The Application Of Novel Multinuclear Catalysts Derived From Dendrimeric Ligands In The Polymerization And Oligomerization Of Unsaturated Hydrocarbons.

By

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Master of Science in the Department of Chemistry, University of the
Western Cape, South Africa.

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Declaration

I, **Rehana Malgas,** declare that **THE APPLICATION OF NOVEL MULTINUCLEAR CATALYSTS DERIVED FROM DENDRIMERIC LIGANDS IN THE POLYMERIZATION AND OLIGOMERIZATION OF UNSATURATED HYDROCARBONS** is my own work and that all sources I have used or quoted have been acknowledged by means of complete references.

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Rehana Malgas

………………………..

Date

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Abstract

G1 and G2 dendrimeric salicylaldimine ligands containing both substituted and unsubstituted aryl rings were synthesized via a Schiff base condensation of the appropriate salicylaldehyde and the peripheral amino groups of the corresponding G1 and G2 polypropyleneimine dendrimers. The new ligands were characterized using FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy, elemental analysis and ESI mass spectrometry. The dendrimeric ligands were converted to multinuclear nickel complexes by reaction with nickelacetate. The metal complexes were characterized by FTIR spectroscopy, elemental analysis and ESI mass spectrometry.

Some of the dendritic complexes were evaluated as catalyst precursors in the oligomerization of α-olefins such as ethylene and 1-pentene, using aluminium alkyls such as $EtAlCl_2$ and modified methylaluminoxane (MMAO) as activators. All the dendrimeric catalysts evaluated are active in the oligomerization reactions. From the oligomerization results it was observed that there is a clear dendritic effect, in that both catalyst activity as well as selectivity are impacted by the dendrimer generation. In most cases it was observed that the second generation complexes show higher activity than the corresponding first generation complexes.

The dendrimeric complexes were also evaluated as catalyst precursors in the vinyl polymerization of norbornene. In this case methylaluminoxane (MAO) were employed as an activator. Once again it was noted that a dendritic effect is operative, with second generation metallodendrimers having a higher activity than the first generation complexes.

Conference Contributions

The following conference presentations based on various aspects of the work covered in this thesis have been made over the past two years.

1 Poster titled, "Catalyst precursors based on periphery modified dendrimeric ligands", S. F. Mapolie, G. S. Smith, S. Ray, S. Ojwach, J. L. van Wyk, R. Malgas, presented at SACI INORG 2005 conference, Kwazulu-Natal, South Africa, April 2005.

2 Poster titled, "Salicylaldimine functionalized dendrimers as synthons for catalytic complexes", S. F. Mapolie, G. S. Smith, S. Ray, S. Ojwach, J. L. van Wyk, R. Malgas, presented at the XVI FECHEM conference on Organometallic chemistry, Budapest, Hungary, September 2005.

3 Poster titled, "Multinuclear nickel complexes as catalyst precursors for the vinyl polymerization of norbornene", R. Malgas, S. F. Mapolie, presented at the Cape Organometallic Symposium (COS), Cape Town, South Africa, October 2005.

4 Poster titled, "Multinuclear nickel catalysts derived from dendrimeric ligands as catalyst precursors for the oligomerization of ethylene", R. Malgas, S. F. Mapolie, presented at the CATSA 2005 conference, Johannesburg, South Africa, November 2005.

5 Oral presentation titled, "Metallodendrimers as mediating agents in organic transformations", S. F. Mapolie, G. S. Smith, R. Malgas, J. Mugo, J. Sibanyoni,

presented at the CATSA 2005 conference, Johannesburg, South Africa, November 2005.

6 Poster titled, "Norbornene and phenylacetylene polymerizations mediated by metallodendrimers", S. F. Mapolie, R. Malgas, J. Mugo, N. Mungwe, presented at the International Conference on Organometallic Chemistry, Zaragoza, Spain, July 2006.

7 Oral presentation titled, "Multinuclear nickel catalysts derived from dendrimeric ligands as catalyst precursors for the oligomerization of ethylene", R. Malgas, S. F. Mapolie, presented at the OATA 2006 conference, Cape Town, South Africa, August 2006.

8 Poster titled, "Multinuclear nickel catalysts derived from dendrimeric ligands as catalyst precursors for the oligomerization of ethylene", R. Malgas, S. F. Mapolie, presented at the 15th International Symposium on Homogeneous Catalysis (ISHC), Sun City, South Africa, August 2006.

9 Oral presentation titled, "Salicylaldimine metallodendrimers as ethylene oligomerization catalysts", R. Malgas, S. F. Mapolie, presented at the Science Faculty Research Open Day, University of the Western Cape, Cape Town, South Africa, November 2006.

10 Oral presentation titled, "Salicylaldimine metallodendrimers as ethylene oligomerization catalysts", R. Malgas, S. F. Mapolie, presented at CATSA 2006, Mosselbay, South Africa, November 2006.

11 Poster titled, “Dendrimers! Norbornene polymerization mediated by multinuclear nickel catalysts”, R. Malgas, S. F. Mapolie, presented at the 9th Annual UNESCO/IUPAC Conference on Macromolecules: Polymers for Advanced Applications, Stellenbosch, Cape Town, South Africa, November 2006.

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Chapter 1

Literature Review:
Olefins and Ethylene Oligomerization Catalysts

1.1 Introduction:

The industrial importance of olefins such as ethylene, butene, pentene and hexene, are briefly discussed in this review. In addition the production of some α-olefins via the process of ethylene oligomerization is also reviewed. The emphasis is based on the most common reported transition metal complexes that are used as catalysts for the oligomerization of ethylene in particular.

1.1.1 The origin of α –olefins and its uses in industry:

Olefins, particularly ethylene, propylene and butenes, are some of the more important basic building blocks of the petrochemical industry.[1] Some of the advantages of these types of compounds are that they are reactive, inexpensive, easily available and readily transformed into a range of useful products. α-Olefins with a carbon number of 4 and higher are of increasing importance since they are the feedstocks for the production of polymers, detergents, lubricants, plasticizers and other useful chemical products.[2]

The most commonly used processes for obtaining α-olefins is the oligomerization of ethylene, and thermal and catalytic cracking of paraffins. Other processes include the dimerization and metathesis of olefins, dehydration of alcohols, dehydrogenation of paraffins and electrolysis of straight chain carboxylic acids. Olefins can be divided into two groups; even carbon number olefins, and uneven carbon number olefins. Short descriptions of each group of olefins are given below.

1.1.1.a. α- Olefins with an even carbon number.

i) Ethylene:

The oligomerization of ethylene is currently the primary source of even carbon number high purity α – olefins. The Shell Higher Olefins Process [SHOP] is the most common ethylene oligomerization process. The four largest producers of linear alpha olefins (LAO's) are SHELL, BP-Amoco, Chevron-Phillips and SASOL.

There is a huge demand for LAO's and the technology to produce it. In response to this demand, the petrochemical company, UOP, has developed a low cost linear-1 process. It is a more economical process for the production of LAO's than other technologies because of the better catalyst utilization and the fact that it is a simpler process.[3] The linear – 1 process is also flexible in varying the C_4-C_8 product yield from 45% - 70% by making simple adjustments to the operating parameters. The highly active catalyst system can be optimized to favour the production of C_4 –C_{10} LAO's.

A general catalytic cycle for the oligomerization of ethylene is shown below in Figure 1.

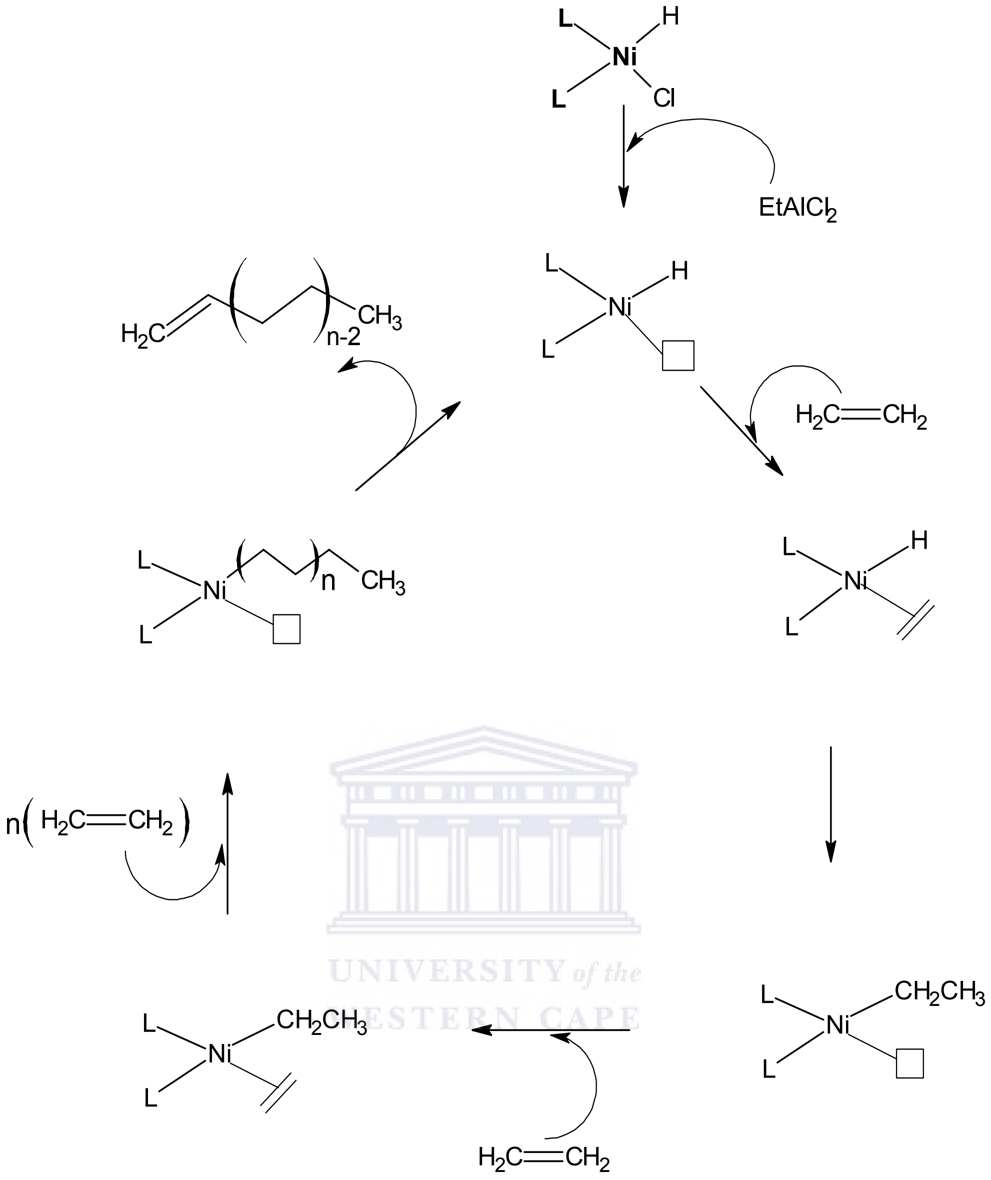


Figure 1.1: General catalytic cycle of ethylene oligomerization.

In Table 1.1, an indication of some of the applications for α-olefins, C_4 to C_{16} is given.

Table 1.1: Industrial use of α-olefins.

α-olefin Fraction	**Application**
C_4	Polyolefin co monomer – low linear density polyethylene [LLDPE], poly-butene-1.
C_6	Polyolefin co monomer[LLDPE], plasticizer alcohol
C_8	Polyolefin co monomer [LLDPE], plasticizer alcohol.
C_{10}	Synthetic lubricants, plasticizer alcohol.
C_{12},C_{14}	Linear alkyl benzene, detergent alcohol.
C_{16}	Alpha olefin sulfonate, detergent additives, oilfield surfactants, alkenyl succinic anhydrides [ASA], wax lubricants.

ii) Butene:

The industrial synthesis of 1-butene is presently achieved using nickel or titanium catalysts[4] via the oligomerization of ethylene. Very few catalytic systems are able to produce selectively 1-butene from ethylene; hence the development of selective catalysts is of great interest.

In general, 1-butene oligomerization differs from that of ethylene oligomerization. Higher alkenes are more reactive over acidic catalysts, while ethylene is readily oligomerized even at low temperatures.[5]

iii) Hexene:

1-Hexene is commonly manufactured by two main processes, the trimerization of ethylene and by the Fischer–Tropsch synthesis followed by purification. 1-Hexene is most commonly used as a co-monomer in the production of linear low density polyethylene. Another use of 1-hexene is for the production of linear aldehydes. 1-Hexene oligomerizes to give dimers, trimers and tetramers in most cases.[6]

1.1.1.b. α-Olefins with an uneven carbon number.

The Fischer-Tropsch process produces α-olefins with an uneven carbon number, such as pentene, heptene and nonene. The production of these α-olefins with odd carbon numbers is unique to South Africa, obtained from the Fischer-Tropch process as operated by SASOL. As a result of high world oil prices and international sanctions during the 1970's, the Fischer–Tropsch technology became increasingly important to South Africa.[7] The decline in world oil prices during the 1980's motivated SASOL to focus on the increased production of chemicals from the Fischer –Tropsch process, as these chemicals could be sold for much higher prices.

The shorter chain olefins such as pentene, heptene and nonene are produced on a large scale by SASOL. Oligomerization of these olefins to longer chain olefins could result in value-added chemicals and be much more profitable to the petrochemical industry in South Africa. Wahner *et al*. studied the oligomerization of 1-pentene using zirconium complexes in the presence of MAO. Products ranging from the dimers of 1–pentene to polymers with Mw =149000 g/mol were formed.[8] The catalysts were active but not very selective. Casagrande *et al*. reported the use of aluminum pillared montmorillonite (APM) and aluminum pillared saponite (APS) as catalysts for the oligomerization of 1-pentene. Both APM and APS were found to be good catalysts. The APM catalyst has a good selectivity to the desired diesel range but its structure was not as stable as the APS catalyst. However the APS catalyst is not as selective as the APM catalyst.[9]

Christoffers and Bergman catalytically dimerized 1-heptene to 2-pentyl-1-nonene with their zirconium metallocene complex without the formation of any higher oligomeric species.[10]

1.1.2. Transition Metal Catalysts for the Oligomerization of Ethylene:

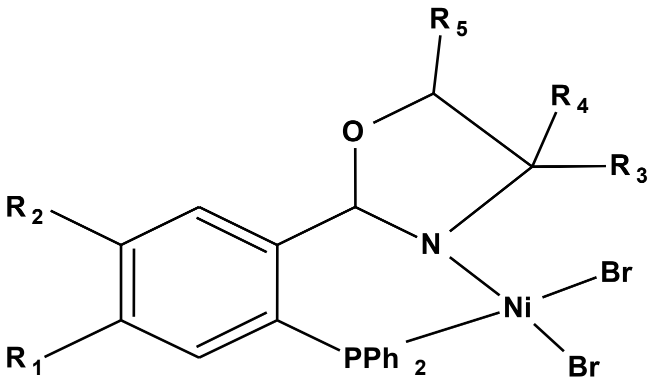
For the past few decades catalytic oligomerization of ethylene has been mainly focused on complexes of nickel, chromium, zirconium and titanium. Group 4 metallocene complexes and related catalyst systems, such as half- sandwich titanium complexes, have also been extensively studied for the oligomerization of ethylene.[11] The development of more efficient and selective catalysts for oligomerization of alkenes by late transition metals is currently of interest.

1.1.2.a. *Nickel:*

In recent years nickel complexes have attracted increasing interest as effective catalysts for short chain olefin polymerization, including ethylene oligomerization. Catalysts for ethylene oligomerization currently used in industry, include neutral Ni(II) complexes bearing bidentate monoanonic ligands.[12] These complexes are the basis of the Shell Higher Olefins Process (SHOP). Ethylene polymerization catalyzed by Ni(II) complexes incorporating α-diimine ligands have been reported by Brookhart *et al.*[13] High activity Ni catalysts that selectively produce oligomers have been obtained by the tailoring of the surrounding ligands. However very few catalytic systems are able to produce selectively 1-butene from ethylene, despite intense research efforts. Developing new ligands in order to obtain selective nickel catalysts is of great interest.[14]

A variety of nickel complexes with P,O (analogous to the Ni precursors used in the SHOP process); P,N; S,S or O,O chelating ligands have been widely studied, predominantly affording linear alpha-olefins with different selectivities in relation to the chain length of the oligomers. Some of these complexes are described below.

Tang[15] *et al*. investigated a series of bidentate Ni(II) complexes bearing phosphino oxazoline ligands. These were fully characterized to reveal a distorted tetrahedral coordination geometry around the nickel center. The complexes are shown in Figure 1.2.



1 R_1=R_2=R_3=R_4=H, R_5=CH_3

2 R_1=R_2=R_3=R_5=H, R_4=C_2H_5

3 R_1 =R_2=R_5=H, R_3=R_5=H

4 R_1 =R_3=R_4= CH_3, R_2=R_5=H

5 R_1 =R_5=H, R_2=OCH_3, R_3=R_4=CH_3

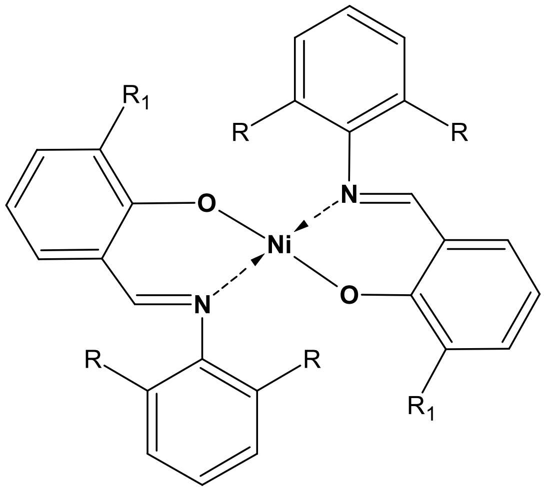
6 R_1=R_2=R_3=R_5=H, R_4=Ph

Figure 1.2: General structure of nickel complex bearing phosphino oxazoline ligand.[15]

These complexes were found to catalyze ethylene oligomerization, with activities up to 1.18 x 10^6 g/mol Ni.h^{-1}, with dimers and trimers being the major products. The ethylene oligomerization activity was found to be affected by the substituents on the ligand framework. Incorporation of sterically bulky and electron donating groups on the carbon atom neighboring the coordinating nitrogen of the oxaline ring led to a decrease in catalytic activity for ethylene oligomerization.

De Sousa[16] *et al*. have described new nickel catalytic systems using 2-pyridylphosphole ligands for the dimerization of ethylene. These catalytic systems are highly efficient and can be associated with high catalytic activities under mild reaction conditions with unusually high selectivities to 1-butene. Ni (2-pyridyl) phosphole complexes are among the very rare catalytic systems selectively affording 1-butene from ethylene. These results hold very promising future prospects since further variations of the ligand structures are possible.

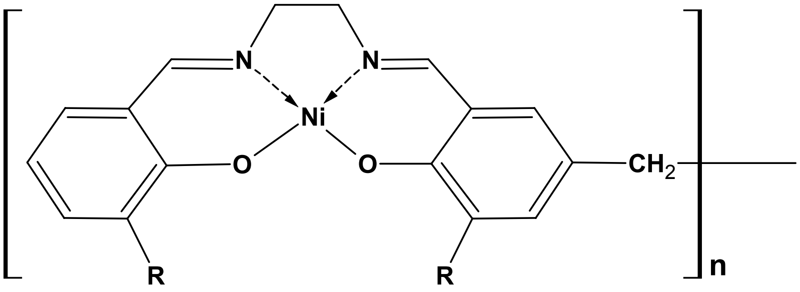
Kim[17] *et al*. reported various phenoxy-imine Ni (II) complexes modulating their structural characteristics by changing the nature of the substituents on the imino and aromatic moieties. These complexes have been investigated as catalyst precursors for the oligomerization of ethylene using various co-catalysts, under different reaction conditions. Indirect evidence of the formation of active species in the presence of ethyl aluminium sulphate (EAS) as a co-catalyst could be obtained using UV-VIS spectroscopy. All Ni complexes in this study exhibited high activities under moderate conditions. The catalytic activity, however, is largely independent of the catalyst structure. An example of these complexes is shown below in Figure 1.3.



Cat	R	R_1
7	Me	H
8	Et	H
9	iPr	H
10	Me	tBu
11	Et	tBu
12	iPr	tBu

Figure 1.3: Phenoxy imine nickel(II) catalysts.[17]

Wu[18] *et al*. investigated the use of poly-salen type Ni (II) complexes as catalysts for the oligomerization of propylene, in the presence of aluminium co-catalysts. They found that when the catalyst, containing a bulky tert-butyl group on the phenolic ring, was used as a precursor, a marked increase in catalytic activity was observed in comparison to those catalysts with a less bulky substituent on the phenolic ring. The selectivity of the catalytic process seemed essentially unaffected with tuning the nature of the poly-salen ligands in the precursors.[18] The general structure of the complexes synthesized by Wu are shown in Figure 1.4.



13 R=H

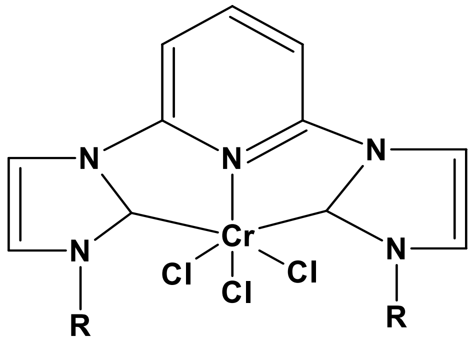
14 R=^{t}Bu

Figure 1.4: Poly-salen type Ni (II) complexes.[18]

1.1.2.b. *Chromium:*

Chromium is one of the most utilized transition metals that catalyze the oligomerization of olefins. Two classes of chromium-based catalysts are used commercially, viz the Phillips catalyst, which is composed of a chromium oxide on an inorganic carrier silica (SiO_2), and the Union Carbide catalyst, which is formed by treatment of silica with low valent organometallic compounds, such as chromocene.[19] The development of non-metallocene chromium catalysts is of increasing interest since these types of complexes may have a higher selectivity towards polymer products.

McGuinness *et al*. described a new class of exceptionally active Cr(III) catalysts for the production of α-olefins. These complexes (shown in Figure 1.5 below) are based on tridentate ligands containing heterocyclic carbene donors. While the rapid development of catalysts based on heterocyclic carbene ligands has been ongoing for over a decade, this report represents the first time that this ligand class has been employed to produce highly active catalysts for olefin oligomerization or polymerization. [20]



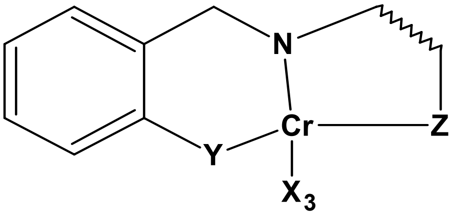
15 R = iPr

16 R=2,6-i-$Pr_2C_6H_3$

17 R=1-adamantyl

Figure 1.5: Cr(III) complexes based on tridentate ligands.[20]

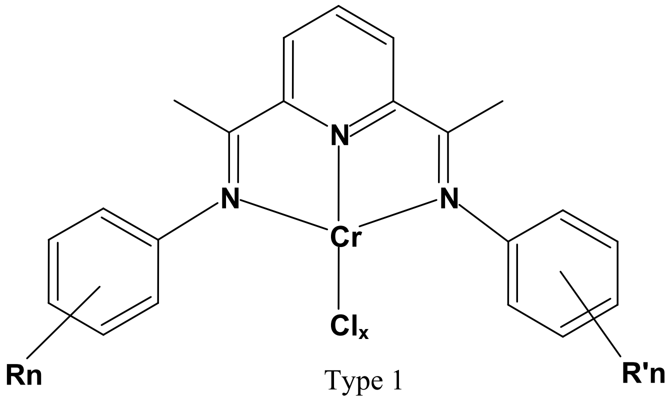
Bluhm *et al*. reported on Cr (III) complexes of tridentate imine and amine ligands with N, P, O and S donor atoms. These complexes were tested as catalysts for the oligomerization and the polymerization of ethylene. The results showed excellent selectivity towards 1-hexene (for the imine complexes) and polymerization to polyethylene (for the amine complexes) when activated with co-catalysts such as MAO, $EtAlCl_2$ and Et_2AlCl.[21] The structure of the amine complex is shown in Figure 1.6.



18 Y=Z=PPh_3, X=Cl

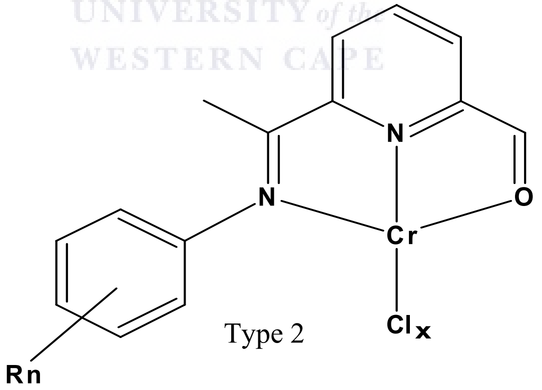
Figure 1.6: Tridentate amine Cr(III) complexes.[21]

Correlations between chromium oxidation state and catalyst productivity are vague. Theopold and Carney reported neutral chromium catalysts that exhibited relatively low activities for polymerization.[22] However, potentially cationic chromium complexes were only marginally more active catalysts. Chromium complexes bearing tridentate pyridine-based ligands, were reported by Small *et al.*[23] These complexes were derived from two types of ligands, type 1 with an N,N,N coordination and type 2 with an N,N,O coordination. Below in Figure 7 is an example of the chromium complexes synthesized by Small.



Type 1

Complex	**Rn**	**R'n**
19	unsub	unsub
20	2-Me	2-Me
21	2-Et	2-Et
22	2-^{i}Pr	2-^{i}Pr
23	2-^{t}Bu	2-^{t}Bu
24	2,6-Me$_2$	2,6-Me$_2$
25	2,5-^{t}Bu	2,5-^{t}Bu



Type 2

X=2,3

Complex	**Rn**
26	2,6-Me$_2$
27	2,6-^{i}Pr
28	2-^{t}Bu

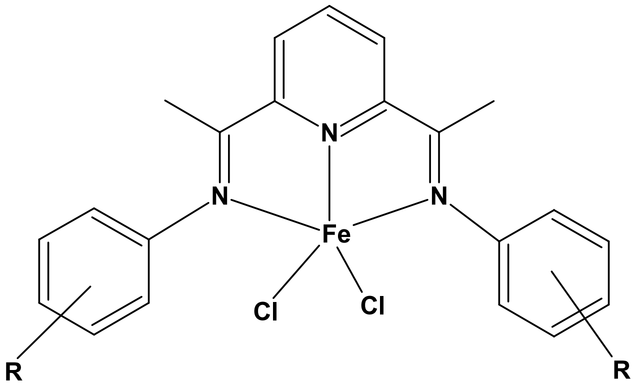
Figure 1.7: Type 1 and type 2 tridentate pyridine-based Cr(III) complexes.[23]

These complexes show high catalytic activity for ethylene oligomerization. From the results it was deduced that Type 1 (N,N,N) catalysts generally produce 1-butene with 99.5% purity, when only two ortho alkyl substituents are present on the aryl rings. However, when size and number of substituents increase, waxes or polyethylene are produced. In the case of the Type 2 (N,N,O) catalysts, only waxes and polyethylene are produced.

1.1.2.c. *Iron*:

A new family of catalysts based on iron complexes containing pyridine bis-imine ligands was discovered independently by Brookhart and Gibson in 1998.[24-27] These complexes are effective catalysts for the oligomerization of ethylene, when activated with methylaluminoxane (MAO), and it also showed high selectivity (~95%) for linear α-olefins. The size and regiochemistry of the substituents on the aryl groups have a controlling effect on the oligomerization of ethylene. A wide range of olefins are obtained when the ortho-substituents on aryl rings are alkyls.

Bluhm *et al*. synthesized iron-based bis(imino)pyridine and acetylimino pyridine complexes as single site catalysts for the oligomerization of ethylene.[28] They investigated the influence of electron donating methoxy- and electron withdrawing trifluoromethyl groups attached to the iminophenyl substituents. The structures of the catalysts are shown below in Figures 1.8 and 1.9.



Complex	R
29	H
30	m-OMe
31	p-OMe
32	m-CF_3
33	p-CF_3

Figure 1.8: Iron-based bis(imino)pyridine complexes.[28]

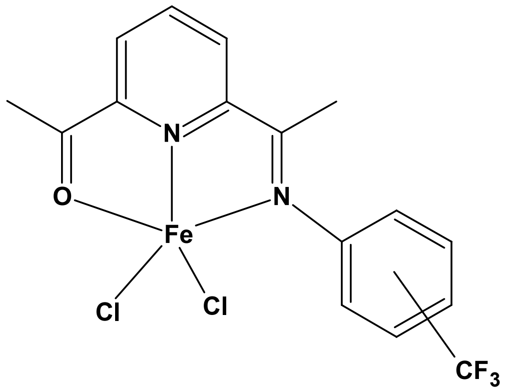


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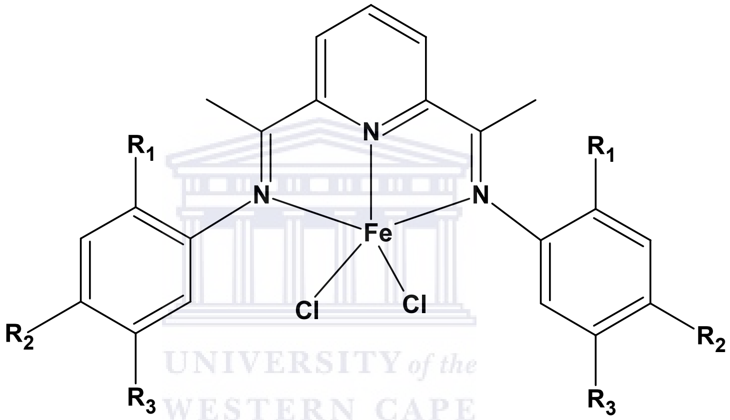
Figure 1.9: Iron-based acetylimino pyridine complex.[28]

The substituted catalysts were found to be active in the presence of MAO as a co-catalyst for the oligomerization of ethylene. The unsubstituted catalyst exhibited good activity but the selectivity to one type of product was poor. The bis(imino)pyridine catalysts produced mostly hexenes and the acetylimino pyridyl catalysts produced mostly butenes.

Zhang *et al.* reported bis (imino) pyridyl iron complexes bearing halogen and alkyl substituents. These complexes (shown below in Figure 1.10) were used as catalysts for ethylene oligomerization. It was found that the complexes exhibit a high catalytic activity. The percent of low molar mass products decreases with an increase of the steric bulk at the ortho-position. The increase in temperature resulted in a decrease in activities and an increase in the yield of low molar weight products.[29]

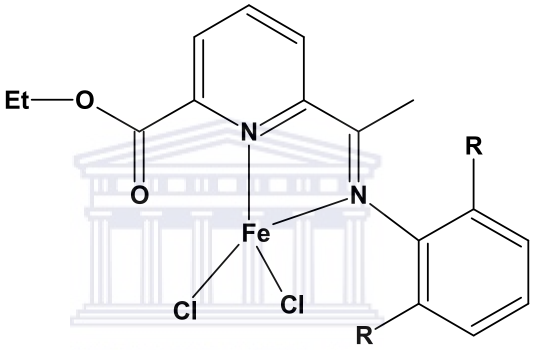


Complex	**R_1**	**R_2**	**R_3**
35	F	CH_3	H
36	Cl	CH_3	H
37	Br	CH_3	H
38	F	H	CH_3
39	Cl	H	CH_3
40	Cl	H	H
41	Cl	F	H
42	F	F	H

Figure 1.10: Bis (imino) pyridyl iron complexes bearing halogen and alkyl substituents.[29]

Since the discovery of the highly active iron catalysts several ferrous based 2, 6 bis(imino) pyridyl complexes, with varying substituents on the aryl rings of the ligand have been investigated. These complexes, however, show poor activity for ethylene oligomerization.

Sun *et al.* reported the synthesis of 2-(carboxylato)-6-iminopyridine-based ferrous complexes. The complexes were studied for their catalytic activities in ethylene oligomerization. Complexes showed considerable activity with butenes, hexenes and a small amount of higher oligomers being obtained.[30] The complexes are shown in Figure 1.11 below.



Complex	R
43	Me
44	Et
45	i-Pr
46	F
47	Cl
48	Br

Figure 1.11: 2-(Carboxylato)-6-iminopyridine-based ferrous complexes.[30]

Mingxing *et al*. reported a series of iron (II) diimine complexes for ethylene oligomerization. All the complexes displayed high activity. It was found that the iron complex with diimine containing iron-halogen bonds and a large π-conjugated system, is favourable for ethylene oligomerization reactions.[31]

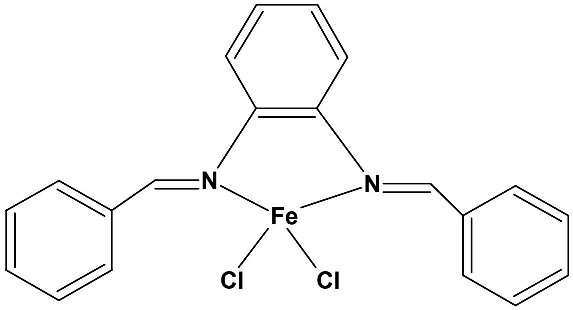


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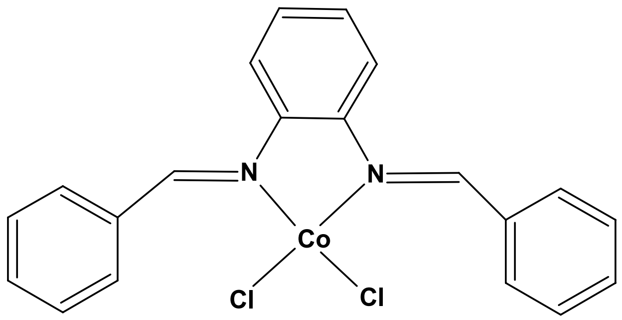
Figure 1.12: Iron (II) diimine complexes.[31]

1.1.2.d. *Cobalt:*

Along with the results of the bis (imino) pyridyl iron complexes, Brookhart and Gibson also reported on the ethylene oligomerization activity of the cobalt analogues of these complexes. Similar types of products were obtained, although the iron complexes exhibited a slightly higher activity than the cobalt complexes.

Qian *et al*. reported on the catalytic properties of a series of Co (II) diimine complexes in combination with ethylaluminoxane (EAO). They found that these cobalt complexes (shown below in Figure 13) display moderate activities for ethylene oligomerization and high selectivity to low carbon olefins. The activities of the catalysts greatly depend on the reaction temperature and A1/Co ratios. At temperatures above 200 ^{0}C, the cobalt (II) diimine complexes display higher catalytic activities and selectivities than their iron (II) diimine analogues, but below 170 ^{0} C, the iron complexes have displayed a higher activity.[32]



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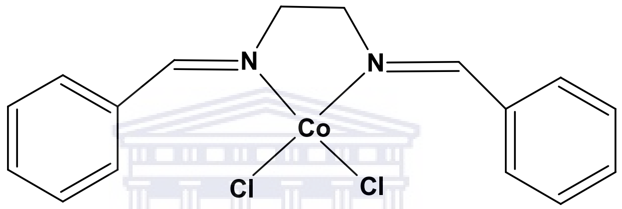

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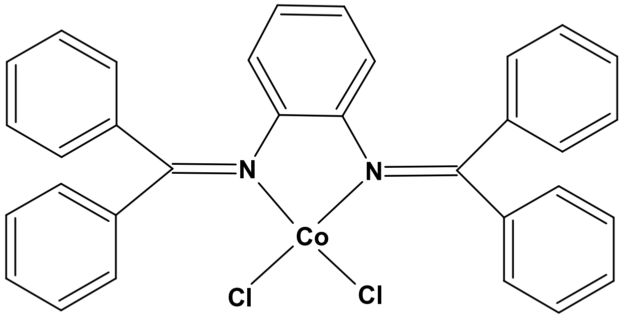


52

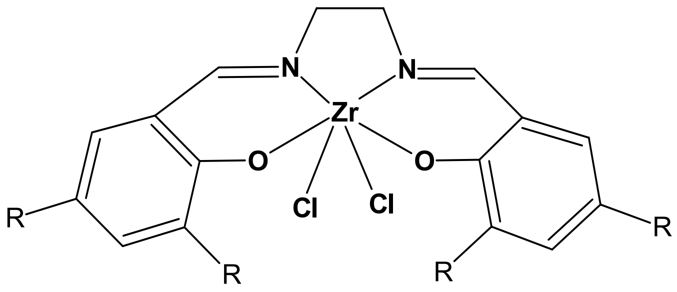
Figure 1.13: Cobalt diimine complexes.[32]

The effect of substituents on the aryl rings of the ligands on ethylene polymerization using Co(II) pyridyl bis-imine catalysts, was investigated by Kim *et al*. In the presence of MAO the complexes exhibit high activities for ethylene polymerization and oligomerization. These cobalt catalysts yielded predominantly 1-butene. It was concluded that the selectivity to yield a specific α-olefin and high molecular weight polyethylene might be tuned by controlling steric bulk around the metal center, metal type and polymerization parameters. [33]

Tellman *et al.* reported the oligomerization of ethylene by cobalt bis(imino) pyridine complexes stabilized by trifluoromethyl substituents. High productivities have been achieved in ethylene oligomerization reactions using these complexes as catalysts. The fluorinated catalysts show greater activities than their non-fluorinated relatives. This suggests that the trifluoromethyl group not only increases the electrophilicity of the metal centers, but also significantly improves catalyst stability. In some cases, the activities of the cobalt complexes surpassed that of the most active iron complexes. [34]

1.1.2.e. *Zirconium:*

Zirconium complexes containing N,O chelating ligands, bi- or tridentate, have been found to be high activity catalysts for polymerization of ethylene, propylene and 1-hexene. Understanding the effects of the electronic and steric properties and the coordination geometry of N,O ligands on ethylene oligomerization is of high interest. The catalytic properties of salen type zirconium complexes are very limited in ethylene oligomerization. Wang *et al.* reported on salen type zirconium complexes that gave rise to efficient catalyst systems for the oligomerization of ethylene to low carbon number linear α-olefins. [35] An example of this type of complexes is shown below in Figure 1.14.



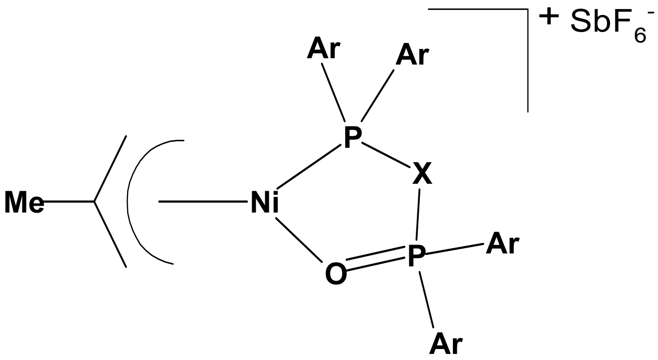
Complex	**R**
53	H
54	^{t}Bu

Figure 1.14: Zirconium Salen type complexes.[35]

They further investigated the influence of substituents on ancillary ligands on the catalytic activity and selectivity in ethylene oligomerization. It was concluded that electron releasing substituents benefit the catalyst system with a cationic transition metal center in an active species, and electron withdrawing groups destabilize the active cationic species resulting in the decrease in catalytic activity.[36]

1.1.2.f. *Palladium:*

Palladium complexes containing phosphino ligands exhibit outstanding catalytic activity in a large number of organic reactions. Brassat *et al.* reported on palladium (II) complexes with bi(phosphine) monoxide ligands. The palladium complexes exhibit moderate activity towards the oligomerization of ethylene. The major products obtained were butenes, as well as a small amount of decenes and dodecenes. The cationic methyl Pd complexes were more active than their allyl analogues.[37] These complexes are shown below in Figure 1.15.

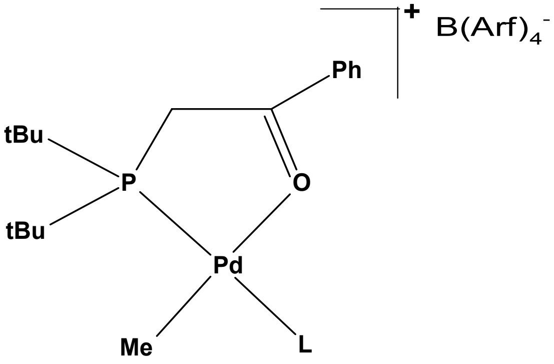


55 X = o-C_6H_4

56 X = NH

Figure 1.15: Palladium (II) complexes with bi phosphine monoxide ligands.[37]

Malinoski *et al*. reported on palladium (II) complexes containing bidentate phenacyldialkylphosphine ligands for the oligomerization of ethylene. Cationic palladium methyl acetonitrile complexes showed modest activity for oligomerization of ethylene to butenes and hexenes. These complexes however, displayed short catalyst lifetimes.[38] The structure of these complexes are shown below in Figure 1.16.



Arf = 3,5 – $(CF_3)_2C_6H_3$

57 L = NCMe

58 L = OEt_2

59 L = C_2H_4

Figure 1.16: Palladium (II) complexes containing bidentate phenacyldiarylphosphine ligands.[38]

1.2 Project Objectives:

The aim of this project is to synthesize dendrimeric Schiff base ligands. The ligand systems are based on dendritic poly (propylene imine) scaffolds and will be obtained via Schiff base condensation with the appropriate aldehydes. These ligands will be complexed to salts of nickel. The ligands and complexes will be fully characterized by using Fourier Transfer Infrared spectroscopy (FTIR), Nuclear Magnetic Resonance spectroscopy (NMR), Mass spectrometry and Elemental Analysis. The new complexes will be catalytically evaluated in the oligomerization of α-olefins such as ethylene and pentene as well as in the polymerization of cyclic alkenes such as norbornene. The efficacy of the different generation catalysts will be compared to each other, to determine whether a dendritic effect exists. Also the effect of substituents on the activity of the complexes will be investigated. Reaction conditions will be optimized in order to obtain highest activity and selectivity.

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Chapter 2

The synthesis of novel nickel complexes derived from dendrimeric salicylaldimine ligands.

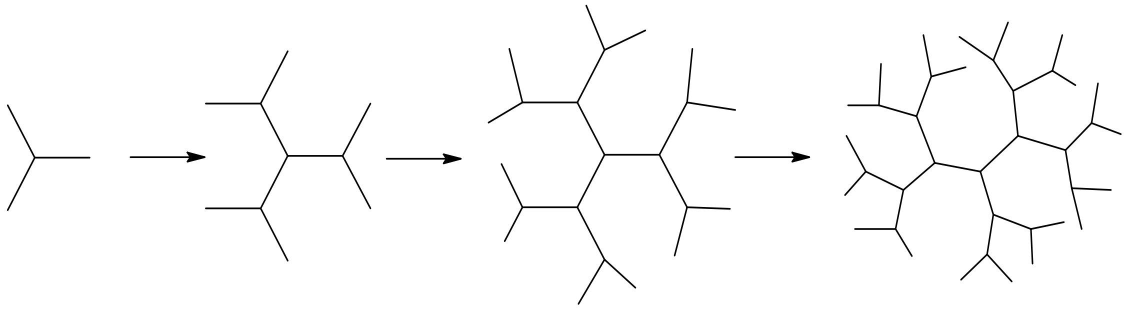
2.1 Introduction:

In this chapter we discuss the synthesis and characterization of dendrimeric salicylaldimine ligand systems, as well as the complexation of these ligands to salts of Ni. A brief overview of these types of ligands is also given below.

2.1.1 Dendrimers:

Dendrimers are a class of three-dimensional macromolecules characterized by a central core and expanding to a periphery that becomes denser with increasing generation number. These molecules have a highly branched structure with a number of end groups. Dendimers are also known as arborols, cascade molecules or starburst polymers. Tamalia *et al*. produced dendritic polymers for the first time during the eighties.[1]

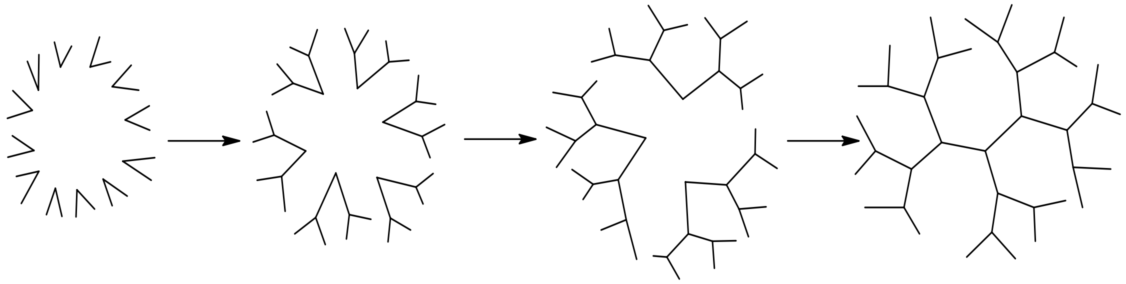
There are two general strategies for synthesizing dendrimers, the divergent approach and the convergent approach. The divergent approach involves growth from a poly functional initiator core, where branching outward is accomplished by an increasing number of terminal branches. The disadvantage of divergent growth is the fact that a large number of monomers have to react successfully with the reactive functional groups of the dendrimer surface. Thus, the higher the generation, the more difficult it becomes to ensure the reaction of all the external functionalities of the dendrimer. [2]



Scheme 2.1

Scheme 2.1 shows the divergent approach to dendrimer synthesis. The Dutch polymer company, DSM,[3] uses the divergent synthetic route on an industrial scale, to produce its ASTRAMOL polypropylene imine dendrimers.

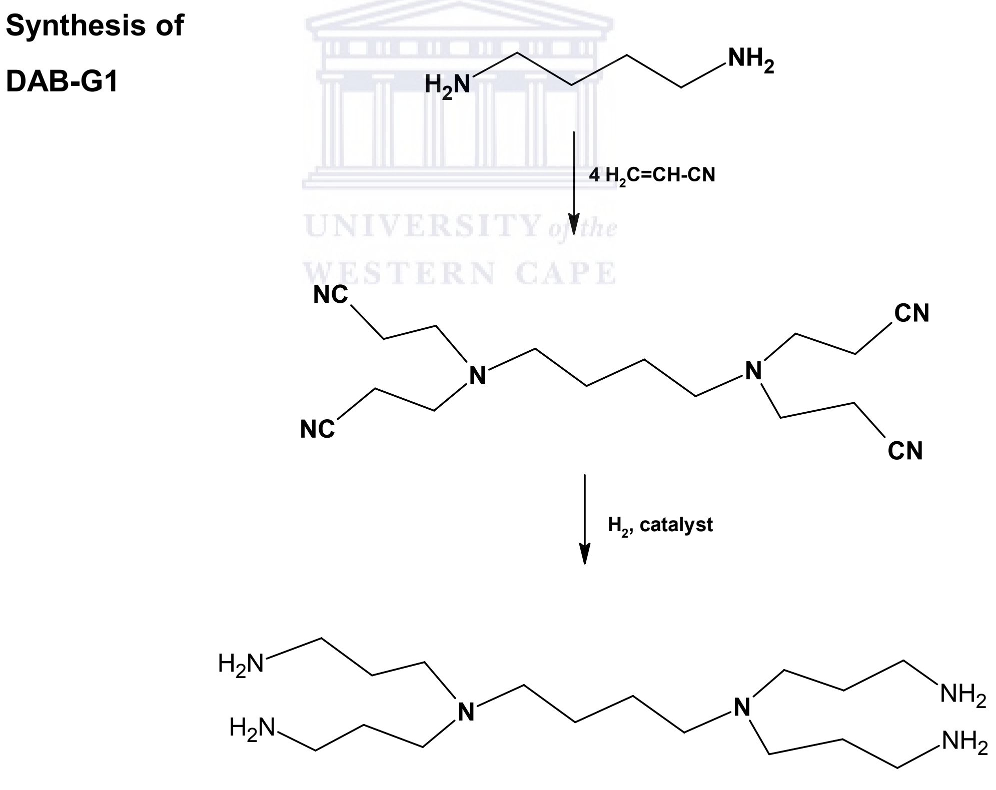
In the convergent approach, complete wedges (dendrons) are prepared first. These are subsequently coupled to the central core. An advantage of the convergent route is the greater control over the separation and purification of the intermediate products.



Scheme 2.2

Scheme 2.2 shows the convergent approach to synthesizing dendrimers. The convergent pathway is more appropriate for laboratory-scale production of tailor-made products. Another advantage of the convergent route, is that by coupling wedges of a different nature to the same core molecule, segment-block or layer-block dendritic molecules can be constructed.[4]

There's a variety of dendrimers based on silicon, nitrogen and phosphorus skeletons. The divergent route to silicon based dendrimers normally starts with tetra-allylsilane or tetra-methyl cyclotetrasiloxanes, four directional centres of branching, and involves repetitive hydrosilylation and alkenylation reactions. Nitrogen-based dendrimers often contains nitrogen as a branching point. An example is the DAB-dend-(NH_2)x dendrimer, which has 1,4 diaminobutane (DAB) as the dendritic core, with $(CH_2)_3$ spacer moieties and NH_2 terminal groups. The synthetic route to the DAB dendrimers is outlined in Scheme 2.3.



Scheme 2.3

Phosphorus based dendrimers has the core and subsequent branching points consisting of pentavalent phosphorus atoms. This type of dendrimer has been constructed divergently up to the 10th generation. The synthesis of these phosphorus-containing dendrimers, starts with $P(S)Cl_3$ reacted with the sodium salt of 4-hydroxybenzaldehyde to give a trialdehyde. Subsequent treatment with $H_2NNMeP(S)Cl_2$, affords the first generation dendrimer.

Dendrimers have been applied as catalysts and nanoscopic reaction vessels, micelle mimics, magnetic resonance imaging agents, immuno diagnostics, agents for delivering drugs into cells, chemical sensors, information processing materials, high performance polymers, adhesives and coatings.[5]

The most common dendrimers are the polypropylene imine dendrimers, the poly (amido amine) dendrimers and the poly (benzylether) dendrimers.

Dendrimers containing metal elements in the framework are known as metallodendrimers. Balzani[6] *et al.* and Newkome[7] *et al.* initiated the incorporation of metal ions to the framework of the dendrimers in the early 1990s.[8] The metals are introduced into the dendritic framework after construction of the dendrimer. The metals can be positioned at various points in the dendritic molecule at the terminal units, the branching centres or the core as shown in Figure 2.1.

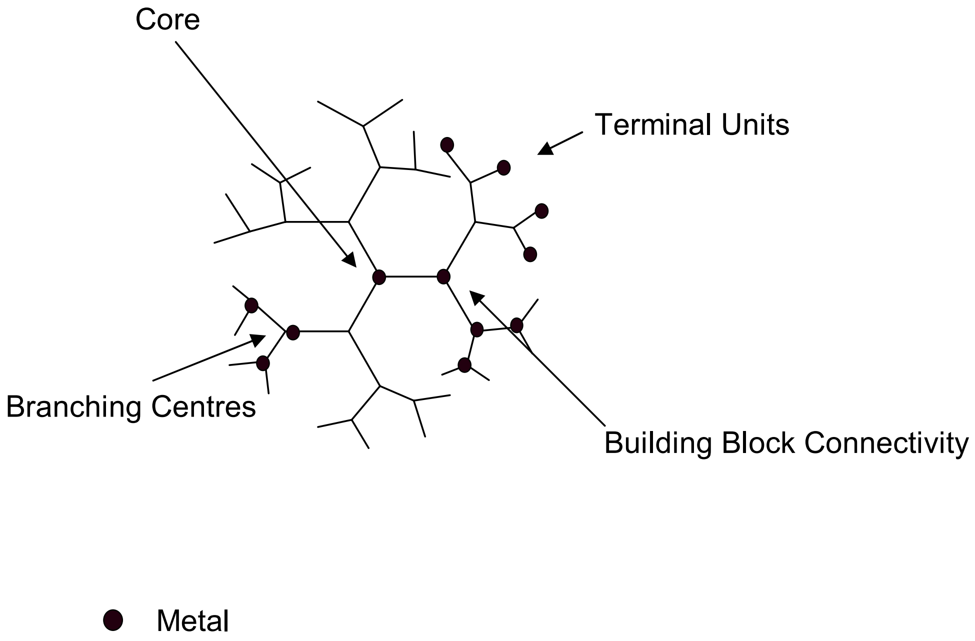


Figure 2.1: Potential positioning of metals within dendritic structures.

Because of its supramolecular structure, metallodendrimers possess physical, optical, electrochemical, photochemical, biological and catalytic properties which might be different to that of small molecules.

Not many examples of dendritic effects of catalyst properties have been reported in literature. Muller *et al.*[9] reported on Ni catalyst systems for the oligomerization of ethylene in which the catalyst, embedded within a dendrimer, was used as a design template. The activity of the core-functionalized dendritic catalyst was compared to the activity of its parent complex. The dendritic catalyst was found to be far more active than its parent complex.

Arevalo *et al.*[10] reported the use of titanium-containing carbosilane dendrimers, in which a phenoxy group was anchored to the dendritic skeleton, as catalysts for the polymerization of ethylene. When metallodendrimer precursors were used, polyethylene with high molecular weight and low polydispersity was produced. The dendritic nature of the catalyst also enforced a higher percentage of crystallinity in the polymer. They concluded that the electronic and steric effects induced by different organometallic units or phenolic ligands, have a big influence on the catalytic activity of these dendrimeric complexes.

The advantages of catalysts based on metallodendrimers are their ability to combine the best properties of homogeneous and heterogeneous catalysis in one system. Their stable structure and size makes them more suitable for recycling than soluble polymer supported catalysts. Dendrimer catalysts can be separated from the product via ultra-filtration.

2.1.2 Salicylaldimine ligands and complexes:

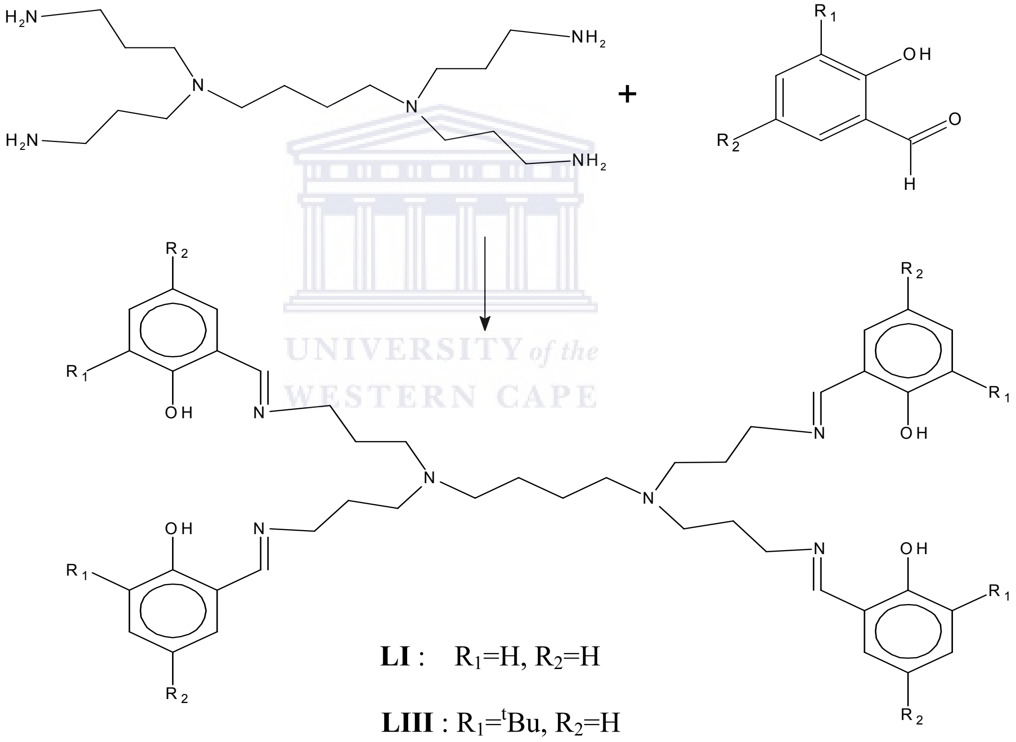
Salicylaldimine ligands is a type of ligand which can be regarded as an N,O chelating system. These types of ligands are synthesized via Schiff Base condensation, where an aldehyde, or ketone is reacted with an amine, to produce an imine. Schiff base ligands are able to stabilize many different metals in various oxidation states, and they can control the performance of metals in many catalytic transformations. Because Schiff bases are stable, they can be stored without any precautions. These ligands are widely used because they can control the coordination properties of the metal, they are moderate electron donors with a chelating structure and they have a low electron counting number. Mononuclear Schiff base complexes are known to be active catalysts for oligomerization and polymerization reactions.[11]

As part of this project, we have anchored different types of salicylaldimine moieties onto the periphery of the generation 1 and generation 2 diaminobutane polypropylene imine dendrimer (ligands **LI-LVI**). Nickel acetate was used to complex ligands **LI-LVI** and to form complexes **I-VI** respectively. Although nickel complexes are reported to be highly active catalysts for oligomerization and polymerization processes, they are not very selective to one type of product. Attempts to synthesize selective catalysts will be made by tailoring the ligands of the complexes.

2.2 Results and Discussion:

2.2.1 Ligand Synthesis.

The synthesis of ligands **LI** and **LII** has previously been reported by Smith[12] in 2003. The same synthetic method was used to prepare a range of dendrimeric salicylaldimine ligands. Ligands **I, III** and **V** was prepared via Schiff base condensation of diaminobutane tetraamine (DAB-(NH_2)$_4$) with the appropriate aldehydes. This reaction is shown below in Scheme 2.4.



LI : R_1=H, R_2=H

LIII : R_1=^{t}Bu, R_2=H

LV : R_1=^{t}Bu, R_2=^{t}Bu

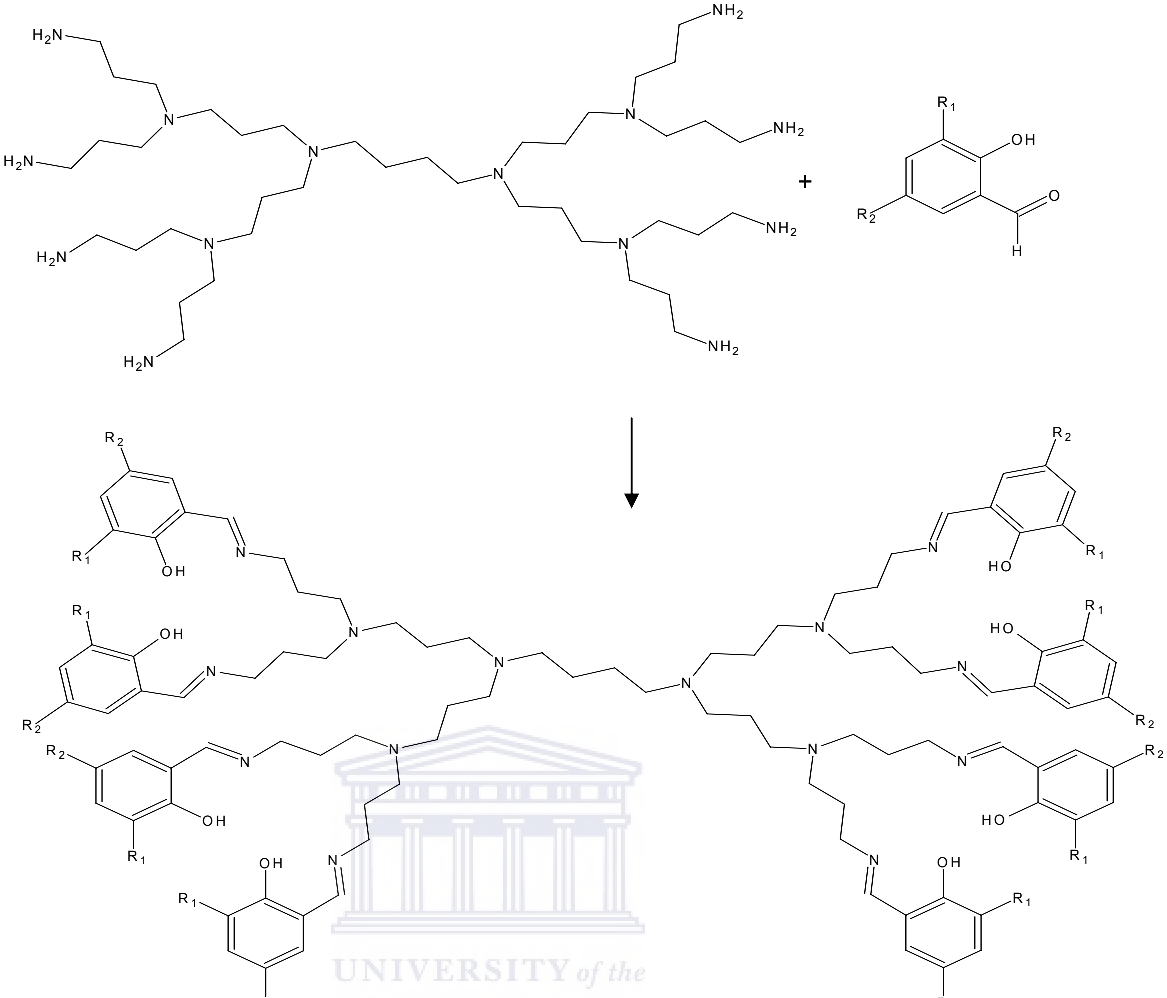
Scheme 2.4

To ensure complete reaction of all the peripheral amino groups with the aldehydes, the reactions had to be carried out over an extended period of three days. In all cases the crude product is initially isolated as a yellow oil. In the case of ligand **LI**, the product could be isolated from the oily residue as a yellow solid by recrystallization from dichloromethane:hexane mixtures. The product was isolated in 90% yield.

Ligand **LIII** was purified by washing the crude oily product with water, isolating a yellow oil as the pure product in 85% yield.

The work-up method for **LV** was different from those previously discussed. In this instance the oily residue was dissolved in dichloromethane, to which water was added. The biphasic mixture was slowly evaporated on a rotary evaporator. As the volume of the dichloromethane is reduced a yellow solid starts precipitating out of the mixture. The product was isolated by decanting the water and drying the product on the vacuum line for 24 hours. The product is a pure yellow solid obtained 90% yield.

The second generation ligands **LII, LIV** and **LVI** were synthesized by reacting diaminobutane octaamine (DAB-$(NH_2)_8$) with the appropriate aldehyde via Schiff base condensation as shown in Scheme 2.5.



LII : R_1=H, R_2=H

L**IV** : R_1=^{t}Bu, R_2=H

L**VI** : R_1=^{t}Bu, R_2=^{t}Bu

Scheme 2.5

The purification of crude product **LII** was initially attempted using the same approach that worked for ligand **LI**. However, no precipitation was observed after cooling the mixture for several days at -4^{0}C. Attempts to purify the material using column chromatography were also not successful as a large amount of the product remained trapped on the silica gel column. It was ascertained that the best way for purifying this ligand was by exhaustive washing of the crude material with large excesses of water. The pure product can be isolated in an 80% yield using this approach.

Attempts were also made to prepare **LII** using other solvents such as water and methanol, instead of toluene. In both cases the yields were not as high and the product could not be isolated in a pure form.

The other generation 2 salicylaldimine ligands **LIV** and **LVI** were isolated using the same work-up methods as for ligands **LIII** and **LV** respectively. **LIV** was obtained as pure yellow oil with an 83% yield whereas **LVI** was obtained as a yellow solid (93% yield).

2.2.2: Ligand characterization.

2.2.2.a: IR Spectroscopy.

The IR spectra of ligands **I-VI** shows peaks in the υ C=N stretching frequency region indicating that the aldehydes have condensed with the amino groups on the peripheries to form the imine. The bands at 3400-3300 cm^{-1} are due to the O-H of the salicylaldimine units. Table 2.1. show the functionalities of these ligands and their corresponding stretching frequencies.

TABLE 2.1.: Ligand IR Stretching frequencies.

Ligand	Functional Group	Stretching Frequency cm^{-1}	Melting Range (^{0}C)	%Yield
LI	O-H	2924	66-68	90
	C=N	1632		
	C-O	1284		
LII	O-H	3058	Oil	80
	C=N	1664		
	C-O	1279		
LIII	O-H	2958	Oil	85
	C=N	1637		
	C-O	1265		
LIV	O-H	2906	Oil	83
	C=N	1618		
	C-O	1224		
LV	O-H	2974	58-62	90
	C=N	1631		
	C-O	1265		
LVI	O-H	2922	68-70	93
	C=N	1632		
	C-O	1274		

2.2.2.b.i: ^{1}H NMR Spectra

The ^{1}H NMR spectra of the salicylaldimine ligands (**LI-LVI**) all show proton signals for the internal branches of the dendrimer, the proton attached to the imine group and the protons from the aryl rings. Ligands **LIII** and **LIV** shows a proton signal at 1ppm indicating the presence of the mono ^{t}Bu substituents on the aryl rings of the ligand at position 3. Ligands **LV** and **LVI** show two proton signals at around 1ppm indicating the presence of the two ^{t}Bu substituents present in the 3 and 5 position on the aryl ring of the ligand. Table 2.2 gives the proton NMR data for ligands **LI-LVI.** Figures 2.2 and 2.3 give the numbered general structures of the ligands that can be compared to the corresponding Table 2.2.

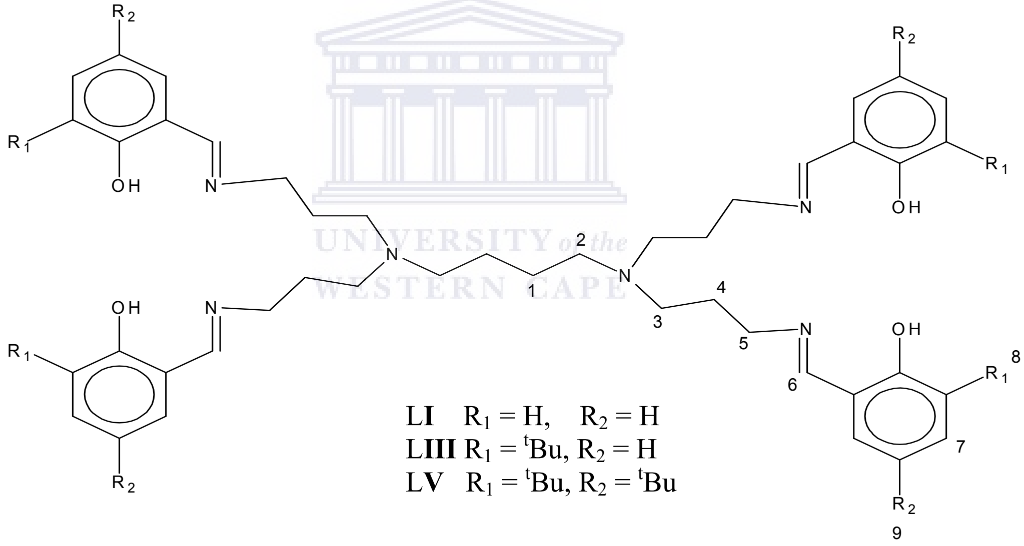
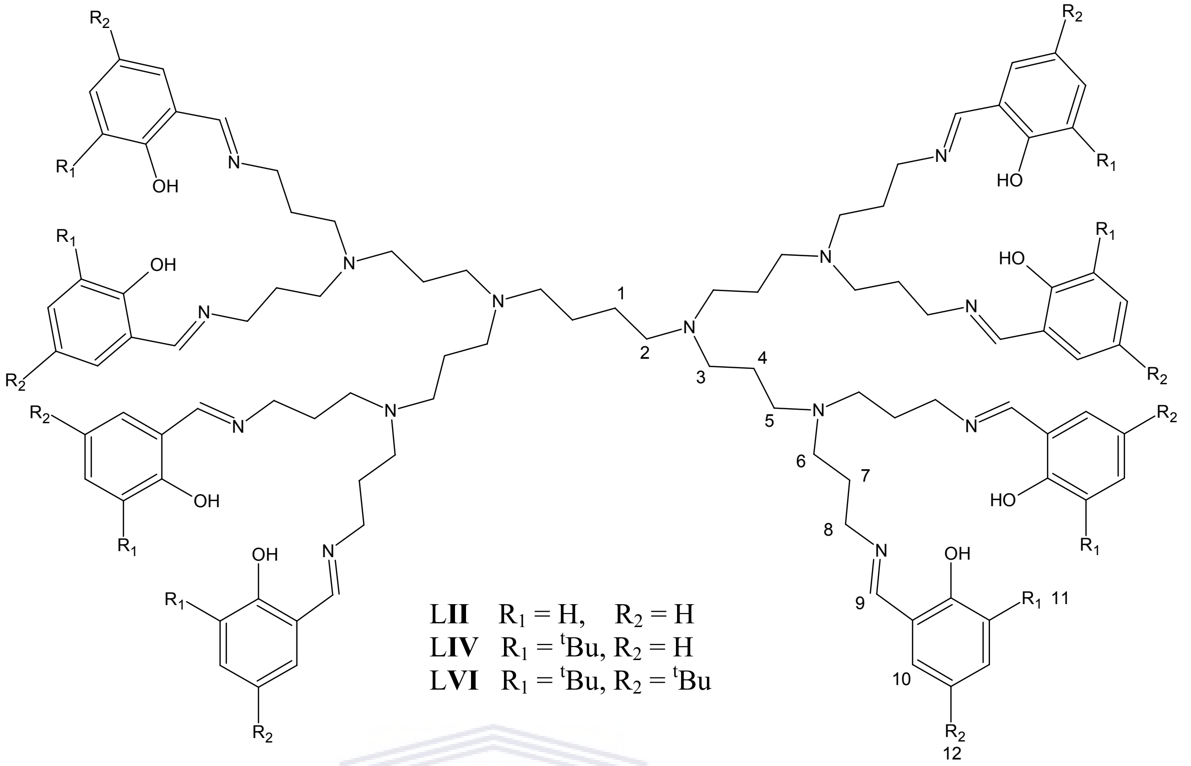


Figure 2.2: General numbered structure of the generation 1 ligands.



LII $R_1 = H$, $R_2 = H$
LIV $R_1 = {}^tBu$, $R_2 = H$
LVI $R_1 = {}^tBu$, $R_2 = {}^tBu$

Figure 2.3: General numbered structure of the generation 2 ligands.

Table 2.2: ^{1}H NMR data for the ligand systems.

Ligand	Assignment	Chemical Shift ppm
LI	1	1.42 (s, b, 4H)
	2	2.42 (t, 4H, $^3J_{H-H}$ = 4.2)
	3	2.57 (b, t, 8H, $^3J_{H-H}$ = 6.4)
	4	1.87 (m, 8H, $^3J_{H-H}$ = 8.4)
	5	3.67 (t, 8H, $^3J_{H-H}$= 5.2)
	6	8.43 (s, 4H)
	7	7.35 (m, 4H, $^3J_{H-H}$ = 7.8)
	8	R_1 = H, 7.35 (m, 4H, $^3J_{H-H}$ = 7.8)
	9	R_2 = H, 7.35 (m, 4H, $^3J_{H-H}$ = 7.8)
LII	1	1.31 (s, b, 4H)
	2	2.45 (t, 4H, $^3J_{H-H}$ = 9.8)
	3	1.61 (t, 8H, $^3J_{H-H}$ = 1.2)
	4	1.90 (m, 8H, $^3J_{H-H}$ = 2.2)
	5	2.32 (t, 8H, $^3J_{-H}$ = 2.0)
	6	2.39 (t, 16H, $^3J_{H-H}$ = 1.5)
	7	2.61 (m, 16H, $^3J_{H-H}$ = 7.0)
	8	3.61 (t, 16H, $^3J_{H-H}$ = 4.2)
	9	8.31 (s, 8H)
	10	7.53 (m, 8H, $^3J_{H-H}$ = 7.2)
	11	R_1 = H, 7.53 (m, 8H, $^3J_{H-H}$ = 7.2)
	12	R_2 = H, 7.53 (m, 8H, $^3J_{H-H}$ = 7.2)

Table 2.2 cont..

LIII	**1**	1.44 (s, b, 4H)
	2	2.40 (t, 4H, $^3J_{H-H}$ = 5.6)
	3	2.53 (b, t, 8H, $^3J_{H-H}$ = 8.6)
	4	1.90 (m, 8H, $^3J_{H-H}$ = 8.8)
	5	3.61 (t, 8H, $^3J_{H-H}$ = 6.6)
	6	8.32 (s, 4H)
	7	7.29 (m, 4H, $^3J_{H-H}$ = 7.4)
	8	R_1 = ^{t}Bu, 1.41 (d, 9H, $^2J_{H-H}$ = 5.2)
	9	R_2 = H, 7.29 (m, 4H, $^3J_{H-H}$ = 7.4)
LIV	**1**	1.45 (s, b, 4H)
	2	2.51 (t, 4H, $^3J_{H-H}$ = 1.4)
	3	1.56 (t, 8H, $^3J_{H-H}$ = 1.2)
	4	1.81 (m, 8H, $^3J_{H-H}$ = 5.8)
	5	2.36 (t, 8H, $^3J_{H-H}$ = 1.2)
	6	2.41 (t, 16H, $^3J_{H-H}$ = 4.4)
	7	2.78 (m, 16H, $^3J_{H-H}$ = 6.4)
	8	3.58 (t, 16H, $^3J_{H-H}$ = 7.6)
	9	8.30 (s, 8H)
	10	7.23 (m, 8H, $^3J_{H-H}$ = 6.6)
	11	R_1 = ^{t}Bu, 1.42 (d, 9H, $^2J_{H-H}$ = 5.2)
	12	R_2 = H, 7.23 (m, 8H, $^3J_{H-H}$ = 6.6)

Table 2.2 cont..

LV	**1**	1.61 (s, b, 4H)
	2	2.40 (t, 4H, $^3J_{H-H}$ = 8.4)
	3	2.55 (b, t, 8H, $^3J_{H-H}$ = 1.0)
	4	1.90 (m, 8H, $^3J_{H-H}$ = 2.6)
	5	3.60 (t, 8H, $^3J_{H-H}$ = 6.4)
	6	8.35 (s, 4H)
	7	7.36 (m, 4H, $^3J_{H-H}$ = 6.2)
	8	R_1 = ^{t}Bu, 1.43 (d, 9H, $^2J_{H-H}$ = 1.8)
	9	R_2 = ^{t}Bu, 1.29 (d, 9H, $^2J_{H-H}$ = 1.6)
LVI	**1**	1.11 (s, b, 4H)
	2	2.51 (t, 4H, $^3J_{H-H}$ = 2.4)
	3	1.58 (t, 8H, $^3J_{H-H}$ = 6.4)
	4	1.81 (m, 8H, $^3J_{H-H}$ = 4.0)
	5	2.36 (t, 8H, $^3J_{H-H}$ = 2.2)
	6	2.41 (t, 16H, $^3J_{H-H}$ = 3.2)
	7	2.71 (m, 16H, $^3J_{H-H}$ = 2.0)
	8	3.57 (t, 16H, $^3J_{H-H}$ = 2.4)
	9	8.32 (s, 8H)
	10	7.26 (m, 8H, $^3J_{H-H}$ = 8.0)
	11	R_1 = ^{t}Bu, 1.28 (d, 9H, $^2J_{H-H}$ = 9.8)
	12	R_2 = ^{t}Bu, 1.43 (d, 9H, $^2J_{H-H}$ = 8.6)

2.2.2.b.ii: ^{13} C NMR Spectra

Table 2.3 contains the ^{13}C NMR data for ligands **LI-LVI.** Figures 2.4 and 2.5 show the numbered general structures of the ligands that can be compared to the corresponding Table 2.3.

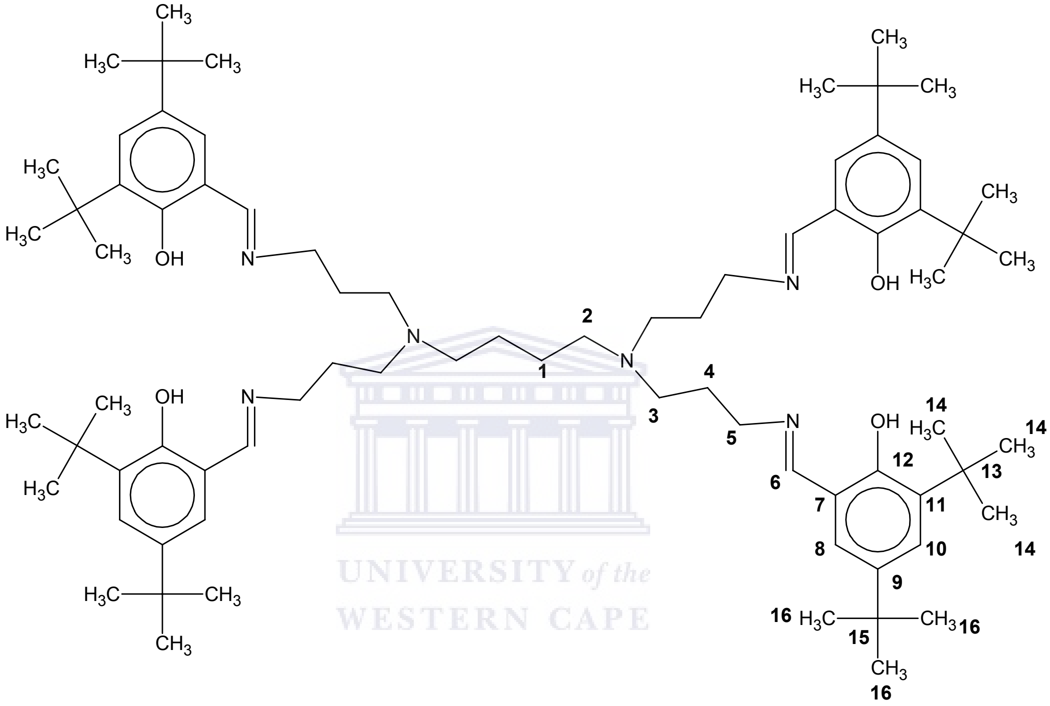


Figure 2.4: General numbered structure for generation 1 ligands.

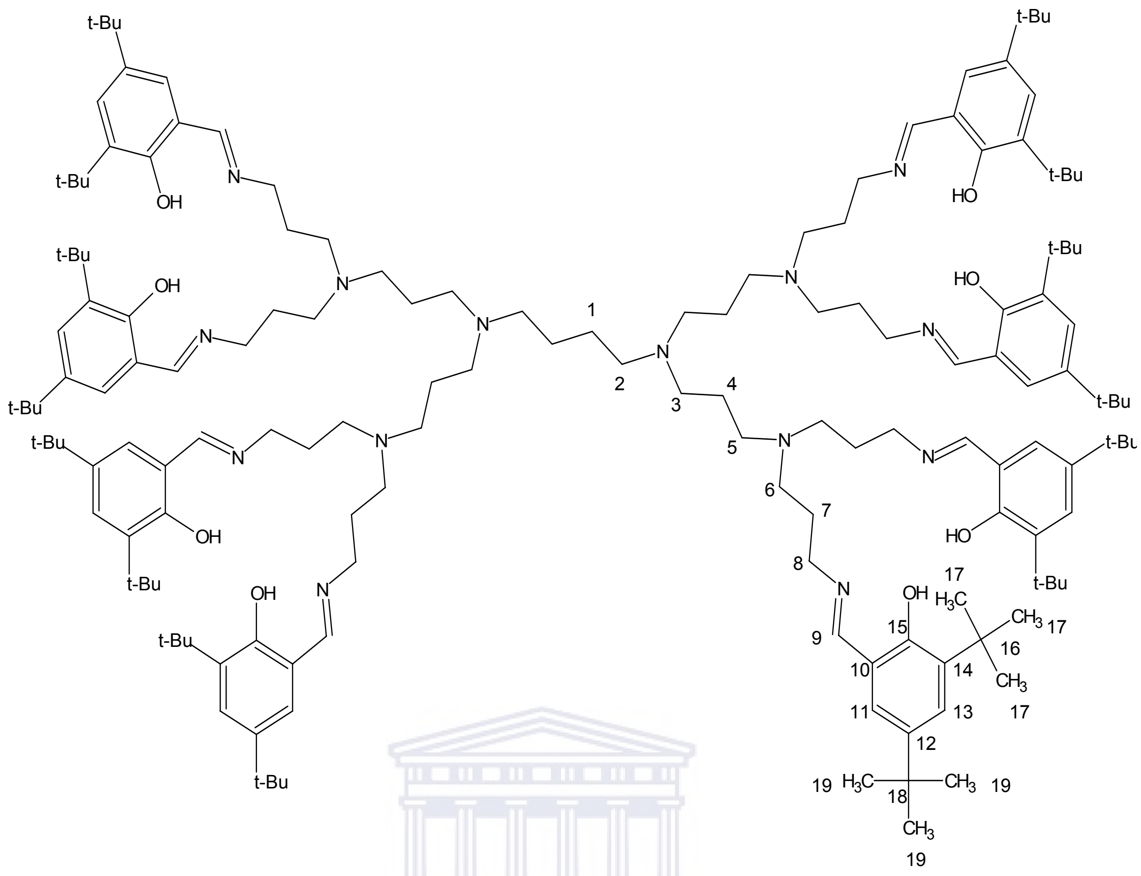


Figure 2.5: General numbered structure for generation 2 ligands.

Table 2.3: ^{13}C NMR data for the ligand systems.

Ligand	Assignment	Chemical Shift
LI	1	25.1
	2	51.4
	3	54.0
	4	28.5
	5	57.3
	6	164.8
	7	116.9
	8	118.8
	9	118.3
	10	131.0
	11	131.9
	12	161.3
LII	1	24.1
	2	52.1
	3	52.2
	4	30.1
	5	52.1
	6	52.2
	7	24.8
	8	57.3

Table 2.3 cont.

	9	164.8
	10	116.9
	11	134.5
	12	118.7
	13	131.9
	14	131.1
	15	161.2
LIII	1	24.9
	2	51.2
	3	53.8
	4	28.2
	5	57.1
	6	165.6
	7	117.6
	8	129.1
	9	118.5
	10	129.5
	11	137.2
	12	160.5
	13	34.8
	14	29.2

Table 2.3 cont..

	1	24.2
	2	53.1
	3	53.2
	4	30.0
	5	53.1
	6	53.2
	7	24.9
	8	60.8
LIV	9	165.4
	10	117.0
	11	134.9
	12	118.1
	13	130.5
	14	129.9
	15	159.8
	16	35.0
	17	29.2
	1	25.2
	2	51.5
	3	54.0
	4	28.5

Table 2.3 cont..

	5	57.4
	6	165.8
	7	117.9
LV	8	126.6
	9	125.6
	10	136.6
	11	139.7
	12	158.2
	13	34.1
	14	29.4
	15	35.0
	16	31.5
	1	23.9
	2	51.5
	3	51.9
	4	28.9
	5	51.5
	6	51.9
	7	24.1
	8	57.6
	9	165.8
LVI	10	117.8
	11	139.8

Table 3.3 cont..

	12	136.6
	13	126.6
	14	125.7
	15	158.2
	16	34.1
	17	29.4
	18	34.9
	19	31.5

2.2.2.c: Elemental Analysis.

Table 2.4 shows the elemental analysis results for the ligand systems. Those ligands isolated as solids (**LI, LV** and **LVI**) give acceptable microanalysis percentage results. Ligands **LII-LIV** were isolated as oils and proved difficult to adequately

Table 2.4: Microanalysis for the ligand systems.

Ligand	Calculated %			Found %		
	C	H	N	C	H	N
LI	72.10	7.70	11.47	71.90	7.90	11.49
LII	71.90	8.03	12.21	70.87	8.28	11.76
LIII	70.29	8.70	8.06	70.84	8.93	8.05
LIV	74.81	9.42	9.54	74.50	8.94	6.83
LV	77.24	10.25	7.11	77.15	10.32	6.72
LVI	76.75	10.31	7.83	76.59	10.56	7.62

2.2.3: Complex synthesis.

The nickel complexes (**I–VI**) were prepared by reacting the previously synthesized ligand systems (L**I**-L**VI**) with nickel acetate tetrahydrate as the metal precursor. All complexes were isolated as green solids with yields ranging from 75-85%. These complexes were purified by adding dichloromethane to the crude solids, filtering the solution by gravity and concentrating the filtrate to produce pure green solid products. This method worked for separating the nickel acetate from the product since the nickel acetate is insoluble in dichloromethane and the product was soluble in this solvent. Figures 2.6 and 2.7 below gives the general structures of the generation 1 and the generation 2 nickel complexes obtained.

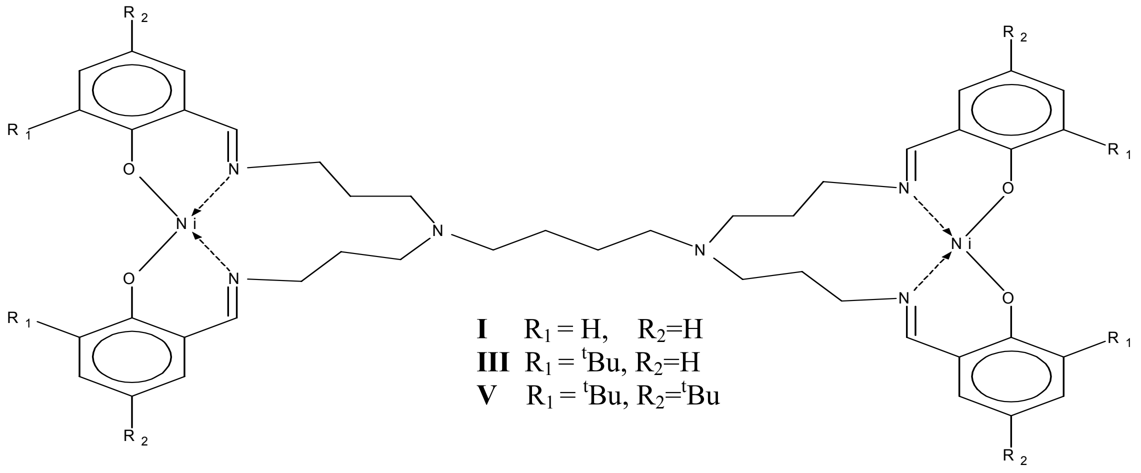


Figure 2.6: The general structure of generation 1 nickel complexes.

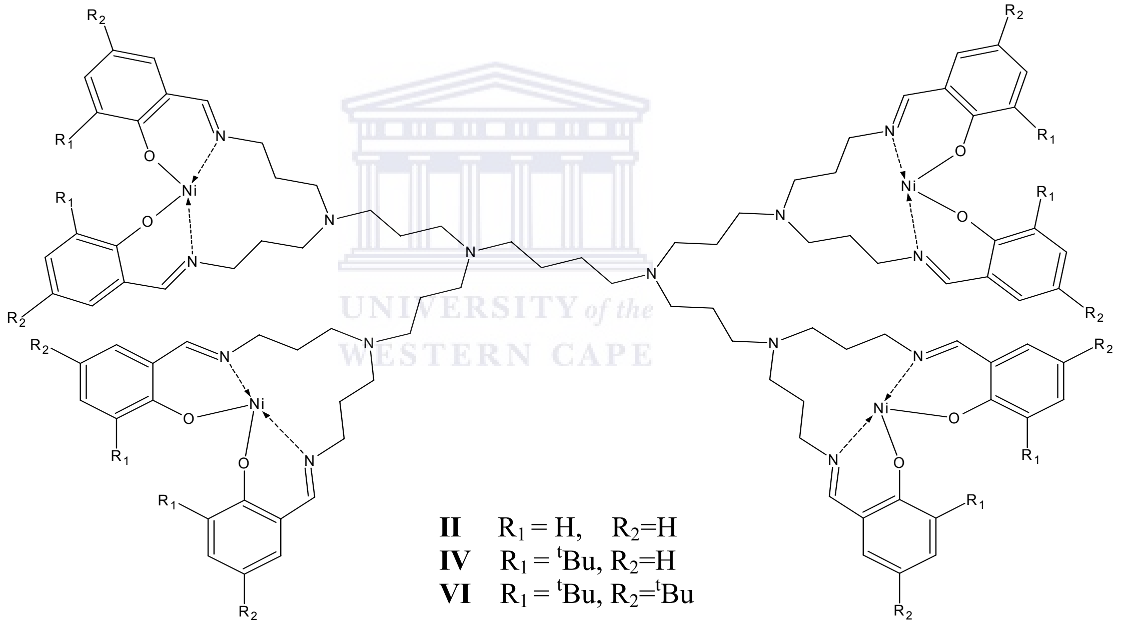


Figure 2.7: The general structure of generation 2 salicylaldimine nickel complexes.

2.2.4: Complex characterization.

2.2.4.a: IR Spectroscopy.

The IR spectra of the nickel complexes **I-VI** show that the bands at the C=N and C-O stretching frequencies has shifted when compared to the ligand spectra. This is due to the effect of the metal on the ligand system. The bands at 3400-3300 cm^{-1} in the ligand spectra, is no longer present in the complex spectra indicating that the metal has coordinated to the O of the ligand. Table 2.5 shows the functionalities of these ligands and their corresponding stretching frequencies as well as their decomposition ranges. After melting, the complexes decompose within a certain temperature range as also indicated in Table 2.5. In general the generation 1 complexes are more thermally stable than the generation 2 complexes as indicated by their decomposition temperatures, with the exception of the di-tertbutyl complexes where the generation 2 complex is more stable than the generation 1 complex with a higher decomposition range.

Table 2.5: Complex IR stretching frequencies.

Complex	Functional Group	Stretching Frequency cm^{-1}	Decomposition Range (^0C)	% Yield
I	C=N	1628	275-278	85
	C-O	1324		
II	C=N	1632	210-215	80
	C-O	1344		
III	C=N	1640	281-283	75
	C-O	1310		
IV	C=N	1630	191-195	82
	C-O	1316		
V	C=N	1630	205-209	78
	C-O	1324		
VI	C=N	1632	217-220	80
	C-O	1324		

2.2.4.b: ^{1}H NMR Spectra.

All the nickel complexes are paramagnetic thus the ^{1}H NMR spectra gave very broad peaks making the results difficult to interpret. However, other analytical techniques such as IR spectroscopy, mass spectrometry and elemental analysis confirmed the structures of the complexes.

2.2.4.c: Elemental Analysis.

Table 2.6 shows the elemental analysis results for the complexes. The calculated values correspond well to the found results, confirming the formulae of the complexes synthesized.

Table 2.6: Microanalysis for the complexes.

Complex	Calculated %			Found %		
	C	H	N	C	H	N
I	62.18	6.08	9.74	62.18	6.15	9.9
II	58.77[a]	6.24	9.79	58.04	6.25	7.08
III	67.30	7.91	7.85	67.18	7.80	7.43
IV	65.47[b]	7.92	8.29	65.61	8.04	8.30
V	70.48	9.63	6.49	70.37	9.33	5.32
VI	68.68[c]	8.95	6.96	68.03	8.98	6.11

[a] Calculated for $C_{100}H_{128}N_{14}O_8Ni_4.2CH_2Cl_2$
[b] Calculated for $C_{132}H_{192}N_{14}O_8Ni_4.1CH_2Cl_2$
[c] Calculated for $C_{160}H_{248}N_{14}O_8Ni_4.1CH_2Cl_2$

2.2.4.d: Mass spectrometry.

The ligands as well as the complexes were analyzed using electron spray mass spectrometry (ESI-MS). The samples were dissolved in DMSO, centrifuged and filtered. A typical example of a ligand mass spectrum and a complex mass spectrum is shown in Figures 2.8 and 2.9.

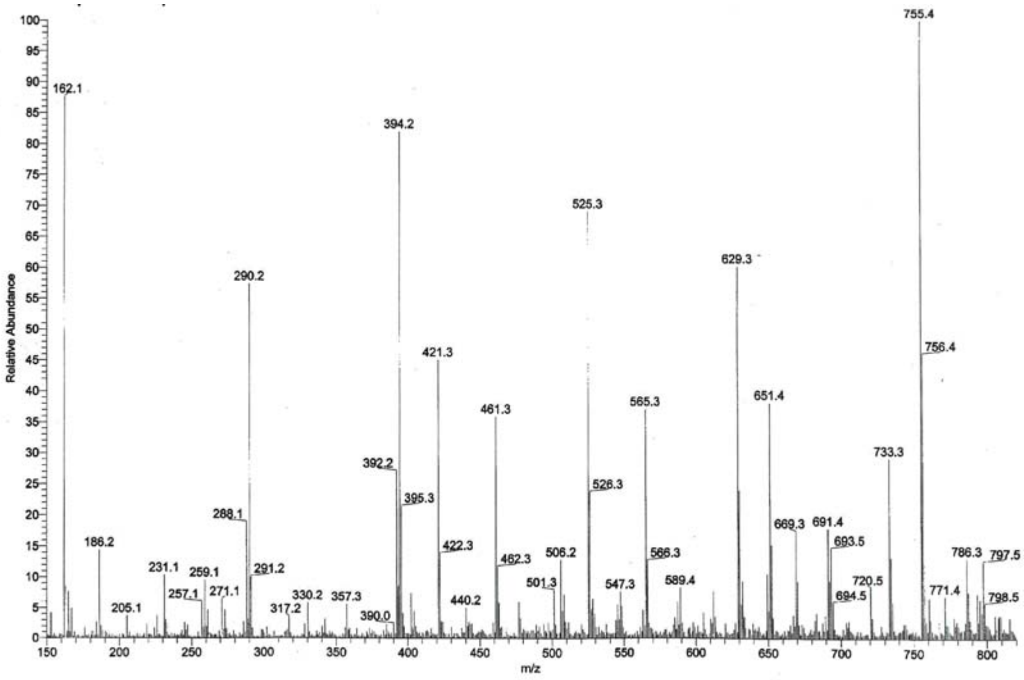


Figure 2.8: ESI-Mass spectrum of generation 1 unsubstituted salicylaldimine ligand.

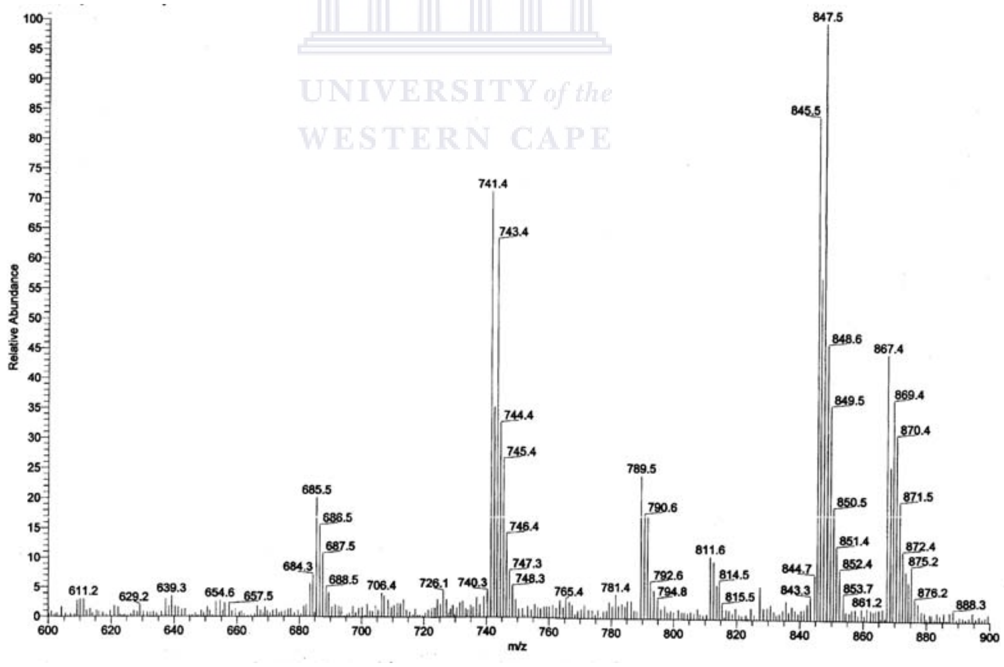


Figure 2.9: ESI-Mass spectrum of generation 1 unsubstituted salicylaldimine nickel complex.

2.3 Conclusion:

Dendrimeric Generation 1 and Generation 2 salicylaldimine ligands have been synthesized. These ligands have been complexed to transition metal salts of nickel. The ligands and complexes have been characterized by FTIR spectroscopy, ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, microanalysis and ESI mass spectrometry. Complexes **II-VI** are new compounds. These complexes can be used as catalysts for several processes. From the selection of complexes synthesized, we will be able to determine whether the generation 1 complexes are better catalysts than the generation 2 complexes. Hence we can deduce whether a dendritic effect exists. The complexes synthesized are unsubstituted complexes, mono ^{t}Bu substituted complexes as well as di ^{t}Bu substituted complexes. Thus we'll be able to determine whether the substituents on the aryl rings of the complexes has an effect on the catalytic activity of the complexes and to what extent that effect is.

2.4 Experimental:

2.4.1: General.

Toluene was dried by refluxing over sodium/benzophenone. The DAB dendrimer range was obtained from Symochem, Netherlands, and used without any further purification. Salicylaldehyde, 3-tertbutyl-2-hydroxy benzaldehyde, 3,5 di tert butyl-2-hydroxy benzaldehyde, 4-tertbutylbenzaldehyde and nickelacetate tetrahydrate were purchased from Sigma Aldrich, and were used without any further purifications. The silica gel used for chromatography was purchased from Merck Chemicals. Infrared spectra were recorded on a Perkin Elmer Paragon 1000PC FT-IR spectrophotometer, using KBr pellets or as a nujol mull on NaCl plates. ^{1}H NMR (200MHz) and ^{13}C NMR (50MHz) spectra were recorded on a Varian XR200 spectrometer, using tetramethylsilane as an internal standard. ESI Mass spectra were done at Stellenbosch University using a Waters API Q-TOF Ultima instrument in V-mode. The source temperature was 100^0C and the desolvation temperature was 350^0C. The capillary voltage used was 3.5kV. Microanalyses were done at the University of Cape Town. Melting points were recorded on a Leitz Microscope Hot Stage 350.

*Synthesis of Ligand **LI**:*

DAB-G1 dendrimer (0.5 g, 1.6 mmol) was added to dry toluene (10 ml) in a Schlenk tube, under nitrogen. Salicylaldehyde (0.77 ml, 6.3 mmol) was added to the solution. The mixture was allowed to stir for 72 hours at room temperature. The solvent was evaporated on a rotary evaporator and a yellow oil was obtained. Dichloromethane (10 ml) was added to the oil, after which hexane (20 ml) was added. This solution was allowed to stand in the fridge for 72 hours at -4^0C. The yellow precipitate obtained was filtered off via vacuum filtration, yield = 90%. M^+ = 733 (ESI-MS).

*Synthesis of Ligand **LII**:*

The generation 2 unsubstituted ligand was synthesized similarly to the ligand **I**, using a 1:8 DAB-G2 dendrimer:salicylaldehyde mol ratio under the same reaction conditions. The solvent was evaporated on a rotary evaporated and a yellow oil was obtained. Dichloromethane (20 ml) was added to the product and the aldehyde was extracted with 30ml water 5 times. The dichloromethane layer was dried over magnesium sulphate after which the latter was filtered off. The filtrate was evaporated via rotary evaporation producing a yellow oil, yield = 80%. M^+ = 1181 (ESI-MS).

*Synthesis of Ligand **LIII**:*

DAB-G1 dendrimer (0.1 g, 0.32 mmol) was dissolved in toluene (5 ml), in a round bottom flask, under nitrogen. 3-tert-butyl-2-hydroxybenzaldehyde (0.25 ml, 1.3 mmol) of was added to the solution while stirring. The mixture was stirred for 72 hours at room temperature. The solvent was evaporated and dichloromethane (10 ml) was added to the product. Unreacted aldehyde was extracted from the product using the same work-up method as for ligand **II** producing a yellow oil, yield = 85%. M^+ = 958 (ESI-MS).

*Synthesis of Ligand **LIV**:*

Ligand **IV** was synthesized and worked-up similarly to that of ligand **III**, using a DAB-G2 dendrimer:hydroxybenzaldehyde mol ratio of 1:8 under the same reaction conditions.

A yellow oil was obtained, yield = 83%. M^{+2} = 1028 (ESI-MS).

Synthesis of Ligand ***LV****:*

DAB-G1 dendrimer (0.3 g, 0.94 mmol) was dissolved in dry toluene (10 ml) in a round bottom flask, under nitrogen. 3,5 di-tert-butyl-2 hydroxybenzaldehyde (0.9 g, 3.3 mmol) was added to the solution. The reaction conditions were the same as for the previously synthesized ligands. A yellow oil was obtained. Dichloromethane (20 ml) was added to the oil and then water (30 ml) was added. The dichloromethane was evaporated on a rotary evaporator and a yellow precipitate formed in the water. The water was decanted and the product was dried under vacuum for 70 hours. The product was a yellow crystalline solid, yield = 90%.

Synthesis of Ligand ***LVI****:*

The same synthetic method and reaction conditions were used to obtain the generation 2 di tert-butyl substituted ligand **VI**. The mol ratio was 1:8 DAB-G2:hydroxybenzaldehyde and the same work-up method used for ligand **V** produced a yellow crystalline solid, yield = 93%. M^{+2} = 1253 (ESI-MS).

Synthesis of Complex ***I****:*

The DAB-G1 salicylaldimine ligand **I** (0.5 g, 0.68 mmol) was added to ethanol (10 ml) in a round bottom flask, under nitrogen. Nickel acetate tetrahydrate (0.34 g, 1.4 mmol) was then added to the solution. The reaction mixture was allowed to stir under reflux for 24 hours. A green precipitate formed. The precipitate was filtered off by vacuum filtration and washed with ethanol and the product obtained is a green solid, yield = 85%.

M^+ = 848 (ESI-MS).

*Synthesis of Complex **II**:*

DAB-G2 salicylaldimine ligand **II** was added to 4 equivalents of Nickel acetate tetra hydrate under the same reaction conditions producing a green solid. The product was dissolved in dichloromethane (15 ml) and the solution was filtered by gravity. The filtrate was concentrated producing a green solid product with a 80% yield.

M^+ = 1833 (ESI-MS).

*Synthesis of Complex **III**:*

DAB-G1 mono tert-butyl ligand **III** (2.8 g, 2.4 mmol) was added to ethanol (10 ml) in a Schlenk tube, under nitrogen. Nickel acetate tetrahydrate (2.39 g, 9.6 mmol) was then added to the solution. The reaction mixture was stirred under reflux for 24 hours forming a green precipitate. The solvent was evaporated via rotary evaporation. The product was dissolved in dichloromethane (15 ml). The solution was filtered by gravity. The filtrate was concentrated and a green solid was obtained, yield = 75%. M^+ = 1070 (ESI-MS).

*Synthesis of Complex **IV**:*

DAB-G2 mono tert-butyl salicylaldimine ligand **IV** was added to 4 equivalents of Nickel acetate tetra hydrate under the same reaction conditions producing a green solid. The product was dissolved in dichloromethane (15 ml) and the solution was filtered by gravity. The filtrate was concentrated producing a green solid product, yield = 82%.

M^+ = 1952 (ESI-MS).

*Synthesis of Complex **V***:

DAB-G1 3,5 tert-butyl ligand **V** (0.2 g, 0.17 mmol) was added to ethanol (10ml) in a Schlenk tube, under nitrogen. 2 mol equivalents of nickel acetate tetrahydrate were then added to the solution. The reaction mixture was allowed to stir under reflux for 24 hours. A green precipitate formed. Solvent was evaporated and a green solid was obtained. Dichloromethane (10 ml) was added to the solid. The solution was filtered by gravity. The filtrate was concentrated. A green solid was obtained, yield = 78%.

M^{+5} = 259 (ESI-MS).

*Synthesis of Complex **VI***:

DAB-G2 3,5 tert-butyl ligand **VI** (0.2 g, 0.08 mmol) was added to ethanol (10ml) in a Schlenk tube, under nitrogen. 4 mol equivalents of nickel acetate tetrahydrate were then added to the solution. The reaction mixture was allowed to stir under reflux for 24 hours. A green precipitate formed. Solvent was evaporated and a green solid was obtained. Dichloromethane (10 ml) was added to the solid. The solution was filtered by gravity. The filtrate was concentrated and a green solid was obtained, yield = 80%. M^{+5} = 542 (ESI-MS).

2.5 References:

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Chapter 3

α-Olefin Oligomerization

3.1 Brief introduction to the oligomerization of α-olefins.

3.1.1: Ethylene Oligomerization.

The oligomerization of ethylene is the most common process for producing linear α-olefins[1] as mentioned in chapter 1 of this thesis. Linear α-olefins are the feedstock for the production of lubricants, waxes, detergents and plasticizers.

In addition, ethylene can be used as a starting material to produce diesel fuels. The demand for diesel fuels is growing rapidly. This is especially true for fuels that emit lower levels of pollutants. Diesel fuel obtained by the oligomerization of olefins such as ethylene has several advantages some of which are the absence of sulphur and aromatics making it environmentally friendly.[2] Diesel fuels correspond to the C_{10}-C_{20} hydrocarbon range. Thus the development of selective ethylene oligomerization catalysts is of industrial importance.

Several mononuclear nickel complexes have been reported to be good catalysts for the oligomerization of ethylene. However in many cases these catalysts are not very selective. They produce a whole range of products instead of just one specific type of product. Selectivity can be achieved by tailoring the surrounding ligands of the catalyst.[3]

Recently dendrimeric complexes have gained increasing interest and are being widely studied in catalytic processes including oligomerization processes. As discussed in Chapter 2, we have synthesized dendrimeric salicylaldimine ligands and complexed these to nickel salts.

Over the past year de Jesus *et al.* [4,5] reported the synthesis of aryloxocyclopentadienyl titanium carbosilane dendrimer complexes as well as iminopyridine dendrimeric carbosilane nickel complexes for the oligomerization and polymerization of ethylene. These researchers prepared the generation 1-4 dendrimeric titanium complexes.[4] These titanium dendrimer catalysts only produce ethylene polymers and no oligomers. In the case of the G1-G3 dendrimeric nickel complexes[5] oligomers as well as polymers of ethylene are obtained. In both instances, methylaluminoxane (MAO) is used as co-catalyst. The effect of dendrimer generation on the activity of the catalysts has also been probed by the above workers. Their results will be discussed in comparison to our results later in this chapter. The structures of the generation 1 titanium and nickel complexes reported by de Jesus *et al.* are shown below in Figures 3.1 and 3.2.

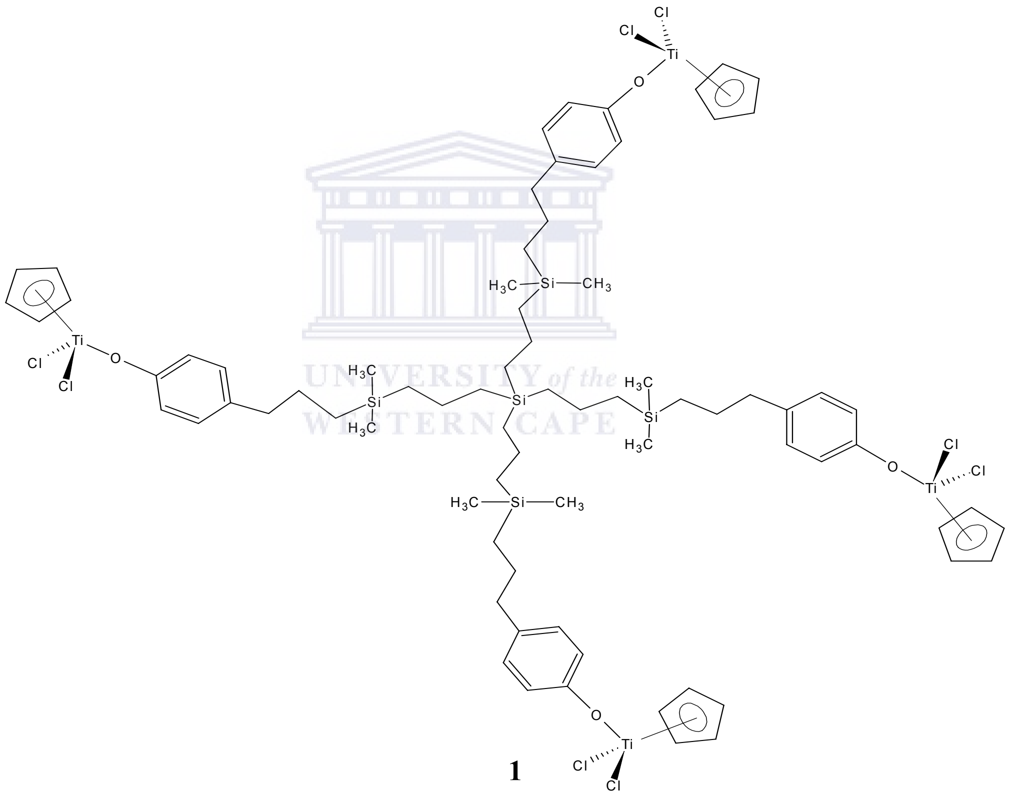

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Figure 3.1: Generation 1 – titanium aryloxocyclopentadienyl carbosilane dendrimer complex.[4]

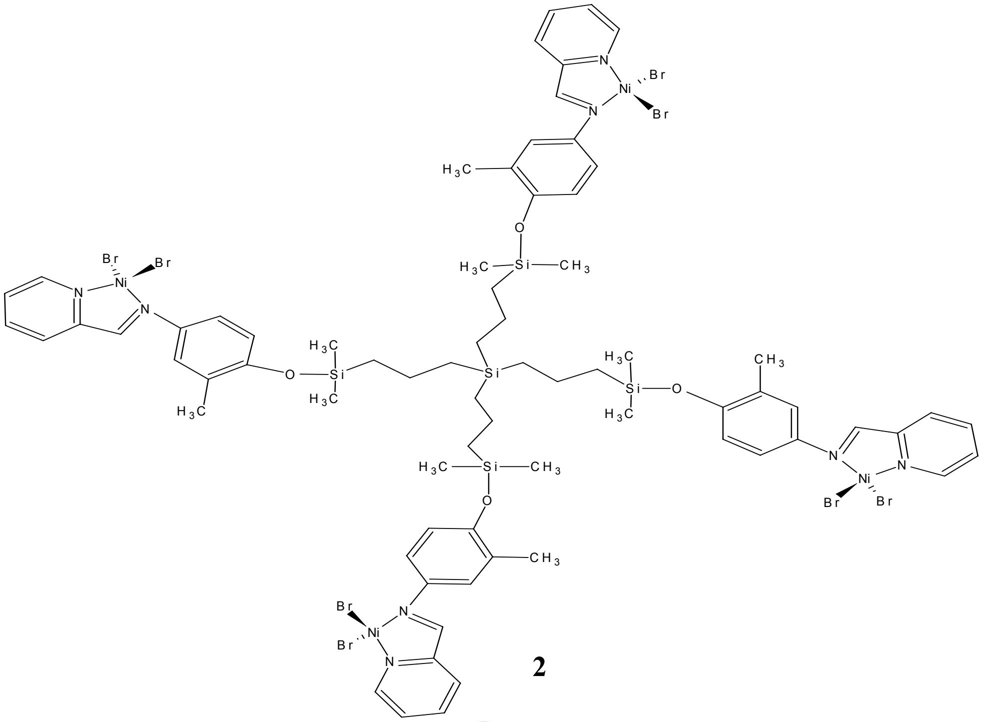

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Figure 3.2: Generation 1 – $ONNMe_2NiBr_2$ dendrimer complex.[5]

Many mononuclear salicylaldimine complexes have also been reported in the literature as good ethylene oligomerization catalysts, some of which have been already discussed in Chapter 1.[6] We therefore prepared for this purpose unsubstituted multinuclear nickel salicylaldimine complexes (**I-II**) as catalyst precursors for oligomerization of ethylene.

3.1.2: 1-Pentene oligomerization.

1-Pentene is an α-olefin that is commonly produced as a byproduct of catalytic or thermal cracking of petroleum, or during the production of ethylene and propylene via thermal cracking of hydrocarbons. 1-Pentene is rarely isolated as a separate compound. It is mostly blended in a mixture with other hydrocarbons to make fuels. The only large-scale commercial manufacturer of 1-pentene is SASOL Ltd, a South African petroleum company. This company produces 1-pentene by the Fischer-Tropsch process. This process converts synthesis gas into a range of hydrocarbons over metal catalysts. The synthesis gas is produced by partial oxidation or steam reforming of coal.[7]

SASOL manufactures a diverse range of products including alcohols, surfactants and paraffins, and ethylene. They also supply plastic adhesives and lubricants to pharmaceutical companies, but their detergent and cleaning industry forms their largest market.[8]

SASOL Ltd. has three operating Fischer-Tropsch plants, one located in Sasolburg and the other two located in Secunda. These plants produce vast amounts of 1-pentene annually as by-products, making it hard to sell since it only has use as a co-monomer and not as fuel.

One way of overcoming this problem is by converting the 1-pentene into more useful products. If 1-pentene can be oligomerized to higher chain olefins, which are more in demand industrially, then the products would be more profitable to sell. C_{10}-C_{20} hydrocarbons falls into the paraffinic diesel range and are possible products of 1-pentene oligomerization. Also, as mentioned previously, diesel produced in this way does not contain any sulphur or aromatics which ordinary diesel fuels do, and thus burns much cleaner causing a decrease in air pollution and subsequently making it more environmentally friendly. C_{25}-C_{30} hydrocarbons fall into the synthetic lubricant and wax range which is also in higher demand in industry than 1-pentene.[9] Thus synthesizing a catalyst that oligomerizes 1-pentene selectively to industrially important products is of great research interest.

However, there are not many reports of pentene oligomerization using transition metal catalysts in the literature. A few research efforts in this field are mentioned below.

Schofer *et al*. synthesized mononuclear scandocene tetramethylaluminate complexes as catalysts for 1-pentene oligomerization.[10] These catalysts produced a large range of oligomers from C_{10}-C_{85}, with some catalysts being more selective than others. The structures of the complexes are shown below in Figure 3.3.

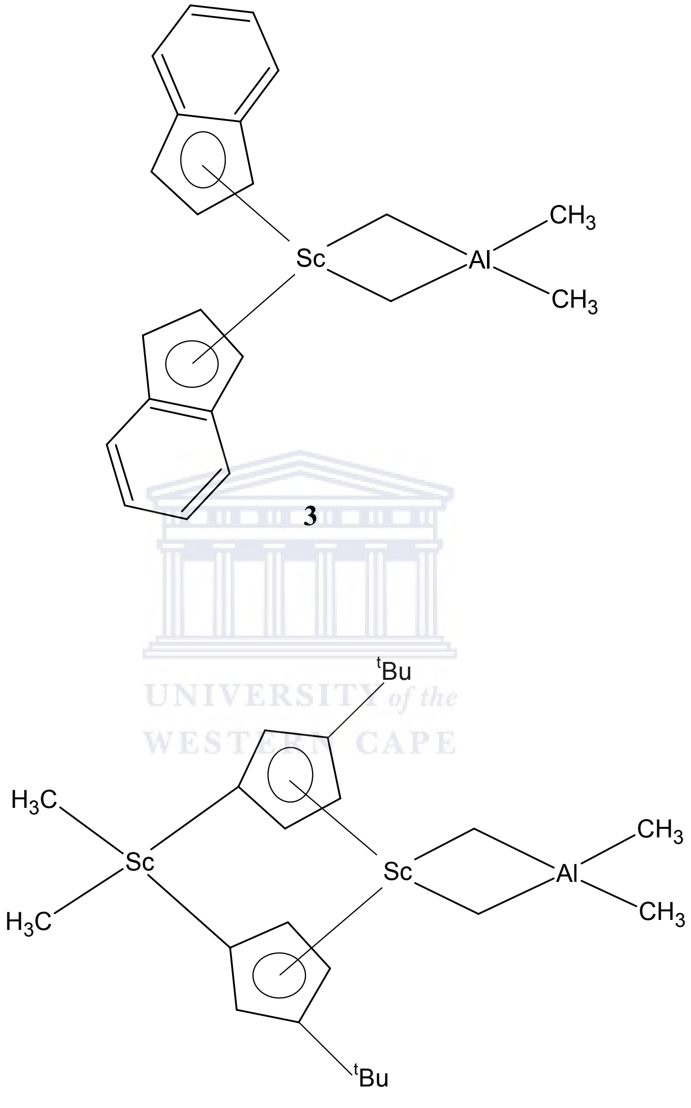

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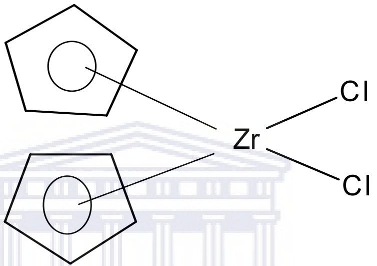
Figure 3.3: Scandium tetramethylaluminate complexes.[10]

For catalyst **3** they found that an increase in reaction time leads to higher molecular weight oligomers being obtained. Catalyst **4** produces mostly dimers of 1-pentene with small amounts of trimers and tetramers also being obtained. However, when the reaction time using this catalyst was increased, the same range of oligomer molecular weights is observed with greater amounts of each oligomers being obtained. Thus reaction time has no effect on the nature of the product for this catalyst but only on the overall yield.

The oligomerization of 1-pentene with hafnocene and zirconocene catalysts were studied by Wahner *et al.*[11] Products ranging from the dimer of 1-pentene to poly-1-pentene were formed. The number average molar mass (M_n) of the poly-1-pentene was 5100g/mol. An example of one of the complexes is shown below in Figure 3.4.

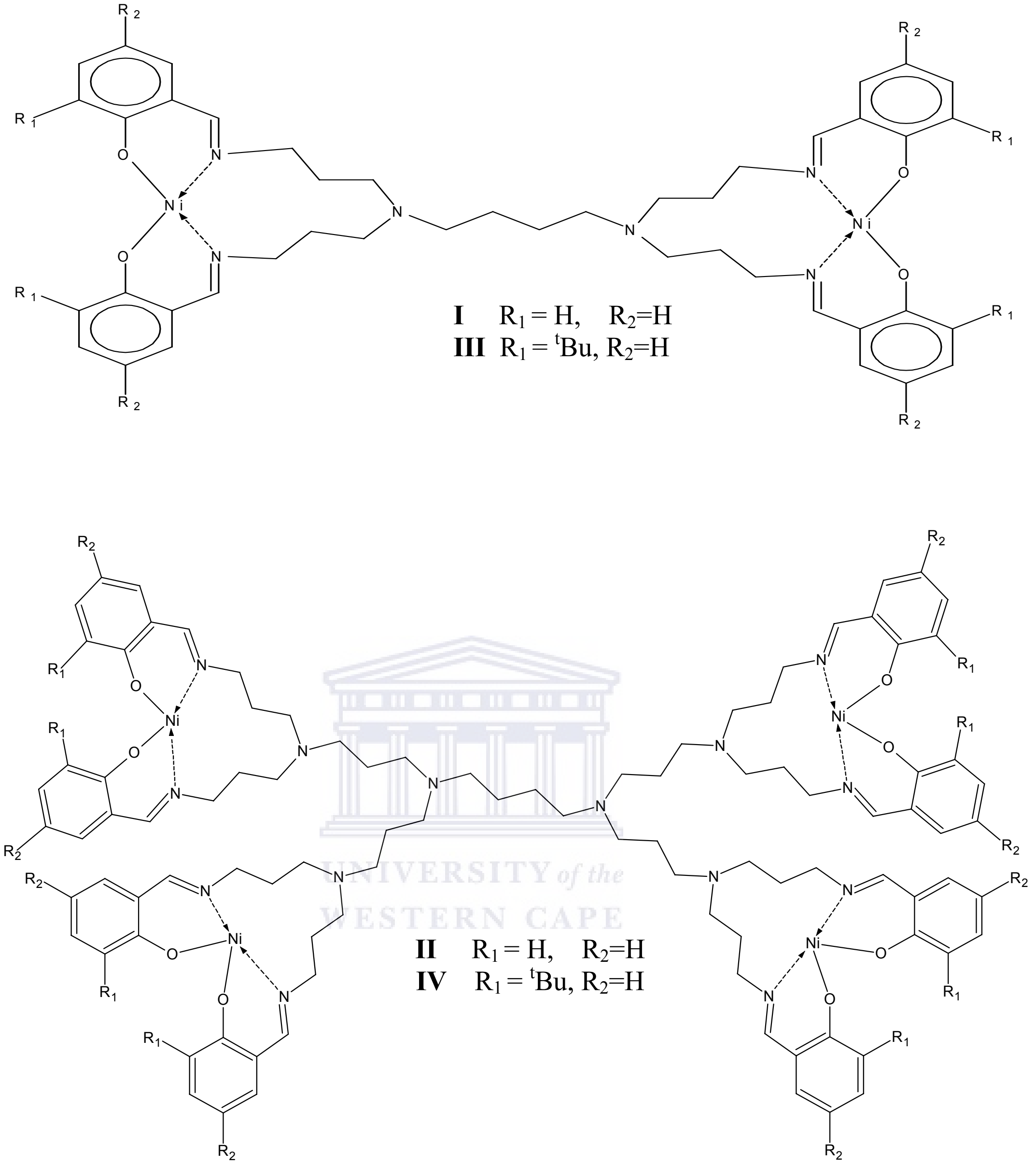


5

Figure 3.4: Zirconium metallocene complex.[11]

Catalyst **5** gave dimers, trimers and tetramers of 1-pentene. Even when the MAO:Metallocene ratio was varied, the tetramer (C_{20}) remained to be the dominant product. At optimum conversion of 80% at a MAO:M ratio of 6000:1, a 1:2:2.2 ratio of C_{10}:C_{15}:C_{20} is obtained.

In this chapter we discuss the results of using unsubstituted complexes **I** and **II** as catalysts for the oligomerization of ethylene. We also report using these complexes (**I** and **II**) as well as the mono substituted nickel complexes (**III** and **IV**) as catalysts for the oligomerization of 1-pentene. The effect of substituents on the activity and selectivity of the catalysts are discussed. The structures of the complexes are shown in Figure 3.5.



I $R_1 = H$, R_2=H

III $R_1 = {}^tBu$, R_2=H

II $R_1 = H$, R_2=H

IV $R_1 = {}^tBu$, R_2=H

Figure 3.5: Generation 1 and generation 2 dendrimeric salicylaldimine nickel complexes.

3.2 Results and Discussion:

3.2.1: Ethylene Oligomerization.

The ethylene oligomerization reactions were carried out in a 300 ml steel autoclave. Methylaluminoxane (MAO, 10% in toluene solution), $EtAlCl_2$ and Et_2AlCl were evaluated as co-catalysts for this process using complexes **I** and **II** as catalyst precursors. Of the three co-catalysts only $EtAlCl_2$ showed activity under the reaction conditions employed. The reaction conditions were kept constant except for the Al:Ni ratios which ranged from 20:1 – 3000:1. The ethylene pressure was kept constant at 5atm. All reactions were performed at room temperature. The metal concentration was kept constant irrespective of the catalyst precursor employed. These reaction conditions are typical of those reported in the literature for ethylene oligomerization reactions. However, it is common practice to vary the pressure and temperature to obtain the optimum reaction conditions for the catalyst precursor used.

3.2.1.a. Activity.

The results for the activity of the generation 1 (**I**) and the generation 2 (**II**) complexes expressed as turn over number (TON) are given below in Table 3.1. TON is defined as the amount (in kg) of total products produced per mol of nickel per hour. The oligomeric products were weighed after evaporation of the solvent via rotary evaporation. The generation 1 (G1) catalyst (**I**) showed optimum activity at an Al:Ni ratio of 500:1 while the generation 2 (G2) catalyst (**II**) showed optimum activity at an Al:Ni ratio of 2000:1. The overall activity of the G2 catalyst is significantly higher than that of the G1 catalyst. However optimum activity for the two catalysts is achieved at a different Al:Ni ratio. Thus for the G2 catalyst to obtain optimum activity, the Al concentration has to be increased four fold to that used in reactions of the G1 catalyst. The reason for this difference in behaviour of the two catalysts could possibly be found in the differences in the architecture of the two dendrimer generations. The G1 catalyst has two tertiary amine units within its internal structure, while the G2 catalyst has six tertiary amine units. In both cases these tertiary amines, being Lewis donor sites, are potential positions for coordinating to the Lewis acidic organoaluminium co-catalyst. It is thought that the co-catalyst, $EtAlCl_2$, first coordinates to these Lewis basic sites before activation of the metal centre occurs. It is well known that N-donor molecules form adducts with Lewis acidic Al complexes.[12-14] Since the G2 catalyst has more N-donor sites it will react with a larger amount of the aluminium alkyl than the G1 catalyst. It therefore requires larger amounts of co-catalyst before the optimum activity is reached.

Table 3.1: Ethylene oligomerization activity of the unsubstituted Ni complexes **I** and **II**.

Entry	**Al:Ni**	**TON[a]** **G1**	**TON[a]** **G2**
1	20	120	42
2	50	556	106
3	100	1088	436
4	200	1400	718
5	500	**2600[b]**	798
6	1000	2000	2086
7	2000	1600	**4020[b]**
8	2500	-	2720
9	3000	-	1972

[a] TON - kg of total products produced per mol of nickel per hour. [b]Optimum activity.

The activity of the generation 2 catalyst is much lower than that of the generation 1 catalyst at Al:Ni ratios lower than the optimum ratio. Also the activities of both catalysts gradually decrease after optimum activity is reached. Our results reflect the general trend observed for the dendrimeric carbosilane nickel complexes reported by de Jesus[5] *et al.* which showed an increase in activity for ethylene oligomerization as the dendrimer generation increased form generation 1 to generation 3. In this case the activity expressed as TON observed for ethylene oligomerization ranged from 293-950 for G1-G3. These workers also observed that polyethylene was being produced concurrently with the oligomers. In addition the generation 1 catalyst produced more polyethylene than the higher generation catalysts. As the dendrimer generation increases, the oligomerization activity increases and the polymerization activity decrease. They also observed higher molecular weights and poly dispersity indexes (PDIs) for polymers produced by higher generation catalysts. We do not observe any polymer formation using our catalysts, even at relatively high Al:Ni ratios which often favours polymerization.

In addition, our dendrimeric nickel complexes are much more active for ethylene oligomerization than the carbosilane nickel dendrimers mentioned above. Our catalyst systems are up to four times more active than the most active catalyst produced by de Jesus *et al*.

The oligomerization activities displayed by our catalysts are also relatively good when compared to some mononuclear ethylene oligomerization nickel catalyst activities in literature. A few of these examples are mentioned below.

Zhang *et al.*[15] reported the use of ketiminato and diimine nickel complexes with a bidentate nitrogen ligand with a six-membered chelating ring as catalyst precursors for ethylene oligomerization using MAO as a co-catalyst. In this case TON values ranging from 81-1800 were obtained depending on the catalyst.

Heinicke *et al.*[16] synthesized P,O chelating phosphonyl phenolato nickel catalysts and obtained TON values ranging from 257-2218 for the oligomerization of ethylene.

Figure 3.4 below shows the plot of ethylene oligomerization activity versus the Al:Ni ratio for the G1 and G2 unsubstituted catalysts **I** and **II**.

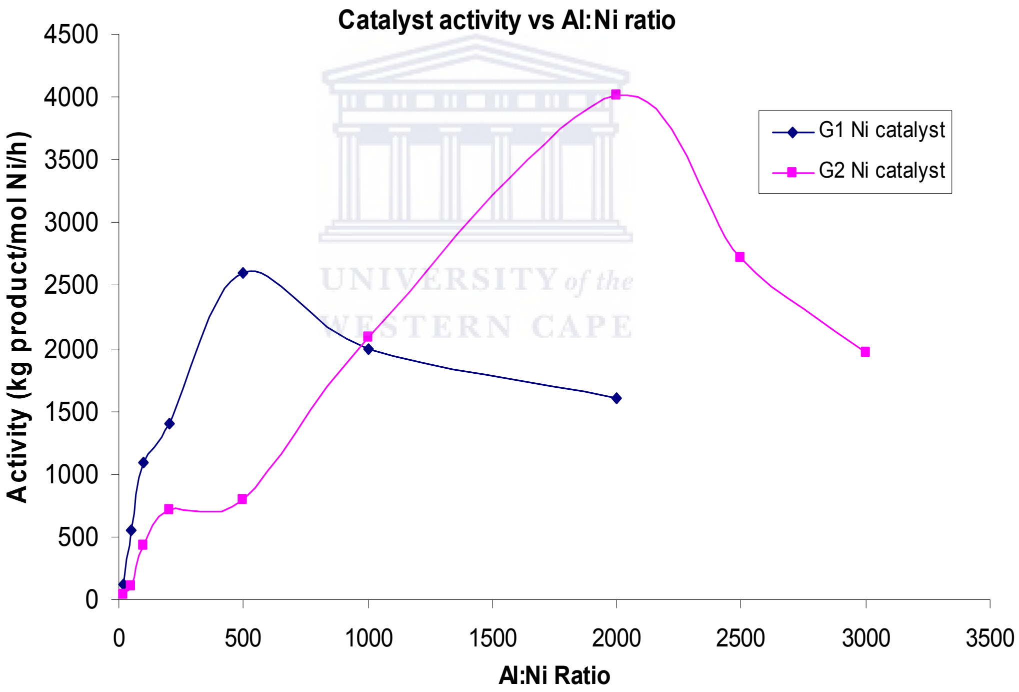


Figure 3.6: Activity of the unsubstituted nickel complexes for ethylene oligomerization.

3.2.1.b. Type of oligomers obtained.

Oligomers obtained from the G1 catalyst (**I**) at an Al:Ni ratio of 20:1-1000:1 were analyzed using gas chromatography (GC). The GC analysis was done on the residues after evaporation of the solvent. The GC results are tabulated in Table 3.2.

Table 3.2: GC results for oligomers obtained using complex **I** as a catalyst.

Al:Ni Ratio	% C_{10}	%C_{12}	%C_{14}	%C_{16+}
20	59	41	-	-
50	58	33	5	4
100	17	57	15	11
200	6	64	12	18
500	1	46	10	43
1000	-	-	-	100
2000	-	-	-	100

The GC results show oligomers ranging from C_{10} to those higher than C_{16}. From the results it is clear that the Al:Ni ratio has an effect on the product selectivity. At low Al:Ni ratios (20:1) the products are exclusively a mixture of C_{10} and C_{12} with C_{10} being formed in a slight excess to C_{12}. As the Al:Ni ratio is increased, we observe a steady decrease in the C_{10} level. Concurrently the C_{12} levels are increasing. In addition we also start observing the formation of longer chain oligomers. At Al:Ni ratios of 100:1 and 200:1, the C_{12} dominates with more than half of the product stream being the C_{12} fraction. It is also noticeable that beyond a 100:1 Al:Ni ratio, the C_{16}^{+} fraction shows a marked increase, until at very high levels of Al:Ni (1000-2000) oligomers with long carbon chains (C_{16}^{+}) are formed exclusively. From the results it would appear that at low levels of Al, the chain transfer process from the active Ni centres to the Al is much more rapid than chain growth. This results in shorter oligomers chains being formed. This is not unusual as often it has been reported that low Al:metal ratios tend to favour oligomerization over polymerization.

GC analysis was also performed on reaction mixtures obtained from reactions using the generation 2 catalyst (**II**). No short chain oligomers were observed in these samples. The only products isolated from the generation 2 catalyst were thick and waxy materials which were yellow-brown in colour. These oligomer samples were analyzed by gel permeation chromatography (GPC) using tetrahydrofuran (THF) as a solvent and against polystyrene standards. The GPC results for the oligomers obtained from the generation 2 catalyst are given in Table 3.3. The molecular weight (M_w) of the oligomers ranged from 72 900g/mol to 94 600g/mol indicating very long chain oligomers. The PDI for the generation 2 catalyst oligomers ranges from 1.57-1.99. The poly dispersity index (PDI) represents the molecular weight distribution. The values obtained are indicative of a relatively uniform distribution of oligomers of similar chain lengths. These results are good when compared to the PDI's obtained from using the previously mentioned nickel catalyst synthesized by Zhang[15], which ranges from 2.24-6.67.

The dendrimeric nickel complexes synthesized by de Jesus *et al* [5] produced oligomers with the PDI's ranging from 2.77-20.12 for the generation 1 – generation 3 complexes. Our dendrimer catalysts produced much better results when compared to those reported in the literature.

TABLE 3.3: GPC results for oligomers obtained from the Generation 2 catalyst.

Al:Ni Ratio	M_w(g/mol)	PDI (M_w/M_n)
20	8.05×10^4	1.59
50	7.29×10^4	1.99
100	7.96×10^4	1.87
200	8.92×10^4	1.54
500	7.59×10^4	1.49
1000	9.46×10^4	1.57

From our results we observe that our two dendrimer systems give very different oligomeric products. Oligomerization using the generation 1 dendrimer complex (**I**) results in short chain oligomers whereas using the generation 2 dendrimer catalyst (**II**) results in very long chains with molecular weights up to 94600 g/mol. Evidently the rate of chain transfer is faster for the generation 1 catalyst than the generation 2 catalyst. The reason for this need to be further investigated.

However, it appears that in the case of the generation 2 catalyst, the rate of the β-hydride elimination process is slowed down relative to that of the generation 1 case. This could possibly be due to the fact that the generation 2 catalyst experience greater steric crowding around the active centre. This would hinder β-hydride transfer from the growing alkyl chain to the metal centre. The retardation of β-hydride transfer would result in longer oligomers chains.

3.2.2: 1-Pentene Oligomerization.

Preliminary reactions have been done on the use of complexes **I-IV** as catalyst precursors for the oligomerization of 1-pentene.

1-Pentene was oligomerized at room temperature using modified methylaluminoxane (MMAO) as a co-catalyst and toluene as a solvent. The nickel amount (25µmol) was kept constant irrespective of the catalyst employed. The pentene:metal ratio was 5000:1 and reaction time was 1 hour. These reaction conditions are typical for pentene oligomerization and were also employed by Schofer *et al.*[10] After the appropriate reaction time, an aliquot of the reaction mixture was taken for GC analysis. The oligomerization reaction was then quenched by adding methanol (10 ml). No precipitate was observed during the quenching process. The solvent was evaporated by rotary evaporation to leave a light powder solid residue.

3.2.2.a: Conversion.

In Table 3.4, the percentage conversion of pentene is given. This gives an idea of the efficiency of the nickel catalysts.

Table 3.4 : % Conversion of 1-pentene to total products.

Al:Ni	Complex I[a]	Complex II[a]	Complex III[a]	Complex IV[a]
100	**58.1**	**86.3**	**71.4**	**68.2**
150	**76.0**	**88.6**	**84.0**	**78.7**
250	**68.0**	**71.4**	**83.4**	**85.6**
300	**71.4**	**71.4**	**82.0**	**85.3**
350	**61.1**	**70.0**	**68.6**	**96.7**

[a] % Conversion of 1-pentene as determined by GC analysis.

The % mass of 1-pentene converted ranges from 58-97%. Complex **IV** (the generation 2 substituted catalyst) gave the highest conversion (97%) at an Al:Ni ratio of 350. Both the generation 2 catalysts (**II** and **IV**) generally exhibit higher activity than the generation 1 analogues (**I** and **III**) although the dendritic effect is not so marked for the substituted salicylaldimine systems as for the unsubstituted salicylaldimine systems. The generation 1 and generation 2 unsubstituted salicylaldimine complexes (**I-II**) show similar trends in terms of conversion relative to the Al:Ni ratio. Both catalysts show optimum activity at an Al:Ni ratio of 150:1, after which the conversion gradually levels off. The substituted generation 1 complex (**III**) follows the same trend exhibited by the unsubstituted catalysts, but the activity of this catalyst is higher than both the generation 1 and generation 2 unsubstituted catalysts. The generation 2 substituted catalyst (**IV**) generally displays the highest activity of all four catalysts. An increase in Al:N ratio leads to an increase in the conversion of 1-pentene using complex **IV** as a catalyst precursor.

3.2.2.b: Selectivity.

The selectivity of these catalysts to produce trimers and tetramers of 1-pentene are given in Tables 3.5-3.8.

Table 3.5: Selectivity of the generation 1 unsubstituted nickel complex **I**.

Al:Ni	**% $^{a}C_{15}$**	**% $^{a}C_{20}$**	**% $^{a}C_{25}^{+}$**
100	**3.0**	**24.3**	**72.8**
150	**1.1**	**44.3**	**54.6**
250	**1.2**	**48.5**	**50.3**
300	**4.5**	**70.5**	**25.0**
350	**1.4**	**63.1**	**35.5**

[a] Mass % oligomer obtained relative to each other.

Catalyst **I** gave trimers, tetramers and higher olefins at various Al:Ni ratios. Trace amounts of C_{10} are also formed. The % of trimer formed by this catalyst is small irrespective of the Al:Ni ratio. We also observe that as the Al:Ni ratio increases, the C_{20} fraction also increase while the C_{25}^{+} fraction generally decreases. At an Al:Ni ratio of 300, this catalyst gives a 70% selectivity to C_{20}. The generation 2 unsubstituted catalyst (**II**) also produced trimers, tetramers and higher α-olefins from 1-pentene as shown in Table 3.6. Only a small percentage of trimer is formed with both C_{20} and C_{25}^{+} being the dominant product. There seems to be no trend regarding the Al:Ni ratio towards selectivity. These are preliminary results and further investigating is necessary.

Table 3.6: Selectivity of the generation 2 unsubstituted nickel complex (**II**).

Al:Ni	**% $^{a}C_{15}$**	**% $^{a}C_{20}$**	**% $^{a}C_{25}^{+}$**
100	**1.9**	**79.2**	**19.0**
150	**0.6**	**22.0**	**77.4**
250	**3.6**	**70.4**	**26.0**
300	**0.8**	**23.3**	**75.9**
350	**13.1**	**58.6**	**28.3**

[a] Mass % oligomers otained relative to each other.

Table 3.7: Selectivity of the generation 1 mono substituted nickel complex (**III**).

Al:Ni	**% $^{a}C_{15}$**	**% $^{a}C_{20}$**	**% $^{a}C_{25}^{+}$**
100	**6.1**	**14.7**	**79.2**
150	**1.9**	**47.9**	**50.1**
250	**0.4**	**9.7**	**89.8**
300	**2.5**	**30.5**	**67.1**
350	**4.8**	**86.5**	**8.7**

[a] Mass % oligomer obtained relative to each other.

The generation 1 mono substituted catalyst (**III**) selectivity results for 1-pentene oligomerization are given in Table 3.7. A small percentage of trimer is formed by this catalyst irrespective of the Al:Ni ratio, and there seems to be no trend in the % of tetramer and % higher olefin formation with regard to Al:Ni ratio. However, at an Al:Ni ratio of 350, 87% of C_{20} is formed by this catalyst, which is more selective to C_{20} than the unsubstituted catalysts discussed previously.

The selectivity of catalyst **IV**, the mono substituted generation 2 complex, is shown in Table 3.8.

Table 3.8: Selectivity of the generation 2 mono substituted nickel complex (**IV**).

Al:Ni	**% $^{a}C_{15}$**	**% $^{a}C_{20}$**	**% $^{a}C_{25}^{+}$**
100	**3.4**	**44.0**	**52.6**
150	**4.4**	**52.9**	**42.6**
250	**5.6**	**19.0**	**75.4**
300	**0.4**	**5.0**	**94.6**
350	**0.1**	**1.0**	**98.9**

[a] Mass % oligomers obtained relative to each other.

As with the other catalysts, a small amount of trimer is formed at all the Al:Ni ratios. Equal amounts of C_{20} and C_{25}^{+} is observed at Al:Ni ratios of 100-150. The production of higher chain oligomers is favoured at increasing Al:Ni ratios. Thus for example at Al:Ni of 350, the reaction yields largely C^{25+} oligomers. This indicates that the higher generation substituted catalyst forms longer chain oligomers than the lower generation unsubstituted catalyst. The substituted catalysts are also more selective towards certain oligomers when compared to the unsubstituted catalysts. The Al:Ni ratio affects the selectivity as well as the activity of all the catalysts but more reactions need to be cared out to establish optimum reaction conditions.

Small amounts of polymeric material were produced concurrently with the oligomers. The masses of the solid material isolated are shown in Table 3.9.

Table 3.9 : Polymeric material isolated.

Al:Ni	**Complex I**[a]	**Complex II**[a]	**Complex III**[a]	**Complex IV**[a]
100	**0.46**	**0.009**	**0.005**	**0.089**
150	**0.126**	**0.022**	**0.039**	**0.106**
250	**0.139**	**0.109**	**0.111**	**0.143**
300	**0.932**	**0.150**	**0.281**	**0.218**
350	**0.276**	**0.191**	**0.251**	**0.329**

[a] Mass of polymeric material in g.

3.3 Conclusion:

Both unsubstituted catalysts **I** and **II** are active in the oligomerization of ethylene. The generation 2 catalyst exhibits higher activity than the generation 1 catalyst. A definite dendritic effect exist. The type of oligomers formed is dependant on the nature of the catalyst. The generation 1 catalyst form short chain oligomers within the C_{10}-C_{20} diesel range. For the generation 1 catalyst, the type of oligomers produced varies with changes in the concentration of co-catalyst used. The oligomers obtained from the reactions using the generation 2 catalyst are long chained oligomers (M_w = 72900-94600g/mol) with a narrow PDI range. From these results we conclude that catalyst selectivity can be tailored by reaction conditions and the nature of the dendritic complex.

All four complexes (**I-IV**) evaluated are active as catalysts for 1-pentene oligomerization. The % conversion of 1-pentene to higher oligomers were very good reaching up to 97% using the generation 2 substituted catalyst (**IV**). In general, the generation 2 catalysts yield higher % conversions than the generation 1 catalysts. The substituted catalysts are more active and selective to certain oligomers than the unsubstituted catalysts. We also observe that the selectivity of the complexes is influenced by the dendrimer generation as well as the presence of substituents on the aryl rings of the ligands of the complexes. In general higher Al:Ni ratios lead to longer chain oligomers. The results of the conversion of 1-pentene to higher oligomers by dendrimeric nickel complexes seem promising although these are preliminary results. Further evaluation using higher Al:Ni ratios and subsequently optimizing reaction conditions will be done.

3.4 Experimental:

3.4.1: Ethylene oligomerization.

Toluene was dried by refluxing over sodium/benzophenone. $EtAlCl_2$ (25 % solution in toluene) was obtained from Sigma Aldrich and used without any further purification. Ethylene (99.9%) was obtained from Afrox and used as is. The GC analyses was done using a Varian CP-3800 with a HP PONA column. The internal standard used for GC analysis was Dodecane. The GPC samples were analyzed at Stellenbosch University using THF as a solvent and polystyrene as a standard, at a temperature of 30^0C.

Reaction conditions:

The catalyst amounts were varied to ensure a constant amount of Ni in the system at 5µmol. $EtAlCl_2$ was employed as a co-catalyst. The reaction time was one hour at room temperature. The ethylene pressure was maintained at 5 atm and the solvent employed was toluene (50 ml). Ethanol (10 ml) was used to quench the reaction. The Al:Ni ratios ranged from 20:1 – 3000:1.

General ethylene oligomerization procedure:

The ethylene oligomerization reactions were carried out in a 300 ml steel autoclave equipped with an overhead stirrer and internal cooling coil. The autoclave was loaded in a nitrogen-purged glove box. The appropriate amount of catalyst corresponding to 5µmol of nickel was suspended in dry toluene (50 ml) in a stainless steel PARR reactor. The required amount of $EtAlCl_2$ was added to the solution using a glass syringe. The reactor was sealed and removed from the glovebox. The reactor was flushed with dry nitrogen 3 times for 5 minutes. The ethylene pressure was set at 5 atm and maintained at this pressure throughout the oligomerization procedure. The reaction was conducted at room temperature for 1 hour. Unreacted ethylene was vented from the reactor at the end of the designated reaction time and the oligomerization was stopped by quenching the reaction mixture with 10 ml of ethanol. The solvent was evaporated via rotary evaporation and the product was weighed.

3.4.2: 1-Pentene oligomerization.

Toluene was dried by refluxing over sodium/benzophenone. 1-Pentene and MMAO (7% in heptane) was obtained from AKZO NOBEL, Netherlands, and used without any further purification. Standard Schlenk techniques were employed for air and moisture sensitive compounds. The GC analysis was done using a Varian CP-3800 with a HP PONA column. Hexadecene was obtained from Sigma Aldrich and used as an internal standard for the GC analysis.

Reaction conditions:

Amount of Ni used was 25µmol. MMAO (7% in heptane solution) was employed as a co-catalyst. Reaction time was one hour at room temperature and the total volume of the reaction mixture was constant at 31ml using toluene as a solvent. The pentene:Ni ratio was kept constant at 5000:1. Methanol (5 ml) was used to quench the reaction. The Al:Ni ratios ranged from 100:1 – 350:1.

General 1- pentene oligomerization procedure:

The appropriate amount of catalyst corresponding to 25µmol of Ni was added to an appropriate amount of dry toluene, in a RB flask, under nitrogen. 13.5ml of 1-pentene was then added to the solution while stirring. Lastly, the oligomerization was activated by the addition of the required amount of modified methylaluminoxane (MMAO). The reaction was allowed to stir at room temperature for 1 hour. A sample was taken from the reaction vessel at the end of the reaction, for GC analysis. The oligomerization then was stopped by the addition of 5ml of methanol. The solvent was evaporated. The non-volatile product was thus isolated.

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Chapter 4

Vinyl Polymerization of Norbornene

4.1 Introduction to Norbornene Polymerization:

There are several ways in which norbornene can polymerize, namely by ring-opening metathesis polymerization (ROMP), cationic and radical polymerization and vinyl polymerization. Each route leads to a different type of polynorbornene with different properties.[1] Figure 4.1. below shows the different routes to polynorbornene.

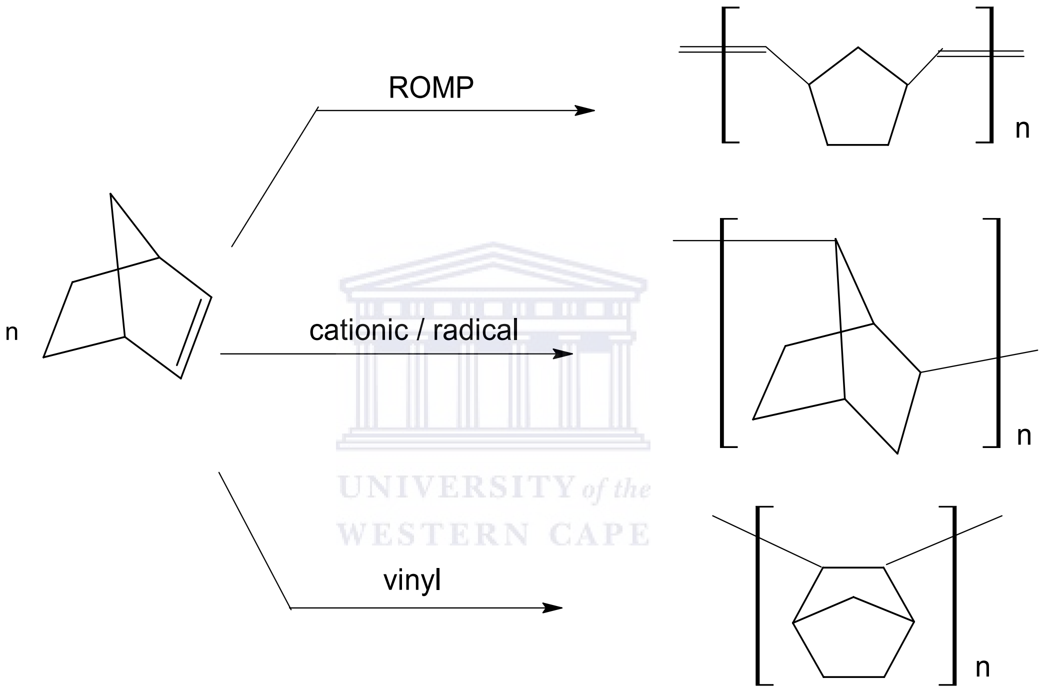

Figure 4.1: Three different routes to polynorbornene.

In the 1950's, Anderson and Merckling first produced norbornene polymers via ROMP.[2] ROMP is the most commonly known route to produce polynorbornene. The metathesis polymer still contains the double bond in the backbone which makes crosslinking or vulcanization possible. The vulcanized product is used as vibration and sound dampening material as well as for engine mounts, shock – proof bumpers and oil sponges.[3]

The radical and cationic polymerization of norbornene was first described in 1967. Polynorbornene obtained via this route is usually a low molar mass oligomeric material. In this case the norbornene framework is rearranged to produce poly (2,7-bicyclo[2,2,1] hept-2-ene) oligomers.[4] There are reports in the literature of several initiators for radical and cationic norbornene polymerization. These include ethylaluminium dichloride ($EtAlCl_2$), azoisobutyronile (AIBN) and tert butyl perpivilate.[5]

Vinyl polymerization of norbornene yields a 2,3 connected polynorbornene. In this instance the double bond is no longer present in the polynorbornene framework. Vinyl polymerization of norbornene is also known as addition polymerization and was first reported by Sartori *et al*.[6]

Polynorbornene obtained via the vinyl addition mechanism has special properties such as a high glass transition temperature, high transparency, high thermal stability and low birefringence.[7] Vinyl polynorbornene films have been applied as cover layers for liquid crystal displays (LCD's).[8] It has also been investigated as a blending ingredient to stiffen polyolefin films. These factors make research in vinyl norbornene polymerization of great interest to industry.

The transition metal complexes of nickel, chromium, palladium, titanium, zirconium and cobalt are reported in literature as good vinyl polymerization catalysts. Nickel and palladium complexes especially display extremely high catalytic activity with excellent performance. A few examples are mentioned below.

Hou *et al.* reported the preparation of acylhydrazone nickel(II) complexes and investigated their catalytic behavior in the vinyl polymerization of norbornene.[9] They used methylaluminoxane (MAO) as a co-catalyst and found these complexes to be highly active for this process. An example of the catalyst is shown below in Figure 4.2.

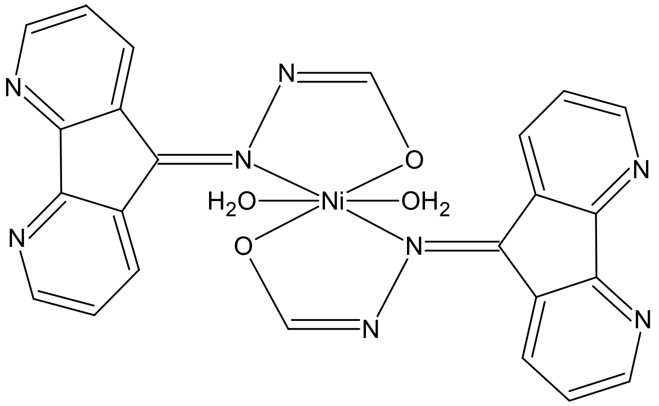

Figure 4.2: Acylhydrazone nickel(II) complex.[9]

They concluded that polynorbornene productivity and molecular weight rely greatly on the ratio of nickel precursor to the amount of MAO and as well as to the monomer concentration.

Chang *et al.* synthesized bis (1-aryliminomethylenylnaphthalen-2-oxy) nickel complexes, which they tested as catalysts for vinyl polymerization of norbornene.[10] When activated with MAO as a co-catalyst, these complexes exhibit good catalytic activity. An example of one of the complexes is shown in Figure 4.3.

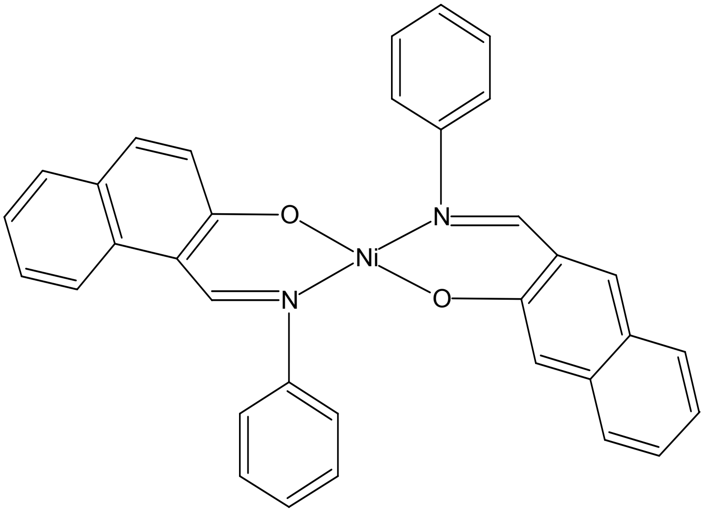

Figure 4.3: Structure of bis (1-aryliminomethyl enylnaphthalen-2-oxy) nickel complex.[10]

N-donor ligand complexes of palladium have also been evaluated by Shin *et al.* as catalysts for the vinyl polymerization of norbornene.[11] Figure 4.4 shows the structure of one such complex.

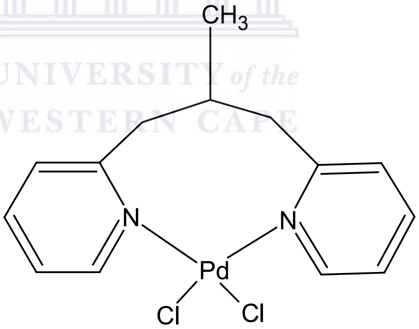

Figure 4.4: 1,3 – di (2-pyridyl) propene palladium complex.[11]

These Pd(II) dipyridyl complexes are very active catalysts, producing high molecular weight polymers. The resulting polynorbornene was insoluble in chlorobenzene, which made characterization difficult.

In this chapter we discuss the use of dendrimeric complexes **I-IV** as catalysts for the polymerization of norbornene, via the vinyl addition process.

4.2 Results and Discussion:

The nickel complexes **I-IV** was evaluated as catalysts in the vinyl polymerization of norbornene. Methylaluminoxane (MAO) was used as an activator employing different MAO:metal ratios. The reactions were performed at room temperature using a constant substrate and metal concentration. 5μmol of nickel was used in all the reactions. The monomer:metal ratio was kept at 5000:1.

These conditions are similar to those employed by Yang[12] *et al.* who used monomeric bis salicylideneiminato nickel catalysts. Reactions were performed over a 30 minute period. Quenching the reaction with a methanol:HCl mixture lead to the formation of the polymer.

4.2.1 **Activity:**

All catalysts evaluated showed activity at the various Al:Ni ratios. The results for unsubstituted salicylaldimine complexes **I** and **II** are tabulated in Table 4.1.

The generation 1 unsubstituted nickel complex (**I**) shows optimum activity of 328 kg.mol^{-1}Ni/h at a Al:Ni ratio of 4000:1 whereas the generation 2 unsubstituted nickel catalyst (**II**) exhibits optimum activity of 792 kg.mol^{-1}Ni/h at Al:Ni ratio of 4500:1. It is evident from these results that the generation 2 unsubstituted complex exhibits higher catalytic activity than the generation 1 unsubstituted complex over a wide range of Al:Ni ratios. The % conversion of norbornene was 84% for the generation 2 (**II**) complex at the optimum activity ratio of 4500:1, while the generation 1 (**I**) complex has a conversion of 34.9% at its optimum Al:Ni ratio of 4000:1. Both catalysts reach optimum activity at relatively high Al:Ni ratios. These ratios are greater than those normally observed for similar mononuclear complexes. Salicylideneiminato nickel complexes synthesized by Yang[12] *et al.* shows optimum activity at an Al:Ni ratio of 2000:1. At this ratio, a TON of 612 is obtained with a 65% conversion of norbornene. In another example, the use of aryliminomethylenylnaphthalen-2-oxy nickel complexes as catalyst precursors, reported by Chang[10] *et al.* shows optimum activity of 390 at an Al:Ni ratio of 10000:1 with an 82.9% conversion. In the latter case, a higher Al:Ni ratio was needed to obtain optimum activity. Both the afore-mentioned cases show lower activities and % conversions when compared to that of our unsubstituted generation 2 (**II**) catalyst. The higher activity of our dendritic system could be due to the increased local concentration of active sites within the dendrimer complex. In our systems, we also note that there is a definite dendritic effect with regards to activity. The generation 2 catalyst shows enhanced activity also related to the increased number of active sites compared to the generation 1 catalyst. The generation 2 catalyst due to its more branched nature might also be more effective in stabilizing the catalyst by preventing deactivation via metal agglomeration.

In Figure 4.5 (a plot of the activity of the G1 catalysts vs that of the G2 catalyst) it can be observed that the generation 2 catalyst needs more MAO to reach the optimum activity than the generation 1 catalyst. Tertiary amine groups within the internal framework of the dendrimer complexes can potentially act as Lewis base sites. Thus the MAO, which is a Lewis acid, first coordinates to these N atoms before activating the metal centres. The same phenomena was observed in ethylene oligomerization reactions and was discussed in detail in Chapter 3. Since the generation 1 catalyst has only two internal N atoms and the generation 2 catalyst has six internal N atoms that can act as Lewis bases, it can possibly explain why the Generation 2 catalyst needs more MAO to reach optimum activity.

Table 4.1: Activity of complexes **I** and **II** for norbornene polymerization.[a]

Entry	MAO:Ni	TON[b] Gen 1 (**I**)	TON[b] Gen 2 (**II**)
1	500	21.6	60
2	1000	37.6	72
3	1500	92	76
4	2000	112	96
5	2500	128	148
6	3000	252	440
7	3500	260	480
8	4000	**328**	520
9	4500	292	**792**
10	5000	252	628

[a]Reaction Conditions: catalyst, 5µmol Ni; time, 30 minutes, solvent, toluene; total volume, 25ml; temperature, room temperature; Monomer:Ni = 5000. [b] TON: Kg of polymer produced per mol of Ni per hour.

A similar reactivity trend is observed for the norbornene polymerization results obtained using the mono ^{t}Bu substituted complexes **III** and **IV** as shown in Table 4.2. The same reaction conditions were applied for these complexes as for the unsubstituted complexes. Once again both catalysts show optimum activity at high Al:Ni ratios. The generation 1 ^{t}Bu substituted nickel complex (**III**) shows an optimum activity of 512kg.mol^{-1}Ni/h at a

MAO:metal ratio of 3500:1 whereas the generation 2 ^{t}Bu substituted nickel catalyst (**IV**) exhibits optimum activity of 640 kg.mol^{-1}Ni/h at a MAO:metal ratio of 4000:1. Complex **IV** (Gen 2) is a more active catalyst than complex **III** (Gen 1), but as in the case of the unsubstituted nickel catalysts, the generation 2 substituted catalyst needs more MAO than the generation 1 substituted catalyst to reach optimum activity. Figure 4.6 shows the activity of the substituted catalysts versus the Al:Ni ratio.

When the activities of the unsubstituted nickel complexes are compared to these of the ^{t}Bu substituted nickel complexes, the generation 1 ^{t}Bu substituted complex exhibits a higher activity than the generation 1 unsubstituted complex. Thus in the case of the generation 1 catalyst, substituents on the aryl rings of the substituted complex aids in monomer insertion.

The unsubstituted mononuclear nickel complexes synthesized by Zhu[13] display lower activity for the vinyl polymerization of norbornene than their phenyl substituted analogues. This indicates that the introduction of an electron withdrawing group into the diketoiminato ligand increased the catalytic activity of the nickel complex. This has been proven when CF_3, a stronger electron-withdrawing group than phenyl, is used as a substituent. The activity increases but the molecular weight of the polynorbornene obtained, decrease. This is due to an increased rate of chain propagation which leads to faster chain transfer reaction causing lower molecular weight polymers.

Table 4.2: Activity of complexes **III** and **IV** for norbornene polymerization.[a]

Entry	MAO:Ni	TON[b] Gen 1 (**III**)	TON[b] Gen 2 (**IV**)
1	500	168	200
2	1000	188	228
3	1500	196	256
4	2000	224	300
5	2500	240	372
6	3000	264	516
7	3500	**512**	540
8	4000	500	**640**
9	4500	448	628
10	5000	440	588

[a]Reaction Conditions: catalyst, 5µmol Ni; time, 30 minutes, solvent, toluene; total volume, 25ml; temperature, room temperature; Monomer:Ni = 5000. [b] TON: Kg of polymer produced per mol of Ni per hour.

However, the generation 2 ^{t}Bu complex are less active as a catalyst than the generation 2 unsubstituted nickel complex. The reason for this could be the steric hindrance caused by the higher generation as well as the ^{t}Bu groups on the aryl rings of the substituted complex. Steric hindrance slows down the coordination of the monomer to the active site into the metal-carbon framing and this will decrease the rate of polymerization.

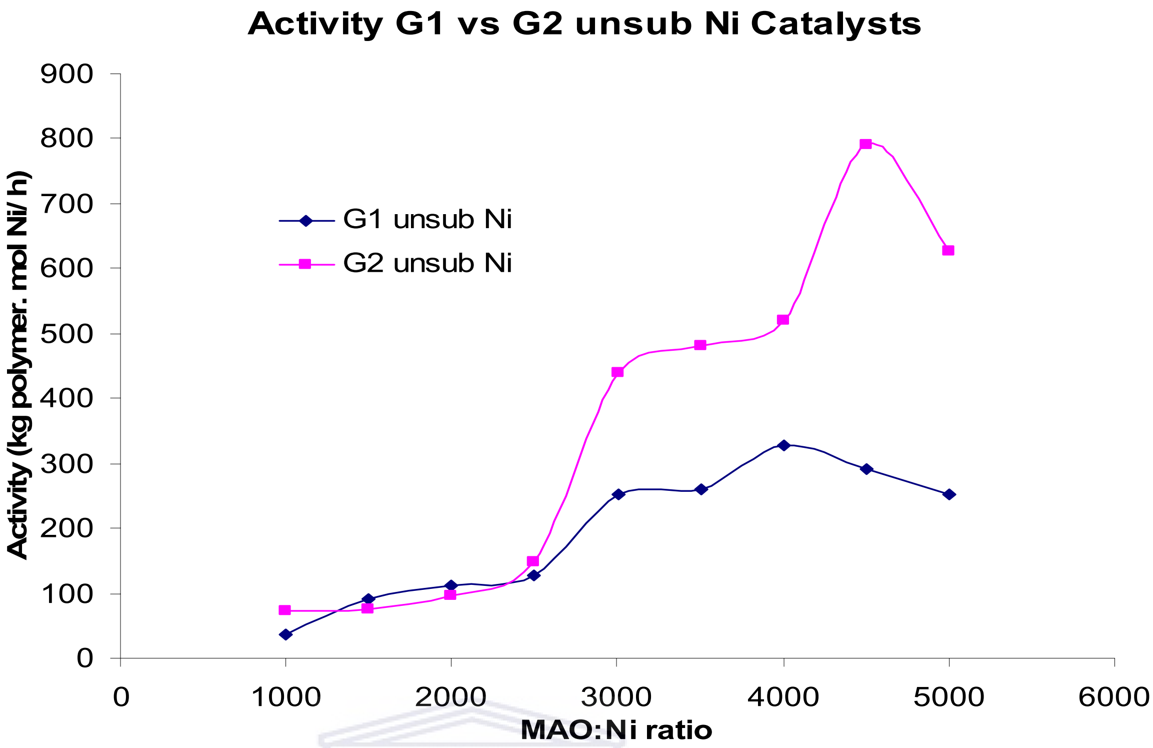

Fig. 4.5: Activity of complexes **I** and **II** for norbornene polymerization.

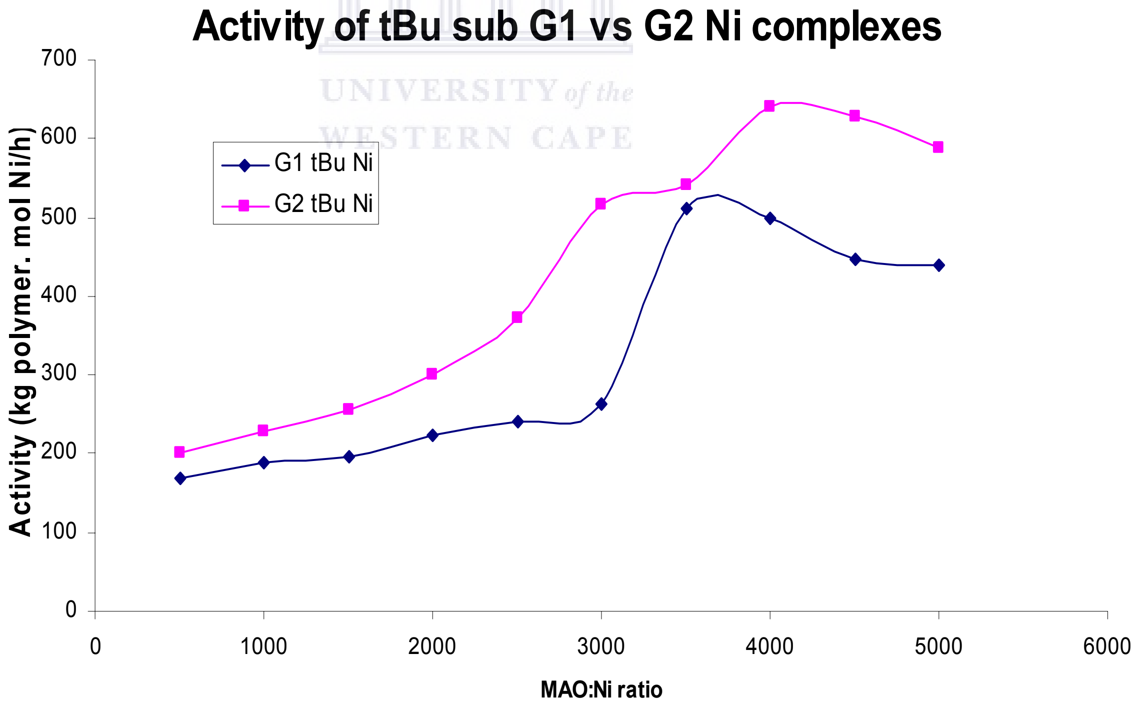

Fig. 4.6: Activity of complexes **III** and **IV** for norbornene polymerization.

4.2.2 Characterization of polynorbornene:

4.2.2.a. ^{1}H NMR.

The obtained polymers are only soluble in hot trichlorobenzene. Thus ^{1}H NMR was carried out in trichlorobenzene spiked with C_6D_6 at 130 ^{0}C. Figure 4.7 below is an example of a proton NMR spectrum of one of the obtained norbornene polymers.

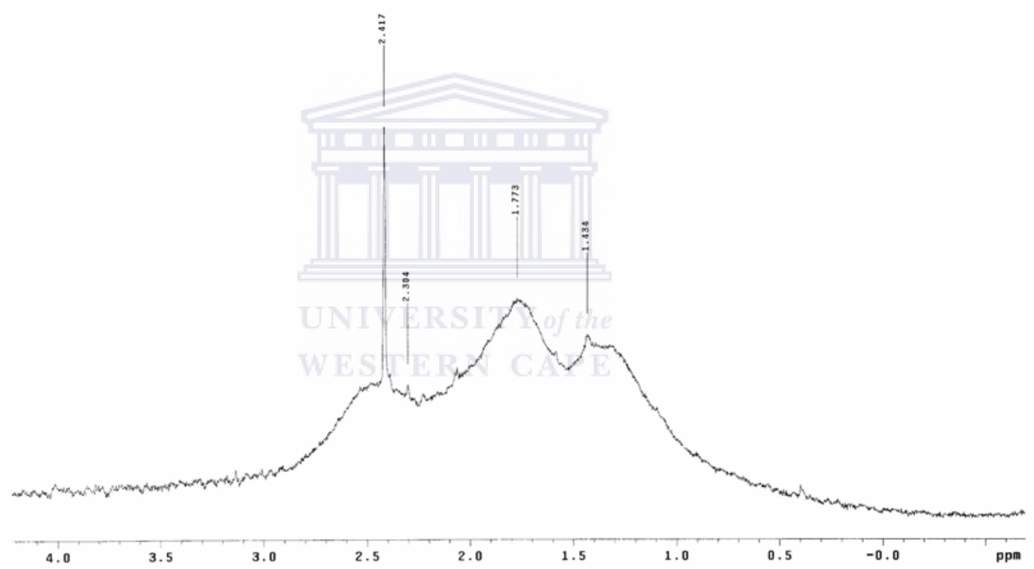

Figure 4.7: ^{1}H NMR spectrum of obtained polynorbornene.

From the ^{1}H NMR spectrum it can be noted that no trace of the C=C bond is present that is usually indicative of polynorbornene formed by ring opening metathesis polymerization (ROMP). In addition, since the product is not a low mass oligomer which it would have been in the case of cationic or radical polymerization, we can deduce that the product is typical of a vinyl addition norbornene polymer. This spectrum resembles that reported by Bao[14] *et al.* who also produced polynorbornene via the vinyl polymerization.

4.2.2.b: Gel Permeation Chromatography (GPC).

Polynorbornene samples obtained from reactions using catalysts **I-IV** at the various optimum Al:Ni ratios as well as at the Al:Ni ratios of 1500 and 3000 were analyzed by high temperature GPC. The polydispersity index (PDI) results are tabulated in Table 4.3, while the molecular weights of the polymers are in Table 4.4.

Table 4.3: PDI results for polynorbornene.

Catalyst	**PDI Al:Ni = 1500**	**PDI Al:Ni = 3000**	**PDI Optimum Al:Ni**
I	2.60	2.51	2.02
II	2.31	2.07	2.31
III	3.10	2.08	2.24
IV	2.46	2.26	2.04

The PDI is defined as the weight average molecular weight (M_w) divided by the number average molecular weight (M_n). This gives an indication of the distribution of chain lengths within the polymer sample. The PDIs for the polymers obtained from reactions using catalysts **I-IV**, ranges from 2.02-3.10. This represents a relatively uniform distribution and these results are very good when compared to PDI values in the literature for polynorbornene formation. For example Sun *et al.*[1] synthesized salicylaldiminato nickel complexes as catalysts for vinyl norbornene polymerization. The PDIs obtained from their polynorbornene ranged from 2.95-6.86 for various Al:Ni ratios.

The previously mentioned nickel complexes reported by Yang *et al.*[12] resulted in polynorbornene with PDI's ranging from 3.17-4.99 for various Al:Ni ratios between 500-2500. In both cases, our polynorbornene molecular weight distribution is narrower.

Bao *et al.*[14] produced polynorbornene with PDI's ranging from 2.28-2.49 using a ketoiminato nickel complex as a catalyst precursor. These results are most similar to our results obtained using our dendrimeric catalyst systems.

When comparing the substituted nickel complexes to the unsubstituted nickel complexes, we observe that in some cases the unsubstituted complexes have a lower PDI range than the substituted complexes. Also, the PDI range at optimum activities for the four catalysts is very narrow, ranging from 2.02-2.31.

The molecular weights of the polynorbornene obtained are given in Table 4.4. The molecular weights range from 512024-765880 g/mol indicating very long polymer chains present. Also, at optimum ratios the molecular weights of the polynorbornene range from 716148-765880 g/mol and are quite similar irrespective of the catalyst used.

From this we can conclude that our dendrimer catalysts produce similar chain lengths of polynorbornene irrespective of the dendrimer generation or the effect of substituents on the aryl rings of the complexes.

Polynorbornene produced by Yang[12] has molecular weights ranging from 6.31x10^5-1.51x10^6 g/mol at Al:Ni ratios between 500-2500.

Table 4.4: Polynorbornene molecular weights.

Catalyst	**M_W** **Al:Ni = 1500**	**M_W** **Al:Ni = 3000**	**M_W** **Optimum Al:Ni**
I	639000	512024	765880
II	688496	738519	720324
III	546270	722262	716148
IV	617162	682993	762387

4.3 CONCLUSION:

Complexes **I-IV** are all active as catalysts for the vinyl polymerization of norbornene. The generation 2 catalysts are more active than the generation 1 catalysts. The steric hindrance caused by the substituents on the aryl rings of complexes **III** and **IV** makes it less active as catalysts than the unsubstituted complexes **I** and **II**. Catalytic activities also rely on the ratio of MAO:metal. The GPC results indicate that the type of polynorbornene formed with regard to chain length, is similar regardless of the catalyst employed. Thus the dendrimer generation as well as the substituents on the aryl ring of the ligand has an affect on the activity of the complexes but not on the chain length or polydispersity of the polynorbornene obtained.

4.4 EXPERIMENTAL:

All work involving moisture and air sensitive compounds such as MAO was carried out using standard Schlenk techniques. GPC analysis was done at Sastech R&D using trichlorobenzene as a solvent at 160 ^{0} C and polystyrene as a standard. Toluene was dried by refluxing over sodium/benzophenone. Norbornene was obtained from Sigma Aldrich and dried over calcium hydride before being distilled. A 5M norbornene stock solution in toluene was prepared. Methylaluminoxane (MAO), a 10% solution in toluene, was obtained from Sigma Aldrich and used without any further purification.

Reaction conditions: The amount of Ni used was 5 µmol in all polymerization reactions. A 10% MAO (1.7 M) solution was employed as a co-catalyst. Reaction time was 30 minutes at room temperature. The norbornene:nickel ratio was 5000:1 and the total volume of the reaction mixture was 25 ml. A 95:5 Methanol:HCl solution was used to quench the reaction.

Typical Polymerization Procedure:

The amount of catalyst corresponding to 5 µmol of nickel was added to an appropriate amount of dry toluene in a Schlenk tube, under nitrogen. 5 ml (25 mmol) of a 5M norbornene in toluene solution was added to the reaction vessel. The required amount of MAO was then added to the reaction solution, to initiate the polymerization. The mixture was allowed to stir for 30 minutes at room temperature. The polymerization was stopped by adding the solution to 200ml of acidic methanol (95:5). A white solid precipitated from solution. The polymers were dried in the oven for 24 hours.

4.5 REFERENCES:

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