Palladium (II) and iron (II) complexes derived from pyridyl-imine ligands as catalyst precursors for 1-hexene oligomerization and norbornene polymerization

by

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DECLARATION

I declare that the dissertation ‘‘**Palladium (II) and Iron (II) complexes derived from pyridyl-imine ligands as catalyst precursors for 1-hexene oligomerization and norbornene polymerization**’’ is my original work and that all the quoted literature and sources used have been indicated and referenced accordingly.

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Pamela Zanele Khuzwayo

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ABBREVIATIONS

°C	degrees Celsius
d	doublet
dd	doublet of doublets
dmso	dimethyl sulphoxide
EWGs	electron withdrawing groups
g	grams
GC-MS	gas chromatography-mass spectrometry
h	hour(s)
HDPE	high density polyethylene
im	imine
i-Pr	isopropyl
IR	infrared resonance spectroscopy
L	ligand
LLDPE	linear low density polyethylene
M	metal
MAO	methylaluminoxane
MMAO	modified methylaluminoxane
Mmol	millimoles
m/z	mass to charge ratio
m	multiplet
NMR	nuclear magnetic resonance
PE	polyethylene
PP	polypropylene
Py	pyridyl-ring
ROMP	ring opening metathesis
s	singlet
t	triplet
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TOF	turn over frequency
UV-Vis	ultraviolet-visible
w/w	weight per weight

ACKNOWLEDGEMENT

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ABSTRACT

Pyridyl-imine ligands **L1**-**L4** were prepared by condensation of pyridine-2-carboxyaldehyde with an appropriate amine. Characterization by NMR spectroscopy, infrared spectroscopy, mass spectrometry and elemental analysis confirmed successful preparation in yields of 64-88%. These ligands were used to prepare Pd(II) complexes **C1**-**C4,** from $PdCl_2(CH_3CN)_2$ and the corresponding pyridyl-imine ligand. ^{1}H-NMR, ^{13}C-NMR, FT-IR, mass spectrometry and elemental analysis confirmed coordination. Attempts to prepare target Fe(II) complexes **C5**-**C8** by reacting the ligands with anhydrous $FeCl_2$ were unsuccessful. Infrared data suggested coordination of ligands to the Fe centre, however mass spectrometry and elemental analysis data revealed that target complexes were not obtained.

Pd(II) complexes **C1**-**C4** were evaluated as catalyst precursors for 1-hexene oligomerization and norbornene polymerization using methylaluminoxane (MAO) as co-catalyst. The oligomerization of 1-hexene was investigated in a neat reaction media at various Al:Pd ratios. All investigated complexes were found to be inactive for the oligomerization of 1-hexene. From ^{1}H-NMR spectroscopy and GC-MS analysis it was observed that the product distribution was mainly a mixture of 2-hexene and 3-hexene isomers. Parameters such as temperature and time did not have any significant influence towards the productivity of 1-hexene oligomers.

Norbornene polymerization studies were carried out with Pd(II) complex **C4** in toluene at room temperature. This complex was found to exhibit good activity for norbornene polymerization, producing a vinyl bicyclic polymer, confirmed with infrared and solid state ^{13}C-NMR spectroscopy. Increasing the amount of co-catalyst (MAO) and temperature did not have any significant influence on the activity and monomer conversion. However, increasing reaction time was observed to have a significant influence on the activity.

CHAPTER 1

LITERATURE REVIEW: PYRIDYL-IMINE METAL COMPLEXES AS HOMOGENEOUS CATALYSTS

1.1 INTRODUCTION

The past five decades have witnessed a number of developments in the catalysis of olefin polymerization. These include for example, the introduction of heterogeneous Ziegler-Natta catalysts by Karl Ziegler and Guilio Natta and the development of homogeneous early transition metal catalysts (metallocenes) by Kaminsky and Sinn.[1,2] Properties such as high catalytic activity and ease of catalyst-product separation have led to the industrial application of Ziegler-Natta catalysts. However, implementation of these catalysts has also been hampered by the presence of multiple active sites which makes it difficult to understand the mechanistic aspects. Additionally, both Ziegler-Natta and metallocene catalysts are presumed to be highly oxophilic and can be easily poisoned by functionalized olefins.[1,2] Of interest to olefin polymerization catalysis to date is the introduction of less oxophilic homogeneous late transition metal (Post-metallocene) catalysts by Brookhart and co-workers.[3]

Homogeneous late transition metal catalysts serve as promising alternatives to heterogeneous catalysts for organic transformations. Compared to conventional Ziegler-Natta catalysts, these systems consist of a single active metal centre, whereby the actual catalytic species is well defined. Furthermore, homogeneous catalysts are reported to produce high yields and selectivities in contrast to heterogeneous catalysts.[3-6] Industrially, difficulty in catalyst-product separation serves as a major setback for homogeneous catalysts. Occasionally homogeneous process systems use low catalyst concentrations compared to heterogeneous catalytic systems, thus eliminating the requirement of recovering the catalyst from the product stream.[6] Among the various coordination systems investigated as homogeneous catalysts, ‘‘pyridyl-imine complexes derived from late transition metals’’ have been extensively studied as polymerization and oligomerization catalysts for both α-olefins (alkene) and cyclic olefins.[7-11]

The ability to regulate catalyst activity and selectivity through modification of the ligand backbone and choice of metal centre, highlights one of the most significant findings made thus far on homogeneous catalysis using pyridyl-imine systems.[12-16] The ease of synthesis and ability to incorporate different functionalities onto the ligand backbone, has played an important role in generating interest in complexes of this nature for catalytic processes such as polymerization and oligomerization of olefins. The interest in the oligomerization and

polymerization of olefins is sparked by the application of olefin oligomers as intermediates or additives for speciality chemicals as well as their application as microelectronic components.[17,18] Metal complexes are often used to catalyse organic transformations of this nature. In this project the main objective was to develop catalysts for norbornene polymerization and 1-hexene oligomerization. This literature review will thus focus on the progress and advances made in recent years on developing transition metal catalysts for olefin polymerization and oligomerization.

1.2 GENERAL OVERVIEW OF OLEFIN POLYMERIZATION

Until the early 1990's little information existed on the polymerization of α-olefins using homogeneous catalysts. Highly oxophilic catalytic systems developed by Karl Ziegler[19], Giulio Natta[19], Hogan and Banks[20], as well as Kaminsky[14] dominated the industry during this time period. In 1953, Karl Ziegler discovered a titanium tetrachloride ($TiCl_4$) complex which in the presence of diethylaluminium chloride [$(C_2H_5)_2AlCl$] as a co-catalyst, was observed to be an active catalyst for the polymerization of ethylene in mild reaction conditions.[1,19] This catalyst was later demonstrated by Giulio Natta to polymerize propylene into polypropylene (PP).[1] Both "Ziegler and Natta were awarded a Nobel prize" for their innovative work in the field of olefin polymerization technology.[19] In 1957, the "first homogeneous Ziegler-Natta catalyst" was introduced by Breslow, Newburg and Karl Ziegler.[21] However, the bis(cyclopentadienyl)titanium dichloride/alkyl aluminium chloride [Cp_2TiCl_2/AlR_2Cl] catalyst gave low polymerization activities for ethylene compared to the heterogeneous systems initially reported by Ziegler and Natta.[21] Unfortunately not much can be said about the mechanistic aspects involving heterogeneous Ziegler-Natta catalysts. Mainly because these systems consist of structurally and reactively different multiple active sites.[1]

In the 1960s, Cossee postulated that polymerization of olefins in the presence of Ziegler-Natta catalysts occurs initially by the generation of a vacant coordination site (Figure 1.1(**a**)), which is thus followed by olefin complexation (Figure 1.1(**b**)).[1] The polymer chain then undergoes a formal migration, which results in the formation of a metal-carbon bond from a four-centre transition state (Figure 1.1(**c**)). A new vacant coordination site is thus created, which allows for another alkene component to insert and chain growth to continue.[1] In the 1970s, another generation of Ziegler-Natta catalysts was discovered. This generation was

made up of catalytic systems which consisted of $MgCl_2$/Lewis base/$TiCl_4$ ternary mixture as the complex component and Al alkyl/Lewis base as the co-catalyst fragment.[21]

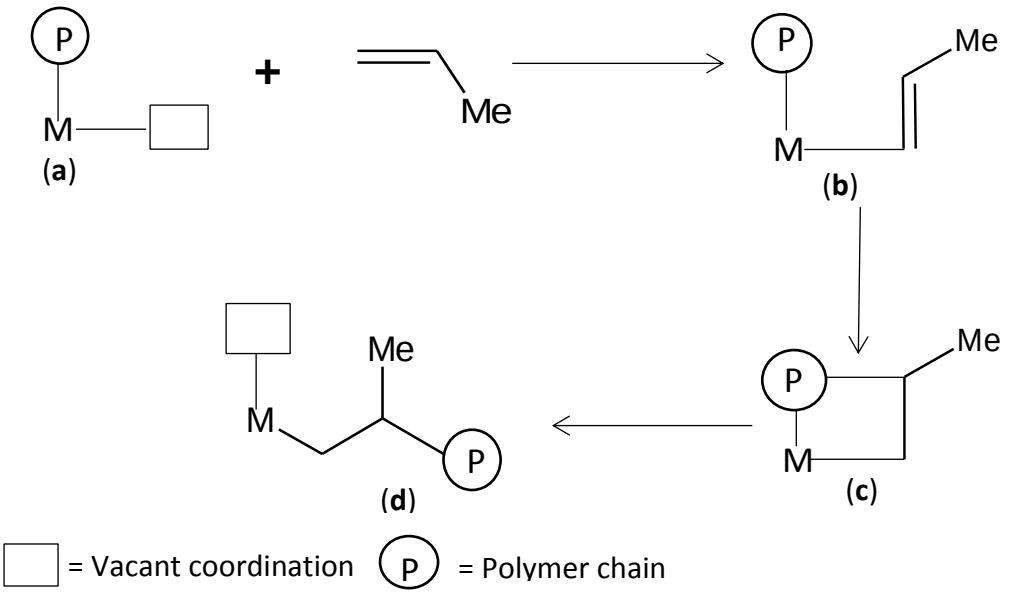


Figure 1.1: Cossee Mechanism for the polymerization of olefins using Ziegler-Natta catalysts.[1]

Phillips-type catalysts with a name originating from the ‘‘founders of J.P Hogan and R.L Banks company name’’, also made a huge impact on the olefin polymerization technology in the early 1950s.[22] This type of polymerization catalyst, is a chromium oxide complex supported on an amorphous material like silica (i.e. $CrOx/SiO_2$).[20,23] Moreover, these catalysts are responsible for ‘‘50 % of the world’s high density polyethylene (HDPE)’’ produced to date.[20] Weckhuysen *et al.* reported that chromium Phillips catalysts are also able to polymerize olefins which do not contain carbon atoms greater than eight and with no branching closer than the fourth position to the double bond.[23] For example, 1-butene, 1-pentene and 1-hexene could be polymerized into high molecular weight branched polymers.[23] Ahmadi *et al.* recently reported on a Cr/SiO_2 and $Cr/Ti/SiO_2$ Phillips catalyst which was used to polymerize ethylene into crystalline and amorphous polyethylene.[20] The $Cr/Ti/SiO_2$ catalyst was reported to give high ethylene polymerization activity compared to the Cr/SiO_2 analogue.[20]

It was not until the late 1970s and early 1980s, that the activity of the biscyclopentadienyl based homogeneous catalytic systems introduced by Breslow and co-workers was

significantly improved with the introduction of methylaluminoxane (MAO) as a co-catalyst.[14,24,25] This type of olefin polymerization catalyst is referred to as a metallocene polymerization catalyst, made up of a single active site and marks a start-up for a new generation of transition metal based complexes.[14,21,23] For example, the highly active Cp_2ZrCl_2/MAO catalyst reported by Kaminsky *et al.* is able to polymerize ethylene to polyethylene with the same average chain length and molecular weight.[21] Furthermore, compared to Ziegler-Natta catalysts, metallocene systems are soluble in organic solvents and have a ligand backbone that can be easily tuned.[26] Keminsky *et al.* also reported on another type of cyclopentadienyl-Zirconium/Hafnium dichloride/MAO catalyst (Figure 1.2) for the polymerization of ethylene and propylene.[26] In general, the hafnium systems were found to be less active compared to the zirconium based analogues

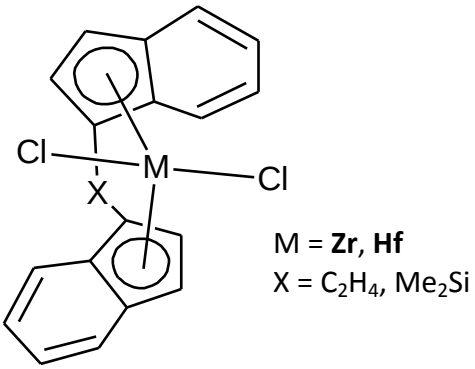
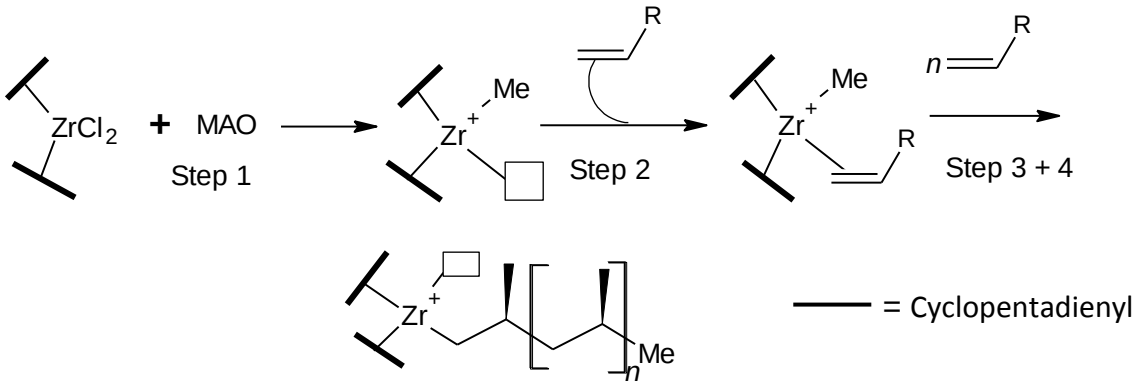


Figure 1.2: Zirconium/Hafnium cyclopentadienyl-dichloride/MAO catalyst reported by Kaminsky *et al.*[26]

Polymerization of olefins by these zirconium/MAO catalytic systems implies that, the metallocene-dichloride metal precursor undergoes a ligand exchange with the co-catalyst (MAO). This allows for one of the Cl^- or CH_3^- species to be abstracted by an Al-centre in MAO, thus forming an active alkylated metallocene cation (Scheme 1.1). An olefin species inserts into this newly created electron-deficient zirconium-alkyl bond of the active species, while at the same time a new free co-ordination position is created (Scheme 1.1 (step 3)).[26] This allows for insertion of another alkene or olefin component, thus enabling growth of a polymer chain (Scheme 1.1 (step 4)).[26]



Scheme 1.1: Olefin polymerization mechanism using zirconocene/MAO catalysts reported by Kaminsky *et al.*[26]

Over the last decades significant developments have occurred in the olefin polymerization technology, through the evolution of catalyst design, i.e. from the discovery of multiple active site Ziegler-Natta catalytic systems to the single active site homogeneous metallocene catalysts. The catalyst evolution has allowed for better understanding of the process technology and the key mechanistic steps involved during the olefin polymerization process.[19,21] Olefin polymerization technologies based on both Ziegler-Natta and metallocene catalytic systems are however, limited by their high oxophilic nature (i.e. ability to react irreversibly with heteroatoms), which then requires additional costs for the purification of the monomer feed.[27] The discovery of late transition homogeneous metal catalysts in the 1990s which are less oxophilic and able to tolerate heteroatoms, highlights some of the most significant break-throughs made thus far in the olefin polymerization technology.[28] In addition to the known polyolefins such as PE and PP, which can be produced with conventional Ziegler-Natta and homogeneous metallocene catalysts, copolymerization of olefins as well as polar co-monomers like vinyl acetate implies development of new polymer materials with different microstructure and rheological properties.[2]

The first ever class of Pd(II) and Ni(II) homogeneous catalysts (Figure 1.3) reported to be tolerant to heteroatoms was introduced by Brookhart *et al.*[11,29,30] These α-diimine complexes produced highly branched high molecular weight polyethylene under mild reaction conditions using MAO as a co-catalyst.[29] Ethylene polymerization using Brookhart's cationic palladium α-diimine complexes could be conducted in the presence of organic esters, ethers and acids which all consist of heteroatoms.[11] These α-diimine complexes thus

paved a way to the production of polymerization catalysts which would allow access to the development of new polymer materials.

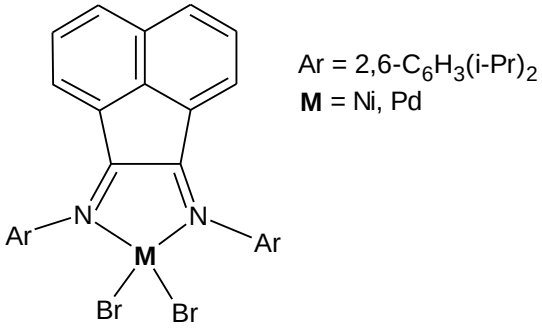
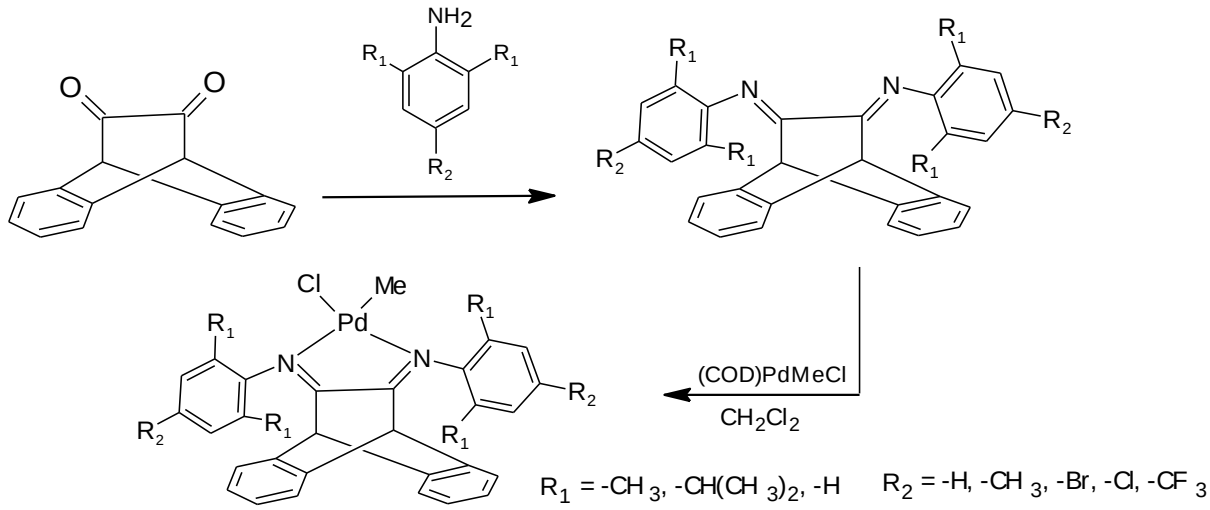


Figure 1.3: α-Diimine Ni (II) and Pd (II) complexes synthesized by Brookhart *et al*.[29]

"Three dimensional α-diimine palladium complexes" with an imine nitrogen consisting of aryl ring substituents such as isopropyl, methyl, chloride, bromide as well as trifluoromethyl were also recently reported by Huo *et al* (Scheme 1.2).[30] These systems were shown to be active for both norbornene homo-polymerization and copolymerization of norbornene with 5-norbornene-2-carboxylic acid methyl ester (NB-$COOCH_3$) using $B(C_6F_5)_3$ as the activator. Upon homo-polymerization of norbornene, it was found that the system containing an isopropyl substituent on the phenyl ring attached to the imino-nitrogen gave a higher activity compared to that consisting of a methyl group.[30] High catalytic activities were observed for all α-diimine palladium complexes activated for the copolymerization of norbornene and NB-$COOCH_3$.



Scheme 1.2: α-Diimine palladium complexes reported by Huo et al. for the polymerization of norbornene.[30]

Brookhart's systems inspired the development of a number of other related diimine complexes derived from late transition metals, such as Fe(II) and Co(II) tridentate catalyst precursors developed by Small *et al*.[31] These tridentate systems were easily prepared by the condensation of an appropriate aniline with 2,6-diacetylpyridine to yield the desired ligand. Generated Fe and Co complexes are activated with modified methylaluminoxane (MMAO) to give the active catalytic species (Figure 1.4).[31]

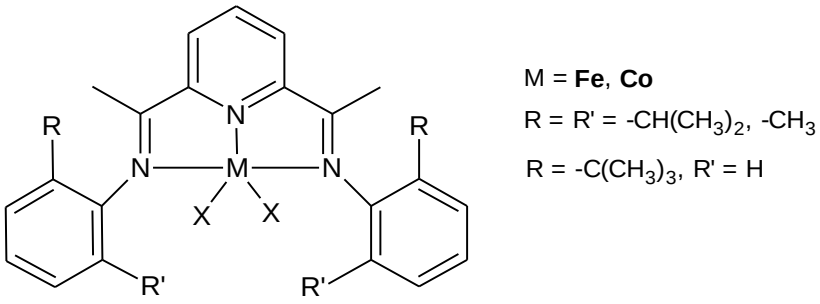
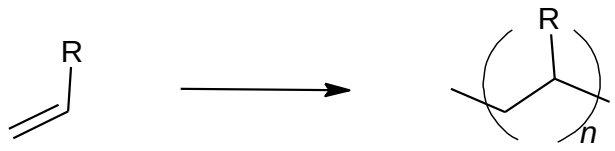


Figure 1.4: Tridentate pyridyl-imine Fe(II) and Co(II) complexes synthesized by Small *et al*.[31]

In contrast to the Ni(II) and Pd(II) diimine complexes, both Fe(II) and Co(II) tridentate pyridine-imine systems reported by Small *et al*. give strictly linear polyethylene compared to the highly branched polyethylene reported by Brookhart *et al*.[11,31] For the Fe(II) systems, it was observed that increasing the bulkiness of the "*ortho* aryl substituents" did not significantly increase the activity. For example the isopropyl substituted iron system yielded a turnover frequency of 0.12 x 10^6/h compared to 0.10 x 10^6/h for the methyl substituted system at 25 °C.[31] However, activities observed for the cobalt systems were shown to decrease slightly with an increase in steric bulk. For instance, at a reaction temperature of 25°C, the methyl substituted cobalt system gave a turnover frequency of 0.08 x 10^6/h compared to 0.04 x 10^6/h observed for both the isopropyl and tert-butyl substituted system.[31]

1.2.1 Polymerization versus Oligomerization

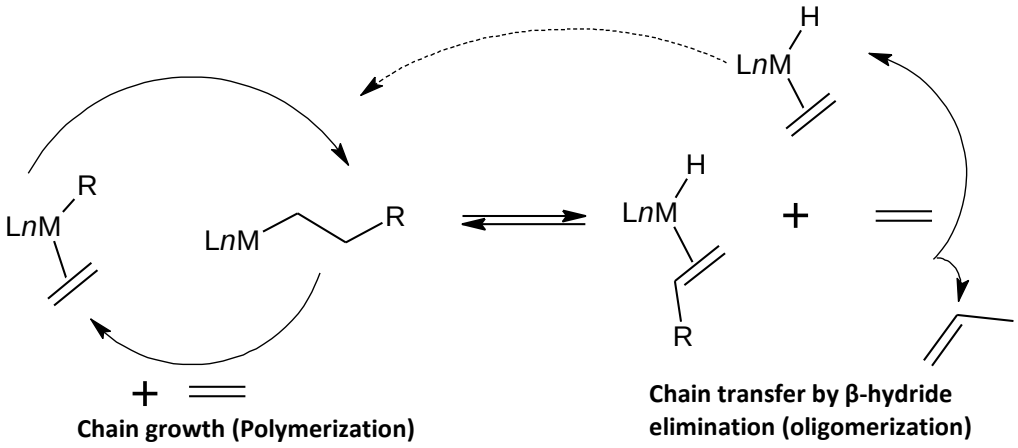
The coupling of carbon bonds according to Scheme 1.3 illustrates how oligomers and polymers can be catergorized.[17] Oligomerization molecules are by definition a subclass of molecules produced through polymerization reactions, and typically consist of low molecular weights.



R = H, -CH $_3$, -CH $_2$CH $_3$,....,C $_6$H$_5$ **Oligomer** : *2<n<100*, **Polymer** : *n>100*

Scheme 1.3: Coupling of C-C bonds to yield oligomers and polymers.[17]

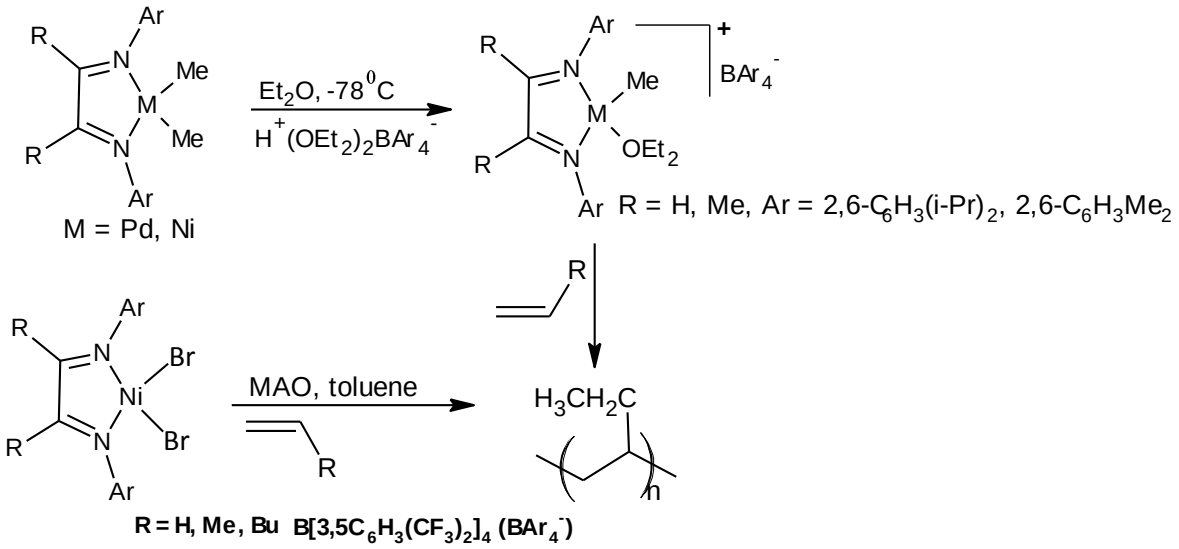
In the presence of a metal catalyst the activation energy for the organic transformation (i.e. polymerization or oligomerization) can be reduced, thus speeding up the transformation and allowing the process to possibly occur even under mild reaction conditions.[19] In general, polymerization and oligomerization of olefins by either heterogeneous Ziegler-Natta catalysts or by homogeneous metallocene or late transition metal catalysts relies on the same basic type of reaction, which involves "chain growth by migratory insertion in an alkyl-complex" (Scheme 1.4).[32] The frequency of the chain transfer reactions via β-H elimination, in which the hydrocarbon chain component is separated from the active metal catalyst, highlights that small difference which exists between polymerization and oligomerization reactions (Scheme 1.4).[32,33]



Scheme 1.4: Olefin polymerization versus oligomerization by late transition metals.[33]

Polymerization and oligomerization of olefins using homogeneous late transition metal catalysts has been clearly shown by Johnson *et al* and Tang *et al*. and depending on the nature of the metal catalyst used during the transformation, chain transfer could potentially be in competition with chain propagation.[39,34,35] Johnson *et al*. reported on α-diimine Ni(II) and Pd(II) complexes with bulky aryl-substituents, for the polymerization of ethylene (Scheme 1.5).[29,34] From this study, it was shown that by using bulky ligand substituents, high

molecular weight polymers are formed as a result of "slow chain transfer relative to chain propagation".[29] By reducing the steric bulk on these systems, Killian and co-workers demonstrated how oligomerization of ethylene was the favoured transformation rather than polymerization.[34]



Scheme 1.5: Ni(II) and Pd(II) α-diimine systems reported by Johnson *et al*.[29]

Tang *et al.* reported on Ni(II) 2-ethylcarboxylate-6-iminopyridyl complexes for the oligomerization and polymerization of ethylene (Figure 1.5).[35] It was shown from both activity and product distribution, how big an influence the ligand environment has on both polymerization and oligomerization of ethylene. For example, activation of the Ni(II) complexes with MAO favoured production of oligomers in high activities compared to polymer production.[35] Of the Ni(II)/MAO catalysts evaluated, the diisopropyl-substituted system gave both ethylene oligomers and polyethylene with considerable amount of polymer activity under the same reaction conditions, compared to a methyl and ethyl substituted analogue.[35] Only traces of polyethylene were observed for the ethyl substituted Ni(II)/MAO complex.

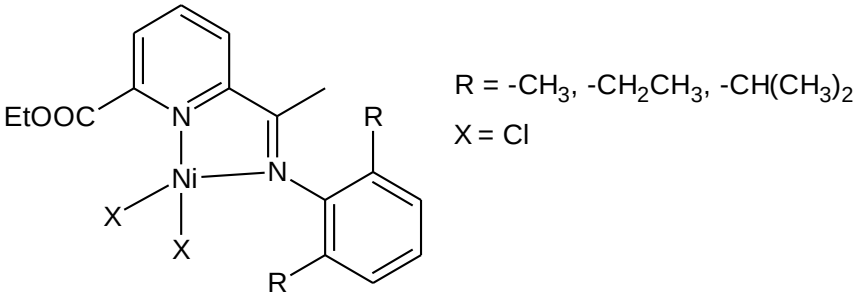


Figure 1.5: Ni (II) 2-ethylcarboxylate-6-iminopyridyl complexes investigated by Tang *et al.* for the polymerization and oligomerization of ethylene.[35]

1.2.2 Overview of olefin monomers

An olefin is a generic term which refers to both linear (i.e. ethylene, propylene, 1-butene, 1-hexene, 1-octene etc.) and cyclic alkenes (i.e. norbornene, cyclopentene, cyclohexene, cyclooctene etc.). Linear olefins in particular can be divided into lower and higher olefins depending on the number of carbon atoms present. Lower linear olefins can be gaseous or liquid in nature and have low boiling points, these are typically olefins from ethylene to pentene (C_2-C_5).[36] Higher linear olefins are normally liquid olefins with higher molecular weights (C_6-C_{20}).[36] Depending on the positioning of the double bond on the alkene chain, the monomer can be referred to as an internal olefin (e.g. 2-propene, 2-hexene) or as a terminal alkene (1-propene, 1-hexene, 1-butene).[37]

Both cyclic and linear olefins have made a huge impact on an industrial and academic scale owing to their demand as monomers for the production of polymers and oligomers.[38,39] The interest in the commercial usage of olefins, comes from the application of olefin polymers and oligomers in the production of consumer goods such as grocery bags, adhesives, engineering plastics, medical applications, prosthetic implants, detergents, synthetic lubricants, surfactants, etc.[34,38,39,40] Commonly used processes for the production of olefins include; catalytic dehydrogenation, metathesis of alkenes, thermal and catalytic cracking of paraffins.[37,41,42] In some selected cases, olefins can be produced through the oligomerization and polymerization of other olefins.[26] Advantages such as low cost, ready availability, a high reactive and easily transformable alkene monomer species into a number of valuable products makes olefins highly valued commercial commodities and of importance both industrially and academically.[26, 39,41,42]

1.3 NORBORNENE POLYMERIZATION

"Norbornene ([Bicyclo(2.2.1)]hept-2-ene)" is a bridged cyclic olefin, which can be polymerized by three methods: "ring opening metathesis (ROMP), vinyl/addition polymerization and cationic or radical polymerization" (Figure 1.6).[43] Each route gives a different structural polymer unit with different properties. For example, properties such as high chemical resistance, low dielectric constant, good UV resistance, high glass transition temperature, excellent transparency, a large refractive index together with a low birefringence have given the vinyl type norbornene polymer increased interest over the past few years.[44]

Out of the three norbornene polymerization routes, the ROMP has received more attention and is commercially applied in the "Norsorex process" for the production of polymer material in a form of moulding powder, using $RuCl_3$/HCl as the metal catalyst.[18,45] This type of polymerization process was reported for the first time by Andersen and Meckling in the 1950s.[46] The type of polymer product obtained with ROMP contains a double bond in the polymer backbone (Figure 1.6). Polynorbornene (PNB) of this nature is occasionally used as an "elastometric vulcanizable material for both sound and vibrational damping".[18] The ROMP of norbornene can be catalysed by metals such as molybdenum, rhenium, ruthenium, tungsten and osmium.[18] The radical polymerization of norbornene was introduced for the first time in 1967, producing a 2.7-connected low molar mass oligomeric material as the final product (Figure 1.6).[18] This type of polymerization has been reported to be initiated by free radicals such as azoisobutyronitrile (AIBN), tert-butyl perpivalate or tert-butyl peracetate as well as $EtAlCl_2$.[18,28]

Vinyl or addition polymerization of norbornene saturates the π-component and leaves the bicyclic structure intact (Figure 1.6).[18,47] This type of polymerization was first reported by Sartori *et al.* in 1963, using $TiCl_4/Al^iBu_3$ as the metal catalyst.[47,48] In 1965 Tsujino *et al*. developed a similar type of catalyst (i.e. $TiCl_4/AlEt_3$) for the vinyl polymerization of norbornene, by varying the alkyl component of the binary system initially developed by Sartori *et al*.[48] From this study it was demonstrated that by increasing the ratio of Al:Ti a mixture of a vinyl type bicyclic structural unit and a metathesis polymer is obtained.[49] Subsequently various catalysts containing transition metals such as nickel, cobalt,

chromium, titanium, zirconium, palladium and iron were investigated for this type of vinyl polymerization route.[7,50]

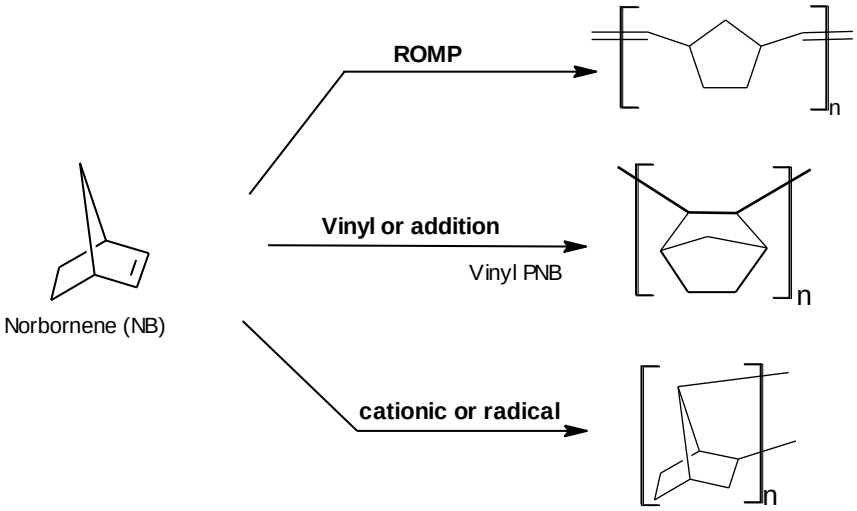


Figure 1.6: Polymer units obtained in the polymerization of norbornene.[51]

In 1967 McKeon *et al*. reported for the first time the vinyl polymerization of norbornene using palladium catalysts with a general formula of the type $Pd(A_2)X_2$, $Pd(B)X_2$ and $[Pd(A)X_2]_2$ respectively.[52] From the reported formulae A represents a neutral monodentate ligand derived from compounds consisting of benzonitrile, trimethyl phosphine, dimethylsulfoxide, carbon monoxide as well as tetrahydrofuran; B is a neutral bidentate ligand derived from 1,5-cyclooctadiene, endodicyclopentadien as well as vinyl cyclohexene.[52] Dichlorobis(benzonitrile) palladium, dichloro(endodicyclopentadien) palladium and palladium diacetate were thus reported by McKeon *et al*. for the polymerization of norbornene at room temperature conditions.[52] The polynorbornene obtained was a vinyl type solid polymer made up of repeating bicyclic structural units.[52] McKeon also reported that the palladium metal was the preferred choice of metal, as it is readily available, highly effective and relatively inexpensinve.[52] It is no surprise that a large part of the research on vinyl polymerization of norbornene has been focussed on palladium based catalysts. In 1976 Gaylord *et al*. also reported on the vinyl polymerization of norbornene using the dichlorobis(benzonitrile)palladium $[Pd(C_6H_5CN)_2Cl_2]$ catalyst which had been previously reported by McKeon *et al*.[53]

Sen *et al.* reported for the first time in 1982 a cationic palladium catalyst (Figure 1.7) for the polymerization of different olefins including norbornene.[54] Polymerization reactions were

conducted in the absence of a co-catalyst, mainly because the active systems consisted of weakly bound acetonitrile ligands.[54] The polynorbornene obtained was however disappointingly insoluble in most organic solvents thus properties such as molecular weight could not be determined.[54] Mehler *et al.* also reported in 1991 on the vinyl polymerization of norbornene using this particular cationic palladium catalyst.[55] Even after increasing the ratio of norbornene to catalyst, the obtained polymer unit still had limited solubility in solvents such as CH_3NO_2.[55]

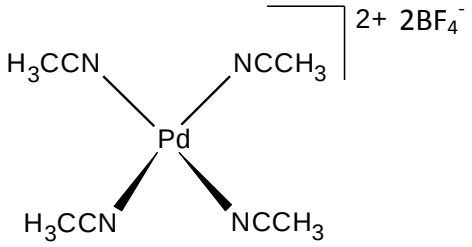


Figure 1.7: Cationic palladium catalyst developed by Sen et al.[54]

Kaminsky *et al.* was another researcher who reported in the year 1991, on the vinyl polymerization of cyclobutene, cyclopentene and norbornene using chiral metallocene based catalysts (i.e. $Me_2Si(Ind)_2ZrCl_2$ and $Et(Ind)_2ZrCl_2$ using MAO as the co-catalyst.[56] It was shown that both catalytic systems gave higher polymerization activity towards cyclopentene and cyclobutene than towards norbornene. In 1993 nickel catalytic systems were presented by Deming *et al.* for the vinyl polymerization of norbornene (Figure 1.8).[57] Deming found that, of the systems investigated the electron deficient π-allylnickel trifluoroacetate complex (Figure 1.8(**a**)) was not active for this particular polymerization.[57] However, compound (Figure 1.8(**b**)) which was recovered as a red homogeneous solution, was observed to be highly active in the absence of a co-catalyst.[57]

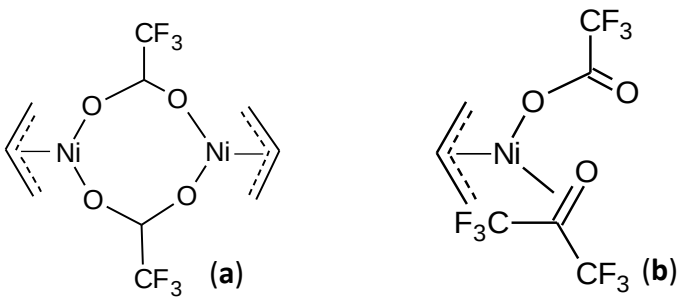


Figure 1.8: Nickel complexes developed by Deming *et al.*[57]

Safir *et al*. introduced for the first time Pd(II) complexes consisting of an internal olefin to stabilize the palladium centre (Figure 1.9).[58] From this study Safir postulated that by using Pd(II) complexes which consist of an internal olefin, factors often related to inhibition of olefin polymerization by chelation and strong donor ligands attached to the metal centre can be eliminated.[58]

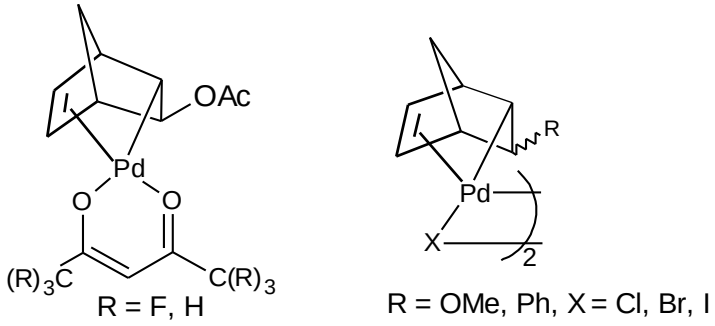


Figure 1.9: Pd(II) complexes investigated by Safir *et al*.[58]

These bicyclic complexes synthesized by Safir and co-worker were evaluated as initiators for the 1,2-insertion polymerization of norbornene and its derivatives. It was reported that "norbornene and diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate" could be polymerized quantitatively in less than 15 minutes by these Pd(II) initiators, using solvents such tetrahydrofuran and tetramethylurea in the presence of air.[58] Other norbornene derivatives such as bicycle[2.2.1]hepta-2,5-diene and diethyl bicycle[2.2.1]hepta-2,5-diene-2,3-dicarboxylate could also be polymerized in quantitative yields.[58] In 1995, Goodall *et al*. reported on a Co-neodecanoate complex (Figure 1.10) capable of polymerizing norbornene through vinyl insertion, using MAO as a co-catalyst.[59] Due to the good solubility of the produced polynorbornene in organic solvents such as cyclohexane, quantitative information such as the molar mass of the polymer (i.e. M_W = 1,600,000 $gmol^{-1}$) could be determined.[59]

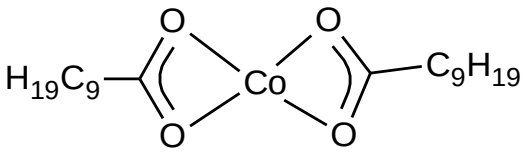
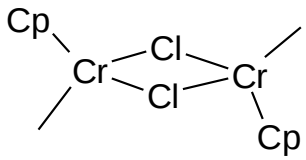


Figure 1.10: Co(II)-neodecanoate complex investigated by Goodall et al.[59]

Three years later after Goodall's discovery, Peuckert *et al*. reported on Cr(III)/MAO homogeneous catalysts with different Cp ligands.(Figure 1.11).[60] Peukert investigated the effect of increasing the "nucleophilicity" of the Cp ligands on the polymerization activity of norbornene. By increasing electron density on the ligand backbone, catalytic activity was significantly increased.[60]



Cp = C_5H_5, $C_5(CH_3)_5$, Indenyl, Fluorenyl

Figure 1.11: Cr(III)/MAO catalysts reported by Peuckert *et al*.[60]

Sen *et al*[54] and Mehler *et al*[55]. demonstrated how the prepared vinyl type polynorbornene is found to be poorly soluble in most organic solvents and how difficult it is to thus obtain quantitative data. In 1998, Kaminsky *et al*. developed hafnium and zirconium metallocene based catalysts for the "copolymerization of cycloolefins such as cyclopentene and norbornene" with ethylene (Figure 1.12).[26] This was one strategy used to eliminate factors associated with the poor analysis of the prepared polynorbornene.

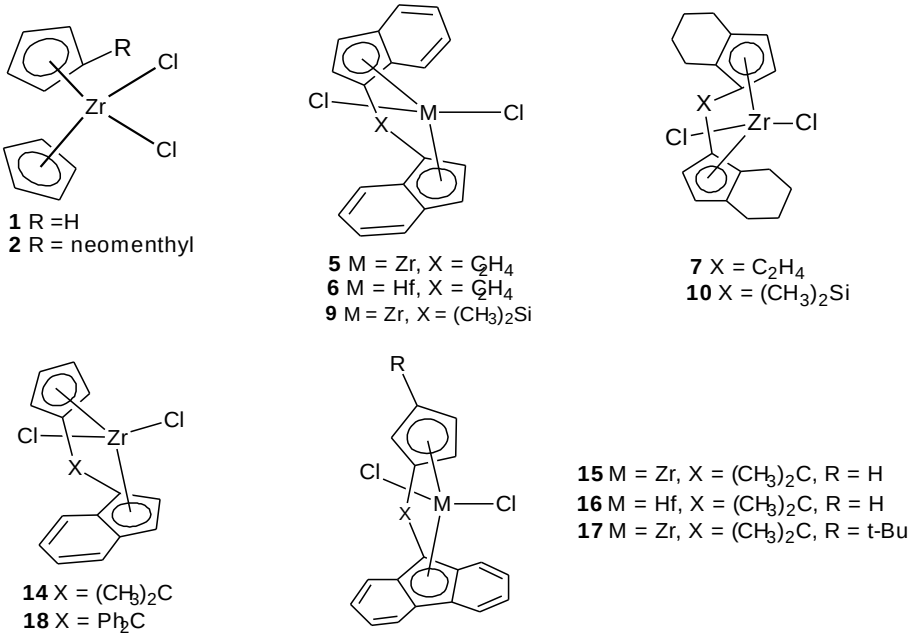


Figure 1.12: Zirconium metallocene complexes reported by Kaminsky et al.[26]

Copolymerization of norbornene with ethylene was also reported to occur via a vinyl type polymerization route (Figure 1.13).[26] Of the systems evaluated, catalysts (Figure 1.12 **5**, **15** & **17**) gave the highest activities in only 10 minutes of reaction time. Catalyst **7** (Figure 1.12) however, gave the lowest activity even after the reaction time was increased to 40 minutes.[26]

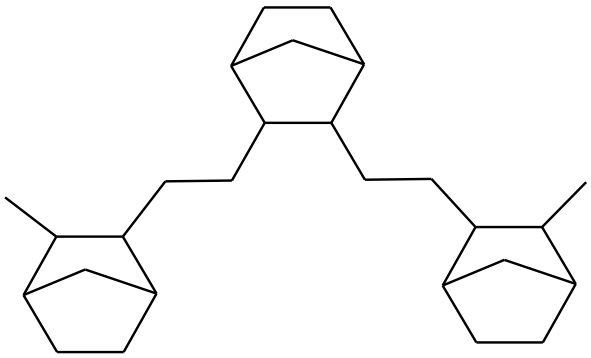


Figure 1.13: Structure of norbornene-ethylene copolymer developed by Kaminsky *et al*.[26]

Homogeneous catalytic systems based on late transition metals have also made a significant impact on the polymerization of norbornene. For example, tridentate and bidentate pyridyl-imine based systems represent some of the catalytic systems which have been investigated in the vinyl polymerization of norbornene in recent years. The increased interest in these particular systems is mainly due to the ease of synthesis of the ligand backbone and the ability to introduce different substituents into the functionality attached to the imine nitrogen. For example, in 2001 Sacchi *et al*. reported on α-diimine Ni(II) and tridentate pyridyl-imine Fe(II), Ni(II) and Co(II) complexes bearing isopropyl and tert-butyl substituted phenyl rings attached to the imine nitrogen (Figure 1.14).[61] These Ni(II), Fe(II) and Co(II) complexes investigated by Sacchi et al. were evaluated for the vinyl polymerization of norbornene using MAO as the co-catalyst.[61] Of the catalysts evaluated, the α-diimine and tridentate Ni(II) catalysts gave the highest activities, only traces of PNB were observed for both the Fe(II) and Co(II) tridentate systems.[61] The high molecular weight PNB obtained was observed to be moderately soluble in most organic solvents.[61]

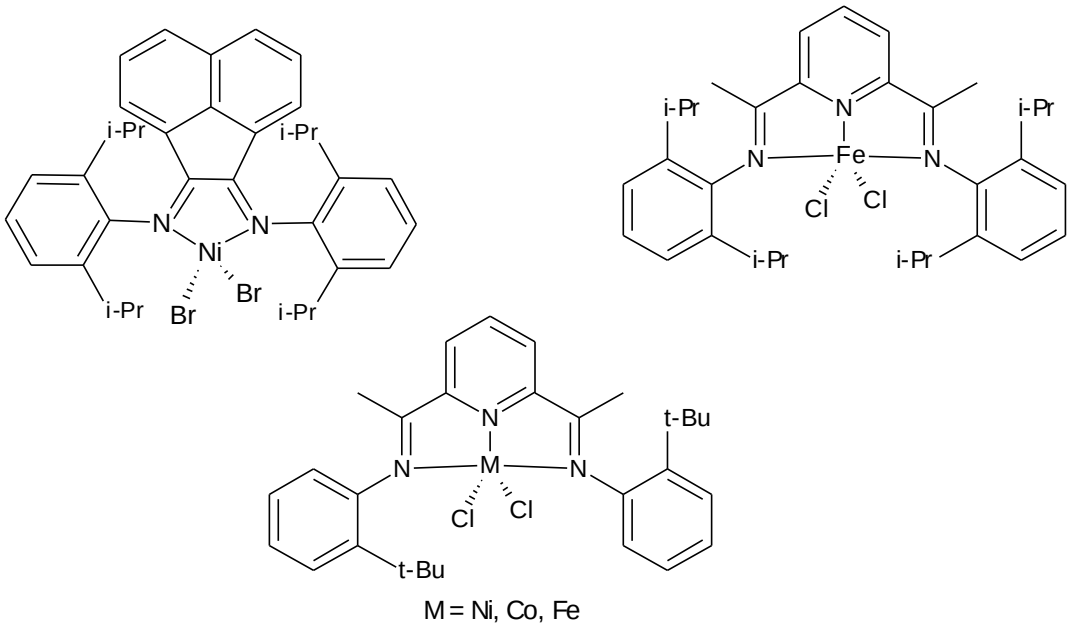


Figure 1.14: α-Diimine and tridentate pyridyl-imine complexes investigated by Sacchi *et al.*[61]

Sun *et al*. reported in 2003 on neutral salicylaldimine Ni(II) complexes, which were investigated as potential catalysts for the vinyl polymerization of norbornene, using MAO as a co-catalyst (Figure 1.15).[50] From this study, it was shown that complexes with an increased "electron withdrawing character" on the ligand backbone (i.e. X = Cl) gave higher activities compared to those carrying an iodine substituent.[50] Increasing the steric hindrance on the ligand backbone did not show any recognizable impact on the polymerization activity.[50]

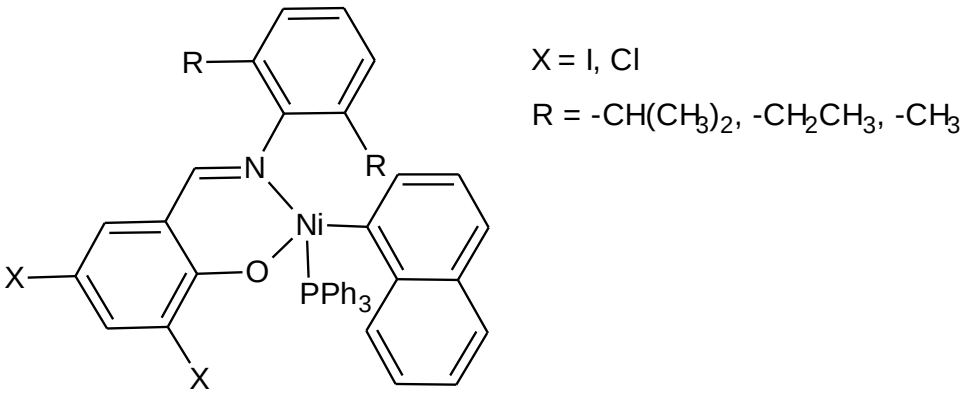


Figure 1.15: Salicylaldimine Ni(II) complexes developed by Sun *et al*.[50]

In 2012, Antonow *et al*. reported on bis(imino)pyridyl nickel(II) complexes which were investigated for the vinyl polymerization of norbornene using MAO as the co-catalyst (Figure 1.16).[47] Their main objective was on investigating the effect observed on the catalytic activity, when different electron-withdrawing groups (EWGs) are introduced in the phenyl rings attached to the imine nitrogen.[47] This group found that for the tridentate systems consisting of meta and para EWGs, higher activities were observed compared to those which had the EWGs on the ortho position.[47]

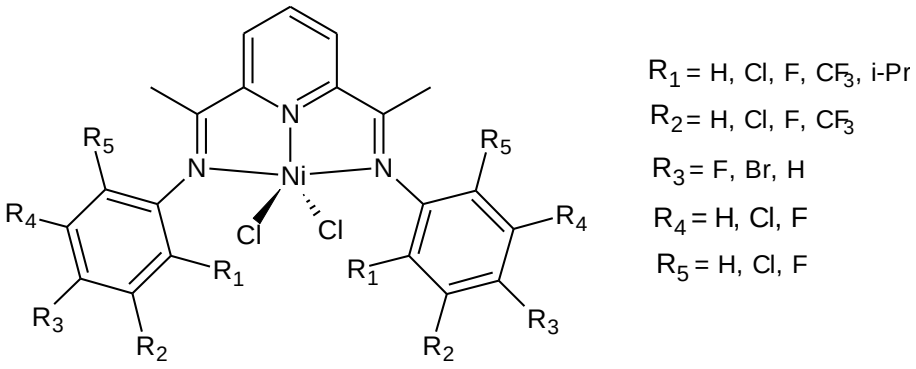


Figure 1.16: Bis(imino)pyridyl nickel(II) complexes developed by Antonow *et al*.[47]

Fe(II), Co(II), Cr(II), Cu(II) and Zn(II) bis(imino)pyridyl complexes consisting of 2.5-ditertbutylphenyl and 2.6-diisopropylphenyl substituents attached to the imine moiety have also been synthesized by Chen *et al*.[8] Out of the five complexes, the Fe(II), Co(II) and Cr(II) containing systems were found to be very active for the vinyl polymerization of norbornene in the presence of MAO as the co-catalyst. Disappointingly, no activity was observed for the systems which consisted of zinc and copper as the metal centre.[8]

Initial reports made by Brookhart *et al.*, Small *et al.* Antonow *et al.* and Chen *et al.* on tridentate and α-diimine systems were structurally symmetrical in nature, meaning that the two different imine nitrogens consisted of the same substituents. In the year 2000, a new class of pyridyl-imine based vinyl type polymerization catalysts were reported by Laine and co-workers.[9] These pyridyl-imine palladium complexes containing a substituted phenyl ring attached to the imino-nitrogen (Figure 1.17) were found to "produce active vinyl type polymerization catalysts for norbornene when activated with MAO".[9]

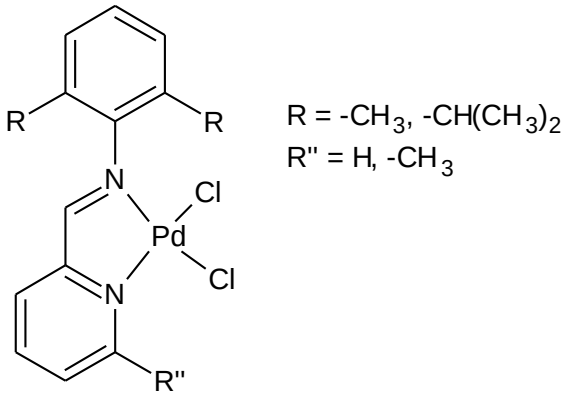
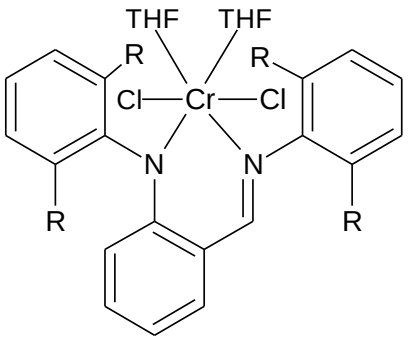


Figure 1.17: Palladium(II) pyridyl-imine complexes reported by Laine *et al*.[9]

These pyridyl-imine based palladium complexes were activated for norbornene polymerization using MAO as a co-catalyst under mild reaction conditions. All three systems were reported to give quantitative polymer yields in only two hours of reaction time.[9] This demonstrates the ability of the substituted phenyl pyridyl-imine ligands to sufficiently stabilize the cationic palladium centre, which is generated in the reaction of the co-catalyst with the respective catalyst precursor.[9] Monomer conversions of up to 100% were reached using catalysts with an isopropyl substituent attached to the *ortho* aryl position. The molecular weight of the polymer unit generated using these systems could not be determined due to its poor solubility.

It has been well demonstrated from the introduction of α-diimine, tridentate and bidentate pyridyl-imine systems how much influence variation of the ligand backbone has on the norbornene polymerization activity.[30,50,61] To date, variation of the ligand backbone is still demonstrated to have an influence on the vinyl polymerization activity of norbornene. For example, Pei *et al.* recently illustrated how a series of anilido-imine chromium complexes were used as catalysts for norbornene polymerization in the presence of MAO (Figure 1.18).[62] The polymerization results for these particular systems showed that activity towards norbornene polymerization increased with a decrease in bulkiness of the ligand backbone.[62] The obtained polynorbornene was a white solid, according to the quantitative data obtained using gel permeation chromatography a low molecular weight polymer was obtained.[62]



R = H, -CH_3, -$CH(CH_3)_2$

Figure 1.18: Chromium anilido-imine complexes derived by Pei *et al*.[62]

1.4 OLEFIN OLIGOMERIZATION

Olefin oligomers and their use as synthetic lubricants, detergents, plasticizers, preparation of sulfurized calcium alkyl-phenate and different kinds of surfactants, have been well researched over the past few years.[33,63,64] However, a large market exists for the production of linear alpha-olefin oligomers, typically α-olefins in the range of C_4-C_{20}.[63-65] These types of olefins are occasionally prepared using ethylene. In addition to being used as feedstock for the production of detergents and plasticizers, they are also used as ‘‘co-monomers in the synthesis of linear low density polyethylene (LLDPE)’’.[32,33,66] As demonstrated, oligomerization of ethylene is an industrially important processes, occasionally used to produce linear α-olefins.[67] The oligomerization of linear α-olefins is however still currently conducted with acidic catalysts such as, the Friedel-Crafts $AlCl_3$ and the solid phosphoric acid catalyst.[66,68] Unfortunately the application of acid catalysts for such organic transformation is limited by their restricted drawbacks: corrosiveness, elevated deactivation rate, poor selectivity and low activity towards production of linear α-olefins.[66,68] Homogeneous catalysts represent a version of catalysts which have been well demonstrated to offer elevated activities and selectivities for strictly linear α-olefins in contrast to acid catalysts.[64,65,66]

1.4.1 Ethylene oligomerization

One of the most significant discoveries made thus far in both polymerization and oligomerization technology is that of Ni, Pd α-diimine and Fe, Co tridentate pyridyl-bis(imine) systems introduced by Brookhart *et al* and Small *et al* over two decades ago.

These systems have since been used as benchmarks for the design of new pyridyl-imine homogeneous catalysts for olefin oligomerization reactions.[27,34,69,70,71] Svejda *et al*. demonstrated for example how catalysts derived from late transition metals have a strong propensity to undergo β-hydrogen elimination during oligomerization processes, especially when coordinated to ligands with reduced steric hindrance (Figure 1.19).[69] From this study oligomerization of ethylene was evaluated using Ni(II) α-diimine complexes which are less sterically hindered, compared to bulky Ni(II) α-diimine systems initially studied for ethylene polymerization.[69,29] These Ni(II) systems investigated by Svejda *et al*. oligomerize ethylene into linear α-olefins as well as linear internal olefins in the presence of MAO, MMAO and Et_2AlCl as co-catalysts.[69]

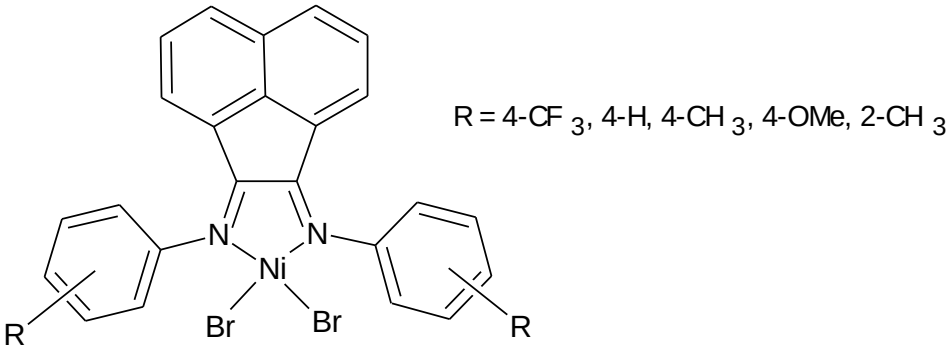
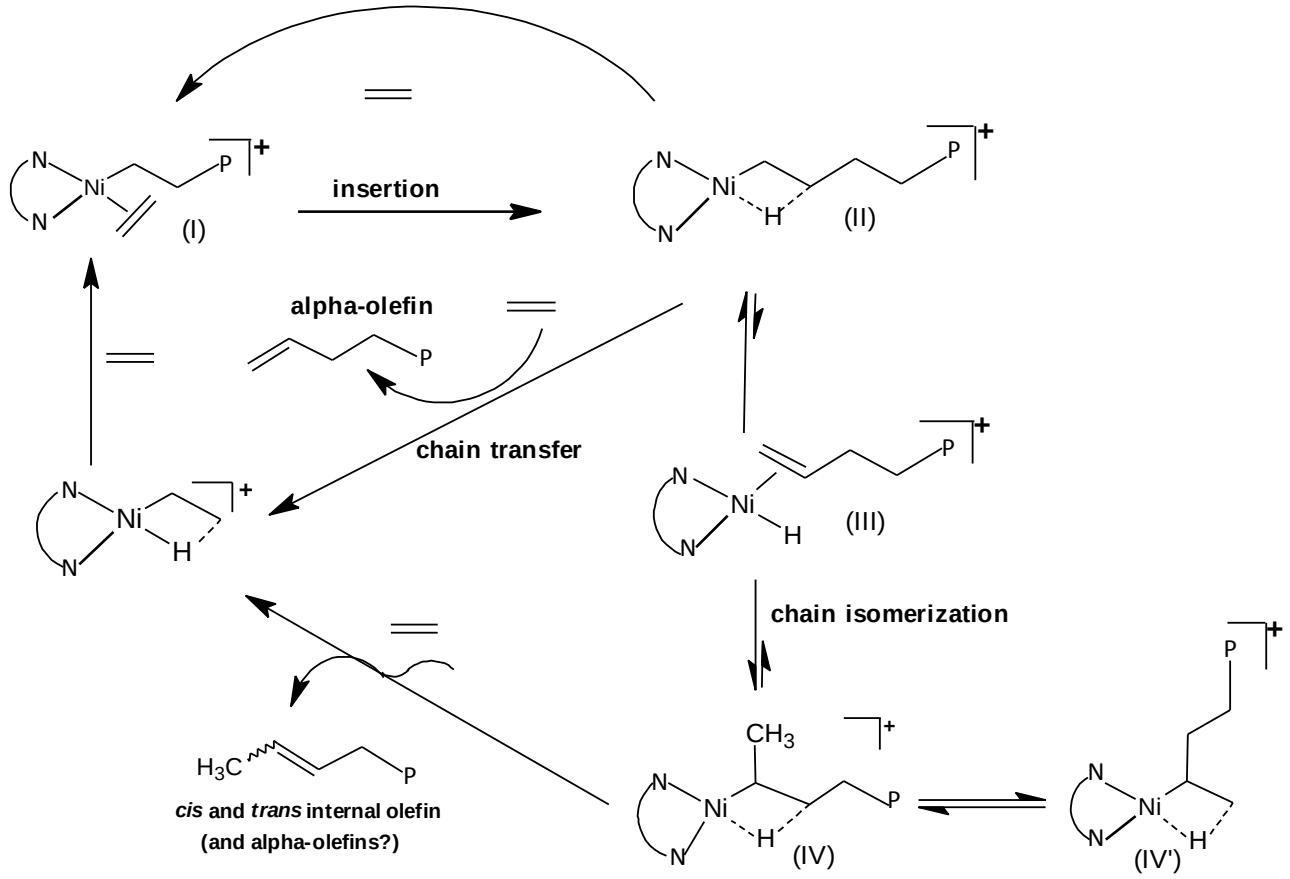


Figure 1.19: Ni(II) α-diimine complexes developed by Svejda *et al*.[69]

The mechanism proposed by Svejda *et al*. demonstrates how both linear α-olefins and linear 2-alkenes are produced (Scheme 1.6).[69] According to the oligomerization mechanism, linear α-olefins are only produced upon migration of the metal centre along the chain, through an olefin hydride species ((II)/(III)).[69] Chain transfer via associative displacement of an olefin from an olefin hydride species (III), followed by another chain transfer from a secondary alkyl agnostic species ((IV)/(IV')) enables production of linear-2-alkenes.[69]



Scheme 1.6: Proposed mechanism for the oligomerization of ethylene to produce linear-α-olefins and linear-2-alkenes.[69]

Tridentate pyridyl-(imine) complexes of iron synthesized by Small *et al*. when activated with MMAO gave ‘‘highly active and selective’’ tridentate Fe(II) catalysts for the oligomerization of ethylene to α-olefins (Figure 1.20).[72] Under similar oligomerization conditions, bulkier catalysts were proven to give reduced activities compared to the less bulky analogues.[72] This was demonstrated by two different entries conducted under the same reaction conditions, the turnover frequency observed for the methyl substituted catalyst was reported to be significantly higher (72 x 10^6 turnovers/h) than that of the ethyl substituted analogue (20 x 10^6 turnovers/h). On average the turnover frequencies given by the methyl substituted catalyst were observed to be much higher compared to the ethyl and isopropyl substituted catalysts. All of the catalytic systems tested gave over 99% selectivities for strictly linear α-olefins.[73] These Fe(II) complexes clearly demonstrate a generation of oligomerization catalysts capable of showing how the ligand backbone influences both selectivity and activity of the catalytic transformation.

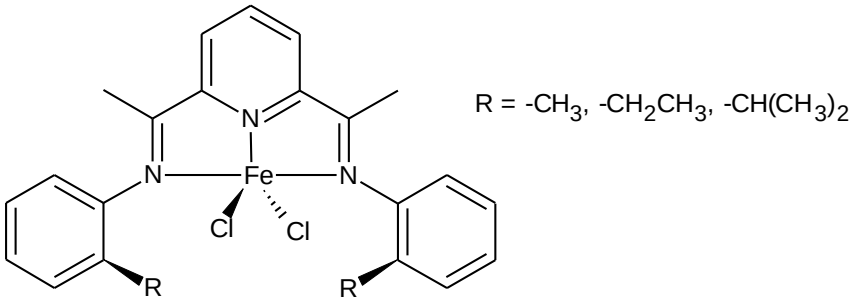


Figure 1.20: Fe(II) tridentate pyridyl bis-imine complexes reported by Small *et al*.[72]

A series of highly active and selective asymmetric tridentate Fe and Co catalysts based on pyridyl-imine ligand systems were developed by Wang *et al*. which have been shown to be active catalysts for the oligomerization of ethylene (Figure 1.21).[9] In this investigation, it was found that on average better selectivities and activities were given by systems carrying bulky substituents on both R^1 and R^2. High activities were observed for the Fe(II) system when the R^1 substituent was varied from a methyl group to a bulky *i*-Pr or Cy substituent while leaving the R^2 substituent as a methyl group.[9] Lowering the bulkiness of the R^2 substituent to an even smaller functionality like a hydrogen group led to even lower activities. On average activities observed for the Co(II) complexes were observed to be similar to the Fe(II) analogues. However, for the Co(II) complexes the least bulky systems gave high activities compared to the bulkier analogues.[9]

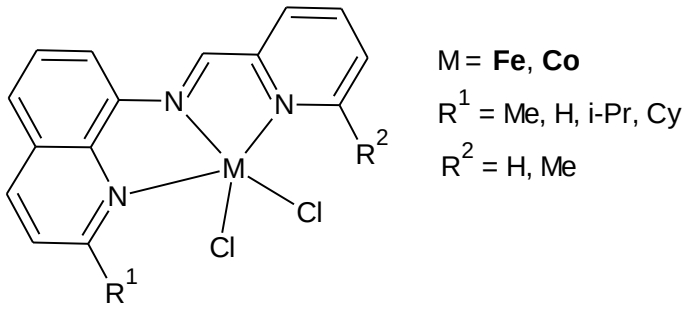


Figure 1.21: Fe(II) and Co(II) tridentate pyridyl-imine systems reported for ethylene oligomerization by Wang et al.[23]

The pyridyl-imine framework has been extensively utilized to design catalytic systems which are capable of oligomerizing a range of olefin monomers including ethylene, propylene, norbornene as well as 1-hexene. This was demonstrated by Meneghetti *et al*. who

synthesized neutral and cationic asymmetrical pyridyl-imine based palladium(II) complexes capable of oligomerizing α-olefins (Figure 1.22).[11]

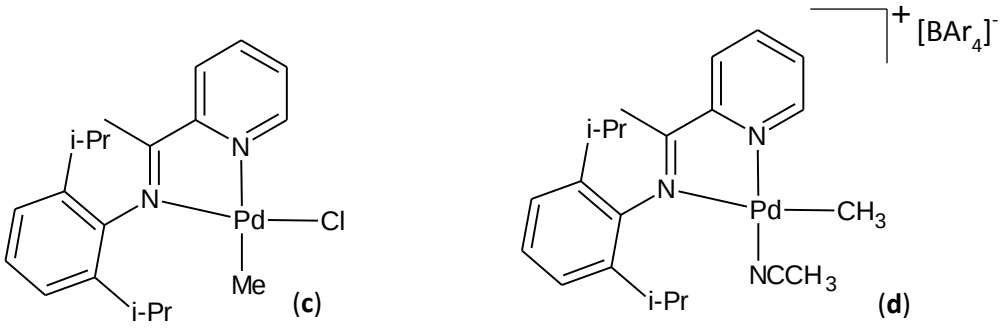


Figure 1.22: Palladium (II) bidentate pyridyl-imine based complexes synthesized by Meneghetti *et al*.[11]

Treatment of the neutral complex (Figure 1.22 (**c**)) with 1 equivalent of $NaBAr'_4$ (Ar = 3.5-$(CF_3)_2$-C_6H_3) resulted in the formation of the catalytically active cationic species (Figure 1.22 (**d**)). Under various temperature and pressure conditions this palladium complex was shown to be active in the oligomerization of ethylene, propylene as well as 1-hexene.[11] Hydrocarbons consisting of even numbers of carbon atoms were the only oligomeric products observed using gas chromatography.

Oligomerization of olefins using tridentate pyridyl-imine systems developed by Small *et al* and Wang *et al* clearly demonstrate how much influence the ligand backbone has on both selectivity and activity. Variation of the ligand backbone as an attempt to design complexes capable of producing highly active catalytic systems was extended to pyridyl-imine based asymmetrical systems. This was well demonstrated by Benito *et al*. who prepared mononuclear nickel(II) pyridyl-imine based complexes (Figure 1.23).[73] Activation with MAO resulted in catalysts which gave low to moderate activities for the oligomerization of ethylene into even olefins, with a molecular weight average (M_n) between 220 to 370.[73] From this study it was well established that the distribution of substituents on the ligand backbone has a significant effect on the catalytic activity of the prepared nickel(II) complexes. This was demonstrated by the activities observed for the nickel pyridyl-imine complexes consisting of either a methyl or a hydrogen substituent on the *ortho* aryl position. The system consisting of a methyl group on the *ortho* aryl position and a hydrogen substituent on the pyridyl ring gave a significantly higher activity compared to the hydrogen

ortho aryl substituted analogue.[73] The complex consisting of a methyl substituent on the pyridyl ring as well as on the *ortho* aryl position did not show any observable activity. These observations clearly indicate how much influence the steric protection of the coordination site has on the resultant activity. According to the results presented by Benito *et al*, increasing or decreasing the bulkiness on both the pyridyl and imine moiety at the same time produced low activities. However, by leaving the pyridyl ring without any steric hindrance while increasing the bulkiness of the imine moiety aryl substituents gave systems which exhibited high activities.

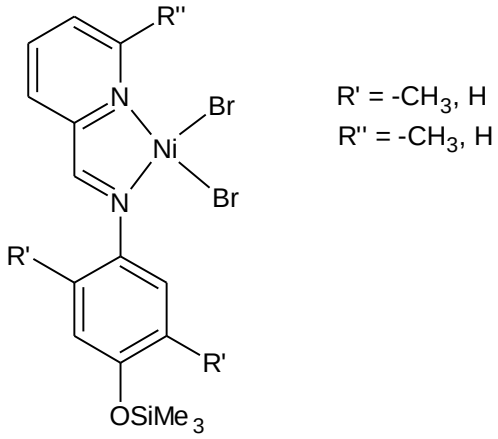
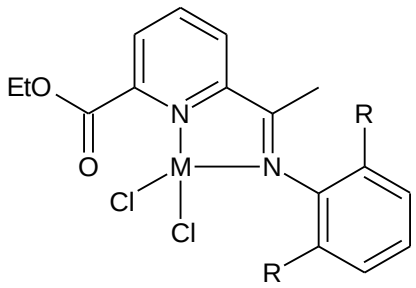


Figure 1.23: Mononuclear asymmetrical pyridyl-imine complexes developed by Benito *et al.*[25]

The idea of varying the aryl substituents attached to the imine moiety was also reported by Sun *et al*. who investigated the oligomerization of ethylene using six different iron and cobalt pyridyl-imine based complexes (Figure 1.24).[15] These complexes produced a range of oligomeric products including butene, hexene and trace amounts of higher oligomers under "mild reaction conditions using MAO as a co-catalyst". Increasing the bulkiness of the aryl substituents on the imine moiety for both ferrous and cobalt systems was shown to give lower catalytic activities.[15] This is however, in contrast to what was reported by Benito *et al* but correlates well with previous reports made by Small *et al.* on bis(imino)pyridyl iron(II) catalysts.[15,72] Introducing other functionalities on the imine phenyl ring such as *ortho* and *para* deactivating directors like halogens, was also found to significantly increase ethylene oligomerization activity. For example, the dichloro substituted iron catalyst exhibited higher catalytic activity compared to both the difluoro and dibromo analogue.[15] Compared to all iron catalysts evaluated for ethylene oligomerization at 20 °C under 10 atmospheric

pressure of ethylene, the dichloro substituted catalyst gave a significantly higher catalytic activity.[15]



R = Me, Et, i-Pr, F, Cl, Br
M = **Fe**, **Co**

Figure 1.24: Ferrous and cobaltous pyridyl-imine based complexes reported by Sun *et al*.[15]

The work reviewed thus far on the oligomerization of olefins, demonstrates how pyridyl-imine based homogeneous catalytic systems have been well investigated in the oligomerization of olefins such as ethylene and propylene, both industrially important olefins. Research work dealing with the oligomerization of heavier olefins as well as 1-hexene using homogeneous catalytic systems based on pyridyl-imine ligands is however limited, this is mainly due to the fact that these type of olefins can be easily incorporated directly as additives in most chemical applications.[74] Despite this fact, oligomers of 1-hexene have a major importance in the gasoline and fuel industry. In the following section, catalytic systems which have been investigated for 1-hexene oligomerization are reviewed.

1.4.2 Higher α-olefins

Alpha-olefins such as 1-octene and 1-hexene are occasionally used as reaction components in a number of productions; for example, they are used as co-monomers in the plastic industry for the synthesis of LLDPE, in the production of lubricants, hydraulic fluids as well as transmission fluids.[74,75,76] Due to their relatively high abundance and low cost, higher α-olefins can be potentially used as renewable resources for fuel synthesis to power heavy machinery such as aircrafts, ships and trucks.[75] Depending on the nature of the chain length and branching, oligomers derived from higher α-olefins are used in the production of fuel (C_{12}-C_{18}), surfactants (C_{12}-C_{20}), lubricants for car engines (C_{10}) as well as in the polymerization of ethylene (C_4-C_8).[75,77] In general oligomerization of higher α-olefins over the past few years has been conducted using catalytic systems derived from early and late transition metals. Oligomerization of higher α-olefins dates back to 1963. Antonsen *et al*.

reported in this particular year on the oligomerization of α-olefins from C_2-C_{12} using a Ziegler type catalyst ($Al_2Et_3Cl_3$-$TiCl_4$-propylene oxide).[78] From this study, it was reported that oligomers derived from higher α-olefins including 1-pentene increase in viscosity depending on the chain length of the monomer.[78] Antonsen also observed that all oligomers obtained using monomers above 1-octene were crystalline in nature at low temperatures.[78] As such, a series of oligomers could be obtained and used as lubricants , due to their unusual viscosities and ability to be easily processed over a wide range of temperatures.[78]

1.4.2.1 Oligomerization of higher α-olefins using early transition metal based catalysts

In 1991, oligomerization of 1-decene and 1-hexene was reported using a reduced chromium catalyst (i.e. Cr/SiO_2), at temperatures ranging from 180-190°C.[79] Characterization using insensitive nuclei enhancement by polarization transfer spectroscopy (INEPT) showed that oligomers derived from either 1-hexene or 1-octene were more selective for methane carbons rather than methylene carbons on the oligomer chain.[79] Oligomerization of 1-hexene and 1-octene over a solid acid catalyst (i.e. SO_4^{-2}/ZrO_2) was reported by de Klerk *et al*.[74] Oligomers obtained from 1-hexene were highly selective for chains ranging from C_{12}-C_{18}. 1-Octene on the other hand gave mainly dimers, no oligomers heavier than C_{16} were observed for this particular monomer.[74] Over the past few years however, oligomerization of higher alpha-olefins such as 1-hexene have been mostly conducted using metallocene based zirconium catalysts. For example, Janiak *et al*. investigated the catalytic activity of several zirconium catalysts in the direct oligomerization of 1-hexene (Figure 1.25).[80,81]

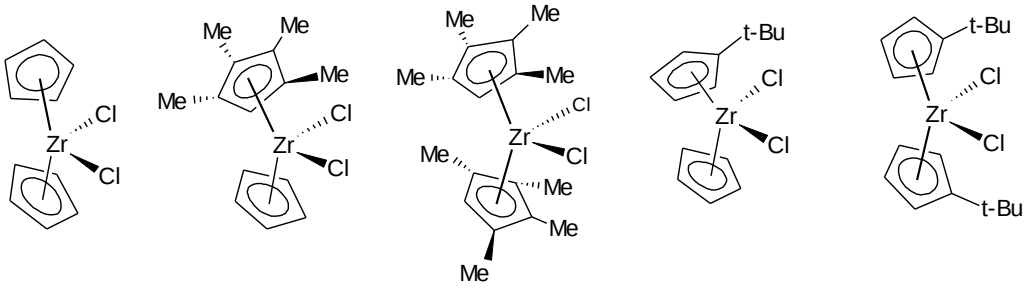


Figure 1.25: Zirconium complexes investigated for the oligomerization of 1-hexene by Janiak *et al.*[80,81]

Majority of the 1-hexene oligomers obtained consisted of an end group with a double bond. For example, vinylidene (Figure 1.26) type oligomers were obtained with tert-butyl substituted zirconocenes as well as for the unsymmetrical methyl substituted Cp_2ZrCl_2/MAO

catalysts.[81] On average the methyl-substituted catalysts were more active compared to the tert-butyl substituted catalysts.

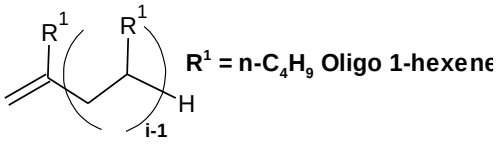


Figure 1.26: Vinylidene type 1-hexene oligomers reported by Janiak et al.[81]

Lian *et al*. reported on another type of zirconium complex, which was investigated as a catalyst for 1-hexene oligomerization in the presence of $B(C_6F_5)_3$ (Figure 1.27).[82] From ^{1}H-NMR studies it was evident that vinylidene type oligomers were also observed using this catalytic system under mild reaction conditions.[82]

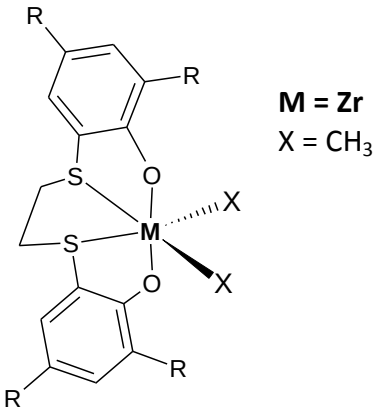


Figure 1.27: Zirconium complex prepared by Lian et al. for the direct oligomerization of 1-hexene.[82]

Recently Harvey *et al*. reported on the selective oligomerization of 1-hexene with Cp_2ZrCl_2/MAO catalyst.[75] To eliminate production of higher molecular weight oligomers and selectively produce low 1-hexene oligomers such as the dimer and trimer units (Figure 1.28), low ratios of Al/Zr were used.[75] These two hexene oligomers are specifically important for the production of jet and diesel fuel.[75]

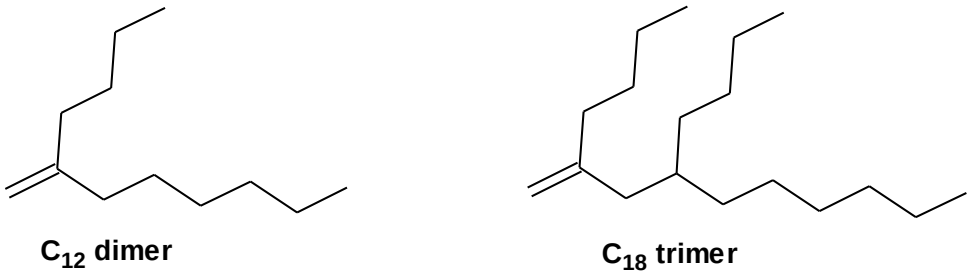


Figure 1.28: 1-Hexene dimer and trimer oligomers produced by Harvey *et al*.[75]

1.4.2.2 Oligomerization of higher α-olefins using late transition metal based catalytic systems

Despite the fact that not much work has been conducted and reported in literature on the oligomerization of higher α-olefins, the work that has been reported thus far also indicates the usage of homogeneous late transition metal catalysts derived from nitrogen donor ligands. Tellmann *et al*. investigated the activity of Co(II) and Fe(II) catalysts based on bis(imino)pyridyl ligands in the oligomerization of 1-hexene in the presence of MAO (Figure 1.29).[83] From gas chromatography and NMR analysis, it was shown that linear dimers were obtained as the principal products. However, internal olefins such as the *E* isomer of 1-hexene were also observed.[83] Up to 19000 g/(g of Co.h) of activity was obtained using the Co catalytic systems.

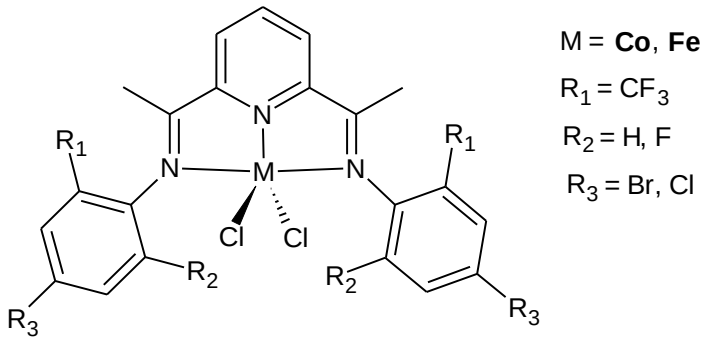
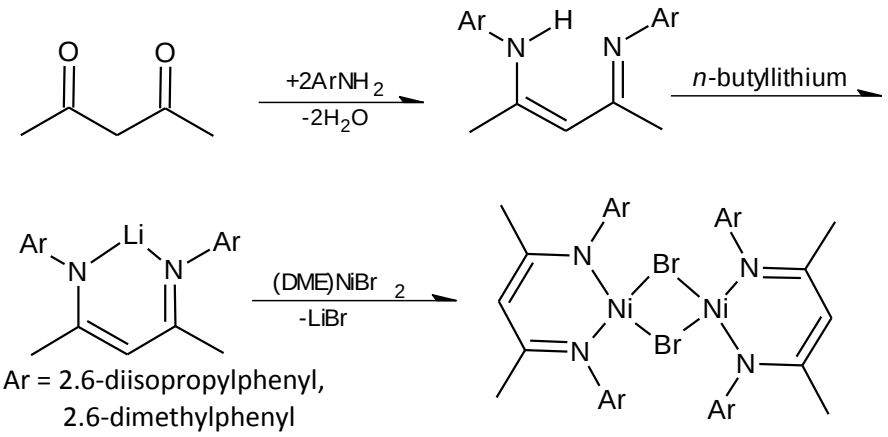


Figure 1.29: Bis(imino)pyridyl complexes investigated for 1-hexene oligomerization by Tellmann *et al.*[83]

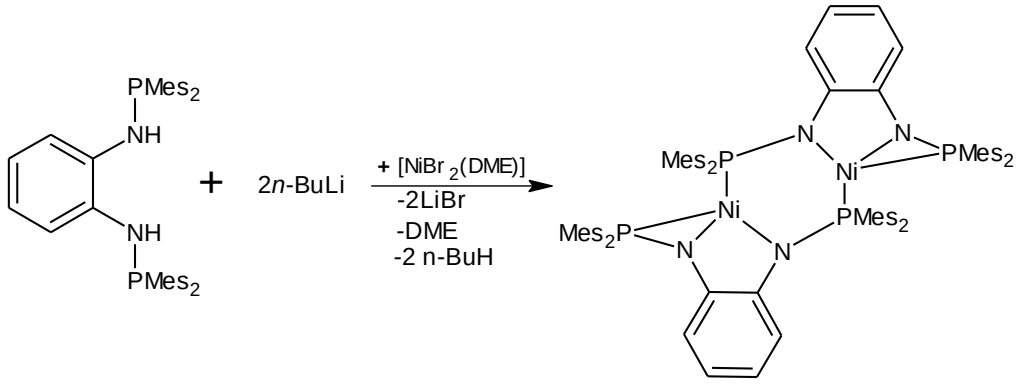
Zhang *et al*. reported on the isomerization and oligomerization of 1-hexene, catalysed with Ni(II) β-diketiminato complexes using MAO as a co-catalyst (Scheme 1.7).[84] From gas chromatography it was observed that C_6, traces of C_7 isomers as well as C_{12} olefin dimers were isolated as products.[84] Zhang *et al*. proposed that the observed isomers and oligomers

could be derived from the "direct β-hydride elimination of the *m-Ni-dodecyl* intermediate" *(m = 5)* during the oligomerization and isomerization process.[84]



Scheme 1.7: Ni (II) β-diketiminato complexes derived by Zhang *et al*. for the isomerization and oligomerization of 1-hexene.[84]

Another type of oligomerization catalyst derived from nitrogen donor ligands was reported not so long ago by Majoumo-Mbe *et al* (Scheme 1.8).[85]This type of catalyst was reported to oligomerize 1-hexene and 1.5-hexadiene into dimeric and trimeric oligomers under mild conditions with MAO as the co-catalyst.[85]



Scheme 1.8: Nickel bisamido complex derived by Majoumo-Mbe *et al*. for the oligomerization of 1-hexene and 1,5-hexadiene.[85]

1-Hexene in particular was oligomerized into 1-dodecene which was the major product, the rest of the product mixture was made of diastereomers, which were however difficult to separate.[85] 1,5-Hexadiene on the other hand was oligomerized into 5-methyleneundeca-1,10-diene which was the major dimer product.[85]

1.4.2.3 Other metal catalysts reported for the oligomerization of higher α-olefins

A class of nonene oligomerization catalysts based on $AlCl_3$, $AlBr_3$ and BF_3 complexes were recently reported.[86] From this study it was demonstrated how the automotive industry has a huge demand for engine lubricants which are able to operate at various temperatures for a longer period, as well as low in volatility.[86] The oligomers produced were mainly dimers, trimers, tetramers and higher oligomers of nonene.[86] It was reported that the dimeric products consisted of a carbon chain ranging from C_{10}-C_{20}. A lower degree of carbon number (i.e. C_{20} or C_{30}) is expected to give fuel with properties which are desirable for a better fuel economy, such as better temperature flow properties, low volatility, viscosity as well as better biodegradability.[86]

More recently Azizov *et al*. reported on the oligomerization of 1-decene using chloroaluminate ionic type catalytic systems ($AlCl_3$, $AlCl_3$:TryEtAHCl, AlCl:DyEtAHCl).[87] These catalysts produced 1-decene oligomers with vinylidene double bonds as well as naphthenic rings at temperatures ranging from 95-100°C.[87] From ^{13}C-NMR spectroscopy, resonance absorption signals of the methyl and methylene protons due to the vinylidene oligomer were observed at 0.98 ppm and 1.28-1.3 ppm respectively.[87]

1.5 OBJECTIVES OF THE STUDY

Homogeneous late transition metal catalysts based on pyridyl-imine ligands constitute an area of interest both industrially and academically. This has largely been due to the easily varied ligand backbone, which enables one to fine tune factors related to activity and selectivity. Although there are a number of reports in the literature on different catalysts for norbornene vinyl polymerization as highlighted, reports on norbornene vinyl polymerization catalysts based on Fe and Pd bidentate pyridyl-imine complexes are scarce. Also, the application of these metal complexes in the oligomerization of higher-olefins is relatively unexplored. It is for the forenamed reasons why this study was undertaken. It was envisaged that this study would generate new scientific knowledge on iron and palladium pyridyl-imine based complexes.

The main objective of this study is to investigate pyridyl-imine complexes containing Pd and Fe centres for 1-hexene oligomerization and norbornene polymerization. Bidentate pyridyl-

imine ligands with an N-alkyl and N-aryl substituent will thus be synthesized and characterized. Fe(II) and Pd(II) complexes of these ligand systems will also be prepared and evaluated as catalyst precursors for 1-hexene oligomerization and norbornene polymerization studies. The effect of steric bulk and the presence of an electron withdrawing group on the phenyl ring attached to the imino nitrogen will thus be evaluated during the oligomerization and polymerization process. Complexes derived from pyridyl-imine ligands have been reported to give considerable activity in the polymerization and oligomerization of lower linear olefins such as ethylene.[9,31,35] Also % conversions as high as 100% were reported by Laine et al. for the vinyl polymerization of norbornene using MAO-containing bidentate pyridyl-imine catalysts.[9]

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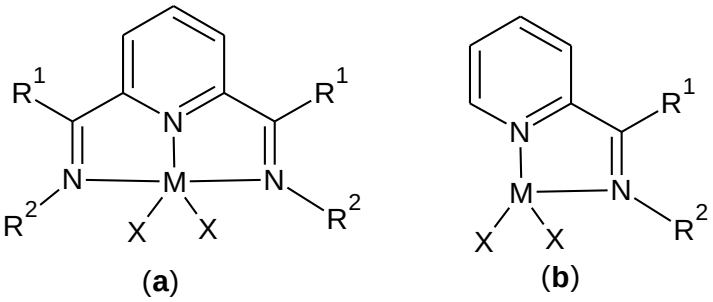
CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF PYRIDYL-IMINE METAL COMPLEXES

2.1 INTRODUCTION

Pyridyl-imines are nitrogen-donor ligands. Typical coordination systems found in literature for such ligands are of the type shown in Figure 2.1. However, the tridentate type (Figure 2.1 (**a**)) are perhaps the most extensively studied class of pyridyl-imine complexes. Coordination systems derived from pyridyl-imine ligands have been known since the late 1990's and have been well investigated as coordination ligands for transition metal complexes as discussed in chapter 1.[1,2,3] The easily varied ligand backbone which is capable of accommodating a variety of transition metals in different oxidation states, highlights some of the important features which enhance the industrial and academic appeal of pyridyl-imine complexes as potential catalysts.[4,5] Factors such as activity and selectivity can now be easily varied or tuned by the choice of substituent attached to imine nitrogen.



M = Metal, **X** = Halogen (Cl, Br)

$\mathbf{R^1}$ = Hydrogen, methyl group, $\mathbf{R^2}$ = Alkyl, aryl group

Figure 2.1: General structures of known pyridyl-imine metal complexes.

For example, *N-alkyl* pyridyl-imine dichloro Pd(II) complexes (Figure 2.2) have been reported by Chen *et al*. to investigate the "effects of alkyl substituents" on ethylene polymerization.[3] These complexes produced only high density polyethylene using methylaluminoxane (MAO) as co-catalyst. It was found that increased length of the alkyl chain attached to the imine nitrogen not only enhances polymer molecular weight, but also reduces catalytic activity of the metal complex. Of the complexes evaluated, a system with a shorter alkyl chain (n = 4) attached to the imine nitrogen gave the highest activity (15.4 Kg/(mol Pd atm h)$^{-1}$).

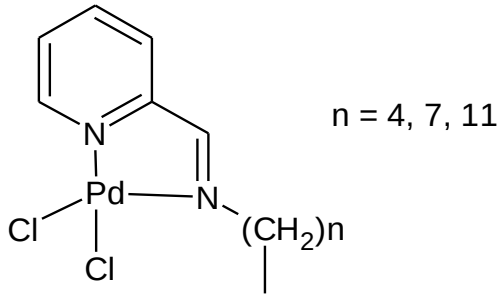


Figure 2.2: Pyridyl-imine Pd(II) complexes with *N-alkyl* substituents attached to the imino nitrogen prepared by Chen *et al*.[3]

Yi *et al*. also reported on the synthesis of N-aryl pyridyl-imine dibromo Ni(II) complexes for polymerization studies of ethylene, using either MAO or Et_2AlCl as co-catalyst (Figure 2.3).[6] From this study, it was demonstred how much influence steric bulk of the ligand backbone has on the product composition. For example, only Ni(II) complexes bearing ‘‘bulky aryl ortho substituents’’ attached to the imine nitrogen were capable of producing polyethylene. Ligands without a bulky character on the aryl ortho position (i.e. R^2 and R^3) gave ethylene oligomers instead. [6]

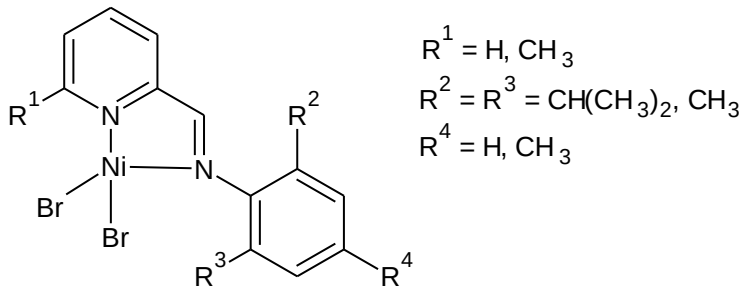


Figure 2.3: Ni(II) pyridyl-imine complexes with *N-aryl* substituents prepared by Yi *et al*.[6]

In addition to being explored as coordination ligands for the synthesis of olefin polymerization and oligomerization catalysts, pyridyl-imine derived metal complexes have been successfully employed in catalytic transformations including hydroboration, hydrogenation, Suzuki cross-coupling as well as Heck coupling reactions .[7,8] Pelagatti *et al.* reported on Pd(II) and Pd(0) complexes derived from pyridyl-imine ligands (Figure 2.4).[9] These complexes were evaluated as potential catalyst precursors for the coupling of iodobenzene and methyl acrylate using Et_3N as the base. Iodobenzene was successfully converted into trans-methylcynnamate in only 2,5 hours of reaction time.

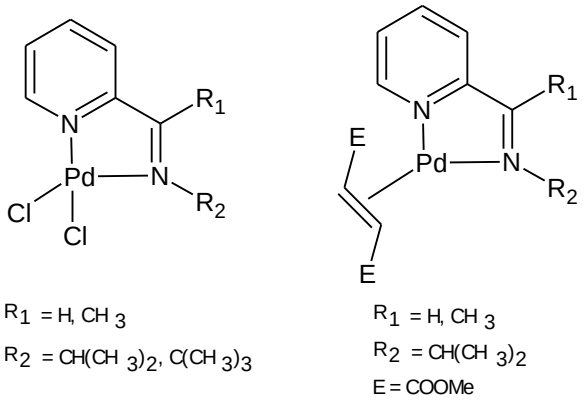


Figure 2.4: Pd(II) and Pd(0) pyridyl-imine complexes prepared by Pelagatti *et al*. for the Heck reaction.[9]

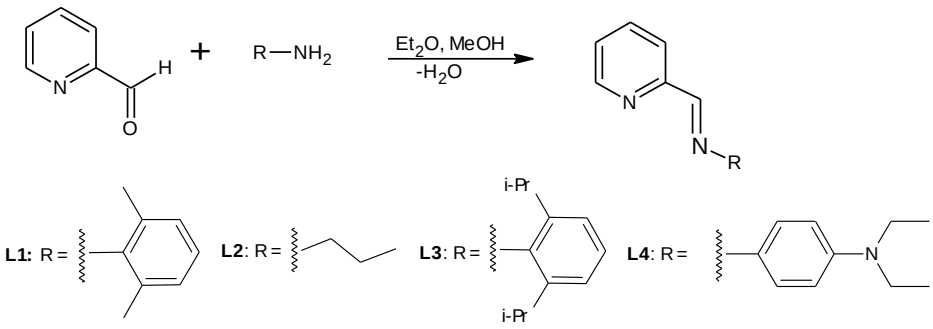
In this chapter the synthesis and characterization of pyridyl-imine ligands and complexes containing Fe and Pd metal centres is described. Analytical techniques such as ^{1}H and ^{13}C-NMR, infrared spectroscopy, mass spectrometry, uv-vis spectroscopy, thermogravimetric analysis (TGA) and elemental analysis were used to characterize prepared pyridyl-imine ligands and corresponding metal complexes.

2.2 RESULTS AND DISCUSSION

2.2.1 Synthesis and Characterization of Pyridyl-imine ligands

In this study pyridyl-imine ligands (**L1**-**L4**) were prepared according to the synthetic procedure reported by Cloete *et al*. which involved the condensation of pyridine-2-carboxyaldehyde with an appropriate amine as shown in Scheme 2.1.[5] Ligands **L1**-**L3** have been prepared and published previously by Cloete et al, Gibson *et al* and Laine *et al*.[1,5,10] However **L4** has not been published previously and thus new to this study. Ligands **L1** and **L2** were obtained as yellow oils, whereas ligands **L3** and **L4** were obtained as green solids. The ligands were obtained in good yields (64 - 88%) and found to be air and moisture stable over a short period. Samples kept in a desiccator appeared to change in colour from yellow to dark brown and from green to black after approximately 2-3 weeks. Hence samples were refrigerated to preserve their composition. The prepared ligands were characterized using a

range of techniques which include ^{1}H and ^{13}C spectroscopy, FT-IR spectroscopy, mass spectrometry and elemental analysis.



Scheme 2.1: Synthesis of pyridyl-imine ligands.

*2.2.1.1 ^{1}H and ^{13}C-NMR spectroscopy characterization of **L1-L4***

The ^{1}H and ^{13}C-NMR spectral data for the prepared pyridyl-imine ligands together with the corresponding assignments is provided in Table 2.1. The presented data corresponds to the structural depictions in scheme 2.1 and previously reported NMR data for similar pyridyl-imine systems.[3] In general, proton signals for **L1** to **L4** of the pyridyl ring were fairly similar in the aromatic region. A typical ^{1}H-NMR spectrum of these ligands is shown using the spectrum of ligand **L4** as an example (Figure 2.5). A doublet is observed at δ8.74 ppm for H-1, followed by a singlet at δ8.68 ppm (H-6), another doublet at δ8.19 ppm (H-4) and lastly two triplets at δ7.99 ppm (H-3) and δ7.50 ppm (H-2) (Figure 2.5). This spectral data is similar to that observed for the pyridyl-imine ligands reported by Cloete *et al*.[5]

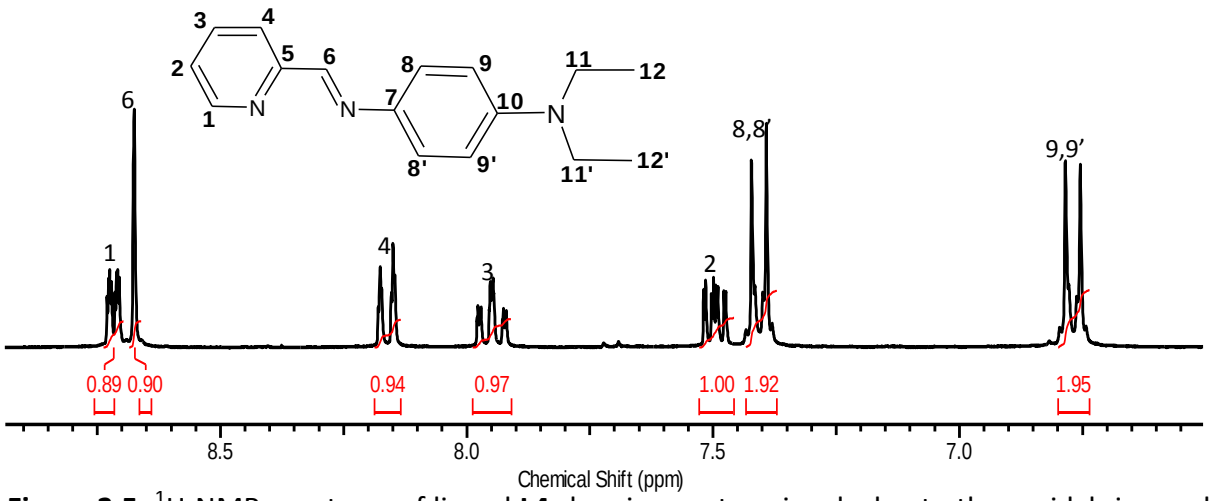
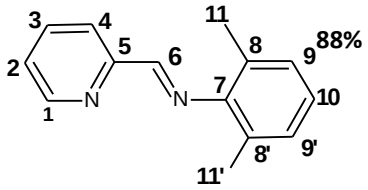
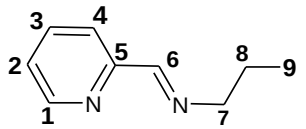
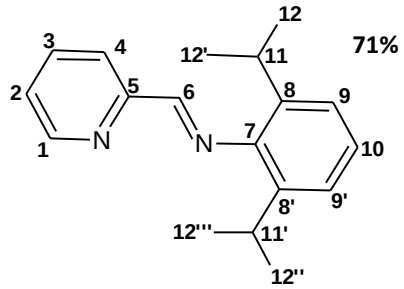
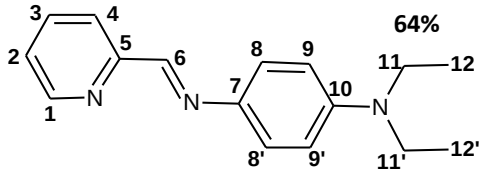


Figure 2.5: ^{1}H-NMR spectrum of ligand **L4** showing proton signals due to the pyridyl ring and imine moiety**.**

Table 2.1: *^{1}H and ^{13}C-NMR data for pyridyl-imine ligands*

Ligand	^{1}H and ^{13}C-NMR chemical shift δ (ppm)
L1  88%	δ_H (DMSO) 2.079 (s, H(**11**,**11'**)) , 6.859-6.908 (d, H-**9**,**9'**), 7.005-7.158 (t, H-**10**)), 7.292-7.300 (t, H-**2**, *J* = 7.54 Hz), 7.709-7.712 (t, H-**3**), 8.207-8.210 (d, H-**4**, *J* = 7.91 Hz), 8.261 (s, H-**6**), 8.615-8.634 (d, H-**1**) δ_C (DMSO) 18.29 (C-**11**,**11'**), 121.23 (C-**8**,**8'**), 124.09 (C-**9**,**9'**), 125.33 (C-**10**), 126.86 (C-**4**), 128.15 (C-**2**), 136.73 (C-**3**), 149.61 (C-**1**), 150.36 (C-**7**), 154.48 (C-**5**), 163.44 (C-**6**)
L2  68%	δ_H (DMSO) 0.97 (t, C(**9**)H_3, *J* = 7.44Hz), 1.76 (m, C(**8**)H_2), 3.65 (t, C(**7**)H_2, *J* = 6.92Hz) 7.30 (t, H-**2**, *J* = 7.49Hz), 7.73 (t, H-**3**), 7.99 (d, H-**4**, J = 7.91Hz), 8.38 (s, H-**6**), 860-8.70 (d, H-**1**) δ_C (DMSO) 11.79 (C-**9**), 23.83 (C-**8**), 63.25 (C-**7**), 121.13 (C-**4**), 124.51 (C-**2**), 136.44 (C-**3**), 149.36 (C-**1**), 154.68 (C-**5**), 161.69 (C-**6**)
L3  71%	δ_H (DMSO) 1.02-1.12 (d, C(**12,12',12'',12'''**)H_3, *J* = 6.78Hz), 2.89 (m, C(**11,11'**)H, *J* = 6.88Hz), 7.01 (d, C(**9,9'**)H), 7.13 (t, H-**10**), 7.28-7.37 (t, H-**2**, *J* = 7.49Hz), 7.70-7.82 (t, H-**3**), 8.19 (d, H-**4**, *J* = 7.91Hz), 8.24 (s, H-**6**), 8.69 (d, H-**1**) δ_C (DMSO) 23.46 (C-(**12-12'''**), 27.98 (C-**11,11'**), 121.34 (C-**8,8**), 123.08 (C-**9,9'**), 124.49 (C-**10**), 125.31 (C-**4**), 136.76 (C-**2**), 137.27 (C-**3**), 148.43 (C-**1**), 149.71 (C-**7**), 154.43 (C-**5**), 162.98 (C-**6**)
L4  64%	δ_H (DMSO) 1.17 (t, C(**12,12'**)H_3, J = 7.06Hz), 3.44 (m, C(**11,11'**)H_2, J = 7.10Hz), 6.74-6.80 (dd, C(**9,9'**)H), 7.37-7.43 (dd, C(**8,8'**)H), 7.50 (t, H-**2**, J = 7.49Hz), 7.99 (t, H-**3**), 8.13-8.19 (d, H-**4**, *J* = 7.96Hz), 8.68 (s, H-**6**), 8.70-8.74 (d, H-**1**) δ_C (DMSO) 12.68 (C-**12,12'**), 44.56 (C-**11,11'**), 111.86 (C-**9,9'**), 121.30 (C-**4**), 123.29 (C-**8,8'**), 124.16 (C-**2**), 136.48 (C-**3**), 138.22 (C-**7**), 147.53 (C-**1**), 149.53 (C-**5**), 154.43 (C-**10**), 155.59 (C-**6**)

Spectra obtained in dmso-d_6 (dimethyl sulfoxide), s, singlet, d, doublet, t, triplet, m, multiplet

Condensation of the amine with the aldehyde was confirmed by the occurrence of the resonance for the imine (HC=N) proton, which was observed as a sharp singlet in the range δ8.20-8.40 ppm for ligands **L1**-**L3**. However, for ligand **L4** this imine proton is observed at a higher chemical shift (δ8.68 ppm). This could be due to the presence of the amine group attached on the para position of the phenyl ring, which potentially removes electron density from the ring and imine moiety. The resonance for the phenyl ring protons on the imino nitrogen are observed as doublets and triplets in the region δ6.859 - 7.43 ppm for ligands **L1**, **L3**, and **L4**. The spectra of ligand **L4** also shows protons of the two ethyl groups as a multiplet due to the C(11,11')H_2 protons and a triplet due to the C(12,12')H_3 protons at δ3.44 ppm and δ1.17 ppm respectively (Table 2.1). This observation indicates that the two ethyl groups attached to the nitrogen are magnetically equivalent.

The resonance for the two magnetically equivalent methyl protons in ligand **L1** are observed as a sharp singlet at δ2.079 ppm. The propyl chain protons for **L2** gave signals on the upper field region at δ3.65 ppm (CH_2), δ1.76 ppm (CH_2) and at δ0.97 ppm (CH_3). The spectra of ligand **L3** containing two isopropyl substituents show a doublet due to the methyl groups and a multiplet due to the CH proton in the regions δ1.02-1.12 ppm and δ2.89 ppm respectively (Table 2.1), indicating that the isopropyl groups on the phenyl ring are magnetically equivalent.

The ^{13}C-NMR data obtained and the corresponding assignments in Table 2.1 showed that all carbons were clearly observed, giving further evidence that the desired ligands were successfully prepared. Chemical shifts were observed in the expected regions and comparable to values observed in literature.[5] The same pattern for the positioning of the pyridyl ring carbons was observed for all four ligands.

In general, aromatic carbons for all ligands **L1**-**L4** in the pyridyl ring were observed in the region δ121-154 ppm in the ^{13}C-NMR spectra. The carbon signal for the imine functionality is observed in the region δ161-163 ppm for ligands **L1** to **L3**. However for ligand **L4**, this carbon is 7 units lower than signals observed for the other three ligands (Table 2.1). The trend observed in terms of the positioning of the chemical shifts for ligands **L1** and **L3** are very similar due to their almost identical structures. Due to the magnetic equivalence of the methyl groups in ligand **L1** and the two isopropyl substituents in ligand **L3**, the carbon

signals of these substituents are observed as a single signal at δ18.29 ppm and δ23.46 ppm respectively. Ligand **L2** on the other hand consists of aliphatic carbons which are not magnetically equivalent, as such the carbon signals of the alkyl chain for this ligand are observed as 3 signals in the range δ63.25 - 11.79 ppm.

*2.2.1.2 Characterization of **L1**-**L4** by infrared, mass spectrometry and elemental analysis*

The elemental analysis data for the prepared ligands were in agreement with the proposed structures in scheme 2.1 (Table 2.2). In addition, the mass spectra showed molecular ion peaks due to $[M+H]^+$.

Table 2.2**: Mass spectrometry and elemental analysis data for ligands **L1-L4

Ligand	Formula	$[M+H]^+$ (Calc)	Anal Found (Calc)%		
		m/z	**C**	**H**	**N**
1	$C_{14}H_{14}N_2$	211.0 (211.3)	79.6 (79.9)	6.55 (6.70)	13.4 (13.3)
2	$C_9H_{12}N_2$	149.0 (149.2)	73.2 (73.0)	7.80 (8.20)	18.1 (18.9)
3	$C_{18}H_{22}N_2$	267.0 (267.4)	81.0 (81.2)	8.10 (8.30)	10.0 (10.5)
4	$C_{16}H_{19}N_3$	254.0 (254.3)	74.7 (75.8)	6.70 (7.60)	15.9 (16.6)

Further characterization with infrared spectroscopy revealed that, the spectra of ligands **L1-L4** show characteristic bands due to the stretching frequencies of the pyridyl ring $\nu(C=N)_{py}$ and imine moiety $\nu(C=N)_{im}$, observed between 1700 and 1400 cm^{-1}. The assignment of these bands is based on literature values obtained for both *N-aryl* and *N-alkyl* pyridyl-imines reported by Cloete *et al*, Gibson *et al* and Sun *et al*.[1,5,6] For all ligands the infrared spectra shows a very strong band around 1644-1650 cm^{-1} assigned to $\nu(C=N)_{im}$, as well as a medium and weak band at around 1587 and 1568 cm^{-1} assigned to $\nu(C=N)_{py}$ (Figure 2.6). The imine band $\nu(C=N)_{im}$ for ligand **L2** was observed at 1649 cm^{-1} which is at a slightly higher wavenumber compared to the other three ligands (Figure 2.6). The higher wavenumber

observed for **L2** is most likely due to the more electron donating propyl chain.

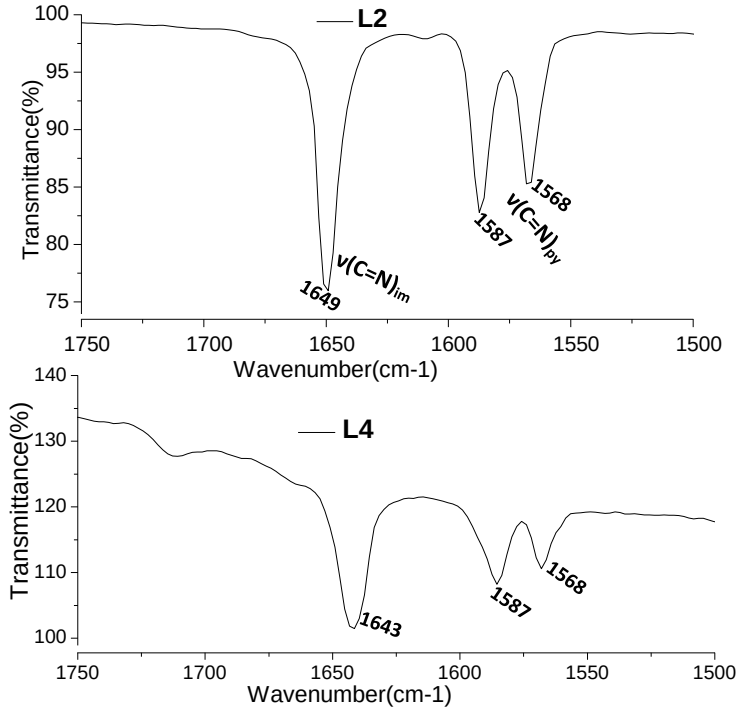
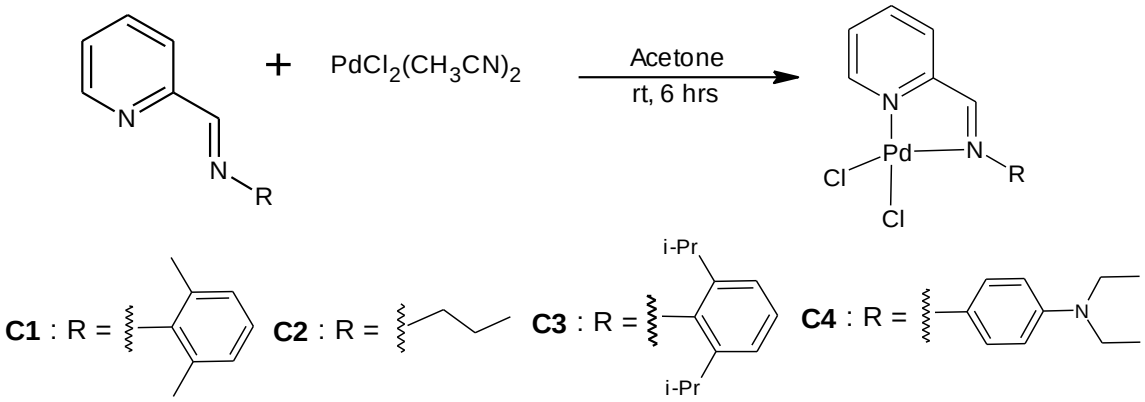


Figure 2.6: Infrared spectra of ligand **L2** and **L4** showing the $\nu(C=N)_{py}$ and $\nu(C=N)_{im}$ bands.

2.2.2 Synthesis and Characterisation of Pyridyl-imine Pd(II) complexes

The Pd(II) complexes (**C1**-**C4**) were prepared by reacting a 1:1 mole equivalent of the appropriate ligand with $PdCl_2(CH_3CN)_2$ as shown in scheme 2.2.[5] Complexes **C1**-**C3** have been previously recovered as yellow solids and found to be insoluble in common organic solvents except dimethyl sulphoxide, however complex **C4** has not been published or reported.[5,10] The complexes were isolated as yellow solids in good yields (52.3 - 91.2%). These metal complexes were observed to be air and moisture stable and were found to be insoluble in most organic solvents (e.g. hexane, toluene, diethylether, ethylacetate) except dimethyl sulfoxide (DMSO). Structural characterization of the synthesized Pd(II) complexes was carried out with ^{1}H and ^{13}C-NMR spectroscopy, FT-IR spectroscopy, mass spectrometry, uv-vis, elemental analysis and thermal gravimetric analysis (TGA).



Scheme 2.2: Synthetic procedure for the preparation of Pd(II) pyridyl-imine complexes.

2.2.2.1 Characterization of Pd(II) complexes by means of ^{1}H and ^{13}C-NMR spectroscopy

The ^{1}H and ^{13}C-NMR spectral data for the prepared Pd(II) complexes are provided in Table 2.3. The proton and carbon spectra obtained for the complexes confirmed that the target pyridyl-imine Pd(II) complexes were successfully prepared. In general, upon complexation the prepared Pd(II) complexes show a "distinct downfield shift" of the proton and carbon signals of the pyridine ring and imine moiety (Figure 2.7). For example, there appears to be a distinct shift of the doublet generally found around δ8.70 ppm assigned to H-1 and the singlet of the imine proton (H-6) which was observed around δ8.30 ppm in the ligand spectra (Table 2.3). These two signals shift downfield to around δ9.0 and δ8.68 ppm respectively on complexation (Table 2.3). However, compared to the free ligand the imine proton for complex **C4** was shifted from δ8.60 ppm to δ8.54 ppm. Coordination of the metal centre is expected to lower electron density around the imine moiety, thus an increased chemical shift is to be observed.[5] Presence of the electron donating propyl chain attached to the phenyl ring in complex **C4** allows for some electron density to be added on the imine moiety, thus the observed decrease in chemical shift**.**

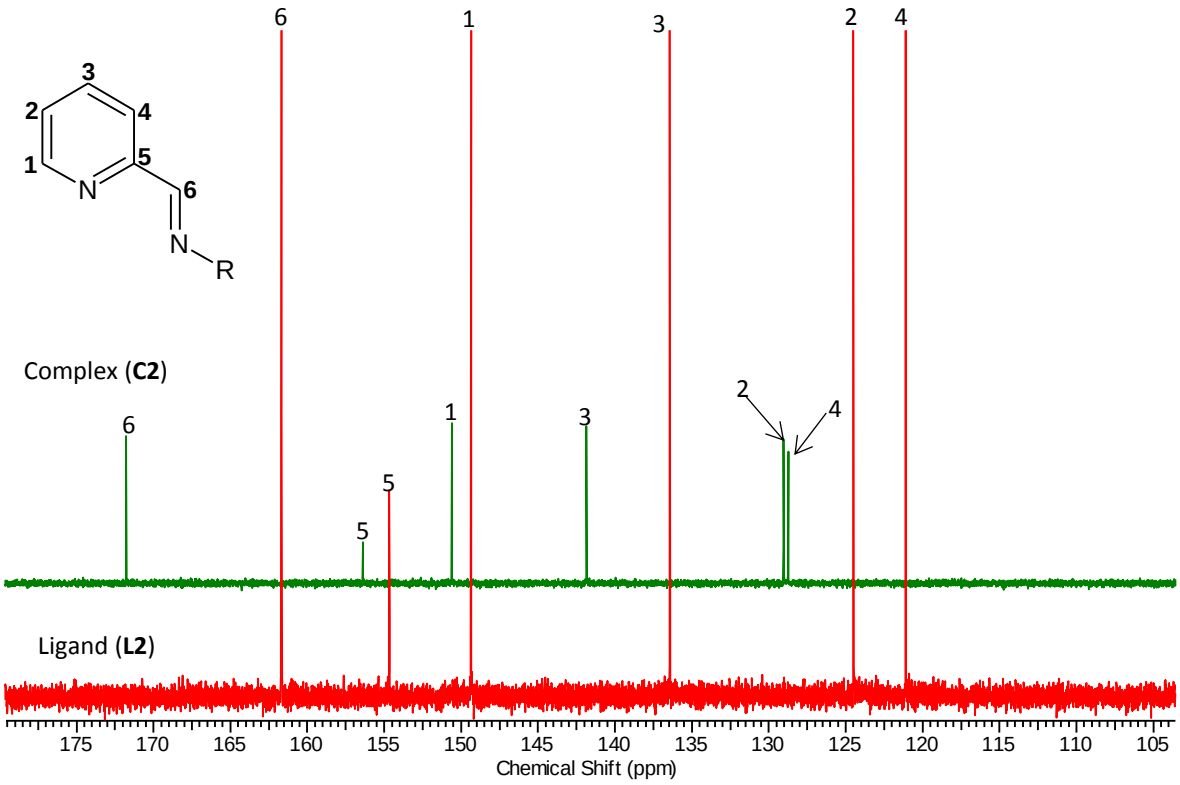
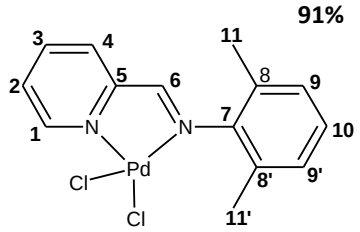
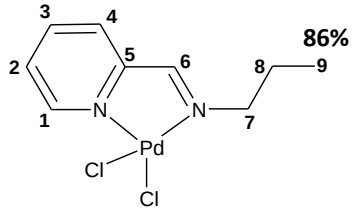
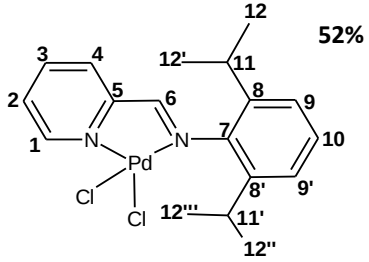
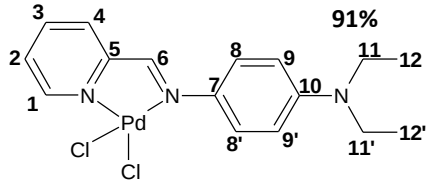


Figure 2.7: ^{13}C-NMR spectrum showing shifts in carbon signals after complexation.

Table 2.3: *^{1}H and ^{13}C-NMR data for Pd(II) pyridyl-imine complexes*

Complex	^{1}H and ^{13}C-NMR chemical shift δ (ppm)
C1 	δ_H (DMSO) 2.278 (s, C(**11,11'**)H_3), 7.109 (d, H-**9,9'**), 7.208 (t, H-**10**), 8.018 (t, H-**2**), 8.144-8.8173 (d, H-**4**), 8.398-8.455 (t, H-**3**), 8.682 (s, H-**6**), 9.057-9.079 (d, H-**1**, *J* 5.75Hz) δ_C (DMSO) 18.71 (C-**11,11'**), 127.90 (C-**8,8'**), 128.12 (C-**9,9'**), 130.10 (C-**10**), 130.28 (C-**4**), 130.60 (C-**2**), 141.81 (C-**3**), 146.13 (C-**1**), 150.75 (C-**7**), 155.69 (C-**5**), 175.25 (C-**6**)
C2 	δ_H (DMSO) 0.88 (t, C(**9**)H_3, *J* = 7.44Hz), 1.779-1.730 (m, C(**8**)H_2), 3.701 (t, C(**7**)H_2, *J* = 7.06Hz), 7.842-7.891 (t, H-**2**, *J* = 7.58Hz), 8.076-8.104 (d, H-**4**), 8.316-8.602 (t, H-**3**, *J* = 7.72Hz), 8.602 (s, H-**6**), 8.958-8.977 (d, H-**1**) δ_H (DMSO) 11.17 (C-**9**), 23.72 (C-**8**), 61.05 (C-**7**), 128.67 (C-**4**), 128.99 (C-**2**), 141.79 (C-**3**), 150.56 (C-**1**), 156.34 (C-**5**), 171.71 (C-**6**)
C3 	δ_H (DMSO) 1.110-1.287 (d, C(**12-12'''**)H_3, *J* = 6.78Hz), 3.219-3.261 (m, C(**11,11'**)H), 7.205-7.230 (d, C(**9,9'**)H), 7.317-7.344 (t, C(**10**)H), 7.988-8.014 (t, H-**2**), 8.033 (d, H-**4**), 8.408-8.460 (t, H-**3**), 8.746 (s, H-**6**), 9.074-9.092 (d, H-**1**) δ_H (DMSO) 24.53 (C-**12-12'''**), 28.53 (C-**11,11'**), 123.49 (C-**8,8'**), 128.71 (C-**9,9'**), 130.29 (C-**10**), 130.34 (C-**4**), 140.90 (C-**2**), 142.02 (C-**3**), 143.29 (C-**1**), 150.97 (C-**7**), 155.30 (C-**5**), 174.52 (C-**6**)
C4 	δ_H (DMSO) 1.07-1.16 (t, C(**12,12'**)H_3), 2.44-2.56 (m, C(**11,11'**)H_2, *J* = 6.97Hz), 6.69 (dd, C(**9,9'**)H, *J* = 9.23Hz), 7.34 (dd, C(**8,8'**), *J = 9.23*Hz), 7.80 (t, H-**2**), 8.09 (d, H-**4**), 8.29 (t, H-**3**), 8.539 (s, H-**6**), 9.041 (d, H-**1**) δ_H (DMSO) 12.95 (C-**12,12'**), 44.35 (C-**11,11'**), 110.29 (C-**9,9'**), 124.20 (C-**4**), 125.48 (C-**8,8'**), 126.31 (C-**2**), 128.35 (C-**3**), 128.91 (C-**7**), 141.51 (C-**1**), 150.31 (C-**5**), 158.78 (C-**10**), 167.72 (C-**6**)

Spectra obtained in DMSO-d_6, s, singlet, d, doublet, t, triplet, m, multiplet

In general, for all complexes (**C1-C4)** it was observed that the two triplets which generally occur around 7.40 ppm (H-2) and at 7.97 ppm (H-3) in the ligand spectrum are significantly shifted downfield to 7.86 ppm (H-2) and 8.35 ppm (H-3) upon complexation. Furthermore the doublet assigned to H-4 and normally located downfield away from these two triplets in the ligand spectrum, moves in between the two triplets when complexation takes place (Figure 2.8). The typical shifting patterns illustrated in table 2.3 for these particular complexes correspond to the results reported by Cloete *et al* on compounds of this nature.

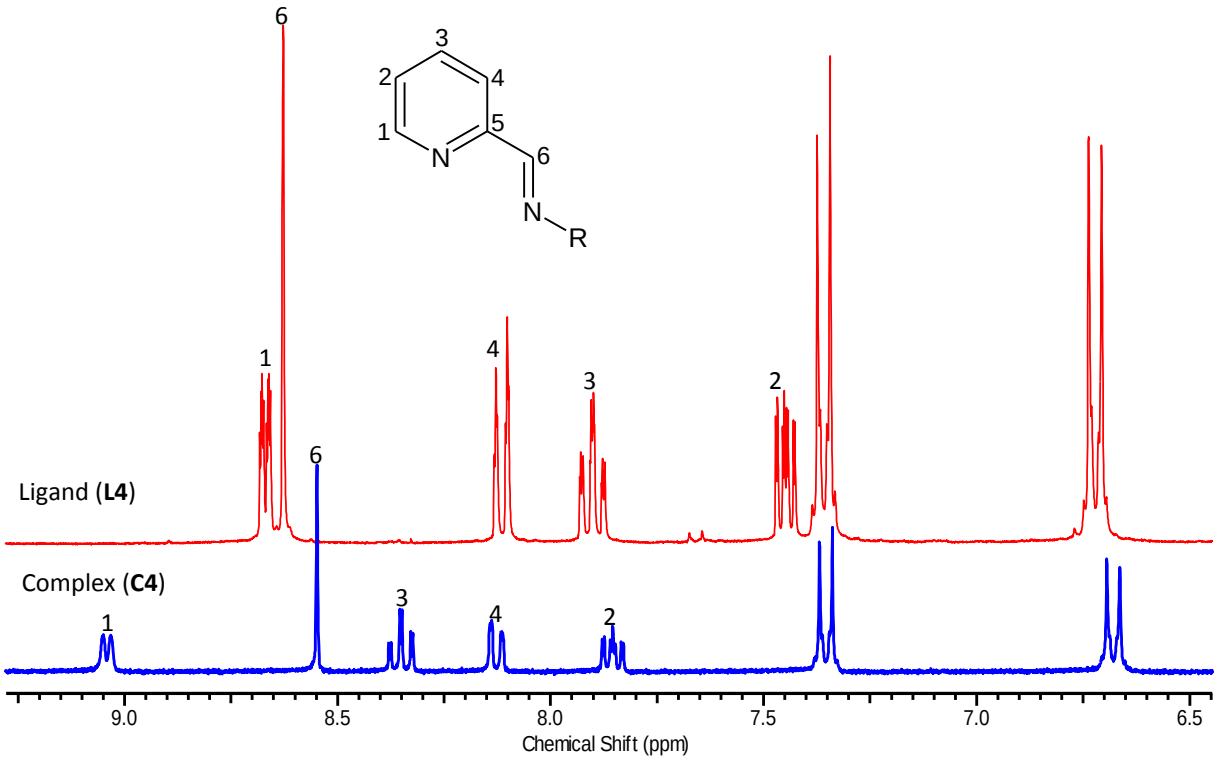


Figure 2.8: ^{1}H-NMR spectrum showing shifts in signals after complexation

2.2.2.2. Mass spectrometry and elemental analysis studies

Mass spectrometry and elemental analysis data for Pd(II) complexes **C1-C4** are provided in Table 2.4. In general, the mass spectrometry data presented for the prepared Pd(II) complexes were in agreement with the expected structures in Scheme 2.2. The elemental analysis data obtained for the Pd(II) complexes confirmed a 1:1 ligand to metal ratio expected for the bidentate pyridyl-imine complexes.. The obtained elemental analysis results for complexes **C1** and **C3**, indicate that these Pd(II) complexes do however exist as hydrated species. Also the increased melting point range observed for these complexes is most likely due to the presence of water molecules within the vicinity of the metal complex.

Table 2.4: *Mass spectrometry and elemental analysis data for Pd(II) pyridyl-imine complexes*

Complex	Formula	$[M+H]^+$(calc)	Anal Found (Calc)		
	M.p (°C)	*m/z*	C	H	N
1	$C_{14}H_{14}Cl_2N_2Pd•1/3H_2O$	391 (391.7)	42.22 (42.72)	3.60 (3.59)	6.89 (7.12)
	210-250				
2	$C_9H_{12}Cl_2N_2Pd$	330 (330.6)	33.10 (33.20)	3.35 (3.72)	8.35 (8.61)
	208-210				
3	$C_{18}H_{22}Cl_2N_2Pd•1/3H_2O$	448 (448.8)	48.49 (48.07)	4.35 (4.93)	5.43 (6.23)
	260-290				
4	$C_{16}H_{19}Cl_2N_3Pd$	431 (431.7)	45.07 (44.62)	4.63 (4.45)	9.42 (9.76)
	180-182				

Calc- Mass calculated for the Pd(II) molecular ion

2.2.2.3 Infrared and uv-vis spectroscopy

Infrared spectra of the palladium metal complexes were obtained to confirm coordination of the ligand to the metal centre (Table 2.5). A significant shift is observed for the $\nu(C=N)_{im}$ band which generally occurs around 1633 - 1649 cm^{-1} on the free ligand (**L1-L4**) to around 1589 - 1593 cm^{-1} for complexes **C1-C4** (Table 2.5). Compared to the free pyridyl-imine ligands, the absorption of the $\nu(C=N)_{im}$ band decreased by approximately 55 cm^{-1} units for the corresponding Pd(II) complex, confirming a strong coordination between the Schiff base ligand and the palladium metal centre. The reported IR data in this study is in agreement with absorption bands observed for the pyridyl ring and imine functionality of typical bidentate pyridyl-imine complexes.[2,4] For example, Yi *et al*. reported on a 45 cm^{-1} decrease for the $\nu(C=N)_{im}$ band of Ni(II) pyridyl-imine based complexes, which was used as confirmation that a strong interaction existed between the nickel metal centre and the corresponding Schiff base ligand.[4]

In general, for all complexes (**C1**-**C4)** a very strong $\nu(C=N)_{im}$ band is observed in between a medium and weak band due to the pyridyl ring (Figure 2.9). For the corresponding ligands this band was observed at a higher wavenumber, followed by the medium and weak band at lower wavenumbers (Figure 2.9). This observation is also in agreement with the findings made by Benito *et al*. regarding bidentate iminopyridyl Ni(II) complexes prepared for olefin oligomerization and polymerization.[2] Both infrared and NMR spectra of the pyridy-imine Pd(II) complexes prepared in this study, indicate that coordination between the metal and ligand occurs via the pyridyl ring nitrogen and the imine nitrogen.

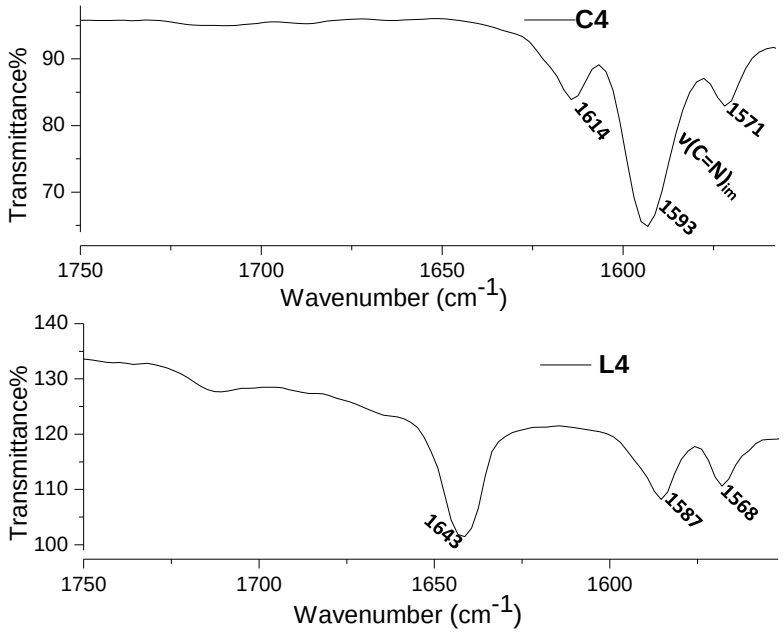


Figure 2.9: Comparison of the pyridyl ring and imine moiety stretching frequencies for the Pd(II) complexes and corresponding ligands.

The uv-vis absorption spectra recorded for Pd(II) complexes **C1**-**C4** showed four characteristic absorption bands at 205 - 215 nm, 239 - 256 nm, 272 - 300 nm and at 294 - 343 nm respectively (Table 2.5). These bands are fairly typical for Schiff base absorption spectra for Pd(II) complexes.[11-15] The first two absorption maxima are due to the π-π^* transition observed for the benzene ring and the pyridyl ring. The third absorption band (272 - 300 nm) has been reported by Salen *et al* and Yousif *et al*. to be due to the ligand charge transfer (C.T) band, which is given by the coordination that exists between the metal and the nitrogen lone pairs.[11,15] The fourth absorption band is attributed to the n-π^* electronic transition due to the C=N chromophore.

Table 2.5: *Infrared and UV-Vis spectroscopic data for Pd(II) pyridyl-imine complexes*

Complex	UV-Vis	Infrared spectra (cm^{-1})		
	λ_{max} (nm)	Imine	Pyridyl ring	
		ν(C=N)	ν(C=N)	
1	211, 256, 300, 343	1595	1620	1569
2	209, 246, 295, 329	1593	1620	1568
3	215, 239, 315, 338	1589	1616	1566
4	205, 245, 272, 294	1593	1614	1571

2.2.2.4. Thermal gravimetric analysis studies for Pd(II) complexes

All pyridyl-imine complexes prepared were subjected to a thermal analysis study. Thermograms obtained for Pd(II) complexes are provided in Figures 2.10. TGA curves obtained for these complexes showed decomposition to proceed via a two-step to four-step process. A gradual decrease of 2% from 34 - 310 °C can be observed for complex **C1** and **C3**. This corresponds to the percentage mass loss (2.4%) of 1/3 H_2O molecules. Both complexes were shown previously using elemental analysis to contain this amount of water. The reported thermal analysis data gives further evidence for the presence of water molecules within the vicinity of the metal complex. Compared to the rest of the Pd(II) complexes **C1** and **C3** are structurally similar, the difference only lies on the isopropyl and methyl substituents attached to the benzene ring. A two-stage and four-stage decomposition process was observed for complex **C2** and **C4** respectively. For example, a percentage mass loss of 36.0% from 34-323 °C can be observed for complex **C2**. This corresponds to the mass loss (35.2%) of two chlorine atoms and the entire alkyl chain. Complex **C4** gave an initial mass loss of 5.8% from 34-193 °C, which corresponds to the mass loss (6.9%) of two CH_3 molecules of the alkyl chain. The second decomposition process of 22.2% took place in the temperature range of 193-310 °C. This corresponds to two chlorine molecules and two CH_2 molecules from the rest of the aliphatic group. Complex **C2** and **C4** are the only systems which consist of an aliphatic chain attached to either the imino nitrogen or the nitrogen which is attached to the phenyl ring, such groups can be easily decomposed. For all four

complexes (**C1**-**C4**) a weight percentage of 24 – 32% is observed, which could be a residue product in a form of PdOx. Akbari *et al.* also reported on a PdOx (27.63%) residue product observed for typical Pd(II) Schiff base complexes.[12]

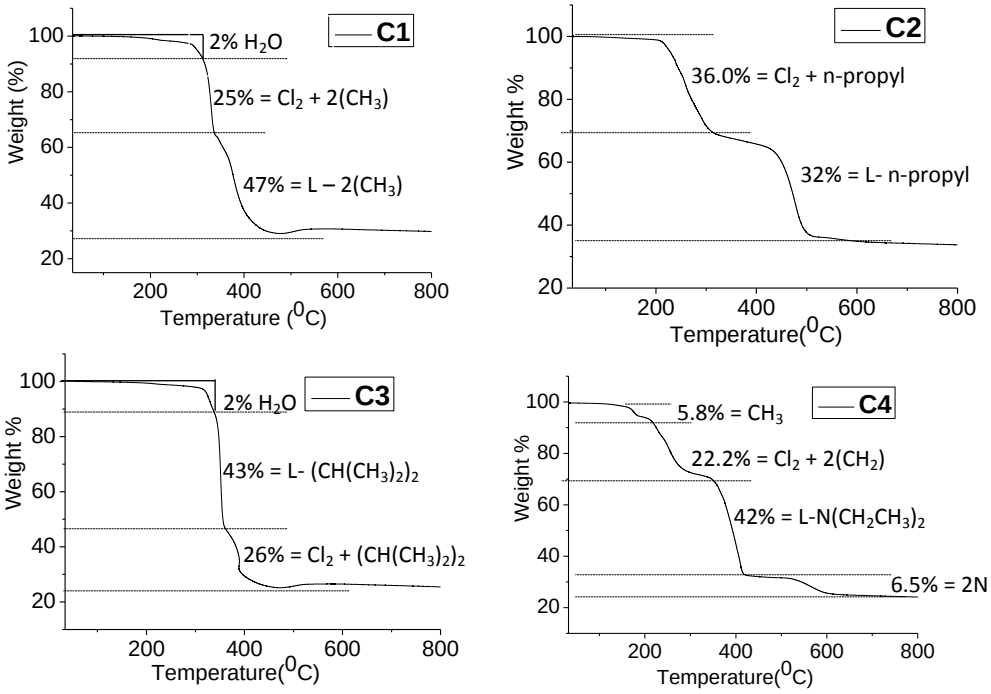


Figure 2.10: Thermograms obtained for the Pd(II) pyridyl-imine complexes.

2.2.3 Synthesis and characterization of Fe(II) pyridyl-imine complexes

In this study the preparation of the Fe(II) analogues was also attempted by reacting the pyridyl-imine ligands in a 1.1:1 mole equivalent with $FeCl_2$, using tetrahydrofuran as the reaction solvent (Figure 2.11).[1] Of the four complexes, only **C6** and **C7** were previously prepared and published as purple solids by Gibson *et al*. A tridentate derivative of complex **C5** has been reported by Small *et al,* however complex **C8** is the only iron system which has not been previously pushed.[16] Purple to dark maroon solids were obtained and isolated by filtration after the reflux period. The recovered solids were observed to be insoluble in most organic solvents (i.e. hexane, toluene, diethyl ether and ethyl acetate) except dimethyl sulfoxide. Purple microcrystalline solids were also reported by Gibson *et al*. upon preparation of iron complexes bearing iminopyridyl ligands.[1] Isolated solids in this study were however observed to change colour from purple to charcoal black after a very short period and these samples were thus kept refrigerated and analysed thereafter. Analysis using NMR spectroscopy could not be performed due to the "paramagnetic nature" of the

complexes. Samples were thus analysed with mass spectrometry, elemental analysis and infrared spectroscopy.

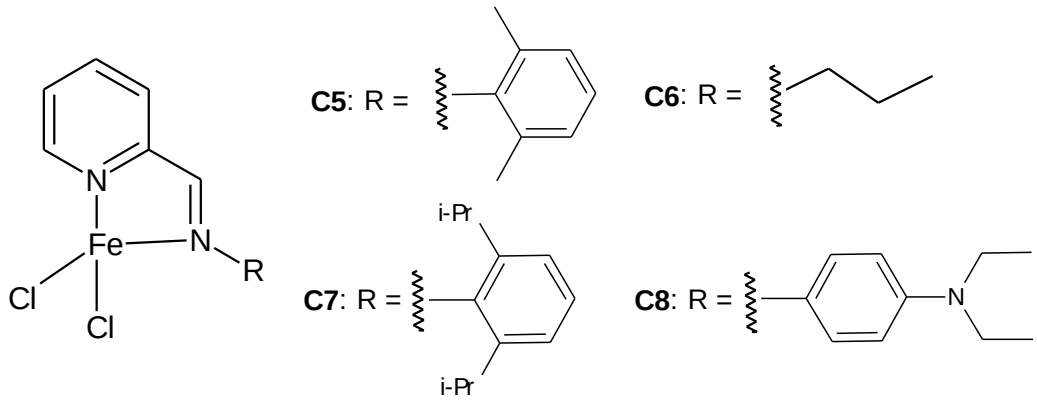


Figure 2.11: General structures of the attempted pyridyl-imine Fe(II) complexes.

2.2.3.1 Characterization by means of infrared spectroscopy

The infrared spectra of complex **C5** showed a band pattern similar to that observed for the Pd(II) complexes (Figure 2.12). A strong $\nu(C=N)_{im}$ band is observed in between a medium and weak band due to $\nu(C=N)_{py}$. A significant shift is observed for the $\nu(C=N)_{im}$ band which occurs at 1633 cm^{-1} on the free ligand (**L1**) to 1595 cm^{-1} in the complex. The rest of the Fe(II) complexes gave a pattern completely different from what is occasionally observed for typical Schiff base metal complexes of this nature (Figure 2.12). This made it difficult to determine the nature of the coordination mode for these particular systems. For example, complex **C6** shows a $\nu(C=N)_{im}$ band at a higher wavenumber followed by the two weak bands at lower wavenumbers as was observed for the free ligand. Compared to the free pyridyl-imine ligand (**L2**) the absorption of the $\nu(C=N)_{im}$ band decreased by approximately 36 cm^{-1} units for the corresponding Fe(II) complex (**C6**). Complex **C8** indicates presence of the strong $\nu(C=N)_{im}$ band which has also been shifted towards a lower frequency, however the two bands due to the pyridyl ring are relatively very weak compared to those observed for the Pd(II) analogue (**C4**).

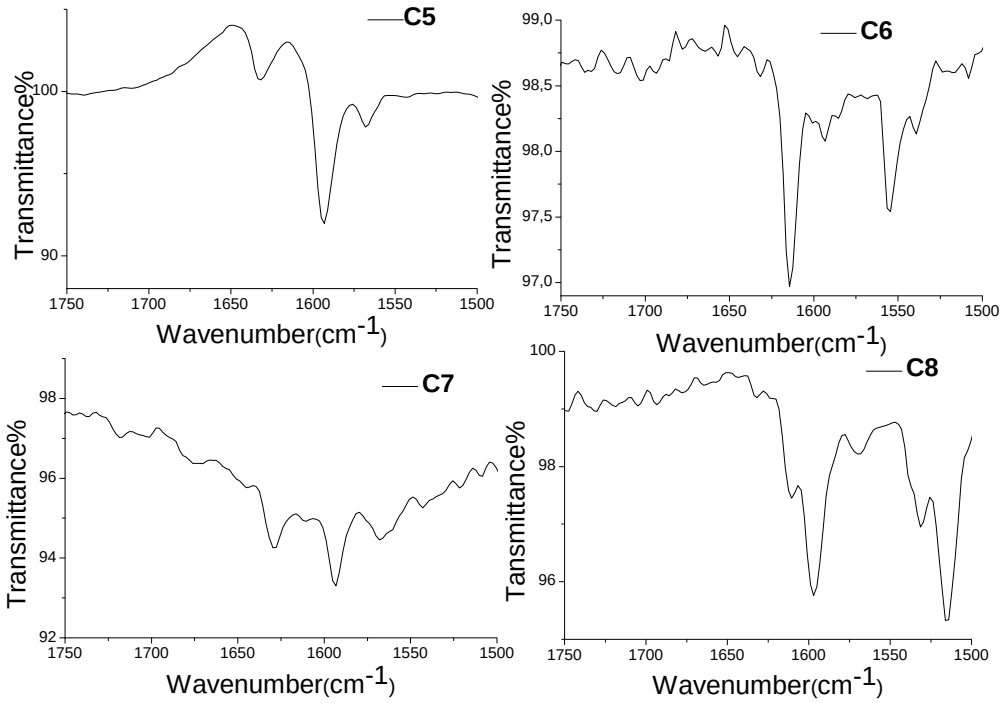


Figure 2.12: Observed imine and pyridyl ring stretching vibrations for the Fe(II) complexes.

*2.2.3.2 Mass spectrometry and elemental analysis studies for complexes **C5-C8***

From the mass spectral data obtained for complexes (**C5**-**C8**) it was observed that none of these systems gave peaks due to the parent ion. However complexes **C5** and **C7** showed molecular ion peaks of appreciable intensity corresponding to [L-$(CH_3)_2$] and [L-$(CH(CH_3)_2)_2$]. In the case of complex **C6** and **C8** fragments due to the free ligand were not observed. Figure 2.13 shows a typical mass spectrum obtained for complex **C6**, it can be observed that the expected molecular ions were not observed anywhere on the spectrum. It is thus difficult to speculate the type of fragmentation pattern observed for these systems.

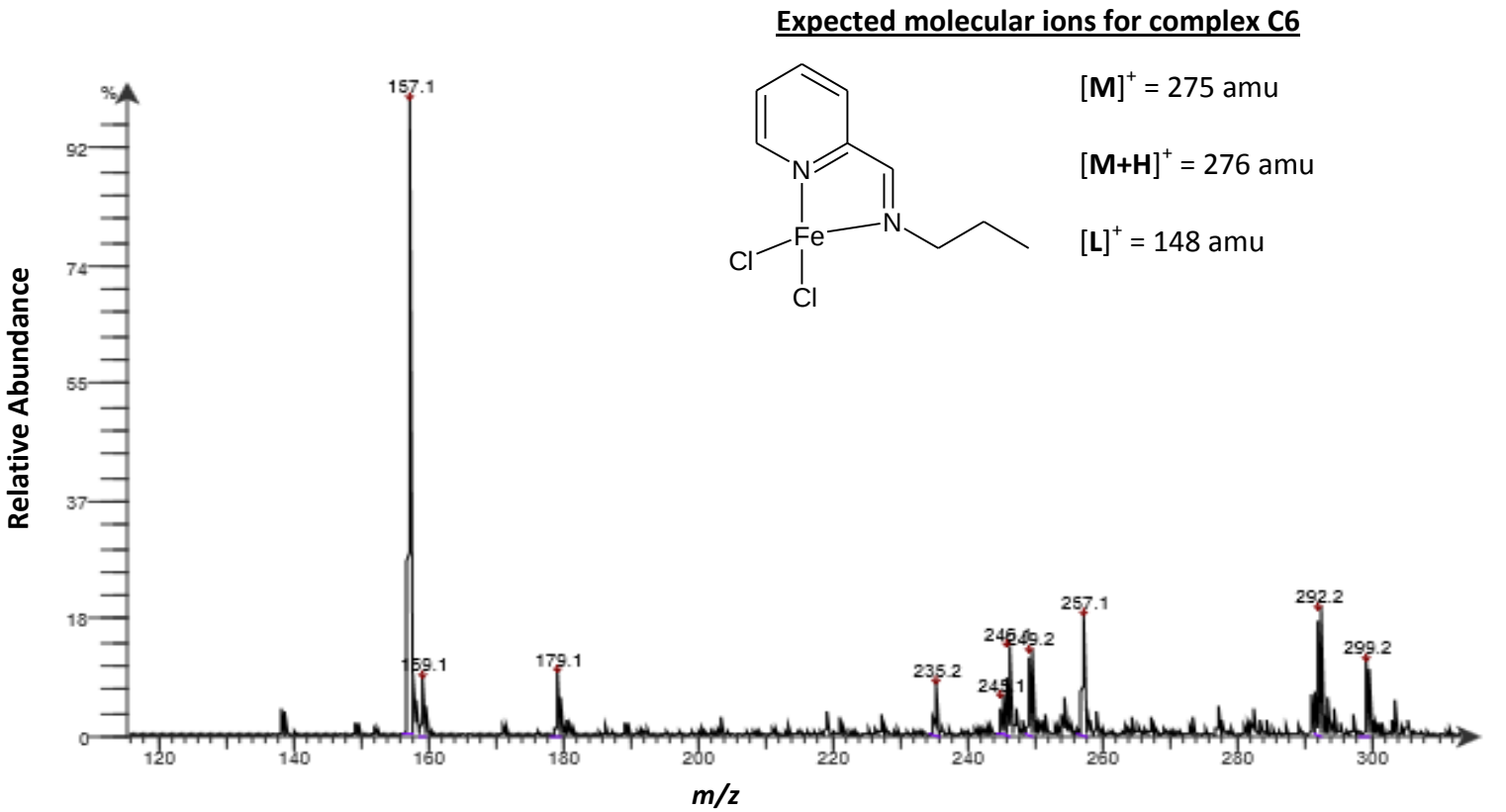


Figure 2.13: ESI mass spectrum of complex **C6** indicating absence of the parent ion and fragments of the free ligand.

The elemental analysis data obtained for complexes **C5-C8** provided additional information suggesting that the expected coordination systems were not obtained. The elemental analysis results for these complexes were not in agreement with the proposed formulations depicted in Figure 2.10 (Table 2.6). Further analysis with thin layer chromatography (eluent: ethyl acetate/hexane) showed that none of these complexes contained any other spots due to organics. This observation suggests that the observed deviation on the obtained elemental analysis results is not due to the presence of unreacted ligand or any other multiple coordination species.

Table 2.6: *Elemental analysis data for Fe(II) pyridyl-imine complexes*

Complex	**Formula**	**Anal Found (Calc)**		
		C	**H**	**N**
5	$C_{14}H_{14}Cl_2N_2Fe$	54.51 (49.89)	3.40 (4.19)	5.47 (8.31)
6	$C_9H_{12}Cl_2N_2Fe$	37.08 (39.31)	3.77 (4.39)	9.44 (10.19)
7	$C_{18}H_{22}Cl_2N_2Fe$	33.12 (54.99)	5.40 (4.39)	8.35 (7.13)
8	$C_{16}H_{19}Cl_2N_3Fe$	38.43 (50.56)	3.74 (5.04)	6.56 (11.06)

2.3 CONCLUSIONS

Bidentate pyridyl-imine complexes containing a palladium metal centre were successfully prepared by the reaction of the pyridyl-imine ligands with $PdCl_2(CH_3CN)_2$ as the metal precursor using a 1:1 ligand to metal ratio. Formation of the desired Pd(II) coordination systems was confirmed by NMR spectroscopy, FT-IR spectroscopy, mass spectroscopy, uv-vis and elemental analysis. The decomposition temperature of these systems was observed to be affected by the type of functionality attached to the imino nitrogen. Pyridyl-imine complexes containing an iron metal centre were also attempted by the reaction of the appropriate pyridyl-imine ligand with $FeCl_2$ as the metal precursor. Analysis using FT-IR spectroscopy indicated that some coordination between the iron metal centre and pyridyl-imine ligand might have occurred. However, analysis using mass spectrometry and elemental analysis confirmed that the target coordination complexes were not prepared. Further analysis to determine the nature of coordination complexes prepared perhaps with single crystal X-ray analysis is still required.

2.4 EXPERIMENTAL

2.4.1 Materials and Instrumentation

All experiments were carried out under an inert atmosphere using standard Schlenk techniques. THF and diethyl ether were distilled from sodium/benzophenone while acetone was distilled from potassium carbonate (K_2CO_3). Solvents were stored over molecular sieves after distillation. Pyridine-2-carboxyaldehyde, propyl-1-amine, 2.6-dimethylaniline, N.N-diethyl-p-phenylenediamine and 2.6-diisopropylaniline were purchased from Sigma-Aldrich and used as received. $PdCl_2(CH_3CN)_2$ was synthesized according to a literature procedure.[17] ^{1}H-NMR (300MHz) and ^{13}C-NMR (300 MHz) spectra were recorded on a Brucker Ultra Shield superconducting magnet spectrometer, using tetramethylsilane (TMS) as the internal standard. Infrared spectra were recorded on a Brucker Tensor 27 ATR Cell spectrophotometer. Elemental analysis was performed by the University of Johannesburg Microanalytical Laboratory. UV-Vis spectroscopy was recorded on a Varian Cary Eclipse (Cary 50) spectrometer. Mass spectrometry analysis was carried out using an advion expression ESI (electron spray ionization) spectrometer.

2.4.2 General procedure for the synthesis of pyridyl-imine ligands L1-L4

The synthesis of the ligands is described using the procedure followed for ligand **L1** as an example. Dry diethyl ether (10 ml) was added to a nitrogen purged Schlenk tube, followed by 2-pyridinecarboxyaldehyde (2.0 ml, 21.0 mmol), while stirring in an ice bath. 2,6-Dimethylaniline (2.6 ml, 21.0 mmol) was added to this solution, followed by magnesium sulphate (1.0 g) and the resultant slurry stirred at room temperature for 3 hours. During this time period the mixture was observed to be a light green colour. The magnesium sulphate was removed by filtration, followed by distillation of the solvent using a rotary evaporator. A light green residue was obtained which was further purified by dissolving in hexane (20 ml) and extracting with water (3×20 ml). The hexane layer collected was dried with magnesium sulphate, filtered and the solvent of the filtrate distilled. A light green to orange oil was obtained which was further dried under reduced pressure for approximately 24 hours. The final ligand product was obtained as a yellow oil.

2.4.3 General procedure for the synthesis of Pd(II) pyridyl-imine complexes C1-C4

The synthesis of Pd(II) complexes is described using the synthetic procedure followed for complex **C1** as an example. To a nitrogen purged Schlenk flask a solution of $PdCl_2(CH_3CN)_2$ (0.16 g, 0.6 mmol) in dry acetone (10 ml) was added. To this well stirred solution, a solution of ligand **L1** (0.12616 g, 0.6 mmol) in 5 ml of acetone was added. During this time period a yellow solid precipitated from solution. The mixture was then stirred at room temperature for 6 hours, after which acetone was removed by decantation. This yellow solid was then washed with hexane (3×20 ml) and then dried under reduced pressure for 24 hours before analysis.

2.4.4 General procedure for the synthesis of Fe(II) complexes C5-C8

Synthesis of Fe(II) complexes is described using the procedure followed for the synthesis of complex **C5**. A solution of the ligand (0.61 mmol, 0.1283 g) in dry THF (15 ml) was added to a well stirred solution of $FeCl_2$ (0.6 mmol, 0.07605 g) in THF (20 ml). The mixture was then refluxed at 60 °C for 24 hours. During this time period the solution was purple in colour and a purple solid precipitated from solution. The reaction mixture was allowed to cool to room temperature and the solid isolated by decantation. The purple solid was then washed with hexane (3×20 ml) and later dried under reduced pressure for 24 hours before analysis. The final product was obtained as a purple solid material (0.0642 g).

2.5 REFERENCES

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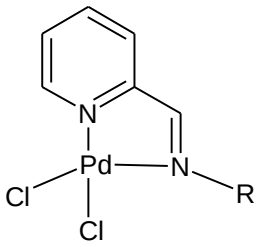
CHAPTER 3

PRELIMINARY CATALYST EVALUATION OF Pd (II) PYRIDYL-IMINE COMPLEXES FOR 1-HEXENE OLIGOMERIZATION AND NORBORNENE POLYMERIZATION STUDIES

3.1 INTRODUCTION

Transition metal complexes derived from pyridyl-imine ligands are known catalysts in the polymerization and oligomerization of olefins.[1-4] One of the most effective systems introduced thus far include less oxophilic "α-diimine Pd(II) and Ni(II) complexes" developed by Brookhart *et al*. as well as Fe(II) and Co(II) tridentate complexes developed by Small et al.[1,2] Treatment of these complexes with methylaluminoxane (MAO) or modified methylaluminoxane (MMAO) results in the production of highly active ethylene polymerization catalysts suitable for the conversion of ethylene to highly branched or linear polyethylene (PE). Furthermore, significant findings have also been made on the polymerization and oligomerization of α-olefins using bidentate pyridyl-imine complexes.[5,6]

Cloete *et al*. demonstrated that varying the functionality attached to the imine nitrogen has a significant influence on the catalytic activity of ethylene polymerization.[7] Bidentate pyridyl-imine Pd(II) complexes were reported in this study to be efficient catalysts upon activation with MAO (Figure 3.1). On average complexes containing an allyl, phenol and a styryl substituent attached to the imine nitrogen were observed to be more active compared to a system bearing a propyl chain or phenyl ring in this position.[7]



R = -$CH_2CH{=}CH_2$, -$C_6H_4CH{=}CH_2$, -C_6H_4OH, -C_6H_5, -C_3H_7

Figure 3.1: Mononuclear Pd(II) pyridyl-imine based complexes investigated by Cloete *et al*. for ethylene polymerization.[7]

Nyamato *et al*. recently reported on less bulky bidentate pyridyl-imine based palladium(II) complexes (Figure 3.2).[8] Using either MAO or $NaBAr_4$ (Ar = 3.5-$(CF_3)_2C_6H_3$) as an activator. These systems were found to be highly active catalysts in the selective dimerization of ethylene to butene. In general, the reported activities for the neutral palladium catalysts (Figure 3.2 (**a**)) were higher compared to the cationic catalysts (Figure 3.2 (**b**)).The structure of the ligand backbone was also reported to have a significant influence on the observed catalytic activity for such palladium systems. A complex bearing a methyl substituent on the

imine carbon and a hydrogen substituent on the pyridyl ring was observed to exhibit a much lower activity compared to a system which consisted of a hydrogen substituent at these positions.

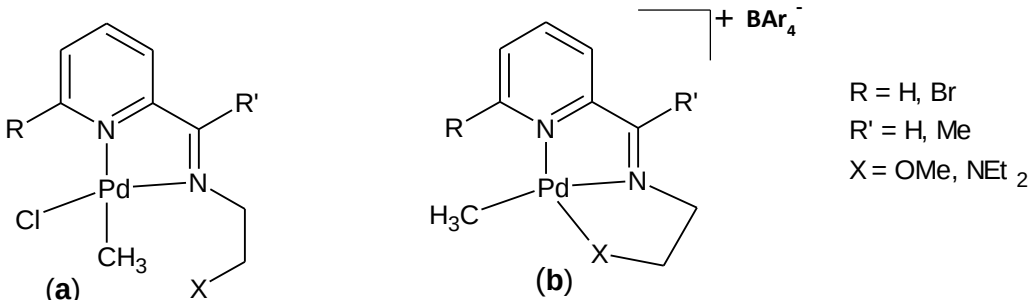


Figure 3.2: Asymmetrical pyridyl-imine based palladium complexes synthesized by Nyamato *et al*. for the dimerization of ethylene.[8]

Pyridyl-imine complexes have also been used in the polymerization of cyclic olefins such as norbornene and its derivatives. Laine *et al*. reported on Pd(II) pyridyl-imine complexes for the vinyl polymerization of norbornene (Figure 3.3).[9] These complexes were treated with MAO, leading to active catalysts which were able to reach up to 100% monomer conversion.[9] None of the palladium complexes evaluated were however capable of producing polynorbornene (PNB) with good solubility in "high boiling point organic solvents such as 1,2,4-trichlorobenzene". Hence properties such as molecular weight and chain length of the obtained polymer could not be determined.[9]

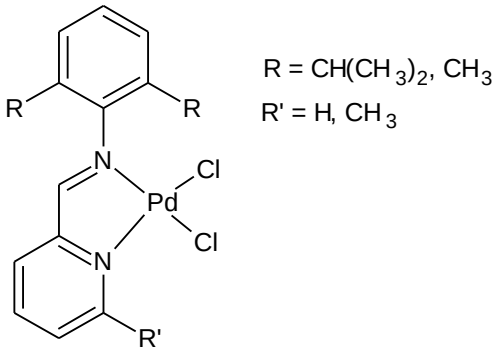


Figure 3.3: Pd(II) pyridyl-imine complexes reported by Laine *et al*. for the vinyl polymerization of norbornene.[9]

To our knowledge the application of bidentate pyridyl-imine complexes in the oligomerization of higher-olefins such as 1-hexene is relatively unexplored. Also, only a few studies have been presented in literature on the vinyl polymerization of norbornene using bidentate pyridyl-imine complexes. Most of the work on the vinyl polymerization of norbornene using pyridyl-imine complexes has been conducted using tridentate systems instead.[10,11] In this chapter Pd(II) pyridyl-imine complexes prepared in this study will be evaluated as potential oligomerization and polymerization catalysts for 1-hexene and norbornene.

3.2 RESULTS AND DISCUSSION

3.2.1 Oligomerization of 1-hexene using complexes C1-C4

Preliminary reactions were conducted using complexes **C1-C4** (Figure 3.4) as catalyst precursors for the oligomerization of 1-hexene. The reactions were performed at room temperature using methylaluminoxane (MAO) as an activator, employing an Al:Pd ratio of 500:1. The reactions were performed as reported by Janiak *et al*. with slight modifications.[12] All experiments were performed over a 1 hour period. The reaction mixture was quenched with acidified methanol (5 ml) which afforded two solvent layers, which were collected using a separating funnel and subsequently analysed by ‘‘proton nuclear magnetic resonance and gas chromatography coupled with mass spectrometry (GC-MS)’’.

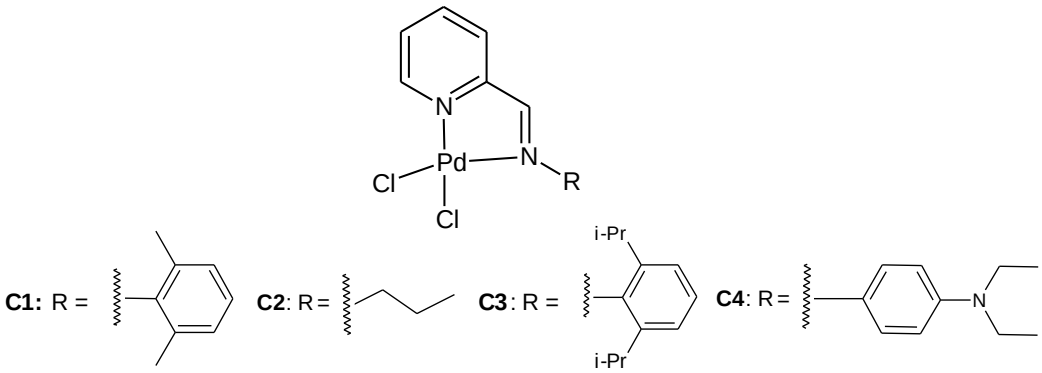


Figure 3.4: Pd(II) complexes evaluated for 1-hexene oligomerization.

The evaluated complexes did not show any activity towards 1-hexene oligomerization, instead isomerization was observed. From the obtained ^{1}H-NMR spectra of the reaction mixtures it was shown that mainly linear inner isomers of 1-hexene were isolated for all

complexes. From the ^{1}H-NMR spectrum it can be observed that the protons of the terminal double bond due to 1-hexene appear as a multiplet at δ4.80 - 5.01 ppm. The protons of the internal double bond due to 2-hexene also appear as a multiplet at δ5.48-5.52 ppm (Figure 3.5). The ^{1}H-NMR spectrum shows no trace of the vinylidene end group (i.e. $CH_2=CR_1R_2$, R_1 = n-C_4H_9 and R_2 = $(CH_2CH_2(R_1))_{i-1}$) bond, which generally appear as broad singlet signals resonating at δ4.67 and δ4.75 ppm (Figure 3.5). These vinylidene end groups are indicative of 1-hexene oligomers which could be derived from β-hydrogen elimination as a chain-termination reaction.[12]

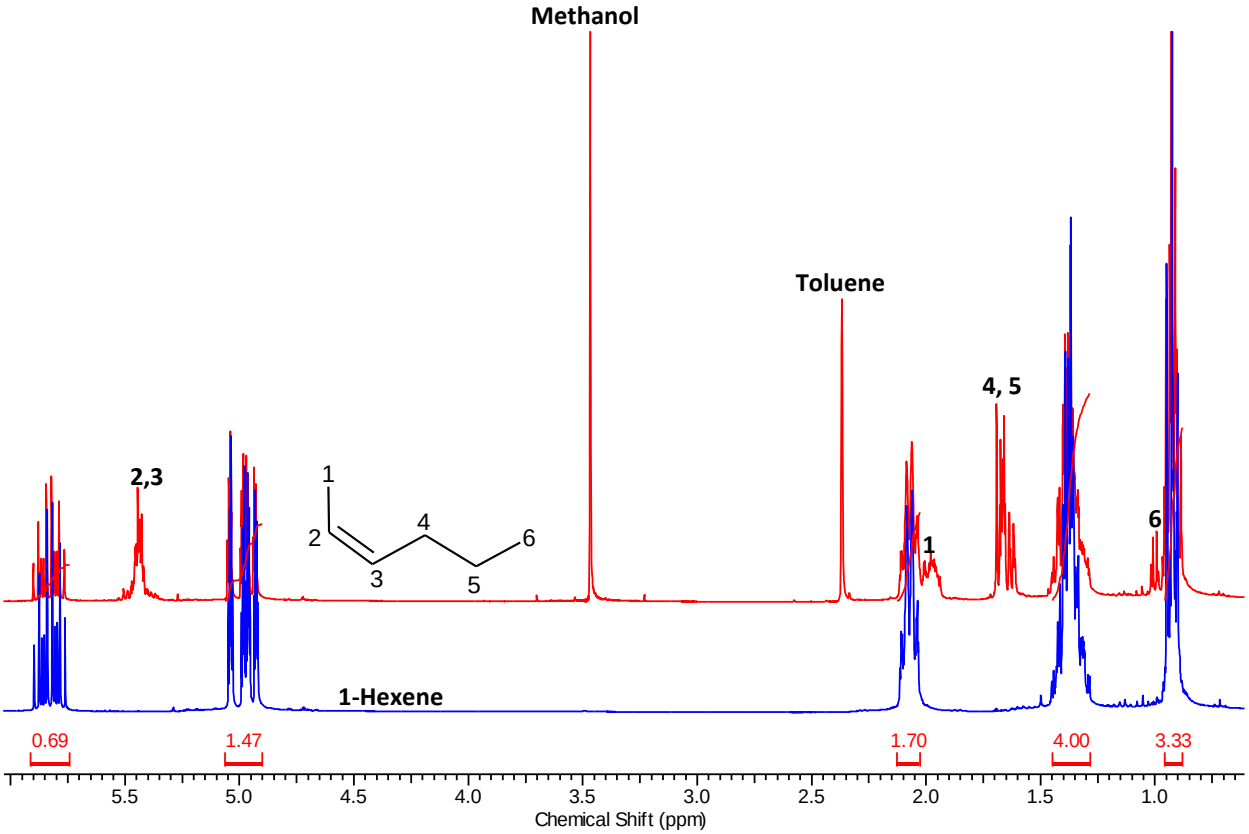


Figure 3.5: ^{1}H-NMR spectra (**top**) indicating presence of 2-hexene in an aliquot prepared using complex **C1**.

Further characterization using GC-MS analysis confirmed that complexes **C1**-**C4** isomerize 1-hexene into linear internal olefins. The results for the preliminary reactions are tabulated in Table 3.1. The GC-MS data library was used to confirm the identity of the peaks along with the mass spectra obtained for each isomer detected (Figure 3.6). Quantification of each isomer relative to the amount of unreacted 1-hexene was however not conducted. Also, the full GC spectrum obtained for each experiment showed additional peaks, which were not identified as either 1-hexene isomers or oligomers (e.g. toluene from the MAO solution). No

significant difference was observed among the product distribution obtained by the four complexes, however in the case of complex **C4** only 2-hexene was observed at this particular ratio (i.e. 500:1).

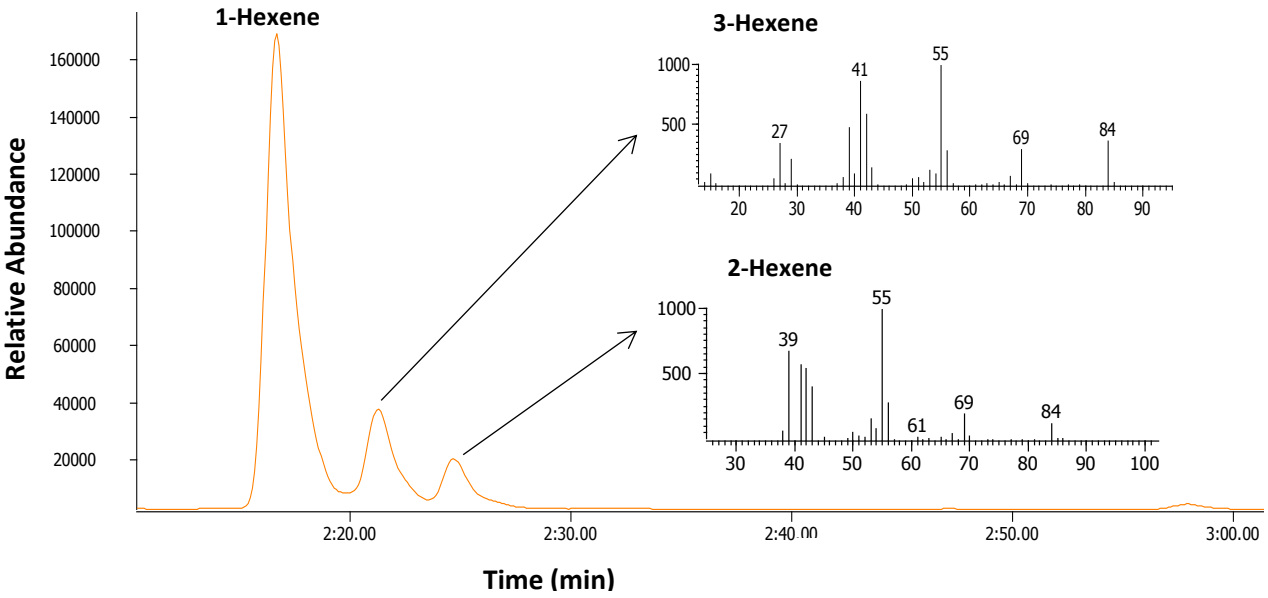


Figure 3.6: GC spectrum of the 1-hexene isomers obtained with complex **C3**.

3.2.1.1 1-Hexene oligomerization at different ratios of Al:Pd

Preliminary reactions conducted for 1-hexene oligomerization using an Al:Pd ratio of 500:1 showed that none of the evaluated complexes were active for oligomerization. Additional studies were thus conducted at different Al:Pd ratios to determine if any of the evaluated complexes (**C1-C4**) will show activity. Data for these studies are shown in Table 3.1, once again only isomerization of 1-hexene was observed for all experiments. Compared to the preliminary studies, no significant difference was observed on the distribution of products for complexes **C1**-**C3**, when the Al:Pd ratio was increased to 1500:1. However for complex **C4**, increasing the ratio of Al:Pd to 1500:1 favours the production of 3-hexene. Moreover, the 3-hexene isomer was the observed product when the Al:Pd ratio was lowered to 250:1.

The % conversion of 1-hexene isomerized by complexes **C1-C4** ranges from 1.74 - 93.3%. Complex **C4** gave the highest conversion (entry 12) when compared to the other three complexes at an Al:Pd ratio of 1000 (Table 3.1). In general, complexes **C1**, **C2** and **C4** show similar trends in terms of the observed monomer conversion relative to the Al:Pd ratio.

Optimum conversion was observed at an Al:Pd ratio of "1000:1", after which the conversion decreases significantly as the ratio of Al:Pd increases (Table 3.1). Complex **C3** gave an optimum conversion at an Al:Pd ratio of 500 (entry 7), this complex also shows a significant decrease in monomer conversion as the Al:Pd ratio is increased to 1500:1.

Table 3.1: *Results of 1-hexene oligomerization by complexes* ***C1****-****C4*** *at various* ***Al:Pd*** *ratios*

Entry	Catalyst	Al:Pd	Conversion (%)	3-Hexene	2-Hexene
1	1	500	25.61	√	√
2	1	1000	48.30	√	√
3	1	1500	15.58	√	√
4	2	500	42.82	√	√
5	2	1000	50.60	√	√
6	2	1500	1.74	√	–
7	3	500	49.64	√	√
8	3	1000	28.56	√	√
9	3	1500	14.11	√	√
10	4	250	57.10	√	–
11	4	500	59.11	–	√
12	4	1000	93.30	√	–
13	4	1500	43.15	√	–
14	4	2000	35.85	–	√

Oligomerization conditions: 1-hexene (42.3 mmol), 1 hour, 25 °C, Pd (3.9 µmol)

Isomerization of 1-hexene has been previously reported by Zhang *et al.* using β-diketiminato Ni(II) bromide complexes.[13] From this study, it was proposed that isomerization of 1-hexene was a result of a metal-hydride mechanism, which involves "insertion of 1-hexene to the Ni-H active species".[13] Zhang and co-workers demonstrated how the coordination wedge of the β-diketiminato complexes had an influence on the selective isomerization of 1-hexene to 2-hexene.[13] Tellmann *et al*. also reported on the production of trimers and dimers of 1-hexene together with a fraction of the 2-hexene, cis isomer using Co and Fe pyridyl-imine tridentate complexes.[14] It was proposed that the increased bulkiness of these systems allows for strong inhibition of β-H elimination and promotion of chain propagation. The tridentate systems reported by Tellmann *et al*. were to a large extent symmetrical and bulkier

compared to the bidentate Pd(II) pyridyl-imine complexes evaluated in this current study, thus the observed strong propensity to undergo oligomerization.

3.2.1.2 Time and temperature variation oligomerization studies using complex C4

The effect of time and temperature was also investigated to determine if these parameters might have any influence towards productivity of 1-hexene oligomers. Among the four complexes evaluated, complex **C4** gave the highest % conversion even at lower Al:Pd ratios (i.e. 250:1, 500:1). This complex was thus subjected to a temperature and time variation study using an Al:Pd ratio of 250:1. In Table 3.2, the results of this study are given. Increasing time and temperature did not show any significant effect in enabling complex **C4** to show catalytic activity towards 1-hexene oligomerization. Once again no oligomerization of 1-hexene was observed. The products obtained by complex **C4** did not show any significant difference from those obtained at room temperature conditions. Moreover, the 3-hexene isomer was still observed to be the favoured product for this complex at an Al:Pd ratio of 250:1 (Table 3.2).

Monomer % conversion gradually increases with an increase in time (Table 3.2). However, after 3 hours of reaction time a slight decline in % conversion was observed (entry 2), this could have been derived from errors such as evaporation of the reaction solution. In terms of temperature, monomer conversion increases until a maximum is reached and thereafter decreases when the reaction temperature was raised to 55 °C (entry 6). The decline in % conversion as temperature increases could be due to the ‘‘deactivation’’ of the metal catalyst.

Table 3.2: *Results of 1-hexene oligomerization catalysed by complex* ***C4****, a time and temperature variation study*

Entry	Al:Pd	Time (hour)	Temperature (°C)	Conversion (%)	3-Hexene
1	250	1	25	57.10	√
2	250	3	25	48.38	√
3	250	5	25	85.38	√
4	250	1	35	12.40	√
5	250	1	45	79.91	√
6	250	1	55	8.49	√

Oligomerization conditions: 1-Hexene (42.3 mmol), Pd (3.9 µmol)

3.2.2 POLYMERIZATION OF NORBORNENE

Polymerization studies making use of complexes **C1**-**C3** as catalyst precursors have been previously demonstrated successfully in the literature.[5,7,9,15] For example, Laine *et al*. reported on the polymerization of norbornene and ethylene using complex **C1** and **C3**.[9] Six years later Cloete *et al*. reported on the polymerization of ethylene using complex **C2** as the catalyst precursor.[7] This system exhibited lower catalytic activity when compared to other pyridyl-imine Pd(II) complexes with more electronegative substituents attached to the imine moiety.[7] In this study, baseline studies were conducted on the use of complex **C4** as a catalyst precursor in the vinyl polymerization of norbornene utilizing an Al:Pd ratio of 250:1.

Norbornene was polymerized at room temperature using methylaluminoxane (MAO) as a co-catalyst and toluene as a solvent. The Pd concentration (3.9 µmol) and that of norbornene (3.20 mmol) was kept constant in all reactions performed. The polymerization reaction was quenched by addition of acidified methanol. A white solid precipitated from solution, which was later washed with methanol and dried in vacuo. These reaction conditions with slight modifications are typical for norbornene polymerization and have been employed by Laine *et al*. who used pyridyl-imine Pd(II) and Ni(II) catalysts. Gao *et al*. also reported on the vinyl polymerization of norbornene using similar reaction conditions,

employing nickel catalysts derived from [N,N] ligands.[15] The isolated polymer samples were insoluble in common organic solvents, including high boiling point solvents like toluene and trichlorobenzene. Thus infrared spectroscopy and solid state ^{13}C-NMR were the two techniques used to confirm that the obtained polymer samples are typical of a vinyl norbornene polymer.

Samples analysed using infrared spectroscopy were indicative that a vinyl type polynorbornene (PNB) was obtained, as no bands due to the double bond appear around 1620-1680 cm^{-1} and at 1334 cm^{-1} (Figure 3.7(**a**)). The existence of vibration bands of the bicyclic unit around 940 cm^{-1}(Figure 3.7(**a**) and (**b**)) further ensures occurrence of a vinyl type polymerization rather than ROMP or cationic polymerization. The type of polymer obtained will consist of a bicyclic structural unit without a double bond. Similar infrared bands indicating disappearance of the double bond were reported by Chen *et al*, Gao *et al* and Pei *et al*. for a vinyl type norbornene polymer prepared using iron and nickel pyridyl-imine based catalysts.[16,17,18]

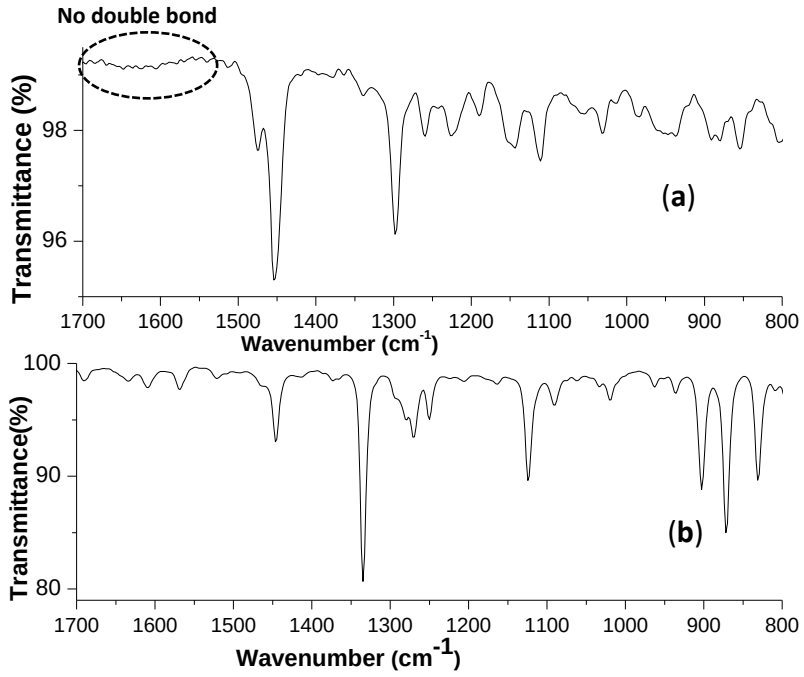


Figure 3.7: Infrared spectra of PNB prepared using complex **C4** (**a**) and unreacted norbornene (**b**)

Further characterization of the isolated polymer material using solid state ^{13}C-NMR, confirmed the disappearance of the bicyclic unit double bond. Figure 3.8 below shows a

spectrum of one of the obtained polynorbornene samples. The spectrum shows separate signals of all carbons of the symmetrical unit, only those of carbons 3 and 4 overlap due to poor resolution. The resonance corresponding to the backbone carbon (C(1)H), bridgehead carbon (C(2)H) and the two carbon bridges ($C(3,4)H_2$) indicative of PNB formed by vinyl polymerization can be noted on the solid state ^{13}C-NMR spectra. The spectrum and assignments resembles that reported by Huang *et al*. who also produced PNB via the vinyl polymerization route.[19]

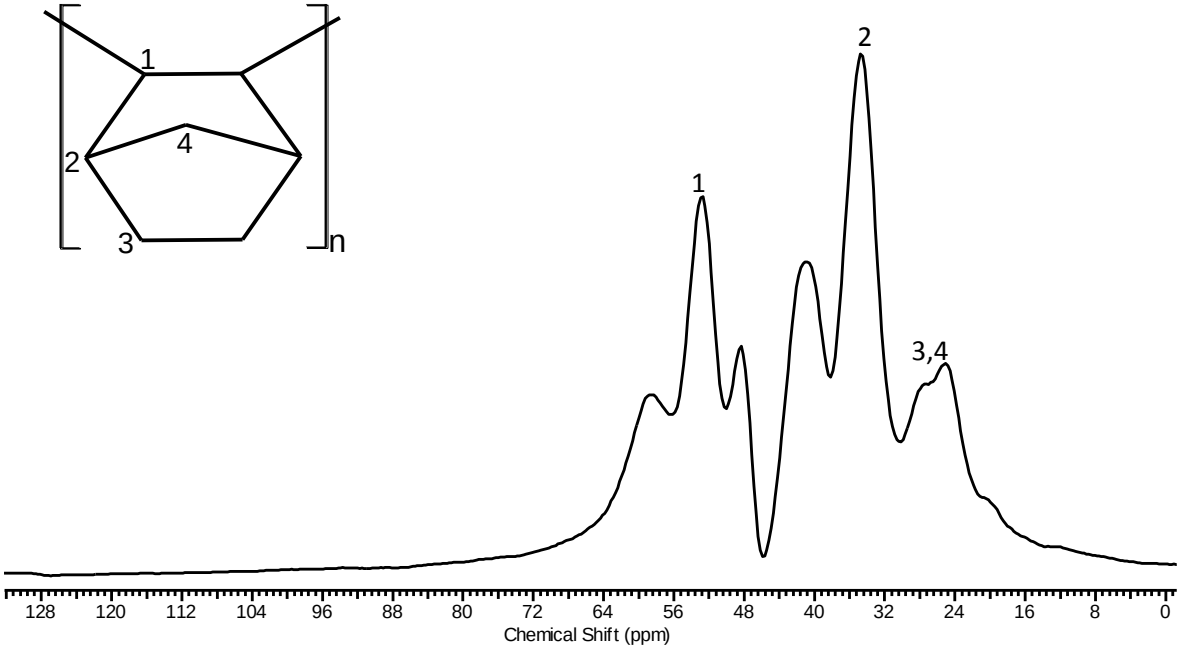


Figure 3.8: ^{13}C-NMR CP/MAS NMR of PNB prepared using complex **C4** as a metal precursor in toluene.

3.2.2.1 Norbornene polymerization at different ratios of Al:Pd

Baseline reactions conducted for norbornene polymerization in 3 hours and 30 minutes using an Al:Pd ratio of 250:1 showed that complex **C4** is active as a catalyst for the vinyl polymerization of norbornene. The catalytic transformation of norbornene was conducted at various Al:Pd ratios, to elucidate the efficiency of this catalyst and the effect of increasing the co-catalyst concentration on the polymerization activity. In Table 3.3, the percentage conversion of norbornene is given.

The conversion % of norbornene ranges from 78.38 - 90.33%. Conversions obtained after 3 hours were comparable to those observed at 30 minutes. The highest conversion was observed at an Al:Pd ratio of 500:1 (Table 3.3: entry 2). Up to 100% monomer conversions were reported by Laine *et al*. on the polymerization of norbornene for 120 minutes using Pd(II)/MAO catalysts of this type.[9]The monomer conversion results demonstrated in Table 3.3 for the two different time periods, show that monomer conversion increases with an increase in Al:Pd ratio until it reaches a plateau and thereafter decreases significantly.

Table 3.3: *Results of norbornene polymerization catalysed by* ***C4*** *at various Al:Pd ratios*

Entry	Time (hours)	Temperature (°C)	Al:Pd	Conversion (%)	TOF x 10^4	PNB Yield (g)
1	0.5	25	250	80.54	5.93	0.1156
2	0.5	25	500	90.33	11.96	0.2332
3	0.5	25	1000	89.74	10.90	0.2125
4	0.5	25	1500	78.38	11.90	0.2318
5	3	25	250	89.33	1.99	0.2334
6	3	35	250	88.65	1.97	0.2346
7	3	45	250	90.27	2.02	0.2358
8	3	55	250	90.27	2.09	0.2441
9	3	25	500	90.24	2.19	0.2567
10	3	25	1000	90.01	2.05	0.2397
11	3	25	1500	89.14	2.11	0.2469
12	3	25	2000	88.34	2.18	0.2557

Polymerization conditions: Toluene (5ml), Pd (3.9µmol), Norbornene (3.20mmol), TOF = g(PNB)/(mol Pd x h)$^{-1}$

In general catalytic activities observed over a 3 hour period were however observed to be lower than those obtained in 30 minutes (Table 3.3). Complex **C4** exhibited optimum activity of 11.96 x 10^4 g(PNB) mol^{-1} Pd h^{-1} at an Al:Pd ratio of 500:1 (entry 2) in only 30 minutes compared to 2.19 x 10^4 g(PNB) mol^{-1} Pd h^{-1} obtained in 3 hours (entry 9). This indicates that increasing the time period has an effect on the activity of complex **C4** towards norbornene polymerization; it also raises a possibility of catalyst deactivation as the reaction time increases. The activities exhibited by complex **C4** were however observed to be lower compared to those previously reported in the literature for other pyridyl-imine palladium complexes.[15] The 2-methoxycarbonyl-6-iminopyridine palladium complexes synthesized by

Shi *et al*. were reported to give activities up to 1.05 x 10^6 g PNB/(mol Pd h) for the vinyl polymerization of norbornene.[15]

In this study complex **C4** was further subjected to a temperature variation study, to ascertain whether or not temperature will have significant influence on the catalytic performance of this complex. The results pertaining to this study are also tabulated in Table 3.3. The lowest monomer conversion and activity observed was at a temperature of 35 °C (entry 6). Activities as high as 2.09 x 10^4 g(PNB) mol^{-1} Pd h^{-1} were reached when temperature was increased to 55 °C (entry 8). On average, the % conversions and obtained activities at higher reaction temperatures did not show any significant difference from those obtained at room temperature conditions in 3 hours. This implies that temperature does not have any recognizable influence on the vinyl polymerization of norbornene using complex **C4**. Huo *et al*. evaluated the thermal stability of an α-diimine palladium complex with 2,4,6-trimethyl groups on the phenyl ring.[20] The activity of this complex went up to a maximum value at 30 °C and thereafter decreased with an increase in temperature. The complex was found to be thermally stable with an activity as high as 2.33 x 10^5 g(PNB) $mol^{-1}h^{-1}$ obtained at 90 °C.[20]

3.3 CONCLUSIONS

The catalytic activity of Pd(II) complexes derived from pyridyl-imine ligands was evaluated in the oligomerization of 1-hexene, using MAO as a co-catalyst. Complexes **C1** to **C4** were observed to be inactive as catalysts for the oligomerization of 1-hexene. All complexes appeared to be more selective towards the formation of 2-hexene and 3-hexene isomers. Oligomerization parameters such as time, temperature and Al:Pd ratio did not have any significant influence towards the productivity of 1-hexene oligomers. In the case of complexes **C1-C3** no significant Al:Pd ratio effect was observed in terms of the product distribution. However, for complex **C4** it was observed that by reducing the Al:Pd ratio to 250:1 only the 3-hexene isomer is obtained. Increasing the ratio to 2000:1 favours the formation of both 2-hexene and 3-hexene isomers. The high affinity for the Pd(II) systems reported in this current study to isomerize 1-hexene, can be hypothesized to be due to the lack of overall bulkiness in the ligand backbone.[14]

Polymerization of norbornene using catalyst **C4/MAO** at various Al:Pd ratios and at elevated temperatures, gave the same vinyl type polymer material which contained the bicyclic unit. This system showed a much more significant time dependence of activity, since the activity of the catalyst showed an increased margin for reactions conducted for half an hour compared to activities observed after 3 hours of reaction time. Polymerization temperature and Al:Pd ratio did not show any significant influence on the observed % conversion and catalytic activity. However, poor solubility of the polymer obtained was a disadvantage seeing that the nature of the PNB was not fully understood.

3.4 EXPERIMENTAL

3.4.1 Materials and instrumentation

All experiments were carried out under a nitrogen atmosphere with standard Schlenk techniques. Toluene was dried over sodium/benzophenone prior to use. 1-Hexene and norbornene were purchased from Sigma-Aldrich and used without further purification. ^{1}H-NMR (300MHz) spectra were recorded on a Brucker Ultra Shield magnetic spectrometer, using tetramethylsilane (TMS) as the internal standard. Solid state ^{13}C-NMR (500MHz) was also performed on a Brucker Ultra Shield magnetic spectrometer. Characterization of oligomerization products and quantification of the amount of norbornene converted to polynorbornene (PNB) was done using a Pegasus 4D GC*GC TOF Mass spectrometer with an agilent 7890B gas column (RXI-5SIL (30.O m x 0.25 mm)). Helium was used as the carrier gas. The analytical conditions used for GC-MS analysis for both polymer and oligomer analysis are as follows: 0.5 µl samples were injected at 200 °C with an ion source temperature kept at 250 °C. An initial oven temperature of 40 °C was used, which was held constant for 0.5 minutes. Ramping was then increased from 20 °C/min to 50 °C, 10 °C/min to 100 °C, with a hold of 0.2 minutes in both temperature ranges. Finally a ramping temperature of 50 °C/min to 280 °C, with a hold of 10 minutes was conducted. Retention times (R_t) were thus given in minutes.

3.4.2 General procedure for the oligomerization of 1-hexene

The Pd complex (3.9 µmol) was placed in a nitrogen purged Schlenk tube followed by 1-hexene (5.25 ml) while stirring. The required amount of MAO was added to initiate the

reaction. The mixture was stirred at room temperature for the required time period and quenched by the addition of acidified methanol (5 ml). A two layer solution was obtained and separated by decantation. An aliquot of the organic layer was taken for GC analysis.

3.4.3 General procedure for the polymerization of norbornene using catalyst C4/MAO

The amount of complex corresponding to 3.9 μmol of Pd was added to an appropriate amount of dry toluene, in a Schlenk tube, under nitrogen. A solution of norbornene (3.20 mmol) in toluene (5 ml) was added to this solution while stirring. The polymerization was initiated by the addition of the required amount of MAO. The Reaction was allowed to stir at room temperature for 3 hours. Polymerization was quenched by the addition of acidified methanol (5 ml). A white solid precipitated from solution, this was washed with methanol (3 x 20 ml) and later dried in vacuo for a period of 3 days.

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CHAPTER 4

SUMMARY

Bidentate pyridyl-imine ligands **L1**-**L4** were successfully prepared from a condensation reaction. Ligands were obtained as yellow oils (**L1** and **L2**) and green solids (**L3** and **L4**), which were found to be air and moisture stable. All ligands were characterized using ^{1}H-NMR, ^{13}C-NMR, infrared spectroscopy, mass spectrometry and elemental analysis. From the ^{1}H-NMR spectra of all ligands, condensation was confirmed by the occurrence of the resonance due to the imine proton around δ8.30 ppm, except for ligand **L4**, in which this proton was observed at δ8.68 ppm. Moreover, infrared spectra of all ligands revealed a strong $\nu(C=N)_{im}$ band around 1650 cm^{-1}, which is preceded by a medium and weak band due to $\nu(C=N)_{py}$. This is a typical trend observed for pyridyl-imine ligands confirming occurrence of condensation.

The Pd(II) complexes **C1**-**C4** of these ligands were successfully prepared from $PdCl_2(CH_3CN)_2$ in good yields (52.3 - 91.2%). Complexes were isolated as yellow solids and found to be air and moisture stable. All complexes were characterized by NMR spectroscopy, mass spectrometry, uv-vis, infrared spectroscopy, thermogravimetric analysis and elemental analysis. ^{1}H-NMR and infrared spectra of all complexes revealed that coordination occurred via the pyridyl-ring nitrogen and the imine nitrogen. For example, upon complexation the infrared spectra of all complexes shows a very strong $\nu(C=N)_{im}$ band in between a weak and medium band due to $\nu(C=N)_{py}$. The ^{1}H-NMR spectra of complexes **C1**-**C3** showed a downfield shift of the imine proton together with the pyridyl ring protons. From mass spectrometry peaks due to the parent ion were clearly observed, moreover the purity of these complexes was confirmed by the obtained elemental analysis results.

In this study the preparation of Fe (II) complexes **C5**-**C8** was also attempted. These complexes were prepared from a tetrahydrofuran solution of anhydrous $FeCl_2$ and the corresponding pyridyl-imine ligands. Purple to dark maroon solids were isolated and found to change colour over a very short period, when exposed to room temperature conditions. Infrared spectra of these complexes suggest coordination, however the mass spectra obtained for these compounds did not show molecular ion peaks corresponding to the

target Fe(II) systems. Also, the obtained elemental analysis data was not in agreement with the target coordination systems. Further characterization of these systems is still required. For example, the use of single crystal X-ray analysis can help elucidate the nature of coordination compounds obtained.

Oligomerization studies of 1-hexene were carried out using Pd(II) complexes **C1**-**C4**. Experiments were conducted in a neat reaction media, using MAO as a co-catalyst. Recovered samples were analysed using ^{1}H-NMR and GC-MS. Preliminary oligomerization experiments conducted at room temperature for 1 hour, indicated that these complexes are inactive in the oligomerization of 1-hexene. ^{1}H-NMR and GC-MS analysis revealed that 2-hexene and 3-hexene isomers were isolated instead.

Further oligomerization studies were thus conducted using different ratios of Al:Pd and varying parameters such as time and temperature. These experiments also showed that evaluated Pd(II) complexes were inactive as catalysts precursors for 1-hexene oligomerization. 2-Hexene and 3-Hexene isomers were also isolated for these studies. Variation of the Al:Pd ratio did not have any significant influence on the product distribution for complexes **C1**-**C3**. In the case of complex **C4,** 3-hexene was the favoured isomer when an Al:Pd ratio of 250:1 was used, regardless of the reaction time or temperature. The 2-hexene isomer was only observed when the Al:Pd ratio was increased.

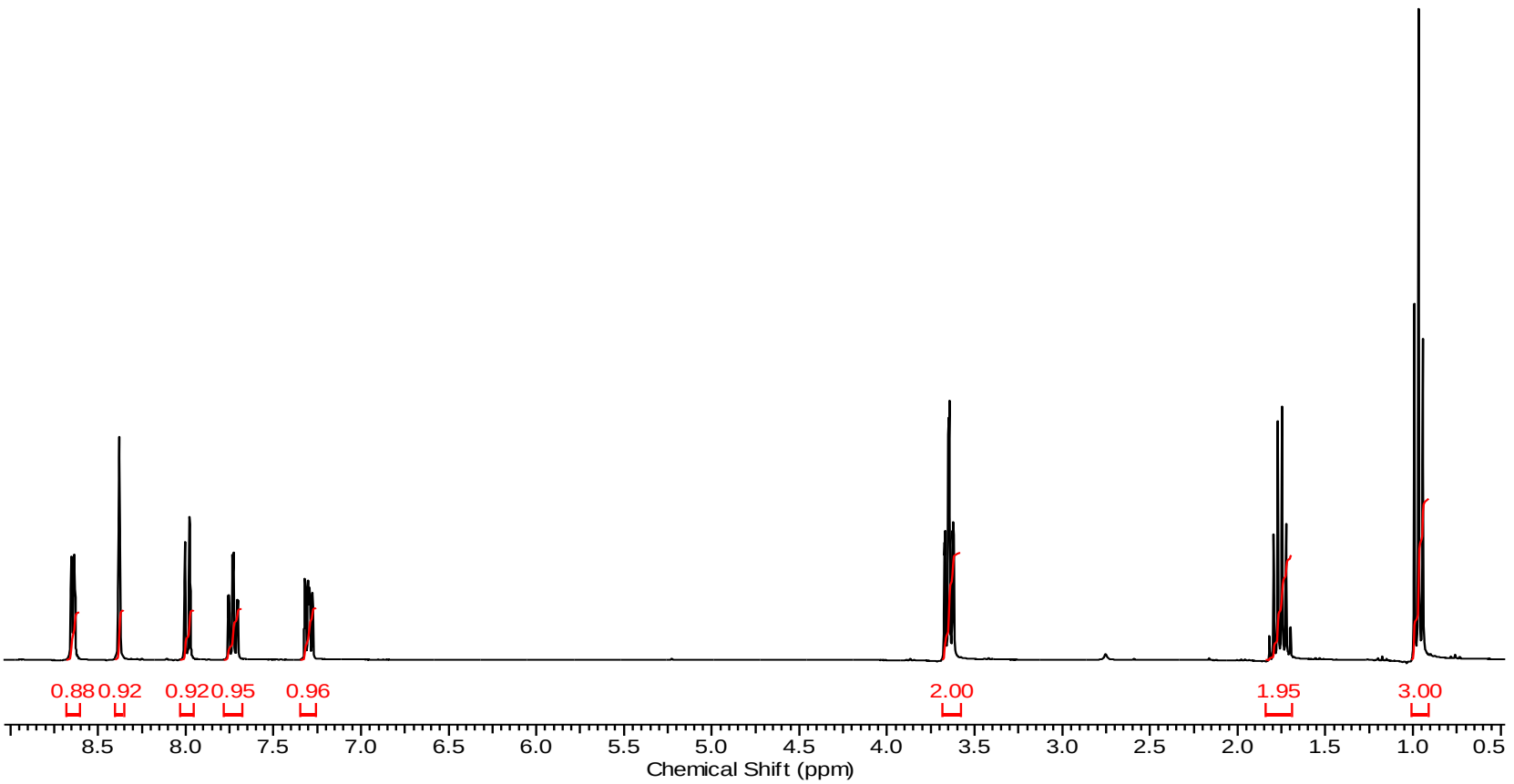
Oligomerization studies conducted in this current study were preliminary, thus experiments are to be repeated to investigate the reproducibility of the obtained results. Also, studies were not attempted at higher temperatures for complexes **C1**-**C3**, thus for comparison future investigation should also include the evaluation of these complexes at higher temperatures. Attaining a more comprehensive study of the reaction conditions and further optimization of the process conditions is still required as future work.

Complex **C4** was also evaluated as a catalyst precursor in the polymerization of norbornene. Polymerization studies were carried out in toluene at room temperature, using different ratios of Al:Pd. Solid state ^{13}C-NMR and infrared spectroscopy were the two techniques used to characterize the obtained white polymer solids. GC-MS analysis was used to determine the percentage of converted norbornene. This complex was found to be active for the vinyl

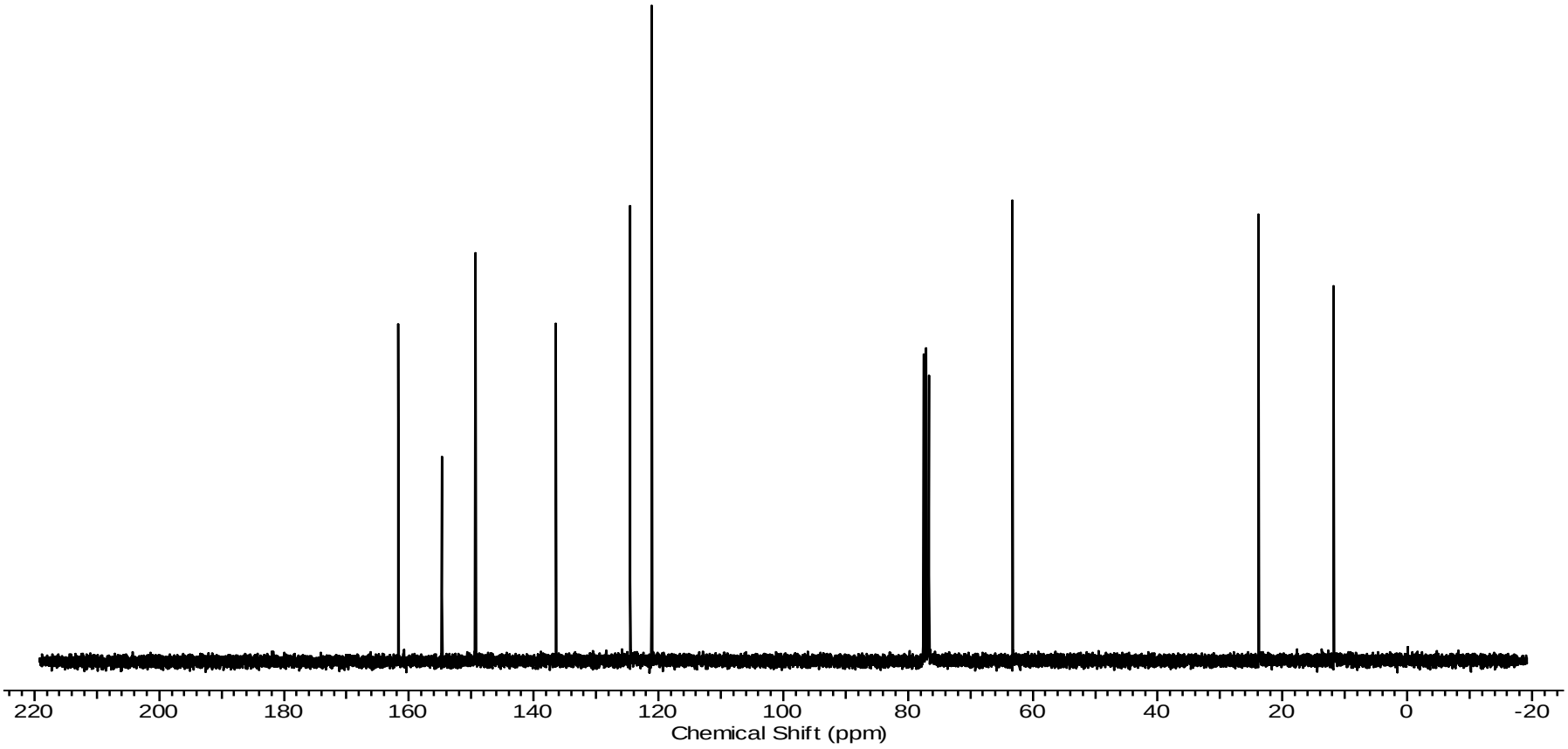
polymerization of norbornene. Infrared and ^{13}C-NMR spectra of all solids confirmed the disappearance of the double bond from the bicyclic unit.

It was revealed that by increasing Al:Pd ratio from 250:1 to 2000:1 as well as temperature from 25 °C to 55 °C does not have any recognizable influence on the catalytic activity and monomer conversion. Time however, showed significant influence on the catalytic activity, with higher activities observed for reactions conducted over half an hour compared to 3 hours of reaction time. The polynorbornene obtained was poorly soluble in most organic solvents including high boiling point solvents, which made it difficult to obtain data related to the polymer molecular weight and chain length. Further optimization of the process conditions is still required, to understand the mechanistic rationale between norbornene and the palladium complex.

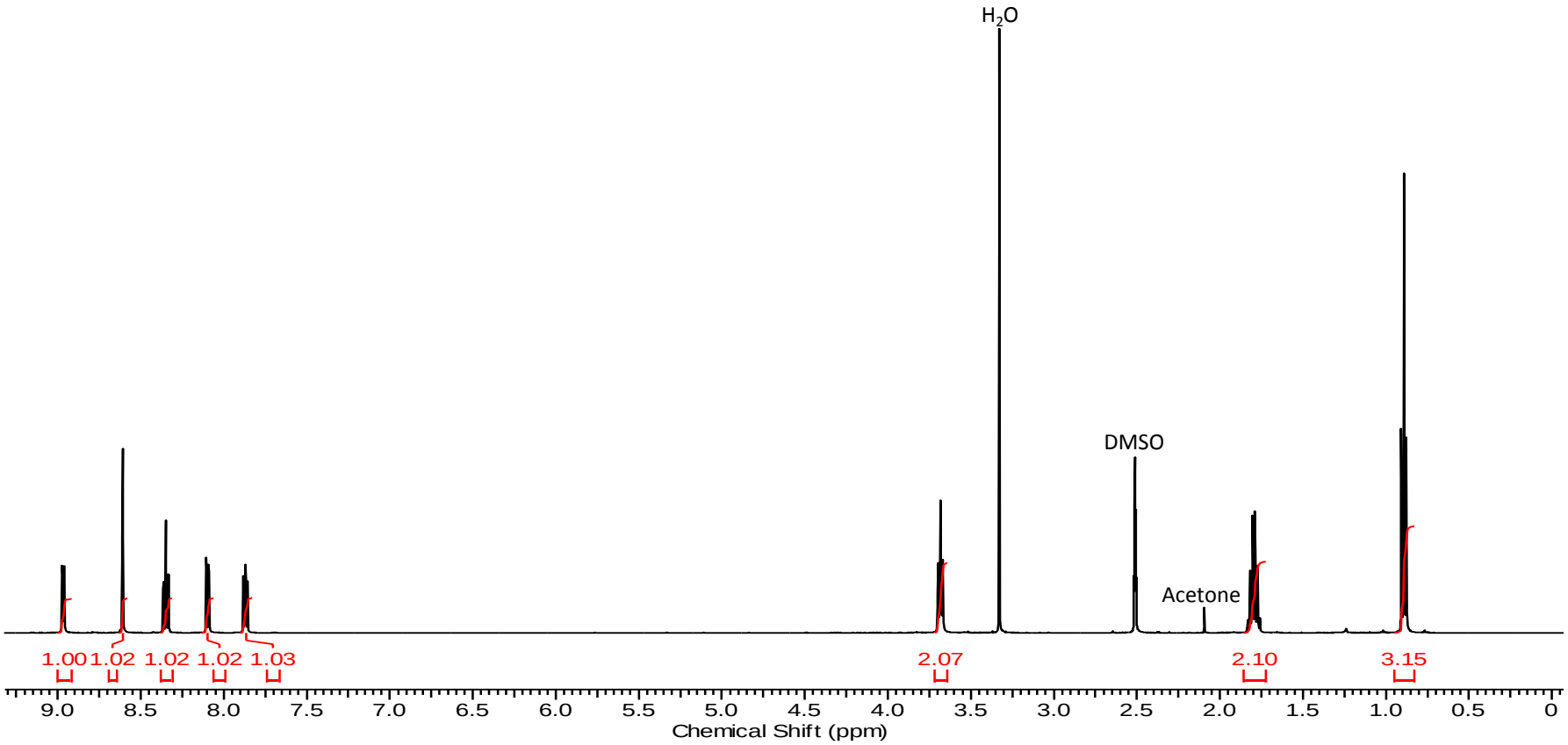
APPENDIX



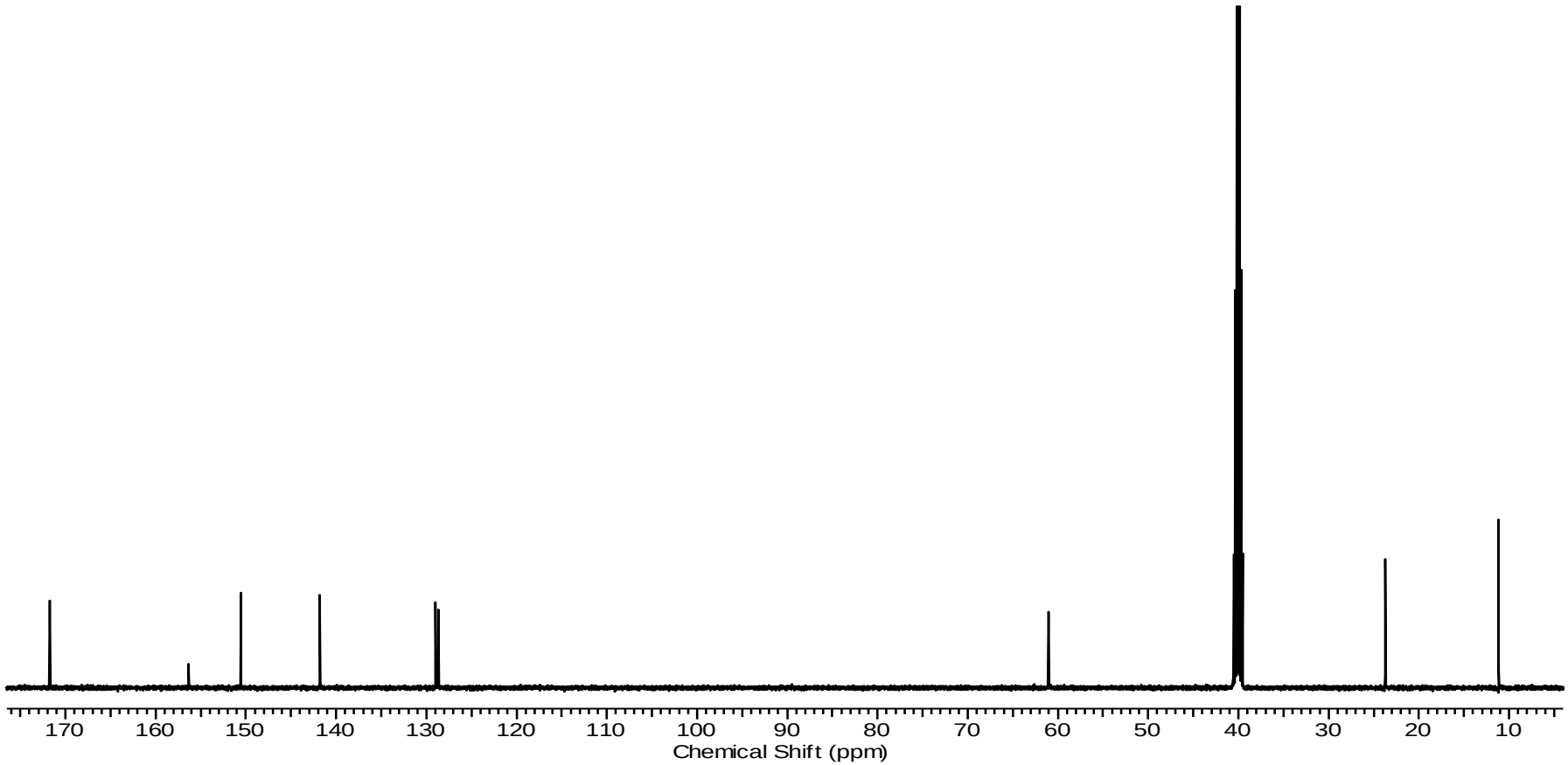
*^{1}H-NMR spectrum of pyridyl-imine ligand **L2***



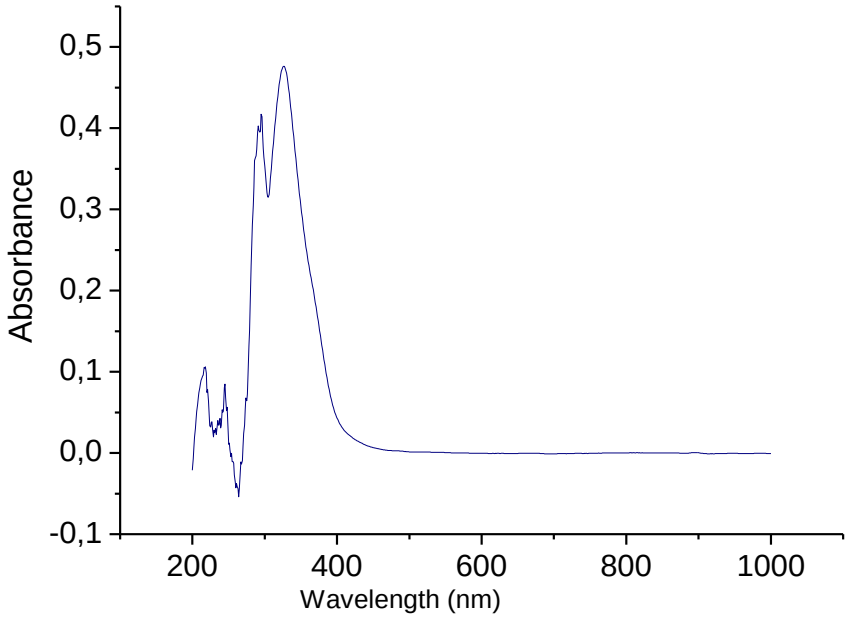
*^{13}C-NMR spectrum of pyridyl-imine ligand **L2***



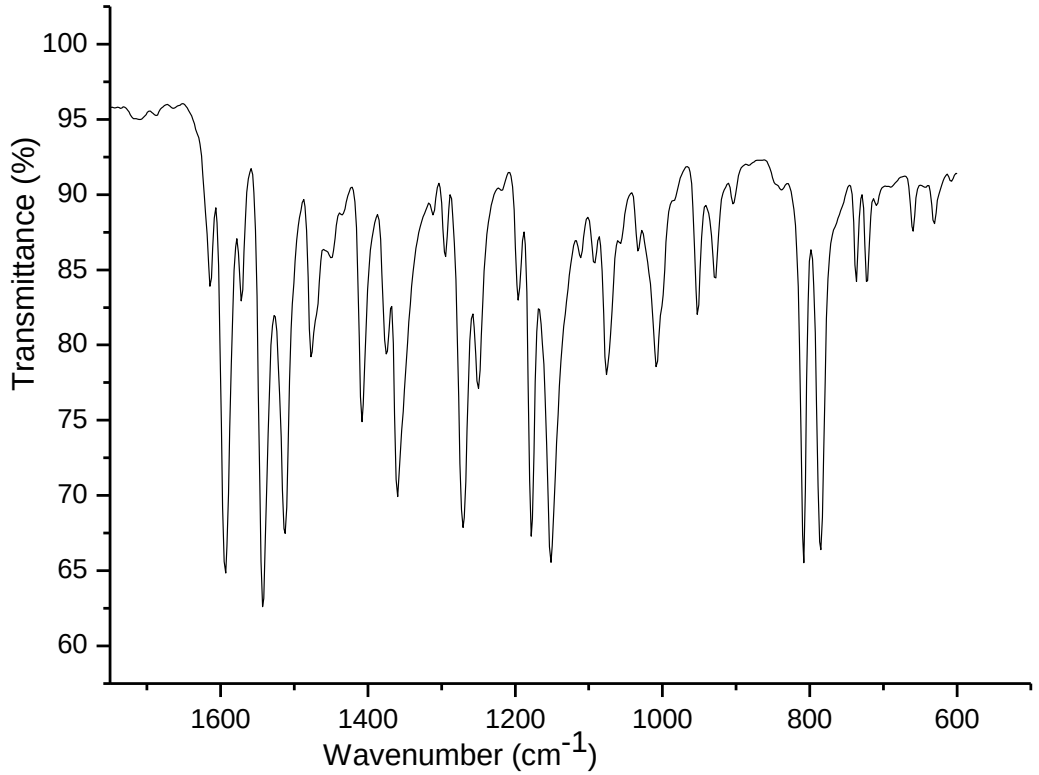
[1]H-NMR spectrum of pyridyl-imine Pd(II) complex ***C2***



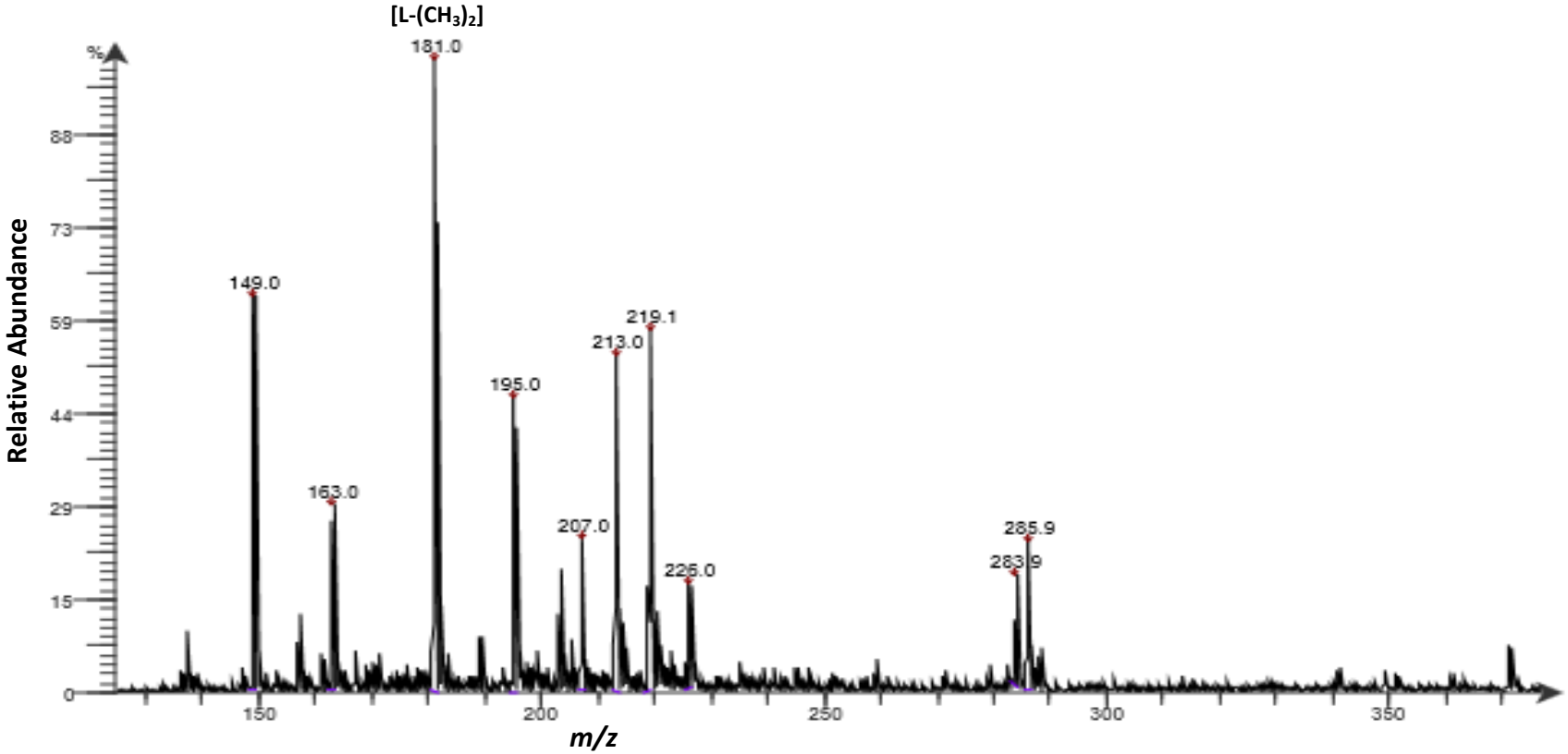
*^{13}C-NMR spectrum of pyridyl-imine Pd(II) complex **C2***



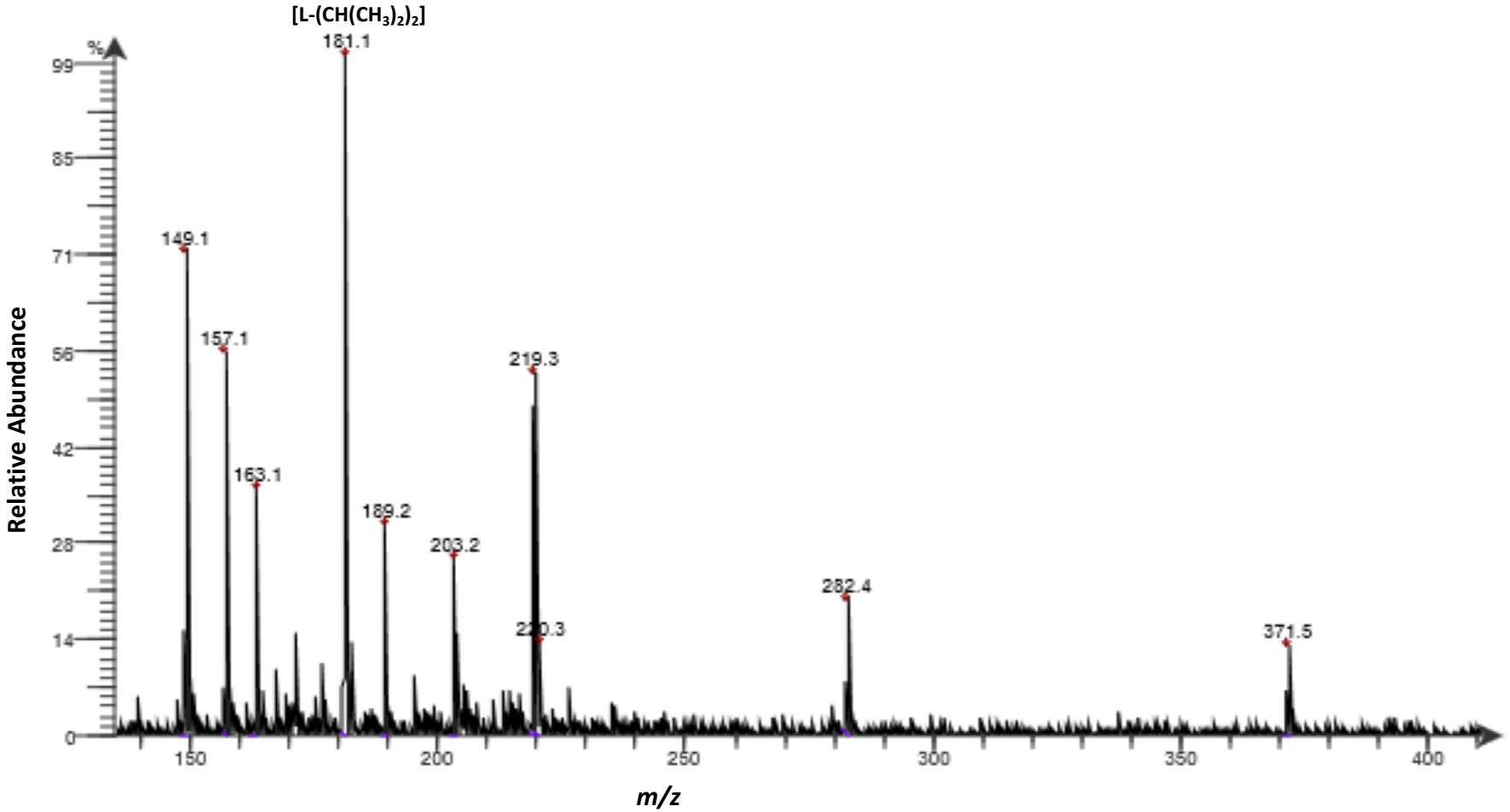
*UV-Vis absorption spectra obtained for Pd(II) complex **C2***



*Infrared spectrum of pyridyl-imine Pd(II) complex **C4***



ESI Mass spectrum of Fe(II) complex ***C5***



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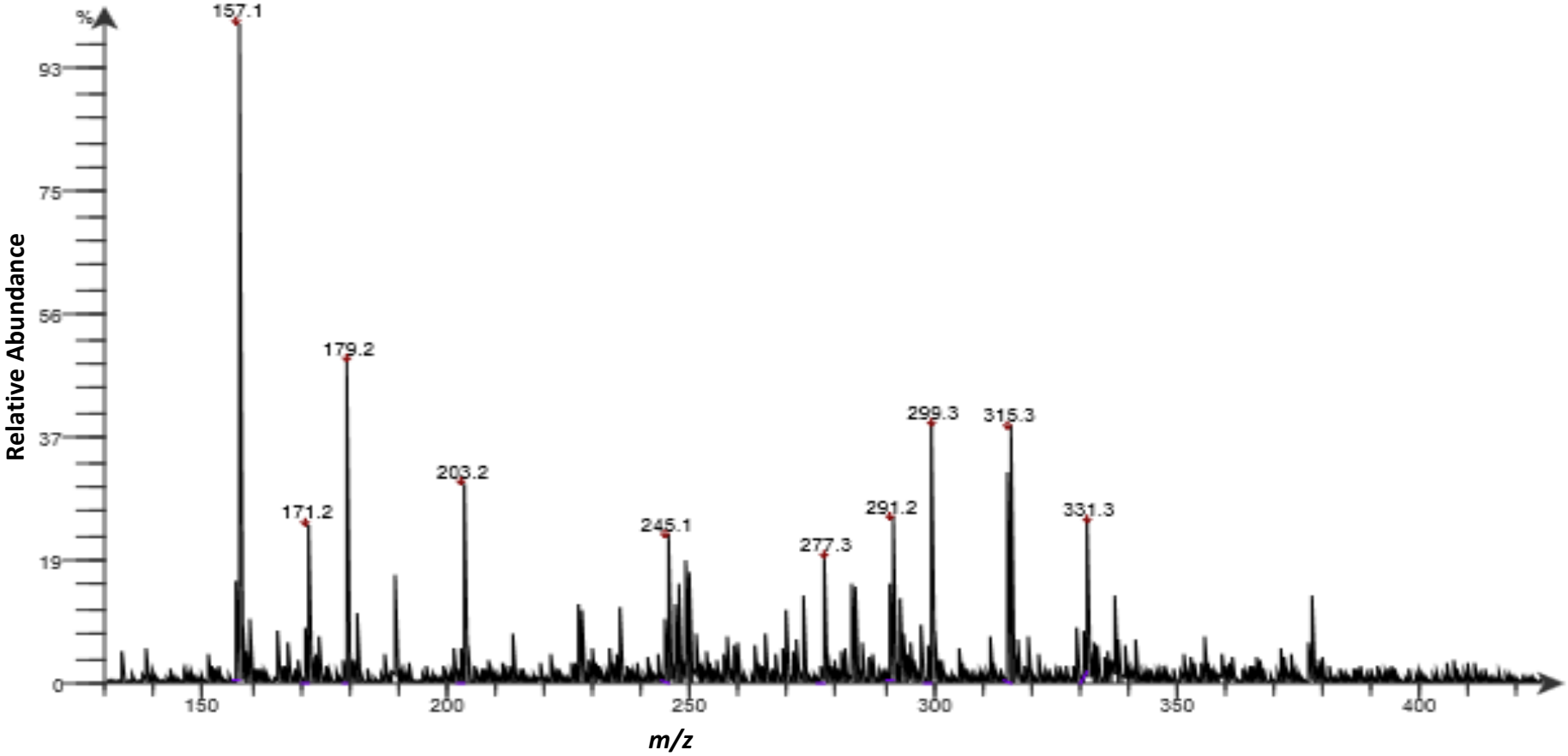

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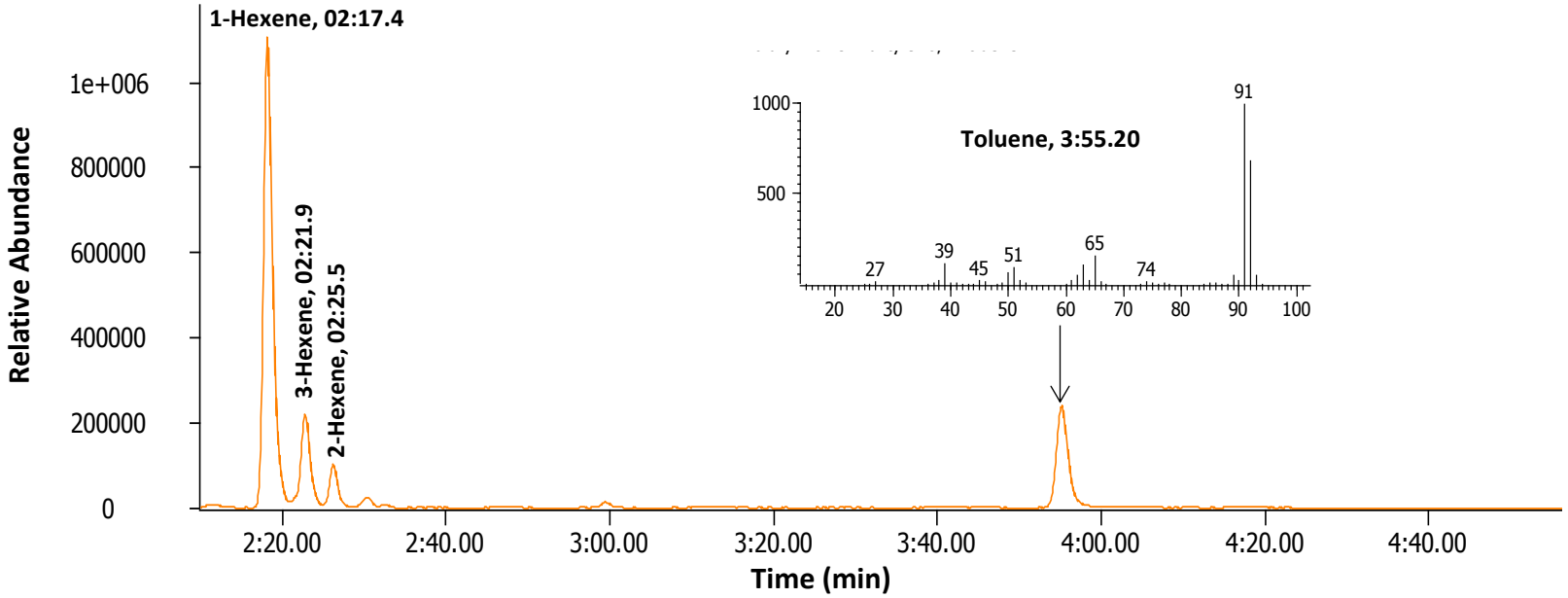
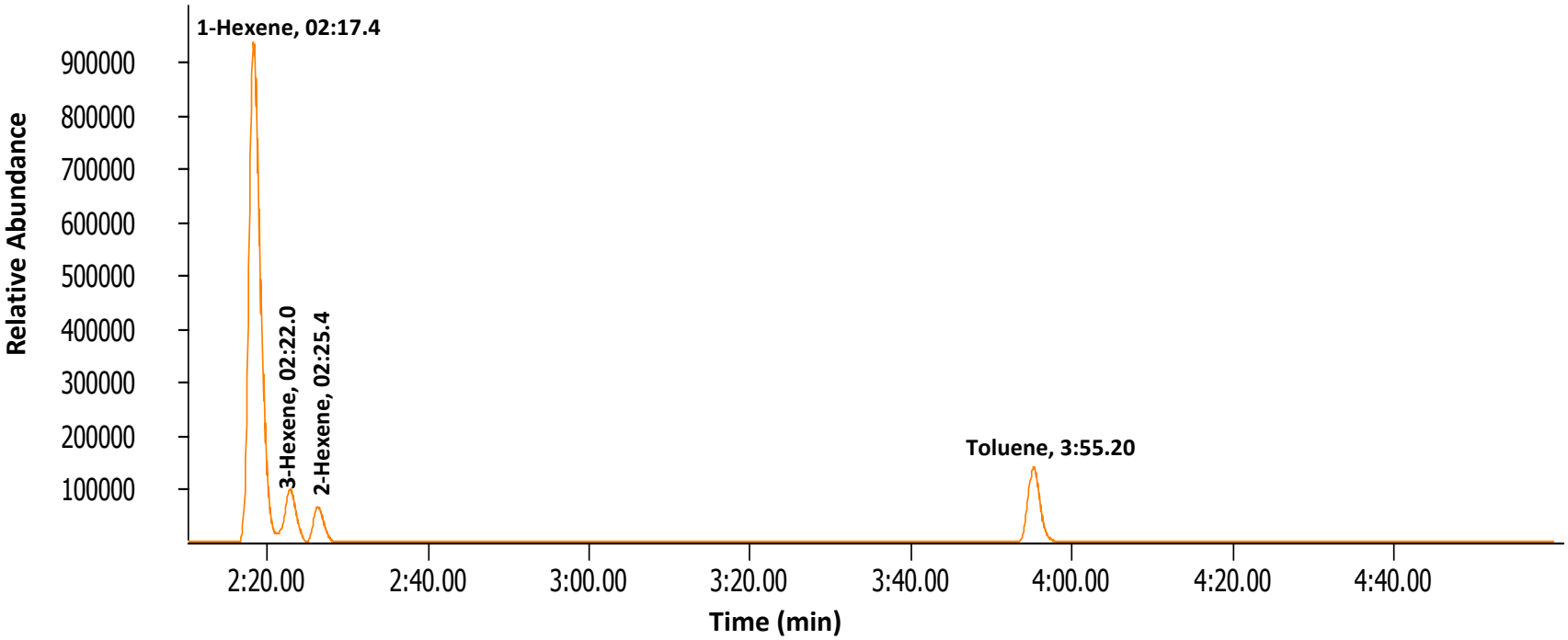
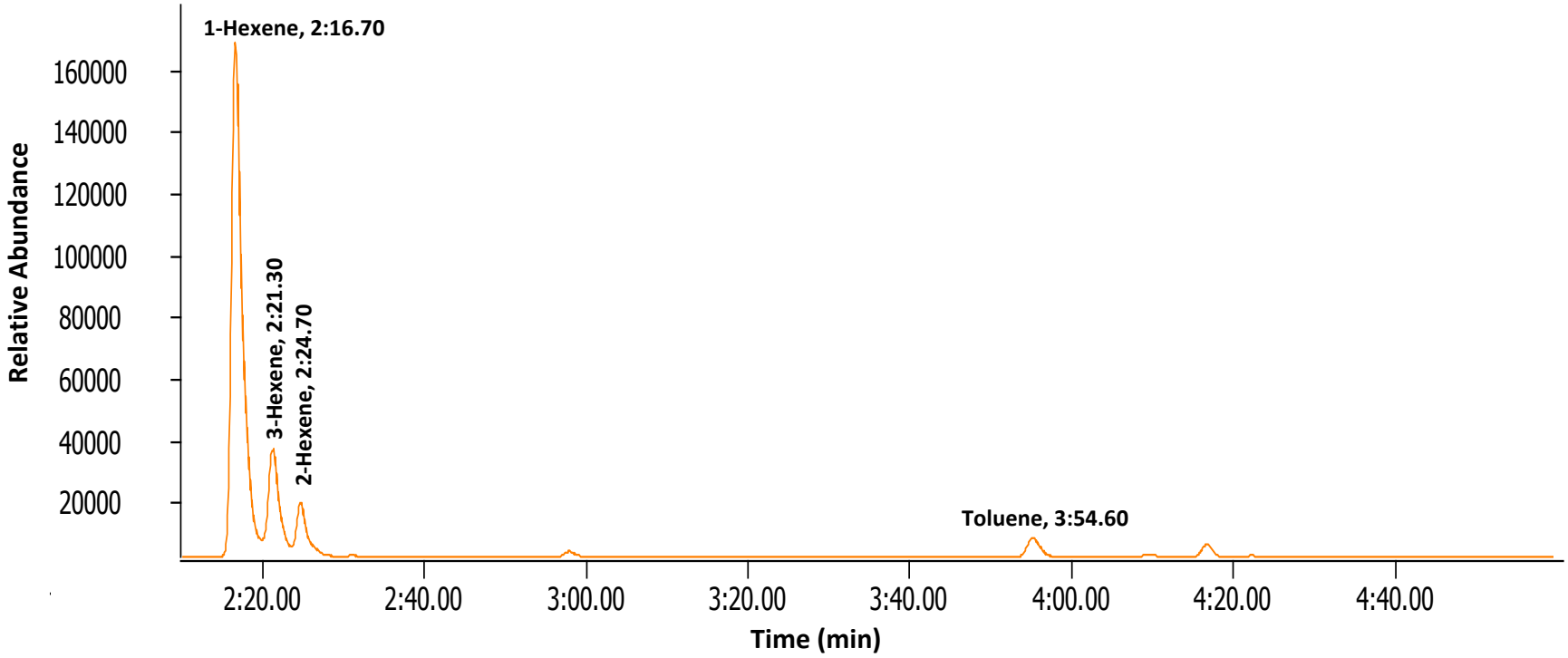


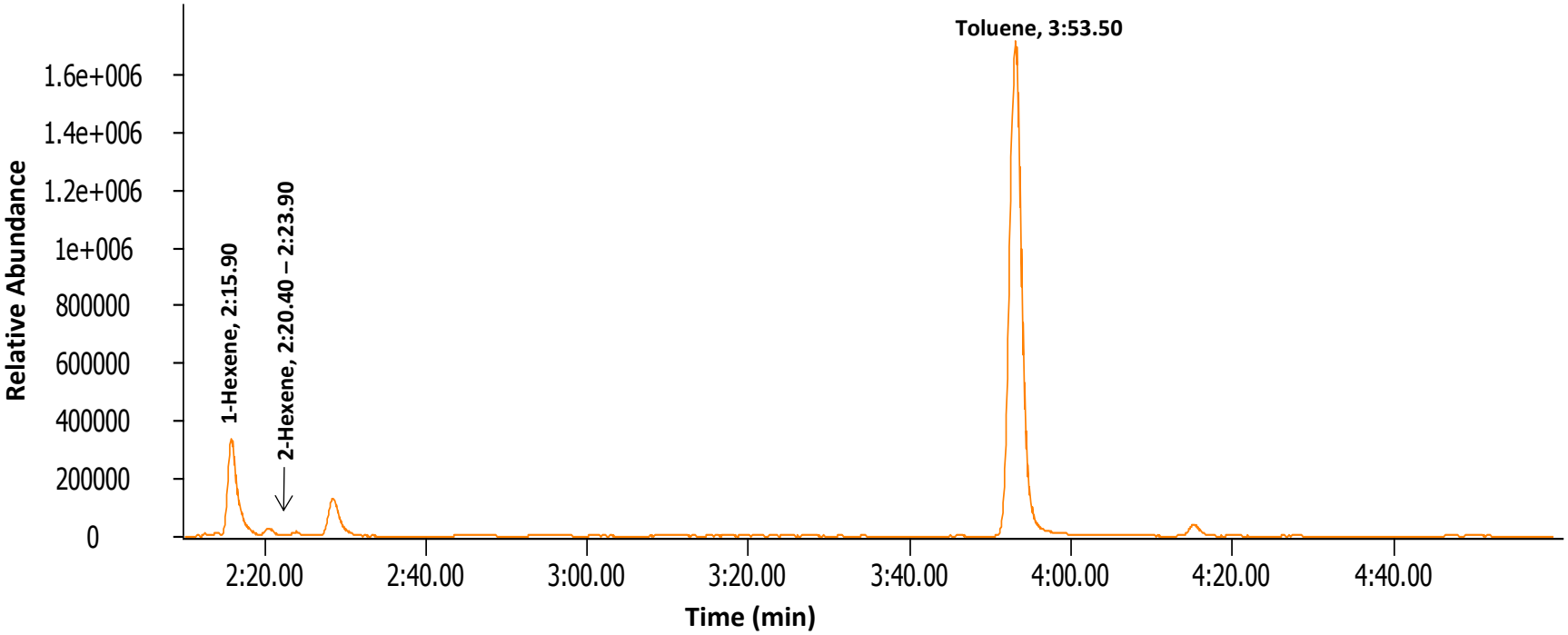
*GC spectrum obtained for compounds isolated using complex **C1** (Entry **1**, Al:Pd ratio of 500:1)*



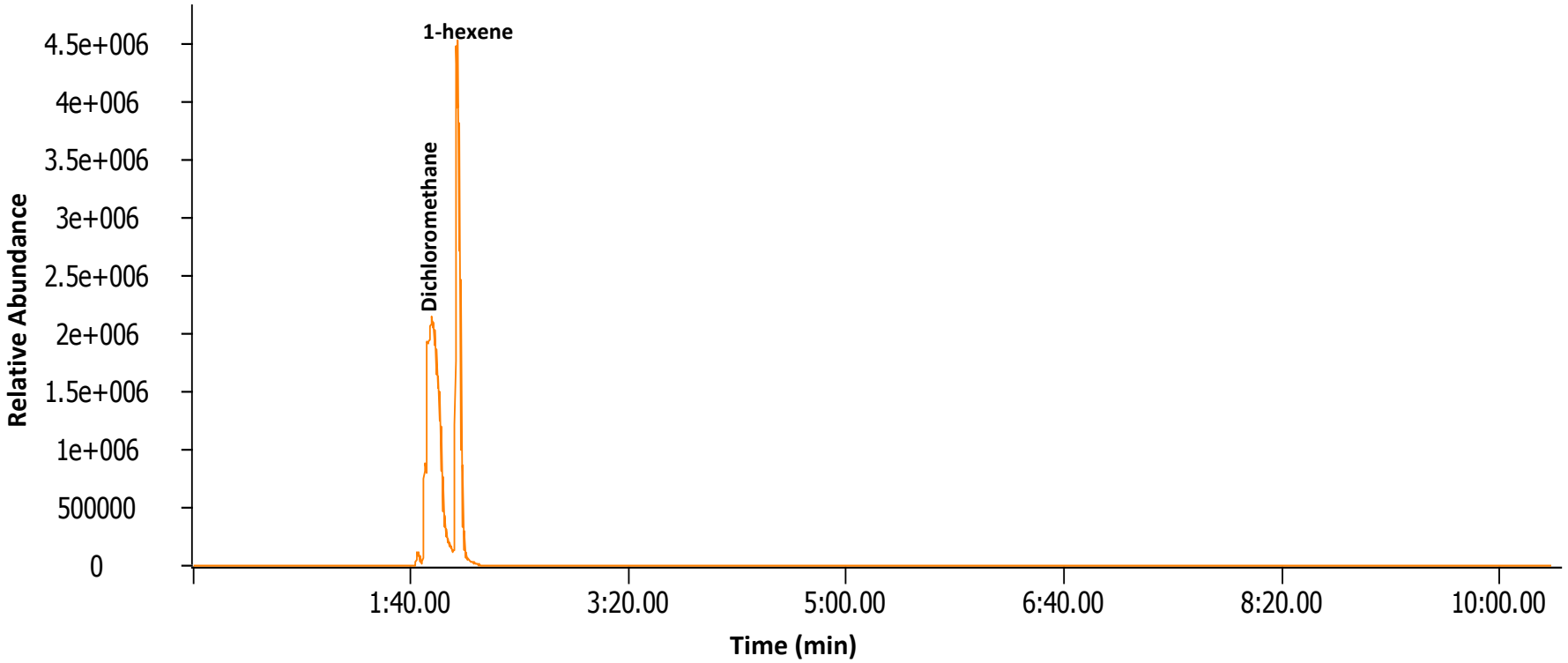
*GC spectrum for compounds isolated using complex **C2** (Entry **4**, Al:Pd ratio of 500:1)*



*GC spectrum obtained for compounds isolated using complex **C3** (Entry **7**, Al:Pd ratio of 500:1)*



*GC spectrum obtained for compounds isolated using complex **C4** (Entry **11**, Al:Pd ratio of 500:1)*



GC spectrum obtained for clean 1-hexene (solvent for analysis = HPLC grade dichloromethane)