# Vinyl-addition polymerization of norbornene catalyzed by (pyridyl)imine Ni(II), Pd(II), Co(II), and Fe(II) complexes.

By

Danielle van der Westhuizen
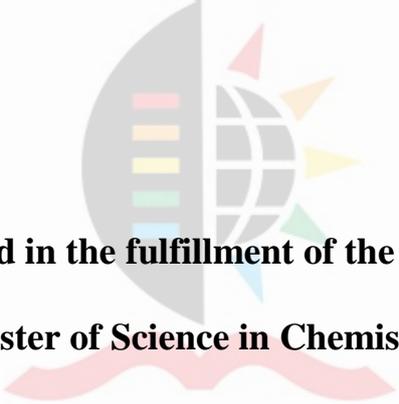
A dissertation submitted in the fulfillment of the academic requirements

for the degree of Master of Science in Chemistry, in the College of

Agriculture, Engineering and Sciences, University of KwaZulu-Natal.

March 2023

Supervisor: Professor Stephen O. Ojwach

DECLARATION:

I, Barend Danielle van der Westhuizen hereby declare that the project **"Vinyl-addition polymerization of norbornene catalyzed by (pyridyl)imine Ni(II), Pd(II), Co(II), and Fe(II) complexes"** is my own work and all other sources used have been sufficiently acknowledged through complete references.

Name: Barend Danielle van der Westhuizen

Signature…………………………. Date…03-03-2023………………………….

As a university supervisor; I approve this MSc dissertation for examination.

Supervisor: Prof Stephen Ojwach

Signature……………………………. Date: 14th August, 2023

DECLARATION: PLAGIARISM

I, Barend Danielle van der Westhuizen, declare that:

1. The research reported in this dissertation, is my original work, except where otherwise acknowledged or indicated, is my own original work.

2. This dissertation has never been submitted in part or full for any examination or degree to any other university.

3. This dissertation does not contain another person's writing, unless specifically acknowledged as being sourced from the researcher. Where other written sources have been quoted, then:

a. Their words have been re-written and the general information ascribed to them has been referenced.

b. Where their exact words have been used, their writing has been placed inside quotation marks, and referenced.

4. This dissertation does not contain any other individual's data, graphs, pictures, or other information, unless acknowledged.

5. This dissertation does not contain text, graphics, or tables copied and pasted from the Internet, unless acknowledged, and the source indicated in the dissertation and in the references sections.

This dissertation is basically a collection of data and material, prepared by myself, presented orally or as posters at conferences, or published as journal articles whereas in some instances, additional material has been included.

Student Name: Barend Danielle vd Westhuizen

Signature: …………………………… Date: …03-03-2023………………………..

ABSTRACT

The thesis reports the syntheses, and structural characterization of (pyridyl)imine transition metal complexes and their applications as pre-catalysts in the vinyl-addition polymerization of norbornene. The bidentate ligand (E)-N-(1-phenylethyl)-1-(pyridin-2-yl)methanimine (**L1**) was synthesized by reactions of 2-pyridine carboxaldehyde with (R)-(+)-α-methyl benzylamine in the presence of p-TsOH and obtained in moderate yields of 64%. On the other hand, the tridentate ligand (E)-1-(pyridin-2-yl)-N-(pyridin-2-ylmethyl)methanimine (**L2**) was obtained by reacting 2-pyridine carboxaldehyde with 2-picolylamine in the presence of p-TsOH in high yields of 90%. Reactions of bidentate ligand **L1** and tridentate ligand **L2** with $NiCl_2$, [Pd(COD)Cl$_2$], $FeCl_2$, and $CoCl_2$ metal salts gave the corresponding complexes [Ni(**L1**)$_2$Cl$_2$] (**Ni1**), [Ni(**L2**)Cl$_2$] (**Ni2**), [Pd(**L1**)Cl$_2$] (**Pd1**), [Co(**L1**)$_3$][2PF$_6$] (**Co1**), [Co(**L2**)Cl$_2$] (**Co2**), [Fe(**L1**)$_3$][2PF$_6$] (**Fe1**), [Fe(**L2**)Cl$_2$] (**Fe2**) in low to moderate yields (18% - 60%). The identities of the isolated complexes were confirmed by characterization with FT-IR spectroscopy, mass spectrometry, elemental analysis, single crystal X-ray crystallography for **Co1**, and nuclear magnetic resonance where applicable. The solid state structure of complex **Co1** was established as *tris*-chelated, containing three ligands to give an octahedral coordination environment.

The metal complexes were evaluated as pre-catalysts in the vinyl-addition polymerization of norbornene to produce poly(2,3-bicyclo[2.2.1]heptene) using modified methyl aluminoxane (MMAO) as the co-catalyst. Complex **Ni1** was the most active with catalytic activity of 22.7 g×10^3$_{(PNBE)}$.mol$_{(M)}$$^{-1}$.h^{-1} followed by complex **Pd1** which showed catalytic activity of 17.6 g×10^3$_{(PNBE)}$.mol$_{(M)}$$^{-1}$.h^{-1} whereas complex **Co1** showed 0.7 g×10^3$_{(PNBE)}$.mol$_{(M)}$$^{-1}$.h^{-1} and complex **Fe1** showed catalytic activity of 0.3 g×10^3$_{(PNBE)}$.mol$_{(M)}$$^{-1}$.h^{-1} concluding that the choice of metal center is of absolute importance to achieve high catalytic activity. The number of electron

donor atoms in the ligand structure influenced catalytic activity as bidentately chelated complex **Ni1** showed catalytic activity of 22.7 g×10^3$_{(PNBE)}$.mol$_{(M)}$$^{-1}$.h^{-1} whereas the tridentately chelated **Ni2** showed catalytic activity of 81.9 g×10^3$_{(PNBE)}$.mol$_{(M)}$$^{-1}$.h^{-1}.

The influence of reaction parameters were investigated using **Ni1** and **Ni2** as pre-catalysts and it was concluded that monomer/metal ratios, co-catalyst/metal ratios, reaction temperatures, reaction times, and solvent choice influenced catalytic activity. A higher monomer/metal ratio of 1250 resulted in catalytic activity of 17.5 g×10^3$_{(PNBE)}$.mol$_{(M)}$$^{-1}$.h^{-1} compared to the value of 6.8 g×10^3$_{(PNBE)}$.mol$_{(M)}$$^{-1}$.h^{-1} obtained from a lower monomer/metal ratio of 625. An optimum co-catalyst/metal ratio of 1500 was established and recorded catalytic activity of 33.7 g×10^3$_{(PNBE)}$.mol$_{(M)}$$^{-1}$.h^{-1}. Polymerization reactions at room temperature gave higher monomer conversions of 70% as opposed to lower conversions of 17% obtained at 50 °C. The choice of solvent influenced catalytic activities of the complexes, with the more polar *o*-chlorobenzene solvent giving the highest monomer conversion of 70% in comparison to 31% obtained in toluene solvent.

Polymers formed from all complexes were of the vinyl type with possible ring-opening metathesis polymeric inserts present in the polymer backbone. Thermal gravimetric analysis and differential scanning calorimetry of the formed polymers demonstrated that polymers formed from complex **Co2** and complex **Fe2** displayed degradation temperatures of 492 °C and 478 °C respectively opposed to polymers formed from complex **Ni2** and complex **Pd2** which gave values of 478 °C and 462 °C.

ACKNOWLEDGEMENTS

DEDICATION

To my wife Anica and my family.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SCHEMES

ABBREVIATIONS

AP	Anionic Polymerization
CHN	Elemental Analysis
COC	Cyclic olefin copolymer
CP	Cationic polymerization
CSD	Cambridge structural database
DSC	Differential scanning calorimetry
DCM	Dichloromethane
ESI-MS	Electron spray ionization mass spectrometry
FT-IR	Fourier transform infra-red spectroscopy
GPC	Gel permeation chromatography
h	Hours
HR-MS	High solution mass spectrometry
LC-MS	Liquid chromatography mass spectrometry
MAO	Methyl aluminoxane
MMAO	Modified methyl aluminoxane
Mp	Melting point
Mw	Molecular weight
NBE	Norbornene

NMR	Nuclear magnetic resonance
PDI	Polydispersity
PhCl	*o*-Chlorobenzene
PhMe	Toluene
PNBE	Poly-norbornene
ROMP	Ring-opening metathesis polymerization
R_T	Room temperature
s	Seconds
SC-XRD	Single crystal x-ray diffraction
SEC	Size exclusion chromatography
T_d	Thermal degradation temperature
T_g	Glass transition temperature
TGA	Thermal gravimetric analysis
TOF-MS	Time of flight mass spectrometry
VAP	Vinyl-addition polymerization
VNBE	Vinyl norbornene
VPNBE	Vinyl poly-norbornene

Chapter One

Introduction to transition metal catalyzed polymerization of norbornene: properties and applications

1.1 General background

Norbornene (NBE) or "bicyclo[2.2.1]hept-2-ene" is a very reactive strained cycloolefin that can be synthetically prepared by a Diels-Alder condensation reaction between ethylene (C_2H_4) and 1,3-cyclopentadiene (C_5H_6) [1, 2, 3]. High yields of NBE can be achieved by maintaining high reaction pressures with an excess amount of ethylene. The traditional Diels-Alder reaction describes a cycloaddition reaction between a conjugated diene and a dienophile [$4\pi + 2\pi$], where the dienophile must consist of at least one π-bond [4, 5]. In the case of NBE synthesis, 1,3-cyclopentadiene will serve as the conjugated diene and ethylene as the dienophile. The general reaction to produce NBE is illustrated in **Scheme 1.1**.

Norbornene (NBE)

Scheme 1.1: Diels-Alder synthesis of norbornene.

NBE and other reactive cycloolefin monomers are of great importance in the world of polymer synthesis, since NBE holds great potential for different structural variations of poly-

norbornenes utilizing homo-polymerization or co-polymerization [5, 6]. NBE polymerization can be achieved *via* three routes for example, ring-opening metathesis polymerization (ROMP), cationic or anionic polymerization, and vinyl addition polymerization (VAP), where the formed polynorbornene's characteristics are route-dependent (**Scheme 1.2**) [7, 8, 9, 5]. These characteristics are also subject to catalyst nature (cationic or neutral), the effect of the steric hindrance experienced, the metal center used, and the size of the chelate ring around the metal center [10, 2].

Scheme 1.2: ROMP-, cationic or radical- and vinyl-type polymerization of NBE [11].

Although it is possible to manipulate the formed polymer's characteristics with the catalyst system used, might desired properties be limited. It is possible to functionalize this strained cyclic olefin to form derivatives that might hold superior properties when polymerized [11]. Further derivatization of NBE (**Figure 1.1**) [5], can be achieved to obtain functionalized monomers consisting of alkyl groups (**1a**), cyclic hydrocarbon groups (**1b**), unsaturated hydrocarbon groups (**1c**), alcohol or ether groups (**1d**), carbonyl moiety groups (**1e**) nitrogen or carborane containing groups (**1f**), chromophore groups (**1g**), fluorene containing groups (**1h**) or halogen-containing groups (**1i**). Polymerization of such functionalized NBE (**Scheme 1.3**) monomers progresses analogues to the polymerization of non-functionalized NBE i.e., *via*

ROMP, VAP, and radical polymerization where catalytic activity might be influenced by substituents [5]. The advantage of polymerizing substituted forms of NBE, include overcoming limitations experienced with high glass transition state temperatures (T_g) and limited solubility as normally obtained from the unsubstituted monomer, therefore making functionalized NBE important in the engineering of high-performance materials with specialized applications [5]. For example, when NBE derivatives containing ester groups are polymerized, the possibility exist to obtain polymers with T_g ranging from -40 °C to 268 °C that are soluble in common organic solvents like dichloromethane, toluene, tetrahydrofuran, and chlorobenzene as opposed to the parent polymer with T_g exceeding 320 °C and insoluble in most of the solvents stated [12].

Figure 1.1: Norbornene derivatives.

Further refinement of polymer applications derived from the NBE monomer, includes the co-,

tri-, or tetra polymerization of NBE (**Figure 1.2**) with other monomers like ethylene [13, 14],

isoprene and octene [15], 1,3-butadiene [16], 1-hexene [17], styrene [18] or propylene [19]. It has been reported that the copolymerization of NBE with the above-stated monomers, showed altered properties as opposed to polymers obtained from the homopolymerization of NBE [20].

Scheme 1.3: Polymerization routes of functionalized polynorbornenes [5].

For example, polymers obtained from copolymerization of NBE with ethylene hold the advantage of having high-glass clarity, good solvent resistance, facile processability, and T_g of 200 °C [13] making it useful in applications such as optics, capacitor films, food, and drug packaging materials and medical diagnostic materials whereby polymers obtained from NBE alone consists of a T_g exceeding 300 °C. This indicates that it is possible to lower the T_g of the obtained monomer while maintaining a polymer with bicyclic units built into the polymer backbone. Further research has proven the altercation of this cyclic olefin copolymer's (COC) T_g by copolymerization of NBE with propylene that resulted in a T_g of 137 °C to 207 °C relative to the NBE insertion rate in the formed polymer [19]. A terpolymer formed from NBE, isoprene, and octene has a resulting T_g of 170 °C to 185 °C with improved solubility in halogenated organic solvents [15]. The solubility of formed polymers intended for optical

applications, are especially important as this determines the polymer's ability to be prepared as a film in solution casting.

Figure 1.2: Examples of norbornene-containing copolymers.

Copolymerization of NBE and polymerization of NBE derivatives, are significant in industrial applications with recognized potential for specialized engineering applications. Since the principles of homopolymerization apply to copolymerization and polymerization of NBE derivatives, the focus for the remainder of this chapter will be on the homopolymerization of unfunctionalized NBE.

1.2 Ring-opening metathesis polymerization of norbornene

Olefin metathesis reactions were first described in the 1950s where the redistribution of C-C double bonds is mediated by metal-containing species to form new C-C double bonds [21]. The generally accepted mechanism for metathesis can be viewed in (**Scheme 1.4**) and its discovery has found various applications mainly in organic synthesis [21]. Olefin metathesis polymerization was developed as an application of the metathesis principle, that well describes the ring-opening metathesis polymerization (ROMP) observed in strained cyclic olefins such as NBE and its derivatives. The process involves the conversion of cyclic olefinic monomers into linear polymers that comprises of olefins in the main polymer chain. Polymers obtained from ROMP methods offer yields of polymers with unique architectures with specialized applications.

Scheme 1.4:Olefin metathesis mechanism proposed by Chauvin [21].

The mechanism of ROMP can be viewed in **Scheme 1.5** [21]. ROMP is usually initiated with the coordination of the cyclic olefin to a metal alkylidene complex followed by a [2+2] cycloaddition that leads to the formation of a metallocyclobutane intermediate to polymer

propagation. A new metal alkylidene is formed when the intermediate undergoes cycloreversion. The sequence of events is repeated midst the propagation stage, until polymerization is terminated by the total consumption of the monomer and the equilibrium is reached. The solution is generally quenched by employing ethyl vinyl ether which interacts with the metal carbene species by removing the metal from a propagating polymer chain. Having a considerably high amount of ring strain makes cyclic olefins like cyclobutene, cyclopentene, and norbornene ideal for ROMP.

Scheme 1.5: Mechanism of ROMP [21].

Ruthenium-based catalysts hold the advantage of having low oxophilicity towards polar functional groups compared to Ti, Ta, W, and Mo complexes [21]. The first recorded ROMP of NBE has taken place in the 1960s but was only well-defined a decade later in 1975 when a Ru-based catalyst complex was used. Advances in Ru-based catalyst research led to the development of the Ru-carbene complexes such as the Grubbs 1st generation complex

synthesized from (PPh$_3$)$_3$RuCl$_2$ by reacting diazo benzylidene and the appropriate phosphine substituent. The Grubbs 1st generation complex allows the utilization of a wider range of monomers for metathesis chemistry employing Ru-based complexes. The Grubbs 2nd generation catalyst displays an extraordinarily high ROMP activity due to the ability of the NHC - ligand to enhance the dissociation of the *trans*-phosphine ligand from the Ru-centre to form a metathesis-active species. This system is often deemed unfavorable because polymers with unregulated molecular weights and high molecular weight distributions are obtained. The 3rd generation Grubbs catalyst also display high activity in living ROMP of NBE and NBE-derivatives yielding polymers with low molecular weight distributions (<1.10) because the system contains a strongly ligating NHC and weakly coordinating halogenated pyridines ensuring high initiation rates.

Figure 1.3: Three generations of Grubbs Ru-based catalysts used in the ROMP [21].

Industrial applications of poly(1,3-cyclopentylenevinylene), obtained by ROMP of NBE, have found critical applications in its vulcanized form in oceanic oil spillage clean-ups. Industrially, this material is known as Norsorex®, Telene®, or Zeonex® [10, 5]. Further applications of these materials showed significance as vibration-absorbing materials such as engine mounts,

shock-proof bumpers, and flexible couplings [10]. Norsorex® was introduced to the market in 1976 by CdF-Chimie in France, and later made its way to the markets of Japan and the USA in 1978 [22]. Norsorex® in its porous form has applications in oceanic oil spills because of its ability to absorb oil volumes of up to 400% of its own weight, and is also used as shape-memory resin and used in optical materials [23, 24, 10]. Commercial production of PNBE *via* ROMP generally entails the utilization of a $RuCl_3$/HCl catalyst in butanol as solvent, which produces a 90 % *trans*-polymer with a high molecular weight and T_g of 37 °C [22, 10]. Other processes, which are less popular employ metal centers such as titanium, niobium, tantalum, chromium, osmium, molybdenum, tungsten, and rhenium [8, 23]. The latter can be seen as the most favorable particularly in the forms of metal halides (e.g., $MoCl_5$, WCl_6), metal oxo-halides (e.g., $WOCl_4$), and alkoxohalides (e.g., $[(RO)_xWCl_{6-x}]$, x = 1-3) [8]. They are generally used in combination with alkylating agents such as R_4Sn, Et_2AlCl, and $AlEt_3$ and promoting agents such as O_2, EtOH, and PhOH [10, 8].

Another advantage of this polymerization route is that it is less sensitive to substituents on the monomer making it more favorable for producing specialty polymers [5]. The disadvantage of PNBE produced *via* ROMP lies in the high level of unsaturation in the polymer's backbone, which causes thermal instability [10]. With more than 20 000 papers published on the ROMP of NBE [21] to produce poly(1,3-cyclopentylenevinylene), where one double bond is retained in every repeated polymeric unit, makes this the best-understood polymerization method of NBE [7, 10, 25, 23]. NBE is considered the ideal strained cyclic olefin for ROMP due to the absence of bulky groups around the double bonds [21].

1.3 Isomerization polymerization of norbornene with cationic, anionic, and radical initiators

The least understood method in NBE polymerization is isomerization polymerization, which is described as utilizing cationic, anionic, or radical agents to rearrange the NBE structure to produce "poly(2,7-bicyclo[2.2.1]hept-2-ene)" oligomers, with low molecular weight, leaving the bicyclic unit of the monomer intact [10, 25, 9]. Isomerization polymerization was first described in 1967 with only a few reports published where high molecular weights were recorded [5]. A lack of data on the physical, thermal, and chemical properties of these type of polymers are evident, resulting from limited studies [11].

Typical initiators for the radical polymerization of NBE would include azoisobutyronitrile (AIBN), *tert*-butyl peracetate, or *tert*-butyl perpivalate whereby cationic polymerization would be initiated by $EtAlCl_2$ [10] and anionic polymerization would be achieved by employing *n*-BuLi and Et_3Al [11]. Bermeshev *et. al* proposed a mechanism for the cationic polymerization of a norbornene derivative, 5-methylene-2-norbornene (MNB) catalyzed by $H_2O/B(C_6F_5)_3$ which acts as the initiating system (**Scheme 1.6**) [11]. Polymerization commences by proton addition to the *exo* methylene group, generated when $B(C_6F_5)_3$ interacts with H_2O. This leads to the formation of the tertiary carbocation (**A**). Transannular rearrangement takes place whereby carbocation **A** rearranges to a sterically less hindered carbocation **B**. Propagation then takes place through the monotonous addition of the monomer's *exo* methylene double bond to carbocation **B** whereafter rearrangement of the formed tertiary carbocation takes place. Transannular polymerization is achieved whereby the cyclic diene monomer then serves as substrate in the cyclopolymerization. Chain termination results from further rearrangement of carbocation **B** to a more stable tertiary cations following a hydride shift or β-proton elimination.

Initiation

$$B(C_6F_5)_3 + H_2O \longrightarrow H^+[B(C_6F_5)_3(OH)]^-$$

Propagation

Termination

$$P_n^+[B(C_6F_5)_3(OH)]^- \xrightarrow{\text{Transfer Reactions}} \text{Dead chains}$$
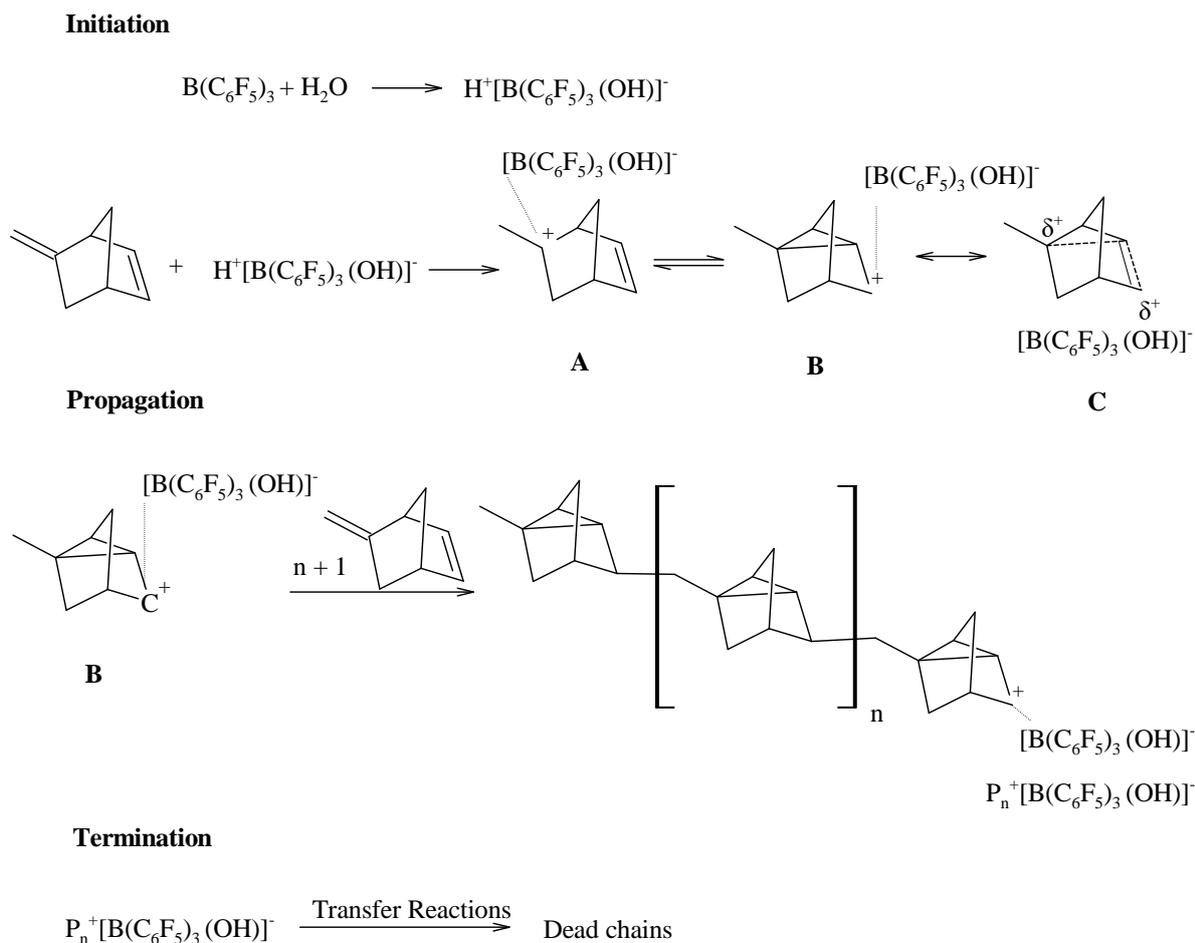
Scheme 1.6: Mechanism for cationic polymerization of a norbornene derivative [11].

1.4 Vinyl-addition polymerization of norbornene

Addition polymers are described as macromolecules formed from monomers consisting of a sp^2 carbon-carbon bond, whereby no byproduct is formed in the polymerization process, as in the case of condensation polymers [26]. The first successful vinyl addition polymerization (VAP) of NBE was reported in 1963 using a TiCl$_4$/Al(*iso*- Bu)$_3$ Ziegler-Natta catalyst system with an Al:Ti of 1:2, to form a cycloaliphatic polymer containing bicyclic structural units that are intact with no double bonds present [27, 28, 29, 30, 10]. The level of saturation achieved during VAP of NBE, is what makes the polymer highly resistant to chemical - and thermal

degradation [5, 31]. The disadvantage of using the traditional Ziegler-Natta catalyst system, is that this system, and also the cationic metallocene systems, are both sensitive to heteroatoms (S, O, N) which negatively affects the stability of catalysts and the co-catalysts [32]. Currently, transition metal complexes activated by methyl aluminoxane (MAO) or cationic complexes with weakly coordinating counter ions like BF_4^- or PF_6^-, are utilized as catalyst systems and generally result in polymers with uniform microstructures following this polymerization method [33, 24, 34]. Vinyl-addition polymerization solely involves interaction with the π - bond, leaving the bicyclic unit of the monomer intact after polymerization [27, 10, 35]. The bicyclic units act as strained rings that contribute to high rigidity in the polymer main chain [25].

The accepted mechanism for the VAP of NBE is conceived when MAO activates the transition metal complex by alkylation to produce the active species with an empty coordination site [36]. The NBE monomer occupies the empty coordination site whereby the metal - CH_3 bond is inserted, resulting in the regeneration of an empty coordination site. The repetition of these steps whereby the coordination site is regenerated leads to polymer chain propagation. Chain growth is eventually terminated by the residual MAO that acts as a chain transfer agent. The mechanism is illustrated in **Scheme 1.7**.
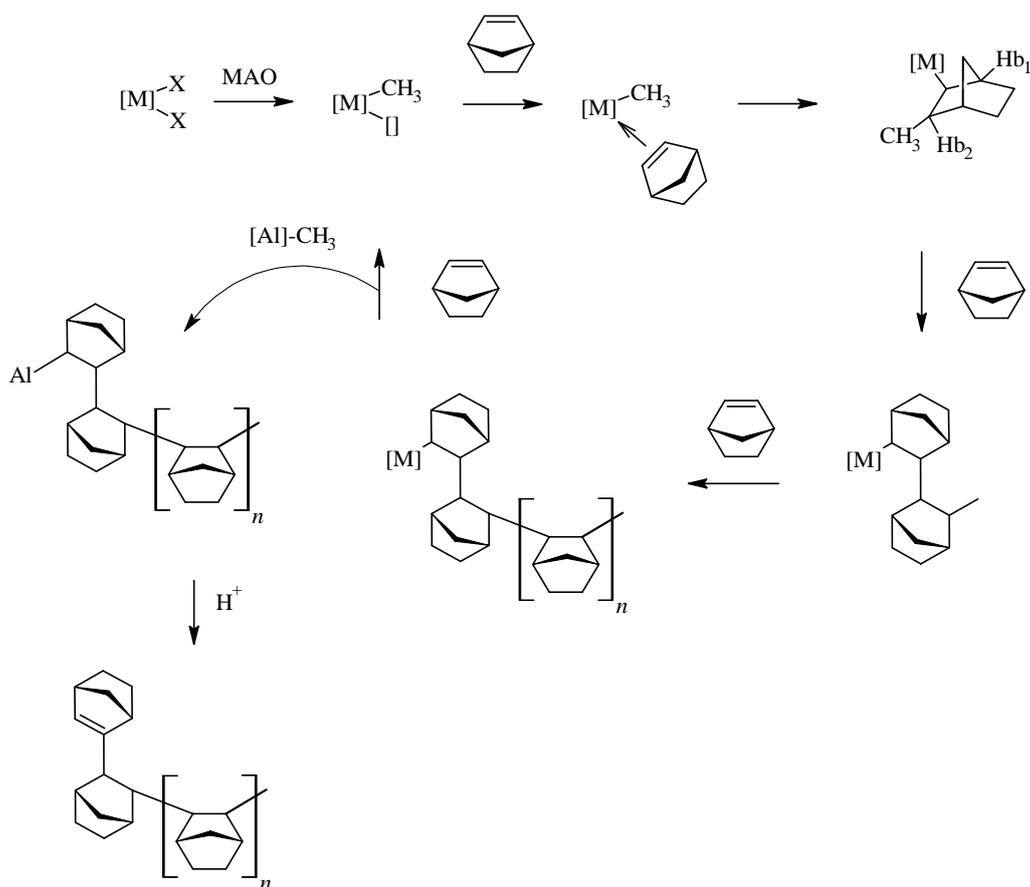
Scheme 1.7: The accepted mechanism for vinyl addition polymerization of norbornene by transition metal-based catalyst complexes [37].

As a result, vinyl PNBE consists of two stereo centers that give rise to the existence of two enantiomers for each monomer repeat unit [37]. The enantiomers consist of exo- and endo-stereo differentiation whereby the macroscopic properties of the polymer are dictated by the microstructure. The solubility of the VPNBE can be described by observing the stereoregularity of the polymer chain. It was found that VPNBE which consists of a high stereoregularity often display insolubility in organic solvents. This indicates that the VPNBE consists of a highly- or semi-crystalline structure. VPNBE that display soluble characteristics in organic solvents like cyclohexane and chlorinated aromatic hydrocarbons often display amorphous structures with low stereoregularity. This explains how the solubility of VPNBE is controlled by the

stereoregularity, and thus in turn is controlled by the catalyst system utilized. In general, catalysts that employ late-transition metals such as nickel(II), cobalt(II) and palladium(II) often deliver VPNBE that are both soluble and easily processable. VPNBE catalyzed by early and mid-table transition metals such as zirconium and chromium generally display insolubility in the same organic solvents. Polynorbornene consists of an exo- and endo-differentiation, that when the R- and S-configurations are considered, indicates that six isomeric stereoregular NBE polymers exist [10]. An exo-exo-enchainment takes place during propagation, and therefore PNBE will undergo conformational conversions to establish more stable conformers. Studying the microstructure of VPNBE with ^{13}C NMR poses challenging due to the bicyclic backbone of the polymer and tacticity investigations of vinyl polymers also proves difficult as the determination and interpretation are less developed than methods for acyclic olefins and ROMP polymers. The insolubility of some NBE polymers also further constrain characterization. The six isomeric stereoregular norbornene polymers, with *cis*-double bond opening assumed, can be seen in **Figure 1.4**. Advantages of a polymer with these characteristics include: high tensile strength, high chemical resistance, optical transparency, low birefringence, high glass transition temperature (T_g) $> 300\ °C$ [12], low dielectric constant, and large refractive indices and moisture absorption [7, 16, 15, 33, 38]. With good dielectric properties and good optical transparency, vinyl-polynorbornene receive a lot of attention from microelectronic and optical device manufacturers as well as applications in new optical information storage media [25, 39, 40]. These manufacturers will typically use vinyl-polynorbornene in deep ultraviolet photoresistors, interlevel dielectrics in microelectronics, as a cover layer for liquid crystal displays and other potential applications in packaging and gas separation [41].
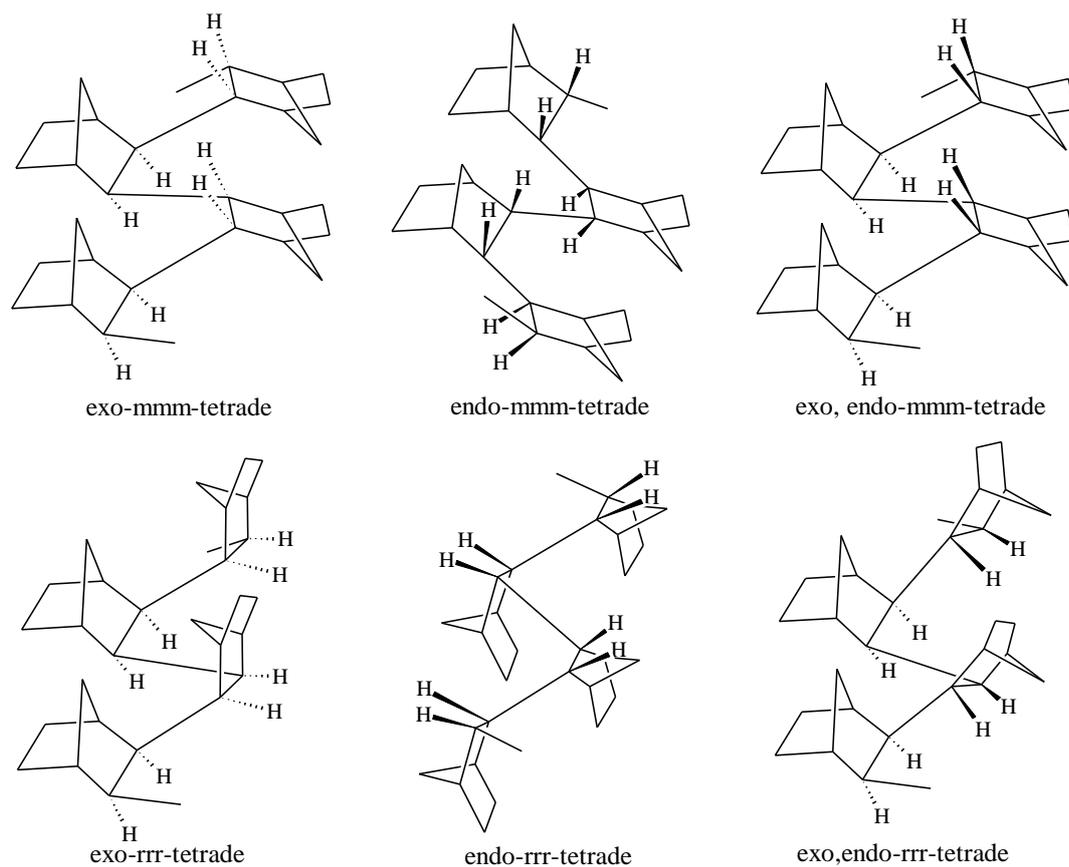
Figure 1.4: The six isomeric stereoregular norbornene polymers, displayed as tetrameric units [10].

In Chapter Two, an overview of the previously reported transition metal complexes employed as pre-catalysts in the polymerization of norbornene is given.

References

[1] Kauffman, George B.; Seymor, Raymond B.; Mason, Stewart M., "Happy and Unhappy Balls: Neoprene and Polynorbornene," *J. Chem. Educ.,* vol. 67, no. 3, pp. 198-199, 1990.

[2] J. Zhang, P. Wang, X. Wang, L. Wang, J. Chen and Z. Zheng, "Vinyl addition polymerization of norbornene catalyzed by b-iminoamine Ni(II) complexes/methylaluminoxane systems," *J. Organomet. Chem.,* vol. 696, pp. 3697-3702, 2011.

[3] E. Finkelshtein, M. Gringolts, M. Bermeshev, P. Chapala and Y. Rogan, J. Membr. Mater., Moscow, Russia: John Wiley & Sons Ltd., 2017.

[4] F. Fringuelli, The Diels-Alder Reaction: Selected Practical Methods, West Sussex, England: John Wiley & Sons, Ltd, 2002.

[5] M. Bermeshev and P. Chapala, "Addition polymerization of functionalized norbornenes as a powerful tool for assembling molecular moieties of new polymers with versatile properties," *Prog. Polym. Sci.,* vol. 84, pp. 1-46, 2018.

[6] J. Ni, C. Lu, Y. Zhang, Z. Liu and Y. Mu, "Norbornene polymerization and ethylene/norbornene copolymerization catalyzed by constrained geometry cyclopentadienyl-phenoxytitanium catalysts," *Polym.,* pp. 211-216, 2008.

[7] J. Meng, X. Li, X. Ni and Z. Shen, "High transparent alternate copolymer of norbornene with isoprene catalyzed by bis(phenoxy-imine) titanium complex," *RSC Adv.,* vol. 6, pp. 19351-19356, 2016.

[8]   G. Floros, N. Saragas, P. Paraskevopoulou, N. Psaroudakis, S. Koinis, M. Pitsikalis, N. Hadjichristidis and K. Mertis, "Ring Opening Metathesis Polymerization of Norbornene and Derivatives by the Triple Bonded Ditungsten Complex Na[W2(μ-Cl)3Cl4(THF)2]·(THF)3," *Polym.,* vol. 4, pp. 1657-1673, 2012.

[9]   H. Liang, J. Liu, X. Li and Y. Li, "Synthesis, structure and norbornene polymerization behavior of neutral palladium complexes," *Polyhedron,* vol. 23, pp. 1619-1627, 2004.

[10] C. Janiak and P. Lassahn, "Metal catalyst for the vinyl polymerization of norbornene," *J. Mol. Catal.,* vol. 166, pp. 193-209, 2001.

[11] M. Bermeshev, B. Bulgakov, A. Genaev, J. Kostina, G. Bondarenko and E. Finkelshtein, "Cationic Polymerization of Norbornene Derivatives in the Presence of Boranes," *Macromol.,* vol. 47, pp. 5470 - 5483, 2014.

[12] S. Breunig and W. Risse, "Transition-metal-catalyzed vinyl addition polymerization of norbornene derivatives with ester groups," *Macromol. Chem.,* vol. 193, pp. 2915-2927, 1992.

[13] I. Tritto, L. Boggioni, G. Scalcione, D. Sidari and N. Galotta, "Novel norbornene copolymers with transition metal catalysts," *J. Organomet. Chem.,* vol. 798, pp. 367-374, 2015.

[14] G. Zanchin, I. Pierro, E. Parisini, J. Marti-Rujas, G. Ricci and G. Leone, "Synthesis, structure and behavior of vanadium(III) diphosphine complexes in the homo- and co-polymerization of ethylene with norbornene: the ligand donor strength and bite angle make the difference.," *J. Organomet. Chem.,* pp. 142-150, 2018.

[15] R. Tanaka, R. Matsuzaki, Y. Nakayama and T. Shiono, "Synthesis of Highly Thermostable Norbornene-Isoprene-1-Octene Terpolymer with Titanium Catalyst," *Polym. Chem.,* vol. 55, pp. 2136-2140, 2017.

[16] S. Yamakawa, D. Takeuchi, K. Osakada, S. Takano and S. Kaita, "Copolymerizationof1,3-butadiene and norbornene catalyzed by Ni complexes," *React. Funct. Polym.,* vol. 136, pp. 19-24, 2019.

[17] H. Y. Jung, S. Hong, M. Jung, H. Lee and Y. Park, "Norbornene copolymerization with a-olefins using methylene-bridged ansa-zirconocene," *Polyhedron,* pp. 1269 - 1273, 2005.

[18] J. Bernard, V. Heroguez and H. Cramail, "Copolymerization of norbornene with norbornene terminated polystyrene macromonomer in the presence of Ni-based/MAO catalytic systems," *Polymer.,* vol. 43, pp. 7251-7256, 2002.

[19] W. Kaminsky, S. Derlin and M. Hoff, "Copolymerization of propylene and norbornene with different metallocene catalysts," *Polymer.,* vol. 48, pp. 7271-7278, 2007.

[20] W. Kaminsky, "Highly active metallocene catalysts for olefin polymerization," *J. Chem. Soc., Dalton Trans.,* pp. 1413-1418, 1998.

[21] S. Sutthasupa, M. Shiotsuki and F. Sanda, "Recent advances in ring-opening metathesis polymerization, and application to synthesis of functional materials," *Polym. J.,* vol. 42, pp. 905 - 915, 2010.

[22] J. Mol, "Industrial applications of olefin metathesis," *J. Mol. Catal. A: Chem.,* vol. 213, pp. 39 - 45, 2004.

[23] S. Aime, A. Arce, O. Chiantore, R. Gobetto, A. Russo and Y. De Sanctis, "Ring-opening polymerization of norbornene by (m-H)2Os3(CO)10 complex," *J. Organomet. Chem.,* vol. 622, pp. 43-46, 2001.

[24] Y. Sato, Y. Nakayama and H. Yasuda, "Controlled vinyl-addition-type polymerization of norbornene initiated by several cobalt complexes having substituted terpyridine ligands," *J. Organomet. Chem.,* vol. 689, pp. 744-750, 2004.

[25] G. Myagmarsuren, K. Lee, O. Jeong and S. Ihm, "Polymerization of norbornene by novel bis(acetylacetonate)palladium/ boron trifluoride etherate catalyst system," *Polymer.,* vol. 45, pp. 3227-3232, 2004.

[26] G. Odian, Principles of Polymerization, 4th Edition., Hoboken, New Jersey: John Wiley & Sons, Inc., 2004.

[27] N. Seehof, C. Mehler, S. Breunig and W. Risse, "Pd2+ catalyzed addition polymerizations of norbornene and norbornene derivatives," *J. Mol. Catal.,* vol. 76, pp. 219-228, 1992.

[28] F. Chang, D. Zhang, G. Xu, H. Yang, J. Li, H. Song and W. Sun, "Synthesis and characterization of new bis(1-aryliminomethylenylnaphthalen-2-oxy)nickel complexes and their catalytic behavior for vinyl polymerization of norbornene," *J. Organomet. Chem.,* vol. 689, pp. 936-946, 2004.

[29] S. Jie, P. Ai, Q. Zhou and B. Li, "Nickel and cationic palladium complexes bearing (imino)pyridyl alcohol ligands: Synthesis, characterization and vinyl polymerization of norbornene," *J. Organomet. Chem.,* vol. 696, pp. 1465-1473, 2011.

[30] P. Xiang and Z. Ye, "Homo- and Co-polymerization of norbornene and methyl acrylate with Pd-diimine catalysts," *J. Organomet. Chem,* vol. 798, pp. 429-436, 2015.

[31] X. Mi, Z. Ma, N. Cui, L. Wang, Y. Ke and Y. Hu, "Vinyl Polymerization of Norbornene with Dinuclear Diimine Nickel Dichloride/MAO," *J. Appl. Polym. Sci.,* vol. 88, pp. 3273-3278, 2003.

[32] T. Younkin, E. Connor, J. Henderson, S. Friedrich, R. Grubbs and D. Bansleben, "Neutral, Single-Component Nickel (II) Polyolefin Catalysts That Tolerate Heteroatoms," *Science,* vol. 287, pp. 460-462, 2000.

[33] L. Benade, S. Ojwach, C. Obuah, I. Guzei and J. Darkwa, "Vinyl-addition polymerization of norbornene catalyzed by (pyrazol-1-ylmethyl)pyridine divalent iron, cobalt and nickel complexe," *Polyhedron,* vol. 30, pp. 2878-2883, 2011.

[34] Y. Huang, J. Chen, L. Chi, C. Wei, Z. Zhang, Z. Li, A. Li and L. Zhang, "Vinyl Polymerization of Norbornene with Bis(imino)pyridyl Nickel(II) Complexes," *J. App. Polym. Sci.,* vol. 112, pp. 1486-1495, 2009.

[35] A. Abu-Surrah, K. Lappalainen, T. Repo, M. Klinga, M. Lesekela and H. Hodali, "Palladium(II) complexes bearing ethylene-bridged S-As and S-SP donor ligands: synthesis, crystal structure and reactivity towards the polymerization of norbornene," *Polyhedron,* vol. 19, pp. 1601-1605, 2000.

[36] Yang H., Li Z., Li Y. and Sun W., "Vinyl Polymerization of Norbornene with Neutral Salicylaldiminato Nickel(II) Complexes," *Organometallics,* vol. 22, pp. 3678-3683, 2003.

[37] G. Vougioukalakis, I. Stamatopoulos, N. Petzetakis, C. Raptopoulou, V. Psycharis, A. Terzis, P. Kyritsis, M. Pitsikalis and N. Hadjichristidis, "Controlled Vinyl-Type Polymerization of Norbornene with a Ni(II) diphosphinoamine/methylaluminoxane catalytic system," *J. Polym. Sci., Part A: Polym. Chem.,* vol. 47, pp. 5241-5250, 2009.

[38] H. Gao, L. Pei, Y. Li, J. Zhang and Q. Wu, "Vinyl polymerization of norbornene with nickel catalysts bearing [N,N] six-membered chelate ring: Important influence of ligand structure on activity," *J. Mol. Catal. A,* vol. 280, pp. 81-86, 2008.

[39] G. Ricci, G. Leone, A. Rapallo, P. Biagini, G. Guglielmetti and L. Porri, "Syndiospecific oligomerization and polymerization of norbornene with titanium catalysts," *Polym.,* vol. 52, pp. 5708-5715, 2011.

[40] D. Lee, J. Lee, J. Ryu, Y. Kim, C. Kim and I. Lee, "Novel Nickel Catalysts Containing Tetradentate Chelating Ligands for the Polymerization of Norbornene," *Bull. Korean Chem. Soc.,* vol. 27, p. 1031, 2006.

[41] X. He and Q. Wu, "Polymerization of Norbornene Using Bis(B-ketoamino)nickel(II)/MAO Catalytic Systems," *J. App. Polym. Sci.,* vol. 101, pp. 4172-4180, 2006.

Chapter Two

A brief review of transition metal complexes used as pre-catalysts for vinyl-addition polymerization of norbornene

2.1 Introduction

Many metal complexes have been reported as catalysts for vinyl-addition polymerization of strained cyclic olefins. These catalysts can be divided into three main groups relative to the catalyst's metal center [42]: the early transition metal catalyst group, the mid-table transition metal catalyst group, and the late transition metal catalyst group. Most research was focused on but not limited to iron, titanium, cobalt, palladium, zirconium, and nickel complexes where the nickel- and palladium complexes display the highest catalytic activity [33, 43, 44, 42, 45]. Catalyst systems based on Schiff base ligands received copious amounts of attention in VAP of NBE [44, 46, 9, 47].

2.2 Early transition metal catalysts for norbornene polymerization

2.2.1 Titanium(IV) complexes as pre-catalysts for norbornene polymerization

The first successful VAP of NBE was reported in the early 1960s using a $TiCl_4$/Al(*iso*- Bu)$_3$ Ziegler-Natta catalyst system with an Al:Ti of 1:2, to form a cycloaliphatic polymer containing bicyclic-structural units that are intact with no double bonds present [48, 43, 44, 49, 42]. In other reports, a similar catalyst such as $TiCl_4$/AlEt$_3$ produced a combination of metathesis polymer and vinyl polymer when the Al:Ti ratio was increased. Saegusa *et. al* illustrated in 1964 that an "amine addition to the system" can redirect the polymerization to exclusively

produce PNBE *via* ROMP [50]. In 2004 Hasan *et. al* tested a Ti-based catalyst by varying the activators (MAO, MMAO, and $Ph_3CB(C_6F_5)_4/Oct_3Al$) and experimental reaction temperatures (20 – 80 °C) [12]. The highest activity was observed when (t-$BuNSiMe_2Flu)TiMe_2$ was activated by $Ph_3CB(C_6F_5)_4/Oct_3Al$ resulting catalytic activities of 4.8×10^6 $g_{(PNBE)}.mol_{(Ti)}^{-1}.h^{-1}$ at 20 °C and molecular weight distribution of 1.41. It was also reported that all systems displayed a high *Mn* ranging from 0.55 to 29.6×10^{-4}. When MMAO was used as co-catalyst a molecular weight distribution of 1.07 was obtained with activity of 2.1×10^6 $g_{(PNBE)}.mol_{(Ti)}^{-1}.h^{-1}$ as the propagation rate was controlled by altering the Al/Ti ratio. All vinyl PNBE obtained displayed good solubility in halogenated aromatic solvents and were thermally stable up to 420 °C. It was also observed that the vinyl PNBE had good optical transparency in the UV-vis region.

In another development, Hu *et. al* reported in 2008 on the synthesis of a novel alkoxyl titanium(IV) complex which contained a pair of chelating benzoin ligands incorporated for the co- and homopolymerization of ethylene and norbornene [13]. They found that upon activation the dimeric complex $[(OC(Ph)HC(Ph)O)TiCl(\mu-OCH(Ph)C(Ph)(n-Bu)O)]_2$ showed good activities for the homopolymerization of ethylene and norbornene, with high-molecular-weight polyethylene and vinyl-type polynorbornene produced. When the catalyst was tested at 50 °C for the VAP of NBE, an activity of 3.58×10^5 $g_{(PNBE)}.mol_{(Ti)}^{-1}.h^{-1}$ was observed. By increasing the temperature, a reduction of catalytic activity was observed and was explained by the destabilization of the active species. They found that by increasing the monomer concentration at 50 °C, the activity and yield further increased. The titanium(VI)-based pre-catalyst can be viewed in **Figure 2.1**.

1

Figure 2.1: Titanium(IV)-based catalyst (**1**) tested by Hu *et. al* as pre-catalysts for norbornene homo- and co-polymerization with ethylene [13].

In 2011 Ricci *et. al* further investigated the polymerization of NBE with titanium-based catalysts such as $TiCl_4$-AlR_2Cl (R = Et, Me, *i*Bu) where higher NBE/$TiCl_4$ molar ratios were used and found that the stereospecificity of the resulting PNBE can be controlled [5]. The polymer fractions were separated using solvent extractions and they concluded that with higher NBE/Ti ratios, polymers with 2,3-*exo*-disyndiotactic stereo structures are obtainable.

2.2.2 Zirconium(IV) complexes as pre-catalysts for norbornene polymerization

Metallocene or half-metallocene complexes of zirconium and titanium have been studied extensively and have shown abilities to produce crystalline, insoluble, and brittle polymers [53, 54, 42]. The structures of metallocenes are commonly called to as "sandwich compounds" whereby a π - bonded metal atom is positioned between two aromatic rings [16]. Metallocene catalysts pose the advantage of having only one type of active site and in addition to this, the chemical structure can be easily modified [16]. This makes it relatively easy to predict the properties of the resulting polyolefins with great accuracy if the catalyst is known. It is thereby

also easy to control the molecular weight, the molecular weight distribution, the resulting content of the copolymer, and the tacticity of the polyolefin by optimizing the reaction conditions. Furthermore, varying the ligands on the metallocene, makes it possible to obtain polyolefins with different microstructures and characteristics. The "metallocene" often refers to metallocene dichloride and can be seen in **Figure 2.2** [42].
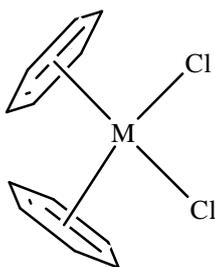
M = Ti, Zr, Hf

2

Figure 2.2: General structure of metallocene pre-catalysts often referred to as sandwich compounds [42].

When metallocenes are utilized in traditional Ziegler systems, whereby an aluminum alkyl serves as co-catalyst for the polymerization of olefins, low activities are generally observed [56]. With the discovery of methyl aluminoxane (MAO) in 1977, the activity of metallocene catalysts increased by a factor of 10 000 and because of this remarkable increase in activity, MAO became a vital component in olefin polymerization [56]. The MAO structure consists of aluminum and oxygen atoms that are alternately arranged whereby methyl substituents saturate the empty valence orbitals. MAO can be synthesized by conducting partial hydrolysis of trimethylaluminum whereby the basic structure obtained consists mainly of four aluminum atoms, three oxygens, and six methyl groups [$Al_4O_3Me_6$] [56]. The aluminum atoms are co-ordinately unsaturated and therefore it is seen that the basic units of mostly four, form a cluster

by joining together. The proposed MAO cluster by Sinn *et. al* can be viewed in **Figure 2.3** [18].
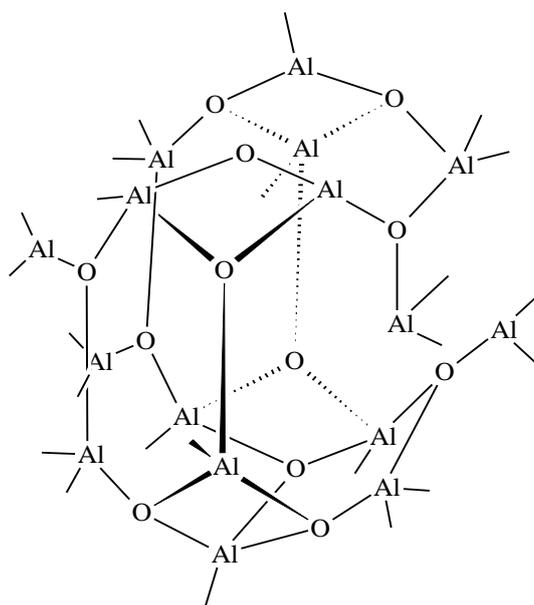
Figure 2.3: The proposed MAO cluster proposed by Sinn *et. al* [18].

It is accepted that MAO initially undergoes a fast ligand exchange reaction with the metallocene dichloride, with subsequent formation of metallocene methyl and dimethyl aluminum compounds. It thus acts as an alkylating agent, establishing a σ-bond between the metal and alkyl group [58]. This is followed by either the Cl^- or CH_3^- being abstracted from the metallocene structure by an Al-center in MAO, thereby forming a metallocene cation along with a MAO anion. With this step, a free coordination site for the monomer is made available. The alkylated metallocene cation serves as the active center and the monomer is now coordinated to the empty coordination site. Hereafter the insertion of the olefin into the zirconium-alkyl bond follows and a new coordination position is created. The last step is repeated, and chain propagation is achieved [56]. The proposed mechanism of olefin polymerization by zirconocenes can be seen in **Scheme 2.8**.
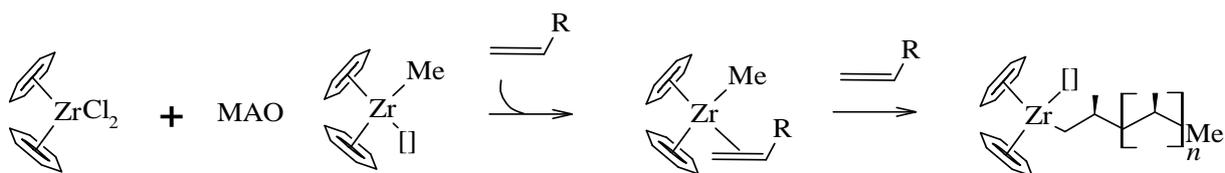
Scheme 2.8: Mechanism for olefin polymerization using metallocene-type complexes as pre-catalysts [56].

A study conducted by Kaminsky *et. al* aimed to investigate the polymerization of cycloolefins such as cyclobutene, cyclopentene, and norbornene employing chiral metallocenes such as Et(Ind)$_2$ZrCl$_2$, Ind = indenyl (**3**), and Me$_2$Si(Ind)$_2$ZrCl$_2$ (**4**) which are illustrated in **Figure 2.4** [59]. When activated by MAO, catalysts **3** and **4** showed higher polymerization activity towards cyclopentene and cyclobutene in comparison with the activity towards norbornene. In a follow-up study, Kaminsky investigated the co-polymerization of ethene and NBE using C$_s$-symmetrical complexes such as [Me$_2$C(Fluo)(Cp)]ZrCl$_2$, Fluo = fluorenyl (**5**), and [Ph$_2$C(Fluo)(Cp)]ZrCl$_2$ (**6**) together with C$_2$-symmetrical pre-catalysts [Me$_2$Si(Ind)$_2$]ZrCl$_2$ (**4**) and [Ph$_2$Si(Ind)$_2$]ZrCl$_2$ (**7**) that can be seen in **Figure 2.5** [21].
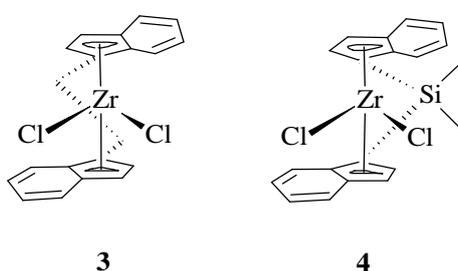
Figure 2.4: Et(Ind)$_2$ZrCl$_2$ and [Me$_2$Si(Ind)$_2$]ZrCl$_2$ zirconocene complexes investigated by Kaminsky *et. al* as pre-catalysts in cycloolefin polymerizations [59].

MAO was utilized to initiate polymerization, under an argon atmosphere in toluene. It was apparent that the polymerization rates were different whereas **5** measured activity of 2.2×10^6 g(copolymer).mol^{-1}(M).bar^{-1}.h^{-1} and 2.4×10^6 g(copolymer).mol^{-1}(M).bar^{-1}.h^{-1} for **6.** The C_2-symmetrical catalysts (**4** and **7**) displayed a decrease in polymerization rates with an increase in norbornene-ethene ratios.

5   **6**   **7**
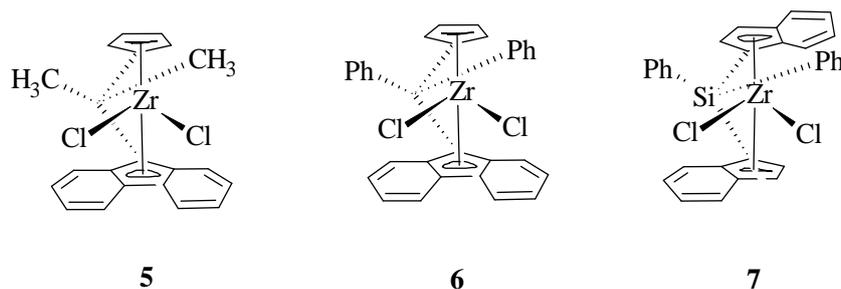
Figure 2.5: [Me$_2$C(Fluo)(Cp)]ZrCl$_2$ (**5**), [Ph$_2$C(Fluo)(Cp)]ZrCl$_2$ (**6**) and [Ph$_2$Si(Ind)$_2$]ZrCl$_2$ (**7**) catalysts tested by Kaminsky *et. al* as pre-catalyst in NBE polymerization [21].

It was evident that research utilizing metallocene systems for the homopolymerization of NBE has been declining since 2001 and research on employing metallocene systems for the co-polymerization of NBE is still actively being investigated [22]. For example, Kaminsky *et. al* investigated the co-polymerization of propylene/norbornene activated by MAO in 2007 with *rac*-[Me$_2$C(Ind)$_2$]ZrCl$_2$, [Me$_2$C(Cp)(Fluo)]ZrCl$_2$, [Ph$_2$C(Cp)(2,7-di^{t}BuFluo)]ZrCl$_2$ and [Me$_2$Si(3-^{t}BuCp)(N^{t}Bu)]TiCl$_2$ whereafter they reported that it was possible to manipulate the T_g of the resulting copolymer by controlling the molar fraction insert of norbornene in the resulting polymer. For instance, when a 0.20 molar fraction of norbornene feed was loaded, a resulting molar fraction of 0.28 of norbornene in the resulting copolymer was obtained with a T_g of 37.9 °C. When increasing the norbornene feed molar fraction to 0.60, a resulting norbornene molar fraction of 0.67 was obtained in the resulting co-polymer with a T_g of 159.3 °C. Although the thermal properties were controllable in this fashion, it came at the expense of

catalytic activity. The catalytic activity with 0.20 molar fraction norbornene in the feed, was in the order of 186 $kg_{(PNBE)}mol^{-1}_{(M)}h^{-1}(molL^{-1})^{-1}_{(monomer)}$ and increasing the norbornene to a molar fraction of 0.60 the activity decreased to 32 $kg_{(PNBE)}mol^{-1}_{(M)}h^{-1}(molL^{-1})^{-1}_{(monomer)}$. This observed trend was consistent for all runs [22].

2.3 Mid-table transition metal catalysts for norbornene polymerization

2.3.1 Chromium(II) and (III) complexes as pre-catalysts for norbornene polymerization

The second group of catalysts is the mid-table transition-metals catalysts in which chromium(III) serves as metal center and are the less popular group of catalysts in vinyl-addition polymerization of NBE [42]. Peuckert *et. al* reported in 1998 on the homo-polymerization of NBE with chromium(III)-based pre-catalyst (**8**) [62]. They found that [RCrMeCl]$_2$, R = fluorenyl , activated by MAO, resulted activity of 1.8×10^4 $g_{(PNBE)}.mol_{(Cr)}^{-1}.h^{-1}$ and formed partly crystalline homo-polymers that are insoluble in typical organic solvents. In a series of polymerizations, they tested different cyclopentadienyl ligands and concluded that the activity of the catalyst increased as the electron-donor characteristics of the ligand increased. The complex is illustrated in **Figure 2.6**.

R = C_5H_5, C_5Me_5, indenyl, fluorenyl
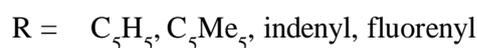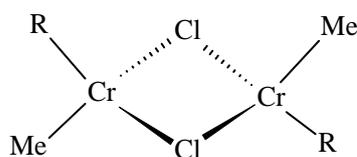
8

Figure 2.6: Chromium(III)-based complex investigated by Peuckert *et. al* as pre-catalyst for the homopolymerization of norbornene [62].

Pei *et. al* reported in 2016 on the homo- and copolymerization of ethylene and norbornene utilizing an anilido-imino chromium(II) complex, activated by MAO, which resulted in good activity for the homopolymerization of ethylene but low activities for the VAP of NBE [24]. Three chromium complexes of $(ArN = CHC_6H_4NAr)CrCl_2(THF)_2$ were synthesized where Ar = phenyl (**9**), 2,6-dimethylphenyl (**10**) and 2,6-diisopropylphenyl (**11**) respectively. By varying the temperature from 20 to 80 °C it was found that the highest activity for the VAP of NBE of 174×10^3 g$_{(PNBE)}$.mol^{-1}$_{(Cr)}$.h^{-1} can be achieved at 60 °C when the phenyl (**9**) group was used as substituent. This indicates that the steric bulk in the *o*-position of the ligand, influences catalytic ability through steric hindrance. This produced a vinyl PNBE with a Mw of 13.6×10^3 g.mol^{-1} and molecular weight distribution of 1.94. From the data, it was concluded that the molecular weight of the polymer decreased when the polymerization temperature increased because the chain transfer reaction accelerates. The catalyst with the incorporated phenyl group can be viewed in **Figure 2.7**.

<table>
<tr><td align="center">**9**</td><td align="center">**10**</td><td align="center">**11**</td></tr>
</table>
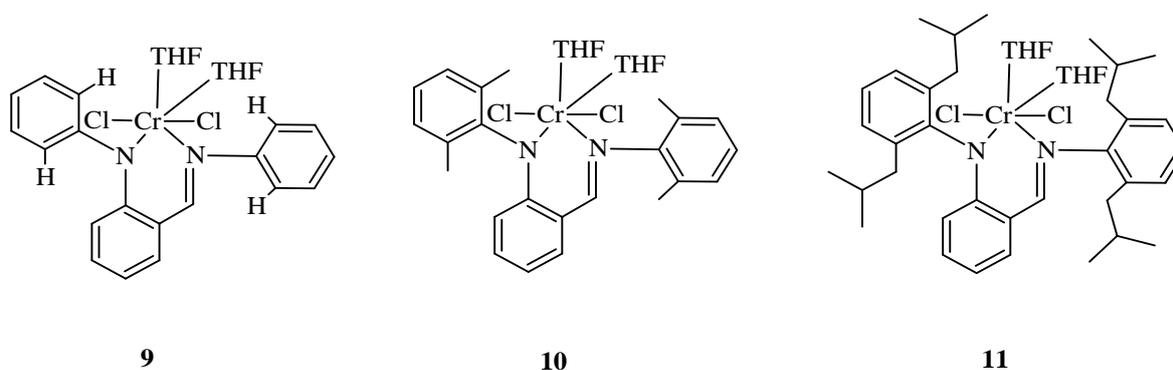
Figure 2.7: Chromium(II)-based complexes synthesized and tested by Pei *et. al* as pre-catalyst for the homo-and-co-polymerization of norbornene and ethylene [62].

2.4 Late transition metal catalysts for norbornene polymerization

The third group of catalysts describes the late transition metals, i.e. copper, cobalt, iron, palladium, and nickel pre-catalysts which in general, are a lot easier to handle than their earlier transition metal counterparts [54, 46, 64, 65]. From the three groups, the late transition-metal catalysts generally display the highest activity and produce polymers with the highest molecular weights which are generally amorphous and soluble [9, 66, 67]. This group also holds the advantage of being less oxophilic in comparison with the early transition metal catalysts and are therefore more tolerant towards functionalized olefins [29]. This group of catalysts are described as the most advanced and important group of catalysts for the vinyl-addition polymerization of NBE where nickel and palladium-based metal complexes serve as the most popular systems used [49, 68, 47].

2.4.1 Copper(II) complexes as pre-catalysts for norbornene polymerization

Carlini *et. al* reported in 2006 on the employment of different bis(salicylaldiminate)Cu(II) complexes with MAO, for the VAP of NBE and found that electron-withdrawing nitro groups present on the chelating ligand, increases the activity of the catalyst and was high molecular weight vinyl-type PNBE obtainable [26]. **Figure 2.8** shows the metal complexes with highest activity and yielded PNBE with the highest molecular weights. At 80 °C, complex **12** resulted activity of 150×10^3 $g_{(PNBE)}.mol_{(Cu)}^{-1}.h^{-1}$ and a polymer with Mw of 432 000 g.mol^{-1} after 1 h. Complex **13** resulted activity of 110×10^3 $g_{(PNBE)}.mol_{(Cu)}^{-1}.h^{-1}$ and **14** resulted activity of 70×10^3 $g_{(PNBE)}.mol_{(Cu)}^{-1}.h^{-1}$ and Mw of 344 000 g.mol^{-1} and 450 000 g.mol^{-1} respectively. All polymerization reactions were carried out in chlorobenzene.

12   **13**   **14**
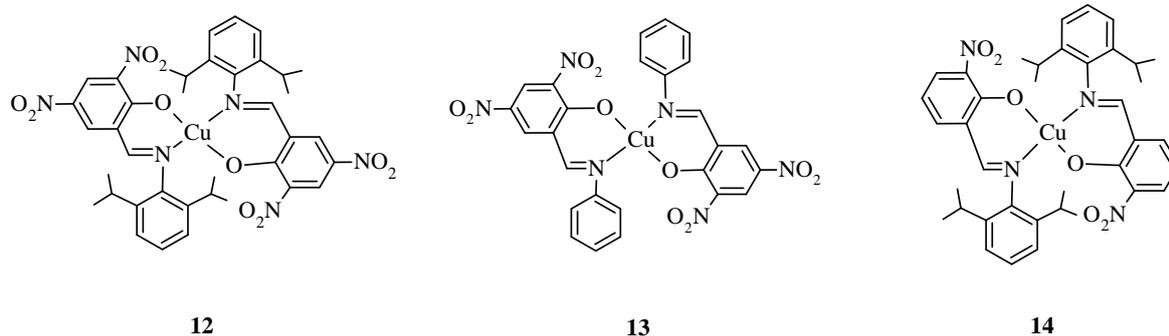
Figure 2.8: Bis(salicylaldimine)Cu(II) complexes investigated by Carlini *et. al* as pre-catalysts for the vinyl addition polymerization of norbornene [26].

A few years later Yu *et. al* synthesized and tested copper(II) (**15**) and nickel(II) complexes bearing tetradentate [O, N, N, O] β-ketoiminato ligands to produce vinyl-type PNBE [69]. When the polymerization was activated by MAO, the copper(II) pre-catalyst showed only trace amounts of polymer formations whereas the nickel(II) based catalyst of complex **15b** resulted activity of 2.44×10^6 $g_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$ leading to all further investigations conducted employing nickel(II) catalysts. The investigated copper(II)-complexes can be seen in **Figure 2.9**.

15
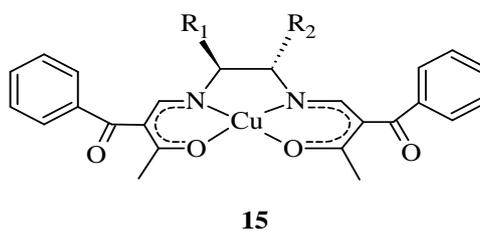
	R₁	**R₂**
Complex **15a**	-C₄H₄-	-C₄H₄-
Complex **15b**	H	H
Complex **15c**	-trans-C₄H₈-	-trans-C₄H₈-

Figure 2.9: Tetradentate copper(II)-based complexes investigated by Yu *et. al* as pre-catalysts for the vinyl addition polymerization of norbornene [69].

2.4.2 Cobalt(II) complexes as pre-catalysts for norbornene polymerization

Goodall *et. al* reported in 1995 on cobalt complexes that allowed NBE to be polymerized *via* ROMP and VAP and that the polymerization route of preference can be controlled through the choice of co-catalyst [70]. ROMP of NBE can be achieved when cobalt salts (**Figure 2.10**) such as Co-*neo*-decanoate (**16**) and Co-acetylacetonate (**17**) are used, together with tri-isobutyl aluminum or triethyl aluminum as co-catalysts. From these systems PNBE of high Mw (720 000 g.mol^{-1}) were obtainable. When Co-*neo*-decanoate was activated by MAO, polynorbornene of the vinyl type formed. These polymers displayed a Mw of 1.6×10^6 g.mol^{-1} and a T$_g$ of 380 °C with good solubility in cyclohexane. The activity of these systems measured unfavourable as a 72 h reaction time was required to achieve 80% monomer conversion.

16   **17**
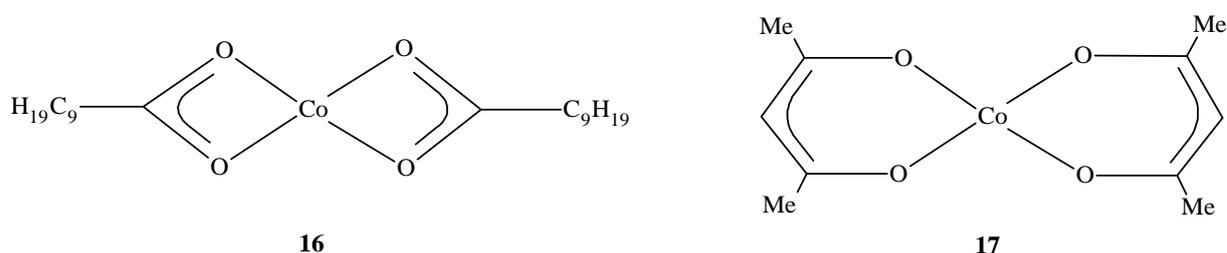
Figure 2.10: Cobalt(II)-based complexes investigated by Goodall *et. al* as pre-catalyst for the vinyl addition polymerization of norbornene [70].

Sato *et. al* reported in 2004 on the successful VAP of NBE with terpyridine cobalt complexes, activated with MAO in chlorobenzene [64]. In their study, they synthesized a series of cobalt(II) complexes that consisted of terpyridine derivatives. Each of the catalysts were evaluated on the catalytic activity during the polymerization of NBE and the catalyst's ability to form polymers with controlled Mw and narrow molecular weight distributions. At room

temperature and after 3 h reaction time, they found that complexes **18**, **19,** and **20** (**Figure 2.11**) yielded 62%, 30%, and 99% respectively. When the catalysts were allowed to react for 12 h all three catalysts resulted in a > 99% yield with molecular weight distributions of 1.22, 1.21, and 1.36, respectively. Further variation of the NBE/Co ratios resulted in a 214 [mol]/[mol] ensuring a > 99% yield with a molecular weight distribution of 1.61, when catalyst **20** was used. This indicated that it was possible to control the Mw and molecular weight distributions by controlling the NBE/Co ratio in the feed and by controlling the steric bulk of the ligand around the active centre might enhance catalytic abilities.
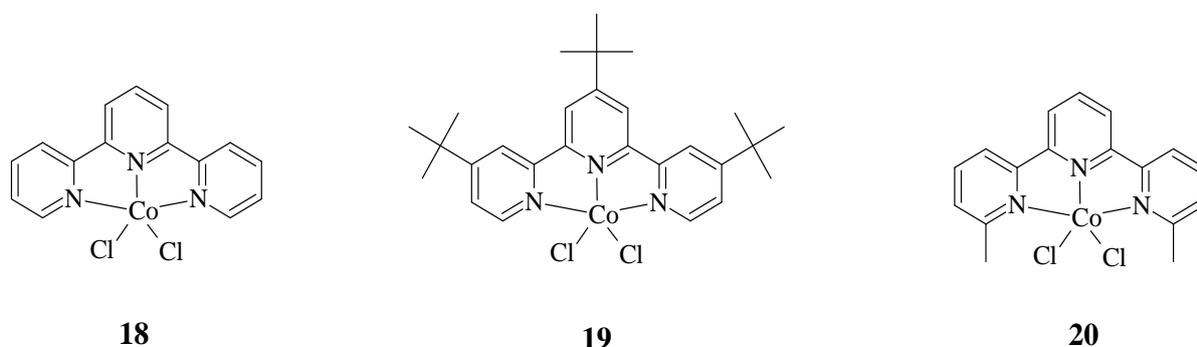
Figure 2.11: Cobalt(II)-based complexes investigated by Sato *et al.* as pre-catalyst for the vinyl addition polymerization of norbornene [15].

Cobalt catalysts were further investigated in 2009 by Leone *et. al* whereby cobalt(II)-phosphine complexes such as $CoCl_2(PR_3)_2$ (PR_3 = di-*tert*-butylphosphine, P^tBu_2H; di-*tert*-butylmethylphosphine, P^tBu_2Me; tricyclopentylphospine, PCp_3), and $CoCl_2(PRPh_2)_2$ (R = methyl, Me; isopropyl, ^iPr; cyclohexyl, Cy) were employed in the homo- and co-polymerization of NBE with ethylene [33]. Here they report on the formation of amorphous and soluble vinyl PNBE, when the polymerization was carried out in 1,2-dichlorobenzene and activated by MAO. $CoCl_2(P^tBu_2Me)_2$ displayed a very high activity of 10.5×10^6 g$_{(PNBE)}$.mol^{-1}$_{(Co)}$.h^{-1} for NBE polymerization delivering an 87% yield after one minute. Vinyl PNBE with a

Mw of 121 800 g.mol^{-1} and a molecular weight distribution of 3.4 was observed. It was concluded that the decrease in a ligand's steric bulk improves catalytic performance. They repeated the polymerization in toluene and found that a 24 h reaction period is required to obtain full monomer conversion with the same catalyst system. Thus, a higher activity can be expected by utilizing a more polar solvent.

R = H; Me   R = Me; ^{i}Pr; Cy   PCp$_3$

21   **22**   **23**
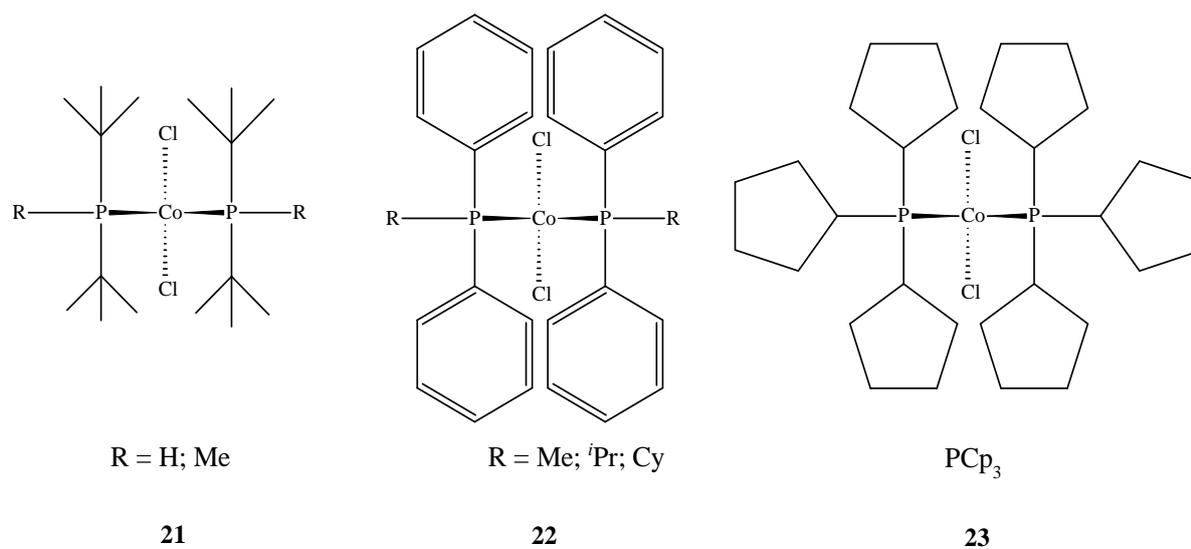
Figure 2.12: Cobalt(II)-based complexes investigated by Leone *et. al* as pre-catalysts for the vinyl addition polymerization of norbornene [33].

2.4.3 Iron(II) complexes as pre-catalysts for norbornene polymerization

In 1998 Brooke *et. al* reported on a highly active iron catalyst for ethylene polymerization [34]. They synthesized tridentate pyridine-diimine ligands by Schiff-base condensation and formed the desired catalysts (**24**) by adding the ligand to the metal salt. The catalyst was activated by MMAO in toluene and the polymerization of ethylene progressed to produce highly linear polyethylene. The iron-based catalyst can be seen in **Figure 2.13**. Brooke stated that "the key to high polymer production using aryl-substituted α-diimine systems is the incorporation on the aryl rings of bulky *ortho* substituents that greatly retard the rate of chain transfer". Chen *et.*

al confirmed Brooke's statement in 2006 by polymerization of NBE with a bulky tridentate bis(imino)pyridyl iron-based catalyst (**25**) which promoted polymerization activities of 9.25×10^6 $g_{(PNBE)}.mol^{-1}_{(Fe)}.h^{-1}$ when MAO was used as co-catalyst [35].

R = *i*-Pr, X = Cl

24   **25**
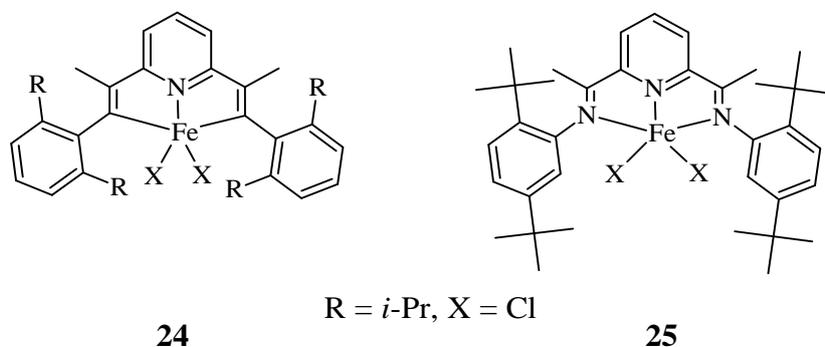
Figure 2.13: Iron(II)-based complex investigated by Brooke *et. al* and Chen *et. al* as precatalysts for the polymerization of ethylene and norbornene [34].

In 2001 Sacchi *et. al* built on the research conducted by Brooke *et. al* by synthesizing the same catalyst complexes. They investigated the effect of solvent polarity, polymerization reaction temperature, and the effect of a chain transfer agent on polymerization activities for NBE when activated by MAO [36]. Different late transition metal centers such as nickel(II), cobalt(II), and iron(II) were used after which it was found that the nickel(II)-based analogue of catalyst (**25**) had the highest activity. Iron(II)-based catalysts showed the lowest activity whereby only trace amounts of vinyl PNBE were produced. From experimental data, iron(II)-based catalyst **24** showed an activity of 0.32×10^3 $g_{(PNBE)}.mol^{-1}_{(Fe)}.h^{-1}$ whereby iron(II)-based catalyst **25** only yielded trace amounts at 50 °C in toluene. The nickel(II)-based catalyst analogue of complex **25** displayed an activity of 4.14×10^3 $g_{(PNBE)}.mol^{-1}_{(Ni)}.h^{-1}$. When the solvent was changed to *o*-dichlorobenzene, no significant increase in polymerization activity was observed for the iron(II)-based catalyst but a dramatic increase to 21×10^3 $g_{(PNBE)}.mol^{-1}_{(Ni)}.h^{-1}$ was observed for the nickel(II)-based catalyst **25**. Interestingly this aligns with statements made by Leone *et. al*

in 2009 with their investigations on cobalt(II)-based catalysts where they found that by increasing the polarity of the solvent, an increase in catalytic activity can be observed.

Benade *et. al* further explored iron(II)-based catalysts in 2011 where they reported on the screening of pyrazolyl complexes of iron(II), cobalt(II), and nickel(II) for the polymerization of NBE [2]. In the range of complexes synthesized iron(II)-based (2-((3,5-dimethyl)-1H-pyrazol-1-ylmethyl)pyridine)Cl$_2$ (**26**) and (2-((3,5-diphenyl)-1H-pyrazol-1-yl)methyl)pyridine)Cl$_2$ (**27**) displayed low activity for NBE polymerization with only a 61% and 50% vinyl PNBE yield respectively after 1 h, when the catalysts were activated with MAO in toluene (**Figure 2.14**). Catalyst **26** produced vinyl PNBE with Mw of 6.47×10^5 g.mol^{-1} and molecular weight distribution of 3.01 where the Mw of NBE from catalyst **27** was not determined. Catalyst **26**'s nickel(II)-based analogue displayed an activity that resulted in a 90% yield, producing a polymer with a Mw of 5.13×10^5 g.mol^{-1} and molecular weight distribution of 2.38.
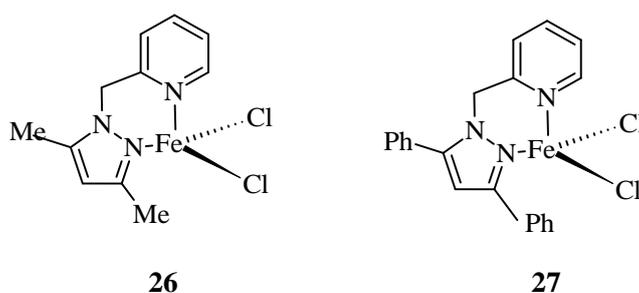
Figure 2.14: Pyrazolyl-pyridine complexes of iron(II) investigated by Benade *et. al* as pre-catalysts in the vinyl addition polymerization of norbornene [22].

2.4.4 Palladium(II) complexes as pre-catalysts for norbornene polymerization

Complexes of especially nickel and palladium received a lot of attention in the homo-polymerization of NBE, since these catalysts display very high activities in olefin- and

cyclo-olefin polymerizations [46, 53]. Palladium(II)-based catalysts used in VAP of NBE date to 1966 and the late 1970s when PdCl$_2$, Pd(C$_6$H$_5$CN)$_2$Cl$_2$, and Pd(Ph$_3$P)$_2$Cl$_2$ gained popularity [42]. In 1988 Sen *et. al* reported on the cationic palladium(II)-based catalyst [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$, illustrated in **Figure 2.5** (**28**), which quickly became the most prevalent used catalyst in NBE polymerizations [75]. This catalyst contained weakly bound acetonitrile ligands and displayed catalytic activity in the absence of a co-catalyst. A 90% yield VPNBE was easily obtainable after 5 minutes when a 100:7 ratio of monomer to palladium(II) was used in nitromethane at 25 °C. Determining the Mw of the VPNBE formed, posed challenging due to the polymer's insolubility in halogenated organic solvents like chloromethane, dichloromethane, tetrahydrofuran, and organic solvents like cyclohexane.
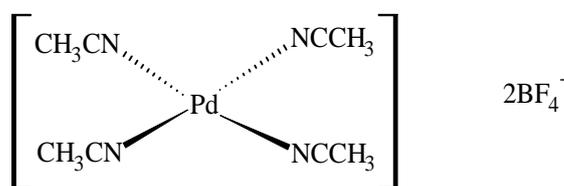
28

Figure 2.5: Palladium(II)-based complex investigated by Sen *et. al* as catalyst for norbornene polymerization [75].

Seehof *et. al* built on the work performed by Sen in 1988 by employing the same catalyst system to successfully polymerize NBE to achieve VPNBE with high Mw and low molecular weight distribution that displayed good solubility in halogenated aromatic solvents [48]. Seehof reported on a [Pd(CH$_3$CN)$_4$][2BF$_4$] catalyst which displayed > 99% yields of vinyl PNBE after 10 minutes at 25 °C in nitrobenzene and chlorobenzene. The

resulting polymer had a Mw of 4.89×10^4 g.mol^{-1} and it was stated that a higher Mw was achievable when the monomer/catalyst ratios were further increased.

Brookhart and team reported a new ([N, N]) palladium(II)- and nickel(II)- based pre-catalyst which polymerize ethylene and α-olefins to give polyolefins with unique microstructures and high molecular masses [76]. But in contradiction to the high activity for ethylene and α-olefins, they show low activity for the homo-polymerization of NBE due to the "nature of the cationic active species, which possess a less planar chelate ring" [53]. Other bidentate ligands such as salicylaldimines catalyst systems hold the advantage of manipulating the steric parameters as well as the electromagnetic parameters of the metal center [29]. This in general, is true for supporting ligands which exhibit the ability to influence the catalytic performance by means of their steric and electronic characteristics [46]. These pre-catalysts were reported highly active for NBE and ethylene polymerization when a bulky substituent is present, which indicates that the nature of the active species and activity trends still lack understanding [53].

In 1996 Reinmuth *et. al* reported on (η^3-allyl)Pd(II) catalysts employed for the VAP of functionalized NBE derivatives [39]. They utilized [(η^3-allyl)Pd(BF$_4$)] and [(η^3-allyl)Pd(SbF$_6$)] for the polymerization of NBE derivatives containing *endo*-linked ester, hydroxyl, and carboxylic acid groups, whereby hexafluoroantimonate ion bearing catalyst displayed slightly higher monomer conversion rates than the tetrafluoroborate Pd(II)-based catalyst. For instance, when bicyclo-[2.2.1]hept-5-en-2-ylmethyl decanoate (*endo/exo*-ratio = 80/20) was used as monomer, [(η^3-allyl)Pd(SbF$_6$)] resulted a 99% yield after 18 h was obtainable at 20 °C, with a Mw of 55×10^3 g.mol^{-1} and molecular weight distribution of 2.19 whereas [(η^3-allyl)Pd(BF$_4$)] only resulted a 74% monomer conversion, Mw of 21×10^3 g.mol^{-1} and molecular weight

distribution of 2.18. In 2004 Liang *et. al* investigated the catalytic activity of neutral palladium complexes, bearing pyrrole-iminato or salicylaldiminato ligands for the VAP of NBE [7]. When activated by MMAO the salicylaldiminato-bearing complexes displayed dominant catalytic activities in comparison to pyrrole-eliminate-bearing complexes and might this be attributed to the difference in stabilization the metal centre experiences. **Figure 2.** (**29**) illustrates the catalyst which displayed a 71% yield when 0.5 µmol of catalyst was used, activated by MMAO, Al/Pd 2000, and NBE/Pd 51 900 at 30 °C in chlorobenzene. The catalyst showed capability of producing 8.52×10^6 g$_{(PNBE)}$.mol$_{(Pd)}^{-1}$.h^{-1} VPNBE when the reaction continued for 10 minutes. They confirmed that the VPNBE obtained, was insoluble in chloroform, benzene, chlorobenzene, 1,2-dichlorobenzene, N, N-dimethylformamide, and N, N-dimethylacetamide and therefore no molecular weights could be determined. VAP of NBE was confirmed by FTIR analysis when no absorption at 1600-1670 cm^{-1} was observed.

29
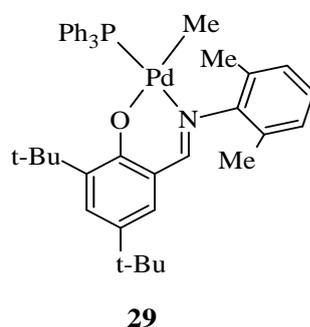
Figure 2.16: Salicylaldiminato catalyst complex investigated by Liang *et. al* as pre-catalyst for vinyl addition polymerization of norbornene [7].

Research done by Myagmarsuren *et. al* in 2006 proved to be of industrial importance as they developed a novel palladium carboxylate/boron trifluoride etherate catalyst system [8]. Pd(carboxylate)$_2$/BF$_3$OEt$_2$ was investigated for its ability to polymerize NBE by varying the cocatalyst/metal ratios, NBE/metal ratios, metal concentrations and varying the reaction

temperature in toluene. An optimum reaction temperature of 25 °C was determined where the catalyst displayed a VPNBE-producing activity of 154.1×10^6 g$_{(PNBE)}$.mol$_{(Pd)}^{-1}$.h^{-1} when a B/Pd ratio of 25 was used. The Mw of the resulting polymer varied between 77 700 and 293 800 g.mol^{-1} with a T$_g$ of 240 to 262 °C. They found that the molecular weight of the resulting polymer decreased at elevated temperatures, the polymer yield and catalytic activity decreases with an increase in monomer concentration and increases with co-catalyst concentrations. The claim of this catalyst being of industrial importance spans from the simplicity of synthesis and ease of use in the VAP of NBE.

Tkach *et. al* built on Myagmarsuren's work in 2008 where they reported on a Pd$_2$(C≡CC$_6$H$_5$)$_2$(C$_5$H$_7$O$_2$)$_3$(BF$_3$)$_2$BF$_4$ (**30**) catalyst (**Figure 2.**) with an activity of 17.6×10^6 g$_{(PNBE)}$.mol$_{(Pd)}^{-1}$.h^{-1} at 25 °C when the polymerization reaction was conducted in toluene, under argon [78]. A polymer was obtained with Mw of 440 000 g.mol^{-1} and T$_g$ of 295 °C, when the reaction was conducted with an NBE/Pd ratio of 3800 and a yield of 61% when the reaction was allowed to continue for 45 s. They concluded that this catalyst proves to be very effective in the polymerization of NBE without the use of a co-catalyst.

30
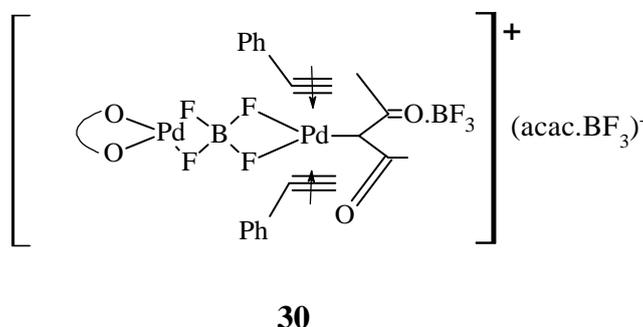
Figure 2.17: Palladium(II)-complex investigated by Tkach *et. al* as catalyst for vinyl addition polymerization of norbornene [78].

Saito *et. al* investigated the VAP of NBE by using a catalyst based on a palladium(0) precursor complex in 2012 [15]. The approach is quite interesting as the aim was to create a palladium(II) complex *in situ* that would promote the polymerization of NBE. This was done by starting with the palladium(0) precursor complex (Pd(dba)$_2$) (dba = dibenzylideneacetone) and then changing the zero-valent complex to a palladium(II) state by conducting an oxidative addition of an alkyl halide in the presence of tricyclohexylphosphine (PCy$_3$). The newly *in situ* generated palladium(II) complex would then contain a metal-to-C σ-bond that would in turn polymerize NBE upon activation by [CPh$_3$][B(C$_6$F$_5$)$_4$]. This system failed to polymerize NBE. An unexpected discovery was made when a mixture of Pd(dba)$_2$/(PCy$_3$)/ [CPh$_3$][B(C$_6$F$_5$)$_4$], without the alkyl halide, proved to be an effective catalyst for the polymerization of VNBE (vinyl norbornene). When polymerization of VNBE was conducted in toluene with VNBE/Pd 1000 and Pd(dba)$_2$/(PCy$_3$)/[CPh$_3$][B(C$_6$F$_5$)$_4$] 1/1/1, the catalyst system resulted yields exceeding 99% when the reaction was allowed to run for 5 h at 40 °C. When the reaction temperatures were increased to 50, 60, and 70 °C respectively, similar yields were obtained. However, it was observed that the molecular weight of the resulting polymer decreased as the temperature increased and may this be due to accelerated chain termination. ^{1}H NMR and FT-IR analyses confirmed that the resulting PNBE was polymerized *via* the addition polymerization route and was soluble in common solvents such as chlorinated- and aromatic solvents as well as tetrahydrofuran.

Xiang *et. al* investigated palladium(II)-diimine catalysts in 2015 with ligands containing different steric characteristics for the homopolymerization of NBE [49]. The experimental setup differs from the conventional Schlenk-technique, but the central premise persists in polymerizing under an N$_2$ atmosphere with controlled reaction temperatures. Xiang *et. al*

conducted polymerization reactions in anhydrous chlorobenzene and sampled the formed polymer at predetermined intervals. No co-catalyst was used, and the reactions were initiated solely by the addition of the palladium(II)-diimine catalyst, dissolved in a small amount of anhydrous chlorobenzene. When the polymerizations were carried out at 25°C for 1 h, all catalysts displayed low activity in comparison with conventional higher yields and activities found when using palladium(II)-catalysts. But of the four catlysts evaluated, the catalyst illustrated in **Figure 2.18** (**31**) displayed the highest activity and yield of 15.5 $\times$ 10^3 g$_{(PNBE)}$.mol^{-1}$_{(Pd)}$.h^{-1} and 20.7 % respectively. When the reaction was allowed to continue for 6 h, a yield of 25.6% was obtained with a noticeable decrease in catalytic activity. The Mw and polydispersity (PDI) were not determined due to the polymer's insolubility in toluene. They concluded that the greater the steric bulk of the diimine ligand the lower the catalytic activity but increase the overall stability of the complex.

31
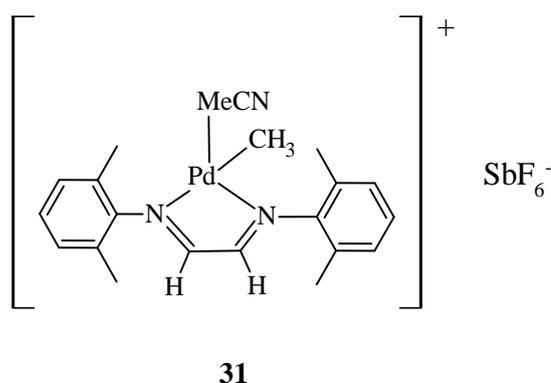
Figure 2.18: Palladium(II)-diimine complex investigated by Xiang *et. al* as pre-catalyst for the vinyl addition polymerization of norbornene [49].

Huang *et. al* described in 2017 that VAP of NBE can be achieved in the presence of water and air [79]. They synthesized a series of air/water-tolerant chiral (S, S)-bis(oxazoline) palladium(II)-alkyl complexes **Figure 2.19** (**32**) and employed each for the polymerization

of NBE in "unpretreated technical grade solvent and monomer" with an excess of activator used. Under controlled conditions, regulated amounts of water were added to the system and the effects were investigated. They found that catalytic activity of 2.2×10^9 $g_{(PNBE)}.mol_{(Pd)}^{-1}.h^{-1}$ was achievable when a NBE/Pd 100 000 was used at 50 °C, for 15 s at a water presence of 11% v/v in technical grade dichlorobenzene, under air and $[Ph_3C][B(C_6F_5)_4]$ as activator. The resulting VPNBE was found to be insoluble in common solvents and therefore no NMR or GPC analyses could be conducted. FT-IR spectroscopy confirmed that polymerization proceeded *via* the vinyl polymerization route, with the absence of double bond peaks at 1620 – 1680, 966, and 735 cm^{-1} regions. DSC analysis indicated a T_g of 317 – 318 °C and TGA analysis confirmed a T_d of 410 °C. The research done by Huang *et. al* contains economic potential since the catalysts employed displayed high activity, can be regarded as environmentally friendly, and can be easily handled.
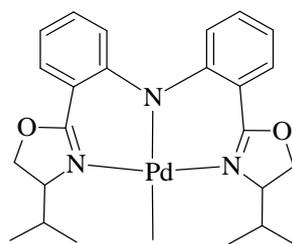
32

Figure 2.19: Chiral palladium alkyl complex investigated by Huang *et. al* as catalyst in vinyl-addition polymerization of norbornene [79].

2.4.5 Nickel(II) complexes as pre-catalysts for norbornene polymerization

Nickel-based catalysts are regarded as some of the most active catalysts for the polymerization of olefins and therefore have been studied extensively. In 2003 Mi *et. al* reported on two novel dinuclear diimine nickel dichloride complexes that have shown moderate activities towards the

VAP of NBE when activated by MAO [31]. In their study, they tested di-μ-chlorodichlorobis{2,6-bisisopropyl-*N*-[1-(2-pyridinyl)ethylidene]phenylamine}dinickel(II) (**33**) as well as di-μ-chlorodichlorobis{2,6-bismethyl-*N*-[1-(2-pyridinyl)ethylidene]phenylamine}dinickel(II) (**34**) and investigated the catalytic activity, as well as the Mw and the microstructure of the resulting polymers. When the polymerization reactions were carried out in solvent mixtures of toluene/dichloromethane, activated by MAO with an Al/Ni ratio of 1600 and allowed to continue for 1 h at 40 °C, complex **33** showed maximum activity of 258×10^3 $g_{(PNBE)}.mol^{-1}_{(Ni)}.h^{-1}$ with an average yield of 21.06%. Complex **34** demonstrated yields of 10.81% with activity of 132.9×10^3 $g_{(PNBE)}.mol^{-1}_{(Ni)}.h^{-1}$ when an Al/Ni of 400 was used at a polymerization temperature of 40 °C. Interestingly enough, lowering the reaction temperature to 0 °C resulted in a twofold increase in both activity and yield for complex **33**. The activity increased to 577.0×10^3 $g_{(PNBE)}.mol^{-1}_{(Ni)}.h^{-1}$ and polymer yield to 46.93% respectively with Al/Ni ratio of 400 in toluene. Mi *et. al* described this observation as advantageous as it was also observed that a lower polymerization temperature delivered higher molecular weight PNBE. Further, they explained this observation was due to *"slower irreversible deactivation of the activated species and less chain transfer"*. For both complexes VPNBE were confirmed and the polymers consisted of a T_g above 240 °C and a T_d of above 400 °C. Complex **33** and **34** can be viewed in **Figure 2.**

33　　　　　　　　　　**34**
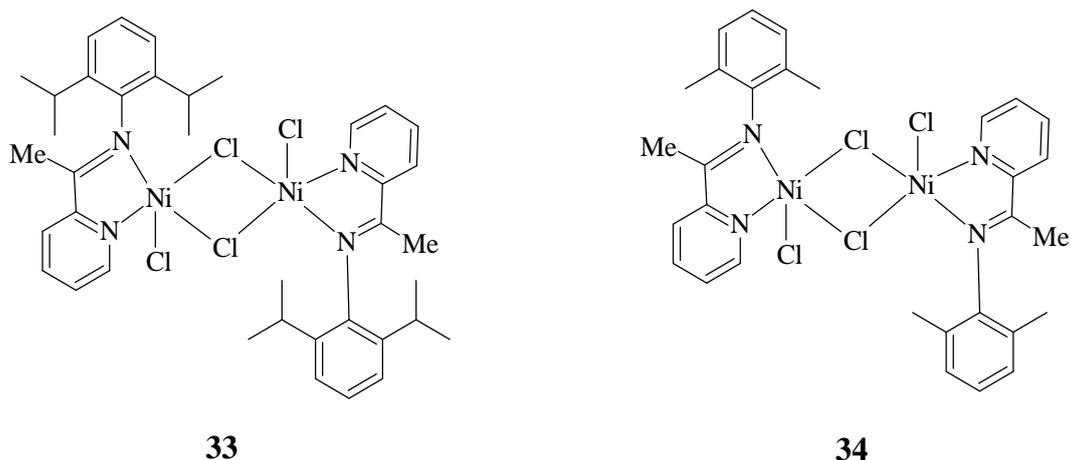
Figure 2.20: Dinuclear diimine nickel dichloride complexes investigated by Mi *et. al* as pre-catalysts for vinyl addition polymerization of norbornene [31].

Sun *et. al* reported similar behavioral observations in 2003 while studying a series of dialkylsalicylaldiminate nickel(II) complexes and their activities toward the VAP of NBE [43]. For the pre-catalyst complex in **Figure 2.21** (**35**) an activity of 2.86×10^8 $g_{(PNBE)}.mol^{-1}_{(Ni)}.h^{-1}$ was observed when the polymerization reaction was conducted in toluene at 25 °C, NBE/Ni 20 0000, 5 μmol catalyst with Al/Ni 2000. After only 20 s a solid white mass formed which could not be stirred and the reaction was quenched with acidic ethanol. By further studying the parameters that affect the VAP of NBE, they employed the same pre-catalyst under variable conditions by altering MAO ratios, polymerization temperatures, and NBE/Ni ratios. This was where a similar observation was made when lowering the polymerization reaction temperature to 0 °C which resulted in the highest Mw PNBE. By increasing the polymerization reaction temperatures, a decrease in Mw and molecular weight distributions were observed, with a yield optimum of 94% at 75 °C. Furthermore, they reported that a MAO ratio of Al/Ni 2000 delivered the highest yield and Mw with relatively low molecular weight distributions. By increasing the Al/Ni ratio to 2500, a decrease in both catalytic activity and polymer Mw were observed. Increasing the NBE/Ni ratios from 2500 to 20 000 resulted in lower yields but higher Mw polymers. The polymers obtained were amorphous and soluble in halobenzene with T_d above

450 °C. It was concluded that polymer Mw, yields, and molecular weight distributions can easily be controlled using this catalytic system.
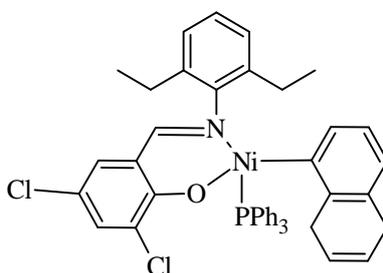
35

Figure 2.21: Nickel(II)-based complexes investigated by Sun *et. al* investigated as pre-catalysts for vinyl addition polymerization of norbornene [43].

Chang *et. al* reported in 2004 on novel bis(1-aryliminomethylenylnaphtalen-2-oxy)nickel complexes, activated by MAO and the employment thereof in VAP of NBE [43]. They reported on synthesizing and characterizing 19 complexes for NBE polymerization. All catalysts displayed yields of over 80% when polymerizations were carried out with Al/Ni 2000, and NBE/Ni 5000 in toluene at 25 °C where the reactions were allowed to continue for 5 h. All complexes tested, displayed the ability to form PNBE with high Mw (5.55×10^5 g.mol^{-1} to 19.2×10^6 g.mol^{-1}) and activities ranging from 7.82×10^4 to 8.95×10^4 g$_{(PNBE)}$.mol^{-1}$_{(Ni)}$.h^{-1}. The complex illustrated in **Figure 2.** (**36**) displayed the highest yield, and activity and formed PNBE with Mw of 8.38×10^6 g.mol^{-1} and narrow molecular weight distribution of 2.07. Further investigations into optimization of reaction conditions by varying the reaction temperature from 0 – 100 °C, found that a reaction temperature of 0 °C proved to be optimum for maximum yields and increased temperatures lead to lower yields. All polymers formed were VPNBE with T$_d$ above 450 °C.
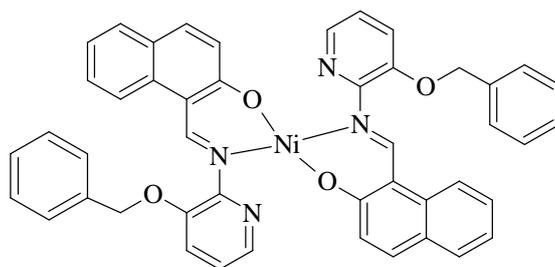
36

Figure 2.22: Nickel(II)-based complex investigated by Chang *et. al* as pre-catalyst for vinyl addition polymerization of norbornene [43].

In 2006 Lee *et. al* also investigated a rigid tetradentate catalyst complex and its ability to polymerize NBE [44]. In this report novel 4,5-substituted-1,2-bis(pyridine-2-carboxamide)-benzene ligands were prepared where alkyl or halide ligands were not present in the coordination sphere and complexation was done to form a nickel(II)-based pre-catalyst. When polymerizations were conducted in chlorobenzene at 70 °C with Al/Ni 1000 and NBE/Ni 1000 and allowed to continue for 10 minutes, the catalyst complex displayed activity of 2.164×10^6 $g_{(PNBE)}.mol^{-1}_{(Ni)}.h^{-1}$ with a yield of 68%. The resulting PNBE consisted of Mw of 3.94×10^5 $g.mol^{-1}$ and molecular weight distribution of 2.79. When a polymerization temperature of 25 °C was tested, it was observed that the catalyst was only capable of half the activity, and only a third of the yield was obtained. The Mw of the formed polymer increased to 9.66×10^5 $g.mol^{-1}$ and the molecular weight distribution decreased to 1.95 indicating that reaction temperatures influence molecular weight and molecular weight distribution of the resulting polymer.

2.5 Rationale of the study

It is evident that the choice of ligand and metal center plays an intricate role in designing a system that displays high activity towards the conversion of NBE to VPNBE. Ligands display high levels of versatility and have shown the ability to regulate the electronic and steric properties of metal centers in complexes. Ultimately, variations in the complex design offer the opportunity to regulate and control molecular weights, solubility, glass transition temperatures, degradation temperatures, and molecular weight distributions of resulting polymers. Great progress has been made in efforts to design systems to afford VPNBE and control key aspects of the resulting polymer's characteristics, but opportunity still exist to expand on the fronts of this knowledge. In this study, bidentate and tridentate systems of nitrogen-donor ligands are to be designed and employed in forming complexes with nickel(II), palladium(II), iron(II), and cobalt(II) (**Figure 2.**). The (pyridyl)imine-bearing complexes hold the potential of forming polymers of industrial interest. The ligands were chosen for their ease of synthesis, their stability in complexes, and their structural similarity to evaluate performance differences between bidentate and tridentate systems.

L1

L2

[M(L1)₂Cl₂]

M = Ni(II) (**Ni1**)

[M(L1)Cl₂]

M = Pd(II) (**Pd1**)

[M(L1)₃][2PF₆]

M = Fe(II) (**Fe1**), Co(II) (**Co1**)

[M(L2)Cl₂]

M = Ni(II) (**Ni2**), Fe(II) (**Fe2**), Co(II) (**Co2**)
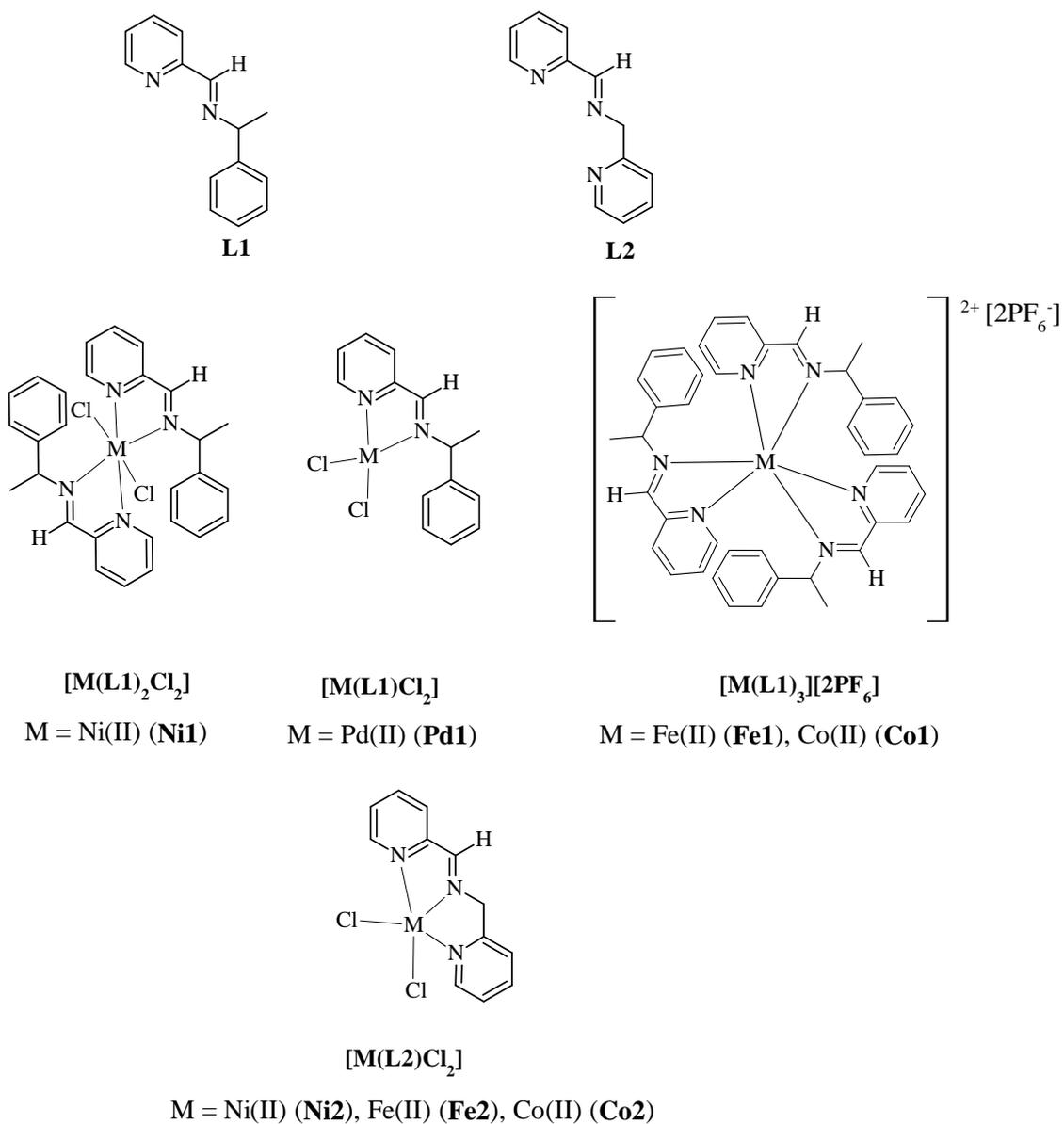
Figure 2.23: The proposed structures of the (pyridyl)imine ligands and their transition metal complexes used in this research.

2.6 Aim and objectives of the study

2.6.1 General aim

To develop active (pyridyl)imine nickel(II), palladium(II), cobalt(II), and iron(II) complexes, with bidentate and tridentate ligand systems, and test as pre-catalysts in vinyl-addition polymerization of norbornene to fully understand the catalytic properties and the influence of reaction parameters on the formation of the resulting vinyl-type polynorbornene.

2.6.2 Specific Objectives

1. To synthesize and characterize bidentate and tridentate (pyridyl)imine ligands and their nickel(II), palladium(II), cobalt(II), and iron(II) metal complexes.

2. To evaluate the catalytic ability of each complex as pre-catalysts in the vinyl-addition polymerization of norbornene.

3. To understand the influence of catalyst structure and reaction parameters on vinyl-addition polymerization of norbornene.

4. To evaluate the microstructure and thermal properties of the resulting polynorbornene.

References

[1] C. Janiak and P. Lassahn, "Metal catalyst for the vinyl polymerization of norbornene," *J. Mol. Catal.,* vol. 166, pp. 193-209, 2001.

[2] L. Benade, S. Ojwach, C. Obuah, I. Guzei and J. Darkwa, "Vinyl-addition polymerization of norbornene catalyzed by (pyrazol-1-ylmethyl)pyridine divalent iron, cobalt and nickel complexe," *Polyhedron,* vol. 30, pp. 2878-2883, 2011.

[3] F. Chang, D. Zhang, G. Xu, H. Yang, J. Li, H. Song and W. Sun, "Synthesis and characterization of new bis(1-aryliminomethylenylnaphthalen-2-oxy)nickel complexes and their catalytic behavior for vinyl polymerization of norbornene," *J. Organomet. Chem.,* vol. 689, pp. 936-946, 2004.

[4] S. Jie, P. Ai, Q. Zhou and B. Li, "Nickel and cationic palladium complexes bearing (imino)pyridyl alcohol ligands: Synthesis, characterization and vinyl polymerization of norbornene," *J. Organomet. Chem.,* vol. 696, pp. 1465-1473, 2011.

[5] G. Ricci, G. Leone, A. Rapallo, P. Biagini, G. Guglielmetti and L. Porri, "Syndiospecific oligomerization and polymerization of norbornene with titanium catalysts," *Polymer,* vol. 52, pp. 5708-5715, 2011.

[6] R. Zhuang, H. Liu, J. Guo, B. Dong, W. Zhao, Y. Hu and X. Zhang, "Highly active nickel(II) and palladium(II) complexes bearing N,N,P tridentate ligand for vinyl addition polymerization of norbornene," *Eur. Polym. J.,* 2017.

[7] H. Liang, J. Liu, X. Li and Y. Li, "Synthesis, structure and norbornene polymerization behavior of neutral palladium complexes," *Polyhedron,* vol. 23, pp. 1619-1627, 2004.

[8] G. Myagmarsurene, J. Park and S. Ihm, "Polymerization of norbornene using novel palladium carboxylate/boron trifluoride etherate catalyst system," *Polymer,* vol. 47, pp. 8474-8479, 2006.

[9] N. Seehof, C. Mehler, S. Breunig and W. Risse, "Pd2+ catalyzed addition polymerizations of norbornene and norbornene derivatives," *J. Mol. Catal.,* vol. 76, pp. 219-228, 1992.

[10] P. Xiang and Z. Ye, "Homo- and Co-polymerization of norbornene and methyl acrylate with Pd-diimine catalysts," *J. Organomet. Chem.,* vol. 798, pp. 429-436, 2015.

[11] T. Saegusa, T. Tsujino and J. Furukawa, *Macromol. Chem.,* vol. 78, pp. 231-233, 1964.

[12] T. Hasan, T. Ikeda and T. Shiono, "Highly efficient Ti-based catalyst systems for vinyl addition polymerization of norbornene," *Macromolecules,* vol. 37, pp. 7432-7436, 2004.

[13] H. Hu, H. Gao, K. Song, F. Liu, J. Long, L. Zhang, F. Zhu and Q. Wu, "Novel bis(benzoin) titanium catalyst for homo- and copolymerization of norbornene with ethylene: Synthesis, characterization and catalytic properties," *Polymer,* vol. 49, pp. 4552-4558, 2008.

[14] J. Zhang, P. Wang, X. Wang, L. Wang, J. Chen and Z. Zheng, "Vinyl addition polymerization of norbornene catalyzed by b-iminoamine Ni(II) complexes/methylaluminoxane systems," *J. Organomet. Chem.,* vol. 696, pp. 3697-3702, 2011.

[15] T. Saito and Y. Wakatsuki, "Addition polymerization of norbornene, 5-vinyl-2-norbornene and 2-methoxycarbonyl-5-norbornene with a catalyst based on a palladium(0) precursor complex," *Polymer,* vol. 53, pp. 308-315, 2012.

[16] W. Kaminsky, "Highly active metallocene catalysts for olefin polymerization," *J. Chem. Soc., Dalton Trans.,* pp. 1413-1418, 1998.

[17] W. Kaminsky, "Highly active metallocene catalysts for olefin polymerization.," *J. Chem. Soc., Dalton Trans.,* pp. 1413-1418, 1998.

[18] H. Sinn, *Macromol. Symp.,* vol. 95, p. 27, 1995.

[19] G. Vougioukalakis, I. Stamatopoulos, N. Petzetakis, C. Raptopoulou, V. Psycharis, A. Terzis, P. Kyritsis, M. Pitsikalis and N. Hadjichristidis, "Controlled Vinyl-Type Polymerization of Norbornene with a Ni(II) diphosphinoamine/methylaluminoxane catalytic system," *J. Polym. Sci., Part A: Polym. Chem.,* vol. 47, pp. 5241-5250, 2009.

[20] W. Kaminsky, A. Bark and M. Arndt, *Macromol. Symp.,* vol. 47, pp. 83-93, 1991.

[21] W. Kaminsky and A. Noll, *Polym. Bull.,* pp. 175-182, 1993.

[22] W. Kaminsky, S. Derlin and M. Hoff, "Copolymerization of propylene and norbornene with different metallocene catalysts," *Polymer,* vol. 48, pp. 7271-7278, 2007.

[23] U. Peuckert and W. Heitz, *Macromol. Rapid Commun.,* vol. 19, pp. 159-162, 1998.

[24] L. Pei, Y. Tang and H. Gao, "Homo- and copolymerization of ethylene and norbornene with anilido-imine chromium catalysts," *Polymers,* vol. 8, p. 69, 2016.

[25] Y. Sato, Y. Nakayama and H. Yasuda, "Controlled vinyl-addition-type polymerization of norbornene initiated by several cobalt complexes having substituted terpyridine ligands," *J. Organomet. Chem.,* vol. 689, pp. 744-750, 2004.

[26] C. Carlini, S. Giaiacopi, F. Marchetti, C. Pinzino, A. Galletti and G. Sbrana, "Vinyl Polymerization of Norbornene by Bis(salicylaldiminate)copper(II)/Methylalumoxane Catalysts," *Organometallics,* vol. 25, pp. 3659-3664, 2006.

[27] P. Hao, S. Song, T. Xiao, Y. Li, C. Redshaw and W. Sun, "Highly active 8-benzoxazolyl- or 8-benzothiazolyl-2-alkylquinolinylnickel(II) complexes for ethylene dimerization and vinyl polymerization of norbornene," *Polyhedron,* vol. 52, pp. 1138-1144, 2013.

[28] X. He and Q. Wu, "Polymerization of Norbornene Using Bis(B-ketoamino)nickel(II)/MAO Catalytic Systems," *J. App. Polym. Sci.,* vol. 101, pp. 4172-4180, 2006.

[29] T. Younkin, E. Connor, J. Henderson, S. Friedrich, R. Grubbs and D. Bansleben, "Neutral, Single-Component Nickel (II) Polyolefin Catalysts That Tolerate Heteroatoms," *Science,* vol. 287, pp. 460-462, 2000.

[30] J. Hou, S. Jie, W. Zhang and W. Sun, "Vinyl Polymerization of Norbornene over Supported Nickel Catalyst," *J. App. Polym. Sci.,* vol. 102, pp. 2233-2240, 2006.

[31] Y. Yu, J. Chen, S. Meng, C. Li, M. Lan and Z. Zhang, "Ni(II) and Cu(II) complexes as catalysts for norbornene vinyl polymerization bearing tetradentate B-ketoiminato ligands," *J. Mol. Cat. A: Chem.,* vol. 380, pp. 104-111, 2013.

[32] L. Goodall, L.H. McIntosh III and L.F. Rhodes, *Macromol. Symp.,* vol. 89, pp. 421-432, 1995.

[33] G. Leone, A. Boglia, A. C. Boccia, S. T. Scafati, F. Bertini and G. Ricci, "Vinyl-type addition polymerization of norbornene and synthesis of norbornene macromonomers in the presence of ethylene catalyzed by cobalt(II)-phosphine complexes," *Macromolecules,* vol. 42, pp. 9231-9237, 2009.

[34] B. L., M. Brookhart and A. Bennett, "Highly active iron an cobalt catalysts for the polymerization of ethylene," *J. Am. Chem. Soc.,* vol. 120, pp. 4049-4050, 1998.

[35] J. Cheng, Y. Huang, Z. Li, Z. Zhang, C. Wie, T. Lan and W. Zhang, *J. Mol. Catal. A: Chem.,* vol. 259, p. 133, 2006.

[36] M. Sacchi, M. Sonzogni, S. Losia, F. Forlini, P. Locatelli, I. Tritto and M. Lichelli, "Vinyllic polymerization of norbornene by late transition metal-based catalysis," *Macromol. Chem. Phys.,* vol. 10, p. 202, 2001.

[37] Sen, A. Sen, T. Lai and R. Thomas, "Reactions of electrophilic transition metal cations with olefins and small ring compounds. Rearrangements and polymerizations.," *J. Organomet. Chem.,* vol. 958, pp. 567-588, 1988.

[38] L. Johnson, C. Killian and M. Brookhart, "New Pd(II)- and Ni(II)-Based Catalysts for Polymerization of Ethylene and a-Olefins," *J. Am. Chem. Soc.,* vol. 117, pp. 6414-6415, 1995.

[39] A. Reinmuth, J. P. Mathew, J. Melia and W. Risse, "(n3-allyl)Pd(II) catalysts for the addition polymerization of norbornene derivatives with functional groups," *Macromol. Rapid Commun.,* vol. 17, pp. 173-180, 1996.

[40] V. Tkach, G. Myagmarsuren, D. Suslov, T. Darjaa, D. Dorj and F. Shmidt, "The Pd2(CH,,CC6H5)2(C5H7O2)3(BF3)2BF4 catalyst for the polymerization of norbornene," *Catal. Commun.,* vol. 9, pp. 1501 - 1504, 2008.

[41] Y. Huang, J. He, Z. Liu, G. Cai, S. Zhang and X. Li, "A highly active chiral (S,S)-bis(oxazoline) Pd(II) alkyl complex/activator catalytic system for vinyl polymerization of norbornene in air and water," *Polym. Chem.,* vol. 8, p. 1217, 2017.

[42] X. Mi, Z. Ma, N. Cui, L. Wang, K. Yucai and H. Youliang, "Vinyl Polymerization of Norbornene with Dinuclear Diimine Nickel Dichloride/MAO," *J. Appl. Polym. Sci.,* vol. 88, pp. 3273-3278, 2003.

[43] Yang H., Li Z., Li Y. and Sun W., "Vinyl Polymerization of Norbornene with Neutral Salicylaldiminato Nickel(II) Complexes," *Organometallics,* vol. 22, pp. 3678-3683, 2003.

[44] D. Lee, J. Lee, J. Ryu, Y. Kim, C. Kim and I. Lee, "Novel Nickel Catalysts Containing Tetradentate Chelating Ligands for the Polymerization of Norbornene," *Bull. Korean Chem. Soc.,* vol. 27, p. 1031, 2006.

Chapter Three

Synthesis and characterization of (pyridyl)imine ligands and their corresponding nickel(II), palladium(II), iron(II), and cobalt(II) complexes

3.1 General background

Schiff bases are compounds possessing azomethine groups (-HC=N-) and are generally prepared following a simple condensation reaction of an aldehyde and a primary amine in the presence of an acid or base catalyst [1, 2, 3, 4]. Transition metals can be reacted with the Schiff bases to achieve coordination between the metal atom and the electron-donating groups present in the ligand structure [5, 6]. Schiff bases are of great chemical importance because chirality and stereogenic centers can be manipulated by synthetic design [5]. Schiff bases were first reported by Hugo Schiff in 1864 and now when used to stabilize cationic metals [5], it has known applications in the field of catalytic transformations [7], oligomerization, and polymerization [8, 9, 10, 11], the refining of metals, photography, electroplating [12], and have illustrated applications in renewable energy resources [6]. Other applications include antibacterial- and antifungal uses in medical technology [13, 1].

Schiff bases have also shown importance as pre-catalysts in the vinyl addition polymerization of norbornene (NBE) when chelated with transition metals to form bi-, tri-, or tetradentate systems containing O, N, or P donor atoms [14, 15, 16, 17, 18]. For example, nickel complexes of Schiff base ligands were recently tested as pre-catalysts in the polymerization of NBE [19, 20, 21]. Hao *et. al* investigated nickel(II) complexes of [N, N, N] – tridentate quinolinyl anilido-imine ligands, which showed moderate activity in the polymerization of NBE [19]. Zhuang and co-workers investigated nickel(II) and palladium(II) complexes which consisted of [N, N, P] –

tridentate ligand systems, whereby high yields and catalytic activities were reported [20]. Jie *et. al* tested nickel(II)-complexes with pyridyl(imine) alcohol ligands which have delivered vinyl-type polynorbornene (VPNBE) with low molecular weight distributions of 2.18 [21]. This confirms that Schiff base ligands, chelated with transition metal centers, are relevant in the effort to find affordable and efficient pre-catalysts for the vinyl-addition polymerization of NBE. Schiff bases are regarded as stable solids and can be stored under moderate conditions. The extensive literature review in previous chapters illustrated the vast number of species that have been employed in recent years to polymerize NBE [22]. In this chapter two Schiff base ligands of [N, N]-bidentate and [N, N, N]-tridentate nature will be synthesized, characterized, and reacted with $NiCl_2$, [Pd(COD)Cl_2], $FeCl_2.4H_2O$ and anhydrous $CoCl_2$ to form corresponding metal complexes.

3.2 Materials and instruments

3.2.1 General instruments and materials

Where applicable, all manipulations of moisture and air-sensitive materials were conducted under Schlenk conditions under nitrogen and a vacuum line. All solvents employed were of analytical grade. Diethyl ether, ethanol (EtOH), dichloromethane (DCM), tetrahydrofuran (THF), and methanol (MeOH) were used as received and no further purification was done. Starting materials: nickel(II) chloride ($NiCl_2$) ($\geq$: 98 %); palladium(II) chloride ($PdCl_2$) ($\geq$: 98 %), anhydrous cobalt(II) chloride ($\geq$: 99 %), Merck; iron(II) chloride ($FeCl_2.4H_2O$) ($\geq$: 98.9 %), univAR, *para*-toluene sulfonic acid monohydrate (p-TsOH) ($\geq$:98.5 %); 2-pyridine carboxaldehyde ($\geq$: 99 %); 2-picolyl amine ($\geq$: 99 %); (*R*-)–(+)-α-methyl benzylamine ($\geq$:98 %) and NMR solvents (deuterated chloroform, $CDCl_3$, and deuterated dimethyl sulfoxide, DMSO-d6) were purchased from Sigma-Aldrich, unless stated otherwise, and used as received without further purification. [Pd(COD)Cl_2] was fabricated by dissolving $PdCl_2$ (1.00 g, 5.65

mmol) in 33 % hydrochloric acid (25 mL) before heating the solution to 50 ˚C. To the cooled solution, ethanol (75 mL) was added, the resulting solution was filtered, and the residue washed with ethanol (20 mL). To the filtrate was added 1,5-cyclooctadiene (1.5 mL) while stirring for 10 min at 40 ˚C. [Pd(COD)Cl$_2$] precipitated immediately as a yellow solid and was filtered before being washed with diethyl ether (15 mL) and dried in air [23]. Yield: 1.48 g, (92%).

NMR spectra were recorded on a Bruker Ultrashield 400 (^{1}H-NMR 400 MHz, ^{13}C-NMR 100 MHz) spectrometer in a CDCl$_3$ or deuterated dimethyl sulfoxide (DMSO-d6) solution at room temperature and chemical shifts (δ) were determined relative to internal TMS and recorded in ppm relative to CHCl$_3$ δ [1]H: 7.26 ppm and δ [13]C: 77.6 ppm and DMSO-d6 δ ^{1}H; 2.50 ppm. Coupling constants (*J*) are reported in Hertz (Hz) and splitting patterns are indicated as singlet (s), doublet (d), doublet of doublet (dd), triplet (t), and multiplet (m). Mass spectra were recorded on an electron spray ionisation mass spectrometer (ESI-MS), liquid chromatography (LC) premier micro-mass spectrometer, and time of flight mass spectrometer (TOF-MS). Elemental analyses (CHN) were conducted on a Thermo Scientific Flash 2000 and infra-red spectra were recorded on a Bruker Alpha II Platinum ATR Spectrometer in the 4000 – 650 cm^{-1} range. Single crystal X-ray diffraction (SC-XRD) evaluation and data collection for complex **Co1** was carried out on a Bruker Apex Duo that contains an Oxford Instrument Cryo, jet operating at 100(2) K, and an uncoated micro source that operates at 30 W power. Data was collected with Mo Kα (λ = 0.71073 (Å)) radiation with the crystal-to-detector distance measuring at 50 mm. Experimental conditions used for data collection are as follows: omega and phi scans with exposures captured at 30 W X-ray power and 0.50 frame widths applying APEX2 [24]. Collected data was condensed using the SAINT [25] program and outlier rejection, scan speed scaling as well as standardized Lorentz and polarization correction factors. A SADABS semi-empirical multi-scan absorption correction was conducted on the

data and the structure of complex **Co1** was solved using direct methods of SHELXS-2014 and WinGX. Non-hydrogen atoms were situated in the differential density map and developed anisotropically with SHELX-2014 [26]. All hydrogen atoms were incorporated as idealized contributors in the least squares procedure and their positions were determined employing a standard riding model with C-H$_{aromatic}$ distances of 0.93 Å and U_{iso} = 1.2 U_{eq} and CH$_{methylene}$ distances of 0.99 Å and U_{iso} = 1.2 U_{eq} and C-H$_{methyl}$ distances of 0.98 Å U$_{iso}$ = 1.5 U_{eq}.

3.2.2 Syntheses of ligands and corresponding transition metal complexes

*3.2.2.1 Synthesis of (E)-N-(1-phenylethyl)-1-(pyridin-2-yl)methanimine (**L1**).*
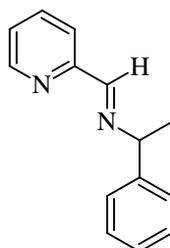
To a solution of 2-pyridine carboxaldehyde (0.75 g, 7.02 mmol) in dichloromethane (10 mL), was added (R)-(+)-α-methyl benzylamine (0.85 g, 7.02 mmol), and catalytic amounts of p-TsOH which was stirred for 24 h at room temperature. After the reaction was complete the solution was filtered, and the solvent was removed in vacuum to obtain crude brown oil. The crude was dissolved in dichloromethane (10 mL), washed with distilled water (15 mL), and the organic layer was dried using Na$_2$SO$_4$, filtered and the solvent was removed in vacuum to obtain bidentate ligand **L1** as a yellow oil. Yield: 0.94 g, (64%). ^{1}H NMR (400 MHz, CDCl3): δ 1.64 (d, 3H, N-CHC<u>H3</u>, 3*J*HH = 6.4Hz) 4.67 (q, 1H, NC<u>H</u>-CH3, 3*J*HH = 6.8Hz), 7.27 (q, 1H, N-C<u>H</u>, 3*J*HH = cluster), 7.36 (t, 2H, <u>H</u>-bz, 3*J*HH = 7.6Hz), 7.45 (d, 2H, <u>H</u>-bz, 3*J*HH = 7.2Hz), 7.71 (ddd, 1H, <u>H</u>-*py*, 3*J*HH = 7.6Hz), 8.11 (d, 1H, H-*py*, 3*J*HH = 8Hz), 8.50 (s, 1H,

N=C<u>H</u>), 8.63 (d, 1H, H-*pyr*, 3*J*HH = 4Hz). ^{13}C NMR (CDCl3): δ 24.54 (<u>C</u>H3), 30.89 (CH3<u>C</u>H), 69.54 (bz-<u>C</u>H), 121.47 (*o*-bz-<u>C</u>), 124.68 (bz-<u>C</u>), 126.71 (bz-<u>C</u>), 127.00 (bz-<u>C</u>), 128.48 (bz-<u>C</u>), 136.49 (py-<u>C</u>), 144.58 (*m*-py-<u>C</u>), 149.33 (*m*-py-<u>C</u>), 154.82 (*m*-py-<u>C</u>), 160.45 (<u>C</u>pyr-CH), 160.45 (<u>C</u>H-pyr). FT-IR (cm^{-1}): ν$_{(C=N)imine}$ = 1644.48. ESI-MS: *m/z* (%) 211 ([M$^+$ + ^{1}H]$^+$, 100%). HR MS-ESI ([M$^+$ - H$^+$]): Calc.: 211.1235; Found: 211.1232. Anal. Calc. for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 75.73; H, 5.57; N, 12.64.

*3.2.2.2 Synthesis of (E)-1-(pyridin-2-yl)-N-(pyridin-2-ylmethyl)methanimine (**L2**).*
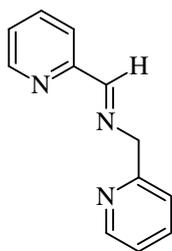
To a solution of 2-pyridine carboxaldehyde (0.53 g, 2.67 mmol) in ethanol (10 mL) was added 2-picolylamine (0.53 g, 2.67 mmol) and catalytic amounts of p-TsOH and the resulting solution was refluxed for 24 h at 80 ˚C. After the reaction, the solution was filtered, and the solvent removed in vacuum to obtain a crude brown oil. The crude was dissolved in dichloromethane (10 mL), washed with distilled water (15 mL), and the organic layer was dried using NaSO$_4$, filtered and the solvent was removed in vacuum to obtain tridentate ligand **L2** as a brown oil. Yield: 0.47 g, (90%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.59 (s, 1H, N=C<u>H</u>) 8.68 (d, 1H, *pyr*-<u>H</u>, $^3J_{HH}$ = 5.6Hz), 7.68 (m, 1H, *pyr*-<u>H</u>), 7.56 (m, 2H, *pyr*-<u>H</u>), 7.36 (m, 1H, *pyr*-<u>H</u>), 5.04 (s, 2H, *pyr-C-2*<u>H</u>), 7.03 (m, 4H, *pyr*-<u>H</u>), ^{13}C NMR (DMSO-d6): δ 161.3 (<u>C</u>-CH$_2$), 158.4 (*o*-<u>pyr</u>-<u>C</u>), 148.9 (*o*-pyr-<u>C</u>), 148.9 (*o*-pyr-<u>C</u>), 137.0 (-N=<u>C</u>), 123.6 (*p*-pyr-<u>C</u>), 123.6 (*p*-pyr-<u>C</u>), 83.5 (*m*-

pyr-<u>C</u>), 76.1 (*m*-py-<u>C</u>), 73.5 (*m*-pyr-<u>C</u>), 69.5 (*m*-pyr-<u>C</u>), 66.3 (N-<u>C</u>H$_2$), FT-IR (cm^{-1}): $\nu_{(C=N)imine}$ = 1670.56. ESI-MS: *m/z* (%) 395 ([2M$^+$ + H], 100%). HR MS-ESI ([2M$^+$ + Na$^+$]): *m/z* Anal. Calc.: 417.1804; Found: 417.1797. Anal. Calc. for C$_{12}$H$_{11}$N$_3$: C, 73.07; H, 5.62; N, 21.30. Found: C, 74.27; H, 5.64; N, 21.35.

*3.2.2.3 Synthesis of [Ni(**L1**)$_2$Cl$_2$] (**Ni1**).*
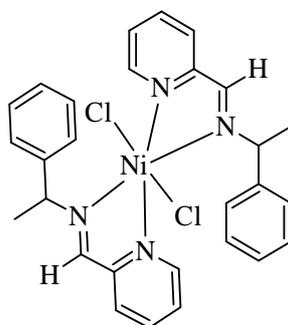
To a solution of ligand **L1** (0.25 g, 1.10 mmol) in dichloromethane (10 mL) was added NiCl$_2$ (0.07 g, 0.55 mmol), and the resulting solution was allowed to stir for 24 h at room temperature. After the reaction, the solution was filtered, and the solvent was removed under vacuum after which diethyl ether (20 mL) was added to precipitate the complex. The mixture was filtered and washed again with diethyl ether (20 mL) and dried in air to obtain complex **Ni1** as a light green powder. Yield: 0.16 g, (53%). FT-IR (cm^{-1}): $\nu_{(C=N)imine}$ = 1598.01, HR MS-ESI ([M$^+$ − Cl]): *m/z* Anal. Calc.: 514.6945, Found: 514.1392; TOF MS-ESI: *m/z* (%) 478.0345 ([M$^+$ − 2Cl$^-$], 31%). Anal. Calc. for C$_{28}$H$_{28}$N$_4$Cl$_2$Ni.CH$_2$Cl$_2$: C, 54.85; H, 4.76; N, 9.24. Found: C, 55.90; H, 4.86; N, 9.34.

*3.2.2.4 Synthesis of [Pd(**L1**)Cl₂] (**Pd1**).*
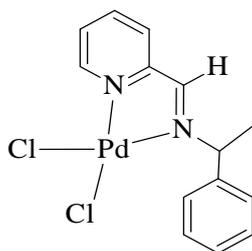
[Pd(COD)Cl$_2$] was prepared according to literature procedures [23].

To a solution of ligand **L1** (0.05 g, 2.37 mmol) in dichloromethane (10 mL) and acetonitrile (1 mL) under N$_2$ was added [Pd(COD)Cl$_2$] (0.67 g, 2.37 mmol) dissolved in dichloromethane (5 mL) *via* cannula. The resulting solution was allowed to stir for 24 h at room temperature. At the end of reaction, the solution was filtered, and the mother liquor concentrated in vacuum. To the resulting solution was added diethyl ether (15 mL) to precipitate the product, after which the mixture was filtered and dried to afford complex **Pd1** as a yellow solid. Yield: 0.55 g, (60%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 1.89 (d, 3H, N-CHC$\underline{H}_3$, $^3J_{HH}$ = 6.8 Hz) 6.09 (q, 1H, NC$\underline{H}$-CH$_3$, $^3J_{HH}$ = 6.8 Hz), 7.45 (m, 5H, $\underline{H}$-bz), 7.66 (m, 2H, $\underline{H}$-pyr,), 7.77 (s, 1H, $\underline{H}$-bz), 8.07 (ddd, 1H, $\underline{H}$-*py*, $^3J_{HH}$ = 6.4 Hz), 9.39 (d, 1H, H-*py*, $^3J_{HH}$ = 4.4 Hz), FT-IR (cm^{-1}): ν$_{(C=N)imine}$ = 1596.21. LR ESI-MS: *m/z* (%) 395 ([M$^+$.(C$_2$H$_3$N) - Cl], 100%); HR MS-ESI ([M$^+$.(C$_2$H$_3$N) - Cl]): *m/z* Anal. Calc.: 393.9298, Found: 394.0150. Anal. Calc. for C$_{14}$H$_{14}$Cl$_2$N$_2$Pd: C, 43.38; H, 3.64; N, 7.22. Found: C, 44.66; H, 3.60; N, 7.29.

*3.2.2.5 Synthesis of of [Fe(**L1**)₃]²⁺[2PF₆⁻] (**Fe1**).*
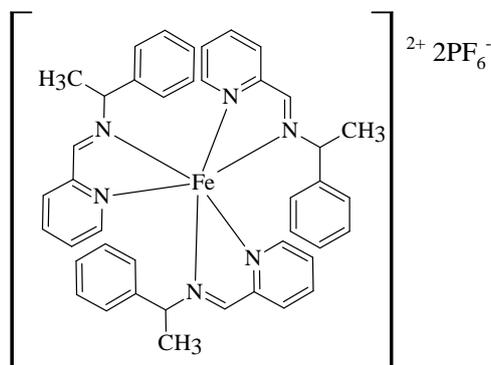
To a solution of ligand **L1** (0.82 g, 2.73 mmol) in dichloromethane (15 mL) under N_2 was added $FeCl_2.4H_2O$ (0.12 g, 0.91 mmol). The resulting solution was reacted for 24 h at room temperature, after which 2 molar equivalents of NH_4PF_6 were added and allowed to react for an additional 24 h at room temperature. After the reaction, the mother liquor was filtered before being concentrated by removing the solvent in vacuum. The complex was precipitated by the addition of diethyl ether (15 mL) after which the mixture was filtered, washed with diethyl ether (15 mL), and dried in air to obtain complex **Fe1** as a dark purple powder. Yield: 0.16 g (18%). FT-IR (cm⁻¹): $v_{(C=N)imine}$ = 1613.54, ESI-MS: *m/z* (%) 687.19 ([M⁺], 8.45%). Anal. Calc. for $C_{42}H_{42}FeN_6P_2F_{12}$: C, 51.56; H, 4.33; N, 8.61. Found: C, 48.22; H, 3.12; N, 8.39.

*3.2.2.6 Synthesis of [Co(**L1**)₃]²⁺[2PF₆⁻] (**Co1**).*
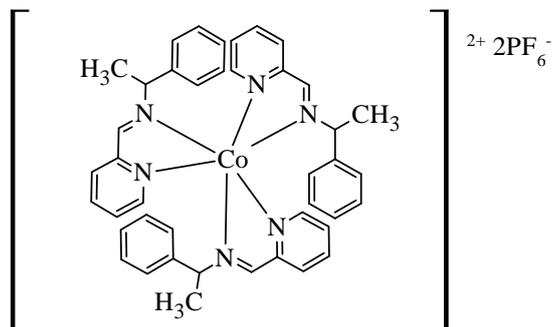
To a solution of ligand **L1** (0.10 g, 0.478 mmol) in dichloromethane (15 mL) was added CoCl₂ (0.02 g, 0.159 mmol). The resulting solution was reacted for 24 h at room temperature, after which 2 molar equivalents of NH₄PF₆ were added and allowed to react for an additional 24 h at room temperature. After the reaction, the mother liquor was filtered before being concentrated by removing the solvent in vacuum. The complex was precipitated by the addition of diethyl ether (15 mL) after which the mixture was filtered, washed with diethyl ether (15 mL), and dried in air to obtain complex **Co1** as a yellow crystalline product. Yield: 0.10 g, (53%). FT-IR (cm⁻¹): $\nu_{(C=N)imine}$ = 1597.90. ESI-MS: *m/z* (%) 834.71 ([M²⁺.(PF₆⁻)], 5%). Anal. Calc. for $C_{42}H_{42}N_6CoF_{12}P_2$: C, 51.5; H, 4.33; N, 8.57. Found: C, 51.69; H, 3.06; N, 8.17.

*3.2.2.7 Synthesis of [Ni(**L2**)Cl₂] (**Ni2**).*
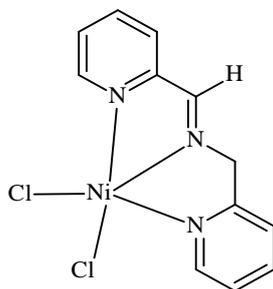
To a solution of ligand **L2** (0.13 g, 0.66 mmol) in dichloromethane (15 mL) was added NiCl₂ (0.09 g, 0.66 mmol), and the resulting solution was stirred for 24 h at room temperature. After 24 h the mother liquor was filtered before being concentrated by removal of the solvent in vacuum. The complex was precipitated by the addition of diethyl ether (15 mL). The mixture was filtered, washed with diethyl ether (15 mL), and dried under a steady flow of N_2 to obtain complex **Ni2** as a light green solid. Yield: 0.10 g, (45%). FT-IR (cm^{-1}): $v_{(C=N)imine}$ = 1603.83 ESI-MS: *m/z* (%) 489 [1/2M + (**L2**) - Cl]$^+$, 100%. Anal. Calc. for $C_{12}H_{11}N_3NiCl_2 \cdot CH_2Cl_2$: C, 37.92; H, 3.18; N, 10.20. Found: C, 37.93; H, 2.88; N, 10.30.

*3.2.2.8 Synthesis of [Fe(**L2**)Cl$_2$] (**Fe2**).*
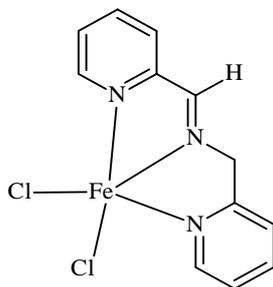
To a solution of ligand **L2** (0.10 g, 0.50 mmol) in dichloromethane (15 mL) was added

FeCl$_2$.4H$_2$O (0.10 g, 0.50 mmol) under N$_2$ and the resulting solution was stirred for 24 h at

room temperature. After 24 h the mother liquor was filtered before being concentrated by

removal of the solvent in vacuum. The complex was precipitated by the addition of diethyl

ether (15 mL). The mixture was filtered, washed with diethyl ether (15 mL), and dried in air to

obtain complex **Fe2** as a brown solid. Yield: 0.05 g, (31%). FT-IR (cm^{-1}): $v_{(C=N)imine}$ = 1601.34.

ESI-MS: *m/z* (%) 477 [1/2M + (**L2** + CH$_3$OH) - 2Cl]$^{2+}$, 100%. Anal. Calc. for C$_{12}$H$_{11}$N$_3$FeCl$_2$:

C, 44.49; H, 3.42; N, 12.97. Found: C, 43.99; H, 2.81; N, 12.05.

3.2.2.9 Synthesis of [Co(L2)Cl₂] (Co2).
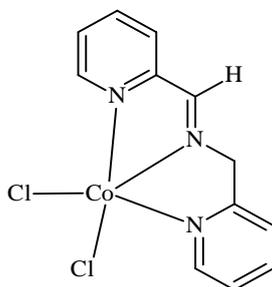
To a solution of ligand **L2** (0.10 g, 0.51 mmol) in dichloromethane (15 mL) was added CoCl₂ (0.07 g, 0.51 mmol), and the resulting solution was stirred for 24 h at room temperature. After 24 h, the mother liquor was filtered before being concentrated in vacuum. The complex was precipitated by the addition of diethyl ether (15 mL). The mixture was filtered, washed with diethyl ether (15 mL), and dried in air to obtain complex **Co2** as a light blue solid. Yield: 0.07 g, (42%). FT-IR (cm^{-1}): $\nu_{(C=N)imine}$ = 1604.32 ESI-MS: *m/z* (%) 488.09 ([M$^+$ - Cl], 100%). Anal. Calc. for C₁₂H₁₁N₃CoCl₂.CHCl₃: C, 34.97; H, 2.71; N, 9.41. Found: C, 34.92; H, 2.71; N, 5.73.

3.3 Results and discussion

3.3.1 Synthesis and characterization of bidentate L1, tridentate L2 and corresponding transition metal complexes

Syntheses of the ligand (E)-N-(1-phenylethyl)-1-(pyridin-2-yl)methanimine (**L1**) and ligand (E)-1-(pyridin-2-yl)-N-(pyridin-2-ylmethyl)methanimine (**L2**) resulted in moderate to high yields (64 - 90%) (**Scheme 3.1**). Reacting (pyridyl)imine ligands (bidentate **L1** and tridentate

L2) to afford corresponding complexes of nickel(II), palladium(II), cobalt(II), and iron(II), were isolated in low to moderate yields (18 - 60%) (**Scheme 3.2** and **Scheme 3.3**).
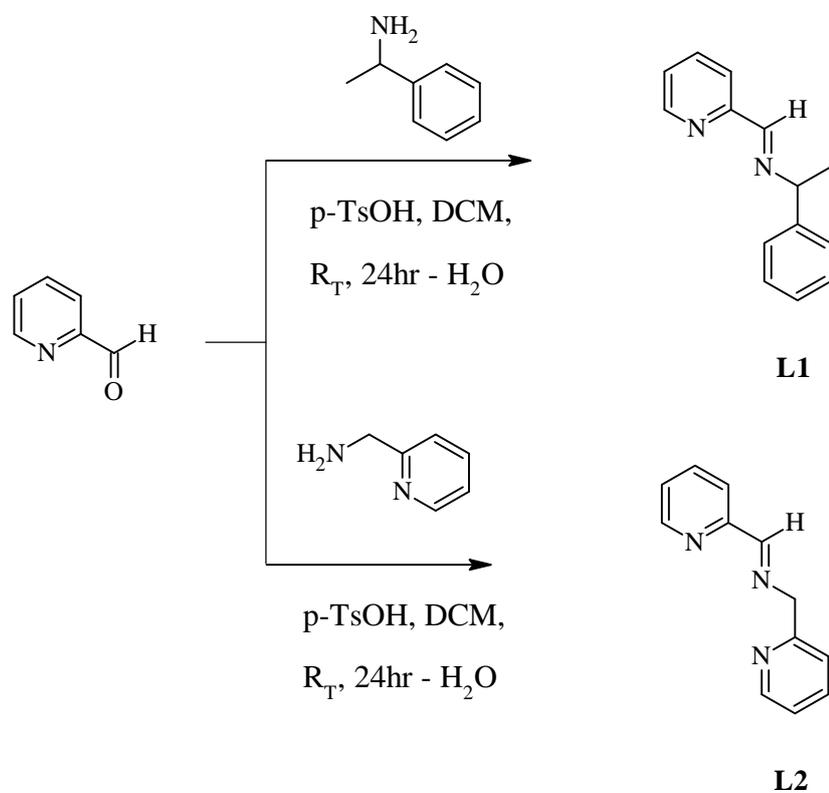
Scheme 3.1: Synthesis of bidentate (E)-N-(1-phenylethyl)-1-(pyridin-2-yl)methanimine (**L1**) and tridentate (E)-1-(pyridin-2-yl)-N-(pyridin-2-ylmethyl)methanimine (**L2**).
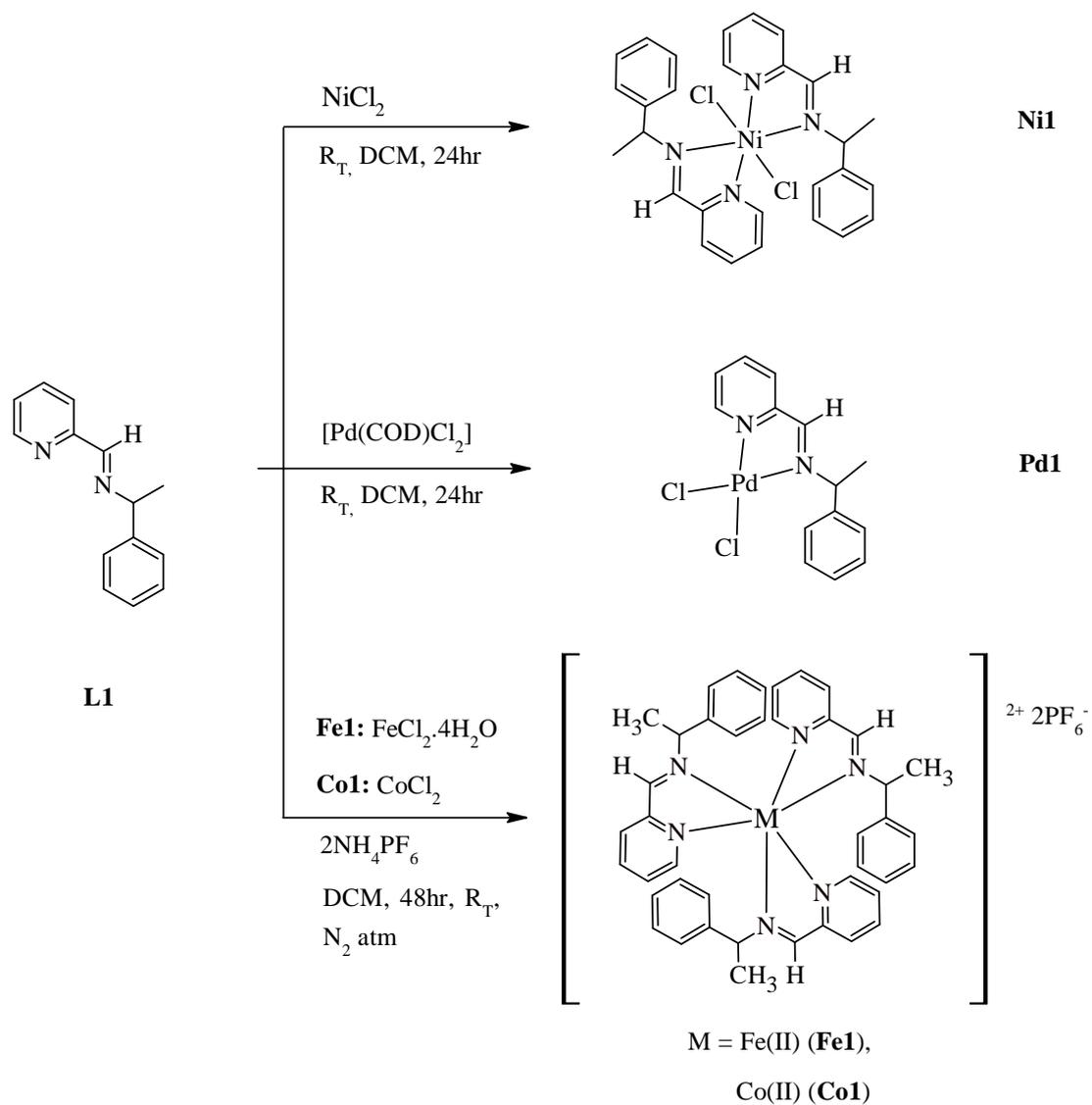
Scheme 3.2: Synthesis of (pyridyl)imine complexes **Ni1**, **Pd1**, **Fe1**, and **Co1** pre-catalysts from bidentate **L1**.
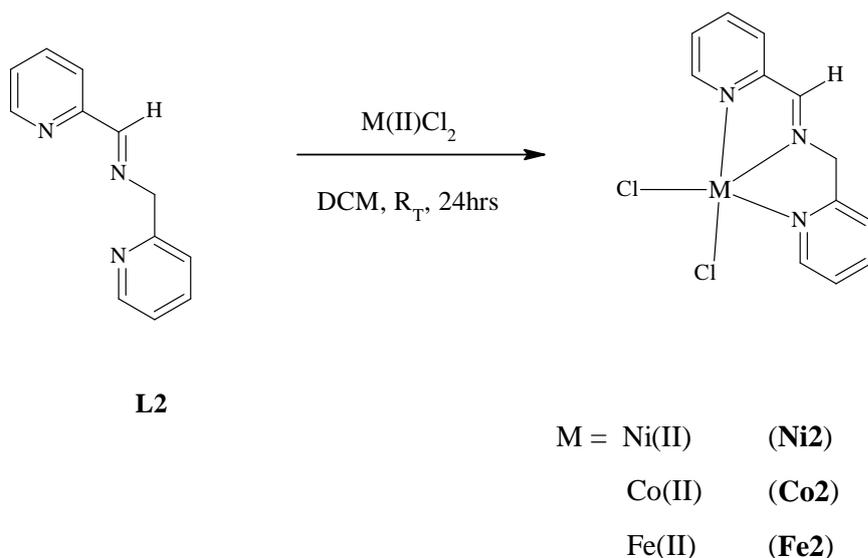
Scheme 3.3: Synthesis of (pyridyl)imine **Ni2**, **Co2,** and **Fe2** pre-catalysts from tridentate **L2**.

The identities of (pyridyl)imine bidentate (E)-N-(1-phenylethyl)-1-(pyridin-2-yl)methanimine (**L1**), tridentate (E)-1-(pyridin-2-yl)-N-(pyridin-2-ylmethyl)methanimine (**L2**)**,** as well as the identities of the corresponding transition metal complexes were confirmed using ^{1}H-NMR, ^{13}C-NMR, FTIR-Spectroscopy, ESI-MS, and elemental analysis. The structure of the novel compound **Co1** was confirmed using SC-XRD. Successful Schiff base formation was confirmed by identifying the signature imine proton peak visible in ^{1}H-NMR spectra for both bidentate **L1** and tridentate **L2**. The imine proton for bidentate **L1** and tridentate **L2** was represented as a singlet at 8.50 and 8.59 ppm respectively. For example, the ^{1}H-NMR spectra for bidentate **L1** can be seen in **Figure 3.1** where the imine proton located on the carbon next to the imine nitrogen, can be distinctly recognized downfield at 8.50 ppm. The aromatic protons were represented by peaks upfield at 7.7 – 7.2 ppm whereby the three protons from the methine group could be seen further upfield as a doublet at 1.63 ppm.
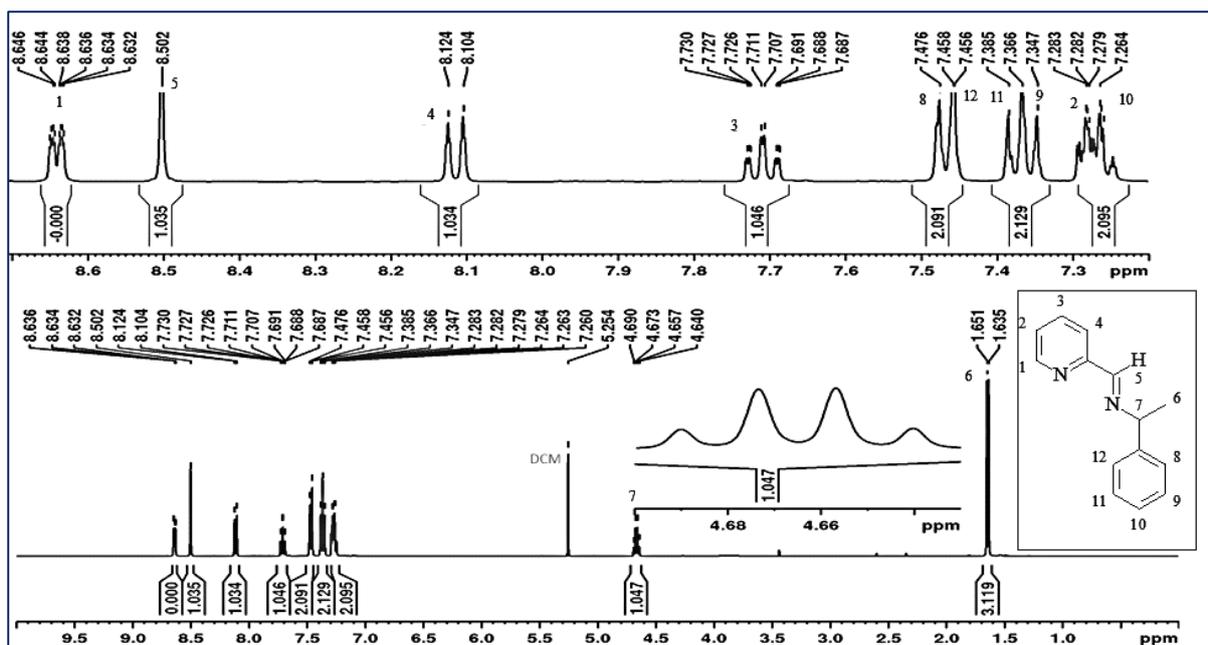
Figure 3.1: ^{1}H-NMR spectra for bidentate **L1** illustrating the imine proton at 8.50 ppm.

Due to the paramagnetic nature of the nickel(II), cobalt(II), and iron(II) metal complexes, ^{1}H-NMR spectroscopic characterization was only conducted for the palladium(II) complex **Pd1**. **Figure 3.2** illustrates the ^{1}H-NMR spectra of complex **Pd1** where the shift of the imine proton signal, indicated successful complex formation. The imine proton for bidentate **L1** was observed at 8.50 ppm whereas the corresponding imine proton for complex **Pd1** was seen at 7.77 ppm. The up-field shift in the imine proton signal can be explained by the deshielding of the imine proton due to the coordination of the nitrogen atom to the palladium(II). These observations were in line with other reports [27, 28]. ^{13}C-NMR spectral analysis accounted for all carbons present in the structure of bidentate **L1** and tridentate **L2** and was consistent with ^{1}H-NMR spectral data. For example, **Figure 3.3** illustrates the ^{13}C-NMR spectra for bidentate **L1**. The methine carbon was seen at 24.54 ppm and the carbon bonded to the imine nitrogen was seen at 30.89 ppm. All aromatic carbons were present at 121.47 to 154.82 ppm and the imine carbon (C=N) was present downfield at 160.45 ppm. This is in good agreement with other literature reports [29].
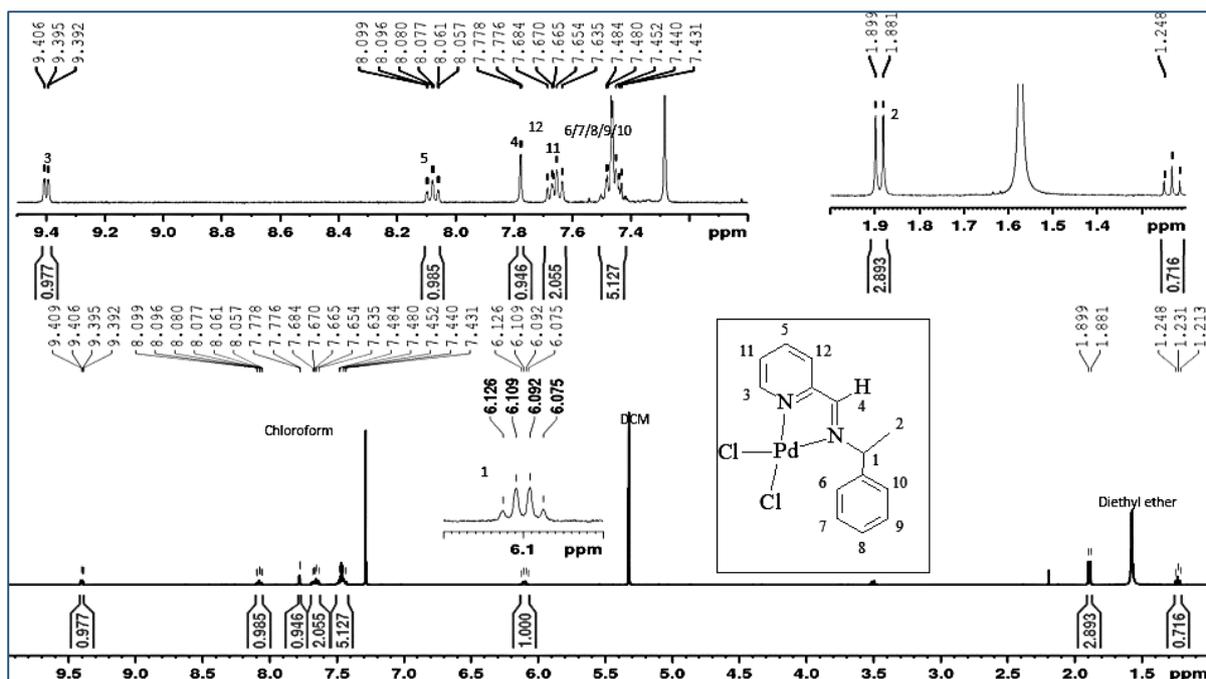
Figure 3.2: ^{1}H-NMR spectra of complex **Pd1** illustrating the clear shift of imine proton at 7.77 ppm.
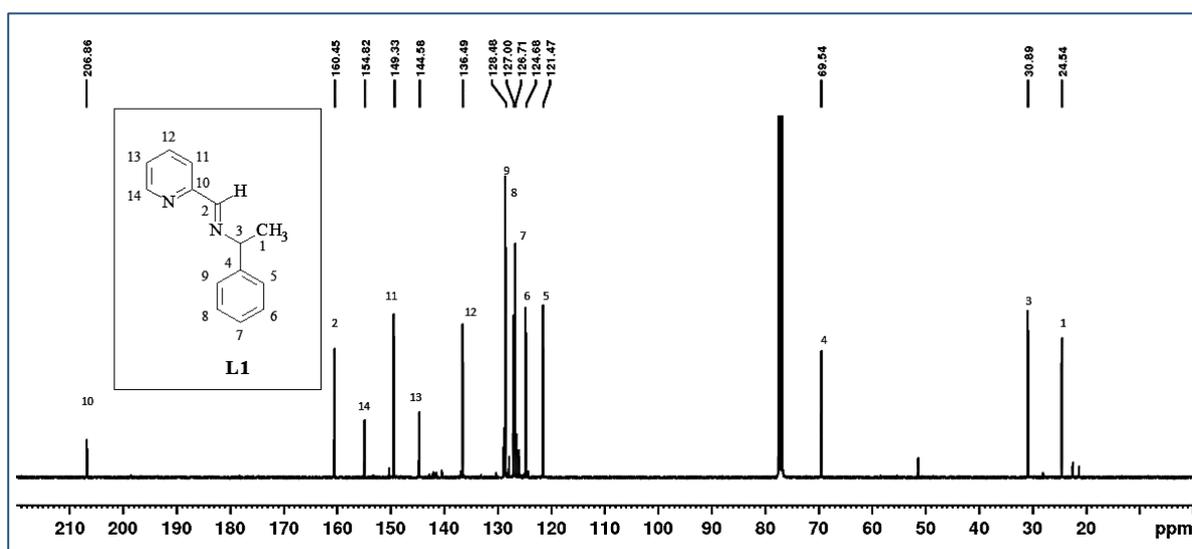
Figure 3.3: ^{13}C-NMR spectra for ligand **L1**, illustrating the imine carbon at 160.45 ppm.

FT-IR spectral analysis of bidentate ligand **L1** and tridentate ligand **L2** confirmed the formation of the ligands with the $v_{(C=N)imine}$ absorption band present between 1670 and 1644 cm^{-1} for both bidentate **L1** and tridentate **L2** [1, 29, 30]. For example, in **Figure 3.4** the imine stretch

vibration of ligand **L1** was seen at 1644.48 cm^{-1} which was a clear indication that the required bond formation (C=N) has taken place. FT-IR spectral analysis was also instrumental in establishing the formation of the corresponding (pyridyl)imine nickel(II), palladium(II), iron(II), and cobalt(II) metal complexes of bidentate **L1** and tridentate **L2**. This was determined by comparing the FT-IR spectra of the uncoordinated ligand with the spectra of the corresponding metal complex.
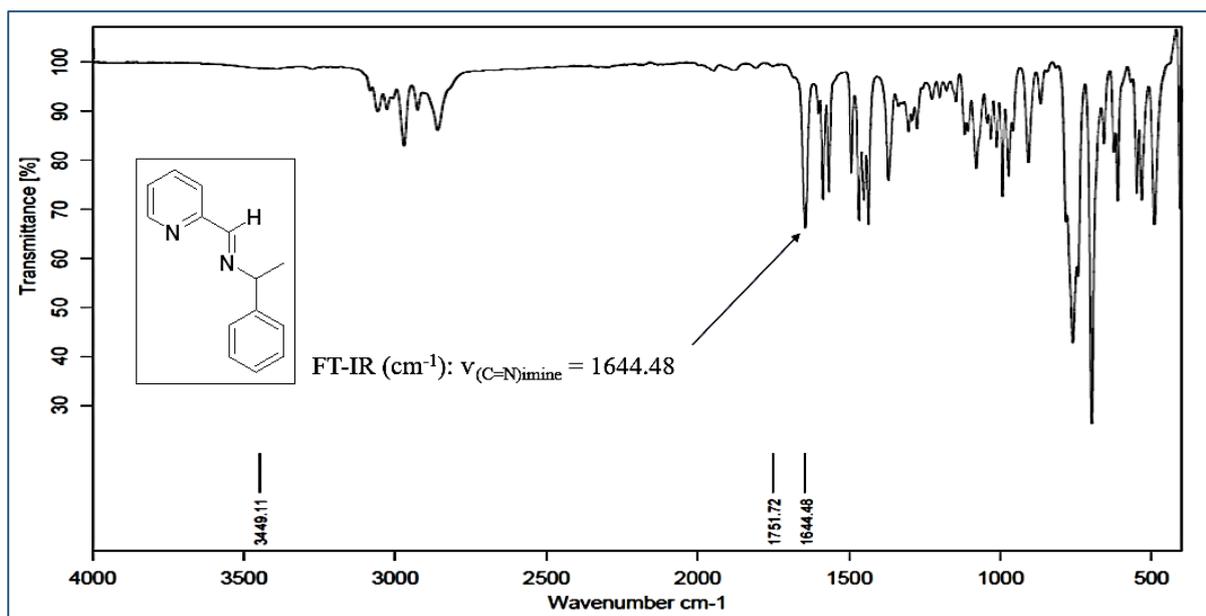
Figure 3.4: FT-IR spectra of ligand **L1**, illustrating the imine bond at 1644 cm^{-1}.

A shift in the $\nu_{(C=N)imine}$ absorption band for all the complexes (**Table 3.1**) relative to the $\nu_{(C=N)imine}$ absorption band of bidentate **L1** and tridentate **L2** were observed. For instance, **Figure 3.5** illustrates the FT-IR spectra of complex **Pd1** and the $\nu_{(C=N)imine}$ absorption band can be seen at 1596.21 cm^{-1} whereas the $\nu_{(C=N)imine}$ absorption band for bidentate **L1** can be seen in **Figure 3.4**, at 1644.48 cm^{-1}. This indicated successful coordination of the metal(II)Cl$_2$ to the imine nitrogen of the ligand [31]. A similar shift in the absorption band was observed by Jie *et. al* [32] whereby the $\nu_{(C=N)imine}$ absorption signal of the ligand was seen at 1642 cm^{-1} and the absorption signal of the corresponding nickel(II) complex at 1616 cm^{-1} [33, 32]. This can be

explained by the decrease of electron density over the -C=N- which alters the absorption characteristics of the functional group. Similar observations have been reported in literature [33, 34, 1, 29].

Table 3.1: $\nu_{(C=N)imine}$ stretch vibrations of ligands and complexes.

	L1	Pd1	Co1	Fe1
$\nu_{(C=N)imine}$	1644.48	1596.21	1597.90	1613.54

	L2	Ni2	Co2	Fe2
$\nu_{(C=N)imine}$	1670.56	1603.83	1604.32	1613.54
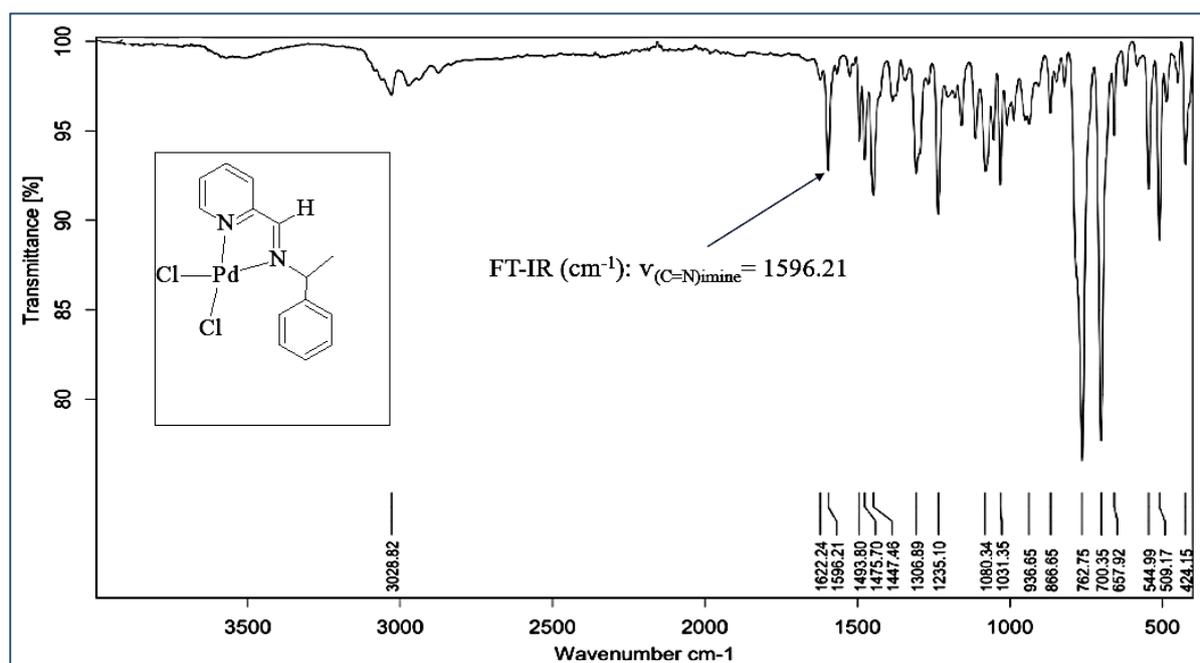
Figure 3.5: FT-IR spectra of complex **Pd1**, illustrating the shift in absorption peak of the imine bond at 1596.21 cm^{-1}.

The Schiff base ligands and the metal complexes were characterized using high-resolution mass spectrometry (HR-MS). The ligands **L1** and **L2** showed the base peaks at m/z= 211.12 (**Figure 3.6**) and m/z = 417.18 corresponding to [M+H$^+$] and [2M+Na$^+$] respectively. This observation clearly pointed to the formation of the ligands. The HR-MS of the metal complexes **Ni1** (**Figure 3.7**), **Co1**, **Fe1**, and **Pd1** showed their base peaks at m/z = 514.69 [M-Cl]$^+$, 834.71 [M]$^{2+}$, 687.19 [M]$^{2+}$ and 393.02 [M]$^{2+}$.C$_2$H$_3$N respectively. The molecular mass of the complexes **Fe1** (976.60 g.mol^{-1}) and **Co1** (979.69 g.mol^{-1}) correspond to [M(**L1**)₃]$^{2+}$ while **Ni1** (550.14 g.mol^{-1}) and **Pd1** (387.60 g.mol^{-1}) corresponds to the formula, [Ni(**L1**)₂]$^{2+}$ and [Pd(**L1**)Cl]$^{2+}$, respectively as showed in the **Table 3.2**. However, the complexes **Ni2** (326.38 g.mol^{-1}), **Co2** (332.62 g.mol^{-1}), and **Fe2** (323.98 g.mol^{-1}) showed signals corresponding to the formula, [M(**L2**)₂Cl]$^+$ rather the molecular mass of the mono(chelated) complexes **Scheme 3.4**.
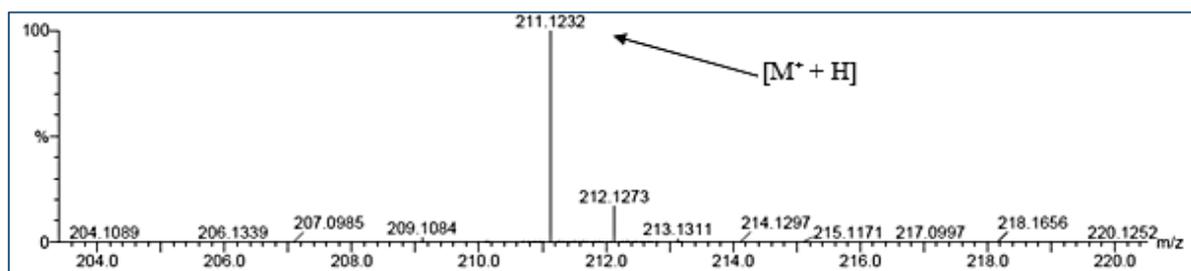
Figure 3.6: HR-MS spectra of ligand **L1**, illustrating found m/z (%) 211.1232 [M$^+$ + H].

For instance, the ESI-MS spectral data of complex **Co2** showed signal, m/z = 488 which correlates with the stable intermediate with the general formula [Co(**L2**)₂Cl]$^+$. This observation could be rationalized by possible rearrangements of the unstable mono(chelated) complex of **Co2** leading to the formation of a more stable bis(chelated) intermediate (**Eq. 1**). More importantly, the simulated and experimental isotopic mass distributions of the complexes showed good agreement (**Figures 3.7**).

$$2[M(\textbf{L2})Cl_2] \xrightarrow{\hspace{2cm}} [M(L2)_2Cl]^+ + [MCl_3]^- \dashrightarrow \quad \textbf{Eq. 1}$$
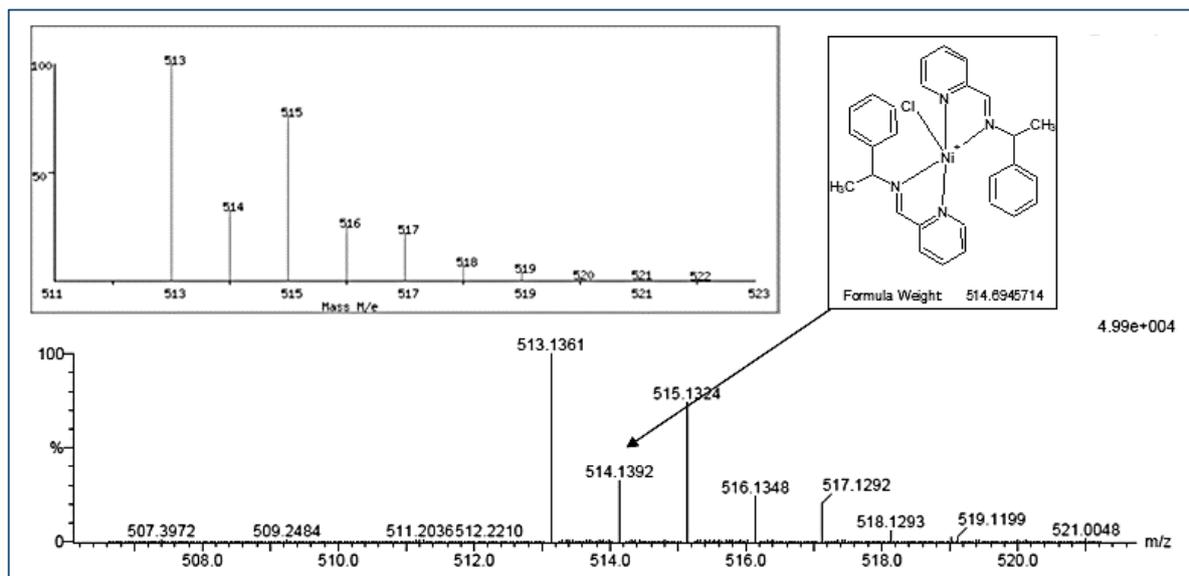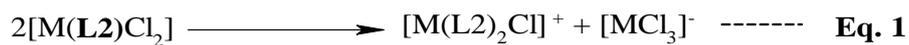
Figure 3.7: HR-MS spectra of complex **Ni1** illustrating complex formation, of ([M^+ - Cl]) at m/z = 514.1392 as well as the theoretical isotopic mass distribution.
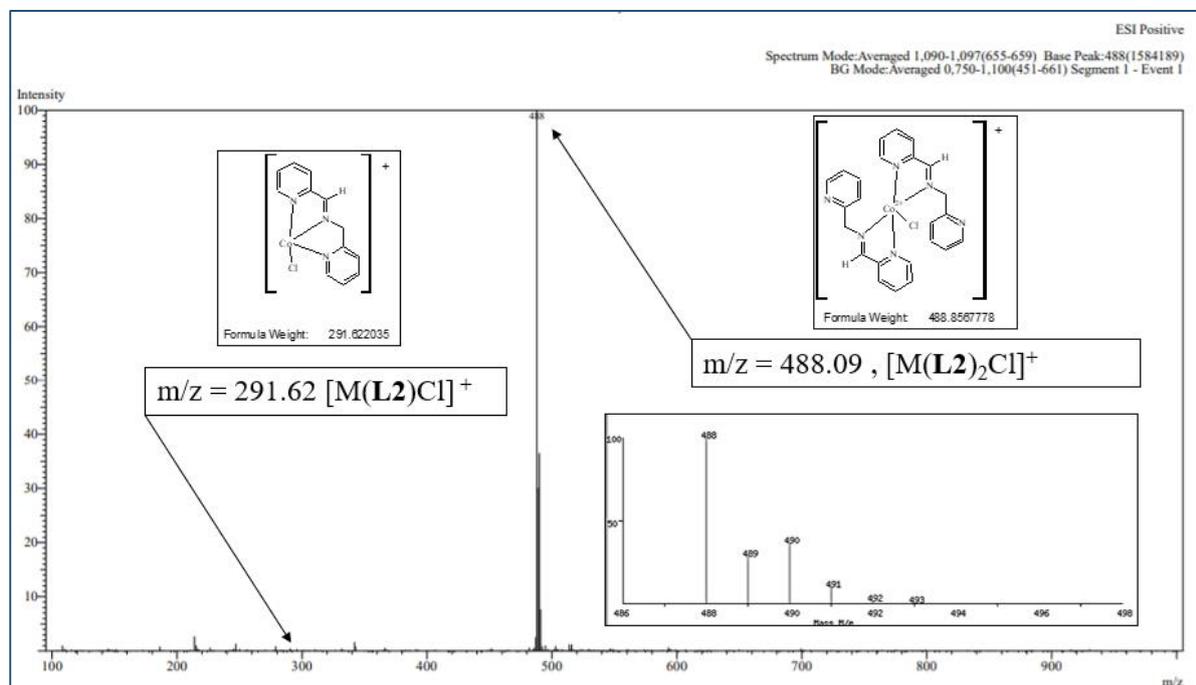
Figure 3.8: ESI-MS spectra of complex **Co2** illustrating the rearrangement to form a bis(chelated) intermediate at m/z = 488 and the theoretical isotopic mass distribution.

Table 3.2: Mass spectral data for both ligands and all metal complexes.

Compound	Formulae	Molar mass (g.mol^{-1})	*m/z* (amu)
L1	$C_{14}H_{14}N_2$	210.27	211.12 (M$^+$ + H)
L2	$C_{12}H_{11}N_3$	197.23	417.18 (2M$^+$ + Na)
Ni1	[Ni(**L1**)$_2$Cl$_2$]	550.14	514.69 (M$^+$ - Cl)
Ni2	[Ni(**L2**)Cl$_2$]	326.38	489 (1/2M$^+$ + (**L2**) - Cl)
Pd1	[Pd(**L1**)Cl$_2$]	387.60	393.02 (M$^+$.(C$_2$H$_3$N) - Cl)
Fe1	[Fe(**L1**)$_3$]$^{2+}$[2PF$_6$$^-$]	976.60	687.19 (M$^+$)
Fe2	[Fe(**L2**)Cl$_2$]	323.98	489 (1/2M$^+$ + (**L2**) - Cl)
Co1	[Co(**L1**)$_3$]$^{2+}$[2PF$_6$$^-$]	979.69	834.71 (M$^+$)
Co2	[Co(**L2**)Cl$_2$]	332.62	488 (M$^+$ - Cl)

Elemental analyses of the corresponding metal complexes provided valuable information on the purity and empirical formulae. The micro-analyses data were consistent with the proposed mononuclear complexes as proposed in Schemes 3.2 and 3.3 of the formulae of [M(L)$_2$Cl$_2$] for complex **Ni1**, and [M(L)Cl$_2$] for complexes **Pd1**, **Ni2**, **Fe2**, and **Co2** as and the general formula for complexes **Fe1** and **Co1** as [M(L)$_3$]$^{2+}$[2PF$_6$$^-$]. The slight deviation from expected theoretical values can be attributed to the hygroscopic nature of the complexes.

3.3.2 Solid state structure of complex Co1

Single crystals suitable for X-ray crystallography analysis of complex **Co1** were grown by slow diffusion of diethyl ether into a concentrated solution of **Co1** in dichloromethane at room temperature. **Table 3.3** gives the data collection and structural refinement parameters for complex **Co1** while **Figure 3.9** presents the molecular structure and relevant bond parameters. To the best of our knowledge, no isostructural similarities of our solid-state structure exist in the CSD (Cambridge Structural Database) [36]. The solid state of cationic complex **Co1** was mononuclear containing three bidentate ligands around the cobalt atom. Two $[PF_6]^-$ counter-anions balanced the charge of the metal center. The average bond lengths of Co-N_{imine} were 2.155 Å, 2.119 Å, and 2.161 Å respectively whereby the average bond lengths for Co-$N_{pyridyl}$ were 2.143 Å, 2.105 Å, and 2.154 Å respectively. The average bond lengths for the two axial Co-N (2.112 Å) were comparable to the equatorial four Co-N bond lengths (2.153 Å) in complex **Co1**. This was comparable with Co-N_{imine} and Co-$N_{pyridyl}$ bond lengths found in reports of similar structures [37, 38, 39]. The selected bond angles 77.4(2), 91.3(2), 96.6(2), N(3)-Co(1)-N(5), N(1)-Co(1)-N(5), N(7)-Co(1)-N(5) respectively for complex **Co1** indicates that the structure is of distorted octahedral geometry since the bond angles deviate from the expected 90º.

Table 3.3: Crystal data for complexes **Co1**.

Parameter	Co1
Empirical formula	$C_{19.25}H_{19.5}Co_{0.5}F_6N_{2.75}O_{0.5}P$
Formula weight	471.81
Temperature (K)	100.01
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P21
α, b, c (Å)	12.0825(8), 13.5875(8), 25.5632(16)
α, β, γ (°)	90, 91.430(2), 90
Volume ($Å^3$)	4195.4(5)
Z	8
ρ_{calc} (g/cm^3)	1.494
μ/mm^{-1}	0.577
F(000)	1926.0
Crystal size/mm^3	$0.165 \times 0.135 \times 0.13$
Radiation	MoKα ($\lambda = 0.71073$)
2Θ range for data collection/°	3.188 to 51.454
Index ranges	$-14 \leq h \leq 14, -16 \leq k \leq 16, -29 \leq l \leq 31$
Reflections collected	76593
Independent reflections	15890 [$R_{int} = 0.0823$, $R_{sigma} = 0.0934$]
Data/restraints/parameters	15890/1/1087
Goodness-of-fit on F^2	1.102
Final R indexes [I>=2σ (I)]	$R_1 = 0.0554$, $wR_2 = 0.1226$
Final R indexes [all data]	$R_1 = 0.0775$, $wR_2 = 0.1302$
Largest diff. peak/hole / e $Å^{-3}$	0.39/-0.42
Flack parameter	-0.011(11)
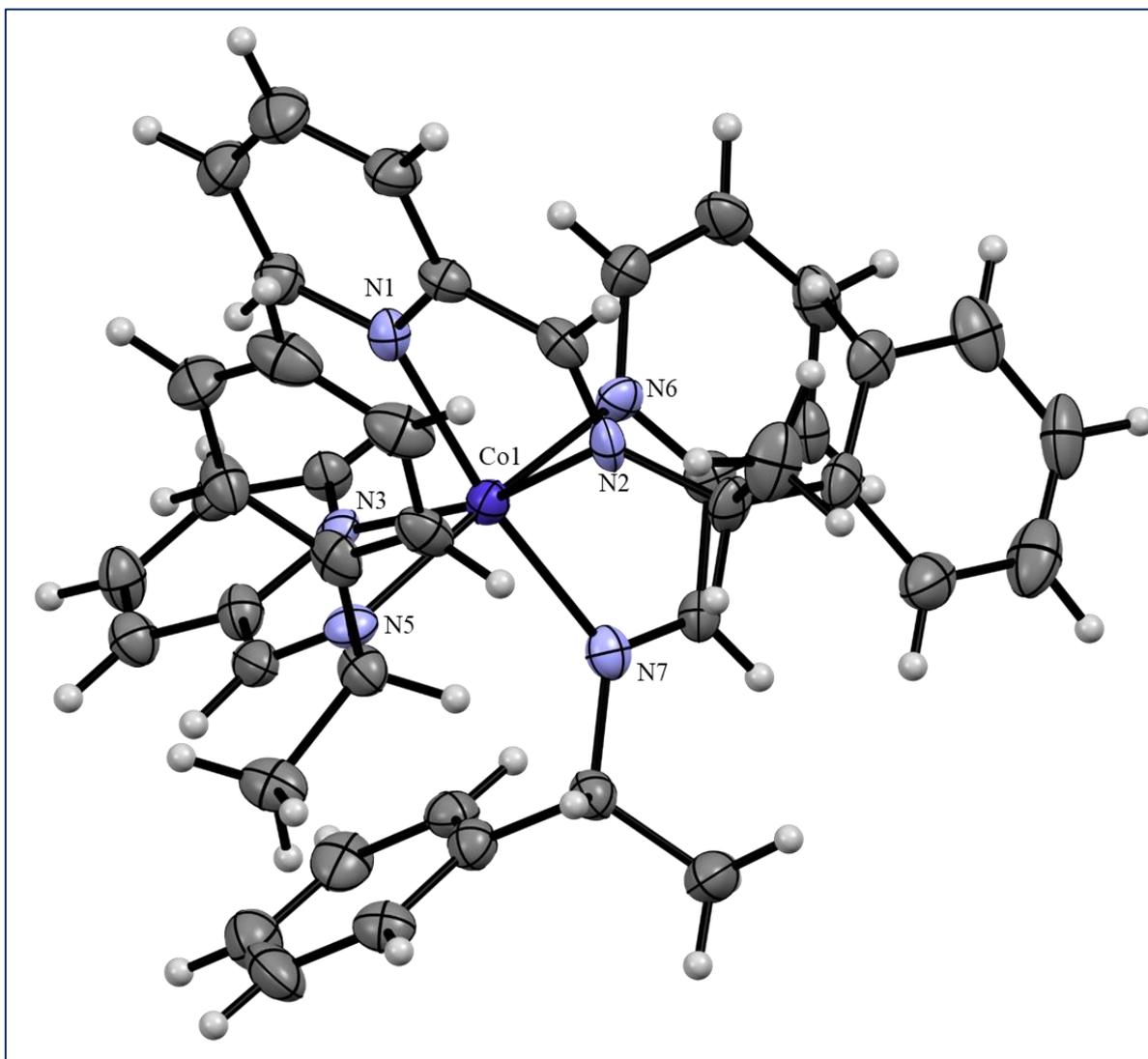
Figure 3.9: Molecular structure of complex **Co1**, with 50% probability thermal ellipsoids. The two anionic counterions $(PF_6)^-$ were emitted for clarity.

3.4 Conclusion

In summary, [N, N] bidentate (pyridyl)imine – and [N, N, N] tridentate (pyridyl)imine ligands were successfully synthesized in good yields. Ligands **L1** and **L2** were successfully reacted with $NiCl_2$ (**Ni1**, **Ni2**), [Pd(COD)Cl$_2$] (**Pd1**), $CoCl_2$ (anhydrous) (**Co1**, **Co2**), and $FeCl_2.4H_2O$ (**Fe1**, **Fe2**) to obtain the corresponding metal complexes in moderate yields. The structures of these complexes were established using FTIR, ^{1}H-NMR, MS, and elemental techniques.

Structural elucidation of novel compound **Co1** was completed by SC-XRD analysis and has confirmed the geometry of the complex to be of octahedral nature, with three bidentate ligands coordinated to the cobalt(II) metal center. Chapter Four reports the application of these complexes as pre-catalysts in the vinyl-addition polymerization of norbornene as well as the thermal and microstructural analyses of the resulting polymers from these complexes.

References

[1] A. Xavier and N. Srividhya, "Synthesis and Study of Schiff base Ligands," *J. of App. Chem.,* vol. 7, pp. 2278-5736, 2014.

[2] C. P.G., "Metl-Salen Schiff base complexes in catalysis: practical aspects.," *Chem. Soc. Rev.,* vol. 33, pp. 410-421, 2004.

[3] R. Nair , A. Shah, S. Baluja and S. Chanda, "Synthesis and antibacterial activity of some Schiff base complexes," *J. Serb. Chem. Soc.,* vol. 71, no. 7, pp. 733-744, 2006.

[4] F. Pelascini, F. Peruch, P. Lutz, M. Wesolek and J. Kress, "Polymerization of norbornene with CoCl2 and pyridine bisimine cobalt(II) complexes activated with MAO`," *Macromol. Rapid Commun.,* vol. 24, pp. 768-771, 2003.

[5] P. Cozzi, "Metal-Salen Schiff base complexes in catalysis: practical aspects," *Chem. Soc. Rev.,* vol. 33, pp. 410-421, 2004.

[6] J. Zhang, L. Xu and W. Wong, "Energy materials based on metal Schiff base complexes," *Coor. Chem. Rev.,* vol. http://dx.doi.org/10.1016/j.ccr.2017.08.007, 2017.

[7] G. Hilt, J. Janikowski, M. Schwazer, O. Burghaus, D. Sakow, M. Broring, M. Druschler, B. Huber, B. Roling, K. Harms and G. Frenking, "Studies of electronic effects of modified pyridine-imine ligands utilized in cobalt-catalyzed meta-selective Diels-Alder reactions," *J. Organomet. Chem.,* vol. 749, pp. 219-223, 2014.

[8] L. Chen, L. Ma, Y. Jiang, J. Liu, C. Li, N. Zhang and J. Wang, "Synthesis and characterization of iron, cobalt and nickel complexes bearing para-phenylene-linked

pyridine imine ligand and their catalytic properties for ethylene oligomerization," *Polym. Bull.,* pp. https://doi.org/10.1007/s00289-020-03119-1, 2020.

[9] Kim, S. Kim, C. Ha and I. Kim, "Highly stereospecific polymerizations of 1,3-butadiene with Cobalt(II) pyridyl bis(imine) complexes," *e-Polym.,* p. 027, 2006.

[10] A. Antonov, N. Semikolenova, V. Zakharov, W. Zhang, Y. Wang, W. Sun, E. Talsi and K. Bryliakov, "Vinyl polymerization of norbornene on nickel complexes with bis(imino)pyridine ligands containing electron-withdrawing groups," *Organometallics,* vol. 31, pp. 1143-1149, 2012.

[11] H. Gao, L. Pei, Y. Li, J. Zhang and Q. Wu, "Vinyl polymerization of norbornene with nickel catalysts bearing [N,N] six-membered chelate ring: Important influence of ligand structure on activity," *Journal of Molecular Catalysis A,* vol. 280, pp. 81-86, 2008.

[12] P. Shamply, M. Nelson, A. Antony and J. Varkey, "Synthesis of salicylaldehyde based Schiff Bases and their metal complexes in aqueous media - characterization and antibacterial study," *Int. J. of Recent Sc. Research,* vol. 9, no. 5B, pp. 26566 -26570, 2018.

[13] R. Nair, A. Shah, S. Baluja and S. Chanda, "Synthesis and antibacterial activity of some Schiff base complexes," *J. Serb. Chem. Soc.,* vol. 71, no. 7, pp. 733-744, 2006.

[14] L. Benade, S. Ojwach, C. Obuah, I. Guzei and J. Darkwa, "Vinyl-addition polymerization of norbornene catalyzed by (pyrazol-1-ylmethyl)pyridine divalent iron, cobalt and nickel complexe," *Polyhedron,* vol. 30, pp. 2878-2883, 2011.

[15] J. Cheng, Y. Huang, Z. Li, Z. Zhang, C. Wie, T. Lan and W. Zhang, *J. Mol. Catal. A: Chem.,* vol. 259, p. 133, 2006.

[16] X. Mi, Z. Ma, N. Cui, L. Wang, K. Yucai and H. Youliang, "Vinyl Polymerization of Norbornene with Dinuclear Diimine Nickel Dichloride/MAO," *J. App. Pol. Sc.,* vol. 88, pp. 3273-3278, 2003.

[17] Pr, L. Pereira and M. Marques, "Performance of a bis(imine)pyridine iron catalyst system in ethylene/norbornene copolymerization with zinc diethyl," *Macromol. Symp.,* vol. 343, pp. 8-17, 2014.

[18] K. Vijayakrishna, S. Padmanabhan, T. Kanna and D. Dakshinamoorthy, "Highly active novel Ni-diimine pre-catalyst containing bis-ketimine ligand for the vinyl polymerization of norbornene," *Polym. Bull.,* vol. 68, pp. 635-645, 2012.

[19] Z. Hao, N. Yang, W. Gao, L. Xin, X. Luo and M. Ying, "Ni complexes bearing N,N,N-tridentate quinolinyl anilido-imine ligands: Synthesis, characterization and catalysis on norbornene addition polymerization.," *J. of Organomet. Chem.,* vol. 749, pp. 350-355, 2014.

[20] R. Zhuang, H. Liu, J. Guo, B. Dong, W. Zhao, Y. Hu and X. Zhang, "Highly active nickel(II) and palladium(II) complexes bearing N,N,P tridentate ligand for vinyl addition polymerization of norbornene," *European Pol. J.,* 2017.

[21] S. Jie, P. Ai, Q. Zhou and B. Li, "Nickel and cationic palladium complexes bearing (imino)pyridyl alcohol ligands: Synthesis characterization and vinyl polymerization of norbornene.," *J. of Organomet. Chem.,* vol. 696, pp. 1465-1473, 2011.

[22] C. Janiak and P. Lassahn, "Metal catalyst for the vinyl polymerization of norbornene," *Journal of Molecular Catalysis,* vol. 166, pp. 193-209, 2001.

[23] D. Drew and J. Doyle, "Cyclic Diolefin Complexes of Pt and Pd," *Inorg. Synt.,* vol. 28, 1990.

[24] B. APex, Bruker AXS, Madison, Wisconsin, USA: SAINT and SADABS, 2010.

[25] G. Sheldrick, *Acta Crystallog. Sec: Found. Crystallog.,* vol. 64, pp. 112-122, 2008.

[26] L. Farrugia, *J. Appl. Crystallog.,* vol. 45, pp. 849-854, 2012.

[27] "Structural studies and applications of water soluble (phenoxy)imine palladium(II) complexes as catalysts in biphasic methoxycarbonylation of 1-hexene.," *J. of Organomet. Chem.,* vol. 942, p. 121812, 2021.

[28] H. Liang, J. Liu, X. Li and Yuesheng, "Synthesis, structure and norbornene polymerization behavior of neutral palladium complexes," *Polyhedron,* vol. 23, pp. 1619-1627, 2004.

[29] N. Ngcobo, S. Akiri, O. Ogweno and S. Ojwach, "Structural elucidation of chiral (imino)pyridine/phosphine palladium(II) complexes and their applications as catalysts in methoxycarbonylation of styrene.," *Polyhedron,* vol. 203, p. 115243, 2021.

[30] R. Kumah, P. Vijayan and S. Ojwach, "Synthesis and applications of (pyridyl)imine Fe(II) complexes as catalysts in transfer hydrogenation of ketones," *Catal. Lett.,* pp. doi.org/10.1007/s10562-020-03311-y, 2020.

[31] Z. Zulu, G. Nyamato, T. Tshabalala and S. Ojwach, "Palladium(II) complexes of (pyridyl)imine ligands as catalysts for the methoxycarbonylation of olefins," *Inorganica Chimica Acta,* p. doi.org/10.1016/j.ica.2019.119270, 2019.

[32] S. Jie, P. Ai, Q. Zhou and B. Li, "Nickel and cationic palladium complexes bearing (imino)pyridyl alcohol ligands: Synthesis, characterization and vinyl polymerization of norbornene," *Journal of Organometallic Chemistry,* vol. 696, pp. 1465-1473, 2011.

[33] R. Kumah, N. Tsaulwayo, B. Xulu and S. Ojwach, "Structural, kinetics and mechanistic studies of transfer hydrogenation of ketones catalyzed by chiral (pyridyl)imine nickel(II) complexes.," *Dalton Transactions,* 2019.

[34] J. Cloete and S. Mapolie, "Functionalized pyridinyl-imine complexes of palladium as catalysts precursors for ethylene polymerization.," *J. of Mol. Cat. A,* vol. 243, pp. 221-225, 2006.

[35] Y. Huang, J. Chen, L. Chi, C. Wei, Z. Zhang, Z. Li, A. Li and L. Zhang, "Vinyl Polymerization of Norbornene with Bis(imino)pyridyl Nickel(II) Complexes," *Journal of Applied Polymer Science,* vol. 112, pp. 1486-1495, 2009.

[36] C. Groom and F. Allen, "The Cambridge Structural Database in retrospect and prospect," *Angew. Chem. Int. Ed.,* vol. 53, pp. 662-671, 2014.

[37] Araujo, C. Araujo, M. Doherty, S. Konezny, O. Luca, A. Usyatinsky, H. Grade, E. Lobkovsky, G. Soloveichik, R. Crabtree and V. Batista, "Tuning redox potentials of bis(imino)pyridine cobalt complexes: an experimental and theoretical study involving solvent and ligand effects.," *Dalton Trans.,* vol. 41, p. 3562, 2012.

[38] C. Bianchini, D. Gatteschi, G. Giabastiani, I. Rios, A. Ienco, F. Laschi, C. Meallo, A. Meli, L. Sorace, A. Toti and F. Vizza, "Electronic influence of the thienyl sulfur atom on the oligomerization of ethylene by Co(II) 6-(thienyl)-2-(imino)pyridine catalysis," *Organometallics,* vol. 26, pp. 726-739, 2007.

[39] C. Vedder, F. Schaper, H. Britzinger, M. Kettunen, S. Babik and G. Fink, "Chiral Fe(II) and Co(II) complexes with biphenyl-bridged bis(pyridylimine) ligands - syntheses, structures and reactivities," *Eur. J. Inorg. Chem.,* vol. 6, pp. 1071-1080, 2005.

Chapter Four

Polymerization of norbornene catalyzed by (pyridyl)imine nickel(II), palladium(II), cobalt(II), and iron(II) complexes as pre-catalysts

4.1 Introduction

Norbornene (NBE), a strained cyclic olefin, can be polymerized *via* three routes [1, 2, 3, 4]; for example, by ring-opening metathesis polymerization (ROMP), here double bonds are still present in the polymer backbone, cationic or radical polymerization and vinyl-addition polymerization (VAP) where the saturated bicyclic unit stays intact. ROMP polymers are widely utilized in vulcanization processes where crosslinking of polymers takes place due to the high level of unsaturation in the polymer backbone. Vinyl-addition polynorbornene (VPNBE) exhibit special characteristics which make it highly sought after for optical applications [5, 6] such as optical information storage, gas separation [7] as well as microelectronics [7, 4]. VPNBE also exhibit good physical properties such as tensile strength and heat resistance [8, 9] as well as good chemical resistance [10]. Norbornene has also shown to perform well in co-polymerizations with isoprene, octene, ethylene, and 1,3-butadiene [11, 12, 9, 13]

Over the past few years literature reports on the VAP of NBE with complexes of nickel(II), palladium(II), cobalt(II), copper(II), iridium(II), titanium(II), and iron(II), displayed good performances and others resulted in industrially undesirable feats [14, 15, 16, 17, 18, 19, 20, 21]. This led to the search for alternate catalyst systems that are economical and have the

potential for industrial applications. In short, the VAP mechanism is known to consist of three major steps. The first entails catalyst activation by alkylation and the creation of an empty coordination site. This is followed by coordination of the monomer to the empty site leading to chain propagation and is concluded with the chain termination step [22]. It can be said that if any of these three major events in the mechanism can be controlled, it might be possible to control polymerization activities and polymeric characteristics such as thermal properties and molecular weights. For instance, it may be possible to increase the activity of a catalyst by increasing the MMAO/M ratio to ensure a higher number of active species present on monomer introduction. Chain length and Mw may be controlled by NBE/M ratios that might increase the rate of monomer insertion and retarding chain transfer.

In this chapter, the synthesized (pyridyl)imine nickel(II) (**Ni1**, **Ni2**), palladium(II) (**Pd1**), cobalt(II) (**Co1**, **Co2**), and iron(II) (**Fe1**, **Fe2**) complexes reported in Chapter Three (**Figure 4.1**), will be tested as pre-catalysts in the VAP of NBE. The microstructure and thermal properties of the resulting polymers from each complex will also be analyzed and compared. An investigation of reaction parameters like polymerization temperature, NBE/M ratios, MMAO/M ratios, and polymerization reaction time as an influence on catalytic performance and polymer thermal properties will also be discussed.
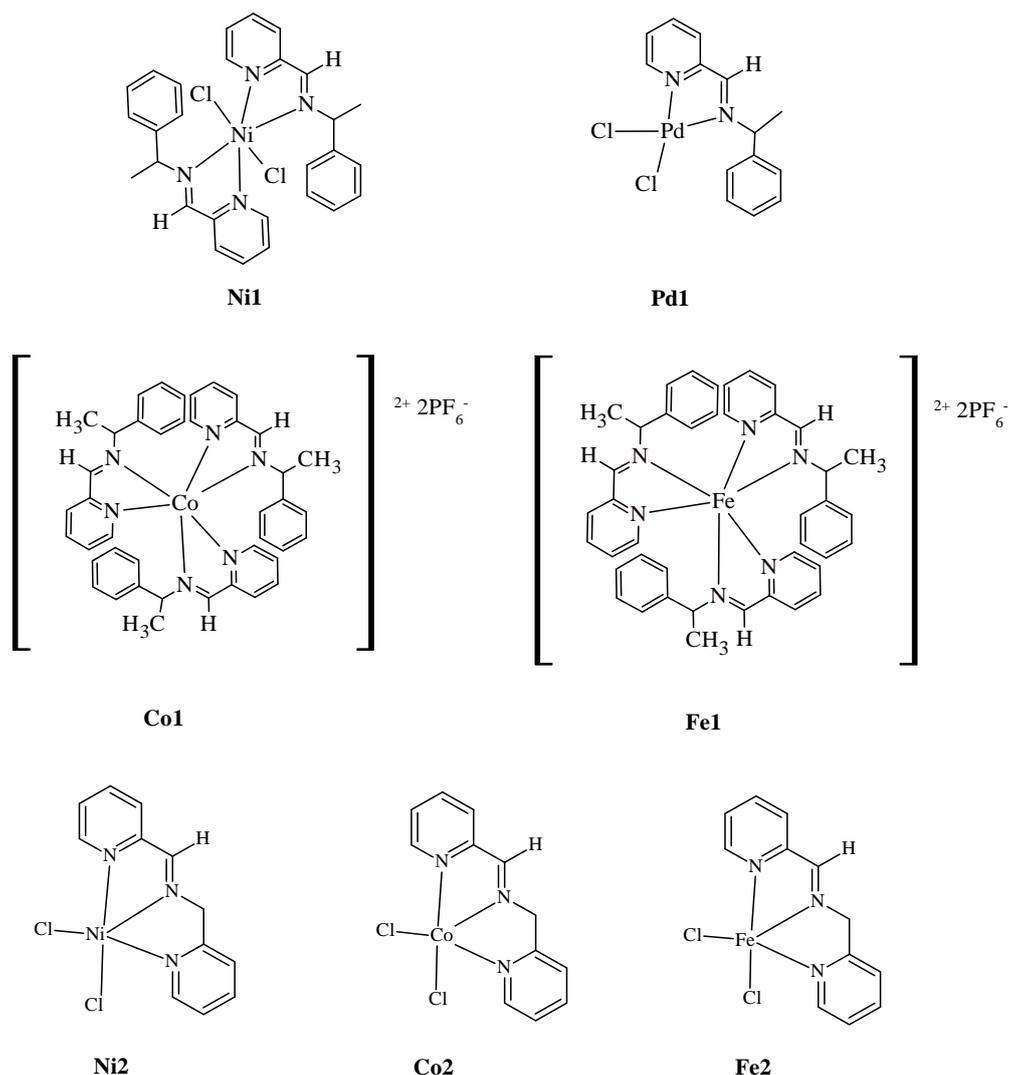
Figure 4.6: Structures of the (pyridyl)imine metal complexes synthesized in Chapter Three, tested as pre-catalysts in norbornene polymerization reactions.

4.2 Experimental Section

4.2.1 General instrumentation and materials

All manipulations of moisture and air-sensitive materials were conducted under Schlenk conditions and nitrogen and vacuum lines. All solvents employed were of analytical grade. Toluene (PhMe), dichloromethane (DCM), and *o*-chlorobenzene (PhCl) were dried by

distillation over $CaCl_2$ onto dried molecular sieves and stored under nitrogen. Ethanol (EtOH) and methanol (MeOH) were used as received and no further purification was done. Starting materials: Norbornene (≥: 99%); modified methyl aluminoxane (MMAO - 12) (7% wt/wt aluminum in toluene methyl aluminoxane solution). Thermal properties of the polymer samples were investigated utilizing a PerkinElmer Thermogravimetric Analyser 4000 (TGA) under atmospheric conditions with a heating rate of 40 °C/min and differential scanning calorimetry (DSC) with a PerkinElmer DSC 4000 and infra-red spectra were recorded on a Bruker Alpha II Platinum ATR Spectrometer in the $4000 – 650$ cm^{-1} range.

4.2.2 General polymerization procedure

All polymerization reactions were conducted in a dry Schlenk tube, equipped with a magnetic stirrer bar. A steady flow of nitrogen ensured the maintenance of an inert atmosphere within the Schlenk tube. Nitrogen was bubbled through a mercury trap to remove impurities before being conveyed through a column packed with silica gel to entrap any moisture carried by the inert gas. Dried solvent stored under nitrogen was transferred in the desired amounts to the Schlenk tube *via* cannula. The solvent was degassed before adding the required amount of pre-catalyst, dissolved in 1 mL of solvent, and was then transferred *via* cannula to the Schlenk tube. The solution was degassed and flushed again with nitrogen. The solution was allowed to stir for 5 min before adding the required amount of MMAO *via* syringe, to pre-activate the catalyst complex. The solution was allowed to stir for 20 minutes, before polymerization was initiated by adding the desired amount of monomer dissolved in 1 mL of solvent *via* cannula and flushing the system again with nitrogen. The polymerization reaction was allowed to continue before coagulation was achieved by the addition of acidic ethanol (10% HCl) to the reaction mixture. Where temperature variations were applicable, lower temperatures were achieved by an external ice-water bath, and elevated temperatures were achieved by an external oil bath.

The amorphous and white polymer was isolated by vacuum filtration and washed several times with acidic ethanol before being dried in air to constant weight.

4.3 Results and discussion

Bidentately chelated **Ni1** and tridentately chelated **Ni2** were used to pre-determine the effects of varying experimental parameters such as ratios of MMAO/M, NBE/M, reaction temperatures, reaction times and solvent choice. Catalytic screening then followed to determine the ability of each metal complex to polymerize NBE under the most favorable conditions determined initially.

4.3.1 Influence of varying MMAO/M ratios on catalytic activity and polymer properties

This was accomplished by varying MMAO/Ni ratios from 500 to 1500, with complex **Ni1** as pre-catalyst (**Table 4.1**, entries 1 – 3) where thermal properties of the resulting polymers were determined with TGA and DSC techniques. Increasing MMAO/Ni ratios showed significance when controlling catalytic activity, as an almost linear increase in both catalytic activity and monomer conversion was observed during the investigation. A MMAO/Ni ratio of 500 displayed trace amounts of polymer formation, indicating that the system can be seen as inactive at these low co-catalyst loadings. Increasing MMAO/Ni ratios to 1000 and 1500 displayed an increased catalytic activity from 22.7 $g \times 10^3_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$ to 33.7 $g \times 10^3_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$ respectively. This is well in line with other literature reports [2, 3, 16, 23, 24]. For instance, Zhang *et. al* reported catalytic activity increased from 0.62 $g \times 10^{-5}_{(PNBE)}.mol_{(M)}^{-1}.h^{-1}$ to 4.48 $g \times 10^{-5}_{(PNBE)}.mol_{(M)}^{-1}.h^{-1}$ when MMAO/M ratios were increased from 200 to 800 respectively [23]. This indicated that MMAO/M ratios are crucial for controlling

catalytic activity and monomer conversion. Varying MMAO/M ratios have showed minimal changes in the T_g and T_d of the resulting polymer. For instance, when MMAO/M ratios of 1000 and 1500 were tested, the T_g of the polymers measured 302 °C and 300 °C respectively. A drop in T_d from 478 °C to 467 °C was also noticeable. This was consistent with other reports wherein it was found that by increasing the MMAO/M from 500 to 2500, a drop in T_d from 463 °C to 456 °C was measured [3].

4.3.2 Influence of varying NBE/M ratio on catalytic activity and polymer properties

The effect of varying the monomer/metal ratio on catalytic activity was tested by polymerization with complex **Ni1**, at varied NBE/M ratios from 625 to 2500 in toluene at room temperature (**Table 4.1**, entries 4-6). The ratio of 625 NBE/Ni (**Table 4.1**, entry 4) showed catalytic activity of 6.8 $g \times 10^3_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$ where doubling the monomer/metal ratio to 1250 (**Table 4.1**, entry 5) increased the catalytic activity to 17.5 $g \times 10^3_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$. Further doubling the monomer loading to NBE/Ni 2500, resulted in a decreased catalytic activity of 300 $g \times 10^3_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$ with trace amounts of polymer formations observed. This indicated that the best monomer/metal loading ratio was 1250 NBE/Ni (**Table 4.1**, entry 5). The lower catalytic activities observed at higher monomer loadings could be associated with larger amounts of impurities in the monomer that might be detrimental to the catalyst's performance. Sun *et. al* reported similar observations when systematic increases of NBE/Ni of 2500, 5000, 10 000, and 20 000 were tested and a consistent decline in monomer conversion from 98% to 78% was observed [3]. Although the monomer conversion rate dropped, a noticeable increase was seen in catalytic activity reported from 0.47 $g \times 10^{-6}_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$ to 265.20 $g \times 10^{-6}_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$. This was consistent with other findings [16, 22, 15]. The opposite was observed in some reports where an increase in NBE/Ni ratio, caused a significant

increase in both monomer conversion and catalytic activity [25, 26, 24]. This implies that the influence of NBE/M ratios on catalytic performance might be system-specific, and that behavioral predictions prove difficult.

Table 4.1: The effect of MMAO/M and NBE/M on catalytic activity and thermal properties of polymers using complex **Ni1** as a pre-catalyst.[a]

Entry	Al/Ni	NBE/Ni	Time (h)	Yield (%)	Activity[b]	T_g (°C)[c]	T_d (°C)[d]
1	500	1250	1	trace	-	-	-
2	1000	1250	1	19	22 700	302	478
3	1500	1250	1	28	33 700	300	467
4	1000	625	2	23	6 800	300	475
5	1000	1250	2	30	17 500	300	476
6	1000	2500	2	trace	300	298	481

[a]Polymerization conditions: Complex **Ni1**; V total = 7.5ml; catalyst: 10µmol, solvent: toluene; R_T, [b]Activity: TOF ($g_{(PNBE)}.mol_{(M)}^{-1}.h^{-1}$); [c]Polymer glass transition state temperature determined by DSC; [d]Polymer degradation temperature determined by TGA.

Variations in T_d resulted when different ratios of NBE/M were tested. For example, by increasing the monomer loading ratio from 625 to 1250 and 2500, a steady increase of T_d from 475 °C, 476 °C, and 481 °C was observed, respectively. No substantial changes in T_g were observed under the same conditions. This was expected as the same observation trends on polymer T_d was made by Sun *et. al*, when increasing the monomer loading ratios in the order of NBE/Ni 2500, 5000, 10 000, and 20 000. This resulted in polymer product formations which consisted of T_d ranging from 456 °C – 458 °C [3]. Similar observations were made by other researchers [26].

4.3.3 Influence of reaction temperature on catalytic activity and thermal properties of polymers

With the implication of altering NBE/M and MMAO/M ratios now understood, it was necessary to investigate the effects of varying polymerization reaction temperatures on both catalytic activity and polymer thermal properties. This was achieved by utilizing complex **Ni2** and conducting polymerization reactions at different temperatures ranging from 0 °C to 50 °C (**Table 4.2**, entries 4, 9 - 10). Polymerization reactions conducted at 0 °C resulted in low catalytic activities (0.50 g×$10^3$$_{(PNBE)}$.mol$_{(M)}^{-1}$.h^{-1}) and by increasing the reaction temperature from 0 °C to 23 °C, a drastic increase in catalytic activity to 81.9 g×$10^3$$_{(PNBE)}$.mol$_{(Ni)}^{-1}$.h^{-1} was observed. Further increasing the polymerization temperature to 50 °C, resulted in a reduction in catalytic activity to 19.90 g×$10^3$$_{(PNBE)}$.mol$_{(Ni)}^{-1}$.h^{-1}. Similar results were reported in literature [2, 25, 27, 28, 17, 24, 29]. For instance, Hao *et. al* investigated the influence of polymerization reaction temperature utilizing a [N, N, N]-tridentately bound nickel system by conducting tests at 20 °C, 40 °C, and 60 °C respectively. It was observed that catalytic activity of 0.68 g×$10^5$$_{(PNBE)}$.mol$_{(M)}^{-1}$.h^{-1} was achieved at 20 °C and a decreasing activity trend to 0.46 g×$10^5$$_{(PNBE)}$.mol$_{(M)}^{-1}$.h^{-1} and 0.18 g×$10^5$$_{(PNBE)}$.mol$_{(M)}^{-1}$.h^{-1} for subsequent tests conducted at 40 °C and 60 °C respectively [24].

Table 4.2: Effect of solvent choice, reaction time, and reaction temperature on catalytic activity and thermal properties of polymers using pre-catalyst **Ni2**.[a]

Entry	Temp (°C)	Time (h)	Solvent	Yield (%)	Activity[b]	T_g (°C)[c]	T_d (°C)[d]
1	23	1	DCM	trace	-	-	-
2	23	1	PhMe/DCM	1.2	1 400	293	475
3	23	1	PhMe	31	36 000	304	476
4	23	1	PhCl	70	81 900	300	478
5	23	0.5	PhCl	30	70 200	ND	ND
6	23	2	PhCl	83	48 600	304	488
7[e]	23	1	PhMe	19	22 700	302	478
8[e]	23	2	PhMe	30	17 500	300	476
9	0	1	PhCl	<1	500	294	479
10	50	1	PhCl	17	19 900	292	474

[a]Polymerization conditions: Complex **Ni2, Ni1**[e]; V total = 7.5ml; Al/Ni: 1000; catalyst: 10µmol, NBE/Ni: 1250. [b]Activity = TOF ($g_{(PNBE)}.mol_{(M)}^{-1}.h^{-1}$); [c]Polymer glass transition state temperature determined by DSC; [d]Polymer degradation temperature determined by TGA.

The thermal properties of the polymers have shown little change when different polymerization reaction temperatures were tested. For instance, the T_g of the polymer formed at 0 °C measured 294 °C, which slightly increased to 300 °C when room temperature polymerization was tested and decreased to 292 °C when a polymerization temperature of 50 °C was tested. Variations in polymerization temperatures did not show any significant influence on the T_d of the resulting polymers which measured 479 °C to 478 °C and 474 °C for polymerization temperatures of 0 °C to R_T and 50 °C respectively. The inability to change the resulting PNBE's thermal characteristics by varying temperature parameters, was not unexpected. Sun *et. al* reported no

T_d changes with varied polymerization temperatures of 0 °C to 100 °C. In both tests a T_d of 453 °C for the resulting polymers were recorded [3].

4.3.4 Influence of polymerization time on catalytic activity and thermal properties of polymers.

After we determined the influence of MMAO/Ni ratios, NBE/Ni ratios, and the influence of polymerization temperatures, we next focused on establishing the influence of polymerization reaction times on monomer conversion and polymer thermal properties. This was accomplished by varying the polymerization reaction time from 0.5 h to 2 h, using complex **Ni2** (**Table 4.2**, entries 4 - 6). Prolonging the polymerization time resulted in a near linear increase in monomer conversion when the polymerization time was doubled from 0.5 h (30%) to 1 h (70%). A smaller increase in monomer conversion was observed when the polymerization was allowed to continue for 2 h (83%) (**Figure 4.2**). The catalytic activity of 70.2 $g \times 10^3_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$ during the initial 0.5 h increased to 81.9 $g \times 10^3_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$ within 1 h but decreased to 48.6 $g \times 10^3_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$ after 2 h. Similar observations were made when polymerization reaction times of complex **Ni1** were increased from 1 h to 2 h. The monomer conversion rate increased from 19% to 30% and catalytic activity decreased from 22.7 $g \times 10^3_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$ to 17.5 $g \times 10^3_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$ concluding that an increase in polymerization reaction time leads to higher monomer conversions.
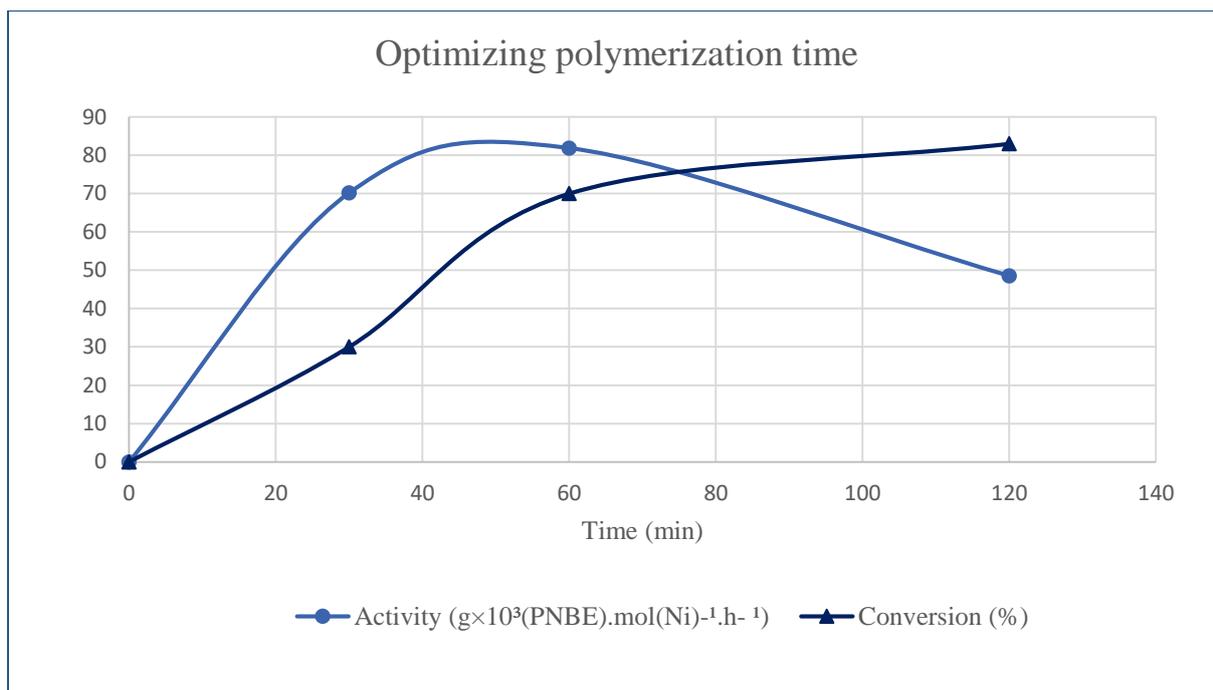
Figure 4.2: The effect of varying polymerization reaction time on catalytic activity and monomer conversion, using complex **Ni2**.

This series of data collections indicated that the catalyst potentially showed the highest activity in the initial stages of polymerization reactions, but as the system is slowly depleted of monomer substrate the activity eventually declined as the monomeric conversion to polymers increased. From the data obtained, it was concluded that the optimal polymerization time is in the order of 1 h if the aim is to benefit from maximum catalytic activity with good monomer conversion. This can be explained by the reduction in diffusion capabilities and kinetic limitations the catalyst experiences due to the solution's systematic increase in viscosity as polymerization proceeds. Similar observations were made in other reports [28, 30, 22, 26]. For instance, Huang *et. al* reported a monomer conversion rate of 6% in a reaction time of 0.25 h. By prolonging the reaction time to 24 h, a conversion rate of 99% was achieved [30]. Similarly, the catalytic activity dropped from 2.4 $g \times 10^6{}_{(PNBE)}.mol_{(M)}{}^{-1}.h^{-1}$ to 0.38 $g \times 10^6{}_{(PNBE)}.mol_{(M)}{}^{-1}.h^{-1}$ with an increase in reaction time from 0.25 h to 24 h respectively.

Thermal properties of the resulting polymers showed changes when different polymerization times were used. For instance, a small increase in T_g of 300 °C to 304 °C can be seen between polymerization times of 1-2 h and a small increase in T_d of 478 °C to 488 °C respectively. This shows that by prolonging the reaction time parameter, it may be possible to enhance the thermal properties of the resulting polymer.

4.3.5 Influence of solvents on catalytic activity of complex Ni1 and thermal properties of the resulting polymers.

With the ramification of varying MMAO/Ni ratios, NBE/Ni ratios, polymerization temperature, and polymerization time now known, the influence of solvent choice was investigated. This was achieved by conducting polymerization reactions in dichloromethane (DCM), toluene (PhMe), *o*-chlorobenzene (PhCl), and dichloromethane/toluene solvent mixtures (**Table 4.2**, entries 1 - 4). Solvent choice has shown significant importance in achieving optimum catalytic activity and monomer conversions. For instance, when polymerizations were conducted in DCM with complex **Ni2**, only trace amounts of the polymer formed concluding the system as inactive in this solvent. When the polymerization reactions were tested in a 1:1 DCM/PhMe solvent mixture, a slight increase of catalytic activity to 1.4 $g \times 10^3_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$ were observed. However, a significant increase in catalytic activity to 36 $g \times 10^3_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$ was observed when polymerizations were conducted in toluene. Conducting polymerizations in *o*-chlorobenzene showed to be the best solvent as this resulted in catalytic activity of 81 $g \times 10^3_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$. This shows that the correct choice of solvent is of vital importance to achieve optimum polymer yields and catalytic activities. Similar observations have been made in previous reports [2, 16, 31, 32, 7, 33]. For instance, Mi *et. al* reported that polymerization in toluene displayed catalytic activity of 169.2 $g \times 10^3_{(PNBE)}.mol_{(M)}^{-1}.h^{-1}$ whereby polymerization in a 5:1 PhMe/DCM solution resulted catalytic activity of 242.5

$g\times10^3$(PNBE).$mol_{(M)}^{-1}$.h^{-1} [2]. This indicated that the solubility of the pre-catalyst in the chosen solvent, influenced the resultant catalytic activities and thermal properties of the resulting polymers. For instance, a T_g of 293 °C was observed when a 1:1 DCM/PhMe system was used, which increased to 304 °C when a toluene solvent system was tested. A slight decrease in T_g to 300 °C was observed when the *o*-chlorobenzene solvent system was tested. The T_d showed fluctuations in measurements ranging from 475 °C to 478 °C for all four systems used, indicating no significant influence. Differences in thermal properties of polymers are suspected to be due to the degree of saturation formed in the polymer backbone whereby a more saturated structure will result in a thermally more stable polymer. The molecular weight of the resulting polymer might also affect thermal properties whereby a higher Mw will contribute to increased thermal stability.

4.3.6 Catalytic screening of nickel(II), palladium(II), cobalt(II), and iron(II) complexes

Upon establishing the influence of varying experimental parameters on the vinyl addition polymerization of norbornene, the next objective was to investigate the effect of ligand/complex structure on polymerization reactions. This was done by catalytic screening of all (pyridyl)imine metal complexes at standardized test conditions as given in **Table 4.3**, entries 1 – 7, and scrutinized according to catalytic activity, monomer conversion, and thermal properties of the resulting polymers. Differences in catalytic activity were observed for complexes consisting of unlike metal centers. For example, complex **Ni1** showed catalytic activity of 22.7 $g\times10^3$(PNBE).$mol_{(Ni)}^{-1}$.h^{-1} as opposed to the catalytic activity of 0.3 $g\times10^3$(PNBE).$mol_{(Fe)}^{-1}$.h^{-1} of complex **Fe1**. Complex **Ni1** also outperformed complex **Pd1** which showed catalytic activity of 17.55 $g\times10^3$(PNBE).$mol_{(Pd)}^{-1}$.h^{-1} whereas complex **Co1** only produced trace amounts of polymer. This illustrates that when metal centres are compared, Ni(II) and Pd(II)-based pre-catalysts dominate in terms of measured activity, relative to activities

observed for Co(II) and Fe(II) based pre-catalysts. Therefore, it can be stated that the observed activities for different metal centres can be organized as **Ni1**>**Pd1**>**Co1**>**Fe1**.

The number of electron-donor atoms present in the ligand showed to influence catalytic activity of the metal complex in the polymerization of NBE. For instance, it was observed that catalytic activity doubled when bidentately chelated complex **Ni1** was compared to tridentately chelated complex **Ni2**. Complex **Ni1** showed catalytic activity of 22.7 $g \times 10^3_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$ where complex **Ni2** resulted catalytic activity of 81.9 $g \times 10^3_{(PNBE)}.mol_{(Ni)}^{-1}.h^{-1}$. Similar observations were made for the (pyridyl)imine- iron(II) and cobalt(II) containing complexes. This can be explained by the stabilization of the active species due to the increased number of electron-donor atoms. These observations have also been reported by other researchers [34, 16, 31]. It can therefore be concluded that the catalytic activity of the formed complexes towards NBE polymerization be categorized as **Ni2 > Ni1** > **Pd1** > **Co2** > **Co1** > **Fe2 > Fe1.** In general, the nickel(II) and palladium(II) catalysts had higher activities compared to activities observed from iron(II) and cobalt(II) and this was consistent with observations made by other researchers [18, 32, 15].

Table 4.3: Catalytic screening of complexes as pre-catalysts for norbornene polymerization.[a]

Entry	Complex	Yield (%)	Activity[b]	T_g (°C)[c]	T_d (°C)[d]
1	**Ni1**	19	22 700	302	478
2	**Pd1**	15	17 600	286	462
3	**Co1**	<1	700	ND	ND
4	**Fe1**	<1	300	202	477
5	**Ni2**	70	81 900	300	478
6	**Co2**	<2	1 500	280	492
7	**Fe2**	<1	500	ND	478

[a]Polymerization conditions: [NBE] = 1.17 g, 0.012 mol; Al/Ni: 1000; NBE/Ni: 1250; V total = 7.5 ml; catalyst: 10 μmol, solvent: chlorobenzene; reaction t: 1 h; R_T. [b]Activity: TOF $(g_{(PNBE)}.mol_{(M)}^{-1}.h^{-1})$; [c]Polymer glass transition state temperature determined by DSC; [d]Polymer degradation temperature determined by TGA.

Investigating the resulting microstructural- and thermal properties of the polymers were imperative as this will serve as key components in determining final industrial applications. Vinyl addition polymerization of norbornene can be confirmed by analyzing the microstructure of the polymer by methods of FT-IR and NMR [2, 3]. For example, the VAP of NBE can be confirmed by the absence of absorption peaks at $1680 - 1620$ cm^{-1} and 960 cm^{-1} which indicates the absence of the *trans* double bond that would be present in the ROMP structure of polynorbornene [2, 35, 36]. Furthermore, the signatory absorption peak at 941 cm^{-1} can be assigned to the bicyclic unit of the monomer that would still be intact in VPNBE. The route of polymerization (vinyl addition) was confirmed for all complexes. For instance, it can be seen in **Figure 4.3** that the peak at 1631.79 cm^{-1} which represents the double bond in the monomers bicyclic unit, is broad and has a low intensity which indicates the formation of a saturated polymer consisting of mainly sp^3 carbons, but sp^2 carbons might still be present [30]. This

indicates that the possibility exists, that although vinyl addition was the main route of polymerization, the polymer may consist of ROMP unit inserts [14, 32]. A peak at 941 cm^{-1} indicates that the bicyclic unit of the monomer is still intact, confirming VPNBE formation. Bao *et. al* reported that it's possible to acquire VPNBE with a low percentage of ROMP unit inserts, and that the number of inserts can be controlled by varying standard polymerization parameters e.g., MMAO/M ratios and reaction temperatures. Sacchi *et. al* made a similar observation and found that it is possible to quantify the insertion rates, using NMR techniques should the polymer display good solubility [32].
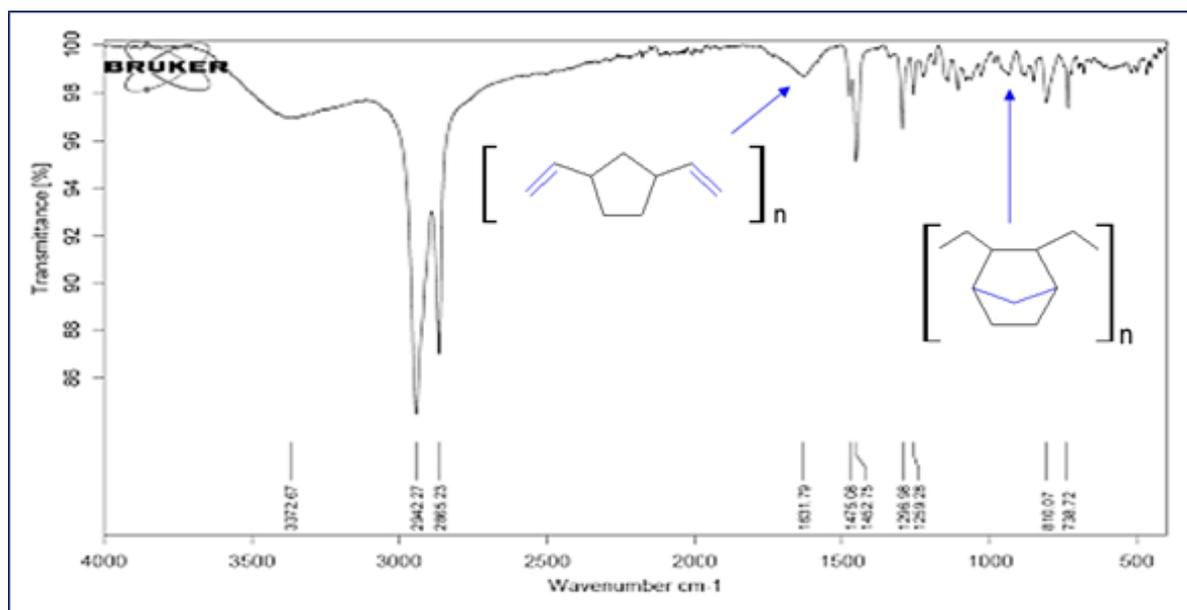
Figure 4.3: FT-IR spectra of vinyl-addition polynorbornene formed from complex **Pd1**, illustrating ROMP unit inserts at 1631.79 cm^{-1} and intact bicyclic units at 940 cm^{-1}.

Glass transition temperature (T_g) and degradation temperature (T_d) play vital roles in polymer industrial applications. It was reported that the choice of metal center strongly influences T_g and T_d [37, 38]. This was shown to be accurate based on the results obtained in **Table 4.3**,

entries 1-7. For example, it was observed that complex **Ni1** produced VPNBE with a T_g of 302 °C, complex **Pd1** a T_g of 281 °C, and complex **Fe1** a T_g of 202 °C. Both complexes **Ni1** and **Ni2** produced polymers with higher T_g than what has been reported in literature. This might indicate significance in industrial applications since enhanced thermal properties can lead to specialized applications. Utilizing different metal centers resulted in different T_d observed for the formed polymers. For instance, the T_d of complexes **Fe2**, **Ni2**, **Co2,** and **Pd1** range between 462 - 492 °C (**Table 4.3**, entries 2, 5 - 7) with increases noticeable between different metal centers. For example, complex **Fe1** resulted in a polymer T_d of 477 °C and complex **Co2** formed a polymer with T_d of 492 °C. The polymer produced by complex **Pd1** showed a T_d of 462 °C, whereas the polymer from complex **Ni2** displayed a T_d of 478 °C. The T_d of polymers formed by complexes **Pd1** and **Ni2** are higher than polymer T_d reported in literature. For example the reported palladium(II)-complexes produce VPNBE with T_d of 410 °C [39], and other nickel(II)-complexes forming VPNBE with T_d ranging from 400 °C – 450 °C [2]. From literature reports, the T_g of VPNBE from cobalt(II)-catalysts are in the range of 380 °C [38], whilst polymers from palladium(II)-catalysts show T_g of 240 – 318 °C [40, 39], and nickel(II)-catalysts produce VPNBE with T_g of 240 °C [2].

4.3.7 Comparison of current complexes with literature catalysts

A brief comparison of the tested pre-catalysts against known catalysts from literature, would further provide clarity on industrial suitability of these complexes. In general, it would make sense to state that a pre-catalyst should be able to convert monomers at an acceptable rate, at moderate reaction temperatures, to achieve high molecular weights and narrow molecular weight distributions. The resulting polymer's application would largely be influenced by the thermal properties measured as well. **Table 4.4** illustrates a summary of some literature catalysts and their properties as discussed in Chapter 2, as well as properties measured from

the best performing pre-catalysts in this study. By comparison, it's clear that the pre-catalysts tested in this study resulted low to moderate activities as opposed to highly active catalysts previously reported. For instance, Huang *et. al* (**32**) reported an extremely active catalyst capable of polymerizing NBE at 2.2×10^9 $g_{(PNBE)}.mol_{(M)}^{-1}.h^{-1}$ whereby the catalyst system reported by Xiang *et. al* (**31**) resulted very low activities of 15.5×10^3 $g_{(PNBE)}.mol_{(M)}^{-1}.h^{-1}$. The best performing catalyst from this study was **Ni2**, measured activity of 81.9×10^3 $g_{(PNBE)}.mol_{(M)}^{-1}.h^{-1}$, which proves to be low compared to the system reported by Huang *et. al.* On the other hand, the resulting thermal properties of the polymers measured significantly higher than previously reported, indicating better stability at elevated temperatures. For instance, the system reported by Sun *et. al* resulted a polymer with T_d of >450 °C whereby the T_d measured for the polymer from **Ni1** and **Ni2** measured 478 °C. These comparisons indicate that although the activities prove low, the thermal properties of the resulting polymers might hold high temperature applications.

Table 4.4: Comparison of the catalytic activities of current and reported catalyst

Catalyst	Catalyst Structure	Activity $(\times 10^3$ $g_{(PNBE)}.mol_{(M)}^{-1}.h^{-1})$	Reference
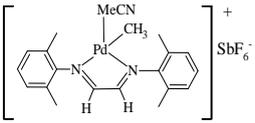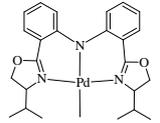
31		15.5	[21]
32		$2\,200 \times 10^6$	[30]
33		242.5	[2]
34		132.9	[2]
35		89.5	[8]
36		2 164	[25]
Ni1		22	-
Ni2		81.9	-
Pd1		17.6	-
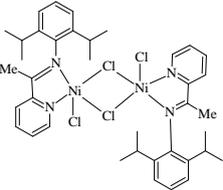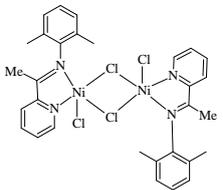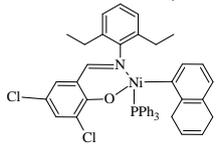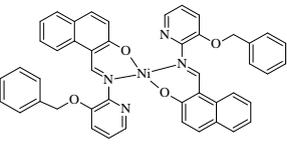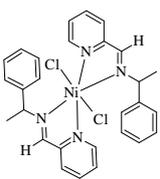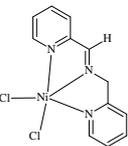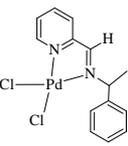
4.4 Conclusions

In conclusion, this chapter demonstrated that (pyridyl)imine complexes of nickel(II), palladium(II), cobalt(II), and iron(II) complexes of bidentate and tridentate nitrogen-donor systems display activity in various degrees towards the vinyl-addition polymerization of norbornene. Catalytic performance is strongly influenced by the choice of metal center and ligand donor system. In the case of ligands tested, the order of catalytic activities for (pyridyl)imine complexes of bidentate **L1** and tridentate **L2** can be expressed as **L2** > **L1**, and the activities for metal centers can be depicted as nickel(II) > palladium(II) > cobalt(II) > iron(II). Optimization studies showed that the catalytic performance of pre-catalysts can be enhanced by increasing the co-catalyst/pre-catalyst ratios as well as monomer/pre-catalyst ratios. An increased polymerization reaction time led to higher monomer conversions where *o*-chlorobenzene resulted as the best solvent of choice for adequate pre-catalyst solubility, high catalytic activity, and monomer conversion. FT-IR analyses of the polynorbornenes formed, showed the polymerization reactions have proceeded *via* the vinyl-addition route for all complexes, with possible ROMP unit inserts present in the polymer backbone. Thermal properties of the resulting polymers are strongly influenced by the choice of pre-catalyst metal center as tridentate (pyridyl)imine complex of cobalt(II) presented the highest thermal degradation temperature of all complexes where bidentate (pyridyl)imine complex of palladium(II) has shown the lowest. Glass transition state temperatures of the resulting polymers are also affected by the choice of pre-catalyst metal center as the formed polymer of bidentate (pyridyl)imine nickel(II) complex resulted in the highest and bidentate (pyridyl)imine complex of iron(II) the lowest.

Thermal properties of the resulting polymers can also be controlled by varying reaction parameters like co-catalyst/pre-catalyst and monomer/pre-catalyst loading ratios, polymerization reaction times, solvent choice, and polymerization reaction temperatures. For instance, by increasing the co-catalyst/pre-catalyst loading ratio the thermal degradation temperature of the resulting polymer decreased where the glass transition state temperature remained unchanged. By increasing monomer/pre-catalyst ratios the thermal degradation temperature increased whereby the glass transition state temperature remained unaffected. By prolonging polymerization reaction times, higher thermal degradation temperatures are obtainable with glass transition temperatures unaltered. Polymerization reactions at room temperature have shown to produce polymers with the highest glass transition state temperature, with thermal degradation temperatures mainly unaffected. Toluene has shown to be the best solvent for high glass transition state polymers whereby the thermal degradation temperatures of polymers remain unaffected by the choice of solvent.

References

[1] Xu. Y.M, K. Li , Y. Wang, W. Deng and Z. Yao, "LMononuclear Ni(II) Complexes with Schiff Base Ligands: Synthesis, Characterization, and Catalytic Activity in NBE Polymerization," *Polymers,* vol. 9, p. 105, 2017.

[2] X. Mi, Z. Ma, N. Cui, L. Wang, Y. Ke and Y. Hu, "Vinyl Polymerization of Norbornene with Dinuclear Diimine Nickel Dichloride/MAO," *J. Appl. Polym. Sci.,* vol. 88, pp. 3273-3278, 2003.

[3] Yang H., Li Z., Li Y. and Sun W., "Vinyl Polymerization of Norbornene with Neutral Salicylaldiminato Nickel(II) Complexes," *Organometallics,* vol. 22, pp. 3678-3683, 2003.

[4] K. Vijayakrishna, S. Padmanabhan, T. Kanna and D. Dakshinamoorthy, "Highly active novel Ni-diimine pre-catalyst containing bis-ketimine ligand for the vinyl polymerization of norbornene," *Polym. Bull.,* vol. 68, pp. 635-645, 2012.

[5] Y. Jang, H. Sung, S. Lee and C. Bae, "Effects of tris(pentafluorophenyl)borane on the activation of zervalent-nickel complex in the addition polymerization of norbornene," *Polymer,* vol. 46, pp. 11301-11310, 2005.

[6] S. Jie, P. Ai, Q. Zhou and B. Li, "Nickel and cationic palladium complexes bearing (imino)pyridyl alcohol ligands: Synthesis, characterization and vinyl polymerization of norbornene," *J. Organomet. Chem.,* vol. 696, pp. 1465-1473, 2011.

[7] D. Lee, J. Lee, J. Ryu, Y. Kim, C. Kim and I. Lee, "Novel Nickel Catalysts Containing Tetradentate Chelating Ligands for the Polymerization of Norbornene," *Bull. Korean Chem. Soc.,* vol. 27, p. 1031, 2006.

[8] Z. Sun, F. Zhu, Q. Wu and S. Lin, "Vinyl polymerization of norbornene with novel nickel(II) diphosphinoamine/methylaluminoxane catalytic system," *Appl. Organomet. Chem.,* vol. 20, pp. 175-180, 2006.

[9] S. Yamakawa, D. Takeuchi, K. Osakada, S. Takano and S. Kaita, "Copolymerizationof1,3-butadiene and norbornene catalyzed by Ni complexes," *React. Funct. Polym.,* vol. 136, pp. 19-24, 2019.

[10] L. Guo, Y. Zhang, H. Mu, L. Pan, K. Wang, H. Gao, B. Wang, Z. Ma and Y. Li, "Efficient addition polymerization of norbornene with polar norbornene derivatives by neutral nickel(II) catalysts," *Chin. J. Polym. Sci.,* pp. doi.org/10.1007/s10118-019-2292-2, 2019.

[11] R. Tanaka, R. Matsuzaki, Y. Nakayama and T. Shiono, "Synthesis of highly thermostable norbornene-isoprene-1-octene terpolymer with titanium catalyst," *J. Polym. Sci., A: Polym. Chem.,* vol. 55, pp. 2136-2140, 2017.

[12] G. Zanchin, I. Pierro, E. Parisini, J. Marti-Rujas, G. Ricci and G. Leone, "Synthesis, structure and behavior of vanadium(III) diphosphine complexes in the homo- and co-polymerization of ethylene with norbornene: the ligand donor strength and bite angle make the difference.," *J. Organomet. Chem.,* pp. 142-150, 2018.

[13] J. Meng, X. Li, X. Ni and Z. Shen, "High transparent alternate copolymer of norbornene with isporene catalysed by bis(phenoxy-imine) titanium complex," *RSC Adv.,* vol. 6, p. 19351, 2016.

[14] F. Bao, X. Lu, H. Gao, G. Gui and Q. Wu, "Vinylic and ROMP of norbornene wit bis(B-ketoamine) Co Complexes," *J. Polym. Sci., Part A: Polym. Chem.,* vol. 43, pp. 5535-5544, 2005.

[15] L. Benade, S. Ojwach, C. Obuah, I. Guzei and J. Darkwa, "Vinyl-addition polymerization of norbornene catalyzed by (pyrazol-1-ylmethyl)pyridine divalent iron, cobalt and nickel complexe," *Polyhedron,* vol. 30, pp. 2878-2883, 2011.

[16] C. Carlini, S. Giaiacopi, F. Marchetti, C. Pinzino, A. Galletti and G. Sbrana, "Vinyl Polymerization of Norbornene by Bis(salicylaldiminate)copper(II)/Methylalumoxane Catalysts," *Organometallics,* vol. 25, pp. 3659-3664, 2006.

[17] H. Gao, L. Pei, Y. Li, J. Zhang and Q. Wu, "Vinyl polymerization of norbornene with nickel catalysts bearing [N,N] six-membered chelate ring: Important influence of ligand structure on activity," *J. Mol. Catal. A: Chem.,* vol. 280, pp. 81-86, 2008.

[18] H. Liang, J. Liu, X. Li and Y. Li, "Synthesis, structure and norbornene polymerization behavior of neutral palladium complexes," *Polyhedron,* vol. 23, pp. 1619-1627, 2004.

[19] X. Xiao and G. Jin, "Functionalized N-heterocyclic carbene iridium complexes: Synthesis, structure and addition polymerization of norbornene," *J. Organomet. Chem.,* vol. 693, pp. 3363-3368, 2008.

[20] J. Ni, C. Lu, Y. Zhang, Z. Liu and Y. Mu, "Norbornene polymerization and ethylene/norbornene copolymerization catalyzed by constrained geometry cyclopentadienyl-phenoxytitanium catalysts," *Polymer,* pp. 211-216, 2008.

[21] P. Xiang and Z. Ye, "Homo- and Co-polymerization of norbornene and methyl acrylate with Pd-diimine catalysts," *J. Organomet. Chem.,* vol. 798, pp. 429-436, 2015.

[22] G. Vougioukalakis, I. Stamatopoulos, N. Petzetakis, C. Raptopoulou, V. Psycharis, A. Terzis, P. Kyritsis, M. Pitsikalis and N. Hadjichristidis, "Controlled Vinyl-Type Polymerization of Norbornene with a Ni(II) diphosphinoamine/methylaluminoxane catalytic system," *J. Polym. Sci., Part A: Polym. Chem.,* vol. 47, pp. 5241-5250, 2009.

[23] J. Zhang, P. Wang, X. Wang, L. Wang, J. Chen and Z. Zheng, "Vinyl addition polymerization of norbornene catalyzed by b-iminoamine Ni(II) complexes/methylaluminoxane systems," *J. Organomet. Chem.,* vol. 696, pp. 3697-3702, 2011.

[24] Z. Hao, N. Yang, W. Gao, L. Xin, X. Luo and Y. Mu, "Nickel complexes bearing N,N,N-tridentate quinolinyl anilidoeimine ligands: Synthesis, characterization and catalysis on norbornene addition polymerization," *J. Organomet. Chem.,* vol. 749, pp. 350-355, 2014.

[25] F. Chang, D. Zhang, G. Xu, H. Yang, J. Li, H. Song and W. Sun, "Synthesis and characterization of new bis(1-aryliminomethylenylnaphthalen-2-oxy)nickel complexes and their catalytic behavior for vinyl polymerization of norbornene," *J. Organomet. Chem.,* vol. 689, pp. 936-946, 2004.

[26] L. Li, P. Gomes, M. Lemos, F. and Z. Fan, "Polymerization of norborene catalyzed by highly active tetradentate chelated a-diimine nickel complexes," *Macromol. Chem. Phys.,* vol. 212, pp. 367-374, 2011.

[27] X. He and Q. Wu, "Polymerization of Norbornene Using Bis(B-ketoamino)nickel(II)/MAO Catalytic Systems," *J. Appl. Polym. Sci.,* vol. 101, pp. 4172-4180, 2006.

[28] Y. Wang, S. Lin, F. Zhu, H. Gao and Q. Wu, "Vinyl polymerization of norbornene with pyrazolylimine Ni(II)/MAO catalytic systems," *J. Appl. Polym. Sci.,* vol. 110, pp. 3590 - 3595, 2008.

[29] F. Pelascini, F. Peruch, P. Lutz, M. Wesolek and J. Kress, "Polymerization of norbornene with CoCl2 and pyridine bisimine cobalt(II) complexes activated with MAO`," *Macromol. Rapid Commun.,* vol. 24, pp. 768-771, 2003.

[30] Y. Huang, J. Chen, L. Chi, C. Wei, Z. Zhang, Z. Li, A. Li and L. Zhang, "Vinyl Polymerization of Norbornene with Bis(imino)pyridyl Nickel(II) Complexes," *J. Appl. Polym. Sci.,* vol. 112, pp. 1486-1495, 2009.

[31] G. Leone, A. Boglia, A. C. Boccia, S. T. Scafati, F. Bertini and G. Ricci, "Vinyl-type addition polymerization of norbornene and synthesis of norbornene macromonomers in the presence of ethylene catalyzed by cobalt(II)-phosphine complexes," *Macromolecules,* vol. 42, pp. 9231-9237, 2009.

[32] M. Sacchi, M. Sonzogni, S. Losia, F. Forlini, P. Locatelli, I. Tritto and M. Lichelli, "Vinyllic polymerization of norbornene by late transition metal-based catalysis," *Macromol. Chem. Phys.,* vol. 10, p. 202, 2001.

[33] A. Antonov, N. Semikolenova, V. Zakharov, W. Zhang, Y. Wang, W. Sun, E. Talsi and K. Bryliakov, "Vinyl polymerization of norbornene on nickel complexes with bis(imino)pyridine ligands containing electron-withdrawing groups," *Organometallics,* vol. 31, pp. 1143-1149, 2012.

[34] U. Peuckert and W. Heitz, *Macromol. Rapid. Commun.,* vol. 19, pp. 159-162, 1998.

[35] R. Zhuang, H. Liu, J. Guo, B. Dong, W. Zhao, Y. Hu and X. Zhang, "Highly active nickel(II) and palladium(II) complexes bearing N,N,P tridentate ligand for vinyl addition polymerization of norbornene," *Eur. Polym. J.,* 2017.

[36] J. Chen, Y. Huang, Z. Li, Z. Zhang, C. Wei, T. Lan and W. Zhang, "Syntheses of iron, cobalt, chromium, copper and zinc complexes with bulky bis(imino)pyridyl ligands and their catalytic behavious in ethylene polymerization and vinyl polymerization of norbornene," *J. Mol. Catal. A: Chem.,* pp. 133-141, 2006.

[37] T. Hasan, T. Ikeda and T. Shiono, "Highly efficient Ti-based catalyst systems for vinyl addition polymerization of norbornene," *Macromolecules,* vol. 37, pp. 7432-7436, 2004.

[38] L. Goodall, L.H. McIntosh III and L.F. Rhodes, *Macromol. Symp.,* vol. 89, pp. 421-432, 1995.

[39] Y. Huang, J. He, Z. Liu, G. Cai, S. Zhang and X. Li, "A highly active chiral (S,S)-bis(oxazoline) Pd(II) alkyl complex/activator catalytic system for vinyl polymerization of norbornene in air and water," *Polym. Chem.,* vol. 8, p. 1217, 2017.

[40] G. Myagmarsurene, J. Park and S. Ihm, "Polymerization of norbornene using novel palladium carboxylate/boron trifluoride etherate catalyst system," *Polymer,* vol. 47, pp. 8474-8479, 2006.

Chapter Five

Final conclusions and future recommendations

5.1 Final Conclusions

The aim of this study included the design and syntheses of (pyridyl)imine bidentate and tridentate metal complexes and the respective catalytic application thereof in the vinyl-addition polymerization of a strained cyclic olefin to produce vinyl-type polynorbornene. The Schiff-base (pyridyl)imine ligands, bidentate **L1,** and tridentate **L2** were designed and synthesized following the condensation reaction between a primary amine and aldehyde in the presence of an acid to afford air-stable products. Ligands **L1** and **L2,** were designed respectively to consist of a bidentate [N, N]- and tridentate [N, N, N]-donor system to be easily chelated with late transition metal groups. The steric bulk of the targeted complexes were taken into consideration during ligand design and has proved to be relevant in catalytic applications. The success of the ligand syntheses and isolations were established using LC-MS, HR-MS, FTIR, ^{1}H-NMR, ^{13}C-NMR, and CHN methods. Chemical analyses confirmed the structural requirements of formed Schiff bases suitable for further employment in metal complex formations with nickel(II), palladium(II), cobalt(II), and iron(II). Ligands **L1** and **L2** underwent successful complexation with late transition metal groups to afford air-stable metal complexes suitable for screening to evaluate catalytic potential. The success of complex formation was established by FTIR, CHN, LC-MS, Single Crystal X-ray Crystallography, and ^{1}H-NMR techniques where was possible and applicable.

The catalytic potential of each complex was evaluated in the vinyl-addition polymerization of strained cyclic olefin; norbornene, and scrutinized categorically for yield, catalytic activity, and the confirmation of the polymerization route followed. Polymerizations were successfully completed in a stepwise and well-planned fashion under Schlenk conditions whereby the metal complexes were activated by alkylation with MMAO, the monomer introduced to the system, and the polymerization quenched with acidic methanol. It was found that nickel(II) and palladium(II) containing complexes (**Ni1**, **Ni2,** and **Pd1**) have shown the highest catalytic activity in comparison to iron(II) and cobalt(II) containing complexes (**Co1**, **Co2**, **Fe1**, and **Fe2**). The stabilization of the metal center with the appropriate ligand-donor system has shown importance to obtain good catalytic activity as differences were observed between systems containing bidentate [N, N] ligands and systems containing tridentate [N, N, N] ligands. The influence of varying polymerization reaction parameters was successfully investigated, and it was found that parameters such as reaction temperatures, solvent type, monomer/metal loading ratios, co-catalyst/metal loading ratios, and reaction times influence catalytic activity as well as thermal properties of the resulting polymers.

Determination of the molecular weight and molecular weight distribution of the resulting polymers will be considered in future as this will further determine the effect of varying experimental parameters on the resulting polymers. This will also assist in concluding the explanation of the observed differences in thermal properties of the polymers. Nuclear magnetic resonance analysis of the resulting polymers also posed challenging due to the resulting polymer's insolubility in common solvents. GPC analyses of the polymers has not been accomplished due to instrument breakages at the University of Stellenbosch. We hope the data will be available before submission of the manuscript from the thesis.

5.2 Future Recommendations

The vinyl-addition polymerization of strained cyclic olefins like norbornene and norbornene derivatives has extensively been investigated where nickel(II) and palladium(II) complexes were employed. Investigations were conducted where the effects of structural changes in pre-catalyst design on catalytic activity were tested. These structural changes to pre-catalysts include variations in the steric bulk of the ligand system, changes in the number of metal nuclei as well as changes in the type and number of electron donor- and withdrawing atoms in the ligand system. This is all evidence of thorough and well-executed research.

However, evidence of the employment of rare earth metals in the polymerization of strained cyclic olefins is still lacking. Neodymium catalyst systems are well established and widely used in the industry for polymerization catalysis of diene monomers. For instance, the utilization of the above stated in the polymerization of 1,3-butadiene to produce high *cis*-content (96.5% +) polybutadiene rubber, with low molecular weight distributions and high linearity which is generally traded as Neodene. This material is of high value in the rubber manufacturing industry, where it is commonly used as a special blend ingredient to establish high abrasion resistance and rebound resilience in rubber compounds used in rubber products such as tires, conveyor belts, and golf ball cores. The utilization of Nd-versatate (**Figure 5.1**) systems where triisobutylaluminum (TIBA) or diisobutylaluminum hydride (DIBAH) are used as co-catalysts and ethyl aluminum sesquichloride (EASC) as halide donor are widely reported on in the polymerization of diene monomers like butadiene.
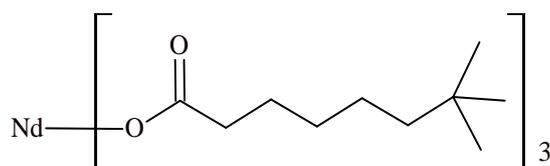
Figure 5.1: Neodymium Versatate complex used for diene polymerization.

It would be interesting to design, synthesize and evaluate this system in the polymerization of strained cyclic olefins and the derivatives thereof and determine the chemical as well as physical characteristics of these polymers. Nd-versatate is predominantly employed for the homo-polymerization of monomers but the utilization in co-polymerization of cyclic olefins with, for instance, isoprene, ethylene, or even styrene could hold significance in the age of specialized polymers and data networks. It is evident from literature that functionalized norbornene derivatives hold unlimited potential in the manufacture and applications of membrane technology suitable for gas separation operations. These norbornene derivatives normally contain functionalities of ester groups as well as SiMe – functionalities. In some cases, have catalyst systems been reported to show great activities toward the polymerization of these functionalized monomers, forming polymers with superior characteristics. It would also be interesting to test a range of rare-earth metal-based catalysts, in the polymerization of functionalized norbornene monomers and evaluate the produced polymers in the field of membrane applications.
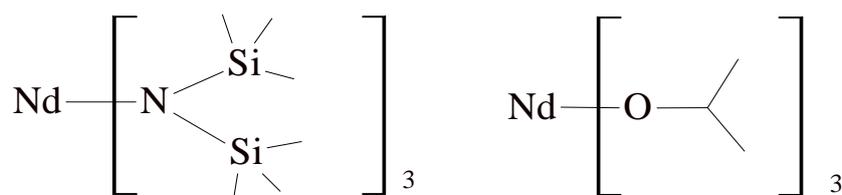

Figure 5.2: Nd-catalysts containing SiMe$_3$ and ether functionalities.