DAB-G1}(\text{Impyr})_4$ **51** (below)

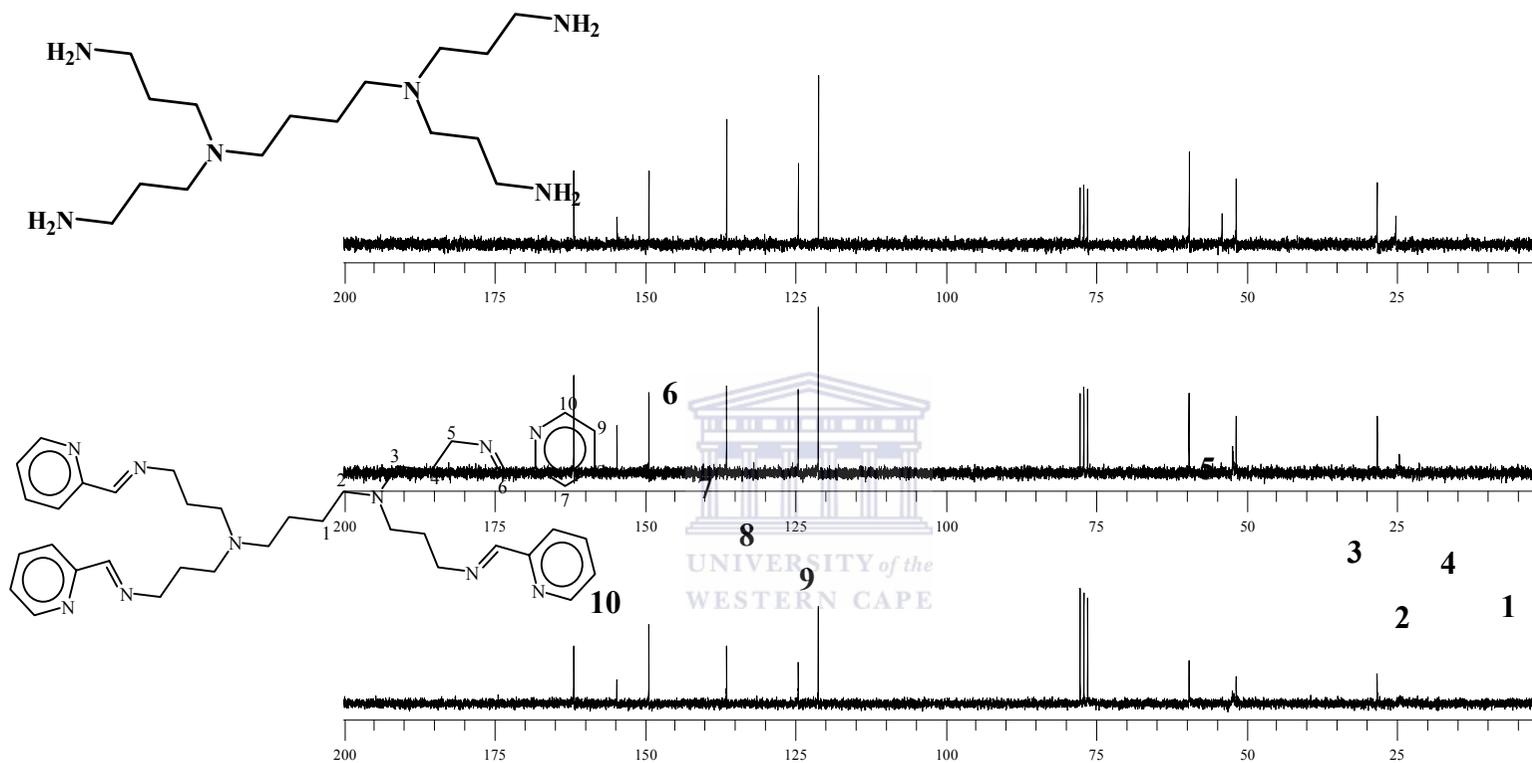


Figure 4.6 ^{13}C NMR spectra of the three generations, $\text{DAB-G1}(\text{Impyr})_4$ (51), $\text{DAB-G2}(\text{Impyr})_8$ (52) and $\text{DAB-G3}(\text{Impyr})_{16}$ (53)

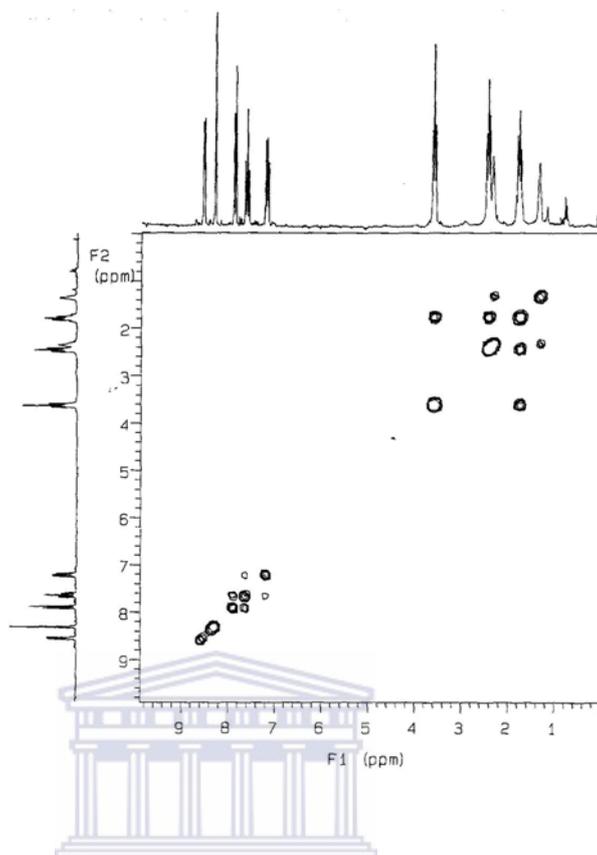


Figure 4.7 2D COSY NMR spectrum of DAB-G3(Impyr)₁₆ (**53**)

IR Spectroscopy

Infrared spectroscopy was used to achieve qualitative information on the end groups in the dendrimers. The IR spectra of the three samples (**51**, **52**, **53**) were recorded as neat oils between NaCl plates. In all three samples, three strong bands are apparent at ~ 1650 , 1587 , and 1567 cm^{-1} . These frequencies are assigned to the C=N vibration and pyridine-ring vibrations, respectively.

Microanalysis

Microanalysis was attempted on all the oils. Despite several purifications and thorough drying under vacuum overnight ($\sim 16\text{h}$), the microanalysis were still slightly outside acceptable limits for the higher generations. It is believed that there is solvent inclusion within the dendrimer. The re-calculated values with solvent inclusion correlate with the found data. Dichloromethane is used during the purification procedures and is not

completely removed, even after thorough drying under vacuum. The presence of dichloromethane can be seen in the ^1H NMR spectra. This phenomenon has also been observed in other poly(propyleneimine) dendrimers functionalized at the periphery with organic groups.²³ Despite these values, other supporting data confirm these to be the correct structures.

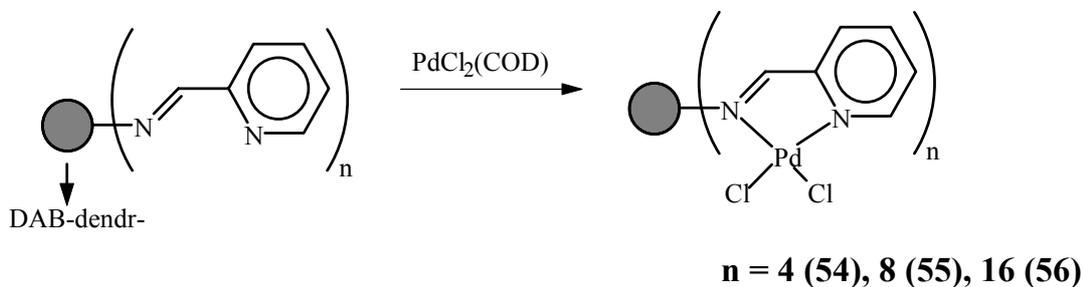
MALDI-TOF Mass Spectrometry

The first generation ligand, DAB-G1(Impyr)₄ (**51**), was studied by MALDI-TOF mass spectrometry. A porphyrinic matrix (10mg in 1ml CHCl₃), which consists of meso-tetrakis(pentafluorophenyl)porphyrin (MW 974.57), was used. The concentration used for the analyte was approximately 15 mg/ml. The matrix solution (20 μ l) and the sample solution (5 μ l) were mixed, and 1 μ l of the resulting solution loaded onto a MALDI plate. The sample was dried before inserting into the vacuum chamber of the MALDI instrument. The MALDI-TOF mass spectrum shows the molecular ion peak (672.80) and correlates well with the calculated monoisotopic molecular mass (672.44). This mass corresponds to a 100% functionalised DAB-G1(Impyr)₄ dendrimer. The spectrum displays a few peaks at lower m/z , which are likely due to the fragmentation of the dendrimer. It was not possible to obtain spectra of the higher-generation dendrimers **52** and **53**. No peaks were observed for the higher generations, using the reflector mode as for the first generation. Structural characterisation with ^1H -NMR, ^{13}C -NMR, IR spectroscopy and microanalysis showed that all of the dendrimer endgroups were functionalised.

4.3.2 Complexation reactions with PdCl₂(COD)

Three new palladium metallodendrimers (**54**, **55**, **56**) were synthesized cleanly by complexation reactions of the dendritic polyimines (**51**, **52**, **53**) with (1,5-cyclooctadiene)palladium(II) dichloride in dry dichloromethane at room temperature (Scheme 4.3). Some of the metallated complex was observed to precipitate during the initial 5-10 minutes after the addition. The reactions were generally allowed to proceed for 24 hours. The peripheral-bound palladium dendrimers were isolated as pale to light orange, amorphous solids, in typical yields of 68-93%. All three complexes were found to be insoluble in most organic solvents. Only the first two generations, compounds **54** and

55, were found to dissolve sluggishly in the polar organic solvent DMSO. Compound **56** is completely insoluble.



Scheme 4.3

¹H NMR spectroscopy

The structure of the new metallodendrimers (**54**, **55**) with PdCl₂ moieties located at the dendritic surface was established by ¹H NMR spectroscopy in DMSO-*d*₆. The ¹H-NMR spectrum of **54** shows broadened peaks and the shift of the peaks is shown in Figure 4.8. The aliphatic protons of the core and side arms occur at chemical shifts slightly downfield to those of the ligand. The peaks due to the aromatic protons of the pyridylimine group are observed to be at lower magnetic fields, as well as a significant downfield shift of the imine proton. This is indicative of the existence of strong coordination of the pyridine nitrogen and the imine nitrogen to the palladium centre. The second generation metallodendrimer shows a similar pattern in its ¹H NMR spectrum.

IR Spectroscopy

The IR spectra of the palladium complexes (Figure 4.9) show only a single absorption peak at ~1598 cm⁻¹, due to the coordinated imine moiety (C=N) and no absorption at 1649 cm⁻¹, which is a characteristic stretching frequency for the free uncomplexed imine system. Lavery and Nelson reported the disappearance of C=N absorptions in the IR spectra of complexes.²⁴ This is ascribed to be an infrared inactive C=N vibration in the Pd(II) complexes. Another plausible explanation could be a reduction in electron density in C=N bond as a result of bonding of the diimine ligand to the metal centre. This would lead to a lower ν(C=N) value.



UNIVERSITY *of the*
WESTERN CAPE

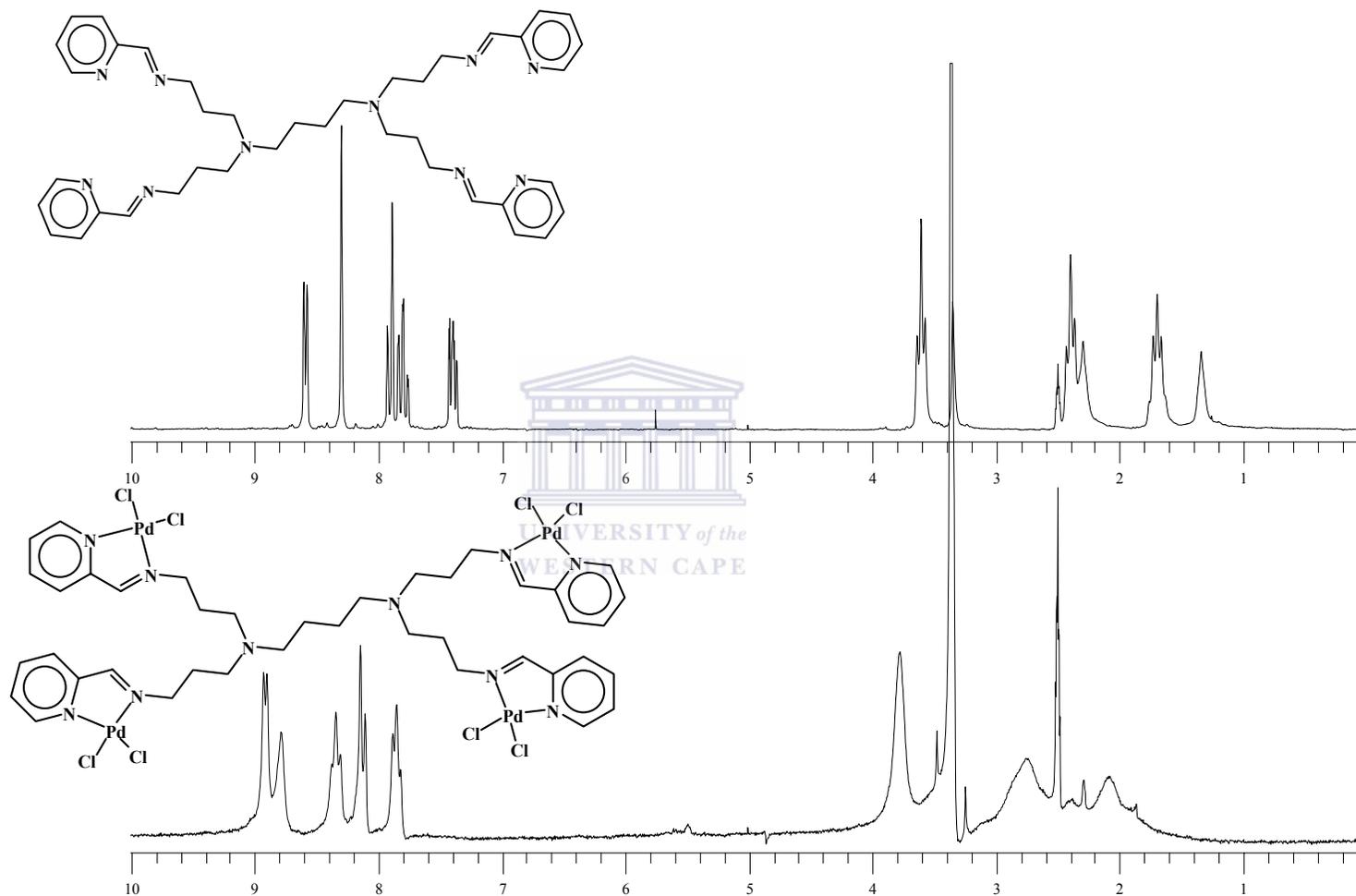


Figure 4.8 ^1H NMR spectra of DAB-G1(Impyr)_4 (above) and $\text{DAB-G1(Impyr-PdCl}_2)_4$ **54** (below) in DMSO-d_6

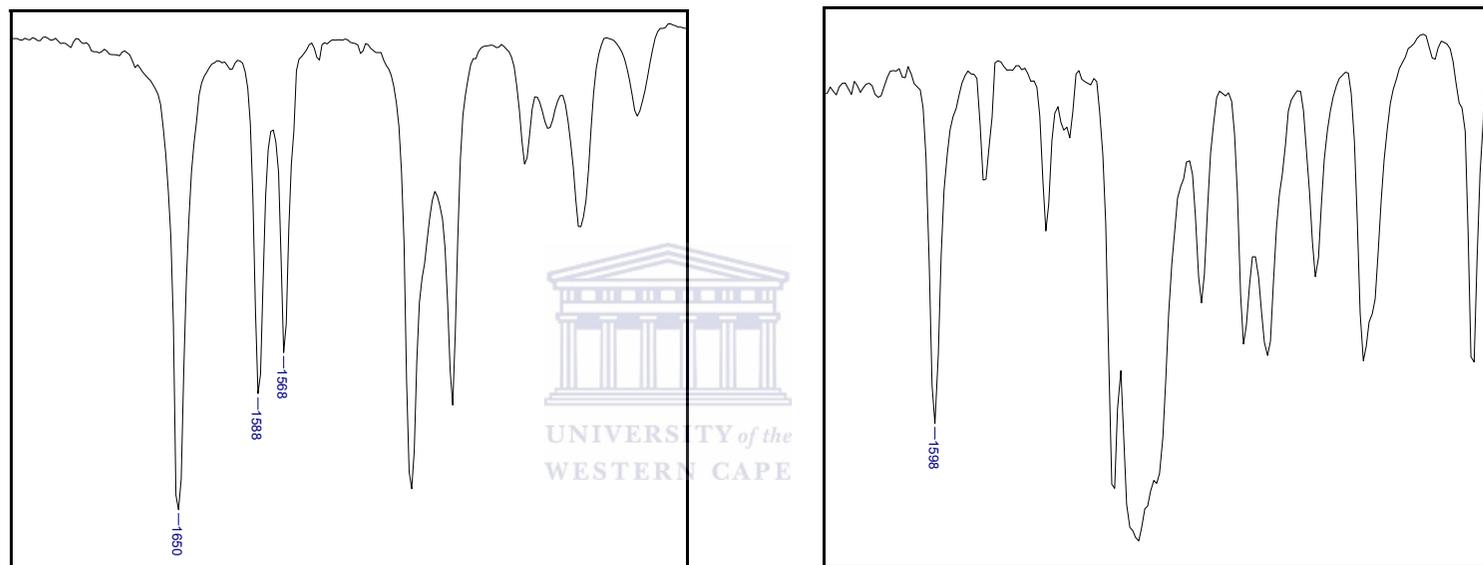


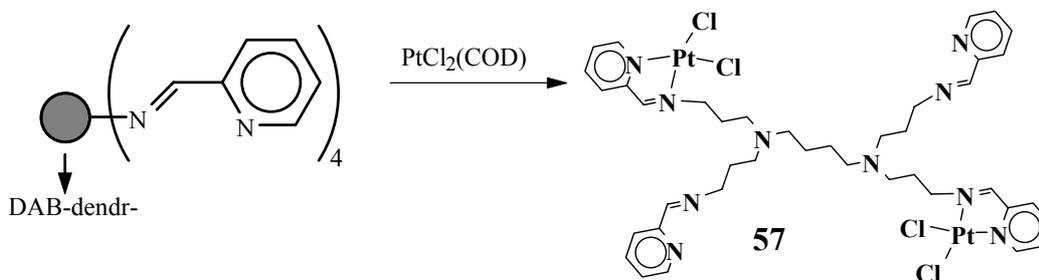
Figure 4.9 IR spectra of first-generation ligand (51) and palladium metallodendrimer (54)

Microanalysis

Microanalysis was attempted on the three palladium metallodendrimers. The experimental values obtained did not correspond with the calculated values. This disparity arises from trace amounts of the solvent CH_2Cl_2 trapped in the dendritic structure. Evidence of this inclusion was observed in the $^1\text{H-NMR}$ spectra, where the included solvent agreed with the residual solvent peak in the $^1\text{H NMR}$ spectrum. The microanalysis data correlates with the re-calculated values, which takes into account solvent inclusion. The results are reported in the experimental section. In addition, the metal composition of **54**, **55**, and **56** was determined by inductively coupled plasma (ICP) analysis. ICP analysis shows that the complex **54** contains 29.11 wt% Pd, **55** contains 26.15 wt% Pd and **56** contains 26.02 wt% Pd. This is in accord with the respective calculated values, 29.88 wt%Pd (**54**), 26.24 wt%Pd (**55**), and 27.03 wt% Pd (**56**), based on the elemental analysis of the solvated complexes. This data confirms the complete metallation of the pyridylimine dendrimers, giving rise to the first, second and third generations containing 4, 8 and 16 Pd centres respectively.

4.3.3 Complexation reactions with $\text{PtCl}_2(\text{COD})$

An experiment, analogous to the reactions using $\text{PdCl}_2(\text{COD})$, was attempted by reacting the ligand DAB-G1(Impyr)₄ (**51**) with $\text{PtCl}_2(\text{COD})$. Dichloromethane solutions of the ligand and the platinum source were mixed at room temperature in a nitrogen-purged Schlenk tube. After a few hours, a light orange solid was seen to precipitate. The reaction was allowed to stir for 24h, and the precipitate collected on a Hirsch funnel. The solid was washed with CH_2Cl_2 and dried under vacuum. The isolated pale orange solid was found to be insoluble in all organic solvents, and dissolves sluggishly in DMSO.



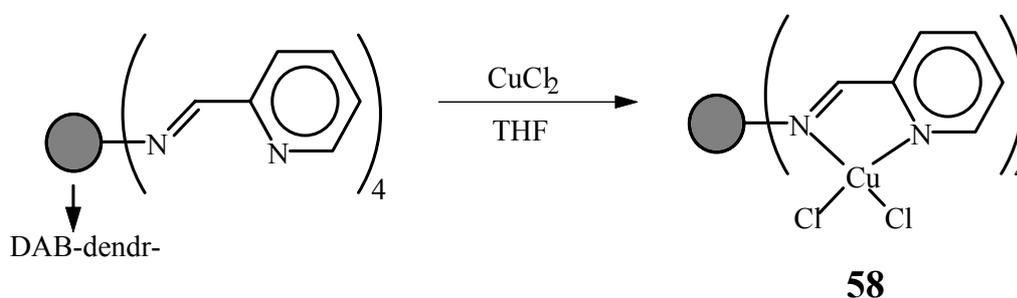
Scheme 4.4

As a result of the insoluble nature of the product, ^1H NMR studies proved to be difficult. Certain peaks due to the pyridine ring are discernible, but it is difficult to distinguish the dendritic core, due to the broadness of the peaks and the poor resolution of the spectrum. Solid-state IR analysis shows a single peak at 1596 cm^{-1} , due to the coordinated imine functional group and is indicative of the bonding of the PtCl_2 moiety with the ligand. This is similar to findings of the analogous palladium complex. Microanalysis data provides supporting information confirming the proposed structure. This correlates with the inclusion of 2 CH_2Cl_2 molecules in the dendritic structure, similar to earlier findings with the palladium analogues. The metal composition (27.22 wt% Pt) of **57** was determined by ICP analysis to contain only half the number of expected platinum centres (Calc. for 28.38 wt% Pt).

4.3.4 Complexation reactions with anhydrous CuCl_2

Reaction of the DAB-G1 (Impyr) $_4$ with anhydrous CuCl_2 (Scheme 4.5) in dry THF, yielded an insoluble green precipitate. The solvent was removed *in vacuo*, the green precipitate thoroughly washed with THF and dried under vacuum. This gave a light green solid, insoluble in most organic solvents. It shows solubility in DMSO, DMF, methanol and water.

^1H NMR spectroscopy, recorded in deuterated DMSO, did not show any well-resolved peaks. A single absorption band at 1592 cm^{-1} observed in the solid-state IR spectrum, is similar and consistent to the analogous metal derivatives of the types of pyridylimine complexes described earlier. Microanalysis data correlate with the inclusion of three CH_2Cl_2 molecules within the proposed structure.



Scheme 4.5

The addition of CuCl_2 to poly(propyleneimine) dendrimers in which the primary end groups had been converted into amides was studied by Meijer *et al.*¹⁷ Their findings revealed that no complexation had occurred, ruling out the possibility of interaction of Cu(II) with the inner tertiary amines. In our case, this would thus also exclude possible coordination of copper to the inner dendritic network. In addition, it is feasible to propose that copper assumes a tetrahedral geometry, giving it paramagnetic character, which is the reason for the broad peaks in the NMR spectrum. Diamagnetic four-coordinated Cu(II) species normally display a square-planar ligand field.

4.3.5 Synthesis of Salicylaldimine-functionalised DAB dendrimers

The past several years has seen substantial progress in the development of salicylaldimine-metal-based complexes.²⁵⁻²⁸ Salicylaldimine ligands came into being in the early 1930's.^{29,30} Their general structure shown in Figure 4.10 is formed by the Schiff base condensation of salicylaldehyde derivatives with a variety of alkyl or aryl diamine compounds.

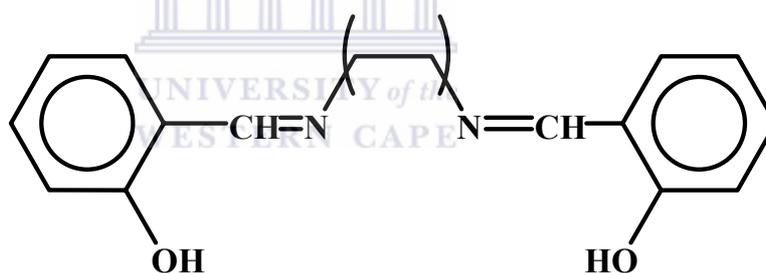


Figure 4.10 General structure of a salicylaldimine ligand

The corresponding metal complexes are formed by the coordination of metal ions through four atoms (Figure 4.11), the imine nitrogens and the oxygens that originate from the aldehyde. This gives rise to tetradentate metal-salicylaldimine complexes, the binding pattern which resembles that of the porphyrin framework in heme-based oxidative enzymes.

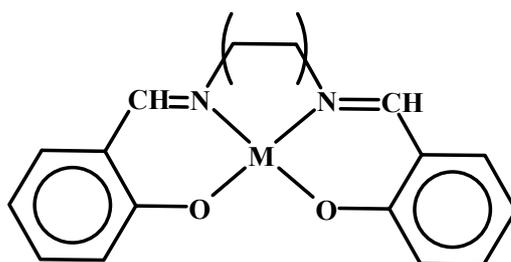


Figure 4.11 Metal-containing salicylaldimine complex

Although the application of metal-salicylaldimine complexes started in the 1990s, a number of metals have been used in recent years as mononuclear active catalysts. Ethylene polymerisation activity has been displayed by zirconium and titanium complexes containing two phenoxy-imine chelate ligands.³¹⁻³⁵ Using MAO as a cocatalyst, these salicylaldiminato metal complexes have attained activities higher than Cp_2ZrCl_2 or Cp_2TiCl_2 . Manganese (III) salicylaldimine complexes of the type shown in Figure 4.12 have been reported to show aerobic oxidation of styrene to benzaldehyde, styrene oxide and phenylacetaldehyde.^{36, 37} Jacobsen and coworkers³⁸ reported the epoxidation of a variety of unfunctional olefins, using similar manganese salicylaldimine-based catalysts. Chromium and cobalt-salicylaldimine complexes effectively catalyse the asymmetric ring-opening of epoxides.^{39, 40}

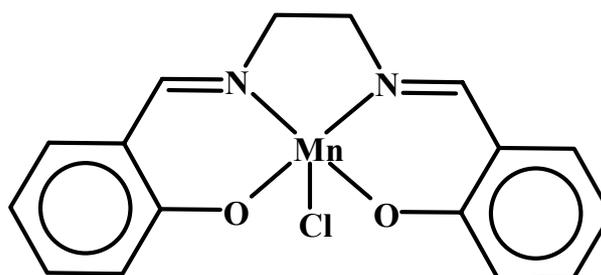


Figure 4.12 Manganese-salicylaldimine complex

There are few reports on metal-salicylaldimine dendritic derivatives. Moors and Vögtle prepared a cobalt-salicylaldimine-based dendrimer (Figure 4.13), with cobalt moieties attached on the periphery of a poly(propylene imine) core.⁴¹

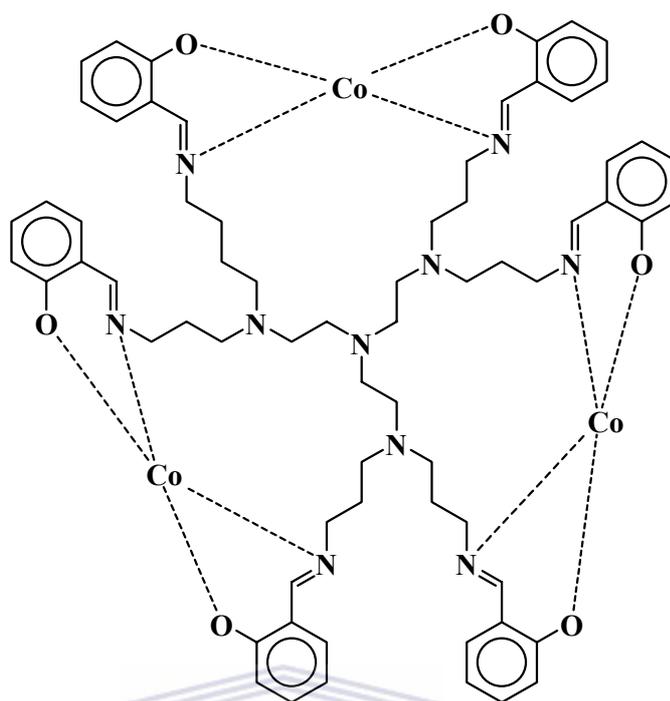
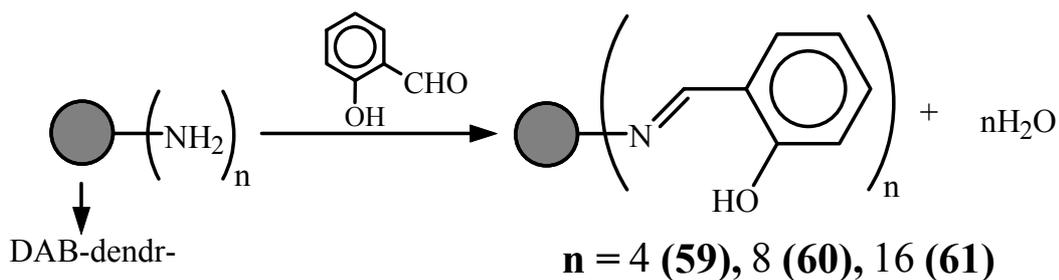


Figure 4.13 Cobalt-salicylaldimine-based dendrimer

Breinbauer and Jacobsen⁴² have also synthesized dendrimer-bound $[\text{Co}^{\text{III}}(\text{salen})]$ complexes, by the covalent attachment of chiral $[\text{Co}^{\text{II}}(\text{salen})]$ units to the periphery of polyamidoamine (PAMAM) dendrimers. They have demonstrated that the complexes act as catalysts and show enhanced catalytic activity in the hydrolytic kinetic resolution of terminal epoxides.

The syntheses of peripheral-functionalized dendrimers with salicylaldimine end-groups as termini have been studied. The first, second and third generations (Scheme 4.6) were synthesized following a parallel procedure to that described for the poly(propyleneimine)-pyridylimine dendrimers (**51-53**), using conventional Schiff-base condensation. Commercial samples of the DAB dendrimers were reacted with salicylaldehyde in toluene solution at room temperature for 48 h. The first generation salicylaldimine dendrimer, $\text{DAB-G1}(\text{Salicyl})_4$ ($x = 4$ (**59**)) was isolated as a bright yellow solid, whilst the second and third generation dendrimers, $\text{DAB-Gn}(\text{Salicyl})_x$ ($x = 8$ (**60**), 16 (**61**)) were obtained as yellow oils. Work-up of the dendrimers entailed thorough washing with either water or hexane again to remove the excess salicylaldehyde.



Scheme 4.6

¹H and ¹³C NMR spectroscopy

Successful reaction between the salicylaldehyde and the DAB dendrimer was established by NMR spectroscopy. In the ¹H-NMR spectrum signals for the CH₂ part of the dendrimer resonate between 1.41 and 3.64 ppm. The triplet at 3.60 ppm in the spectrum of DAB-G1(Salicyl)₄ (Figure 4.14) is assigned to the CH₂ adjacent to the newly-formed imine moiety and confirms the modification of the periphery of the dendrimer. Further proof is given by the signal at 8.32 ppm of the CH proton of the imine group. An additional peak in the spectra of the higher generations is noticed. This is due to the inclusion of CH₂Cl₂ in the dendritic cavities. The purification procedures were similar to that of the pyridyl ligand, using dichloromethane again, as this solvent is not completely removed, even after extensive drying under vacuum. This phenomenon has also been observed in other poly(propyleneimine) dendrimers functionalized at the periphery with organic groups.²³

The ¹³C NMR spectra for the three generations show identical spectra (Figure 4.15). The dendrimer part displays characteristic signals in the region 25 - 57 ppm for the aliphatic carbons, and 116 - 164 ppm for the aromatic and imine carbons.

IR Spectroscopy

Infrared spectroscopy was used to obtain qualitative information on the end groups in these salicylaldimine dendrimers. The solution IR spectra of the three dendrimers, **59**, **60**, and **61**, recorded in CH₂Cl₂, all display two strong absorbances at ~1620 and 1578 cm⁻¹. These frequencies are assigned to the C=N vibration.

Microanalysis

Microanalytical data for the first-generation salicylaldimine dendrimer (**59**) corresponded to the calculated values for this compound. However, the higher generation dendrimers (**60, 61**), which were yellow oils, gave values outside the acceptable limits of the calculated values. These results were achieved despite several purifications and extensive drying under vacuum. It is thought that there may be solvent inclusion within the dendritic framework, as evidence for CH₂Cl₂ inclusion is seen in the ¹H-NMR spectra.



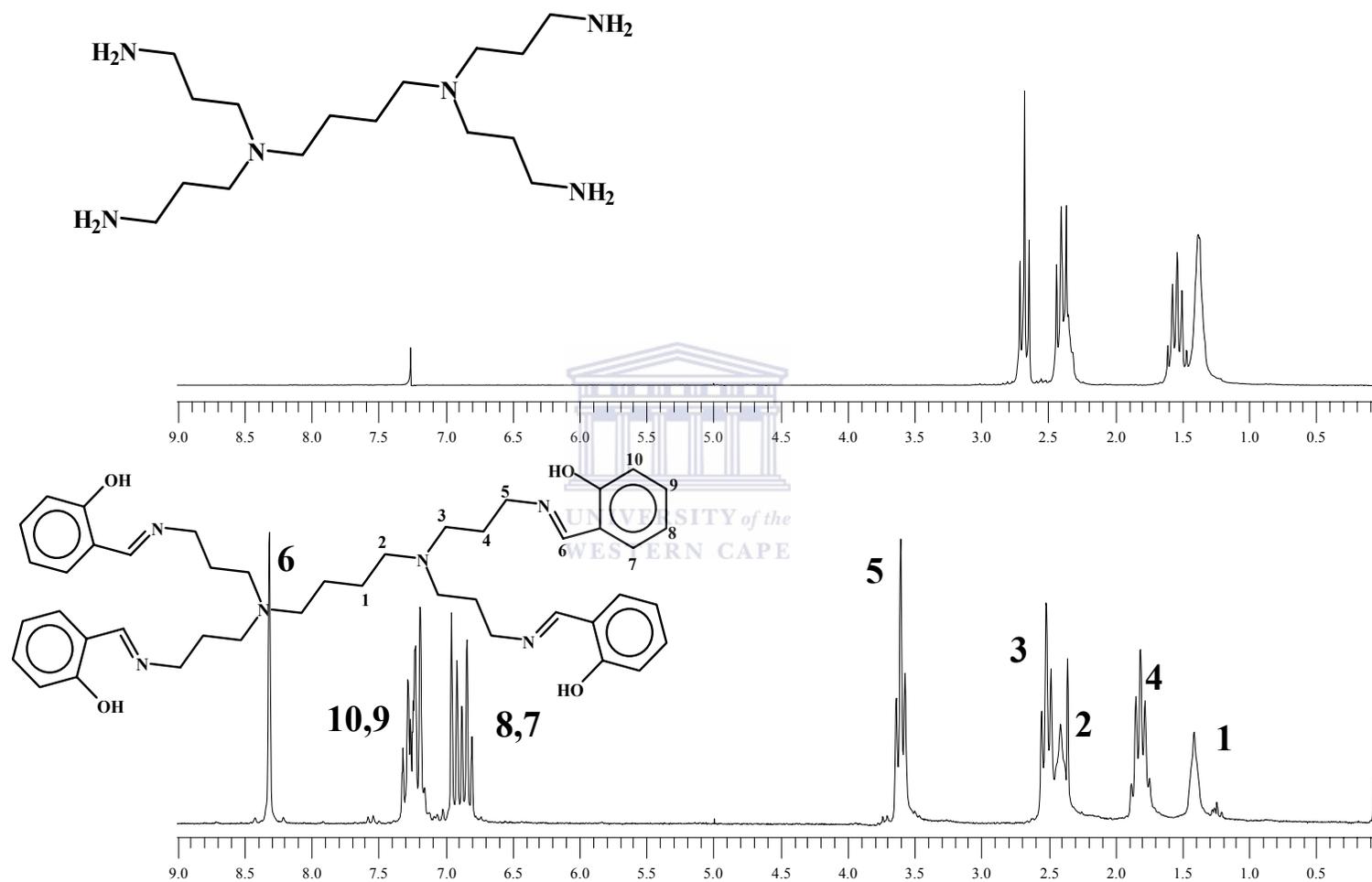


Figure 4.14 ^1H NMR spectra of $\text{DAB-G1}(\text{NH}_2)_4$ (above) and $\text{DAB-G1}(\text{salicyl})_4$ **59** (below)

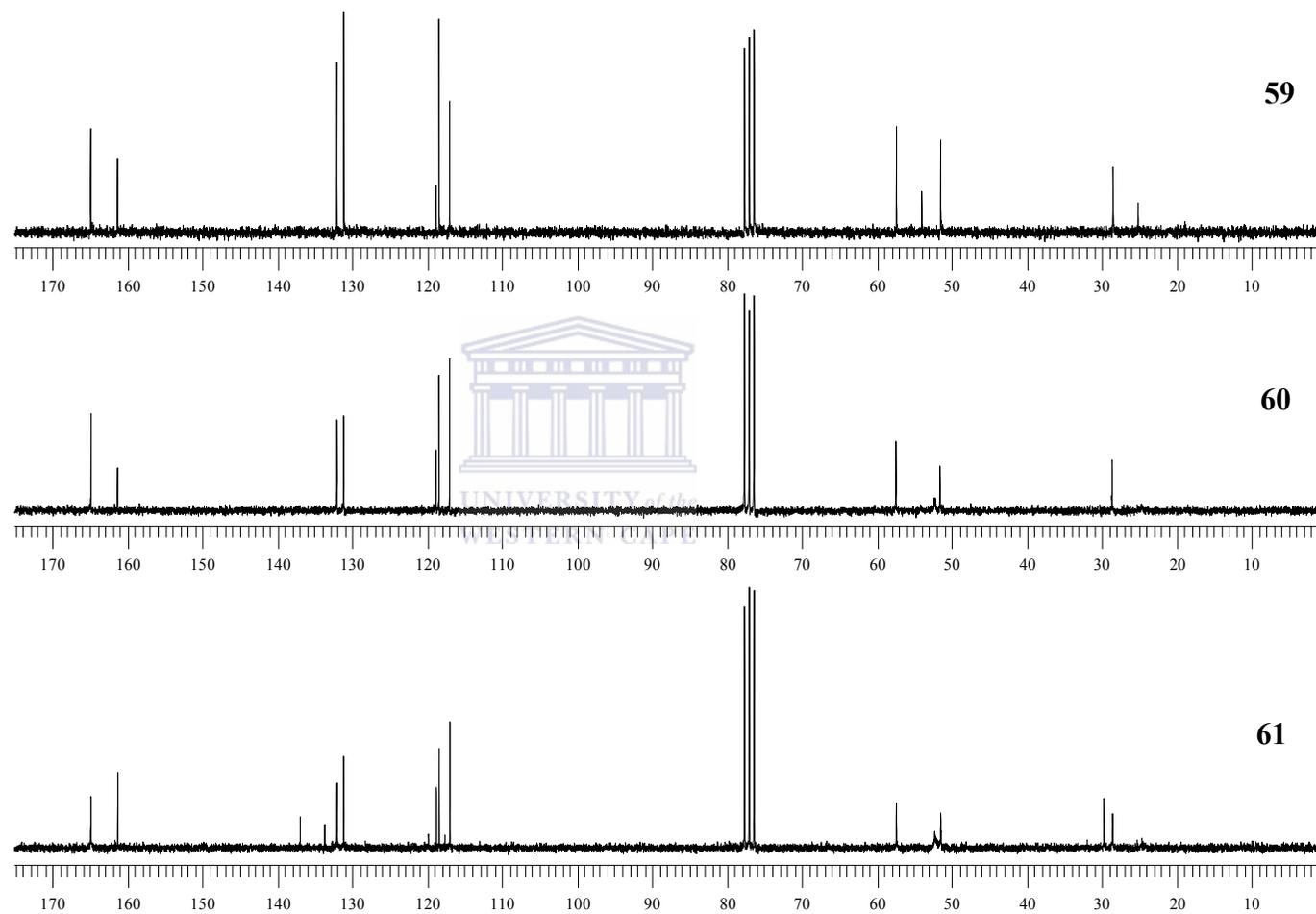
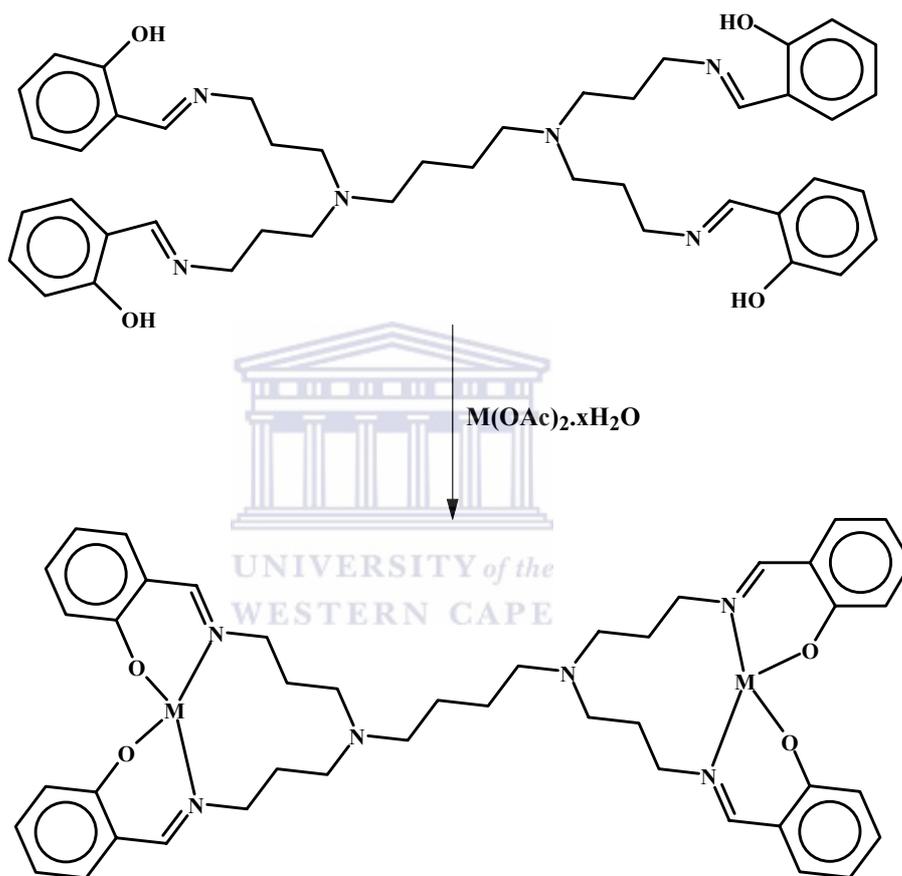


Figure 4.15 ^{13}C NMR spectra of the three generations, DAB-G1(Salicyl)₄ (**59**), DAB-G2(Salicyl)₈ (**60**) and DAB-G3(Salicyl)₁₆ (**61**)

4.3.6 Reactions of DAB-G1(Salicyl)₄ with M(OAc)₂.xH₂O(M = Cu, Ni) and FeCl₂.4H₂O

The syntheses of transition metal complexes of the first generation salicylaldimine dendrimer **59** were attempted. This was performed by refluxing the ligand (**51**) and a slight excess of the desired metal acetate in ethanol. The general reaction pathway is shown in Scheme 4.7. In most cases, the metal complex precipitated during the course of the reaction. The precipitate was washed with ethanol and dried under vacuum.



Scheme 4.7

Reactions with Ni(OAc)₂.4H₂O and Cu(OAc)₂.H₂O yielded green solids (**62,63**), which are soluble in chlorinated solvents, such as dichloromethane and chloroform. The reaction with FeCl₂.4H₂O yielded a red-brown solid (**64**), insoluble in most organic solvents.

A few examples of nickel(II) salicylaldiminato complexes have been studied.⁴³⁻⁴⁴ These compounds are all red-brown in colour and diamagnetic, suggesting square-planar structures.⁴³ This coordination environment holds true for similar copper complexes.⁴³⁻⁴⁵

Bearing this in mind, and the inability to acquire well-resolved NMR spectra for the nickel(II) and copper(II) complexes, it seems likely that the prepared nickel and copper complexes are paramagnetic and accordingly have a tetrahedral coordination around the metal centre.⁴⁶ However, we were not able to grow suitable single crystals to substantiate this. Paramagnetic NMR studies and UV-VIS spectrometry provide some information as to these structures, and these are discussed in the text hereafter.

Paramagnetic ¹H NMR Spectroscopy of Ni(II) (62) and Cu(II) (63) complexes

Initial NMR studies of the complexes **62** and **63** in deuterated chloroform shows broadened peaks, with poor resolution in their spectra. This occurs for the range from 0 - 12 ppm, which is considered to be the diamagnetic region of the spectrum. Paramagnetic systems, like these transition metal ion complexes, are associated with unpaired electrons. The presence of unpaired electrons has a profound influence on the NMR spectra of their solutions. The origin of the effects stems from the large value of the electronic magnetic moment, which is approximately 650 times that of the proton. The influence of paramagnetic species on NMR spectra results in a significant shift in the NMR signals.

⁴⁷

For the soluble Ni(II) (**62**) and Cu(II) (**63**) paramagnetic complexes, we recorded spectra using 0.003M solution, data block size 1K, acquisition time 0.256s and relaxation delay 0s at 293K. Using these parameters over a wider spectral width, more peaks are observed. The ¹H NMR paramagnetic spectra were recorded over the range from +50 ppm to -50 ppm. The peaks associated with the aromatic protons for complex **62** (Figure 4.16) are shifted downfield to 15-30 ppm. The peak that can be assigned to the proton of the imine moiety occurs at 25.37 ppm and correlates with the integration for the proposed complex. The aliphatic protons of the poly(propyleneimine) dendritic network range from -20 to 0 ppm. However, the assignment of all these peaks is not possible, due to the uncertainty in this realm of the paramagnetic spectrum, that is, in the region outside the 0 - 12 ppm range.

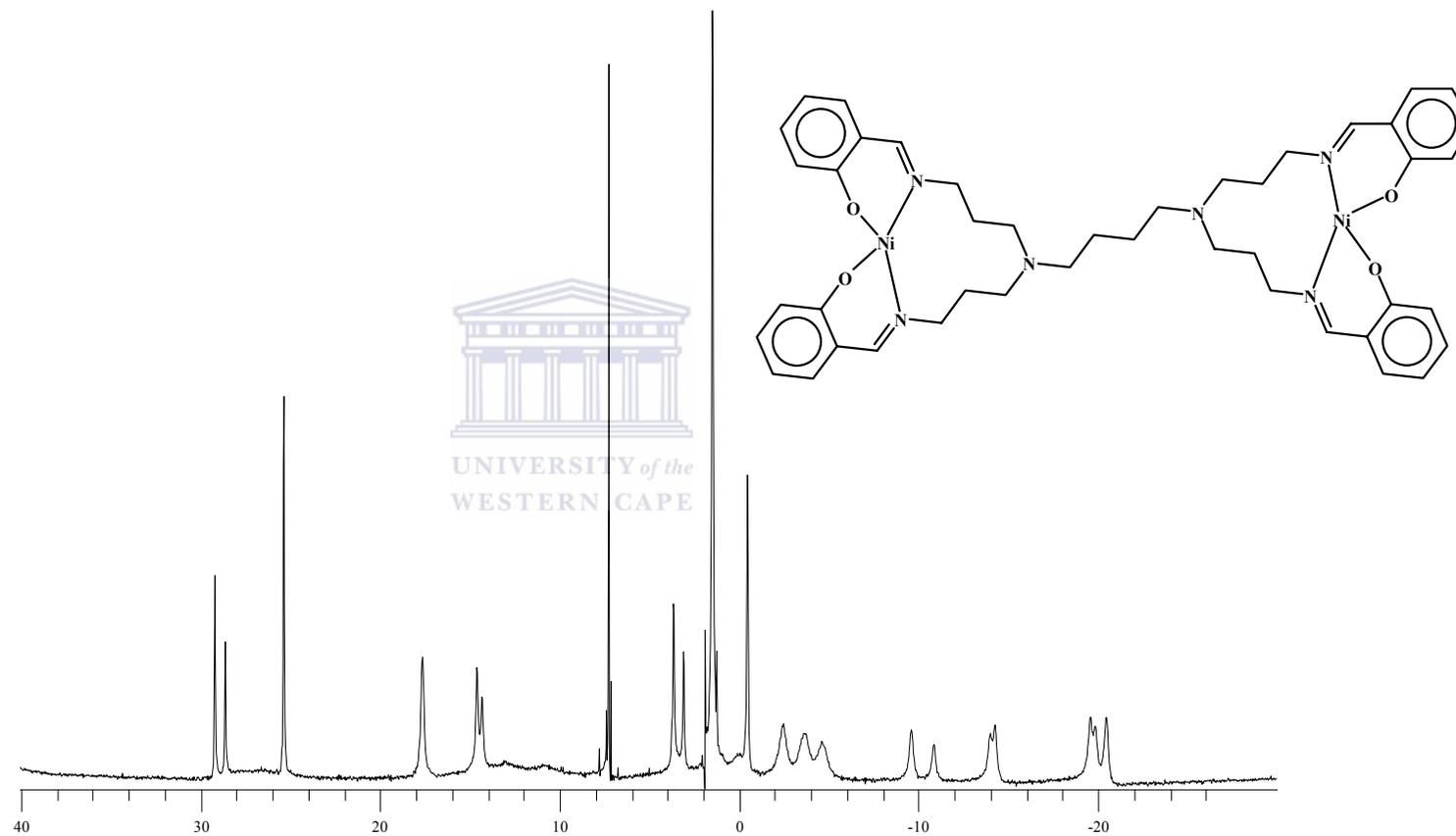


Figure 4.16 Paramagnetic ^1H NMR spectrum of complex 62

IR Spectroscopy

Complexation of the metal acetates to the salicylaldimine ligand, shows a distinct shift toward lower energies for the C=N stretching absorption band. For example, the free ligand shows a $\nu(\text{C}=\text{N})$ stretch at 1580 - 1613 cm^{-1} . In complexes, the bands shift to lower frequencies and appear at 1535 - 1599 cm^{-1} , indicating the coordination of the salicylaldimine ligand to the metal. The presence of several bands of medium intensity in the 2700 - 2900 cm^{-1} range, are ascribed to the C-H symmetrical and asymmetrical stretching due to the propylene dendritic network. Another distinguishing feature is the C-O vibration, which occurs at 1279 cm^{-1} in the Schiff base ligand and shifts to 1345 cm^{-1} upon complexation.

UV-VIS Absorption Spectra

The UV-VIS spectra of the metal-containing salicylaldiminato complexes **62** and **63** were studied in methylene chloride. For the free ligand, the absorption spectra showed bands at 237, 254 and 277 nm. These are assigned to the $\pi - \pi^*$ type transitions of the benzene ring. The band from the $\pi - \pi^*$ transition, which involves the molecular orbital of the C=N chromophore, is found at 314 nm. Upon coordination, this absorption band shifts towards lower energies. The absorption spectra of the nickel(II) (**62**) and copper(II) (**63**) complexes exhibit one d-d band at 374 nm and three ligand bands. These results add to our proposal of tetrahedral geometry about the metal centre and correlates with literature findings of similar complexes.

Microanalysis

The nickel (**62**) and copper (**63**) complexes precipitated from the reaction mixture as solvated complexes. The microanalytical data correlate with the inclusion of EtOH in the dendritic complex. Atomic absorption spectrometric analysis results indicate that nickel and copper exist in the salicylaldiminato complexes, in accord with the proposed general structure in Scheme 4.7. The results for the iron complex (**64**) do not correspond with the general complex shown in Scheme 4.7. Instead, the elemental analysis for carbon, hydrogen and nitrogen correlates with the proposed tetranuclear complex shown in Figure 4.17.

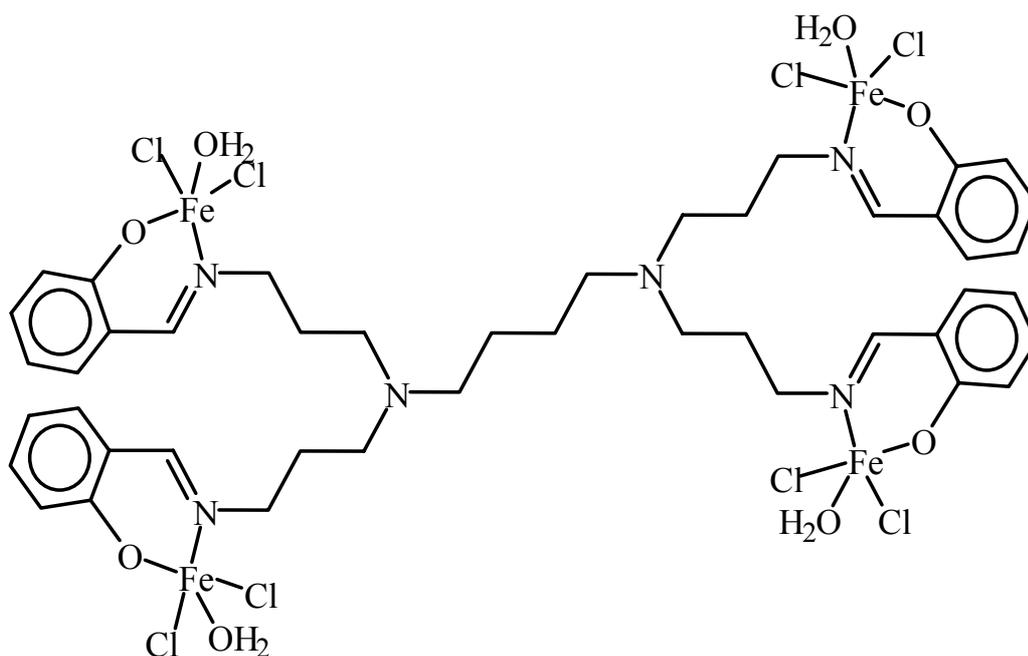


Figure 4.17 Proposed iron salicylaldimine complex (**64**)

The analysis of the metal composition, performed by atomic absorption spectroscopy, gave an iron content of 16.67%, close to the expected metal content (17.08%) for the proposed complex. This serves to confirm the presence of four iron centres in the complex. The loss of water, as presented in the TG trace for compound **64**, provides evidence for the presence of aqua ligands in the complex. All the results are given in the experimental section.

4.4 Conclusions

The preparation of two types of new metallodendrimers has been described, with metal-containing moieties located on the periphery of the dendrimer. Both types of metallodendrimers are based on the commercially available DAB dendrimer.

The first type of dendrimer includes compounds that contain pyridylimine ligands on the surface. These have been synthesized up to the third generation by the Schiff-base condensation reactions of the DAB dendrimer with 2-pyridinecarboxaldehyde. Complexation reactions of these ligands, using various metal sources such as PdCl₂(COD), PtCl₂(COD) or CuCl₂, afforded the corresponding metallated complexes. These metallodendrimers were insoluble in most organic solvents and only the first-generation dendrimers dissolved sluggishly in highly polar, aprotic solvents such as DMSO. Supporting data in the form of ¹H NMR and IR spectroscopy, elemental and ICP analysis confirm the integrity of the proposed metallodendrimers.

The second type of dendrimer was prepared by functionalising the terminal amine groups of the DAB dendrimer with salicylaldehyde. This gives rise to dendrimers with 4, 8 or 16 salicylaldiimine units on the periphery for the first, second and third generations respectively. Metallation reactions of the dendrimers with various metal acetates (MOAc₂, M = Ni, Cu) and using FeCl₂·4H₂O, yielded largely paramagnetic solids (Ni, Cu) or insoluble, intractable materials (Fe). Paramagnetic NMR studies of the nickel and copper complexes revealed significant upfield shifts of the aromatic and imine protons, indicating the coordination around the metal centre. The reaction with iron yielded a tetranuclear metal complex.

4.5 Experimental

All reactions and manipulation were carried out using a dual vacuum/nitrogen line and standard Schlenk techniques. Toluene and tetrahydrofuran (THF) were dried over sodium/benzophenone and distilled under nitrogen before use. Dichloromethane was dried and distilled over P₂O₅. Absolute ethanol was dried and distilled over iodine/Mg turnings. DAB-Am₄, DAB-Am₈, DAB-Am₁₆, 2-pyridinecarboxaldehyde and salicylaldehyde were purchased from Sigma-Aldrich. Anhydrous CuCl₂ was obtained from Riedel de-Hahn. PdCl₂(COD)⁴⁸ and PtCl₂(COD)⁴⁹ were prepared according to literature procedures. ¹H-NMR (200MHz) and ¹³C NMR (50MHz) spectra were recorded on a Varian XR200 spectrometer, using tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin Elmer Paragon 1000PC FT-IR spectrophotometer, using either solution cells with NaCl windows or DRIFTS (diffuse reflectance infrared transmission spectroscopy) in a KBr matrix. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. MALDI-TOF analyses were carried out on a Perseptive Biosystems-Voyager-DE STR mass spectrometer, equipped with a nitrogen laser (337nm) and operated in reflector mode. Irradiance intensity and accelerating voltage were at 20kV for the sample. UV-Vis absorption spectra were recorded on a GBC UV/VIS 920 Spectrometer in CH₂Cl₂ (3 x 10⁻⁴ M) solution. AA spectroscopy was conducted on a Phillips PU9100 spectrophotometer. The operating lamp current was 12 mA, while the slit width was 0.2nm. An air-acetylene flame was used. Inductively coupled plasma (ICP) analysis was carried out on a Varian Liberty II, radial ICP spectrometer, with a plasma gas flow of 15.0 L/min, a nebulizer pressure of 190kPa and an inner gas flow of 1.5 L/min. Readings were taken using a sample aspiration rate of 15 rpm

4.5.1 Synthesis of DAB-G1(Impyr)₄ (51)

A round-bottomed flask was charged with dry toluene (60 ml). Anhydrous MgSO₄ (~ 5 g) was transferred to the flask. 2-Pyridinecarboxaldehyde (0.271 g, 2.53 mmol) was syringed into the round-bottomed flask and the mixture stirred at room temperature. A sample of the DAB-dendr-(NH₂)₄ (0.200 g, 0.633 mmol) was dissolved in 5ml of dry toluene. This toluene solution was added dropwise to the stirring mixture of the aldehyde and MgSO₄, and the reaction allowed to proceed at room temperature for 2 days. The reaction mixture was filtered by gravity and the solvent removed from the filtrate by rotary evaporation with

gentle heating (~40 EC). The residual oil was extracted with hot MeOH and the solvent removed from the extract. The remaining oil obtained from the extract was dissolved in CH₂Cl₂ (20 ml) and washed copiously with water (7x50ml). The organic layer was collected, dried over anhydrous MgSO₄ and filtered by gravity. Removal of the solvent by rotary evaporation yielded compound **51** as an orange oil. Yield = 0.325 g (76%).

Anal. Found : C, 70.53%; H, 8.20%; N, 20.59%. Calc. for C₄₀H₅₂N₁₀: C, 71.40%; H, 7.79%; N, 20.82%. ¹H NMR (200 MHz, CDCl₃) : δ 1.40 (br m, 4H, H-1); 1.84 (qn, 8H, H-4); 2.40 (br t, 4H, H-2); 2.51 (t, 8H, H-3); 3.67 (t, 8H, H-5); 7.28 (t, 4H, H-9); 7.70 (t, 4H, H-8); 7.92 (d, 4H, H-7); 8.36 (s, 4H, H-6); 8.60 (d, 4H, H-10).

¹³C NMR (50 MHz, CDCl₃) : δ 24.7, 27.8, 51.2, 53.6, 59.1, 120.7, 124.0, 136.0, 148.9, 154.1, 161.4; IR (neat oil, NaCl plates) : ν = 1649, 1588, 1567 cm⁻¹ (C=N);

MS (MALDI-TOF) calcd (C₄₀H₅₂N₁₀) 672.44, found 672.80

4.5.2 Synthesis of DAB-G2(Impyr)₈ (**52**)

A sample of the DAB-dendr-(NH₂)₈ (1.75 g, 2.26 mmol) was dissolved in 5ml of dry toluene and mixed with 2-pyridinecarboxaldehyde (1.92 g, 17.9 mmol). The same procedure as for **51** was followed. Compound **52** was isolated as an orange oil.

Yield = 1.06 g (32%). Anal. Found : C, 70.17%; H, 8.49%; N, 20.18%. Calc. for C₈₈H₁₂₀N₂₂.½CH₂Cl₂ : C, 69.54%; H, 7.97%; N, 20.16%. ¹H NMR (200 MHz, CDCl₃) : δ 1.33 (br m, 4H); 1.53 (br m, 8H); 1.80 (qn, 16H); 2.35-2.49 (overlapping m, 36H); 3.63 (t, 16H); 7.22 (t, 8H); 7.62 (t, 8H); 7.90 (d, 8H); 8.32 (s, 8H); 8.56 (d, 8H).

¹³C NMR (50 MHz, CDCl₃) : δ 24.6, 28.2, 51.7, 52.3, 54.2, 59.5, 121.1, 124.5, 136.4, 149.3, 154.6, 161.8; IR (neat oil, NaCl plates) : ν = 1650, 1589, 1568 cm⁻¹ (C=N).

4.5.3 Synthesis of DAB-G3(Impyr)₁₆ (**53**)

A sample of the DAB-dendr-(NH₂)₁₆ (0.200 g, 0.119 mmol) was dissolved in 5ml of dry toluene and mixed with 2-pyridinecarboxaldehyde (0.250 g, 2.33 mmol). The same procedure as for **53** was followed. Yield = 0.152 g (41%). Anal. Found : C, 70.59%;

H, 8.63%; N, 20.26%. Calc. for C₁₈₄H₂₅₆N₄₆.½CH₂Cl₂ : C, 70.24%; H, 8.21%; N, 20.42%. ¹H NMR (200 MHz, CDCl₃) : δ 1.38 (br m, 4H); 1.58 (br m, 24H); 1.84 (br qn, 32H); 2.42-2.53 (overlapping m, 84H); 3.67 (t, 32H); 7.25 (t, 16H); 7.68 (t, 16H); 7.95 (d, 16H); 8.36 (s, 16H); 8.60 (d, 16H).

^{13}C NMR (50 MHz, CDCl_3) : δ 24.5, 28.2, 51.7, 52.3, 59.5, 97.4, 121.2, 124.5, 136.4, 149.3, 154.6, 161.8; IR (neat oil, NaCl plates) : ν = 1649, 1587, 1567 cm^{-1} (C=N).

4.5.4 Synthesis of DAB-G1(Impyr-PdCl₂)₄ (54)

A Schlenk tube was evacuated and then filled with nitrogen. PdCl₂(COD) (0.170 g, 0.597 mmol) was transferred to the Schlenk tube. This was dissolved in dry CH₂Cl₂ (15 ml). The pyridylimine ligand, DAB-G1(Impyr)₄ (93.4 mg, 0.139 mmol), was dissolved separately in dry CH₂Cl₂ (5 ml). This solution was added to the Schlenk tube and the mixture stirred at room temperature under nitrogen. After a few minutes, an orange precipitate formed. The reaction was allowed to proceed for 2 days, and the solid collected on a Hirsch funnel. The solid was washed with CH₂Cl₂ and dried under vacuum, yielding complex **54** as an amorphous, light orange solid. Yield = 0.178 g (93%).

M.p. : 270EC (dec., without melting); Anal. Found : C, 33.48%; H, 3.99%; N, 9.00%.

Calc. for C₄₀H₅₂N₁₀Pd₄Cl₈·1½CH₂Cl₂ : C, 33.01%; H, 3.67%; N, 9.28%.

^1H NMR (DMSO-d₆) : 2.29 - 2.78 (br signals, core), 3.78 (br t, 8H, -CH₂-N=), 7.85, 8.20, 8.35, 8.90 (br, pyridine), 8.76 (br s, -N=CH-);

I.R. (Nujol between NaCl plates) : ν = 1599 cm^{-1} (C=N).

4.5.5 Synthesis of DAB-G2(Impyr-PdCl₂)₈ (55)

PdCl₂(COD) (0.170 g, 0.595 mmol) was transferred to a nitrogen-purged Schlenk tube and dissolved in dry CH₂Cl₂ (15 ml). The pyridylimine ligand, DAB-G1(Impyr)₈ (0.105 g, 0.0706 mmol) was dissolved separately in dry CH₂Cl₂ (5 ml) and mixed with the palladium solution. Same procedure as for **54**. Complex **55** is an orange solid.

Yield = 0.190 g (93%). M.p. : 200EC (onset of dec., no melting before 300EC);

Anal. Found : C, 34.45%; H, 4.38%; N, 9.03%. Calc. for C₈₈H₁₂₀N₂₂Pd₈Cl₁₆·4CH₂Cl₂ : C, 34.07%; H, 3.98%; N, 9.50%.

^1H NMR (DMSO-d₆) : 2.29 - 2.78 (br signals, core), 3.78 (br t, 8H, -CH₂-N=), 7.85, 8.20, 8.35, 8.90 (br, pyridine), 8.76 (br s, -N=CH-); I.R. (Nujol between NaCl plates) : ν = 1599 cm^{-1} (C=N).

4.5.6 Synthesis of DAB-G3(Impyr-PdCl₂)₁₆ (56)

PdCl₂(COD) (0.0735 g, 0.257 mmol) was transferred to a nitrogen-purged Schlenk tube and dissolved in dry CH₂Cl₂ (15 ml). The pyridylimine ligand, DAB-G1(Impyr)₁₆ (40.0 mg, 0.0128 mmol) was dissolved separately in dry CH₂Cl₂ (5 ml) and mixed with the palladium solution. Same procedure as for 54. Yield = 64.2 mg (84%).

M.p. : 297EC (dec., no melting); Anal. Found : C, 35.38%; H, 4.40%; N, 8.66%.

Calc. for C₁₈₄H₂₅₆N₄₆Pd₁₆Cl₃₂.7CH₂Cl₂ : C, 35.06%; H, 4.16%, N, 9.84%;

I.R. (Nujol between NaCl plates) : $\nu = 1599 \text{ cm}^{-1}$ (C=N).

4.5.7 Synthesis of DAB-G1(Impyr-PtCl₂)₄ (57)

PtCl₂(COD) (0.222 g, 0.594 mmol) was transferred to a nitrogen-purged Schlenk tube and dissolved in dry CH₂Cl₂ (20 ml). The pyridylimine ligand, DAB-G1(Impyr)₄ (0.100 g, 0.149 mmol) was dissolved separately in dry CH₂Cl₂ (5 ml) and mixed with the platinum solution. Same procedure as for 54. Complex 57 is an orange solid.

Yield = 0.148 g (57%). M.p. : 251EC; Anal. Found : C, 36.63%; H, 4.65%;

N, 9.86%. Calc. for C₄₀H₅₂N₁₀Pt₂Cl₄.2CH₂Cl₂ : C, 36.69%; H, 4.11%; N, 10.19%.

I.R. (Nujol between NaCl plates) : $\nu = 1597 \text{ cm}^{-1}$ (C=N).

4.5.8 Synthesis of DAB-G1(Impyr-CuCl₂)₄ (58)

A Schlenk tube was evacuated and purged with nitrogen. The pyridylimine ligand, DAB-G1(Impyr)₄ (0.103 g, 0.153 mmol) was transferred to the Schlenk tube. This was dissolved in dry THF (5 ml). Anhydrous CuCl₂ (80.1 mg, 0.595 mmol) was dissolved separately in dry THF and added dropwise to the Schlenk tube. The reaction mixture was allowed to stir at room temperature for 3 days, during which a green solid precipitated. The solvent was removed *in vacuo* and the residue washed with THF. After drying under vacuum, a green solid was obtained. Yield = 0.132 g (71%).

M.p.: 154-156EC (dec.); Anal. Found : C, 35.01%; H, 4.35%; N, 9.78%. Calc. for

C₄₀H₅₂N₁₀Cu₄Cl₈.3CH₂Cl₂ : C, 35.20%; H, 3.96%; N, 9.55%.

I.R. (DRIFTS) : $\nu = 1600 \text{ cm}^{-1}$ (C=N).

4.5.9 Synthesis of DAB-G1(Salicyl)₄ (**59**)

A sample of the DAB-dendr-(NH₂)₄ (2.00 g, 6.32 mmol) was dissolved in 5ml of dry toluene and mixed with salicylaldehyde (3.21 g, 26.3 mmol). The same procedure as for **51** was followed. This yielded ligand **59** as a bright yellow solid. Yield = 4.01 g (86%). M.p. = 52E-53EC. Anal. Found : C, 71.86%; H, 7.54%; N, 11.12%. Calc. for C₄₄H₅₆N₆O₄ : C, 72.10%; H, 7.70%; N, 11.47%.

¹H NMR (200 MHz, CDCl₃) : δ 1.41 (br m, 4H); 1.81 (qn, 8H); 2.41 (br t, 4H); 2.51 (t, 8H); 3.60 (t, 8H); 6.88 (m, 8H); 7.19-7.32 (m, 12H); 8.32 (s, 4H).

¹³C NMR (50 MHz, CDCl₃) : δ 25.1, 28.4, 51.5, 54.0, 57.4, 117.0, 118.4, 118.8, 131.1, 132.1, 161.3, 164.9; IR (CH₂Cl₂), ν(C=N) cm⁻¹ : 1633(s), 1582(m).

4.5.10 Synthesis of DAB-G2(Salicyl)₈ (**60**)

A sample of the DAB-dendr-(NH₂)₈ (0.500 g, 0.647 mmol) was dissolved in 5ml of dry toluene and mixed with salicylaldehyde (1.38 g, 11.3 mmol). The same procedure as for **51** was followed. Ligand **60** was isolated as a bright yellow oil.

Yield = 0.977 g (94%). Anal. Found : C, 70.02%; H, 7.62%; N, 10.98%. Calc. for C₉₆H₁₂₈N₁₄O₈·½CH₂Cl₂ : C, 70.30%; H, 7.89%; N, 11.89%.

¹H NMR (200 MHz, CDCl₃) : δ 1.38 (br m, 4H); 1.54 (br m, 8H); 1.78 (qn, 16H); 2.36-2.52 (overlapping m, 36H); 3.57 (t, 16H); 6.78-6.94 (m, 8H); 7.16-7.31 (m, 24H); 8.29 (s, 8H).

¹³C NMR (50 MHz, CDCl₃) : δ 28.6, 51.5, 52.3, 57.4, 117.0, 118.4, 118.8, 131.1, 132.0, 161.3, 164.7; IR (CH₂Cl₂), ν(C=N) cm⁻¹ : 1633(s), 1582(m).

4.5.11 Synthesis of DAB-G3(Salicyl)₁₆ (**61**)

A sample of the DAB-dendr-(NH₂)₁₆ (0.103g, 0.0610 mmol) was dissolved in 5 ml of dry toluene and mixed with salicylaldehyde (0.229 g, 1.88 mmol). The same procedure as for **51** was followed. This gave ligand **61** as a bright yellow oil.

Yield = 0.154g (62%). Anal. Found : C, 70.73%; H, 7.54%; N, 11.12%. Calc. for C₂₀₀H₂₇₂N₃₀O₁₆·CH₂Cl₂ : C, 70.20%; H, 7.93%; N, 11.68%.

¹H NMR (200 MHz, CDCl₃) : δ 1.38 (br m, 4H); 1.55 (br m, 24H); 1.76 (br qn, 32H); 2.39-2.47 (overlapping m, 84H); 3.55 (t, 16H); 6.80-6.92 (m, 16H); 7.15-7.30 (m, 48H); 8.27 (s, 16H).

¹³C NMR (50 MHz, CDCl₃) : δ 28.5, 29.7, 51.5, 52.2, 57.4, 116.9, 118.4, 118.8, 131.1,

132.0, 161.3, 164.9; IR (CH₂Cl₂), $\nu(\text{C}=\text{N})$ cm⁻¹ : 1633(s), 1582(m).

4.5.12 Synthesis of DAB-G1(Salicyl₂-Ni)₂ (**62**)

A sample of the ligand, DAB-G1(Salicyl)₄ **59** (0.301 g, 0.410 mmol) was partially dissolved in dry absolute ethanol (30 ml), and heated to boiling. Ni(OAc)₂·4H₂O (0.206 g, 0.828 mmol) was carefully added (slight effervescence) and the yellow solution turned green immediately upon addition. The mixture was refluxed for 3h, during which time a green solid precipitated. The reaction mixture was cooled to room temperature, filtered and the insolubles washed thoroughly with EtOH. A dark green, semi-crystalline solid was collected. Yield = 0.132 g (37%).

M.p. : Does not melt below 300EC; Anal. Found : C, 60.10%; H, 5.61%; N, 9.33%. Calc. for C₄₄H₅₂N₆O₄Ni₂·EtOH : C, 59.22%; H, 5.87%; N, 9.42%.

IR (DRIFTS), $\nu(\text{C}=\text{N})$ cm⁻¹ : 1598(s), 1533(s); $\nu(\text{C}-\text{O})$ cm⁻¹ : 1348(s). $\lambda_{\text{max}} = 374$ nm

4.5.13 Synthesis of DAB-G1(Salicyl₂-Cu)₂ (**63**)

Prepared as for complex **62** using Cu(OAc)₂·H₂O as the metal source.

Green amorphous solid isolated. Yield = 0.139 g (38%).

M.p. : 264EC (melts with dec.); Anal. Found : C, 60.80%; H, 5.96%; N, 9.35%. Calc. for C₄₄H₅₂N₆O₄Cu₂·½EtOH : C, 60.12%; H, 5.96%; N, 9.56%.

IR (DRIFTS), $\nu(\text{C}=\text{N})$ cm⁻¹ : 1599(s), 1533(s); $\nu(\text{C}-\text{O})$ cm⁻¹ : 1349(s). $\lambda_{\text{max}} = 374$ nm

4.5.14 Synthesis of DAB-G1(Salicyl₂-Fe)₂ (**64**)

Prepared as for complex **62** using FeCl₂·4H₂O as the metal source.

Dark red solid collected. Yield = 0.198 g (37%).

M.p. : Does not melt below 300EC; Anal. Found : C, 40.37%; H, 4.86%; N, 6.53%. Calc. for C₄₄H₆₀Cl₈Fe₄N₆O₈ : C, 40.40%; H, 4.62%; N, 6.42%.

IR (DRIFTS), $\nu(\text{C}=\text{N})$ cm⁻¹ : 1600(s), 1544(s); $\nu(\text{C}-\text{O})$ cm⁻¹ : 1313(s).

4.6 References

1. I. Cuadrado, M. Morán, C.M. Casado, B. Alonso and J. Losada, *Coord. Chem. Rev.*, 1999, **193-195**, 395.
2. M.A. Hearshaw and J.R. Moss, *Chem. Commun.*, 1999, 1.
3. O.A. Matthews, A.N. Shipway and J.F. Stoddart, *Prog. Polym. Sci.*, 1998, **23**, 1.
4. A.W. Bosman, H.M. Janssen and E.W. Meijer, *Chem. Rev.*, 1999, **99**, 1665.
5. R.M. Crooks, B.I. Lemon III, L. Sun, L.K. Yeung and M. Zhao, *Topics in Curr. Chem.*, 2001, **212**, 81.
6. C. Gorman, *Adv. Mater.*, 1998, **4**, 295.
7. G.E. Oosterom, J.N.H. Reek, P.C.J. Kamer and P.W.N.M. van Leeuwen, *Angew. Chem. Int. Ed.*, 2001, **40**, 1828.
8. D. Astruc and F. Chardac, *Chem. Rev.*, 2001, **101**, 2991.
9. G.R. Newkome, E. He and C.N. Moorefield, *Chem. Rev.*, 1999, **99**, 1689.
10. J.M. Benito, E. de Jesus, F. Javier de la Mata, J.C. Flores, R.Gómez and P. Gómez-Sal, *J. Organomet. Chem.*, 2003, **664**, 258.
11. J.W.J. Knäpen, A.W. van der Made, J.C. de Wilde, P.W.N.M. van Leeuwen, P. Wijkens, D.M. Grove, G. van Koten, *Nature*, 1994, **372**, 659.
12. K. Vassilev, J. Kreider, P.D. Miller, W.T. Ford, *React. Funct. Polym.*, 1999, **41**, 205.
13. R. van Heerbeek, P.C.J. Kramer, P.W.N. van Leeuwen and J.N.H. Reek, *Chem. Rev.*, 2002, **102**, 3717.
14. L.J. Twyman, A.S.H. King and I.K. Martin, *Chem. Soc. Rev.*, 2002, **31**, 69.
15. I. Anggurell, G. Muller, M. Rocamora, O. Rossell and M. Seco, *J. Chem. Soc., Dalton Trans.*, 2003, 1194.
16. E.M.M. de Brabander-van den Berg, E.W. Meijer, *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 1308.
17. A.W. Bosman, A.P.H.J. Schenning, R.A.J. Janssen, E.W. Meijer, *Chem. Ber.*, 1997, **130**, 725.
18. K. Takada, D.J. Diaz, H.D. Abruna, I. Cuadrado, B. Gonzalez, C.M. Casado, B. Alonso, M. Moran, J. Losada, *Chem. Eur. J.*, 2001, **7**, 1109.
19. I. Cuadrado, M. Moran, C.M. Casado, B. Alonso, F. Lobete, B. Garcia, M. Ibisate, J. Losada, *Organometallics*, 1996, **15**, 5278.
20. A. Salmon, P. Jutzi, *J. Organomet. Chem.*, 2001, **637-639**, 595.

21. M.T. Reetz, G. Lohmer, R. Schwickardi, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 1526.
22. G.S. Smith, R. Chen and S.F. Mapolie, *J. Organomet. Chem.*, 2003, **673**, 111.
23. J.F.G.A. Jansen, E.M.M. de Brabander-van den Berg and E.W. Meijer, *Science*, 1994, **266**, 1226.
24. A. Lavery and S.M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1984, 615.
25. E.N. Jacobsen, *Acc. Chem. Res.*, 2000, **33**, 421.
26. T.P. Yoon and E.N. Jacobsen, *Science*, 2003, **299**, 1691.
27. T. Katsuki, *Synlett*, 2003, 281.
28. D.A. Atwood and M.J. Harvey, *Chem. Rev.*, 2001, **101**, 37.
29. J.V. Dubsy and A. Sokol, *Collect. Czech. Chem. Commun.*, 1931, **3**, 548.
30. P. Pfeiffer, E. Breith, E. Lübbe and T. Tsumaki, *Liebigs Ann. Chem.*, 1933, **503**, 84.
31. N. Matsukawa, S. Matsui, M. Mitani, J. Saito, K. Tsuru, N. Kashiwa and T. Fujita, *J. Mol. Cat. A: Chem.*, 2001, **169**, 99.
32. S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa and T. Fujita, *J. Am. Chem. Soc.*, 2001, **123**, 6847.
33. S. Matsui and T. Fujita, *Catalysis Today*, 2001, **66**, 63.
34. S.-I. Ishii, J. Saito, M. Mitani, J.-I. Mohri, N. Matsukawa, Y. Tohi, S. Matsui, N. Kashiwa and T. Fujita, *J. Mol. Cat. A: Chem.*, 2002, **179**, 11.
35. J. Saito, M. Mitani, J.-I. Mohri, Y. Yoshida, S. Matsui, S.-I. Ishii, S.-I. Kojoh, N. Kashiwa and T. Fujita, *Angew. Chem. Int. Ed.*, 2001, **40**, 2918.
36. S.P. Varkey, C. Ratnasamy and P. Ratnasamy, *J. Mol. Cat. A : Chem.*, 1998, **135**, 295.
37. T. Katsuki, *Coord. Chem. Rev.*, 1995, **140**, 189.
38. E.N. Jacobsen, W. Zhang, A. R. Muci, J.R. Ecker and L. Deng, *J. Am. Chem. Soc.*, 1991, **113**, 7063.
39. K.B. Hansen, J.L. Leighton and E.N. Jacobsen, *J. Am. Chem. Soc.*, 1996, **118**, 10924.
40. J.M. Ready and E.N. Jacobsen, *Angew. Chem. Int. Ed.*, 2002, **41**, 1374.
41. R. Moors and F. Vögtle, *Chem. Ber.*, 1993, **126**, 2133.
42. R. Breinbauer and E.N. Jacobsen, *Angew. Chem. Int. Ed.*, 2000, **39**, 3604.
43. S.J. Guber, C.M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1805.

44. R.H. Holm, *J. Am. Chem. Soc.*, 1960, **82**, 5632.
45. B.J. McNelis, L.C. Nathan and C.J. Clarke, *J. Chem. Soc., Dalton Trans.*, 1999, 1831.
46. Z. Li and C. Jablonski, *Inorg. Chem.*, 2000, **39**, 2456.
47. J. Kowalewski (Eds.: D.M. Grant and R.K. Harris), *Encyclopedia of Nuclear Magnetic Resonance*, John Wiley and Sons, Inc., New York, 1996, **5**, 3456.
48. L. Chatt, L.M. Vallarino and L.M. Venanzi, *J. Chem. Soc.*, 1957, 3413.
49. J.X. McDermott, J.F. White and G.M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.



CHAPTER 5

Catalytic Reactions using Metallo dendrimers

5.1 Introduction

Catalysis is one of the most important technologies in modern times and has made a great impact on our industrial economy. The importance of catalysis and the dependence on it is illustrated in Figure 5.1. This diagram shows how we depend on it to produce new materials, fuels (an energy source), and even require it for our health, to ensure the proper functioning of our bodies through enzymatic catalysis.

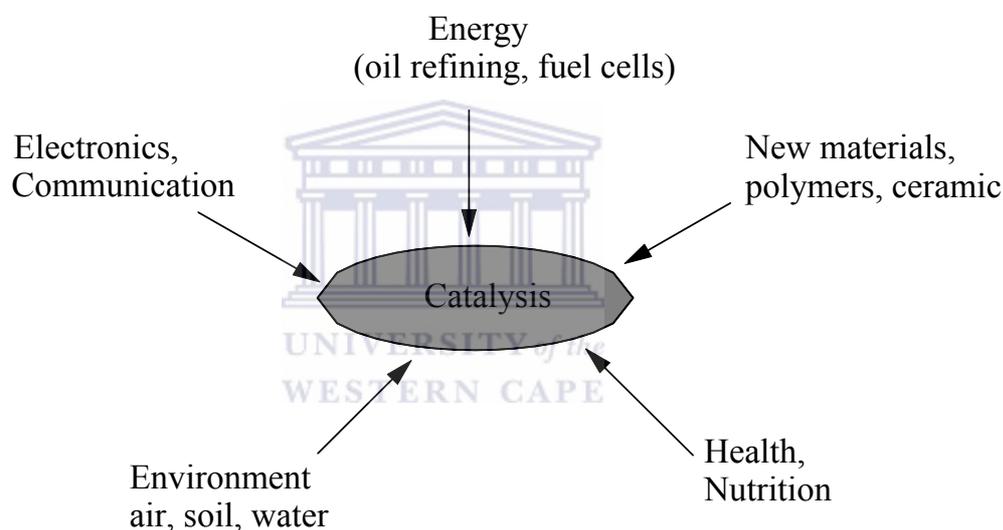


Figure 5.1 Importance of Catalysis

Catalysis has been broadly defined as ‘a process whereby a reaction occurs faster than the uncatalysed reaction, the reaction being accelerated by the lowering of the activation energy of the process in the presence of a catalyst’. This definition has been brought into prominence in the polyolefin industry, which has seen the large-scale production of polymers. The polyolefin industry is a multibillion dollar a year industry, producing a range of polymers. The methods employed focus mainly on early transition-metal catalysis, using conventional Ziegler-Natta catalysis. However, these catalysts are highly oxophilic and do not tolerate other functional groups in the olefins. There is a growing desire to obtain greater control of the resultant polymer’s properties. The drive to obtain

highly active, selective catalysts, has led to an emphasis on ligand-metal complex design and the synthesis of late-transition metal-containing complexes as α -olefin polymerisation catalysts.

Late-transition metal complexes are not commonly used in current industrial processes. The first industrial application of such systems was the Shell Higher Olefin Process (SHOP), in which a neutral Ni catalyst containing P-O chelating ligand effects the oligomerisation of ethylene to linear $C_4 - C_{20}$ olefins. A number of reports of late transition metal complexes as olefin polymerisation/oligomerisation catalysts appeared in the 1990's.¹⁻³ The synthesis of polyolefins has grown significantly since the discovery of methylaluminoxane (MAO), which is used as a co-catalyst for olefin polymerisation. Brookhart and coworkers reported new Pd(II)- and Ni(II)-based catalysts bearing bulky, neutral α -diimine ligands for ethylene polymerisation in 1995.⁴⁻⁵ The spate of work in this field stems from the fact that α -diimine ligands are well-known to stabilise organometallic complexes. More recently, iron (II)- and cobalt(II)-based / MAO catalyst systems were reported by Brookhart⁶ *et al* and Gibson⁷ *et al*, which showed capability of polymerizing ethylene. These examples all show homonuclear metal diimine complexes capable of ethylene polymerisation, but no account is given of multinuclear metal-containing diimine complexes attached to dendrimers, being used to polymerize ethylene.

The interest in dendrimers and metal-containing dendrimers has also brought with it a myriad of potential new applications.⁸⁻⁹ For example, polyamidoamine (PAMAM) dendrimers are used as carriers for DNA, peptide antigens and agrochemicals.¹⁰ Research into the synthesis of metal-containing dendrimers and their specific use as catalysts is supported by a spate of recent excellent reviews and other articles.¹¹⁻¹⁸ Dendrimers are useful scaffolds for the design of catalytic systems. This interest has been ascribed to the well-defined architecture and specific number of active sites in the dendrimer. Our studies have focused solely on peripheral functionalized poly(propyleneimine)-pyridylimine metallo dendrimers, as discussed in Chapter 4. One of the motivations for studying these multinuclear catalyst precursors is that these systems have high local concentrations of active sites within the same molecule. In addition, we wished to compare the new multinuclear systems with mononuclear catalysts with regard to activity, molecular weight

distribution and polymer properties. This we had hoped might lead to enhanced catalyst activity.

Peripheral-functionalized dendrimers have numerous catalytic sites located on the surface of the dendrimer, thus allowing free, unhindered interaction with substrates. This accessibility should ideally enable faster reaction rates and give higher catalytic activities, when compared with conventional linear polymeric supports. The first example of a catalytically active peripheral-functionalized metallodendrimer was reported by van Koten and co-workers in 1994.¹⁹ They had functionalized the surface of a polysilane dendrimer with diaminoarylnickel(II) complexes (Figure 5.1). The dendrimers were then used in Kharasch-type additions of polyhalogenoalkanes to olefins.

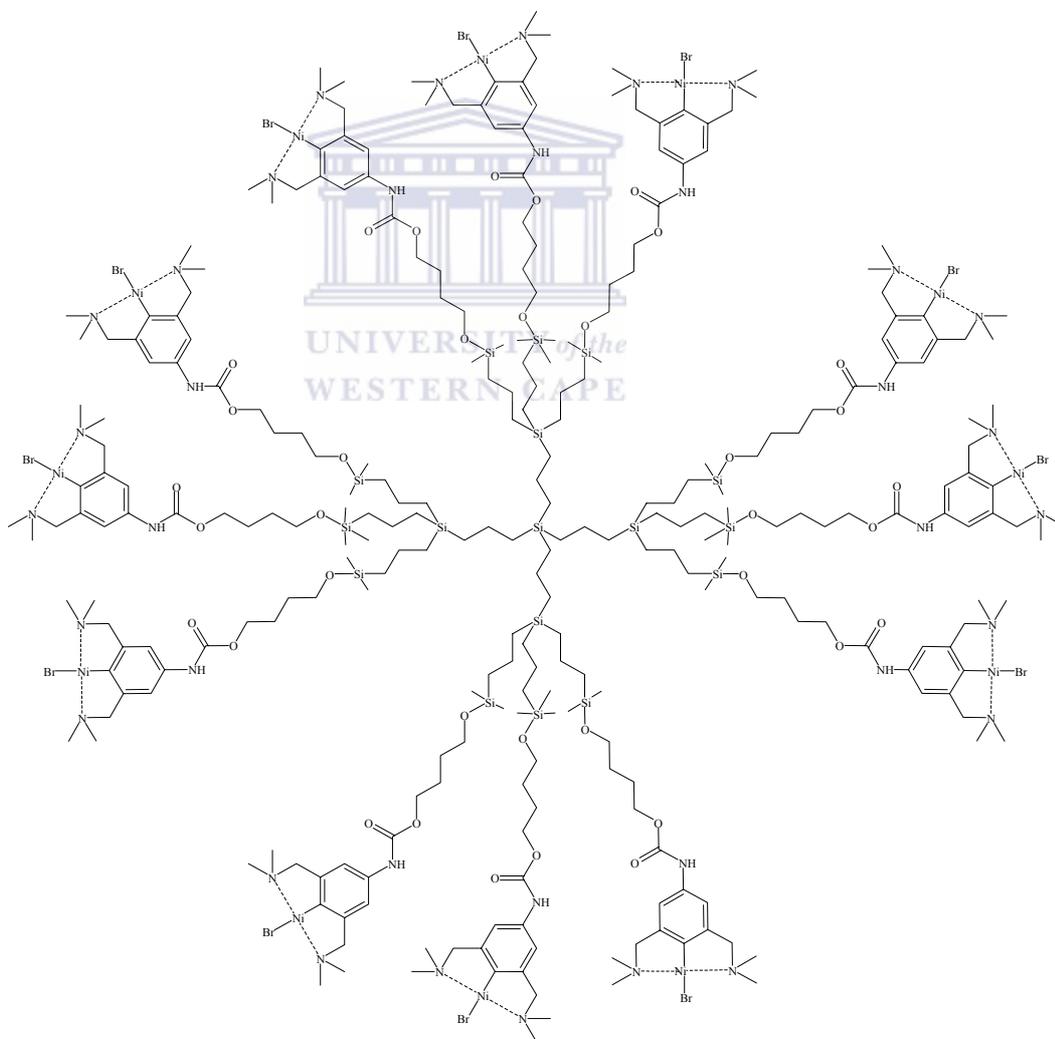


Figure 5.2 Polysilane dendrimer prepared by van Koten and coworkers

The synthesis of phosphorus-based dendrimers with palladium complexes on the periphery was reported by DuBois and co-workers.²⁰ These are generally small dendrimers containing 12 or 15 phosphorus atoms that have been metallated with $[\text{Pd}(\text{MeCN})_4][\text{BF}_4]_2$. These complexes have been shown to exhibit catalytic activity for the electrochemical reduction of CO_2 . The prolific use of metal-containing dendrimers in catalysis has also set a precedent for many transition-metal catalysed organic transformations.²¹⁻²⁴

Astruc and Chardac⁹, as well as van Leeuwen¹⁴ *et al*, have recently reviewed several examples of other surface-bound metallo dendrimers and their application as catalysts or catalyst precursors. In addition, metal-containing dendrimers also have potential applications in host-guest chemistry, liquid-crystals, ion exchange materials and many more.²⁵⁻²⁷

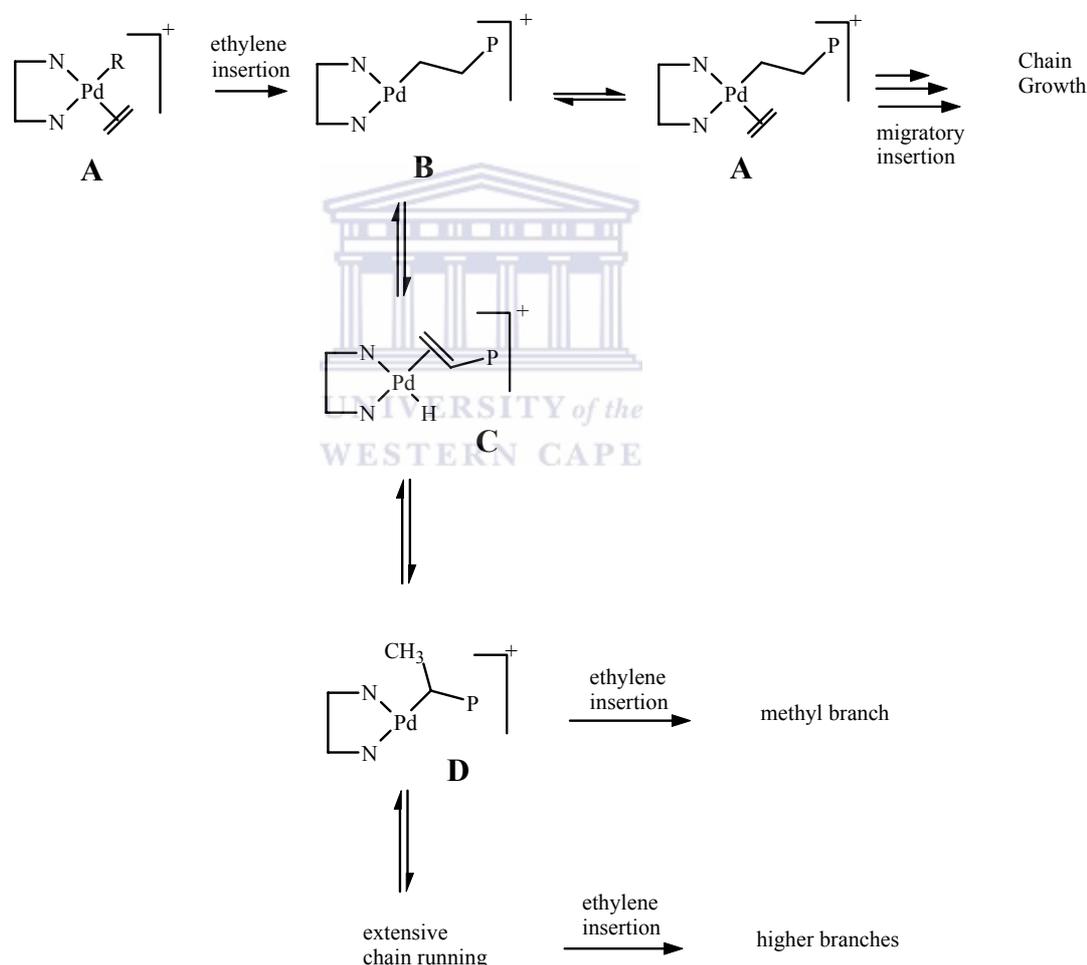
In this chapter we describe the use of the poly(propyleneimine) iminopyridyl metallo dendrimers (**54**, **55**, **56**, **57**, **58**), described in Chapter 4, to catalyze the polymerisation of ethylene. The preliminary results of this work have been published by us.²⁸ The use of the metallo dendrimer **54** as an active Heck cross-coupling catalyst is also discussed in the following text.

5.2 Late Transition Metal Catalysts For Ethylene Polymerisation

5.2.1 Mechanistic Considerations

There is a general consensus that, as far as olefin polymerisation is concerned, the catalytically active species is a coordinatively unsaturated cationic alkyl complex. In the context of palladium α -diimine complexes, such complexes are generated using aluminoxanes such as methylaluminoxane (MAO). Although the structure of MAO is not fully known, it does afford high catalyst activities. The role that MAO fulfils in the polymerisation process is to alkylate the dihalide catalyst precursor and then abstract a methide anion, to generate the active species. Large excesses of MAO are normally required to achieve an active polymerisation catalyst. The large excess is necessary to drive the equilibrium of the abstraction reaction toward the cationic product. The mechanism that olefin polymerisation follows after activation with MAO is depicted in Scheme 5.1.

The limiting step is a migratory insertion step to yield the intermediate **B**. This creates a vacant site which allows for coordination of another ethylene molecule, thus reverting to a similar state as **A**. The process of migratory insertions is repeated and leads to continuous chain growth, generating linear polymers. Alternatively, metal migration (chain running) along the alkyl chain may occur during the intermediate state **B** via β -H elimination / readdition reactions, giving rise to intermediates **C** and **D**. Insertion reactions following the metal migration pathway give rise to more branched polymer chains. A number of factors, such as ethylene pressure and the size of the substituents around the active centre, can affect the extent of branching in the polymer chain.



Scheme 5.1

5.2.2 Catalytic Evaluation of DAB-G1(Impyr-PdCl₂)₄ (54) at 3 atm

Ethylene polymerisation studies were carried out in a stainless steel 300ml Parr autoclave using the palladium dendrimer, DAB-G1(Impyr-PdCl₂)₄ (54), from Chapter 4 as catalyst precursor. The active catalyst is generated *in situ* in toluene by the addition of methylaluminoxane as activator and polymerisations were performed in the presence of ethylene at 3 atm initially. This afforded granular polyethylene, which was filtered, washed with acidified ethanol and dried in a vacuum oven at 80 EC. The polymerisation results with precatalyst, DAB-G1(Impyr-PdCl₂)₄, are summarized in Table 5.1. For comparison, the polymerisation results of the previously reported mononuclear pyridylimine palladium complexes (65)²⁹ (Figure 5.3) are also included.

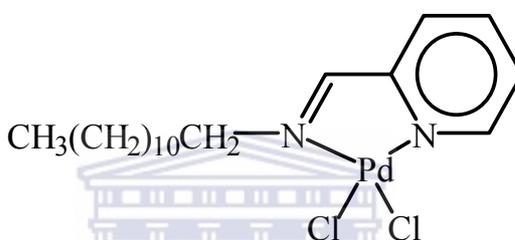


Figure 5.3 Mononuclear Iminopyridyl Palladium Catalyst Precursor (65)

The results collected in Table 5.1 show that the new metallo dendrimer, DAB-G1(Impyr-PdCl₂)₄, is an active ethylene polymerisation catalyst under the conditions described. Activities for this precursor ranged from 0.87 to 118 kg.mol⁻¹.h⁻¹, using Al/Pd ratios between 500 and 1500. Figure 5.5 shows the effect of Al:Pd molar ratio on catalytic activity. There is a significant increase in catalytic activity with an increase in the Al:Pd ratio. It was found that a ratio of Pd:Al = 1:1000 gave the optimum activity, thereafter the catalytic activity began to decrease. These activity values were found to be higher than activities for analogous mononuclear and binuclear palladium diimine systems, reported by Mapolie *et al.*^{29,30} The higher activity could possibly be ascribed to the increased local concentration of catalytic sites within the multinuclear precursor. In addition, their activity can also be ascribed to the higher stability of the dendritic core in comparison with the mononuclear complex. The overall activity is, however, lower than the highly bulky catalyst precursors reported by Brookhart and co-workers⁴⁻⁵, and certain metallocene dendrimers prepared by Seyferth³¹ *et al.*, who reported activities of 5760 kg.mol⁻¹.h⁻¹.

Kaminsky and co-workers³² have prepared dendritic zirconocene complexes for ethylene polymerisation. They have shown that the analogous monomeric zirconocenes were ten times more active ($60900 \text{ kg}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$) than the dendritic zirconocenes. Breinbauer and Jacobsen have modified poly(amidoamine) dendrimer endgroups with $[\text{Co}(\text{salen})]$ catalysts, for testing in asymmetric ring opening of epoxides.³³ Their studies, however, showed that the modified dendrimers were better catalysts than monomeric or dimeric $[\text{Co}(\text{salen})]$ compounds. Reetz *et al*²¹ have also shown that their phosphine-terminated dendrimers exhibit higher catalytic activity compared with that of the analogous monomeric complexes. They attributed this to the higher thermal stability of the dendritic complexes.

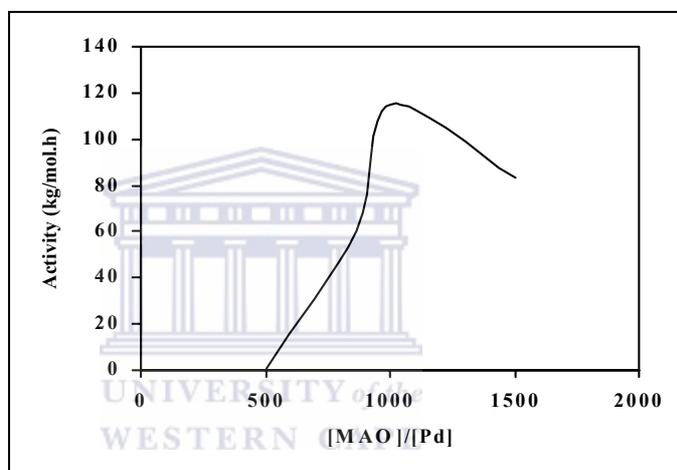


Figure 5.4 Graph of MAO: Pd ratio vs Activity for DAB-G1(Impyr-PdCl₂)₄ (54)

The stability of our metallo dendrimer is also attested to by its greater activity over analogous mononuclear complexes. Previous studies³⁴ have shown that a greater steric bulk around the reaction centre leads to a suppression of side reactions as well as to a decrease of “backbiting”, which is responsible for low molecular weight polymers. The dendritic core and pyridylimine moieties are bulky substituents situated above and below the axial positions of the square planar complex, and in so doing, retard the rate of chain transfer. High molecular weight polyethylene was obtained ($M_w = 14.07 \times 10^5$) at a ratio of Pd:Al = 1:1000, and is comparable with catalytically active metallocenes and certain Pd-containing complexes.

Table 5.1 : Ethylene polymerisation using DAB-G1(Impr-PdCl₂)₄ (54) as precatalyst

Precursor ^a	[MAO]/[Pd]	Ethylene Pressure (atm)	PE yield (g)	Activity (kg.mol ⁻¹ .h ⁻¹)	10 ⁻⁵ M _n ^b	10 ⁻⁵ M _w ^b	M _w /M _n	T _m (EC) ^c
54	500	3	0.0221	0.87	4.21	10.91	2.59	137.18
54	866	3	2.7764	60.34	4.91	13.56	2.76	137.95
54	1000	3	3.1761	118.01	4.87	14.07	2.89	137.59
54	1500	3	2.3938	83.55	4.95	12.41	2.51	137.30
Mononuclear (65)	100	5	0.1817	3.78	3.84	8.08	2.11	138.02
Mononuclear (65)	260	5	0.7314	15.24	4.07	8.53	2.10	137.80
Mononuclear (65)	1040	5	1.1236	23.41	4.52	9.19	2.03	137.75

^a Polymerisation performed in dry toluene at 3 atm of ethylene, 25 EC, 3h, using ~2.0 μmol palladium complex activated with MAO.

^b Molecular weight data was determined by high temperature (160 EC) GPC vs polystyrene standards.

^c Determined by differential scanning calorimetry (DSC)

The polydispersity indices for these polymers were found to average around 2.7, slightly higher than other transition metal catalysts that average around 2.2. In all cases, a unimodal molecular weight distribution curve was observed. This indicates that only one kind of active species is present during the polymerisation reaction.

The melting point temperatures (T_m) as determined by differential scanning calorimetry (DSC) average around 137°C. A representative DSC thermogram is shown in Figure 5.5. The DSC thermograms resemble those usually obtained for linear HDPE and therefore allude to the formation of high-density polyethylene (HDPE), which typically has a T_m of 135°C. High temperature $^1\text{H NMR}$ spectroscopy (Figure 5.6) shows only one signal in the spectrum for polyethylene. This confirms the polymeric material to be linear in nature with no evidence of any branching. An illustration of part of a polyethylene microstructure is given in Figure 5.7.

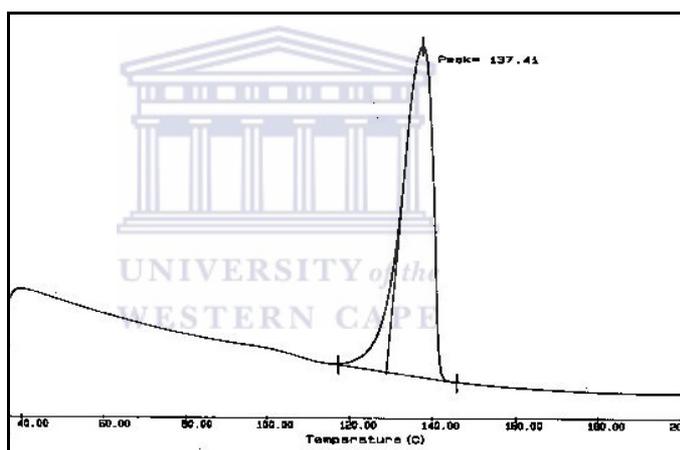


Figure 5.5 DSC thermogram of polyethylene

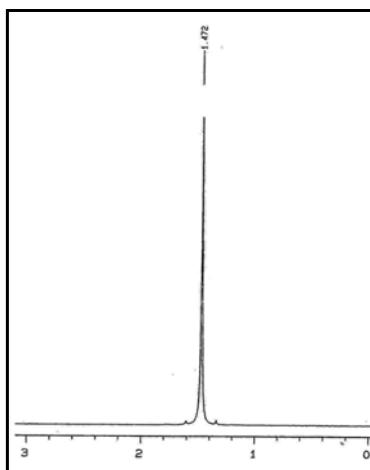


Figure 5.6 High temperature ^1H NMR spectrum of polyethylene

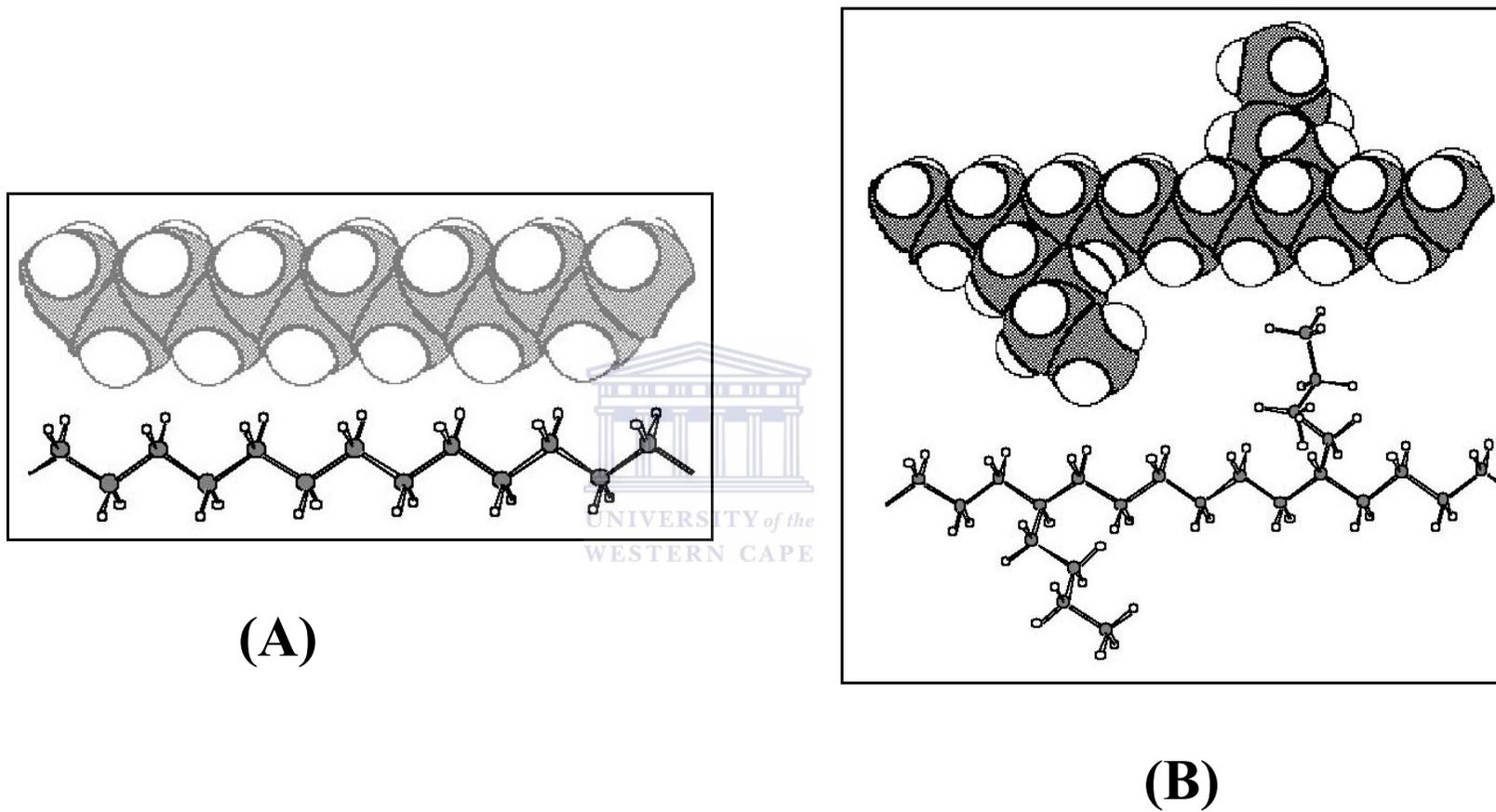


Figure 5.7 Part of a Linear (A) and a Branched (B) Polyethylene Molecule

5.2.3 Catalytic Evaluation of DAB-G1(Impyr-PdCl₂)₄ (**54**) and DAB-G2(Impyr-PdCl₂)₈ (**55**) at 5 atm

The results of the first-generation metallo dendrimer, DAB-G1(Impyr-PdCl₂)₄ (**54**), and second-generation metallo dendrimer, DAB-G2(Impyr-PdCl₂)₈ (**55**), conducted at 5 atm of ethylene pressure, are shown in Table 5.2. This shows that they are both active ethylene polymerisation catalysts under these conditions. Using both catalyst precursors, the morphology of the obtained polyethylene was the same as with previous runs. White granular solids were obtained.

Metallo dendrimer, DAB-G1(Impyr-PdCl₂)₄ (**54**), shows a general increase in catalyst activity at 5 atm, when comparing with similar runs conducted at 3 atm. This is expected since the diffusion of ethylene into solution is more pronounced due to increased ethylene concentration. The molecular weight remains largely unaffected by an increase in ethylene pressure. The second-generation metal-containing dendrimer, DAB-G2(Impyr-PdCl₂)₈ (**55**), displays lower activities, when compared with the first-generation metallo dendrimer under similar conditions.

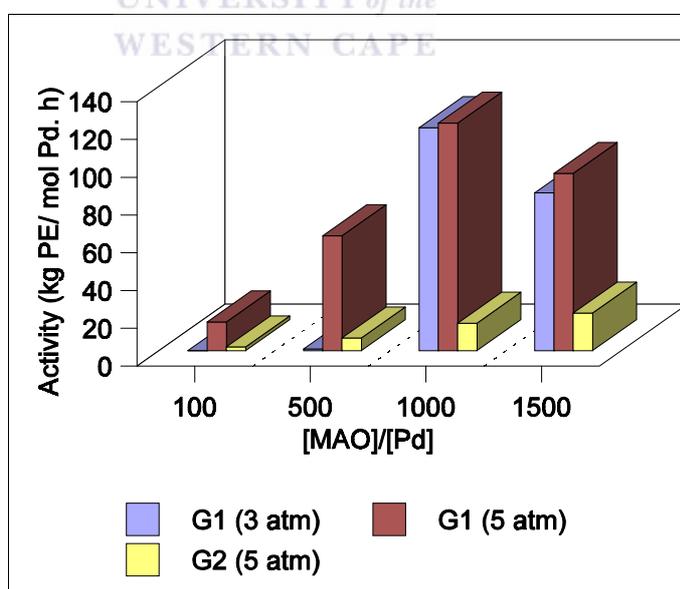


Figure 5.8 Graph of MAO: Pd ratio vs Activity for DAB-G1(Impyr-PdCl₂)₄ (**54**) and DAB-G2(Impyr-PdCl₂)₈ (**55**)

Table 5.2 : Ethylene polymerisation using DAB-G1(*Impyr-PdCl*₂)₄ (**54**) and DAB-G2(*Impyr-PdCl*₂)₈ (**55**) as precatalysts

Precursor ^a	[MAO]/[Pd]	Ethylene Pressure (atm)	PE yield (g)	Activity (kg.mol ⁻¹ .h ⁻¹)	10 ⁻⁵ M _n ^b	10 ⁻⁵ M _w ^b	M _w /M _n	T _m (EC) ^c
54	100	5	0.5132	15.16	4.47	14.48	3.24	136.25
54	500	5	2.0581	60.78	3.04	10.37	3.41	136.83
54	1000	5	4.0778	120.43	3.02	10.42	3.45	136.83
54	1500	5	3.4197	93.78	2.81	9.10	3.24	136.96
55	100	5	0.0611	1.95	3.66	14.09	3.85	137.16
55	500	5	0.2142	6.65	3.27	10.01	3.06	137.12
55	1000	5	0.4543	14.47	2.69	10.22	3.80	136.88
55	1500	5	0.622	19.81	2.53	10.14	4.01	136.83

^a Polymerisation performed in dry toluene at 5 atm of ethylene, 25 EC, 3h, using ~2.0 μmol palladium complex activated with MAO.

^b Molecular weight data was determined by high temperature (160 EC) GPC vs polystyrene standards.

^c Determined by differential scanning calorimetry (DSC)

The lower activity observed is quite surprising, since one would expect higher activities, using complexes containing a greater local concentration of potential catalytic active sites. These findings mirrored those by Jacobsen³³, who found that lower generation dendrimers were better catalysts than high-generation dendrimers. Van Koten¹⁹ *et al* based their lower catalytic activity upon increasing the dendrimer generation on not all the sites being metallated in their dendrimer complex. ¹H-NMR spectroscopy and ICP analysis revealed that complete metallation had occurred for the second generation. Thus we ruled out the possibility of incomplete metallation. Therefore, it is proposed that the decreased reaction rate is due to the more difficult mass transport with increasing steric bulk of the dendritic wedges. Upon increasing the dendrimer generation, the steric bulk increases, making accessibility restricted, due to possible entanglement of the dendritic arms. Therefore, mass transport would be very difficult in this dense network. One may also propose that all of the metal sites are not activated by MAO, which may account for the drop in activity. Detty and co-workers^{35,36} reported examples of phenylseleno-modified poly(benzyl ether) dendrimers, where the order-of-magnitude in catalytic rate increases with increasing dendrimer generation. They attributed the increased catalytic activity to an increase in the density of selenium groups and a possible increase in selenium-selenium interactions. There is also a noticeable increase in the polydispersity of the polyethylene samples upon increasing the dendrimer generation. It would thus appear that the nature of the catalytically active species changes with the increasing number of potential active sites, causing the polydispersity to increase.

Application of the third generation metallo dendrimer, DAB-G3(impyr-PdCl₂)₁₆ (**56**), was not attempted. It is thought that, following the trends of the second generation, much lower catalytic activities can be expected, since the third generation has even greater constraints, coupled with complete insolubility in all organic solvents.

5.2.4 Catalytic Evaluation of DAB-G1(Impyr-PtCl₂)₂ and DAB-G1(Impyr-CuCl₂)₄ at 5 atm

The first-generation metallo dendrimers, DAB-G1(impyr-PtCl₂)₂ (**57**) and DAB-G1(impyr-CuCl₂)₄ (**58**) have been tested as catalyst precursors towards ethylene polymerisation. The active catalysts are generated *in situ* by methylaluminoxane (MAO) activation. These complexes were shown to catalyse the polymerisation of ethylene, but at lower activities than that of the palladium analogue (Figure 5.9). The activities for the platinum and copper first-generation dendrimers were 25.15 and 6.60 kg PE/ (mol M.h) respectively. This lower activity can possibly be attributed to their lower solubility, in comparison with the palladium analogue. The polyethylene produced using the complexes **57** and **58** show similar properties to that produced by the palladium metallo dendrimers. Generally, the polymers resemble those of highly linear polyethylene (T_m . 137 EC), and appears to be high density polyethylene. The polyethylenes have high molecular weights, and show a unimodal molecular weight distribution curve, comparable with the polymers obtained using the palladium complexes as catalysts.

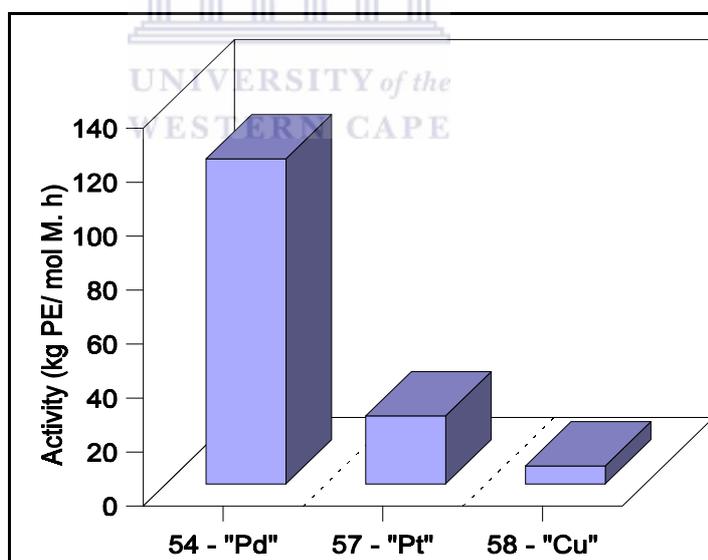


Figure 5.9 Graph of Catalyst Activity as a Function of Metal for complexes 54, 57, and 58.

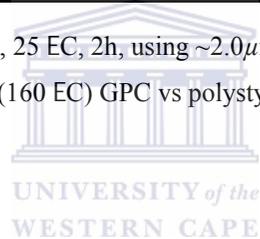
Table 5.3 : Ethylene polymerisation using DAB-G1(Impyr-PdCl₂)₄ (**54**), DAB-G1(Impyr-PtCl₂)₂ (**57**) and DAB-G1(Impyr-CuCl₂)₄ (**58**) as precatalyst

Precursor ^a	[MAO]/[Pd]	Ethylene Pressure (atm)	PE yield (g)	Activity (kg.mol ⁻¹ .h ⁻¹)	10 ⁻⁵ M _n ^b	10 ⁻⁵ M _w ^b	M _w /M _n	T _m (EC) ^c
54	1000	5	4.0778	120.43	3.02	10.42	3.45	136.83
57	1000	5	0.4611	25.15	3.05	8.42	2.76	136.94
58	1000	5	0.0393	6.60	2.60	8.01	3.08	136.81

^a Polymerisation performed in dry toluene at 5atm of ethylene, 25 EC, 2h, using ~2.0μmol metal complex activated with MAO.

^b Molecular weight data was determined by high temperature (160 EC) GPC vs polystyrene standards.

^c Determined by differential scanning calorimetry (DSC)



5.3 Heck reactions using metallodendrimer, DAB-G1(Impr-PdCl₂)₄ (54)

The Heck reaction is widely used in organic transformations in the synthesis of various substituted olefins, dienes and precursors to conjugated polymers.³⁷⁻³⁹ This cross-coupling reaction of electron-rich organohalides and pseudohalides with a wide range of olefins, is catalysed by a Pd(0) complex, formed *in situ* from Pd(OAc)₂, Et₃N and PPh₃ (Figure 5.10).

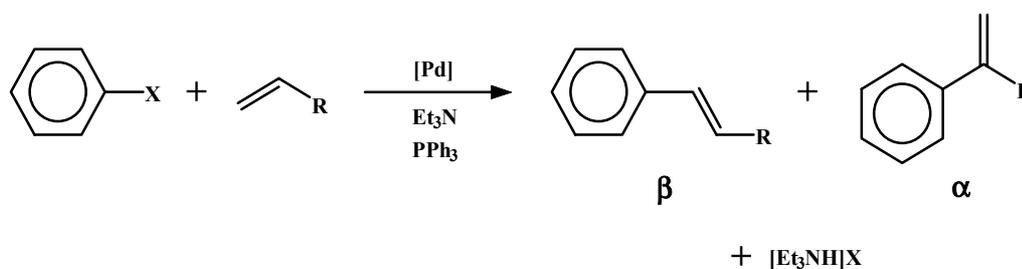


Figure 5.10 Classical Heck Reaction

The classical conditions for the Heck reaction involve heating a mixture of the olefin, the halide, a catalytic amount of Pd(OAc)₂ and several equivalents of triethylamine in acetonitrile until the reaction is complete.^{40,41} Typical Heck procedures use Pd(II) salts and a reducing agent to generate Pd(0) *in situ*. A stoichiometric excess of an amine such as Et₃N is part of the reaction mixture, serving both as a base to trap the HX given off as a by-product and as a reducing agent for Pd. The regiochemistry of the Heck reaction is usually determined by the nature of the R group on the olefin. Electron withdrawing groups lead almost exclusively to the β-arylated products, whereas electron-donating substituents usually lead to a large proportion of the α-arylated product. Heck reactions have found wide application in the preparation of a range of compounds from natural product to fine chemical synthesis.⁴² In addition, this cross-coupling reaction uses cheap and readily available olefins as coupling partners.

The proposed mechanism for the Heck reaction is depicted in the catalytic cycle shown in Figure 5.11. The first step in the cycle entails the oxidative addition of an organohalide (R-X) to the Pd(0) complex, forming a *trans* palladium complex. This is followed by coordination of the olefin to the Pd(II) centre and insertion into the Pd-C bond. The β-elimination of the substituted olefin releases the new cross-coupling product. When monosubstituted olefins are used, the β-hydrogen removed is the one that leads

preferentially to an *E*-double bond. Reductive elimination of HX, which reacts with Et₃N to form the salt [Et₃NH]X, regenerates the active catalyst Pd(0) complex.

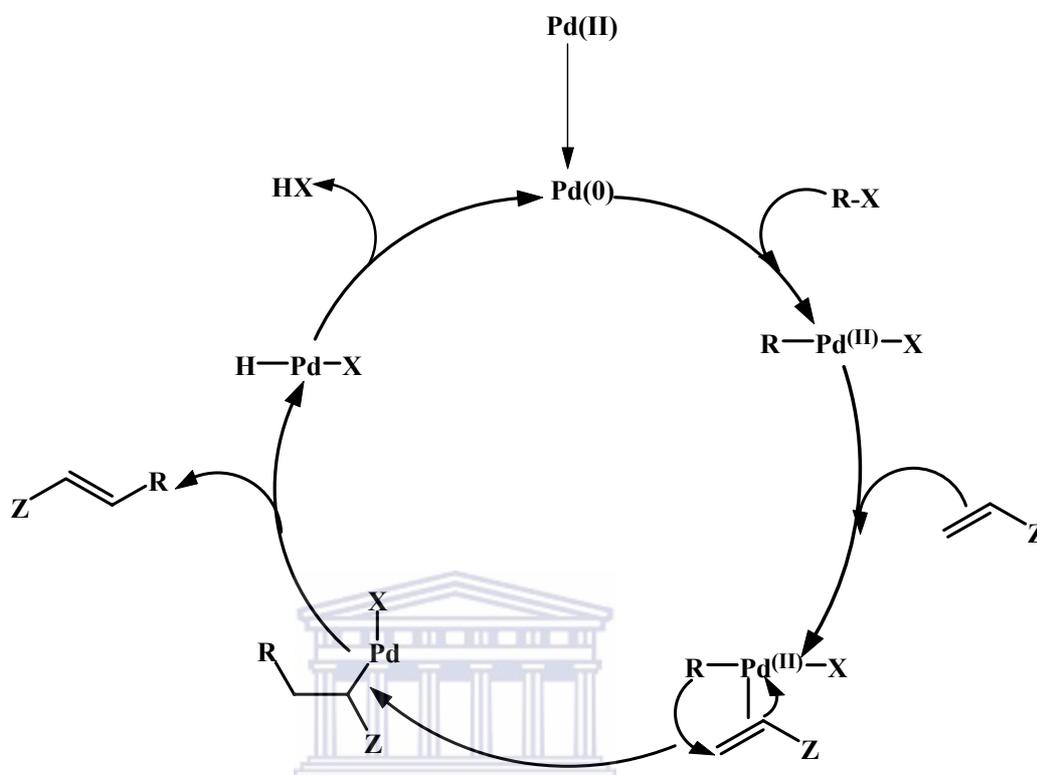


Figure 5.11V Mechanism for the Heck Reaction

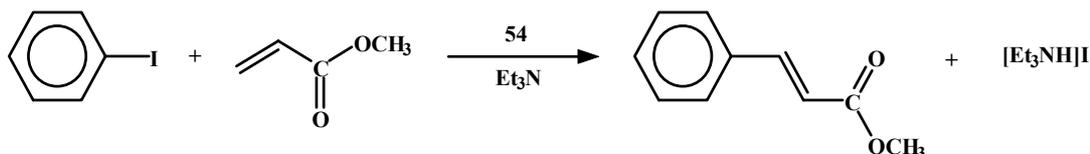
Since the discovery of the Heck reaction, there have been increasing reports of synthetic applications, improvements of traditional Heck conditions, studies of regio- and stereoselectivity and new discoveries on mechanistic features.^{43,44} Traditionally, homogeneous catalytic systems have been used and are highly effective, although heterogeneous catalysts are preferred.⁴⁵ Techniques demonstrating the immobilisation of various complexes are well-documented.⁴⁶⁻⁴⁸ Palladium catalysts, in particular, have been used successfully for a variety of organic reactions.⁴⁹⁻⁵¹ For example, Teranishi and co-workers have immobilised palladium on phosphinated polystyrene⁵², for various carbon-carbon bond forming reactions. Hallberg⁵³⁽ⁱ⁾ *et al.* and Zhang⁵³⁽ⁱⁱ⁾ *et al.* also reported polymer-supported catalysts in Heck arylation reactions. Clark and co-workers⁵⁴ prepared novel palladium catalysts supported on chemically modified mesoporous silica gel, for use in the coupling of aryl iodides with olefins. Dendritic-metal complexes are becoming increasingly popular in various catalytic processes, as they offer the advantages of acting

as both heterogeneous and homogeneous catalyst precursors. These materials would ideally be recoverable and recyclable, and yet still maintain high activity. The use of dendrimeric supports have also found particular application in the Heck reaction.^{21,55} The best example is Reetz's dendritic phosphine^{21,55(ii)}, DAB-*dendr*-[N(CH₂PPh₂)₂]₁₆, bearing P-centres on the periphery, coordinated to palladium catalysts. Alper and co-workers⁵⁵⁽ⁱⁱⁱ⁾ affixed polyamidoamidodiphosphonated dendrimers on the surface of silica, and complexed these to form a palladium-dimethyl TMEDA complex. These catalysts are effective in coupling aryl bromides with butyl acrylate and styrene, and could be reused with a moderate loss in activity. Recent reports involving Pd(II)/diazobutadiene systems⁵⁶ as active catalysts for the Heck arylation of olefins, prompted us to investigate the application of the first-generation metallo dendrimer (**54**), DAB-G1(impyr-PdCl₂)₄, as a potential Heck cross-coupling catalyst precursor.

Our studies focused largely on complex **54**, DAB-G1(impyr-PdCl₂)₄, as the palladium source, although some reactions with the second generation dendrimer were also carried out. All reactions were performed in refluxing acetonitrile. Iodobenzene was chosen as the organohalide substrate. When aryl iodides are used, the addition of phosphine is not required, which, in fact, inhibits the reaction.⁵⁷ Reactions involving less reactive aryl bromides and chlorides require bulky electron-donating phosphines.⁵⁷ Added phosphines are normally required for the oxidative addition step. Under standard Heck conditions, both phosphines and their palladium complexes are prone to decomposition. Excess phosphine is therefore required, reducing the reaction rate, necessitating higher palladium loading. Cross-coupling reactions were attempted with a range of olefins. These include methyl acrylate, styrene and 1-octene. Triethylamine was used to remove hydrogen iodide formed as a by-product during the reaction. All the reactions start after a short induction period of ~5 min for the mononuclear complexes and ~ 10 min for the dendritic complex, in which the initial orange suspension becomes a dark red solution. No attempts were made to recover the catalyst at the end of the reaction.

5.3.1 Catalytic reactions with Methyl Acrylate

Complex **54** effectively catalyses the arylation of methyl acrylate (Equation 5.1) in refluxing acetonitrile (82EC) over 8h. Using palladium loadings of 0.288 mmol Pd, the aryl iodide was converted to the desired product, methyl-3-phenylprop-2-enoate (methyl cinnamate). The consumption of iodobenzene was monitored and analysed by GC-MS. The conversion of iodobenzene was calculated based on *n*-hexadecane as internal standard.



(5.1)

The dendritic complex **54** shows a 78% conversion after 1h and eventually leads to a 96% conversion after 8h (Figure 5.12). This reaction leads to the regiospecific formation of the *trans* isomer, methyl cinnamate, as the major product. A minor amount of the β,β -disubstituted product was found, which is normally only observed in considerable yields in certain reactions where the combined use of high temperature and high pressure is required. A control reaction (no ligand) was run, using only PdCl₂ at the same palladium concentration as for the dendritic complex. This was found to be an active catalyst with a 91% conversion at 8h. It however shows much lower conversion during the initial stages of the reaction, showing less than 50% conversion after 2h reaction time. With respect to catalyst activity, the dendritic complex **54** shows a higher conversion and the reaction proceeds at a much faster initial rate compared to the palladium salt. During the reaction with PdCl₂, partial decomposition to residual palladium metal, as palladium black was observed. This is possibly the reason for the lower activity. Primary particles formed in solution upon reduction have a tendency to agglomerate to form larger metallic particles. Palladium is generally kept in solution as its phosphine complex, rather than precipitating out as the metal. For complex **54** no undesired formation of elemental Pd was observed. The dendrimer-bound catalyst therefore acts as a good support and retards the tendency to agglomerate and precipitate from solution.

Pittman and Ng⁵⁸ coordinated palladium(0) catalysts to polymer matrices and have shown that these resin-attached catalysts reduce catalyst agglomeration, a phenomenon observed for homogeneous palladium(0) catalysts.

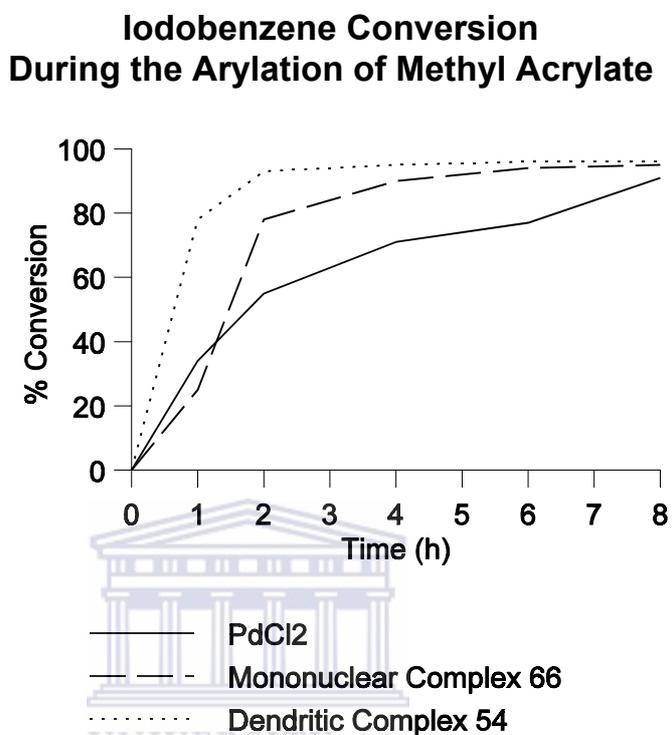


Figure 5.12 Conversion as a Function of Time for the Arylation of Methyl Acrylate with Iodobenzene

The known mononuclear complex, dichloro-*N*-*n*-propyl-2-pyridylmethyl-iminepalladium(II) (**66**)⁵⁹ (Figure 5.13), also effectively catalyses the reaction of iodobenzene with methyl acrylate, with a 95% conversion of iodobenzene in 8h. However, the initial rate is far slower, in comparison with the dendritic complex **54**, with only a 25% conversion after 1h.

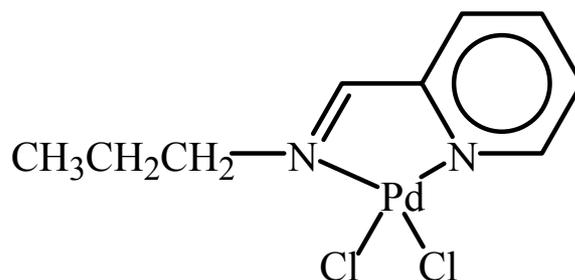


Figure 5.13 Dichloro-N-n-propyl-2-pyridylmethyliminepalladium(II) (**66**)

This catalyst also shows high activity as a Heck catalyst, even though small amounts of palladium black were observed after the reaction was stopped. This lends weight to our proposal that complex **54** acts as a better support, preventing catalyst agglomeration and the precipitation of catalytically inactive palladium metal. The mononuclear complex **66** also shows a slightly higher activity than the palladium salt, PdCl₂. This ligand effect is attributed to the σ -donating and low π -accepting abilities of the α -diimine ligand bonded to palladium. The rate of formation of the coupled product using **54** exceeds that of the mononuclear palladium complex **66** and the salt PdCl₂. After 8h, the reactions using the three different catalysts were nearly complete, showing over 95% conversion of iodobenzene. In the case of the reaction using complex **54** as catalyst, most of the conversion occurs during the first hour of the reaction (~78%).

The second generation palladium metallo dendrimer, DAB-G2(impyr-PdCl₂)₈ (**55**), mentioned in CHAPTER 4, was also used as a catalyst precursor in the reaction of methyl acrylate with iodobenzene. Qualitatively, the same order of catalyst activity was found (Figure 5.14). Catalyst **55** gave about 92% conversion of iodobenzene in 8h. It is noted that catalyst **55** showed a lower conversion after 1h of reaction (39%) compared to the first generation dendrimer **54** after the same amount of time. Obviously, **55** needs time to develop full catalytic capacity, as this complex is sterically more bulky than the first generation. In addition the longer induction period required for **55**, suggests that a relatively longer time is needed for **55** to develop the catalytically active palladium(0)

compared to **54**. In addition, diffusion effects of the substrate can also be a limiting factor, as the greater steric bulk and entanglement of the dendritic arms of the second-generation could limit accessibility to the active sites.

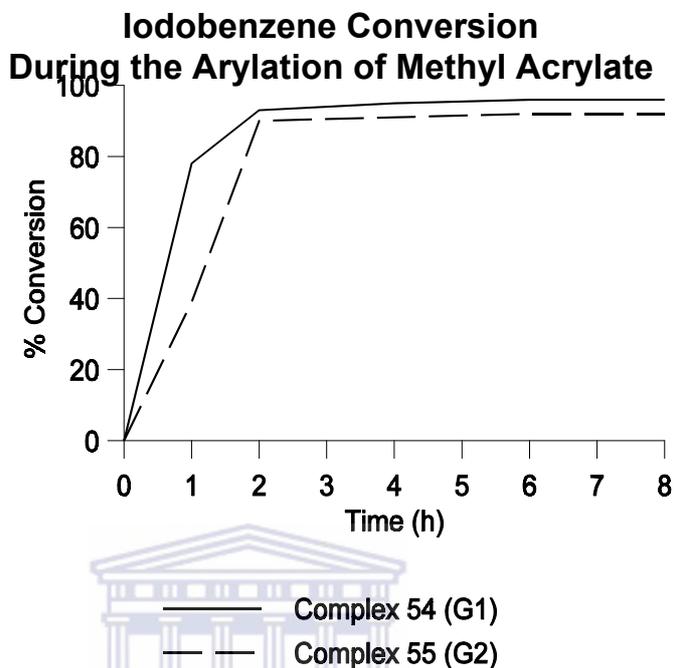
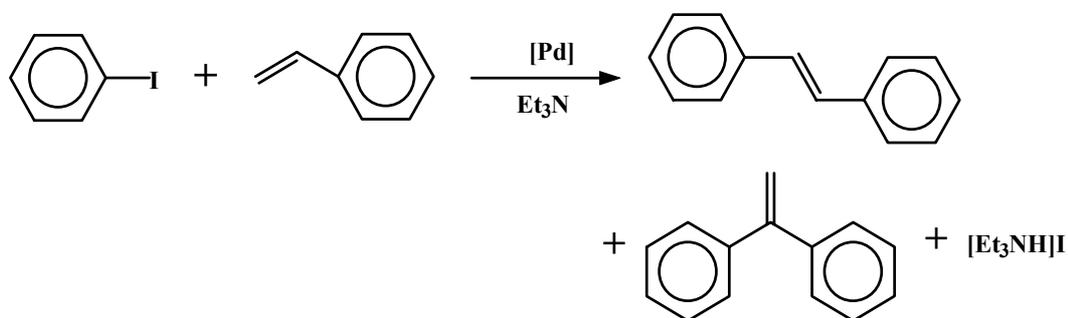


Figure 5.14 Conversion as a Function of Time for the Arylation of Methyl Acrylate with Iodobenzene

5.3.2 Catalytic reactions with Styrene

In the reaction of iodobenzene and styrene, the three palladium sources used in the aforementioned Heck reaction, also successfully catalyse this reaction to yield the product, *trans* 1,2-diphenylethylene or stilbene (Equation 5.2)



(5.2)

Two conclusions are apparent from these reactions. First, the consumption of iodobenzene is a slower reaction and the slower rate is independent of the type of catalyst used (Figure 5.15). This is a similar observation to the findings of Heck⁴⁰ and other groups. Secondly, the rate of reaction, as was the case with methyl acrylate, is dependent on which palladium source is introduced to catalyse the reaction. By comparing the rate of consumption of iodobenzene, the catalysts can be arranged in the following order for the conversion of iodobenzene:



Much lower conversions are observed for PdCl₂ (31%) and the mononuclear iminopyridyl complex **66** (47%) over 8h, in comparison with the dendritic complex **54** (86%). It seems that catalyst agglomeration is more pronounced for PdCl₂ and the mononuclear complex in this reaction with the less active styrene, than is the case with methyl acrylate. In comparison with the methyl acrylate reaction, the catalyst **54** also shows a lower conversion of iodobenzene. This is partly due to a competing side-reaction, in which polystyrene precipitates out of solution. Catalytic polymerisation of styrene has not been observed with neutral Pd(II) compounds⁶⁰, such as Pd(PhCN)₂Cl₂, PdCl₂ and Pd(OAc)₂, and was not observed in our reaction with PdCl₂ either. A small amount of polystyrene was found to precipitate for the mononuclear complex, but the formation of polymer (0.432 g) was more significant for the dendritic complex **54**. This equates to 14% of styrene, that is used to form polystyrene during the reaction. Since the reaction is conducted in stoichiometric amounts, this value correlates with the 86% conversion of iodobenzene. A control reaction performed with the same substrates under the same conditions, but in the absence of any palladium, revealed no polystyrene formation. This rules out thermal polymerisation of styrene and suggests that the dendritic complex **54**, under the optimum reaction conditions, could also potentially catalyse the polymerisation of styrene. This finding is currently under further investigation in our lab.

The regioselectivity of this reaction is also lower compared to that of the methyl acrylate reaction. In this reaction, a mixture of the β -arylated and α -arylated products were

observed, with the β -product more dominant. As was the case in the methyl acrylate reaction, a small amount of the β,β -disubstituted product was also found.

Iodobenzene Conversion During the Arylation of Styrene

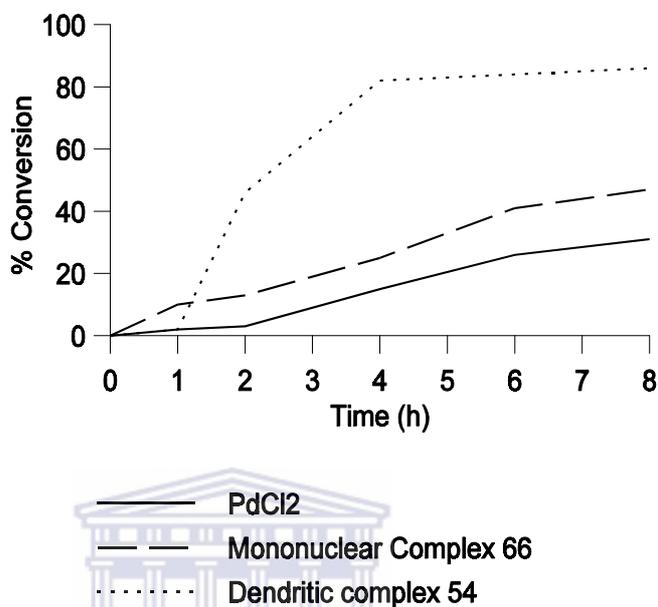
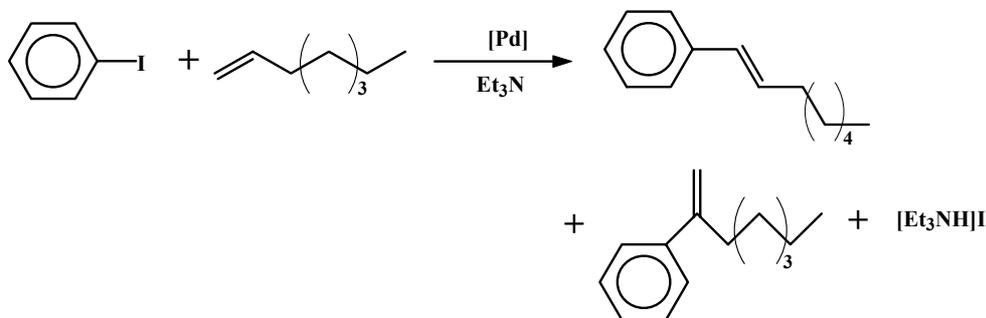


Figure 5.15 Conversion as a Function of Time for the Arylation of Styrene with Iodobenzene

5.3.3 Catalytic reactions with 1-Octene

The reaction of 1-octene and iodobenzene shows the dendritic complex **54** to be a highly effective Heck catalyst precursor, responsible for a 91% conversion of iodobenzene after 8h. However, a mixture of products were obtained (Equation 5.3).



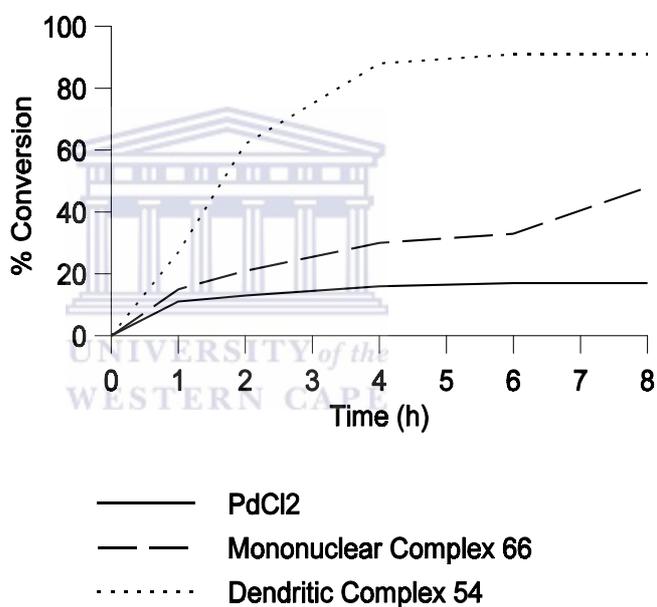
(5.3)

The high conversion of iodobenzene indicates that the dendritic complex **54** is a highly efficient catalyst precursor, capable of coupling iodobenzene with both electron-deficient

or electron-rich olefins. This comparison is also drawn with respect to the mononuclear complex and PdCl₂, which show a much slower rate of conversion over the same period. However, the use of more electron-donating substituents in the olefin, sees a drastic decrease in regioselectivity, as a mixture of arylated products, *cis/trans* isomers and β,β-disubstituted compounds are formed. This is similar to findings with other catalytic systems reported in the literature.⁵⁶

Iodobenzene Conversion During the Arylation of 1-Octene

Figure 5.16 Conversion as a Function of Time for the Arylation



of 1-Octene with Iodobenzene

5.4 Conclusions

The first generation metallodendrimer, DAB-G1(impyr-PdCl₂)₄ (**54**), and the second generation metallodendrimer, DAB-G2(impyr-PdCl₂)₈ (**55**), were used as catalyst precursors in ethylene polymerisation and Heck cross-coupling reactions.

Both metallodendrimers produced highly linear, high density polyethylene with high molecular weights. Complex **54** has a higher activity than similar iminopyridyl mono- and bi-nuclear precatalysts. This can possibly be ascribed to the increased local concentration and greater number of catalytically active sites within the same molecule and the greater stability of the dendritic complex. The optimum ratio of Pd:Al was found to be 1:1000. The second generation metallodendrimer displays a lower catalyst activity than the first generation analogue. A plausible explanation is the more difficult mass transport with increasing steric bulk of the dendrimer. Accessibility to the active sites is also restricted, due to possible entanglement of the dendritic arms. Lower activities can also be attributed to the lower solubility of the second generation compared to the first generation.

Complex **54** proved to be a very active and efficient catalyst precursor in Heck coupling reactions. The dendritic complex successfully achieved high conversions of the aryl halide, in the coupling of iodobenzene with electron-deficient or electron-rich olefins. However, electronic factors seems to play a decisive role in determining the regiochemistry of the reaction. Reactions with methyl acrylate, an electron-deficient olefin, yield mainly β -arylated products, whilst the electron-rich olefin, 1-octene, yielded a mixture of arylated products, *cis/trans* isomers and β,β -disubstituted compounds. With respect to catalyst activity, the dendritic complex **54** generally shows a higher conversion and the reactions proceed at a faster reaction rate compared to the mononuclear iminopyridyl palladium analogue and the palladium salt, PdCl₂. Qualitatively, the catalyst activity did not change dramatically on increasing the dendrimer generation. The initial slower conversion of the second generation metallodendrimer **55** is brought on by the longer induction period required for the catalyst to achieve its full catalytic potential.

5.5 Experimental

The loading of the 300 mL Parr autoclave took place in a nitrogen-purged glove-box. All solvents were dried over the appropriate drying agent and distilled prior to use. Ethylene (99.9%) was purchased from AFROX (South Africa). Methylaluminoxane (10% wt.) in toluene was purchased from Aldrich and used as received. PdCl₂ and triethylamine were obtained from Merck. Iodobenzene was obtained from Hopkin and Williams Ltd, and distilled prior to use. Methyl acrylate was purchased BDH Chemicals. Styrene and 1-octene were purchased from Aldrich. The catalyst precursors were prepared according to the method described in Chapter 4. ¹H NMR (200MHz) and ¹³C NMR (50MHz) spectra were recorded on a Varian XR200 spectrometer. The NMR spectra for polyethylene were recorded in 1,2,4-trichlorobenzene at 120EC, using deuterated benzene as an internal reference. DSC data were obtained at the University of Cape Town on a Perkin-Elmer PC7 Series Thermal Analysis System, at a scanning rate of 10EC/min under N₂ gas-purge with a flow rate of 30ml/min. High-temperature gel permeation chromatography (GPC) was performed by the Polymer Institute (Stellenbosch). A PL-GPC 220 high temperature chromatograph was used, with three columns packed with a polystyrene/divinylbenzene copolymer. The analyses were performed in 1,2,4-trichlorobenzene stabilised with 0.0125% of 2,6-di-tert-butyl-4-methylphenol at 140EC. A calibration curve was established with monodisperse polystyrene standards. GC-MS analyses were performed on a Finnigan MAT GCQ GC / mass spectrometer, equipped with a HP5-MS column.

General Procedure For Ethylene Polymerisation

The catalyst precursor (~2.00μmol) was suspended in dry, degassed toluene (50 ml) in a 300ml stainless steel Parr autoclave. The appropriate amount of methylaluminoxane (10% w/v toluene solution of MAO) was added and an additional 50 ml of toluene added to the solution. The autoclave was sealed, removed from the glovebox and flushed with ethylene. Ethylene was introduced to a pressure of 3 atm and maintained at this pressure throughout the polymerisation. Polymerisation was conducted at 25/C for 3 hours. At the end of the polymerisation, the unreacted ethylene was vented and the reaction quenched with ethanol (20 ml). The resulting polymer suspension was poured into 245 ml of ethanol/HCl (7:1) to remove any palladium residues and left to stand overnight. After filtration, the polymer was washed with ethanol and dried at 80/C in a vacuum oven to constant weight.

General Procedure For Heck Reaction

Iodobenzene (30 mmol), triethylamine (30 mmol) and 30 mmol of an olefin substrate (methyl acrylate, styrene or 1-octene) were mixed in a two-necked round-bottomed flask fitted with a condenser. The mixture was dissolved in 30 ml of dry acetonitrile. The palladium catalyst (0.282 mmol) was added and the mixture heated at 82 EC in an oil bath. Samples of ~0.25 ml were withdrawn periodically by syringe, diluted in dichloromethane and analysed by GC-MS. The conversions were calculated based on *n*-hexadecane as internal standard.



5.6 References

1. G.J.P. Britovsek, V.C. Gibson and D.F. Wass, *Angew. Chem. Int. Ed.*, 1999, **38**, 428.
2. B.L. Small, M. Brookhart and A.M.A. Bennett, *J. Am. Chem. Soc.*, 1998, **120**, 4049.
3. S.D. Ittel, L.K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169.
4. L.K. Johnson, C.M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414.
5. C.M. Killian, D.J. Tempel, L.K. Johnson and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 11664.
6. B.L. Small and M. Brookhart, *Macromolecules*, 1999, **32**, 2120.
7. G.J.P. Britovsek, V.C. Gibson, S. Mastroianni, D.C.H. Oakes, C. Redshaw, G.A. Solan, A.J.P. White and D.J. Williams, *Eur. J. Inorg. Chem.*, 2001, 431.
8. R.M. Crooks, B.I. Lemon III, L.Sun, L.K. Yeung and M. Zhao, *Topics in Curr. Chem.*, 2001, **212**, 81.
9. D. Astruc and F. Chardac, *Chem. Rev.*, 2001, **101**, 2991.
10. R.F. Barth, D.M. Adams, A.H. Soloway, F. Alam and M.V. Darby, *Bioconjugate Chem.*, 1994, **5**, 58.
11. G. Eric Oosterom, J.N.H. Reek, P.C.J. Kamer and P.W.N.M. van Leeuwen, *Angew. Chem. Int. Ed.*, 2001, **40**, 1828.
12. B. Romagnoli and W. Hayes, *J. Mater. Chem.*, 2002, **12**, 767.
13. M.A. Hearshaw and J.R. Moss, *Chem. Commun.*, 1999, 1.
14. R. van Heerbeek, P.C.J. Kamer, P.W.N.M. van Leeuwen and J.N.H. Reek, *Chem. Rev.*, 2002, **102**, 3717.
15. L.J. Twyman, A.S.H. King and I.K. Martin, *Chem. Soc. Rev.*, 2002, **31**, 69.
16. I. Angurell, G. Muller, M. Rocamora, O. Rossell and M. Seco, *J. Chem. Soc., Dalton Trans.*, 2003, 1194.
17. K. Vassilev, J. Kreider, P.D. Miller, W.T. Ford, *React. Funct. Polym.*, 1999, **41**, 205.
18. G. van Koten and J.T.B.H. Jastrzebski, *J. Mol. Cat. A: Chem.*, 1999, **146**, 317.
19. J.W.J. Knapen, A.W. van der Made, J.C. de Wilde, P.W.N.M. van Leeuwen, P. Wijkens, D.M. Grove and G. van Koten, *Nature*, 1994, **372**, 659.

20. A. Miedaner, C.J. Curtis, R.M. Barkley and D.L. DuBois, *Inorg. Chem.*, 1994, **33**, 5482.
21. M.T. Reetz, G. Lohmer and R. Schwickardi, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1526.
22. H. Brunner, *J. Organomet. Chem.*, 1995, **500**, 39.
23. H.-F. Chow and C.C. Mak, *J. Org. Chem.*, 1997, **62**, 5116.
24. P. Bhyrappa, J.K. Young, J.S. Moore and K. Suslick, *J. Mol. Catal. A: Chem.*, 1996, 109.
25. J.F.G.A. Jansen, E.M.M. de Brabander-van Berg and E.W. Meijer, *Science*, 1994, **266**, 1226.
26. A. Cherestes and R. Engel, *Polymer*, 1994, **35**, 3343.
27. Y.H. Kim, *J. Am. Chem. Soc.*, 1992, **114**, 31.
28. G. Smith, R. Chen and S.F. Mapolie, *J. Organomet. Chem.*, 2003, **673**, 111.
29. R. Chen and S.F. Mapolie, *J. Mol. Catal. A: Chem.*, 2003, **193**, 33.
30. R. Chen, J. Bacsá and S.F. Mapolie, *Inorg. Chem. Commun.*, 2002, **5**, 724.
31. D. Seyferth, R. Wyrwa, U.W. Franz and S. Becke, *Chem. Abstr.*, 1997, **127**, 263179p.
32. W. Kaminsky, R. Engehausen, K. Zoumis, W. Spaleck and J. Rohrmann, *Makromol. Chem.*, 1992, **193**, 1643.
33. R. Breinbauer and E.N. Jacobsen, *Angew. Chem. Int. Ed.*, 2000, **39**, 3604.
34. D.P. Gates, S.A. Svejda, E. Ounte, C.M. Killian, L.K. Johnson, P.S. White and M. Brookhart, *Macromolecules*, 2000, **33**, 2320.
35. C. Francavilla, F.V. Bright and M.R. Detty, *Org. Lett.*, 1999, **1**, 1043.
36. C. Francavilla, M. D. Drake, F.V. Bright and M. R. Detty, *J. Am. Chem. Soc.*, 2001, **123**, 57.
37. I. Beletskaya and A.V. Cheprakov, *Chem. Rev.*, 2000, **100**, 3009.
38. G.T. Crisp, *Chem. Soc. Rev.*, 1998, **27**, 427.
39. J.T. Link and L.E. Overman, *Chemtech*, 1998, **28**, 19.
40. R.F. Heck, *Acc. Chem. Res.*, 1979, **12**, 146.
41. R.F. Heck, *Org. React.*, 1982, **27**, 345.
42. (a) L.E. Overman, D.J. Ricca and V.D. Tran, *J. Am. Chem. Soc.*, 1993, **115**, 2042;
(b) J.-M. Gaudin, *Tetrahedron Lett.*, 1991, **32**, 6113;

- (c) L.F. Tietze and W. Buhr, *Angew. Chem. Int. Ed.*, 1995, **34**, 1366.
43. A. de Meijere and F.E. Meyer, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 2379.
44. W. Cabri and I. Candiani, *Acc. Chem. Res.*, 1995, **28**, 2.
45. A. Hallberg and L. Westfelt, *J. Chem. Soc., Perkin Trans. 1*, 1984, 933.
46. M. Poyatos, F. Marquez, E. Peris, C. Claver and E. Fernandez, *New J. Chem.*, 2003, **27**, 425.
47. (i) J. Lieto, D. Milstein, R.L. Albright, J.V. Minkiewicz and B.C. Gates, *Chemtech*, 1983, 46.
(ii) D.C. Bailey and S.H. Langer, *Chem. Rev.*, 1981, **8**, 109.
48. D.D. Whitehurst, *Chemtech*, 1980, 44.
49. B.M. Trost and R.W. Warner, *J. Am. Chem. Soc.*, 1983, **105**, 5940.
50. R.S. Drago, E.D Nyberg and A.G. El A'mma, *Inorg. Chem.*, 1981, **20**, 2461.
51. N.L. Holy and S.R. Shelton, *Tetrahedron*, 1981, **37**, 25.
52. M. Terasawa, K. Kaneda, T. Imanaka and S. Teranishi, *J. Organomet. Chem.*, 1978, **162**, 403.
53. (i) C.-M. Andersson, K. Karabelas and A. Hallberg, *J. Org. Chem.*, 1985, **50**, 3891.
(ii) Z. Zhang, Y. Pan, H.W. Hu and T. Y. Kao, *Synthesis*, 1991, 539.
54. J.H. Clark, D.J. Macquarrie and E.B. Mubofu, *Green Chemistry*, 2000, 53.
55. (i) D.P. Catsoulacos, B.R. Steele, G.A. Heropoulos, M. Micha-Screttas and C.G. Screttas, *Tetrahedron Lett.*, 2003, **44**, 4575.
(ii) M.T. Reetz, *Top. Catal.*, 1997, **4**, 187.
(iii) H. Alper, P. Arya, S.C. Bourque, G.R. Jefferson and L.E. Manzer, *Can. J. Chem.*, 2000, **78**, 920.
56. G.A. Grasa, R. Singh, E.D. Stevens and S.P. Nolan, *J. Organomet. Chem.*, 2003, *in press*.
57. A.F. Littke and G.C. Fu, *J. Org. Chem.*, 1999, **64**, 10.
58. C.U. Pittman, Jr. and Q. Ng, *J. Organomet. Chem.*, 1978, **153**, 85.
59. R.K.Y. Ho and S.E. Livingstone, *Aust. J. Chem.*, 1965, **18**, 659.
60. P.M. Maitlis, In "The Organic Chemistry of Palladium", Chapter I, Vol. II, Academic Press, New York, 1971.

CHAPTER 6

General Conclusions

The primary objective was to use conventional synthetic methodologies to prepare new metal-containing polymers and dendrimers. These would add to the development in the field of materials science.

The synthesis and characterisation of new metal-carbon σ -bonded and π -bonded organometallic polyesters were investigated. The synthetic method entailed first preparing the bifunctional organometallic monomers. These were reacted with terephthaloyl chloride to produce organometallic polyesters. Generally, low molecular weight oligomers were obtained, with an average degree of polymerisation of four. Reactions with the dendritic wedge did not provide pure products, due to the instability of the Fp-dendritic benzyl bromide. Attempts to synthesize metal-containing polyurethanes using the same organometallic bifunctional monomers, produced largely insoluble materials that limited the extent of complete characterisation.

A second approach to preparing metal-containing polymers, based on the same condensation polymerisation principles, was used. In this case, a bifunctional organic monomer was polymerised first to yield a preformed organic polymer. In this manner, polyesters (with pendant vinyl groups) and polyimines (with α -diimine moieties along the backbone) were prepared. Hydrozirconation reactions with the polyesters were attempted and were unsuccessful. The desired metal-containing polymers were not isolated. This is due to interaction of Schwarz's reagent with the ester functionality, which hindered isolation of the desired products. Reaction of the polyimines with $\text{PdCl}_2(\text{COD})$ yielded largely insoluble, intractable palladium-containing oligomeric polyimines that limited the extent of characterisation.

A number of new poly(propyleneimine) iminopyridyl metallodendrimers were prepared. These dendrimers were synthesized by first functionalising three generations of the commercially available DAB dendrimer with 2-pyridinecarboxaldehyde. This yielded poly(propyleneimine) dendrimers with iminopyridyl moieties located on the periphery.

These dendrimers were isolated as orange oils and tended to include solvent within the structure, even after extensive drying. Complexation reactions using either PdCl₂(COD), PtCl₂(COD) or CuCl₂ produced the corresponding metallodendrimers with MCl₂ (M = Pd, Pt, Cu) units on the periphery. The metallodendrimers showed poor solubility, and were characterised by infrared spectroscopy, ¹H NMR spectroscopy and microanalysis.

Functionalisation of commercial samples of the DAB dendrimer with salicylaldehyde produced three generations of poly(propyleneimine) salicylaldimine ligands, having 4, 8 or 12 units on the periphery. The first generation ligand was reacted with various metal acetates of the general formula, M(OAc)₂.xH₂O (M = Ni, Cu) and with FeCl₂.4H₂O, to produce new metal-containing salicylaldiminato dendrimers. The iron complex was insoluble, limiting characterisation to IR spectroscopy and microanalysis. Paramagnetic ¹H NMR, infrared spectroscopy, and UV-Vis studies of the Ni(II) and Cu(II) complexes provide some information to the formation of the corresponding complexes.

The final section of this work describes several catalytic reactions. Ethylene polymerisation studies using the poly(propyleneimine) iminopyridyl metallodendrimers were attempted. These compounds were activated using MAO as co-catalyst, and produced linear, high molecular weight polyethylene. The first generation palladium dendrimer showed higher activity than its analogous mononuclear complex. The second generation palladium dendrimer showed lower activity than the first generation. Catalyst activity as a function of the metal also decreased in the order Pd > Pt > Cu.

The first generation palladium dendrimer also proved to be a highly effective cross-coupling catalyst, between iodobenzene and using either methyl acrylate (electron-deficient), styrene or 1-octene (electron-donating) as olefins. The dendritic complex showed a marked increase in activity over mononuclear palladium complexes, which tend to agglomerate in solution. The reactions were regiospecific for electron-deficient olefins like methyl acrylate, yielding the β-arylated product. However, poor selectivity was observed for more electron-donating olefins, such as 1-octene, giving a mixture of arylated products and isomers.