METALLODENDRIMERS AS CATALYSTS FOR C-C COUPLING REACTIONS

By

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DECLARATION

I, **Anna Manana Moletsane,** declare that "**METALLODENDRIMERS AS CATALYSTS FOR C-C COUPLING REACTIONS."** is my own work and it has never been presented in any form at any research institution before. All sources I have used or quoted have been acknowledged by means of complete references.

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Anna Manana Moletsane

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Date

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CONFERENCES

The following conference presentations based on various aspects of the work covered in this thesis have been made:

8 - 11th November, 2009

Catalysis Society of South Africa (CATSA), 2009 (Goudini Spa)

Anna M. Moletsane, Martin O. Onani, Selwin F. Mapolie

Poster presentation: The development of new catalysts for olefin polymerization/oligomerization based on cyclometallated ferrocenylimine metallodendrimers

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Anna M. Moletsane, Martin O. Onani, Selwin F. Mapolie

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ABSTRACT

In this work, we describe the synthesis of ferrocenylimine and G1 dendrimeric N,N′ ligands, and their palladium(II) complexes. The ligands **L1** – **L4** were synthesized following Schiff base condensation reactions. The ferrocenylimine ligands **L1** and **L2** were prepared from ferrocenecarboxaldehyde and 1,3-diaminopropane or DAB-4-$(NH_2)_4$, while the G1 dendrimeric N,N′ ligands **L3** and **L4** were prepared from DAB-4-amine and 2-pyridinecarboxaldehyde or 2-quinolinecarboxaldehyde.

The air and moisture stable ligands were obtained in fairly good yields of over 65 %. All the ligands were observed to be soluble in common organic solvents. They were characterized by FTIR spectroscopy, ^{1}H-NMR spectroscopy, ^{13}C-NMR spectroscopy, micro-analysis and ESI-mass spectrometry.

A reaction of the ligands with $PdCl_2$(COD) or $PdCl_2(MeCN)_2$ gave palladium(II) complexes **C1** – **C4** in good yields of over 70%. The complexes were observed to be stable. However, the complexes did not dissolve in common organic solvents. These were characterized by FTIR spectroscopy and ^{1}H-NMR and ^{13}C-NMR spectroscopy.

All the complexes were screened for activity towards Heck coupling model reaction of iodobenzene with styrene. The complexes catalyzed the coupling of styrene with iodobenzene, giving over 60 % conversions. However, complex **C3** was found to be the most active catalyst, yielding 75% conversion without formation of palladium black.

ABBREVIATIONS

ATR	Attenuated total reflectance
br	Broad
$CDCl_3$	Deuterated chloroform
COD	1,5-Cyclo-octadiene
Cp	Cyclopentadienyl
DAB	Diaminobutadiene
DAB-Fc	Diaminobutadiene tetraferrocenylimine
DCM	Dichloromethane
DMSO	Dimethyl sulphoxide
ESI-MS	Electron spray ionization- mass spectrometry
Et	Ethyl
Et_3N	Triethylamine
FTIR	Fourier transform infrared spectroscopy
G1	Generation one
GC	Gas chromatography
***i*-Pr**	Iso-propyl
m	multiplet
MAO	Methylaluminoxane
M^+	Molecular ion
Me	Methyl
MeCN	Acetonitrile
$MgSO_4$	Magesium sulphate
m.p.	Melting point
Mw	Molecular average weight

m/z	Mass to charge ratio
NMR	Nuclear magnetic resonance
PAMAM	Poly(amidoamine)
Ph	Phenyl
ppm	Parts per million
PPI	Poly(propylene imine)
qn	quintet
s	singlet
t	triplet

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CHAPTER 1: LITERATURE REVIEW

METALLODENDRIMERS AS CATALYSTS FOR C-C COUPLING REACTIONS

1.1 AN INTRODUCTION TO DENDRIMERS

Dendrimers are well defined macromolecules which have found widespread application in a number of different fields. Included amongst these are applications in catalysis [1], sensors [2], drug delivery systems [3] and electronic devices [4]. Dendrimers form a special type of material because of their nanosized, hyperbranched, and well-defined nature of their macromolecular structures [5]. Dendrimers have three basic architectural features: a core, repetitive branch units, and terminal functional groups as illustrated in figure 1.1. The chemical and physical properties of dendrimers depend strongly on the chemical structure of all three components as well as on the overall size and the dimensionality of the dendrimer. Larger dendrimers are generally spherical in shape and contain interior void spaces while lower generation materials are usually flat and open. The terminal groups largely, but not solely, determine solubility and adsorption properties of dendrimers.

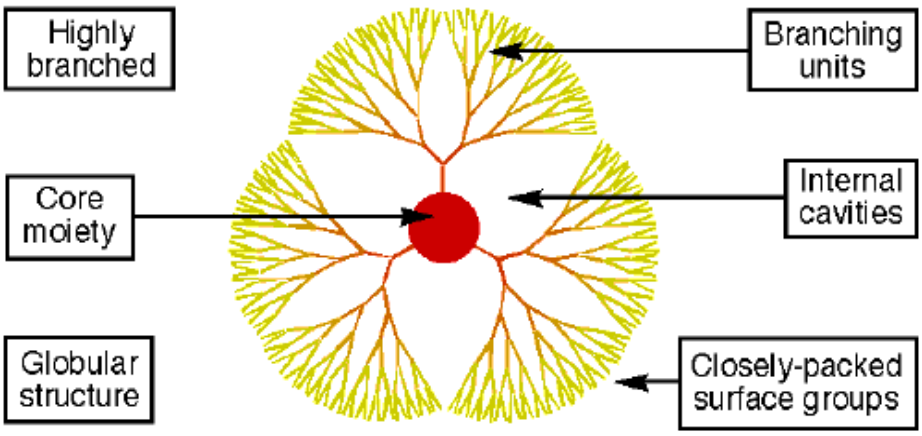
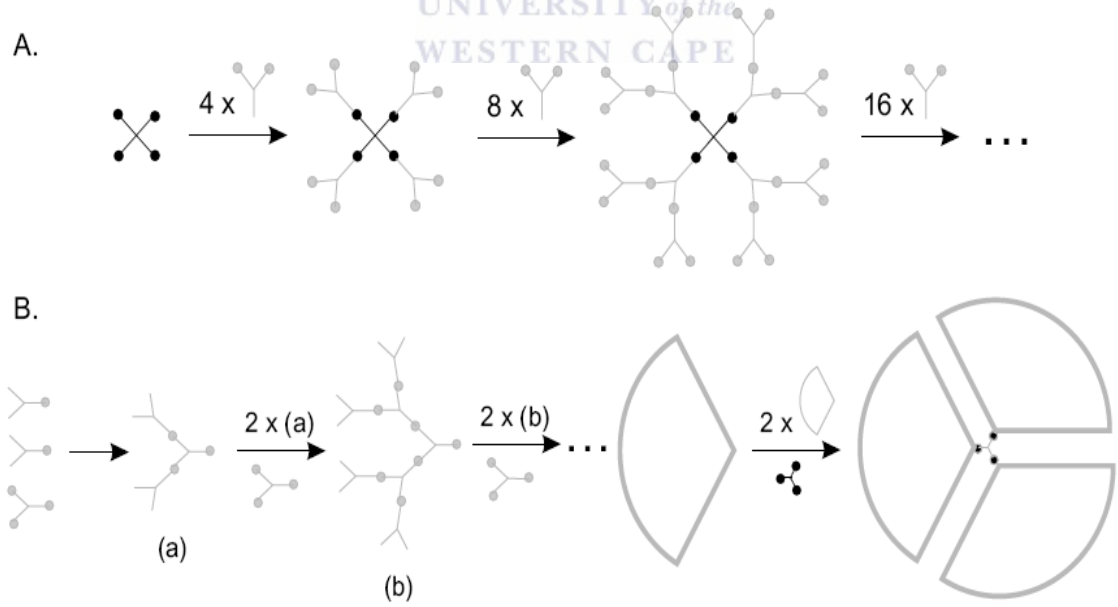


Figure 1.1 Diagram illustrating structure of a dendrimer [5]

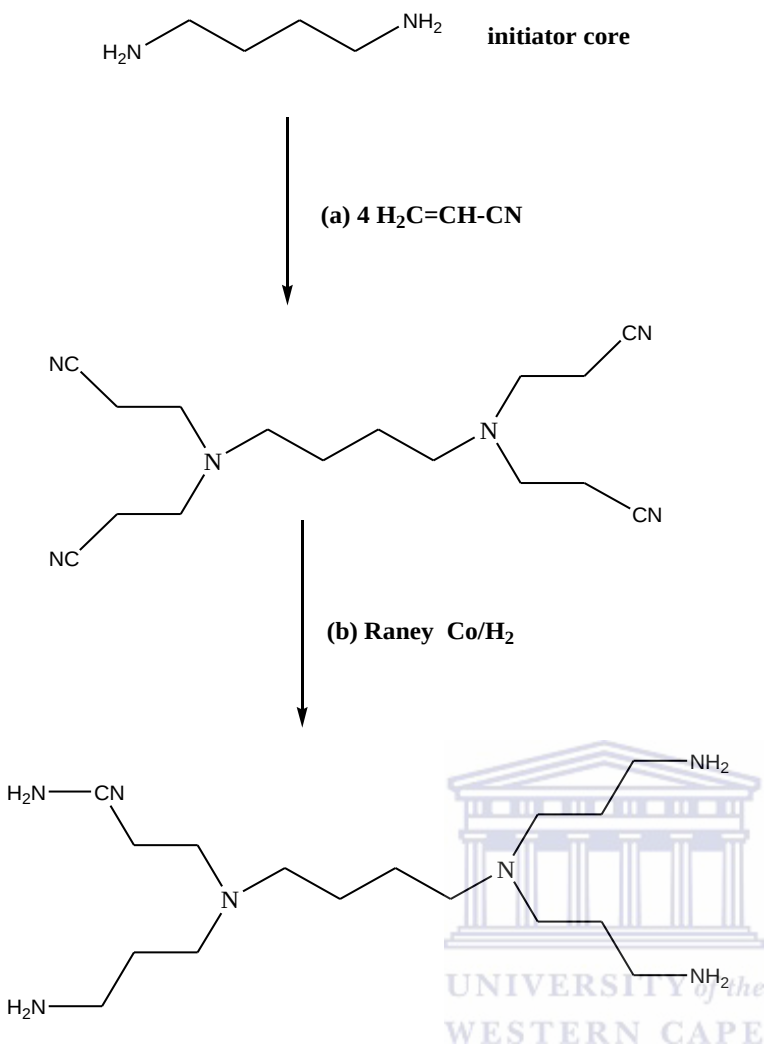
Dendrimers are generally prepared using either the divergent method or the convergent synthesis method [6] as shown in scheme 1.1. In the divergent method, the dendrimer grows outwards from a multifunctional core unit towards the dendrimer surface. The core reacts with monomer molecules containing one reactive and two dormant groups giving the first generation dendrimer. The new periphery of the molecule is then activated for subsequent reactions with more monomer. The process is repeated for several generations and a dendrimer is built up layer by layer. The maximum size or generation is governed by steric crowding at the periphery. The convergent methods were developed as a response to the short-comings of the divergent synthesis [7]. In the convergent approach, the dendrimer is constructed stepwise, starting from the periphery and progressing inwards towards the core. When the growing branched polymeric arms, called dendrons, are large enough, they are attached to a multifunctional core molecule.



Scheme 1.1 The divergent growth method (A), the convergent growth method (B) [6]

Dendrimers synthesized by either method contain defects, but the problem is less pronounced for materials prepared by the convergent method, because it has several advantages. The desired product is relatively easy to purify, because the impurities are very different in size from the fully assembled dendrimers and can therefore be easily removed by chromatography and the occurrence of defects in the final structure is minimised. It also becomes possible to introduce subtle engineering into the dendritic structure by precise placement of functional groups at the periphery of the macromolecule. However, this method does not allow the formation of high generations because of steric problems that occur in the reactions of the dendrons and the core molecule. Accordingly, the convergent approach is typically limited to the synthesis of generation 8 (G8) and lower dendrimers, while up to G10 dendrimers can be prepared through the divergent method [7].

Poly(propylene imine) (PPI) dendrimers are synthesized via the reaction sequence as shown in scheme 1.2. This repetitive reaction sequence involves a Michael addition of two equivalents of acrylonitrile to a primary amine, followed by hydrogenation of the nitrile groups to primary amines. The commercially available PPI dendrimers are usually terminated with amino groups.



Scheme 1.2 Preparation of DAB-G1 [7]

The first dendrimers were synthesized divergently by Vögtle in 1978 [8], Denkewalter and co-workers at Allied Corporation as polylysine dendrimers in 1981 [9], Tomalia at Dow Chemical in 1983 [10] and Newkome in 1985 [11]. In 1990, a convergent synthesis was introduced by Mingjun Liu [12]. Dendrimers then experienced an explosion of scientific interest because of their unique molecular architecture and this resulted in over 5,000 scientific papers and patents published by the end of 2005.

There is a variety of dendrimers based on silicon, nitrogen and phosphorus skeletons. The divergent route to silicon based dendrimers normally starts with tetra-allylsilane or

tetramethylcyclotetrasiloxanes as four directional centres of branching, and involves repetitive hydrosilylation and alkenylation reactions.

Advantages of dendrimers:

- They are perfectly defined macromolecules, i.e. their polydispersity is 1.00, and a number of dendritic generations can be constructed for a given series.
- They have a globular shape resulting in formidable encapsulation properties. In other words, their supramolecular properties are specific and well defined due to flexible design.
- They are able to achieve precise functions that are not accessible with polymers [13].

1.2 METALLODENDRIMERS

Dendrimers can be functionalized at the core, within the branches and at their terminal. As mentioned above, dendrimers consist of a central core and emanating from this are several branches leading to a number of successive, well-defined generations, the introduction of metal centres may occur at various branching points within the dendrimer or they may be found on the periphery of the dendritic molecule, creating different metallodendrimer topologies [14,15]. Dendrimers can therefore serve as supports for transition metal complexes.

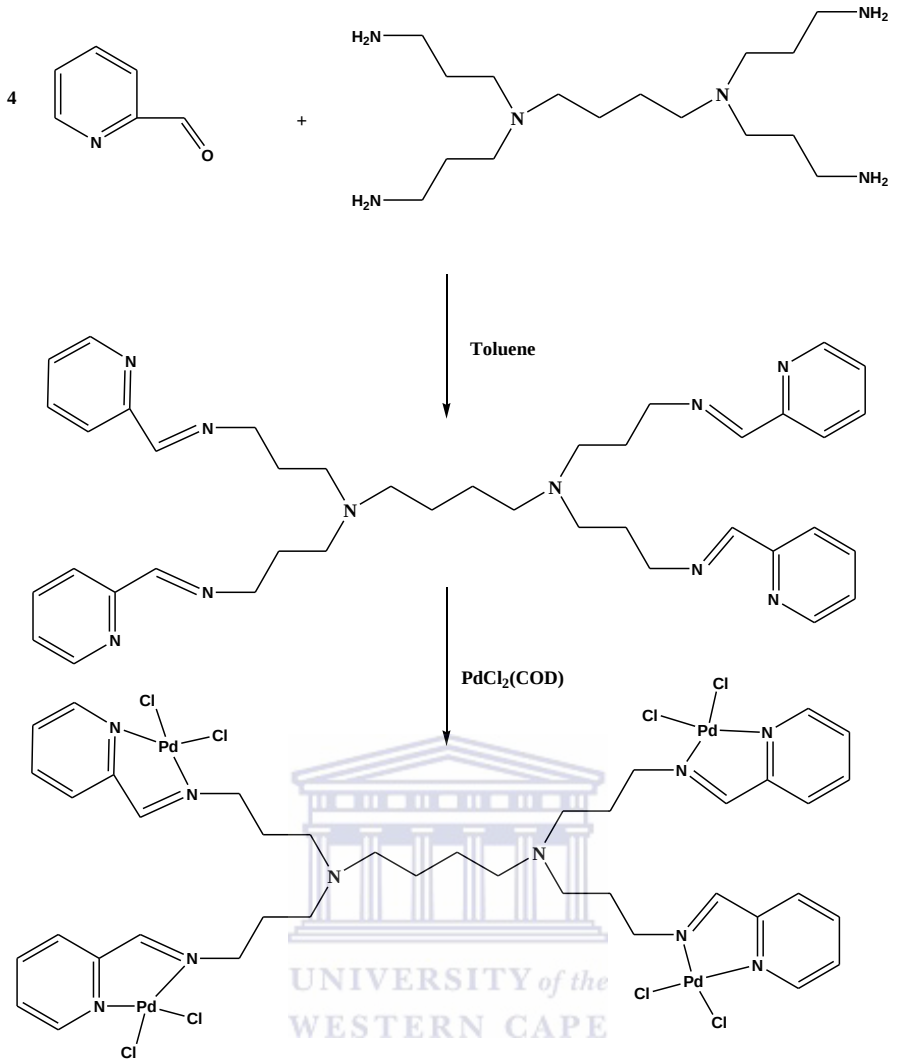
Incorporation of metal ions into the framework of the dendrimers was initiated by Balzani *et al*. [16] and Newkome *et al*. [17] in the early 1990s. The metals were introduced into the dendritic framework after construction of the dendrimer. The metals can be positioned at various points in the dendritic molecule *viz.* at the terminal units, the branching centres or the core, i.e. there are two means of introducing metal ions into dendrimers: either as structural

metal ions or as nonstructural metal ions [18]. Nonstructural interior metal ions can be reduced to yield dendrimer-encapsulated metal and semiconductor nanoparticles. Metallodendrimers are the principal focus of this chapter. Poly(amidoamine) (PAMAM) and poly(propylene imine) dendrimers, which are two commercially available families of dendrimers, are in many cases monodisperse in size. Accordingly, they have a generation-dependent number of interior tertiary amines. These are able to complex a range of metal ions including Cu^{2+}, Pd^{2+}, and Pt^{2+} [18]. The maximum number of metal ions that can be absorbed within the dendrimer interior depends on the nature of the metal ion, the dendrimer type, and the dendrimer generation. For example, a generation six PAMAM dendrimer can contain up to 64 Cu^{2+} ions. Nonstructural interior ions can be chemically reduced to yield dendrimer-encapsulated metal nanoparticles. As each dendrimer contains a specific number of ions, the resulting metal nanoparticles are in many cases of nearly monodisperse size. Nanoparticles within dendrimers are stabilized by the dendrimer framework; that is, the dendrimer first acts as a molecular template to prepare the metal nanoparticles and then as a stabilizer to prevent agglomeration. These composites are useful for a range of catalytic applications including hydrogenations and Heck chemistry [19].

There are three general categories of metal-ion-containing dendrimers. The first is composed of dendrimers that use metal ions as an integral part of their chemical structure. This includes, for example, dendrimers having an organometallic core and dendrimers that use metal ligation to assemble the dendrimeric branches into a complete dendrimer. The second type consists of dendrimers that have peripheral groups that are good ligands for metal ions. The surface functional groups of such dendrimers are usually distinct from the rest of the molecule, that is, they are added after the dendrimer has been synthesized. The third group of metal-ion-containing dendrimers contains internal ligands that result in the partitioning of the

metal into the dendritic interior. Most of the metal-ion containing dendrimers reported so far belong to the first and second types discussed above. These dendrimers are usually referred to as organometallic dendrimers.

The synthesis of metallodendrimers has in recent years, like the more linear metal-containing polymers, developed at a prolific rate. For example, a number of metallodendrimers based on poly(propylene imine) dendrimers with a diaminobutane core, [(DAB-$(NH_2)_n$] have been developed by Smith and Mapolie [20], where they have functionalized the periphery of DAB with [$PdCl_2$(COD)]. They were able to prepare first generation poly(propylene imine) pyridylimine palladium metallodendrimer (Scheme 1.3) and fully characterize the structures by ^{1}H-NMR, ^{13}C-NMR, IR spectroscopy and elemental analysis. This dendrimer was employed in ethylene oligomerization/polymerisation and Heck coupling reactions.



Scheme 1.3 Preparation of first generation pyridylimine palladium dendrimer [20]

Malgas-Enus *et al*. further reported multinuclear nickel complexes derived from (G1) and (G2) dendrimeric salicylaldimine ligands based on the poly(propylene imine) dendrimer scaffolds of the type, DAB-$(NH_2)_n$ (n = 4 or 8, DAB = diaminobutane) [21]. These complexes were evaluated as catalysts precursors in the polymerization of norbornene, using methylaluminoxane (MAO) as co-catalyst. All four catalysts evaluated were found to be active for norbornene polymerization giving polymers with moderate to high molecular weights and low polydispersity indices. The polymerization results indicate that there is some sort of dendritic effect, in that the catalyst activity appears to be influenced by the dendrimer

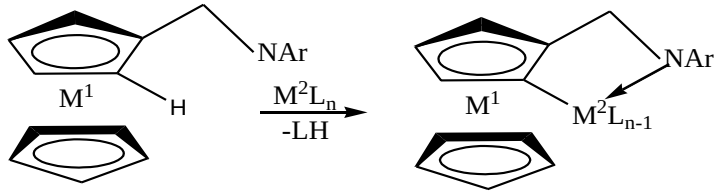
generation. In another report, Cuadrado and co-workers functionalized the periphery of DAB-$(NH_2)_n$ dendrimers with cobaltocenium moieties [22]. They were able to prepare the first four generations and fully characterize the structures by ^{1}H-NMR, ^{13}C-NMR and IR spectroscopy as well as elemental analysis. Electrochemical studies were also performed using cyclic voltammetry and these showed that the metal centres underwent reversible redox processes. The same group also previously incorporated ferrocenyl units onto the periphery of the same dendrimer system.

Benito *et al.* [23] recently reported a series of dendrimers containing nickel and palladium complexes with N,N′-pyridylimine ligands and found that the dendrimer generation affects the nature of the polymerization products. They recently, also synthesized and characterized new carbosilane dendrimers containing N,N′-pyridylimine complexes of molybdenum and platinum at their periphery. Related to this work, there are a few reports in the literature describing alkylpyridylimino palladium moieties bound to the periphery of poly(propylene imine) – also known as DAB – dendrimers or iron bis(imino)pyridyl-terminated carbosilane dendrimers [24]. Schultz *et al.* [25] studied poly(propylene imine) dendrimers with (E)-stilbene or (E,E)-1,4-distyrylbenzene chromophores attached to the four NH_2 groups of the first generation PPI and to the eight NH_2 groups of the second generation PPI. The DAB dendrimer employed as starting material has a diaminobutane core and amino group as termini. This compound was first synthesized by Meijer *et al*. in 1993 and is now commercially available [26].

1.3 INTRODUCTION TO FERROCENYLIMINES

The discovery of ferrocene marked a major milestone and turning point in the evolution of modern organometallic chemistry, and it not only renewed and expanded the concept of chemical bonds which inspired new fields in chemistry, but also laid a foundation for the widespread development of the chemistry of ferrocene and other metallocenes. The synthesis and isolation of ferrocene was first reported independently by two research groups, Kealy and Pauson from Duquesene University in late 1951 [27] and Miller *et al.* from British Oxygen Company in early 1952 [28].

A half century later, ferrocene chemistry has developed into one of the most fruitful fields in organometallic chemistry and still attracts a great deal of interest. One of the most exciting developments in this area over the last two decades is the cyclometallation of ferrocene derivatives. The cyclometallation reaction is defined as a chemical process involving chelation-controlled regioselective C-H bond activation of a ligand with a metallating reagent to form new C-M bonds as well as metallocycles. The cyclometallation of ferrocene and other metallocenes derivatives results in the formation of planar chiral cyclometallated metallocenes as shown in scheme 1.4 and this product distinguishes the reaction from the cyclometallation of any other type of ligands, and shows great potential in asymmetric synthesis.



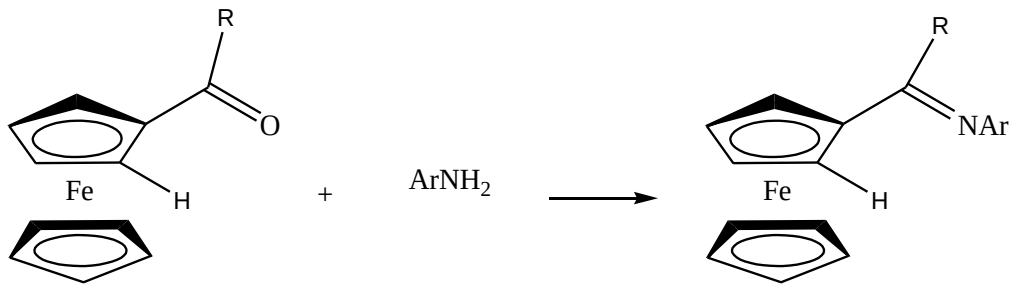
N= electron donating group
M^1= Fe, Ru, etc, M^2= Hg, Pd, Pt, etc.

Scheme 1.4 Cyclometallated metallocenes with planar chirality [67]

The chemistry of cyclometallated complexes has become one of the most advanced areas in organometallic chemistry as mentioned above. Since the first example of cyclopalladated metallocene that was reported by Alper in 1974, there has been considerable interest in the synthesis of cyclometallated ferrocene derivatives containing coordinating groups, especially nitrogen donor ligands, by direct cyclometallation with transition metals such as palladium, platinum and mercury [29]. The advantages of DAB core dendrimers could further be utilized by utilized by incorporating these ferrocenylimines at the periphery. Other ferrocenyl based precursors which could be significant are discussed below.

1.3.1 Schiff base type ferrocenylimines

Ferrocenylaldimines and ferrocenylketimines can generally be prepared by the direct condensation of acylferrocenes with amines. By using formylferrocene (**1**), acetylferrocene (**2**), and benzoylferrocene (**3**) together with amines (**4**) as starting materials, the corresponding ferrocenylaldimines (**4**) and ferrocenylketimine (**5**) and (**6**) can be prepared, (Scheme 1.5). Ferrocenylimines can be prepared under different reaction conditions. An example is the preparation of the ferrocenylketimine (**6)**. It was found that compound **6** existed as two isomers in solution (2D NOESY determination), with the *trans* isomer was present in 90%. The X-ray crystal structure of compound **6** disclosed a *trans* conformation, that is the ferrocenyl moiety and the *N*-phenyl ring lie on different sides of the C=N bond [30]. The interesting feature of this molecule is the specific arrangement of the two phenyl rings and the substituted Cp ring around the C=N plane. Other procedures have been also reported for the synthesis of similar ferrocenylimines [31-33], involving tedious multiple Dean–Stark condensation operations and/or the use of molecular sieves as promoters in some cases.



R= H (**1**), CH_3 (**2**), Ph (**3**)

R= H (**4**), CH_3 (**5**), Ph (**6**)

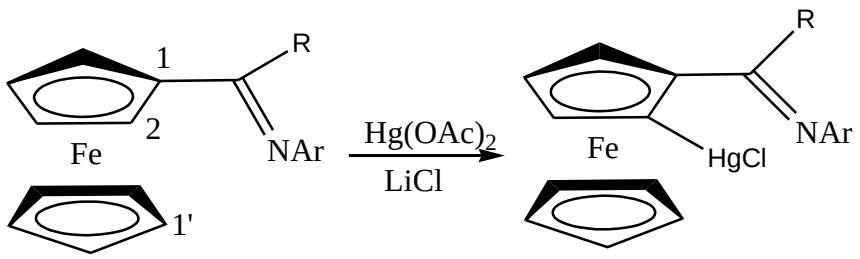
Scheme 1.5 Preparation of ferrocenylimines [30]

1.4 CYCLOMETALLATION OF FERROCENYLIMINES

1.4.1 Cyclomercuration of ferrocenylimines

Mercuration of ferrocene derivatives has been extensively investigated in organic and organometallic chemistry. Organomercury compounds are valuable intermediates for organic synthesis, thus permitting a variety of further transformations such as halogenation, transmetallation and C-C bond formation.

Mercuration is a generally mild reaction and the resultant organomercury compounds are very stable and easy to handle. This provides excellent opportunities to investigate the reaction mechanism, stereochemistry, and selectivity. Direct mercuration of substituted azobenzenes, phenylhydrazones and benzylideneanilines, has previously been reported. However, the development of cyclomercuration of ferrocenylimines appeared only recently [34-36]. The cyclomercuration of **4**–**6**, has been reported. The reaction of ferrocenylimines with mercuric acetate followed by subsequent treatment with lithium chloride proceeded smoothly to produce predominantly 2-chloromercurated ferrocenylimines (Scheme 1.6).

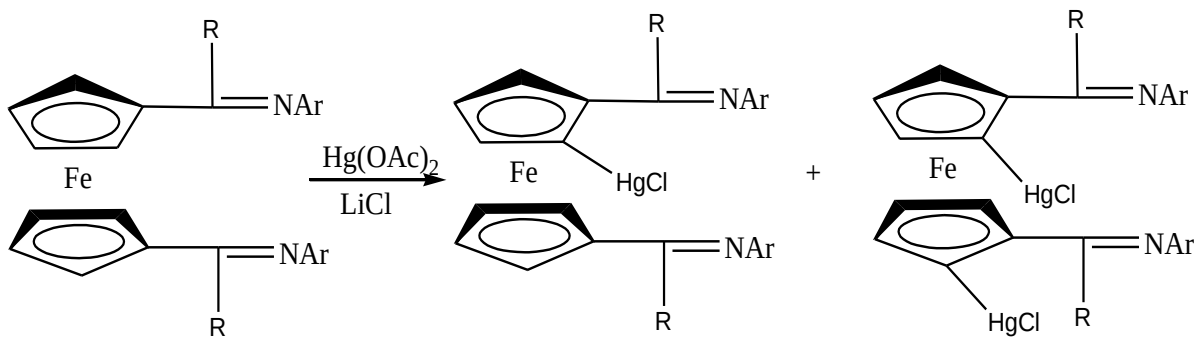


R= H (**4**), CH_3(**5**), Ph (**6**)

R= H (**7**), CH_3(**8**), Ph (**9**)

Scheme 1.6 Cyclomercuration of monoferrocenylimines [34]

It was observed that N-Hg intramolecular coordination played an important role in this reaction and that the effect of an aryliminomethyl group (ArN=CH-) on ferrocene can be twofold: steric and electronic. Electronically, this group will deactivate the substituted Cp ring towards electrophilic substitution, and sterically, this substituent can inhibit the attack at the 2′-position of the substituted Cp ring. Wu and co-workers [34] expected the mercuration of aryliminomethylferrocene should have occurred predominantly on the 1′-position due to the higher reactivity of the unsubstituted Cp ring. However, mercuration occurred predominantly on the 2′-position.The regiospecificity of this reaction suggested that mercury is directed into the *ortho*- position by coordination of mercury to the imino nitrogen with subsequent electrophilic substitution. The chromatographic and spectral properties of the 2-mercurated products showed the presence of an intramolecular N-Hg coordination *via* a five-membered ring in these molecules, and this was further confirmed by single-crystal X-ray structure analysis. Even the reaction of bisferrocenylimines with mercuric acetate and subsequent treatment with LiCl led to the formation of mono and double cyclomercurated derivatives [34-36] (Scheme 1.7).



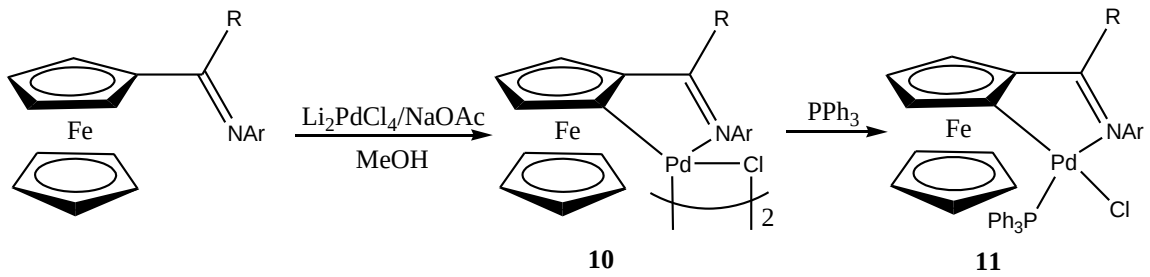
Scheme 1.7 Double cyclomercuration of bisferrocenylimines [34]

1.4.2 Cyclopalladation of ferrocenylimines

In the past ten years great effort has been made to achieve the synthesis of palladacycles having $[C, N, X]^-$ (X= N, O, P, S) groups, due to a wide variety of interesting and novel applications in different fields such as organic or organometallic synthesis and in the synthesis of polynuclear organometallic complexes. In addition these compounds have also found application in homogeneous catalysis and in chiral recognition or discrimination, mainly due to the potential hemilability of the σ(Pd-X) bond in these systems. Five-membered palladacycles with nitrogen donors have generated considerable interest because they are easily synthesized, thermally stable, insensitive to air, and show high activity for various coupling reactions. For example, it was reported that ortho-palladated imines are highly reactive in Heck and Suzuki reactions to afford quantitative yields with very high TONs as reported by Mu and co-workers. [37]. They prepared a series of novel amphiphilic ferrocenylimines as well as their cyclopalladated complexes which were thermally stable and insensitive to oxygen and moisture. These compounds displayed good activity in the Heck reactions of a variety of arylhalides with ethyl acrylate or styrene and in the Suzuki-Miyaura cross-coupling reaction of aryl bromides with phenylboronic acid in bulk solution.

The initial favourable results obtained with cyclomercuration of ferrocenylimines discussed later herein and the long-term interest in intramolecular coordination chemistry by researchers such as Wu and co-workers [38] prompted them to carry out the cyclometallation reaction via the use of transition metal complexes of Pd and Pt, as metallating reagents.

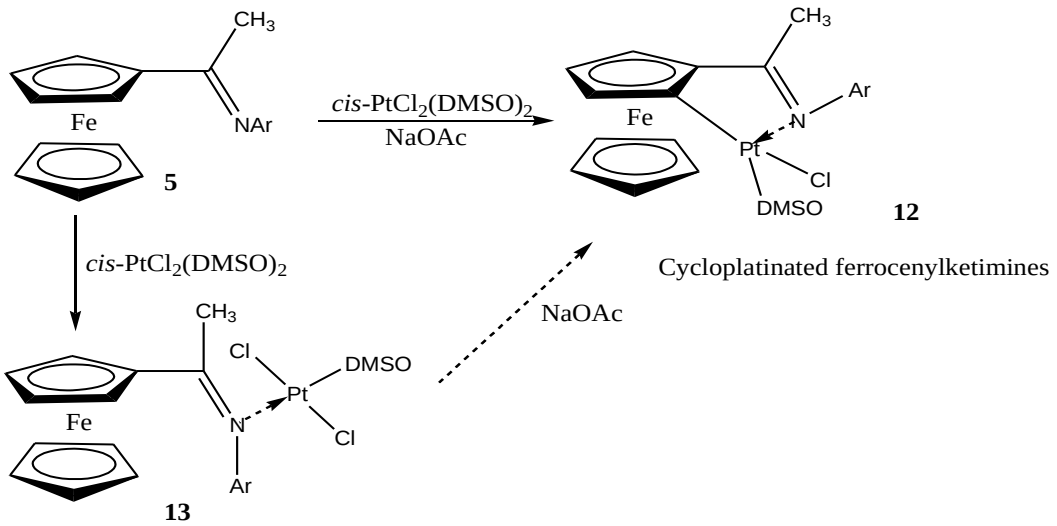
Duff *et al.* [39] have previously shown that an acetate ion promotes internal metallation reactions. It was further demonstrated that the acetate ion not only serves as an acid binding agent consuming the hydrogen chloride liberated in the cyclopalladation, but participates in the formation of the reaction transition state as well [40,41]. In addition, as expected Wu and co-workers also found that Schiff base type ferrocenylketimines such as **5** underwent cyclopalladation readily when treated with molar equivalents of Li_2PdCl_4 and NaOAc to produce a red crystalline solid, assigned to be a chloro-bridged binuclear palladium complex, **10**, which was converted into the monomeric derivative **11** quantitatively by treatment with triphenylphosphine as shown in scheme 1.8 [38]. It was also found that the reaction of **5** with Li_2PdCl_4 in the absence of NaOAc yielded a small amount of **10**, together with a considerable amount of the complex, $Cl_2Pd(PPh_3)_2$. The X-ray crystal structure of cyclopalladated ferrocenylimines indicated that the substituted Cp ring was palladated in an *ortho*-position and formed a five-membered metallocycle as expected.



Scheme 1.8 Cyclopalladation of ferrocenylimines [38]

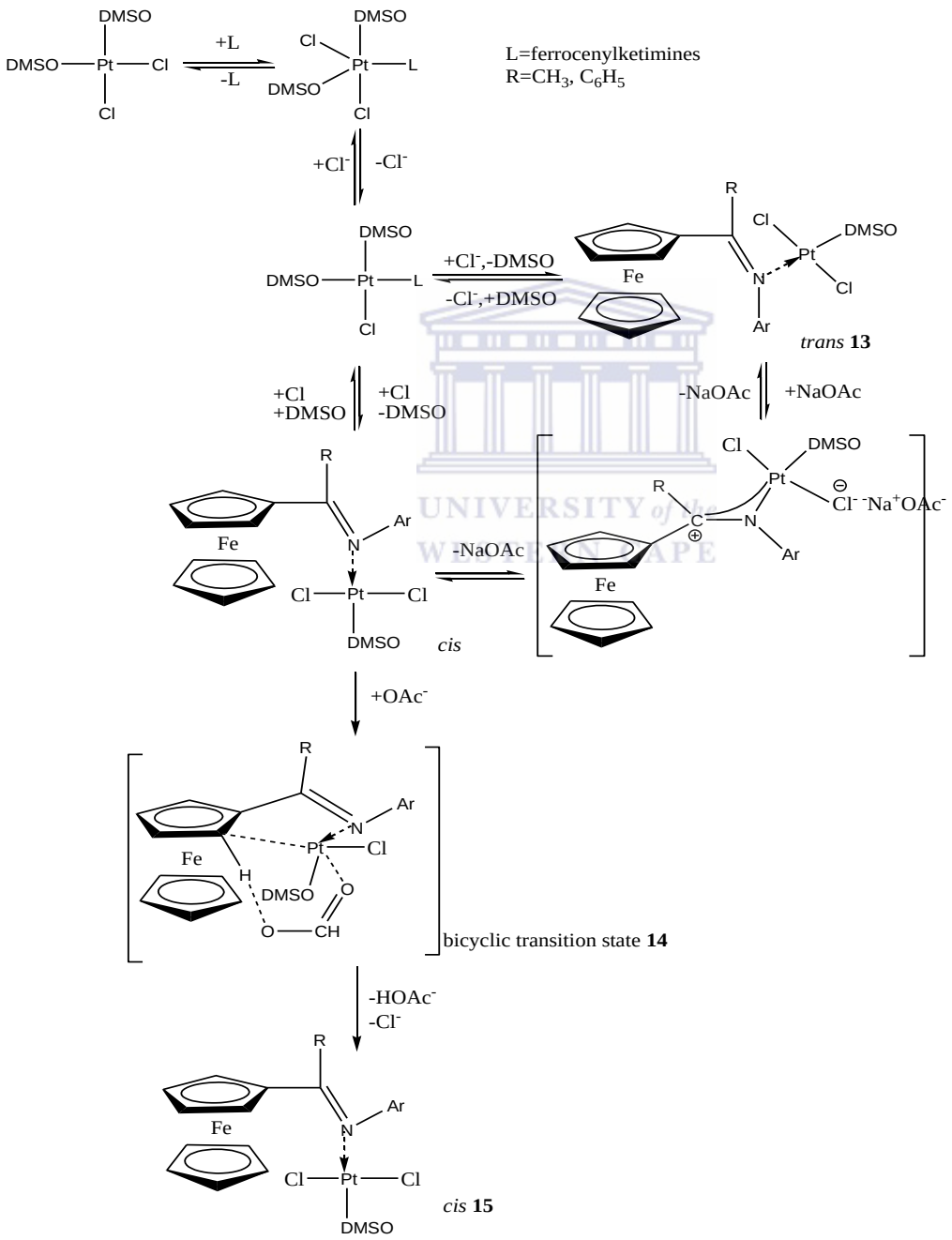
1.4.3 Cycloplatination of ferrocenylimines

In contrast to the intensive studies on intramolecular cyclomercuration and cyclopalladation, there are only a few examples concerning the cycloplatination of nitrogen-containing ferrocene derivatives. The first example of a cycloplatinatedferrocene derivative was synthesized by Sokolov and Troitskaya via transmetallation [42]. The direct cycloplatination of ferrocene derivatives was achieved by using the *cis*-$PtCl_2(DMSO)_2$ as the precursor [43-50]. The bis(hexafluoroacetylacetonato) platinum was also found to be a useful platination reagent for 2-ferrocenylbenzothiazoline to afford a novel trinuclear Pt(II) complex, which has a six-membered Pt_3S_3 ring with thiolate bridging [51]. However, the *cis*-$PtCl_2(DMSO)_2$ is still most commonly used in direct cycloplatination. The reaction of ferrocenylimine **5** with *cis*-$PtCl_2(DMSO)_2$ in the presence of NaOAc led to the cycloplatinated compounds **12** (Scheme 1.9). In the absence of NaOAc, however, the coordinated complex **13** was obtained. Several experimental examples have shown that **13** is a stable intermediate before ring closure. Scheme 1.10 shows the proposed mechanism of cycloplatination of ferrocenylimines.



Scheme 1.9 The reaction of ferrocenylimines **5** with *cis*-$PtCl_2(DMSO)_2$ [51]

The X-ray crystal structures show that the C=N bond adopts a *trans* configuration in complex **13**, as opposed to a *cis*-configuration in compound **15**. Therefore, a transition state, **14** might be involved in the conversion of **13** into **15**. Excellent linear correlations existed between ^{195}Pt chemical shifts and Hammett constants of the substituents on the N-phenyl rings in both **13** and **15**, suggesting the existence of N-Pt intramolecular coordination as well as n–π conjugation between the nitrogen and the N-phenyl ring.

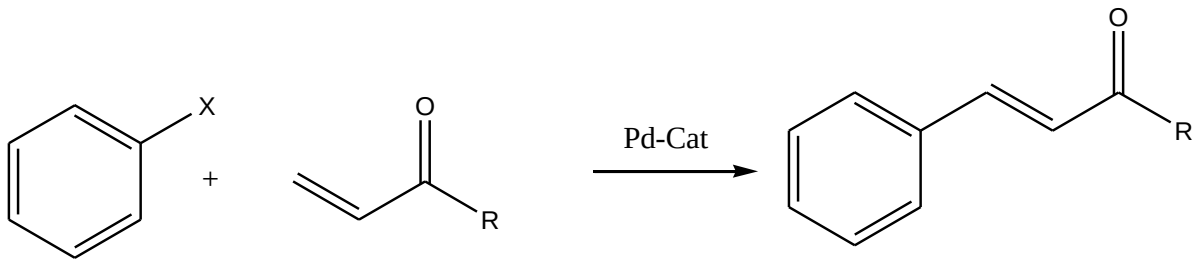


Scheme 1.10 Schematic diagram of cycloplatination [51]

1.5 APPLICATION OF PALLADIUM CATALYSTS TO C-C COUPLING REACTIONS

For the past thirty years, transition metal-catalyzed coupling reactions have experienced a renaissance since the first discovery of the Ullmann reaction a century ago. The metal complexes catalyzed cross-coupling reactions are probably the most popular synthetic methods for the formation of C-X (X: C, N, O, etc.) bonds in modern chemistry. Remarkable success in the application of this strategy has been well documented in the synthesis of numerous organic compounds. With various metals being employed in coupling reactions, palladium probably is the most frequently chosen transition metal mostly due to its excellent efficiency in this type of reaction [52]. We shall therefore only give a general overview of the application of the palladium based catalysts. The applications for Heck and Suzuki coupling reactions are described below.

1.5.1 Heck C-C coupling reactions

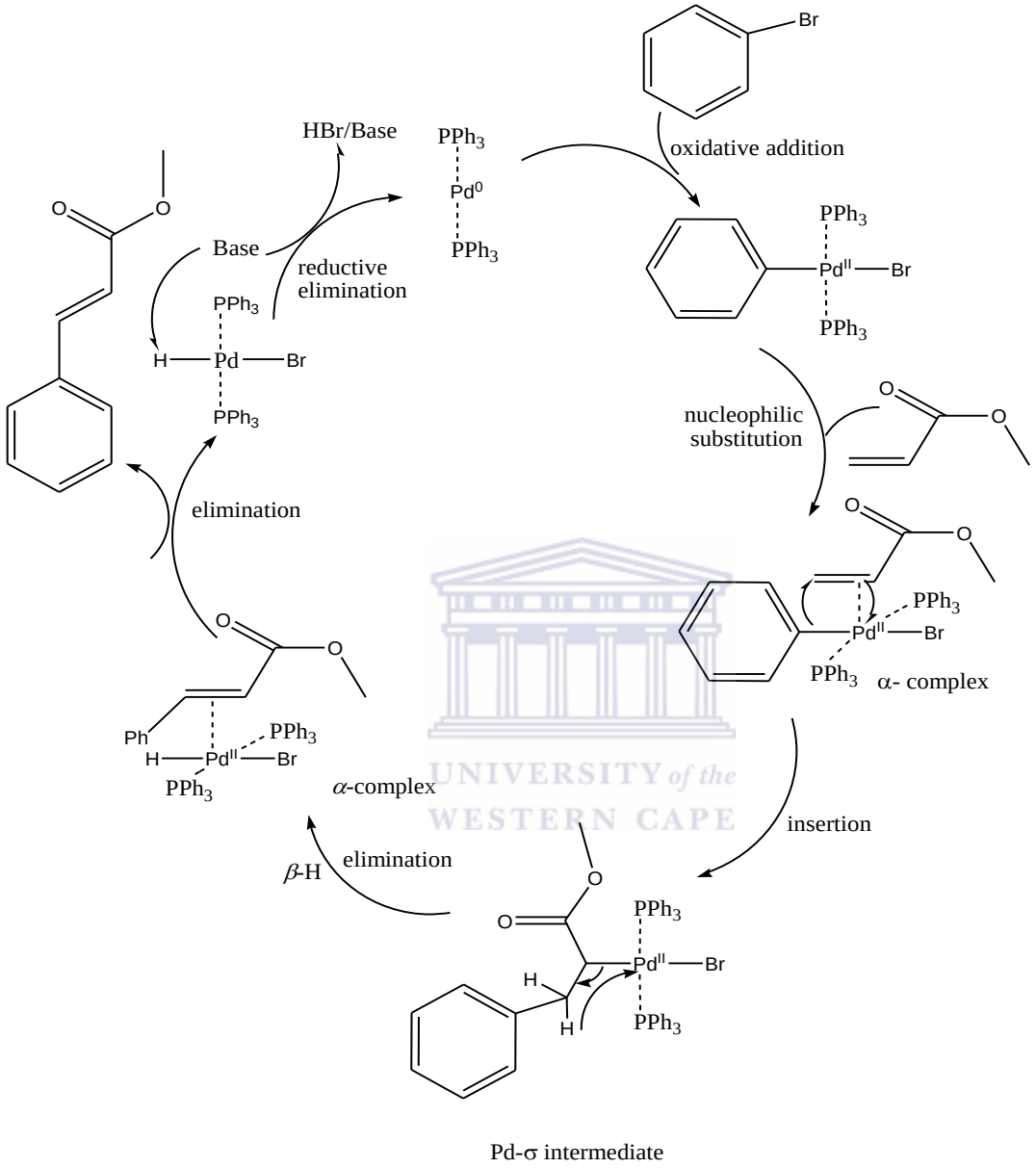


X= I or Br

Scheme 1.11 General method for Heck-coupling reactions [53]

The Heck coupling reaction is referred to as the palladium-catalyzed C-C coupling between aryl halides or vinyl halides and activated alkenes in the presence of a base. Recent developments in terms of the catalysts employed and reaction conditions used have resulted

in a much broader range of donors and acceptors being amenable to the Heck reaction. Below is a general mechanism for Heck-coupling reactions (Scheme 1.12) [53].



Scheme 1.12 Mechanism of the Heck reaction [53]

After being firstly discovered by Heck, who is amongst the winners of the Chemistry Nobel prize in 2010, the reaction has attracted considerable attention and various systems using palladium catalysts have been reported. Arylation of olefins by Heck coupling is an important synthetic method for the formation of carbon-carbon bonds. These reactions are usually

catalyzed by palladium catalysts. To generate the catalyst and quench the acid (HX) liberated during the reaction, various organic (Et_3N) or inorganic bases (K_2CO_3, Cs_2CO_3, NaOAc, K_3PO_4, Na_3PO_4) are employed [54]. Generally, two types of catalysts commonly employed are the coordination complexes of palladium salts such as $Pd(OAc)_2$ or $PdCl_2$ with ligands PPh_3 or PR_3 [55], as well as the cyclopalladium phosphine catalysts [56]. The use of nitrogen-containing catalysts in this reaction is still rare.

An example where nitrogen-containing catalysts are used for Heck coupling is that reported by Smith and Mapolie [20] based on (propylene imine)-iminopyridyl-palladium dendrimers, bearing palladium moieties on the periphery (Scheme 1.3). These complexes were found to be effective catalyst precursors for Heck coupling. The dendritic complexes achieved high conversions in the reaction of iodobenzene with methyl acrylate, styrene and 1-octene. Reactions with electron-deficient olefins yielded mainly β-arylated products, whilst electron-rich olefins yielded a mixture of arylated products (α, β), *cis*/*trans* isomers and β,β-disubstituted compounds. Generally, the metallodendrimer led to higher conversions and the reactions proceeded at a faster reaction rate, when compared to reactions using an analogous mononuclear palladium complex or the palladium salt, $PdCl_2$.

Palladacycles have also emerged over the last few years or so as a new family of palladium catalysts in carbon–carbon and carbon–heteroatom bond forming reactions. Wu and co-workers found novel kind of palladacyclic catalysts [67]. They have investigated their applications in catalytic reactions. In doing so, they developed a mild and efficient method for Heck-type reactions of arylboronic acids with olefins catalyzed by cyclopalladated ferrocenylimines. Their results represented the first examples involving the palladacycles as the catalysts for such coupling reactions.

1.5.2 Suzuki C-C coupling reactions

Suzuki cross coupling reactions are an extremely versatile methodology for the generation of carbon-carbon bonds [57]. This is a reaction of an aryl- or vinyl-boronic acid with an aryl-, vinyl- or an alkyl-halide catalyzed by palladium. It is widely used to synthesize styrenes and substituted biphenyls. The Suzuki reaction of aryl halides/triflates with boronic acids has been one of the most widely studied owing to its applicability and the low toxicity of the reagents [58]. There is currently much interest in the development of catalysts that can activate aryl chlorides since these substrates are cheaper and more readily available than the corresponding bromides and iodides [59].

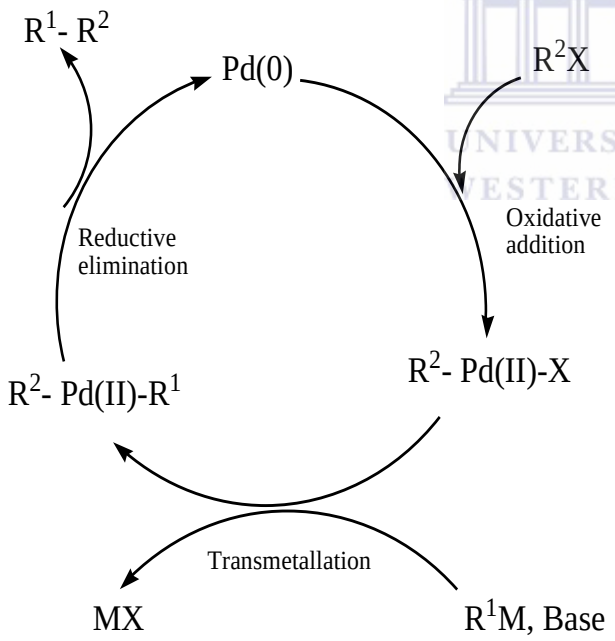
Moreover, palladacyclic catalysts are amongst the most active catalysts for forming carbon–carbon and carbon–heteroatom bonds [60-62]. A large number of phosphorus, nitrogen or sulfur based palladacycles derived from phosphines, phosphites, phosphinites, amines, imines, oximes or thioethers have been synthesized and used in the Suzuki reaction. The advantages of such palladacyclic catalysts include their ease of synthesis, facile modification and convenience of handling (insensitivity to air or moisture).

Reaction mechanism:

By analogy to the other cross coupling reactions, the catalytic cycle of the Suzuki coupling reaction involves three basic steps: 1) oxidative addition, 2) transmetallation and 3) reductive elimination. A general catalytic cycle for the Suzuki coupling reaction is given in scheme 1.13.

It is reported that the efficiency of palladium as catalysts originates from its ability to activate C-X bonds (X=I, Cl, Br, O), when it is zerovalent, by an oxidative addition step which provides an organopalladium(II) complex that will then be prone to react with nucleophiles.

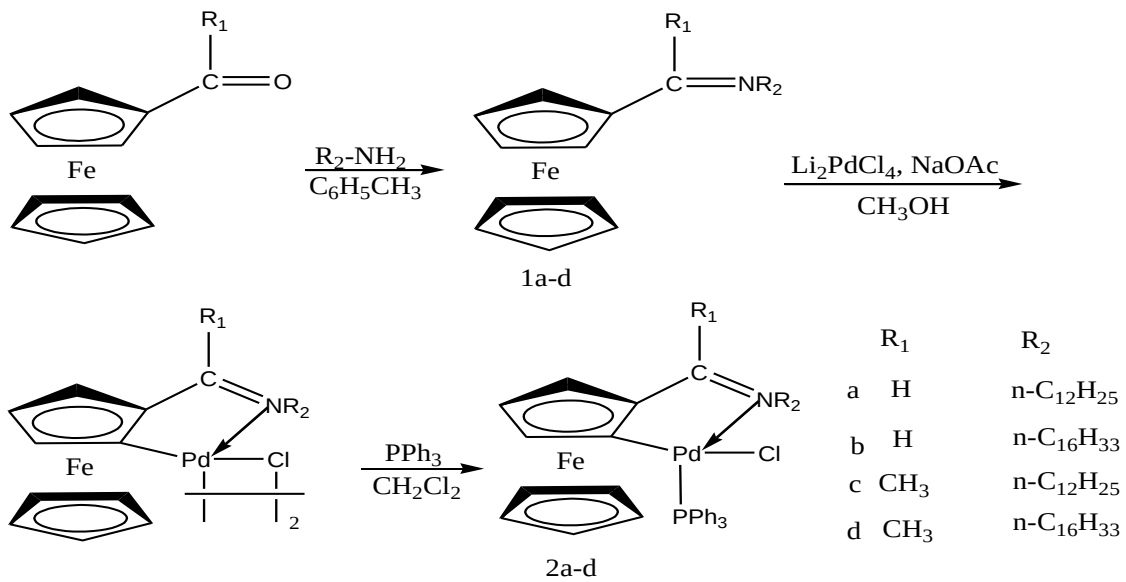
This step is often the rate limiting step in the catalytic cycle and a large variety of palladium(0) catalysts or precursors can be used for this reaction. For example, $[Pd(0)L_4]$ where L=phosphine is most commonly used since they are air stable. Palladium(II) complexes along with reducing agents are also used. The mechanism of the oxidative addition step is elucidated by means of electrochemical techniques (as the metal is oxidized) such as steady state voltammetry, transient voltammetry, cyclic voltammetry and reaction kinetics. The transmetallation step between the organopalladium(II) complex and the organoboron compound does not usually proceed in the absence of base due to the low nucleophilicity of organic groups on the boron atom with the next step which is the reductive elimination, takes place directly from the *cis* complex. The *trans* compound only reacts after its isomerization to the corresponding *cis*-complex.



Scheme 1.13 A general catalytic cycle for the Suzuki coupling reaction [63]

Most of the palladacycles show considerable activity with activated aryl chlorides but only limited activity with deactivated substrates [64]. It was recently reported, however, that

isolated or *in situ* formed secondary [65] or tertiary [66] phosphine adducts (L = $HP(tBu)_2$, $HPCy_2$ or PCy_3, $PtBu_3$) of dimeric phosphorus- or nitrogen-containing palladacycles (Scheme 1.14) efficiently promote the Suzuki coupling of both activated and deactivated aryl chlorides. Wu *et al.* investigated the cyclometallation of ferrocenylimines and applications of these systems [67]. They have found that cyclopalladated ferrocenylimines are effective for the Heck reaction [68] and the dimerization of arylmercurials [69]. These complexes also showed good activity in the Suzuki coupling reaction of aryl iodides and bromides with aryl boronic acids. In contrast, only activated aryl chlorides gave good results [70]. However only in very few cases have Suzuki coupling of sterically hindered substrates been investigated with palladacycles. Bedford *et al.* reported recently that phosphonito-based palladacycles in the presence of PCy_3 were efficient catalysts for the Suzuki coupling reactions of sterically hindered substrates [71] and Mu *et al.* [37] also reported amphiphilic cyclopalladated complexes that displayed good activity in the Suzuki–Miyaura cross-coupling reaction of aryl bromides with phenylboronic acid in bulk solution.



Scheme 1.14 Cyclometallated metallocenes with planar chirality [67]

1.6 CONCLUDING REMARKS

Dendrimers are well structured macromolecules with a wide range of uses including catalysis. Many derivatives of dendrimers have been prepared, among them monometallic and bimetallic in nature. Specifically, the DAB dendrimer has been recently investigated and reported to possess significant applications such as C-C coupling reactions. Most of the metal precursors were always easily identified by using the well-known characterization techniques of IR, $^{1}H/^{13}C$-NMR spectroscopy and elemental analysis. The mechanisms of these reactions are well established and are discussed in the literature.

The cyclomercuration [34], cyclopalladation [37] and cycloplatination [43-51] of some ferrocenylimines have been reported by several researchers as documented. From all the reports it was found that those reactions occur predominantly at the *ortho*-position of the substituted cyclopentadienyl (Cp) ring to afford the corresponding cyclomercurated and cyclopalladated derivatives. All these complexes were applied in C-C coupling reactions, in one way or another. The notable usage was Heck [44] and Suzuki [71] coupling reactions as well as polymerization. In the reported reactions, none of them had the ferrocenylimine anchored on the DAB-periphery. Therefore, on the basis of these findings, the aims and objectives of our study are outlined below.

1.7 AIMS AND OBJECTIVES OF THE STUDY

A number of metallodendrimers based on poly(propylene imine) dendrimers with a diaminobutane core [DAB-$(NH_2)_n$] have previously been reported. They have been successfully used in the oligomerization/polymerization of alkenes as well as Heck and Suzuki coupling reactions [1-2]. The aim of the study is to prepare metallodendrimers and test their potential as catalysts for Heck C-C coupling reactions.

The objectives of this study were as follows:

- To prepare Schiff base ligands including ferrocenylimines via condensation reaction of the appropriate aldehydes/ketones with a range of amines including monofunctional, bifunctional and dendritic amines.
- To react the imines with palladium salts to obtain the desired palladium-imine complexes.
- To characterize the complexes using fourier transfer infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), mass spectrometry and Elemental Analysis.
- To evaluate the prepared complexes for their potential as catalysts in Heck coupling of arylhalides and styrene.

The remaining chapters of this thesis report on the preparation of ligands and complexes (Chapter 2) and the preliminary catalysis results (Chapter 3).

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CHAPTER 2:

SYNTHESIS AND CHARACTERIZATION OF IMINE LIGANDS AND THEIR PALLADIUM COMPLEXES

2.1 INTRODUCTION

2.1.1 Ferrocenyl-containing dendrimers

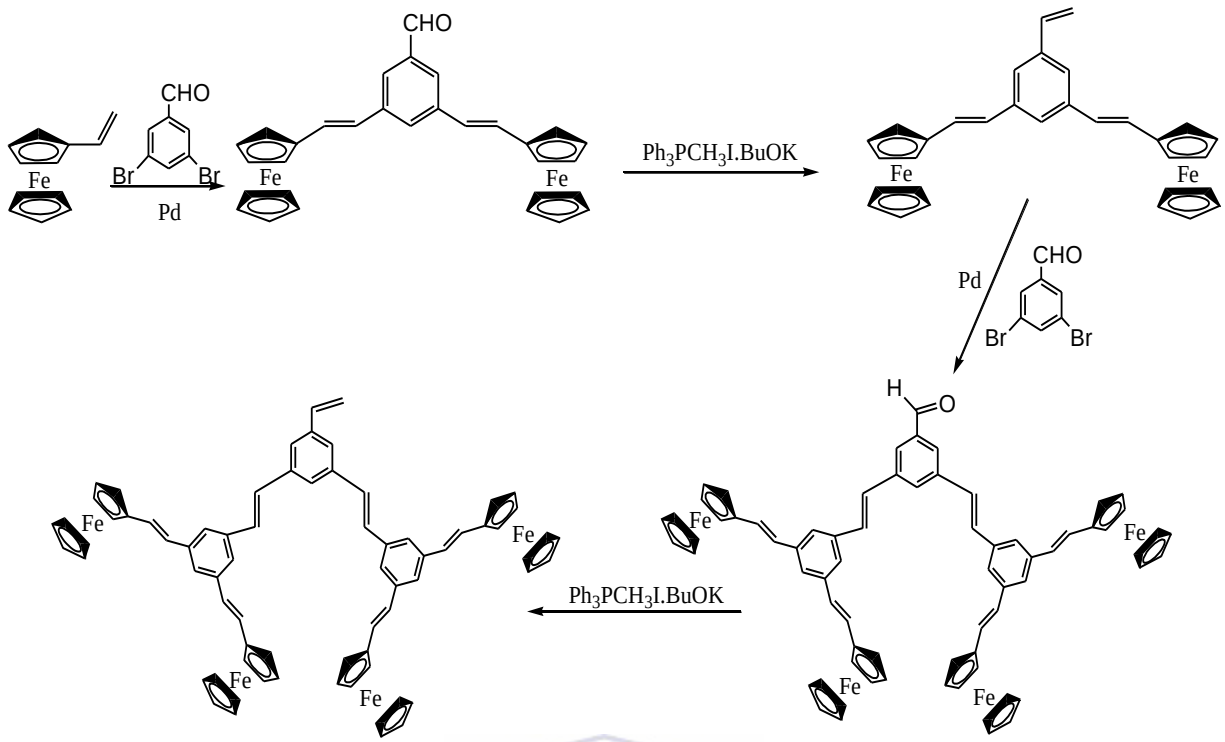
Over the last three decades, much attention has been devoted to the chemistry of ferrocenyl complexes since ferrocene combine together chemical versatility with high thermal stability properties. These properties, together with the exceptional electrochemical properties of ferrocene, make ferrocene-based complexes good compounds for the preparation of new materials with applications in organic synthesis[1], catalysis [2] and materials science [3]. Combining two or more ferrocenyl fragments together connect to give compounds with linked ferrocenes which could lead to even more interesting materials of intercommunication, since intermetallic electronic communication could afford a wide range of new applications. Thus many studies have been undertaken regarding intramolecular electron-exchange reactions and are reported [3-6].

Metal-containing long-chain conjugated systems have emerged as an important category of materials. The impetus for developing these materials is based on the premise that conjugated chains containing metals are expected to possess properties significantly different from those of conventional organic conjugated oligomers. Examples of these properties include: electrical conductivity, magnetic behaviour, thermal stability, nonlinear optical (NLO) effects, and even superconductivity. Because of the special electronic and chemical properties of ferrocene, many efforts have been directed towards the incorporation of a ferrocene moiety into a polymer [1,2] in order to investigate novel properties such as those mentioned above. Although there have been many studies reported where metallocene-containing long-chained conjugated systems have been obtained [3,6], there is still a lack of systematic description of

syntheses leading to useful starting materials. In fact, the bottleneck to the development of organometallic push–pull oligomers is the lack of systematic approaches to the syntheses of long-chained conjugated systems. All the metal-containing polymers that have been reported have in common the fact that they are only conducting if charge carriers can be delocalized over both the metal and the organic fragments. In this regard, Peris and co-workers focused their attention on the fabrication, characterization and study of several types of ferrocene-containing conjugated oligomers, paying special attention to the relation between their chemical structures and physical properties [7].

One of the richest areas of metallocene chemistry has been that of linked metallocenes [3]. Much of the interest in these species is concerned with the interaction between metal centres. Many studies have been conducted during the last decade, regarding intramolecular electron-exchange reactions [3–6] and the number of papers devoted to describe the synthesis and electronic properties of new polymetallocenyl compounds has grown enormously in the last few years [5].

Peris [7] described several phenyl-ethenylferrocenyl containing oligomers, especially with (i) pendant electron-accepting groups (nitro, pyridine, nitrile and heterometallic complexes derived from the coordination of the two latter terminations), (ii) linked ferrocenes, and (iii) two-dimensional star-shaped structures (or metallodendrimers). It was established that Pd-mediated C=C bond formation is an effective method for the synthesis of conjugated ferrocenyldendrimers and can be extended to the design of higher generation dendrimers (Scheme 2.1).

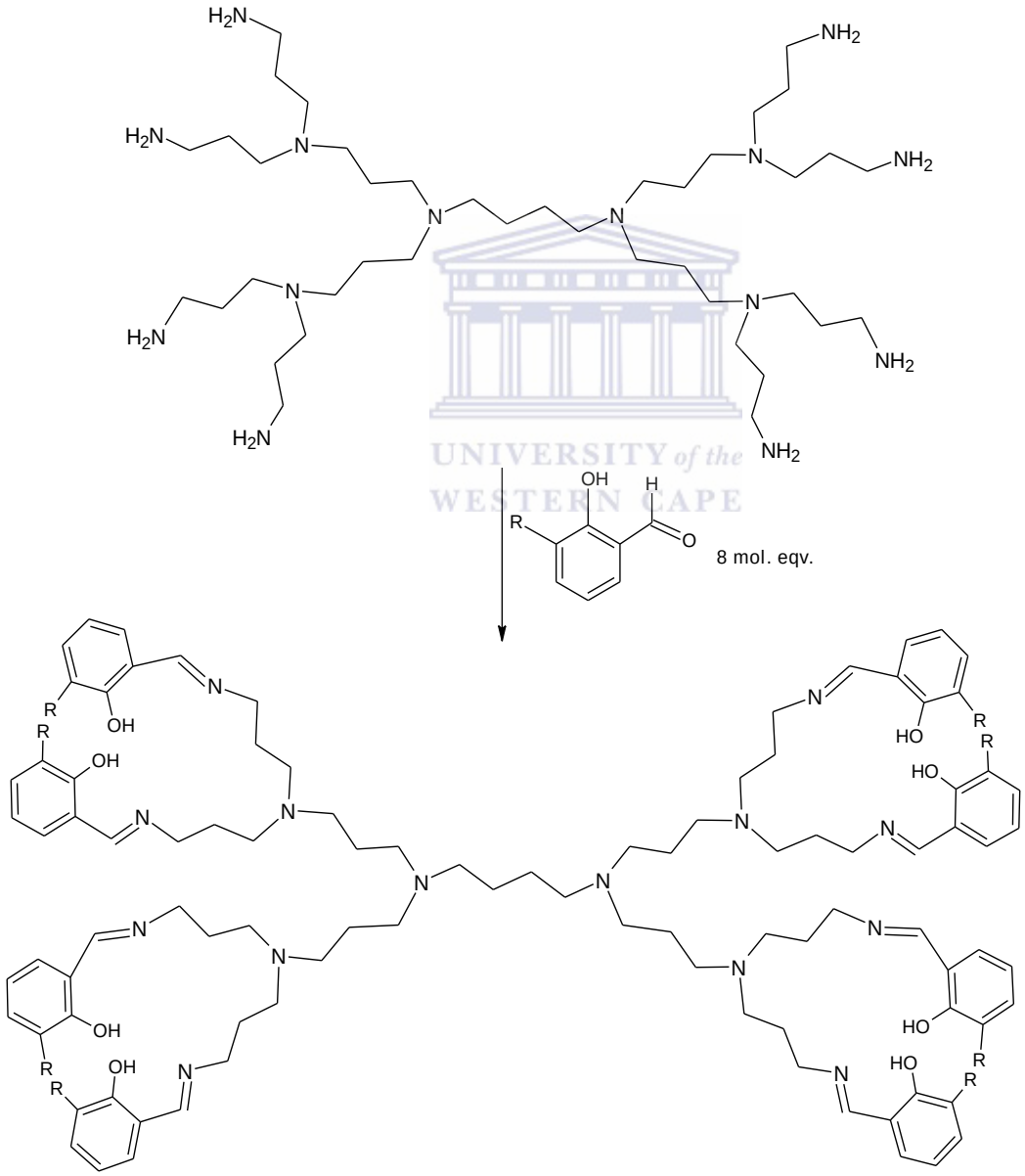


Scheme 2.1 Synthetic route to ferrocenyl-containing dendrimers [7]

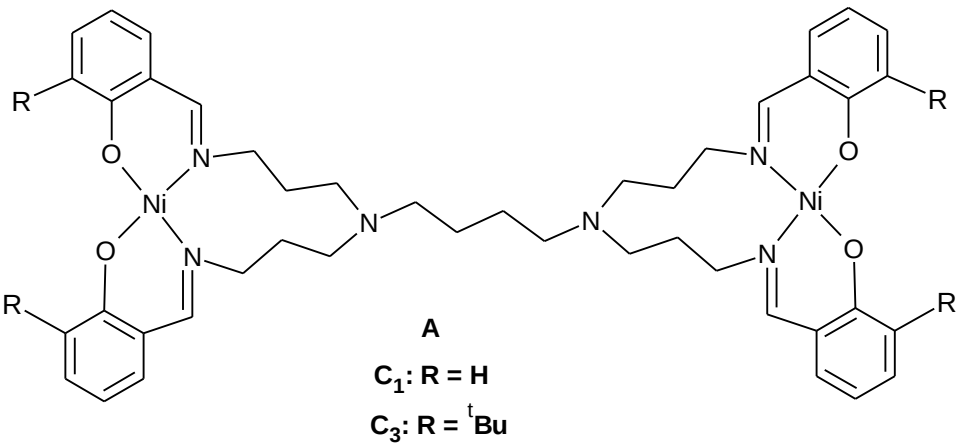
2.1.2 Iminopyridyl-containing dendrimers

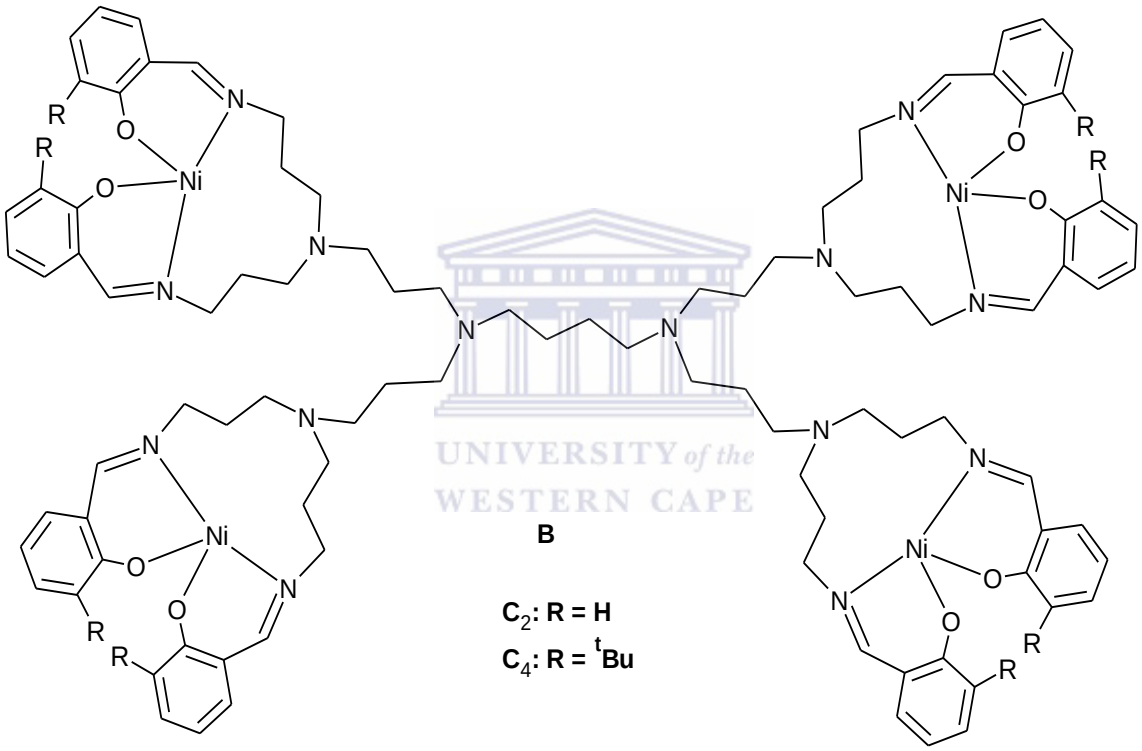
A large number of metallodendrimers are now known and numerous reviews on the application of dendrimers in catalytic reactions have been published [8]. Various examples of dendritic scaffolds have been used to immobilize homogeneous catalysts, including carbosilanes [9], polyamidoamines [10], poly(propylene imine)s [11] and polyarylethers [12], to name a few. More pertinent to our research are poly(propylene imine) dendrimers, and particularly to this study, the peripheral functionalization of this scaffold with palladium complexes.

Examples of such palladium complexes have been reported in the literature. Malgas-Enus *et al*. developed four multinuclear nickel complexes derived from generation 1 (G1) and generation 2 (G2) dendrimeric salicylaldimine ligands based poly(propylene imine) dendrimer scaffolds of the type, DAB-$(NH_2)_n$ (n = 4 or 8, DAB = diaminobutane) (Scheme 2.2 and Scheme 2.3) [13]. The Ni catalysts based on these dendrimers were found to be active for norbornene polymerization giving polymers with moderate to high molecular weights and with low polydispersity indices.



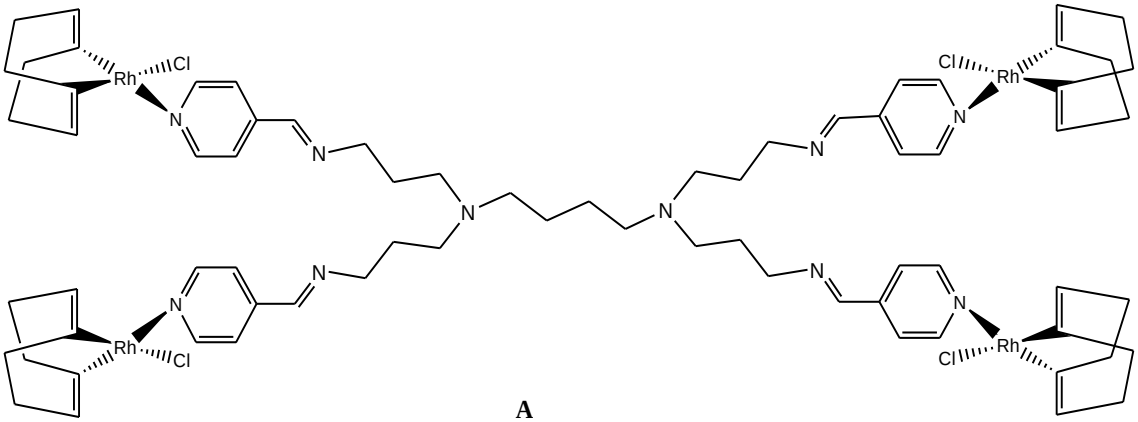
Scheme 2.2 Synthetic method to dendrimeric salicylaldimine ligands [13]



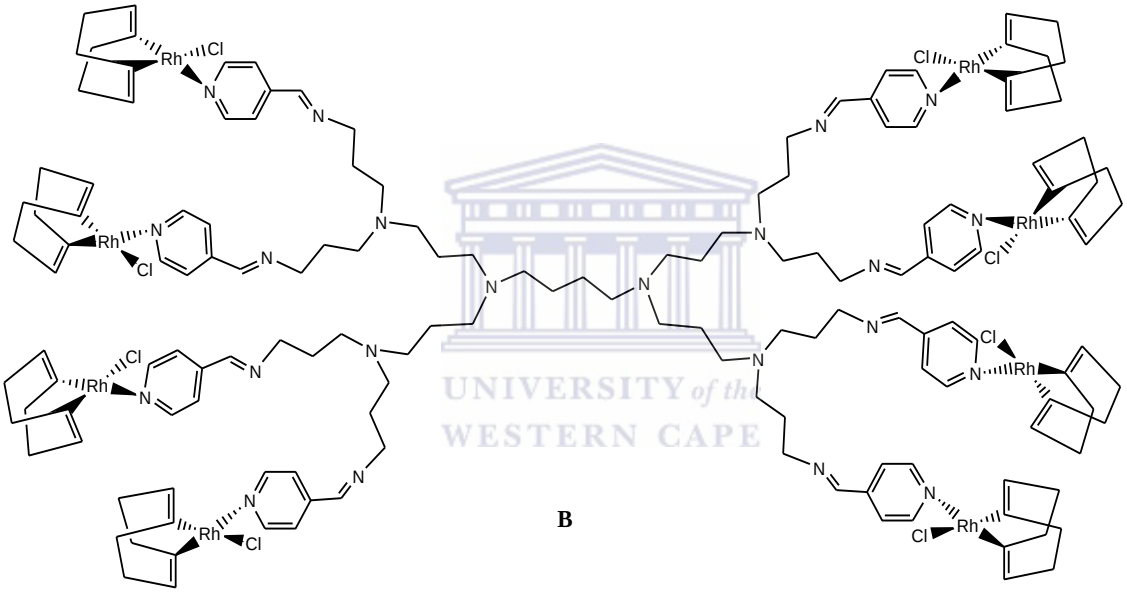


Scheme 2.3 Synthetic method to G1 (A) and G2 (B) dendrimeric salicylaldimine nickel complexes [13]

Most recently, Antonels *et al.* synthesized the first and second generation rhodium(I) poly(propylene imine) metallodendrimers, containing monodentate iminopyridyl units (Scheme 2.4) [14].



A



B

Scheme 2.4 Tetra- (A) and octanuclear (B) rhodium(I) iminopyridyl complexes [14]

Based on the literature, a number of syntheses were carried out to achieve the aim and objectives of this research project.

2.2 EXPERIMENTAL PROCEDURE

2.2.1 Materials and Instruments

All reactions were carried out using a dual vacuum/nitrogen line and standard Schlenk techniques, unless stated otherwise. All solvents were dried over the appropriate drying agent and distilled prior to use. Toluene was dried over sodium benzophenone and distilled under nitrogen prior to use. Dichloromethane was dried over phosphorus pentoxide and distilled under nitrogen prior to use. Acetonitrile and hexane were dried over calcium hydride and distilled under nitrogen prior to use. Methanol was dried over magnesium turnings and iodine and distilled under nitrogen prior to use. DAB-amine dendrimer (generation 1 and 2), ferrocenecarboxaldehyde, 2-pyridinecarboxyaldehyde, 6-methyl-2-pyridinecarboxaldehyde, quinoline-2-carboxaldehyde, acetylferrocene, benzoylferrocene, styrene, iodobenzene, 1,5-cyclooctadiene, $PdCl_2$ and were obtained from Sigma Aldrich, and were used without any further purification. $PdCl_2$(COD) [15] and $PdCl_2(MeCN)_2$ [16] were prepared by following literature methods. The silica gel (70-230 Mesh) used for chromatography was dried in the oven prior to use. Anhydrous $MgSO_4$ was used as the dehydrating agent. Complex **C5** was obtained from Prof S.F Mapolie's research laboratory (University of Stellenbosch) and was used without further purification.

The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian XR200 (200 MHz) spectrometer, using tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin–Elmer Precisely Spectrum-100 FTIR spectrometer, using ATR. Microanalyses were performed on a Server 1112 Series Elemental analyzer by the Microanalytical Laboratory of the University Of Cape Town, South Africa. ESI-MS analyses were carried out at the University of Stellenbosch, South Africa. Melting points were recorded on a Stuart

SMP melting point apparatus using open capillaries and are uncorrected. GC analyses were performed on an Angilent Technologies 7890A GC system using Agilent 19091J-413: 325 °C: 30 m x 320 µm x 0.25 µm HP-5 5% Phenyl Methyl Siloxan: HP-5 column.

Oven programmed: 50 °C for 1 min, then 15 °C/min to 133 °C for 12 min, then 5 °C/min to 138 °C for 3 min, then 10 °C/min to 200 °C for 8 min. Post run temperature 40 °C.

Injection vol (1 µL), DCM vol (8 µL). Heater 250 °C, Pressure 90.389 kPa, Total flow 66 mL/min, Septum purge flow 3 mL/min. Gas saver 20 mL/min after 2 min.

2.2.2 Preparation of ferrocenylimine ligands

2.2.2.1 Preparation of N,N′-bis(ferrocenyl)propyl-1,3-diimine ligand, L1

L1 was prepared by a procedure reported by Mu *et al.* [20]. A Schlenk tube was charged with dried toluene (30 mL). Anhydrous $MgSO_4$ (~3g) was transferred to the tube containing toluene and the mixture stirred at room temperature. Ferrocenecarboxaldehyde (0.27 g; 1.26 mmol) was added to the flask and the mixture was stirred at room temperature. A solution of 1,3-diaminopropane (0.05 g; 0.63 mmol) in toluene (5 mL) was added dropwise to the stirring mixture of the aldehyde and $MgSO_4$. The reaction mixture was then allowed to reflux under nitrogen for 6 h. In order to follow the progress of the condensation reaction, the infrared spectra of the solution was recorded every 30 min. After the reaction was judged to be complete (i.e. after 12 h), it was stopped and the reaction mixture allowed to cool to room temperature. The mixture was carefully filtered through Celite to remove $MgSO_4$ and the filtrate was brought to dryness under vacuum. An orange solid obtained (Yield, 73%). ^{1}H-NMR (200 MHz, in $CDCl_3$): δ = 2.00 (m, H-1, J = 7.6 Hz); 3.53 (t, H-2, J = 7 Hz); 4.18 (s, H-6); 4.37 (pseudo t, H-4, J = 1.8 Hz), 4.64 (pseudo t, H-5, J = 1.8 Hz); 8.15 ppm (s, H-3). (Scheme 2.5 used for numbering system).^{13}C {^{1}H}-NMR (in $CDCl_3$): δ =161.1, 91.2, 80.8, 70.3, 69.5, 69.1, 68.4, 68.3, 67.7, 66.3, 59.5, 45.9, 28.1 ppm. IR: ν=1644.8, cm^{-1} (C=N).

Anal. Calc. for $C_{25}H_{26}Fe_2N_2$: C, 64.42; H, 5.58; N, 6.02; [M^+], m/z = 466.8441. Found: C, 63.33; H, 5.64; N, 6.47; [M^+], 467.0881. Melting point: 130-135 ^oC.

2.2.2.2 Preparation of DAB-Fc ligand, L2

DAB-Fc ligand was synthesized similarly to the ligand **L1**. A mixture of ferrocenecarboxaldehyde (0.25 g; 1.17 mmol) and DAB-4-amine (0.10 g; 0.30 mmol) was dissolved in 60 mL of dry toluene and refluxed under nitrogen in the presence of $MgSO_4$ (~5.0 g). The yellow reaction mixture was allowed to reflux under nitrogen for 18 h. The yellow solid obtained (66% yield). ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.61 (br m, 4H, H-1′, J = 7.6 Hz); 2.17 (qn, 8H, H-1); 2.35 (br t, 4H, H-2′, J = 6.6 Hz); 2. 49 (t, 8H, H-3′, J = 7 Hz); 3.46 (t, 8H, H-2, J = 7 Hz); 4.17 (s, 5H, H-6); 4.35 (pseudo t, 2H, H-7, J = 1.8 Hz); 4.62 (pseudo t, 2H, H-5, J = 1.8 Hz); 8.08 (s, 4H, H-3). (Scheme 2.5 used for numbering system).^{13}C-NMR ($CDCl_3$): δ = 25.1, 28.4, 51.9, 54.1, 60.1 ($CH_{2,\ aliphatic}$); 70.2 (C3 and C4 of subst. Cp ring), 69.0 (C of unsubst. Cp ring), 69.6 (C2 and C5 of subst. Cp ring), 160.8 (CH_{imine}). IR: ν=1644.8, cm^{-1} (C=N). Anal. Calc. for $C_{60}H_{72}Fe_4N_6$: C, 65.48; H, 6.59; N, 7.64; [M^+], m/z = 1220.1103. Found: C, 62.42; H, 6.95; N, 7.27; [M^+], 1221.5331. Melting point: 150-155 ^oC.

2.2.3 Preparation of G1/G2 poly (propylene imine) dendrimeric ligands

2.2.3.1 Preparation of G1 poly (propylene imine) dendrimeric ligand, L3

The ligand was prepared by using reported procedures by Malgas *et al.* [13,17] and Smith *et al.* [18,19]. A 100 mL Schlenk tube was charged with nitrogen gas followed by 15 mL of dry toluene and 3 g of anhydrous $MgSO_4$. Then 2-pyridinecarboxyaldehyde (0.23 g, 2.17 mmol) was dissolved into the toluene by stirring at room temperature for 5 minutes. A sample of

DAB-dendr-$(NH_2)_4$, generation one (0.18 g, 0.56 mmol) was dissolved in dry toluene (10 mL). This colourless solution was added to the stirring solution of the aldehyde and $MgSO_4$ by means of a syringe. The colourless mixture was allowed to stir at room temperature for 2 days. The mixture was filtered by gravity and the solvent was removed by rotary evaporator leaving colourless oil. The product was then dissolved in dry DCM (10 mL) and washed with de-ionised water (7 x 30 mL) to remove any unreacted DAB. The organic layer was separated, dried over anhydrous $MgSO_4$ and the later filtered by gravity. The ligand **L3** was obtained as yellow oil. Yield = 71%. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.4 (br m, 4H, H-1, J = 5.8 Hz); 2.42 (t, 4H, H-2, J = 6.6 Hz); 2.53 (t, 8H, H-3, J = 6.6 Hz); 1.85 (qn, 8H, H-4, J = 5.8 Hz); 3.68 (t, 8H, H-5, J = 6.6 Hz); 8.36 (s, 4H, J = H-6); 8.97 (d, 4H, H-8, J = 8.5 Hz); 7.71 (t, 4H, H-9, J = 6.6); 7.29 (t, 4H, H-10, J = 6.6 Hz); 8.63 (d, 3H, H-11, J = 8.5 Hz). (Scheme 2.9 used for numbering system). ^{13}C-NMR ($CDCl_3$): δ = 25.0, 22.7, 25.5, 28.6, 52.1, 54.4, 60.0, 162.2, 121.6, 124.9, 136.8, 150.0, 155.0. IR: ν=1648 cm^{-1} (C=N).Anal. Calc. for $C_{40}H_{52}N_{10}$: C, 69.62; H, 7.93, N 20.13; [M$^+$], m/z = 672.80. Found: C, 69.61; H, 8.13; N, 20.58; [M$^+$], m/z = 673.4742.

2.2.3.2 Preparation of G1 poly (propylene imine) dendrimeric ligand, L4

L4 was prepared by using a similar procedure used for the preparation of **L3**. The starting materials used were an appropriate amount of quinoline-2-carbaldehyde (0.34 g, 2.17 mmol) and a sample of DAB-dendr-$(NH_2)_4$ generation 1 (0.18g, 0.56mmol). In a similar way, **L4** was obtained as a yellow. Yield = 90%. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.45 (m, 4H, H-1, J = 5.8 Hz); 2.44 (t, 4H, H-2, J = 6.6 Hz); 2.56 (t, 8H, H-3, J = 6.6 Hz); 1.89 (qn, 8H, H-4, J = 5.8 Hz); 3.76 (t, 8H, H-5, J = 6.0 Hz); 8.55 (s, 4H, H-6); 8.11 (d, 4H, H-8, J = 8.5 Hz); 8.09 (d, 4H, H-9, 8.0 Hz); 7.25 (s, 4H, H-10); 7.73 (d, 4H, H-12, J = 8.5 Hz); 7.70 (t, 4H, H-13, J = 6.6 Hz); 7.53 (t, 4H, H-14, J = 6.6 Hz); 8.12 (d, 4H, H-15, J = 8.5 Hz).(See Scheme 2.9 for

numbering system).^{13}C-NMR ($CDCl_3$): δ = 22.0, 25.2, 28.2, 51.7, 54.1, 59.6, 162.4 118.3, 127.3, 136.5, 147.7, 129.4, 129.5, 127.6, 128.8, 154.8. IR: ν = 1643 cm^{-1} (C=N). Anal. Calc. for $C_{56}H_{60}N_{10}$: C, 70.87; H, 8.07, N, 18.69; [M$^+$], m/z = 873.2120. Found: C, 70.19; H, 8.24; N, (19.10); [M$^+$], m/z = 874.0211.

2.2.4 Preparation of ferrocenyliminedichloroPd(II) complexes

2.2.4.1 Preparation of [propyl-1,3-diimine]dichloroPd(II) complex, C1

In a Schlenk tube, **L1** (0.20 g; 0.43 mmol) was dissolved in 20 mL of dried DCM at room temperature. With stirring, Pd(COD)Cl_2 (0.13 g; 0.43 mmol) was dissolved in 10 mL of dry DCM and added dropwise to the stirring reaction mixture. This resulted in the formation of a red precipitate within 10 min. The reaction mixture was stirred at room temperature for a further 12 h in order to optimize the yield. The precipitate was then allowed to settle and the bottom of the Schlenk tube and the solvent was removed using a syringe and the crude product washed with DCM (4 X 10 mL) to remove unreacted starting materials. The product was isolated as a red solid (62% yield). ^{1}H-NMR (200 MHz, in $CDCl_3$): δ = 2.56 (m, H-1); 3.70 (t, H-2); 4.14 (s, H-6); 4.36 (t, H-5), 4.73 (s, H-4); 7.84 ppm (s, H-3). ^{13}C {^{1}H}-NMR (in $CDCl_3$): δ = 169.8, 116.6, 73.5, 73.2, 72.9, 72.4, 70.2, 69.7, 63.3, 31.0 ppm.IR: ν=1626 cm^{-1} (C=N). Decomposition Point: 159°C.

2.2.4.2 Preparation of [DAB-Fc]dichloroPd(II) complex, C2

Method 1: To a Schlenk tube, **L2** (0.08 g, 0.28 mmol) was added, and then 20 mL of dried DCM was added at the mixture heated at 40 ºC. When the ligand had completely dissolved, $PdCl_2$(COD) (0.15, 0.14 mmol) dissolved in 10 mL of DCM was added dropwise to the stirring reaction mixture. The reaction was cooled in order to allow the precipitate to settle.

The supernantant liquid was removed using a Pasteur pipette. A red precipitate formed was isolated. Yield = 52%. The red solid obtained was characterized by ^{1}H-NMR and IR spectroscopy and melting point. ^{1}H-NMR (200 MHz, in DMSO): δ = 2.60 (m, H-1); 3.70 (t, H-2); 4.14 (s, H-6); 4.36 (t, H-5), 4.73 (s, H-4); 7.84 ppm (s, H-3). ^{13}C {^{1}H}-NMR (in DMSO): δ = 128.3, 69.8, 69.7, 39.0, 38.6, 38.2, 27.4 ppm. IR: v=1626 cm^{-1} (C=N). Decomposition Point: 159°C.

Method 2: The above reaction was repeated, but the ratios of **L2** to $PdCl_2$(COD)were varied from 1:2 to 1:4. Under nitrogen, a solution of $PdCl_2$(COD) (0.5, 0.176 mmol) was added to a heating solution of **L2** (0.482 g, 0.44 mmol) and the precipitate was isolated. Yield = 74%. ^{1}H-NMR (200 MHz, $CDCl_3$):δ = 1.21 (br m, 4H, H-1'); 2.64 (qn, 8H, H-1); 1.56 (br t, 4H, H-2'); 2.32 (t, 8H, H-3'); 3.40 (t, 8H, H-2); 3.81 (s, 5H, H-6); 4.551 (d, 2H, H-4); 4.80 (d, 2H, H-5); 7.26 (s, 4H, H-3). ^{13}C-NMR ($CDCl_3$): δ = 27.4, 38.2, 38.6, 39.0, 39.4 ($CH_{2,\ aliphatic}$); 39.8 (C3 and C4 of subst. Cp ring), 40.2 (C of unsubst. Cp ring), 40.7 (C2 and C5 of subst. Cp ring), 128.3 ($CH_{,\ imine}$). IR: v=1626 cm^{-1} (C=N). Decomposition Point: 170°C.

2.2.5 Multinuclear [G-1 DAB-dendr-(NH_2)n-imine]dichloroPd(II) complexes

2.2.5.1 Multinuclear [G-1_DAB-dendr-(NH_2)$_n$-1-(2-pyridyl)-imine]dichloroPd(II) complex, C3

The dendrimeric palladium dichloride complex **C3** of pyridylimine ligand was synthesised by the same method employed by Malgas *et al.* [13,17] and Smith *et al.* [18,19]. Palladium bis (acetonitrile) dichloride precursor (0.14g, 0.55 mmol) was transferred to a 100 mL Schlenk tube followed by 10 mL of dry acetonitrile, upon stirring at room temperature under nitrogen a deep-red solution was observed. Separately G-1pyridine-dendrimeric ligand (**L3**) (0.10g, 0.14 mmol) was dissolved in 5 mL of dry acetonitrile. This colourless solution was added drop-wise into the stirring solution of the palladium precursor. Immediately a yellow

precipitate formed. This reaction was allowed to proceed for two hours. After the removal of solvent, an orange solid residue was obtained which was washed with dry DCM (10 mL x 7) in order to remove any unreacted substrate. The product was isolated as a light-orange solid. Yield = 82%. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.4 (br m, 4H, H-1); 2.42 (t, 4H, H-2); 2.53 (t, 8H, H-3); 1.85 (qn, 8H, H-4); 3.68 (t, 8H, H-5); 8.36 (s, 4H, H-6); 8.97 (d, 4H, H-8); 7.71 (t, 4H, H-9); 7.29 (t, 4H, H-10); 8.63 (d, 3H, H-11). ^{13}C-NMR ($CDCl_3$): δ = 22.7, 25.5, 28.6, 52.1, 54.4, 59.9, 162.2, 121.6, 124.9, 136.8, 149.7, 155.0. IR: ν=1599 cm^{-1} (C=N). Decomposition Point: 200°C.

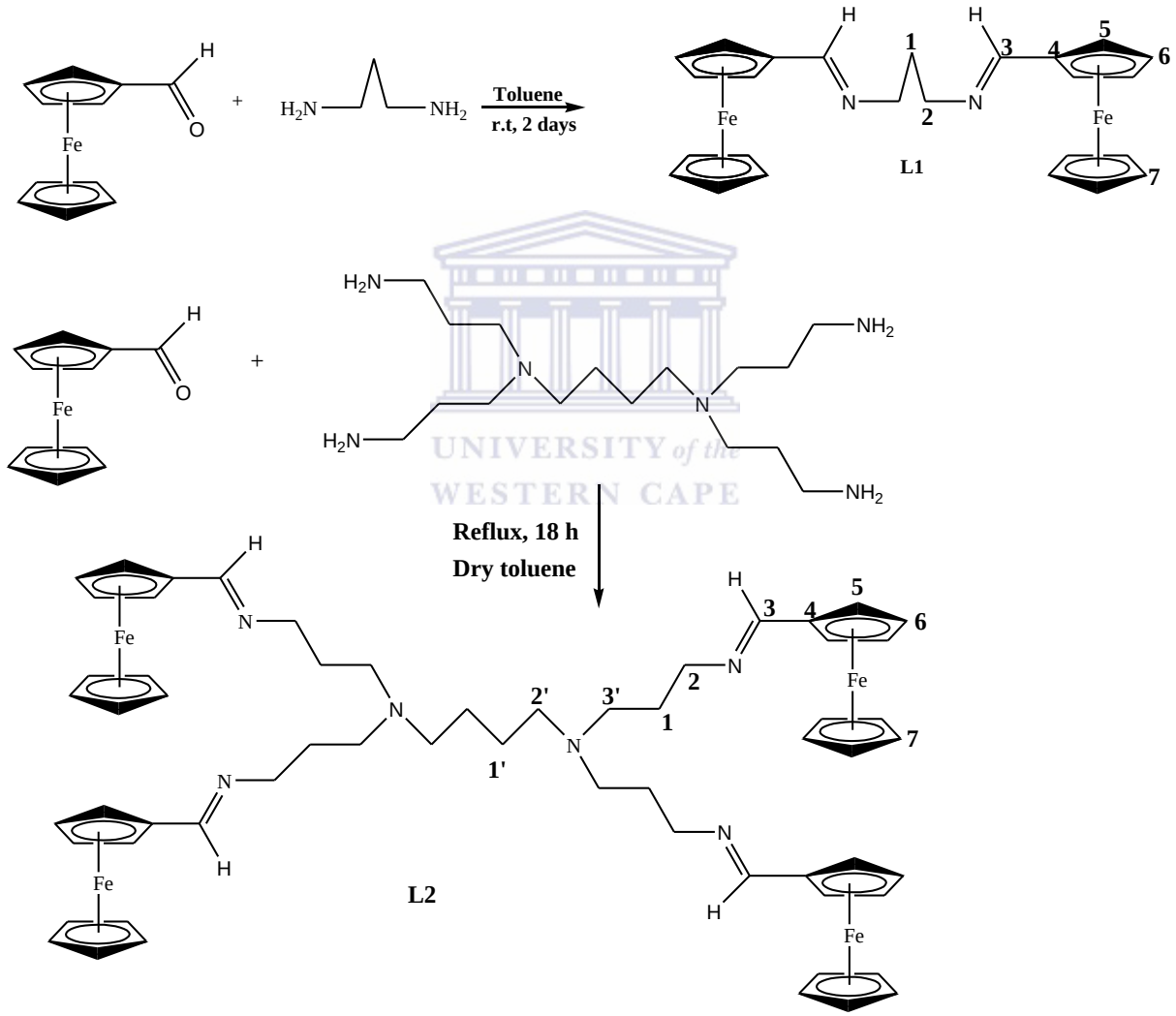
2.2.5.2 Multinuclear [G-1 DAB-dendr-(NH_2)$_n$-1-(2-quinolyl)-imine]dichloroPd(II) complex, C4

Complex **C4** was prepared analogously to **C3**. Palladium bis (acetonitrile) dichloride precursor (0.13 g, 0.59 mmol) was transferred to a 100 mL Schlenk tube followed by 10 mL of dry acetonitrile, upon stirring at room temperature under nitrogen gas a deep-red solution was observed. Separately G-1_quinoline-dendrimeric ligand (**L4**) (0.13 g, 0. 19 mmol) was dissolved in 5 mL of dry acetonitrile. This colourless solution was added drop-wise into the stirring solution of the palladium precursor. Immediately a yellow precipitate formed. This reaction was allowed to proceed for two hours. After the removal of solvent, an orange solid residue was obtained which was washed with dry DCM (10 mL x 7) in order to remove any unreacted substrate. The product was isolated as a deep-orange solid. Yield = 74%. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.45 (m, 4H, H-1); 2.44 (t, 4H, H-2); 2.56 (t, 8H, H-3); 1.89 (qn, 8H, H-4); 3.76 (t, 8H, H-5); 8.55 (s, 4H, H-6); 8.11 (d, 4H, H-8); 8.09 (d, 4H, H-9); 7.25 (s, 4H, H-10); 7.73 (d, 4H, H-12); 7.70 (t, 4H, H-13); 7.53 (t, 4H, H-14); 8.12 (d, 4H, H-15). ^{13}C-NMR ($CDCl_3$): δ 22.0, 25.2, 28.2, 51.7, 54.1, 59.6, 162.4, 118.3, 127.3, 136.5, 147.7, 129.4, 129.5, 127.6, 128.9, 154.7. IR: ν=1598 cm^{-1} (C=N). Decomposition Point: 200 °C.

2.3 RESULTS AND DISCUSSION

2.3.1 Synthesis of ferrocenylimine ligands, L1 and L2

The ligands were prepared according to the general procedure described by Mu *et al.* for most ferrocenylimines as indicated earlier [20]. A general synthetic route for the ferrocenylimines is shown in scheme 2.5.



Scheme 2.5 Synthetic route to ferrocenylimine ligands, **L1** and **L2**

The ferrocenylimines were successfully synthesized by the condensation of ferrocenecarbaldehyde with the corresponding amines (1,3-diaminopropane and DAB-4-$(NH_2)_4$), respectively, in the presence of $MgSO_4$ as the dehydrating agent. For the synthesis of **L2**, a large excess of $MgSO_4$ with longer reaction time was needed to force the displacement of the equilibrium in favour of the product, due to its steric bulk. These compounds, **L1** and **L2** were obtained in 73 and 66% yields, respectively. The ligands were found to be thermally stable and not sensitive to air and moisture. The compounds were found to be highly soluble in most of the common solvents (chloroform, dichloromethane, toluene, ethyl acetate), slightly soluble in petroleum ether, hexane and alcohols, and insoluble in water.

2.3.1.1 Characterization of ferrocenylimine ligands, L1 and L2

The ligands were characterized using solid-state infrared, proton and carbon 13 nuclear magnetic resonance spectroscopy, elemental analysis, mass spectrometry and melting point measurements. Since our aim was to prepare DAB-Fc, the spectra used for illustration and discussion are biased towards it. Therefore, the discussion will be on **L2** and **C2**. Structures shown in the spectra only illustrate the arms and the first two carbons of the dendrimeric core.

2.3.1.2 FTIR spectroscopy of ferrocenylimines ligands, L1 and L2

The IR spectra of the ligands were compared to that of the starting materials. The IR spectrum of **L2** (Figure 2.1) showed an intense sharp band 1644 cm^{-1}. The spectrum of the free imine **L1** also showed an intense sharp band at 1651 cm^{-1}. These bands was assigned to the stretching frequency of the C=N bond, and the ligands did not exhibit the absorption band

due to the asymmetrical stretching of the aldehyde group [ν(C=O)] expected at around 1661 cm^{-1}.

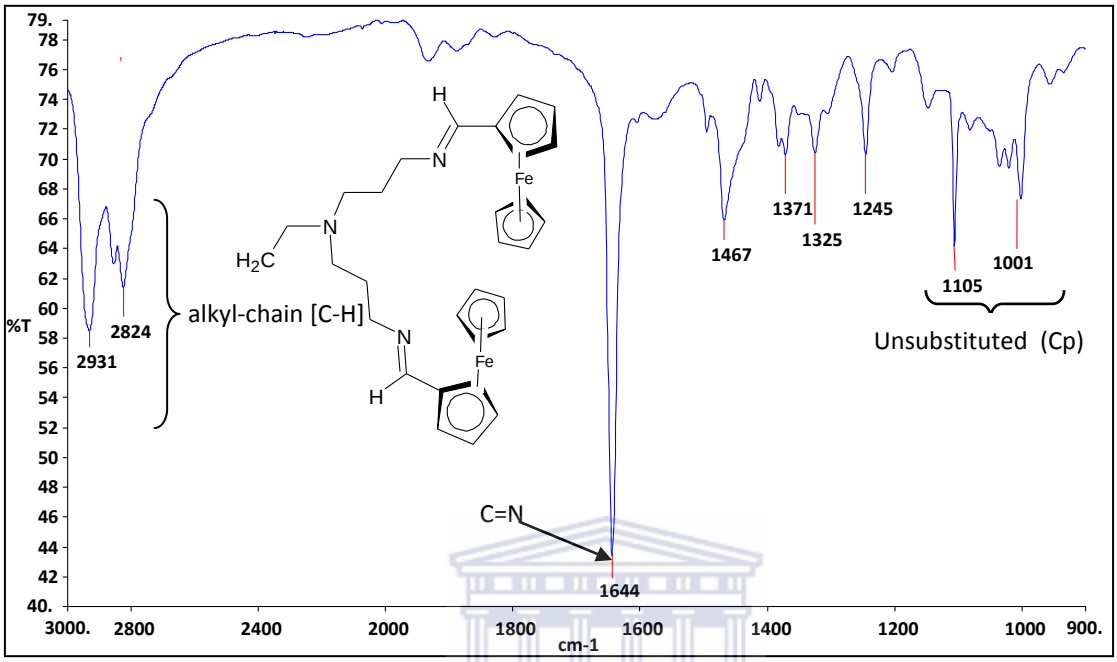


Figure 2.1 IR spectrum of [DAB-Fc], **L2**

The IR spectra of the two ligands were consistent with that of a mono-substituted ferrocene structure, showing absorptions at 1000 and 1100 cm^{-1}, which most importantly indicated an unsubstituted Cp ring [21]. Zhao et al [22] also observed similar results. The (C-H) bond stretching frequencies of the butyl and propyl chains were observed in the regions 2800- 2920 cm^{-1}. The results are in good agreement with those previously reported for related Schiff-base condensation reactions in preparation of ferrocenylimines [20].

2.3.1.3 ^{1}H and ^{13}C-NMR spectra of ferrocenylimines ligands, L1 and L2

The spectrum in figure 2.2 is a typical example of the ^{1}H-NMR spectrum of ferrocenylimines. The ^{1}H-NMR spectra of the ligands were consistent with the reported literature results related to the compounds of ferrocenylimines [2].

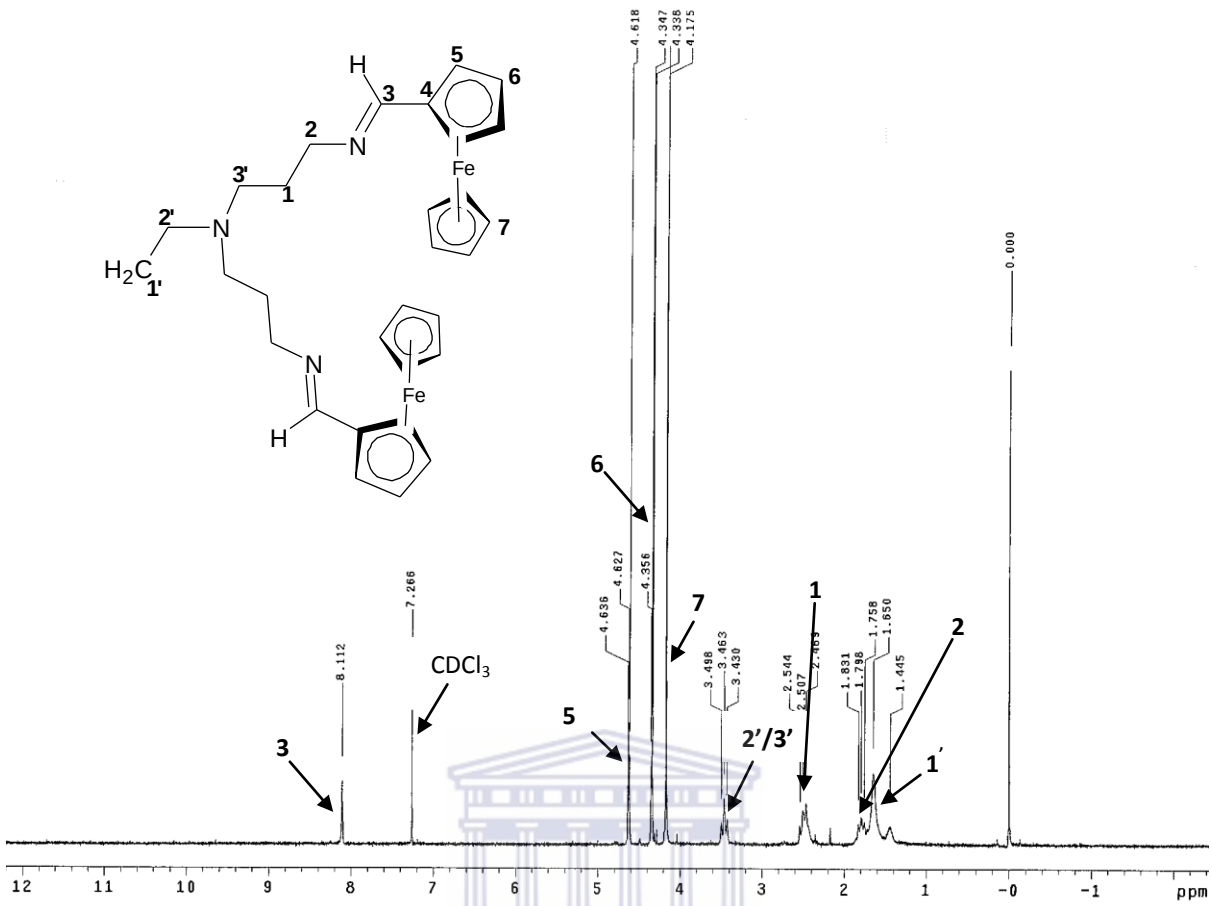


Figure 2.2 ^{1}H-NMR spectrum of [DAB-Fc], **L2**

Strong evidence of the Schiff-base condensation reaction was confirmed by an observed proton signal (singlet) at around δ 8.11 ppm which is due to the H bonded to the iminic carbon (**H**C=N). The observed chemical shift values for the imine proton are within the range 8.26- 8.76 ppm reported by Smith *et al*. [18,19].

The ^{1}H-NMR spectrum of the ligands showed three types of non-equivalent proton signals of the cyclopentadienyl rings. A strong singlet signal at around 4.17 ppm was due to protons of the unsubstituted Cp-ring (H-10) and two triplet signals due to the protons of the substituted Cp-ring at around 4.35 (H-9) and 4.62 ppm (H-8). The ^{1}H-NMR spectra patterns in the aromatic region are very similar to those of the starting materials. The ^{1}H-NMR spectra of the

ligands indicated strongly that the starting materials were converted to the corresponding ferrocenylimine products, by showing no aldehyde proton (**H**C=N) peak in the region 9.99 ppm.

Further confirmation was observed in the ^{13}C-NMR spectrum of the ligands. The following spectrum in figure 2.1 is a typical example of the ^{13}C-NMR spectra obtained for the prepared ferrocenylimines. All the peaks were assigned and the results summarized in Table 2.2.

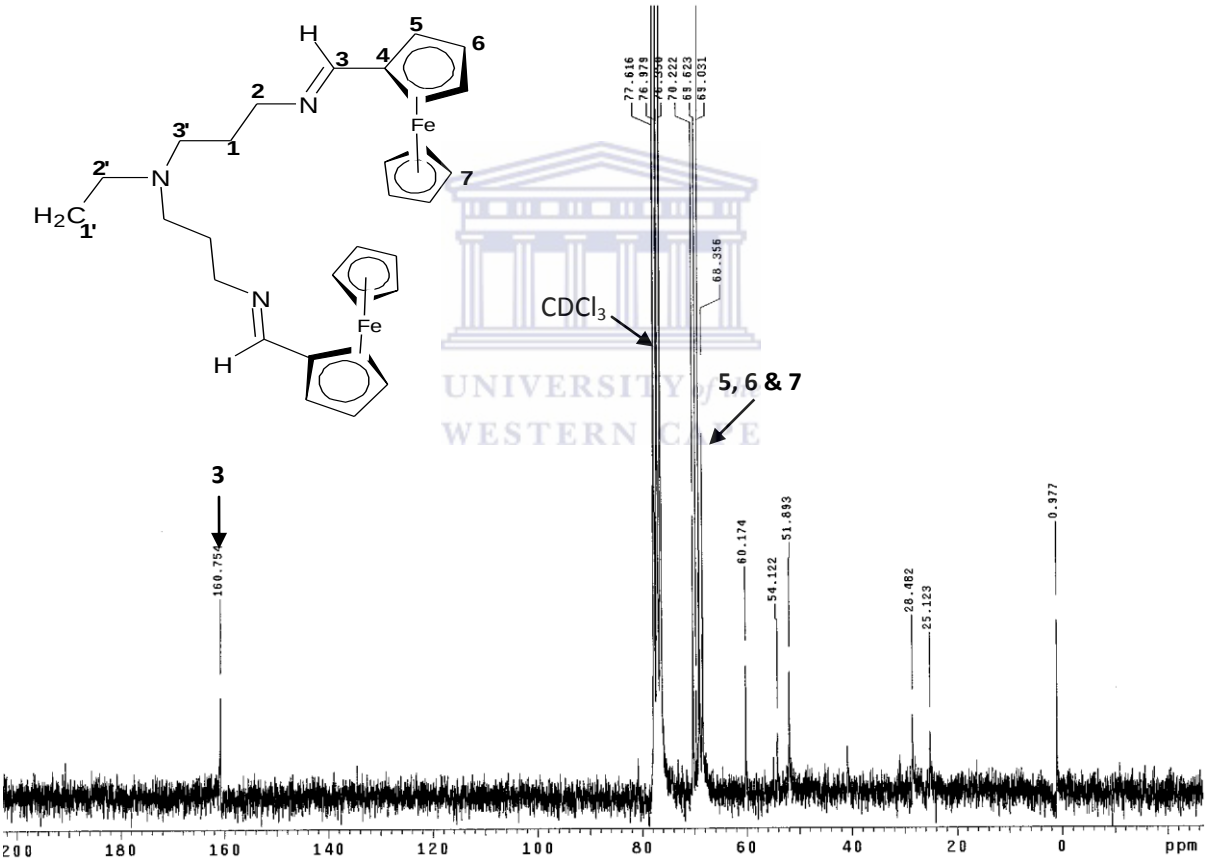


Figure 2.3 ^{13}C-NMR spectrum of [DAB-Fc], **L2**

The C=N signals appeared at 161.05 and 160.75 ppm in the ^{13}C-NMR spectrum for **L1** and **L2** respectively. These results are consisted with what is reported in the literature [22,23].

2.3.1.4 ESI mass spectrometry

Further characterisation of the ligands was done by using electron spray ionization mass spectrometry which confirmed the molecular mass of the expected compounds (**L1** and **L2**). The parent ion of **L1** was observed at m/z 467.0881 from the spectrum obtained (Figure 2.4). A possible fragmentation pattern is also shown in scheme 2.6. The compound **L1** seems to lose one of the unsubstituted cyclopentadienyl rings and Fe atom first, followed by the second cyclopentadienyl ring. The last fragment is due to the ferrocenyl unit. A similar fragmentation pattern was observed for **L2**, the only difference is that the compound is bulkier and loses the unsubstituted cyclopentadienyl rings and Fe atoms first, followed by the second cyclopentadienyl ring. However, they were peaks above m/z 567 which could not be easily assigned neither could they be trapped solvents.

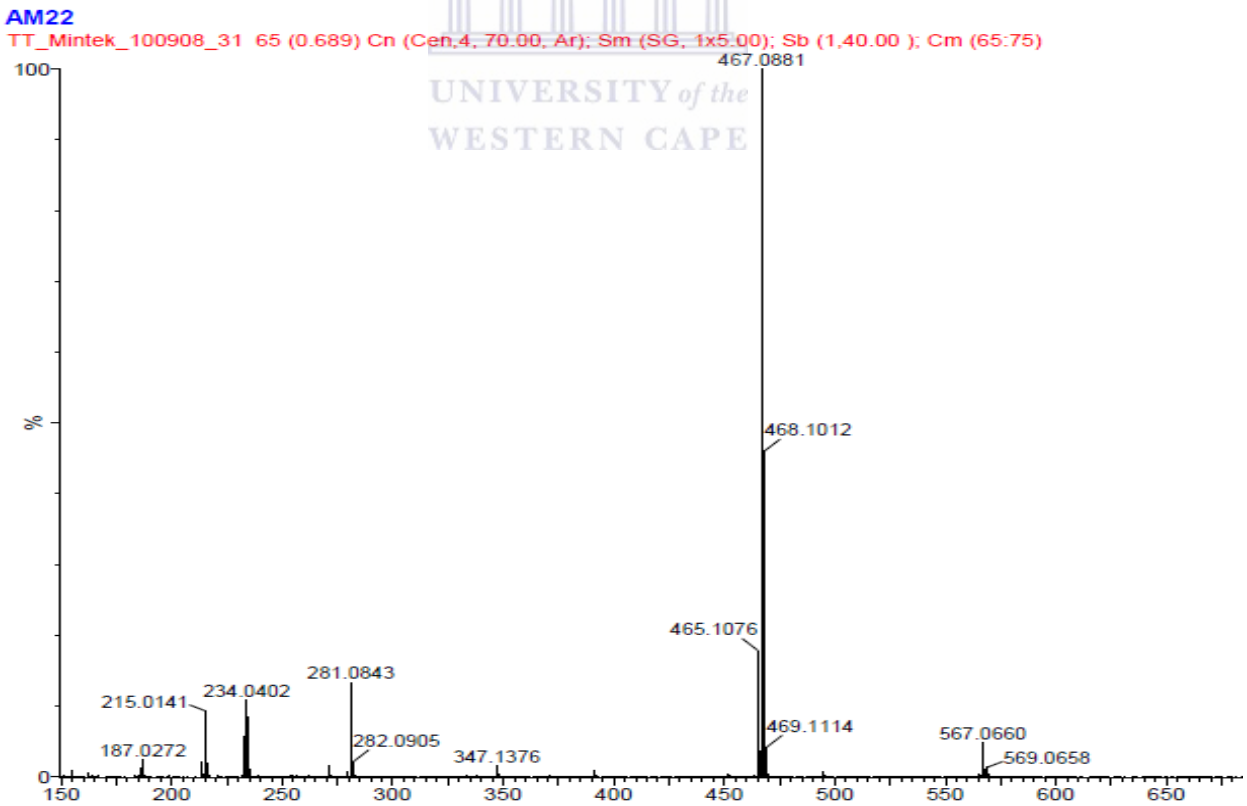
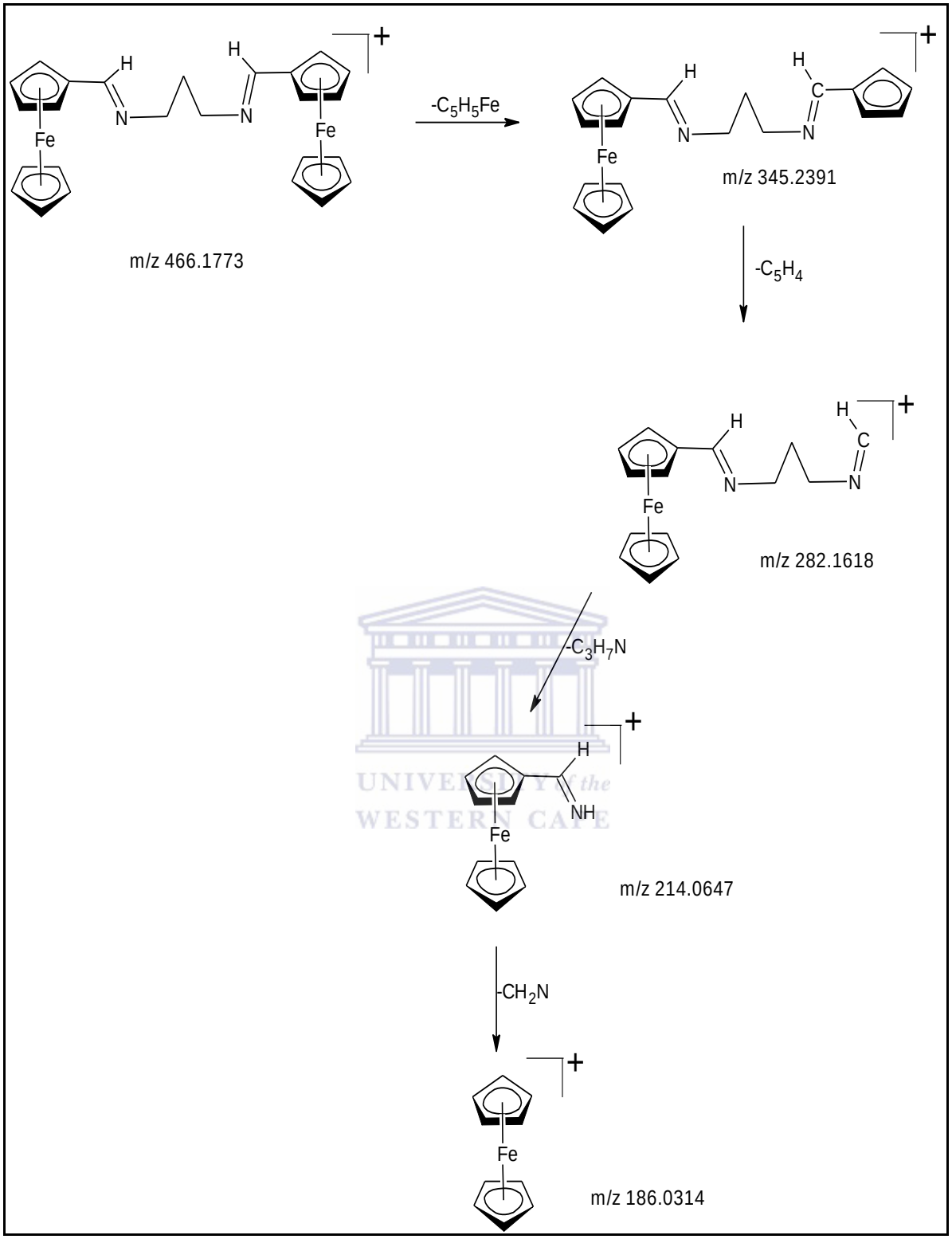


Figure 2.4 ESI mass spectrum of **L1**



Scheme 2.6 Possible fragmentation pattern of ferrocenylimines ligand, **L1**

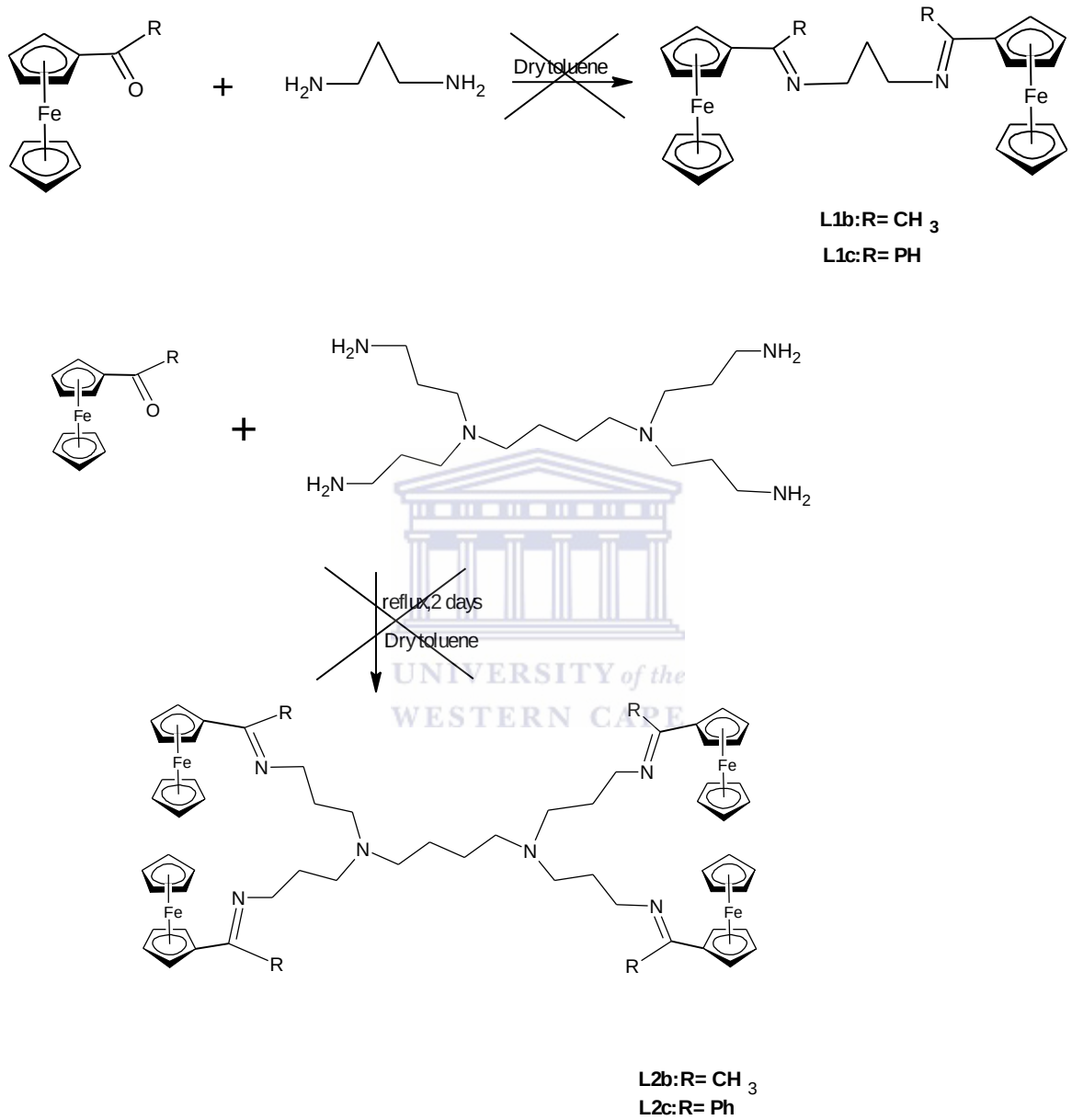
2.3.2 Attempted synthesis and characterization of ferrocenylketimines ligands

In view of the results obtained in the preparation of **L1** and **L2** by reaction of ferrocenecarboxaldehyde with the appropriate amines, we decided to explore whether it could be possible to achieve the synthesis of ferrocenylketimines using different strategies. Previous reports have shown that the preparation of ferrocenylaldimines and ferrrocenylketimines via condensation of the acyl ferrocenes with amines without solvent is successful [23,24]. Unfortunately, this green chemistry technique did not work for us.

Attempts to prepare the above mentioned ferrocenylketimines following the same reaction conditions as for the ferrocenylaldimines did not produce the expected results. In each case, an oil or solid was obtained which contained a mixture of the imine product and the acylferrocene starting material. The thin layer chromatography (TLC) spotting revealed that the acylferrocenes were present in higher quantities. No appropriate solvent system could be developed and attempts to separate these mixtures were unsuccessful.

Literature reports have revealed that as the steric bulk at the imino carbon atoms increases (where R is Me, Et, *i*-Pr or Ph), longer reaction times or forceful reaction conditions are required for the condensation reaction to take place [25]. Wu and co-workers [26] have described preparations of methylsubstituted-ferrocenylketimines [$Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CMe{=}NC_{12}H_{25})$] and [$Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CMe{=}NC_{16}H_{33})$]. In all cases, large excess of amines and molecular sieves were used with long reaction times to force the displacement of the equilibria to the product. Still, further attempted preparation of ferrocenylketimines, **L1(b)**, **(c)** and **L2(b)**, **(c)**, (Scheme 2.7) under the listed reaction conditions gave no desired ferrocenylketimine products: acetylferrocene, or benzoylferrocene, corresponding amine (1,3-diaminopropane, DAB-4-$(NH_2)_4$), dry toluene solvent, refluxed for 2 days and after every 12

h additional amines (0.01 mmol) and molecular sieves were added to try to force the displacement of the equilibria to the right. In each case, the anticipated products were not obtained and unreacted acylferrocenes recovered.



Scheme 2.7 Synthetic route to ferrocenylketimines.

Since we thought that the relatively high temperature could be causing the decomposition of the products, the reactions were repeated using a lower boiling point polar solvent *viz*. methanol. However, this did not lead to any product formation either; instead the

acylferrocenes were recovered unchanged. In another attempt, under more forcing reaction condition, Dean-Stark apparatus was employed: Acetylferrocene, or benzoylferrocene, the corresponding amine (1,3-diaminopropane, DAB-4-$(NH_2)_4$), dry toluene solvent, were refluxed for 3 days. For our condensation attempts using Dean-Stark method, still the desired product was not obtained, with once again unreacted acylferrocene recovered. Similar ferrocenylimine ligands have however been prepared by Lopez *et al.* using this procedure [27], so it is not clear why we were unable to obtain pure ferrocenylketimines, or if the literature is actually reporting accurate results.

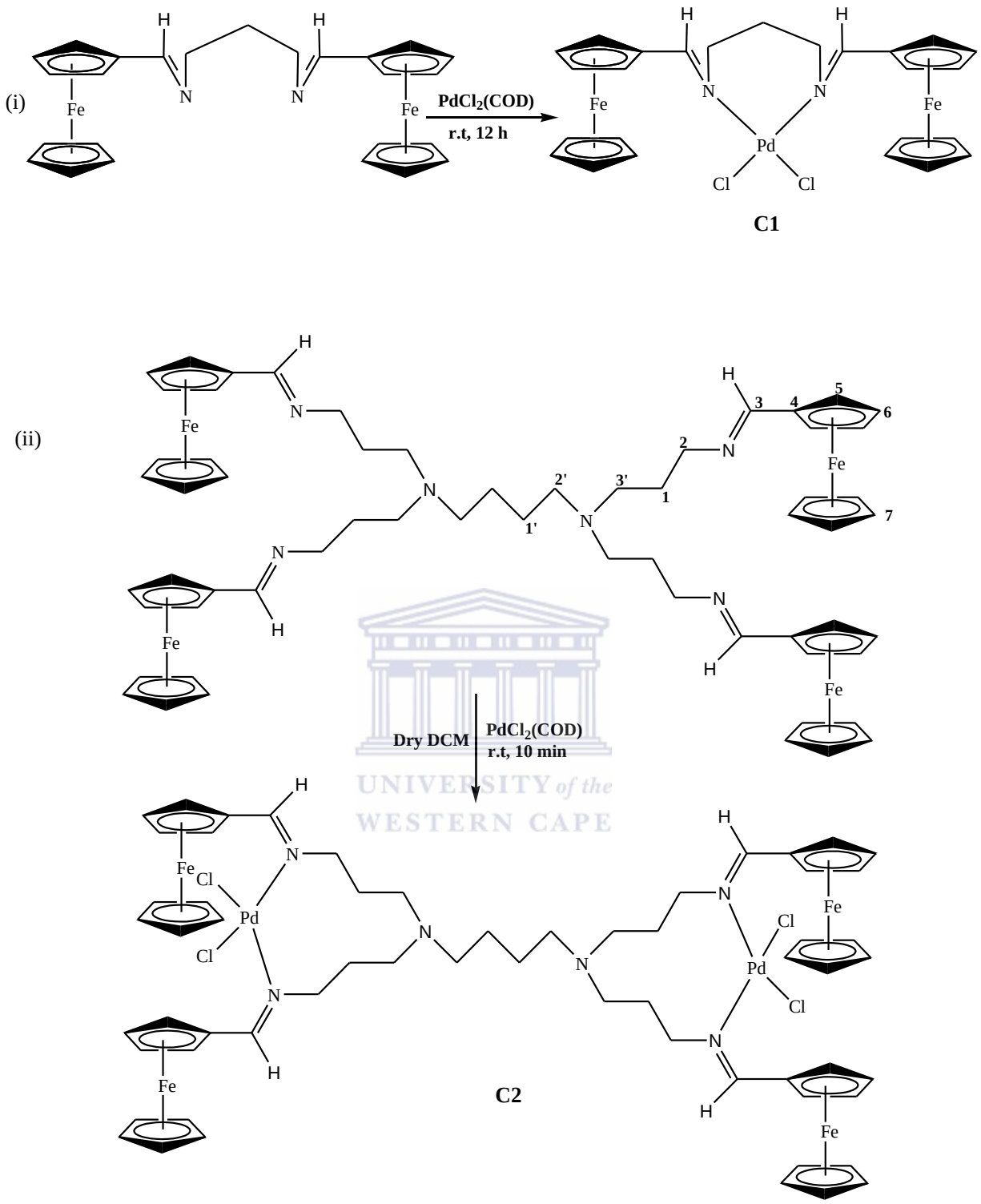
Another group, Imrie *et al.* reported the solvent-free synthesis of ferrocenylimines [28]. The group discovered that in the majority of cases, the ferrocenylimines could be prepared by heating a solution of the ferrocenylaldehyde and aromatic amine in solvents such as anhydrous methanol or ethanol. This research group has also utilized this method before, and found thermal sensitivity as one of the problems associated with the preparation, which the ferrocenylimines suffered by undergoing a degree of decomposition during the heating process. To avoid this problem and to fit in more closely with the principles of green chemistry, they conducted reactions in a solvent-free environment.

So, we concluded that this could also be one of the possible reasons for the failure to obtain the desired ferrocenylketimines. The presence of the imino carbon facilitates this reaction and thus its absence hinders the protonation process with eventual formation of the condensation products. The mechanism is illustrated ahead in scheme 2.9. We again attempted the synthesis of the target molecules by following the “General procedure for the reaction of ferrocenylaldehyde and aromatic amines without solvent”. The acylferrocenes and corresponding amines were added to a test tube fitted with a stirrer bar. The two compounds

were stirred at room temperature. In some cases, a gum-like compound formed and in others the mixture turned into a melt. In cases where the starting materials were less reactive, the test tube was immersed in a constant temperature water bath at 50 $^{\circ}$C. The melt which formed was stirred, while being monitored by TLC for the disappearance of acylferrocenes. A TLC study of the product was done initially using dichloromethane as the developing solvent and no separation of components occurred Therefore another solvent system was developed with varying ratios of dichloromethane/hexane and dichloromethane/ethyl acetate. All these attempts did not give the pure products separation. The NMR and IR spectroscopy studies still showed traces of unreacted acetylferrocene and benzoylferrocene, but with products.

2.3.3 Synthesis and Characterization of ferrocenylimine-chloropalladated complexes, C1 and C2

The ligands **L1** and **L2** were complexed by using palladium metal salts to give complexes **C1** and **C2,** respectively. These compounds **C1** and C**2** were prepared according to an adapted general procedure [20]. The complexes precipitated out of solution within 10 min, but were allowed to proceed for a longer period of time in order to optimize product yields. The compounds exhibited low solubility in common solvents used. The complexes were isolated as red solids in 62 and 74% yields, respectively. Due to insolubility problems, poorly resolved NMR spectra were obtained, but good IR spectra were obtained from the ATR technique. The preparation is presented in scheme 2.8.



Scheme 2.8 Synthetic route to ferrocenylimine-chloropalladated complexes, **C1** and **C2**

2.3.3.1 FTIR spectroscopy of complexes C1 and C2

A typical IR spectrum for ferrocenylimines Pd(II) complexes is given in figure 2.5.

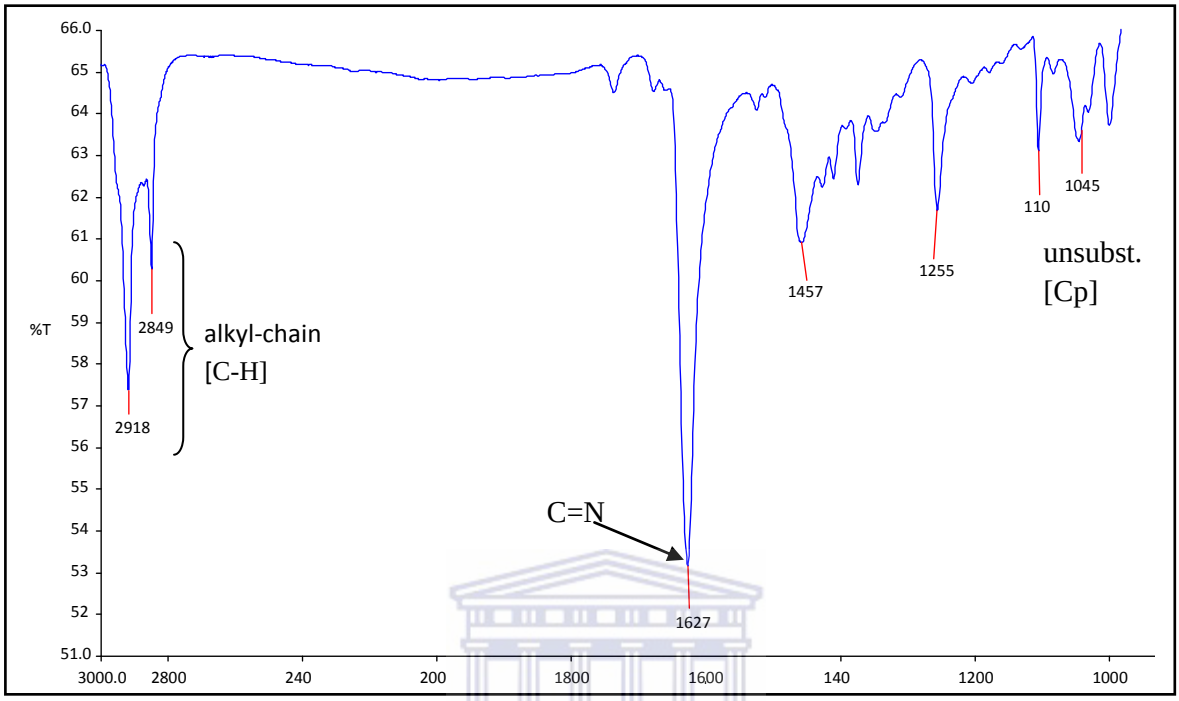


Figure 2.5 IR spectrum of [DAB-Fc]$PdCl_2$, **C2**

The most outstanding feature observed in the infrared spectra of the complexes of **C1** (Figure 2.5) and **C2** is the band due to the stretching frequency of the C=N group appearing at lower frequency than for the corresponding free ligand {1651 cm^{-1} (**L1**) or 1644 cm^{-1} (**L2**)}. Moreover, comparing the IR spectrum of **L2** with that of **C2**, the C=N absorption has shifted to a low value of 1627 cm^{-1}, indicating that the imine was coordinated to the palladium centre through the nitrogen centre. Similarly, The IR spectrum of **C1** showed a characteristic band at 1626 cm^{-1} due to the coordination of the imine moiety (C=N) to Pd. No absorption at 1651 cm^{-1} was observed which is a characteristic stretching frequency for the free uncomplexed imine ligand system. The aliphatic chain of the core and side arms was observed in the region 2800- 2918 cm^{-1}. Similar observations reflect the literature findings, for example Zhao *et al.* [22,29]. Their cyclopallated ferrocenylimine Pd(II) complexes were observed to have shifted

from 1642 cm^{-1} by 3-5 cm^{-1}, indicating that nitrogen was coordinated to palladium through its lone pair. Their spectra also did not show any uncoordinated imine.

2.3.3.2 ^{1}H-NMR spectroscopy of ferrocenylimine palladium complexes, C1 and C2

The ^{1}H-NMR spectra of the palladium(II) complexes further confirms that complexation had taken place. The spectrum in figure 2.6 is example of the spectra obtained for ferrocenylimine. The compounds exhibited low solubility in $CDCl_3$ and DMSO solvents and due to that; very poor NMR spectra were obtained. The complexation was identified with the observation of the imine proton. But the important peaks were assigned and the results summarized in Table 2.1.

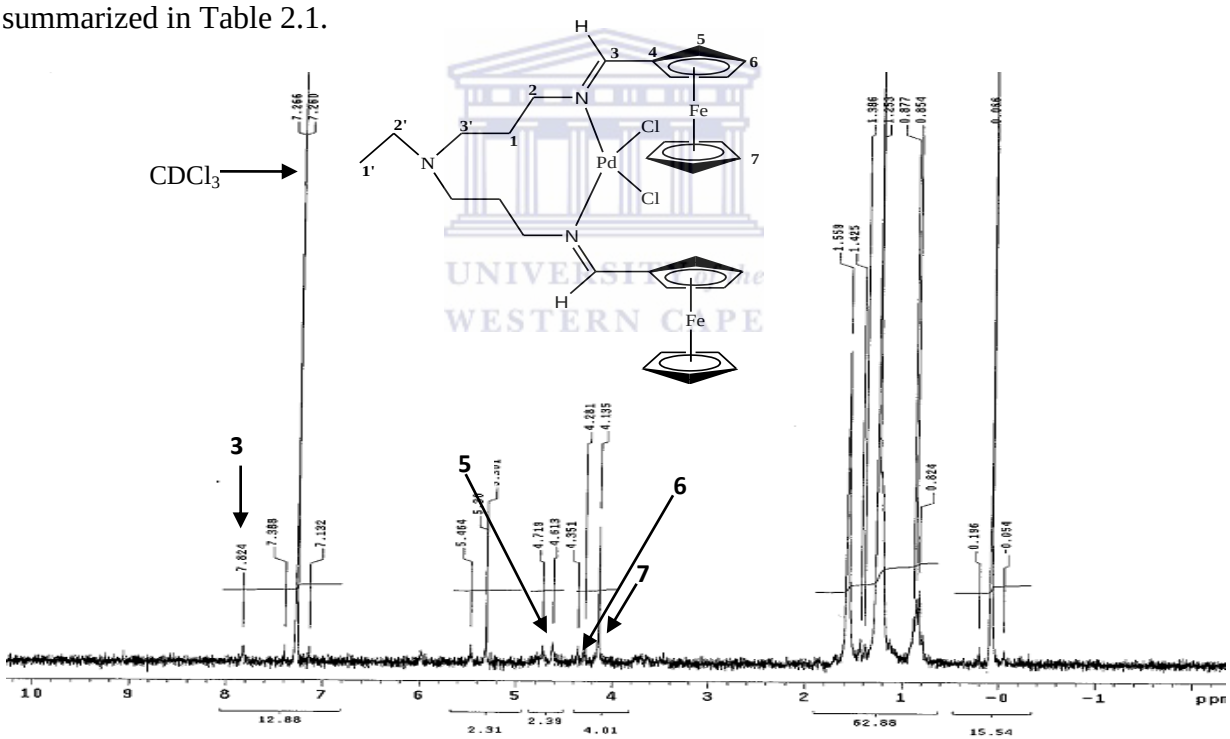


Figure 2.6 ^{1}H-NMR spectrum of [DAB-Fc] Pd(II), **C2**

A shift upfield of the singlet of the proton attached to the imine carbon (**H**C=N) from 8.11 ppm in the free ligand to 7.82 ppm in complex **C2** was observed. A similar observation was seen in the literature, for example Lopez *et al.* [30]. The iminic protons in their complexes had shifted from 8.42 to 8.38 ppm. The CH_2 signals (H-5) adjacent to the imine carbon of the

dendritic imine ligand **L2**, shifted upfield form 2.18 to 1.56 ppm which could only be as a result of the complexation of the $PdCl_2$ moieties to the iminic nitrogen. The same trend was observed for **C1.** The chemical shift of the imine-proton was observed upfield at 7.82 and not at 8.15 ppm, which is characteristic of the free imine ligand **L1**.

2.3.3.3 ^{13}C-NMR spectroscopy of ferrocenylimine palladium complexes, C1 and C2

The spectrum in figure 2.7 is a typical example of the spectra obtained for ferrocenylimines.

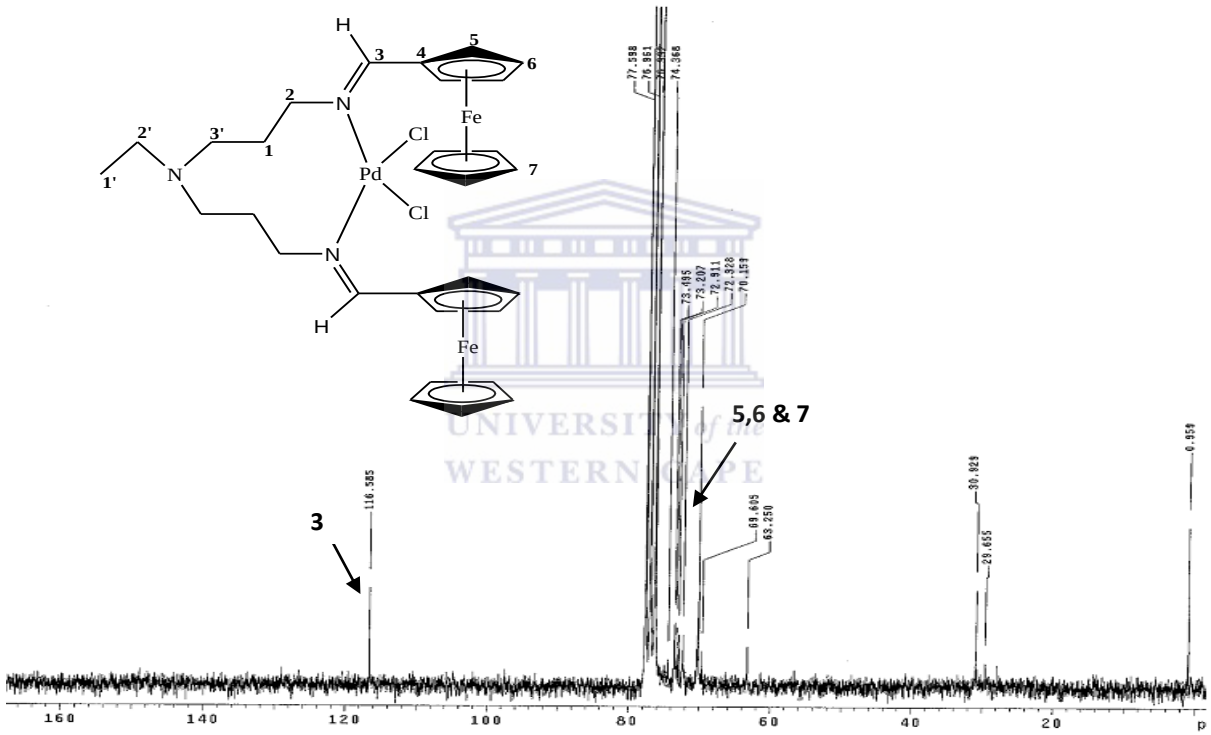


Figure 2.7 ^{13}C-NMR spectrum of [DAB-Fc] Pd(II), **C2**

A shift in the signal of the iminic carbon (**C**=N) of complex **C2** from 160.6 ppm to 116.6 ppm was observed. The C=N chemical shift of **L1** appeared at 169.8 ppm compared to 161.1 ppm of the complex **C1**. The same phenomenon was reported by Malgas-Enus *et al.* in related imino-palladum complexes [13,17]. Even though very poor spectra were obtained, the attempt to assign all peaks was made and the results summarized in Table 2.2.

Table 2.1 ^{1}H-NMR data of ferrocenylimine ligands (**L1** and **L2**) and complexes (**C1** and **C2**)

Protons	L1	L2	C1	C2
H-1	2.04(m,2H,J=7.6)	2.45 (m,8H,J=7.6)	1.56 (m, 2H)	2.48 (m, 8H)
H-2	3.52(t,4H,J=7.0)	2.18 (t,8H,J=6.6)	3.62 (t, 4H)	3.32 (t, 8H)
H-3	8.15 (s, 2H)	8.11 (s, 4H)	7.27 (s, 2H)	7.82 (s, 4H)
-	-	-	-	-
H-5	4.64 (t,4H,J=1.8)	4.62 (t,4H,J=1.8)	4.61 (d,4H)	5.22 (d,4H)
H-6	4.37 (t,4H,J=1.8)	4.35(t,4H,J=1.8)	4.28 (d,4H)	4.55 (d,4H)
H-7	4.16 (s,10H)	4.17 (s,2H)	4.12 (s,10H)	3.81(s,2H)
H-1’		1.61 (m, 4H)		1.61 (m, 4H)
H-2’		3.46 (t,8H,J=6.6)		3.2 (t, 8H)
H-3’		3.46 (t,8H,J=6.6)		3.2 (t, 8H)

NMR Solvent: **L1, L2** and **C2:** $CDCl_3$; **C1**: DMSO-d_6, Units = ppm

Table 2.2 ^{13}C-NMR data of ferrocenylimine ligands **L1** and **L2**, and complexes **C1** and **C2**

Carbons	L1	L2	C1	C2
C-1	32.4	25.1	30.9	27.9
C-2	59.6	60.2	63.3	39.4
C-3	161.1	51.9	169.8	39.0
C-4	80.8	40.9	77.0	38.6
C-5	69.1	28.5	74.4	38.2
C-6	70.3	160.7	72.9	128.3
C-7	66.3	70.2	70.2	74.0
C-8		69.6		73.6
C-9		69.0		72.1
C-10		68.4		69.7

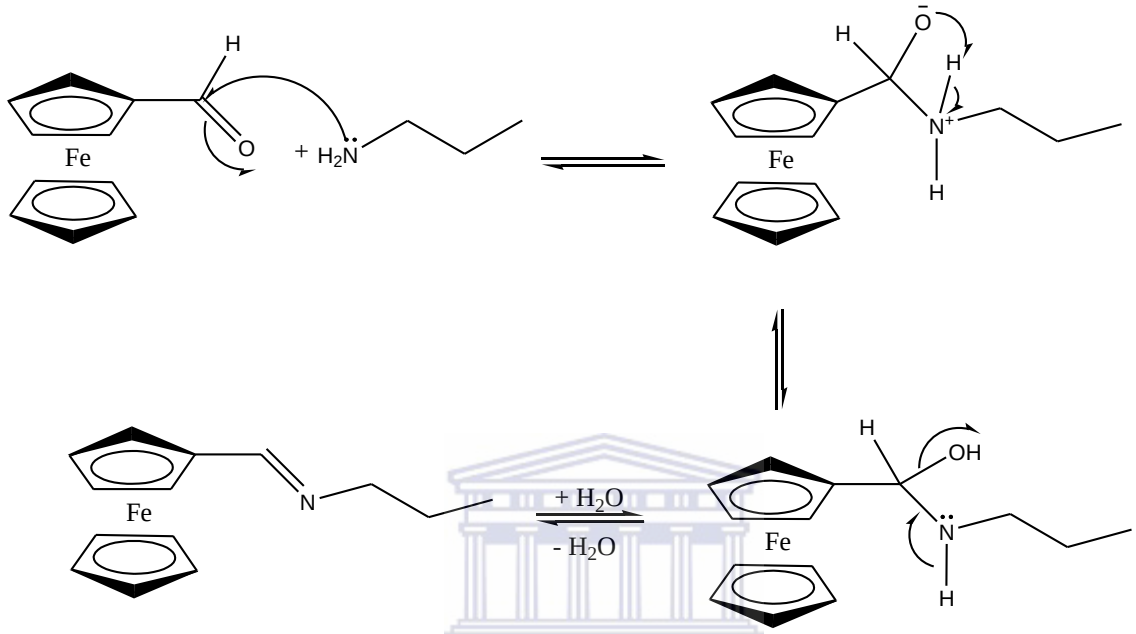
NMR Solvent: **L1** and **L2:** $CDCl_3$; **C1** and **C2**: DMSO-d_6, Units = ppm

The analytical data for the ferrocenylimine ligand (**L1** and **L2)** and complexes **(C1** and **C2)** are given in Table 2.3. It was observed that the ligands were not completely dry when the elemental analysis was done. Since the complexes were prepared in CH_2Cl_2 and were insoluble, they precipitated out of solution and were filtered and allowed to dry. The data revealed that 0.75 mol, 0.25 mol, and 0.5 mol of CH_2Cl_2 were trapped in ligand **L2**, complexes **C1** and **C2**, respectively. A similar observation was made by Nketo [31]. Chemsketch software showed that the compounds were in excess of the expected values. However, the experimental values were in acceptable range.

Table 2.3 Characterization data of ferrocenylimineligands (**L1** and **L2**), and complexes (**C1** and **C2**)

Compound	**Molecular Formula**	**Micro-analysis Calculated (Found)**		
		%C	**%H**	**%N**
L1	$C_{25}H_{26}Fe_2N_2$	64.42 (63.33)	5.58 (5.64)	6.02 (6.47)
L2	$C_{60}H_{72}Fe_4N_6.0.75CH_2Cl_2$	62.64 (62.42)	6.32 (6.95)	7.21 (7.27)
C1	$C_{44}H_{60}N_{10}.0.25CH_2Cl_2$	70.87 (70.19)	8.07 (8.24)	18.69 (19.10)
C2	$C_{88}H_{120}N_{22}.0.5CH_2Cl_2$	69.62 (69.61)	7.93 (8.13)	20.13 (20.58)

Scheme 2.9 depicts a possible reaction mechanism for the formation of our Schiff-base ferrocenylimines. First, the amine nitrogen acts as a nucleophile, attacking the carbonyl carbon to form a hemiacetal. Then the nitrogen is deprotonated, leaving a C=N double bond (an imine) and a displaced water molecule [32].

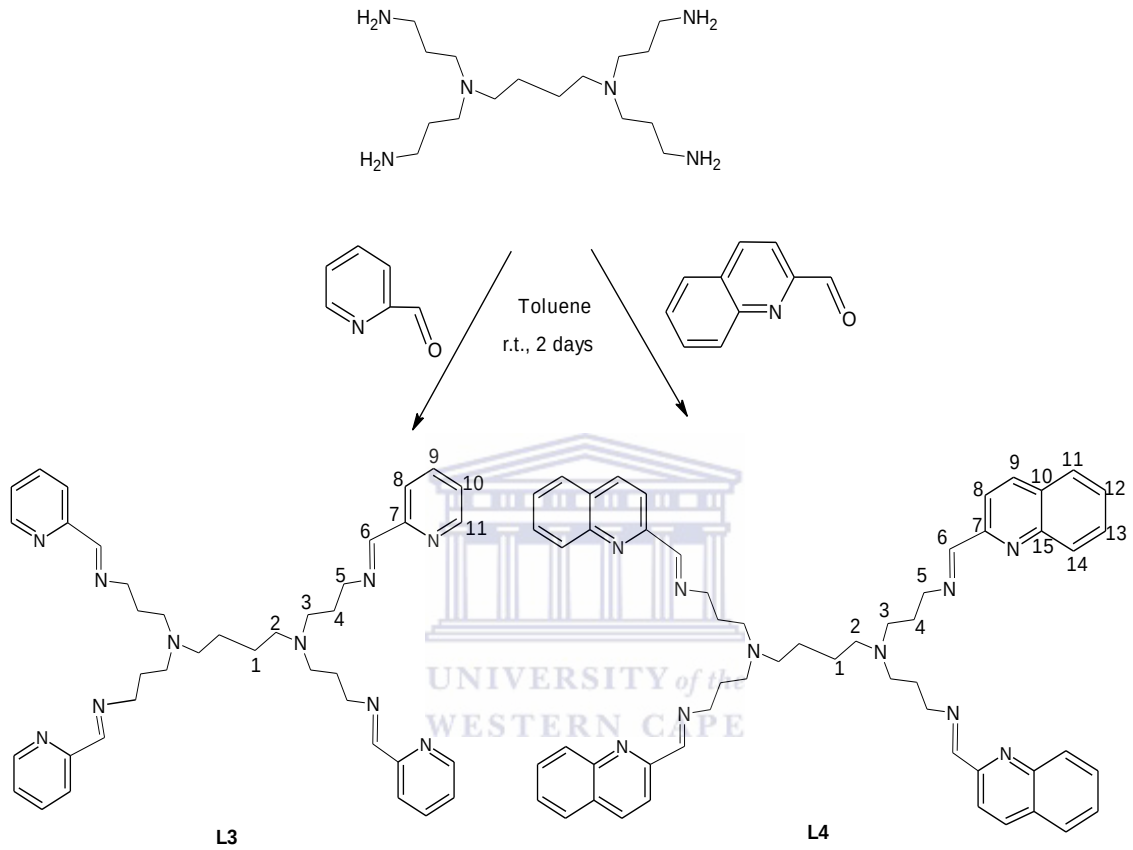


Scheme 2.9 Proposed reaction mechanism for the formation of Schiff-base ferrocenylimines

2.3.4 Synthesis of [G-1 DAB-dendr-(NH_2)-1-(2-pyridyl- and quinolyl)-imine ligands, L3 and L4

The ligands **L3** and **L4** were synthesized through Schiff-base condensation reactions of DAB-4-amine with the appropriate aldehydes (2-pyridinecarboxaldehyde and 2-quinolinecarboxaldehyde, respectively) in dry toluene in the presence of anhydrous magnesium sulphate, again following a literature report [18]. As discussed earlier, the

anhydrous magnesium sulphate served to remove water that was formed as a by-product during the reaction process yielding corresponding imine products as illustrated in scheme 2.10.



Scheme 2.10 G1 dendrimeric N,N′-donor ligands, **L3** and **L4**

The preparation of the dendrimeric ligands was carried out over an extended period of time to ensure complete modification of peripheral amino groups of the PPI-dendrimer with the corresponding aldehyde. Ligand **L3** was obtained as an orange oil and ligand **L4** was obtained as a yellow solid with yields of 71% and 90%, respectively. The oil was purified by washing extensively with water followed by extraction with dichloromethane to remove any unreacted aldehyde from the product. Ligand **L4** was obtained in a pure form and no further

purification was necessary. Both ligands were found to be soluble in most common solvents including dichloromethane, chloroform and toluene. They were found to be stable at room temperature and did not show any signs of decomposition in solution. Table 2.4 shows the analytical data for multifunctional dendrimeric ligands **L3** and **L4**. Similarly, 0.3 and 0.2 mols of CH_2Cl_2 were trapped in **L3** and **L4,** respectively. A similar observation was made with **L2**, mentioned in the previous section.

Table 2.4 Analytical data for multifunctional dendrimeric diimine ligands **L3** and **L4**

Dendrimeric ligands	**Molecular Formula**	**Micro-analysis Calculated (Found)**		
		%C	**%H**	**%N**
L3	$C_{40}H_{52}N_{10}$ .0.3 CH_2Cl_2	68.82 (68.88)	7.46 (7.65)	20.07 (19.79)
L4	$C_{56}H_{60}N_{10}$ .0.2 CH_2Cl_2	75.86 (75.70)	6.79 (7.06)	15.75 (16.37)

2.3.4.1 Characterization of [G-1 DAB-dendr-(NH_2)-1-(2-pyridyl- and quinolyl)-imine ligands, L3 and L4

The ligands were characterized using solid-state infrared, proton and carbon-13 nuclear magnetic resonance spectroscopy, elemental analysis, mass spectrometry and melting point measurements. The discussion of the details will follow.

2.3.4.2 FTIR spectroscopy of [G-1 DAB-dendr-(NH_2)-1-(2-pyridyl and quinolyl)-imine ligands, L3 and L4

Infrared spectroscopy was used to confirm the ligands prepared and figure 2.8 shows the IR spectrum of **L4**.

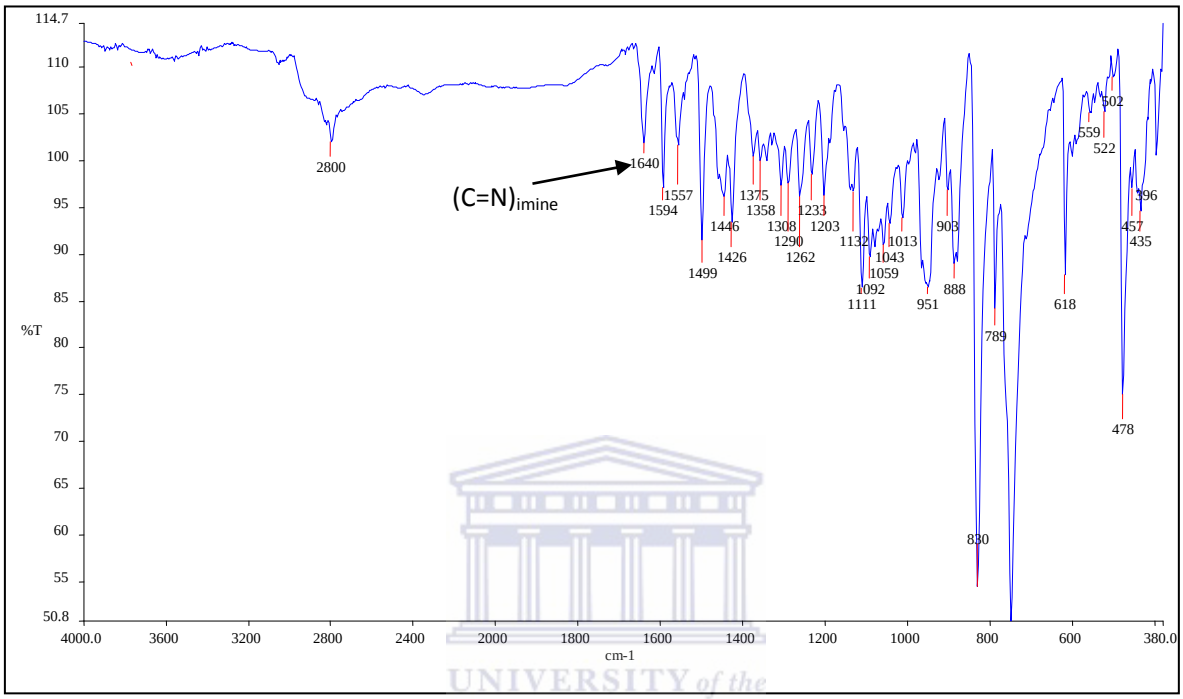


Figure 2.8 FTIR spectrum of [DAB-Fc], **L3**

Infrared spectra of dendritic ligands were obtained using an ATR accessory. The IR spectra of ligands **L3** and **L4** showed characteristic bands for free imine systems, υ(C=N), at 1649 and 1640 cm^{-1}, respectively. In the case of the pyridine based ligands this is consistent with the data obtained for monofunctional ligands. For quinoline based ligands the υ(C=N) stretching frequency is significantly lower than observed for monofunctional ligands because of the extent of electron delocalisation around the quinoline ring.

The infrared spectra of the pyridylimine ligands showed a strong band which appeared at 1587, assigned to the pyridine-ring υ(C=N) and υ(C=C) vibrations. However, for the

quinolylimine ligand **L4**, two strong bands were observed in the regions 1594 and 1557 cm^{-1}, also ascribed to the quinoline-ring υ(C=N) and υ(C=C) vibrations respectively. The absence of the aldehyde (C=O) stretching frequencies in both IR spectra of **L3** and **L4** around 1718-1720 cm^{-1}, confirmed that the aldehyde had reacted with the amine groups to form the corresponding imine ligands. A similar observation was made by Nketo [31]. Her infrared investigation of pyridylimine ligands showed three strong bands which appeared in the regions 1647-1650, 1567-1590 and 1550-1573 cm^{-1}, assigned to imine υ(C=N) vibrations and pyridine-ring υ(C=N) & υ(C=C) vibrations respectively. However , for the quinolylimine ligand, different infra-red spectra were obtained which show strong bands in the range 1642-1644, 1595-1596, 1557-1561 and 1502-1504 cm^{-1}, ascribed to υ(C=N) vibration of the imine functionality and quinoline-ring υ(C=N) and υ(C=C) vibrations respectively. As reported in this section before, absence of (C=O) stretching frequency in the range 1700-1750 cm^{-1} confirmed that the aldehyde had reacted with the amine.

2.3.4.3 ^{1}H and ^{13}C{^{1}H}-NMR studies of dendrimeric ligands (L3 and L4)

Both the ^{1}H and ^{13}C-NMR spectra of the dendritic ligands were obtained in deuterated chloroform. The spectrum in figure 2.9 for **L4** is a typical example of the spectra obtained for dendritic imine ligands. Evidence of the condensation reaction is clearly seen in the ^{1}HNMR spectra by the shift of CH_2 signals adjacent to the NH_2 of the starting dendritic polyamine, to a new downfield position as a result of the CH_2 group now being adjacent to an imine moiety. This signal appears around 3.67 and 3.45 ppm for **L3** and **L4**, respectively. The proton signals for internal branches of the dendrimer are seen between δ 1.19 - 3.50 ppm and these results correlate well with previous results by Malgas *et al.* [13,17] and Smith *et al.* [18,19] and van Wyk *et al.* [33]. The protons assigned to the aryl pyridine and quinoline units are observable downfield between δ 7.22 - 7.83 ppm as expected. These individual peaks were

assigned and summarized in Table 2.5. ^{1}H-NMR spectra of ligands **L3** and **L4** showed a proton signal at 8.36 and 8.25 ppm respectively indicating the presence of the iminic protons (**H**C=N). The ^{1}HNMR spectra of the samples show an absence of any aldehydic peak (**H**C=O) which usually appears at about 9.99 ppm.

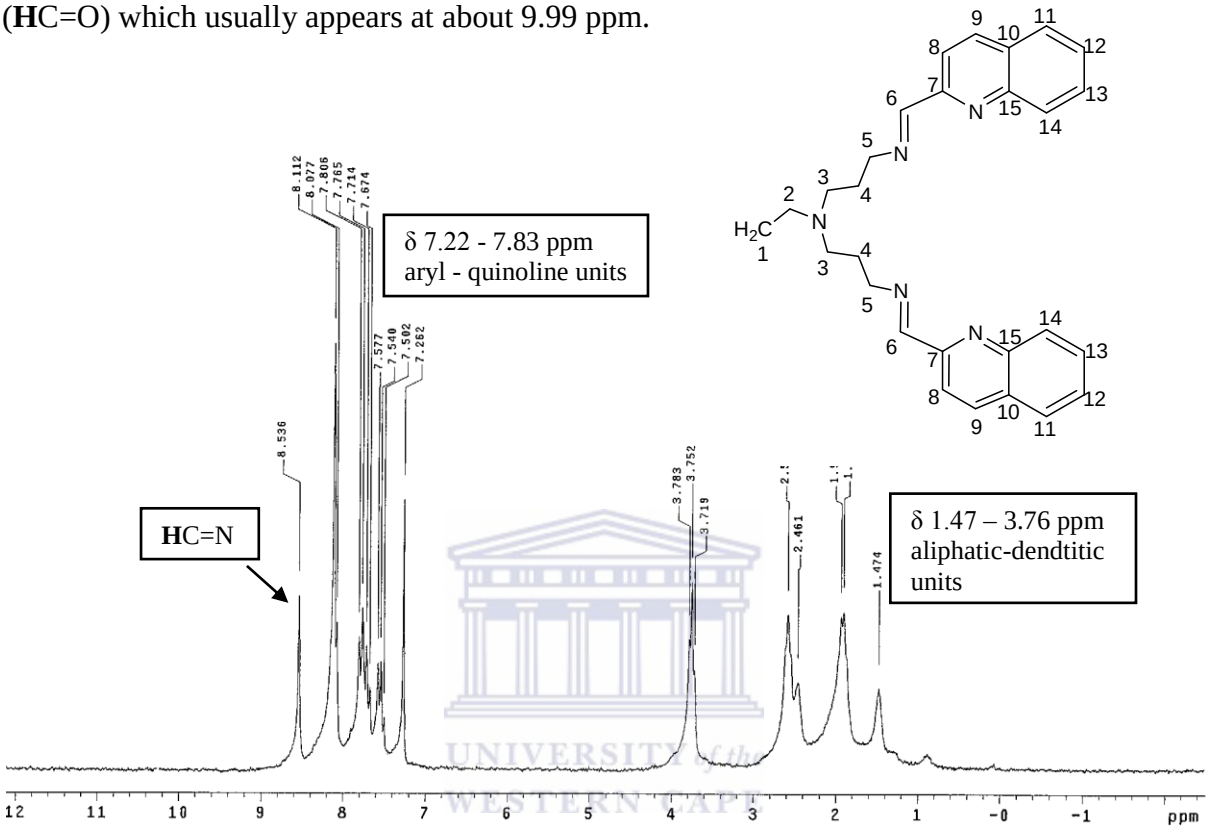


Figure 2.9 ^{1}H-NMR spectrum of **L4**

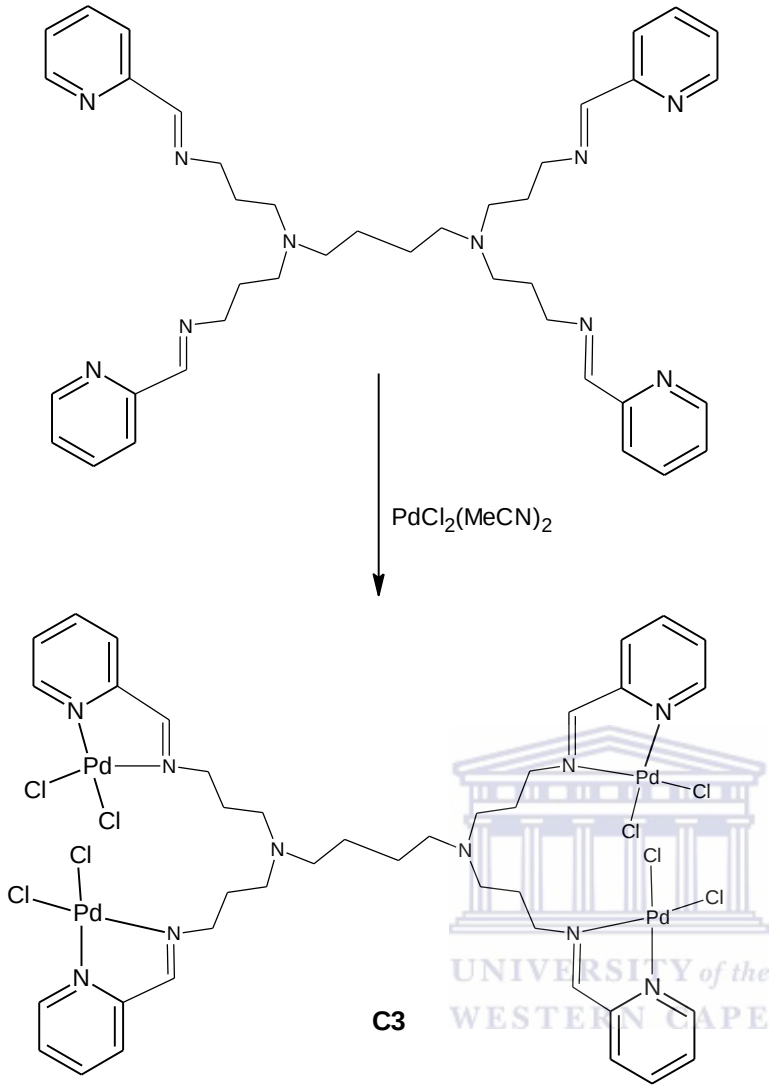
Similarly, the ^{13}C-NMR spectra of the iminopyridyl ligand **L3** and quinolyl ligand **L4** showed a signal for *C*=N carbon appearing downfield at 154.1 and 162.5 ppm respectively, also confirming the formation of the imine moiety. Other chemical shifts observed in **L3** include those of the aliphatic-CH_2 carbons in the region 24.7 - 59.1 ppm as well as the aromatic-CH carbons of the pyridyl ring in the region 120.7 - 161.4 ppm. However, in the case of **L4** the peaks due to the carbons of the internal branches of the dendrimer are found in the region 28.1 - 59.5 ppm and that of the quionolyl ring in region 118.4 - 154.5 ppm. Both proton and carbon-13 nuclear magnetic resonance spectra of the dendritic ligands **L3** and **L4** indicated strongly that the starting materials were converted to the corresponding imine

products. The ten remaining carbon atoms in the quinolyl region behaved as if in ten different magnetic environments. As a result, ten sets of signals were displayed in this region as indicated in Table 2.5. These observations are in agreement with the previously reported by Malgas *et al.* [13,17] and Smith *et al.* [13,17] and van Wyk *et al.* [33].

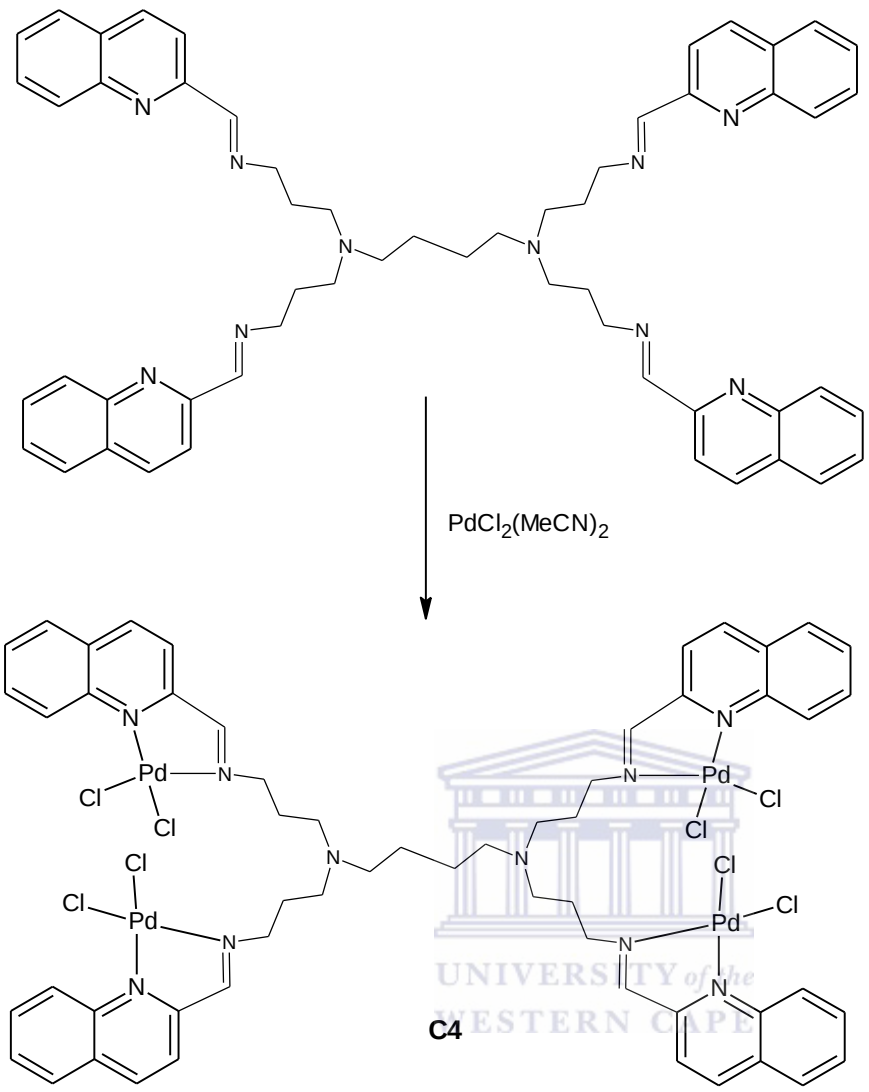
2.3.5 Synthesis of multinuclear dendrimeric Pd(II) complexes, C3 and C4

Complexes **C3** and **C4** were prepared by a modified procedure previously reported by Malgas *et al.* [13,17], Smith *et al*. [18,19] and van Wyk *et al.* [33]. The complexes were synthesized by reacting the imine ligands with $[PdCl_2(CH_3CN)_2]$ in dry DCM/MeCN under nitrogen atmosphere. The products were purified by washing extensively with DCM/MeCN to remove any unreacted imine ligand or $[PdCl_2(CH_3CN)_2]$. The pure products were obtained as yellow solids in yields of 82% for **C3** and 74% for **C4**. The products isolated were multinuclear dendrimeric Pd(II) complexes, as shown in scheme 2.11 and 2.12. The multinuclear complexes were only slightly soluble in DMSO and not in common organic solvents such as DCM, chloroform and toluene. The complexes precipitated immediately out of solution as the imine ligand was added to the palladium precursor due to its low insolubility. As a result, very poor NMR spectra were obtained. From the NMR the most important iminic peaks were observed. Complex **C5** was obtained from Stellenbosch University and was used in the next Chapter.

The structures of the metallodendrimers with $PdCl_2$ moieties bonded to pyridylimino and quinolylimino units were confirmed by ^1H and ^{13}C-NMR spectroscopy in DMSO-d_6 and solid state FTIR spectroscopy.



Scheme 2.11 Dendrimeric Pd(II) complex, **C3**



Scheme 2.12 Dendrimeric Pd(II) complex, **C4**

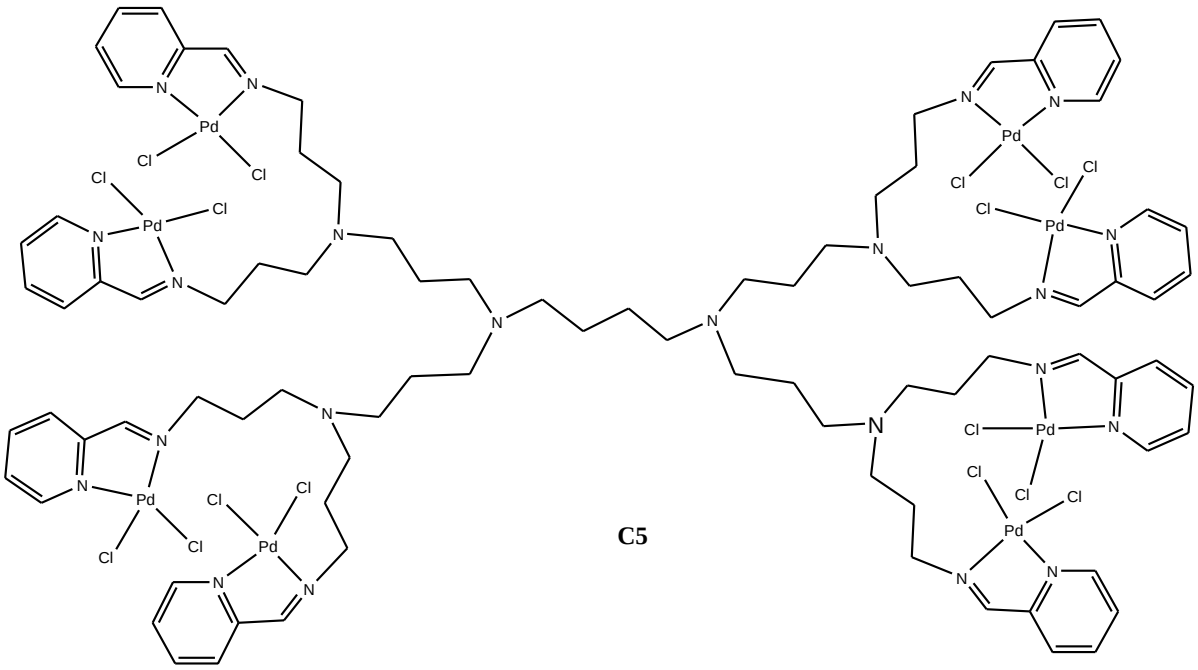


Figure 2.10 G2- Dendrimeric Pd(II) complex, **C5**

2.3.5.1 FTIR spectroscopic studies of C3 and C4

The IR spectrum of **C4** is shown below in figure 2.11 and the results summarized in Table 2.4 include the υ(C=N) stretches for the complexes.

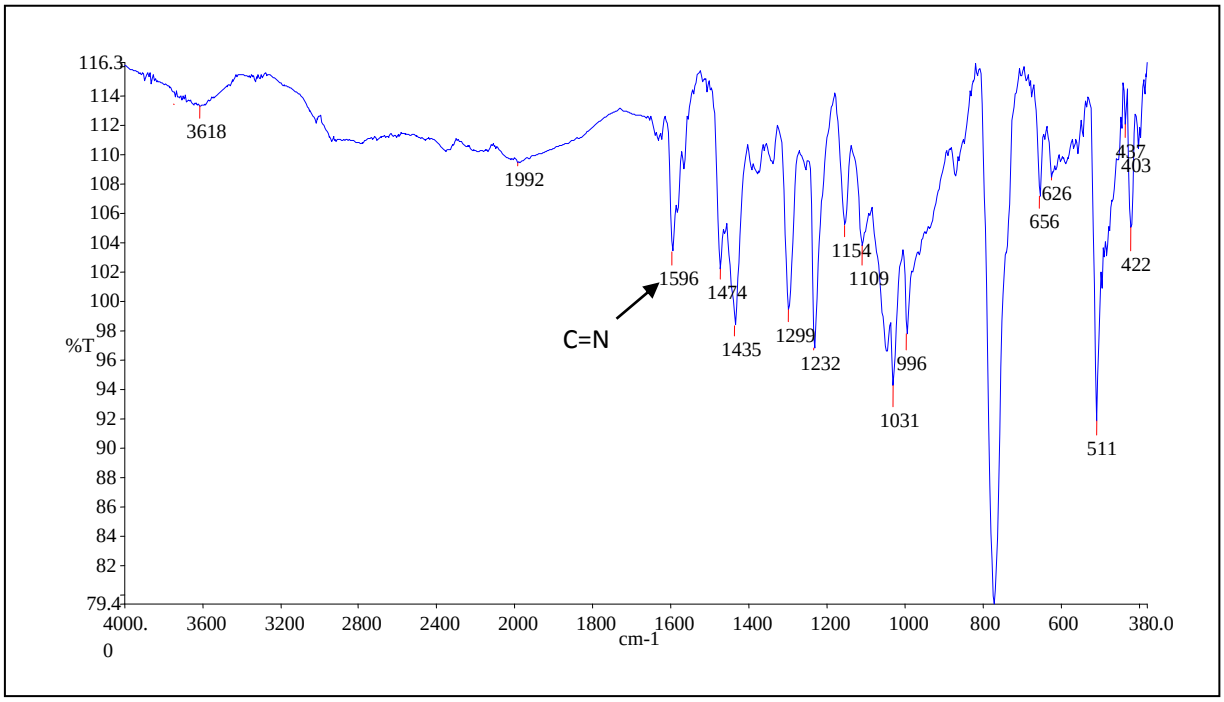


Figure 2.11 The IR spectrum of **C4**

Infrared spectroscopy was also used as an investigation tool to determine the coordination of the dendrimeric ligands to the palladium precursor to form the desired complexes. Coordination was confirmed by an absorption band due to the imine (C=N) vibrations appeared at lower wave numbers as compared to the dendrimeric ligands. This shift is as a result of the reduction of the electron density of the C=N bond arising from the electron flow from the ligand to the metal centre. The C=N absorption frequencies are greatly reduced in intensity, which indicate the coordination interaction between imino nitrogen atoms and the palladium metal centre. Similar observations were made by Smith et al. in their imino-pyrridyl palladium dendritic complexes. The absorption frequencies for their dendritic ligands were observed to have shifted from around 1645 cm^{-1} of a free ligand to values between 1590 and 1599 cm^{-1}. In the case of our pyridine based palladium complex **C3**, the υ(C=N) vibrations shifted from 1648 cm^{-1} (ligand) to 1612 cm^{-1}(complex) and in the case of **C4**, the υ(C=N) vibrations shifted from 1640 cm^{-1} (ligand) to 1596 cm^{-1} (complex).

2.3.5.2 ^{1}H and ^{13}C{^{1}H}-NMR spectroscopic studies of dendrimeric complexes, C3 and C4

The multinuclear dendrimeric Pd(II) complexes, **C3** and **C4** were further characterized by NMR studies in DMSO-d_6. Due the insolubility character of the complexes **C3** and **C4**, ^{1}H and ^{13}C -NMR spectra with very poor resolution were obtained. The proton NMR spectra of these complexes showed broadened peaks as compared to their analogous ligands. NMR signals due to aliphatic protons of the dendrimer core, side-arms and those of the pyridine/quinoline ring occur at chemical shifts similar to those of the parent ligands. The only difference is the fact that in the complexes there is a slightly downfield shift. The shift occurs drastically for the proton of the imine moiety (HC=N) and the protons of the CH_2 group adjacent to the imine moiety (H_2C-N=CH). This is due to coordination of the imine

ligand to the metal centre via the pyridine/quinoline nitrogen and imine nitrogen. In the case of pyridine based palladium complex **C3**, the signal for the imine proton shifted from 8.36 ppm (ligand) to 8.91 ppm (complex) and in the case of **C4**, it shifted from 8.25 ppm (ligand) to 8.59 ppm (complex). A similar observation was made by Smith *et al.* [17,18].

Carbon-13 nuclear magnetic resonance spectroscopy was also used to investigate ligand complexation. All complexes gave relatively poor quality spectra because of the poor solubility of these compounds. Even so all peaks were able to be assigned to the corresponding carbons and the results are tabulated in Table 2.6. A shift in the iminic carbon signal was observed when comparing the ligand spectrum with that of its complex. In the case of the pyridine based palladium complex **C3**, the imine carbon signal shifted from 154.1 ppm (ligand) to 155.0 ppm and in the case of **C4**, it shifted from 162.5 ppm (ligand) to 169.3 ppm (complex) and these results are in good agreement with similar compounds reported in the literature.

^{1}H and ^{13}C-NMR spectroscopy in DMSO-d_6 and solid state FTIR spectroscopy were used as characterization analytical techniques to determine the formation of the multinuclear dendrimeric Pd(II) complexes, **C3** and **C4**.

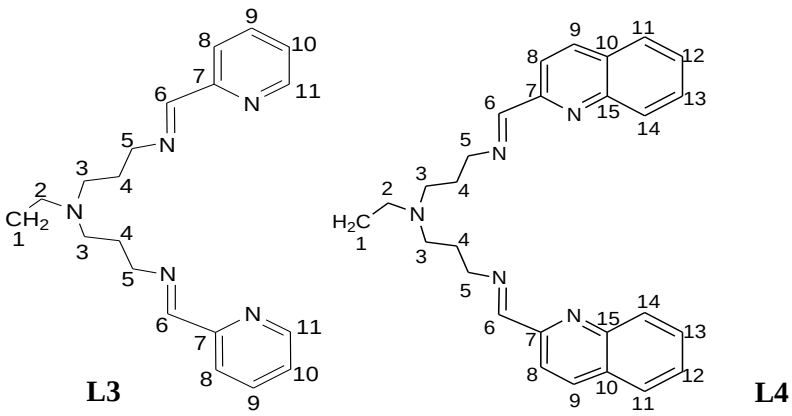


Figure 2.12 Illustration of two arms and the first two carbons of the dendrimeric core.

Table 2.5 ^{1}H-NMR Chemical shifts of multi-functionalised dendrimeric ligands, **L3** and **L4** and complexes, **C3** and **C4**

Protons	**L3**	**L4**	**C3**	**C4**
H-1	1.4 (m,4H)	1.19 (m,4H,J=6.2)	3.926 (m,4H)	2.84 (m,4H)
H-2	2.40 (t,4H)	2.18 (t,4H,J=6.6)	4.26 (t,4H)	3.76 (t,4H)
H -3	2.51 (t,8H)	2.30 (t,8H,J=7.0)	4.85 (t,8H)	3.91 (t,8H)
H-4	1.84 (qn,8H,J=7.8)	1.65 (qn,8H,J=6.6)	4.264 (qn,8H)	3.84 (qn,8H)
H-5	3.67 (t,8H,J=6.6)	3.47 (t,8H,J=6.6)	6.27 (t,8H)	4.22 (t,8H)
H-6	8.36 (s,4H)	8.25 (s,4H)	8.90 (s,4H)	8.59 (s,4H)
H-7				
H-8	7.92 (d,4H)	7.79 (d,4H)	9.09 (d,4H)	6.05 (d,4H)
H-9	7.70 (t,4H,J=7)	7.52 (d,4H)	8.50 (t,4H)	8.23 (d,4H)
H-10	7.28 (t,4H,J=7.6)		7.11 (t,4H)	
H-11	8.60 (d,3H)	7.48 (d,4H)	9.09 (d,3H)	8.81 (d,4H)
H-12		6.98 (m,4H,J=7.0)		9.32 (m, 4H)
H-13		7.26 (m,4H,J=7.6)		9.5 (m,4H)
H-14		7.39 (d,4H,J=7.6)		8.85 (d,4H)

NMR Solvent: **L3** and **L4:** $CDCl_3$; **C3** and **C4**: DMSO-d_6, Units = ppm

Table 2.6 $^{13}C\ \{^{1}H\}$-Chemical shifts of multi-functional dendrimeric ligands **L3** and **L4**, and complexes **C3** and **C4**

Protons	**L3**	**L4**	**C3**	**C4**
C-1	22.7	28.1	24.7	21.1
C-2	28.6	51.7	27.8	38.2
C -3	25.5	54.0	28.6	38.6
C-4	52.1	58.6	51.2	23.9
C-5	54.4	59.5	53.6	39.0
C-6	155.0	162.5	154.1	169.3
C-7	60.0	147.8	59.1	138.0
C-8	121.6	129.7	120.7	129.4
C-9	124.9	128.7	124.0	128.3
C-10	136.8	136.5	136.0	130.8
C-11	149.7	127.7	148.9	79.6
C-12		118.4		57.8
C-13		127.3		69.0
C-14		127.7		114.1
C-15		154.8		145.3

NMR Solvent: **L3** and **L4:** $CDCl_3$; **C3** and **C4**: DMSO-d_6, Units = ppm

2.4 CONCLUSION

Ferrocenylimine ligands **L1** and **L2** as well as dendrimeric generation 1 ligands **L3** and **L4** were synthesised via Schiff base condensation reactions of appropriate amine and the corresponding aldehydes. The ligands were obtained in very good yields of about 70%.

By complexing these ligands, with the transition metal salts of palladium, $[PdCl_2(COD)]$ or $[PdCl_2(MeCN)_2]$, the desired palladium complexes, **C1-C4** were obtained. All the complexes showed very low solubility toward common solvents used. Due to this, very poor NMR spectra were obtained. The ligands and complexes were characterized by FTIR spectroscopy, ^{1}H-NMR spectroscopy, ^{13}C-NMR spectroscopy, microanalysis and mass spectrometry. These complexes were used as catalysts in Heck coupling reactions of iodobenzene and styrene in the following chapter 3.

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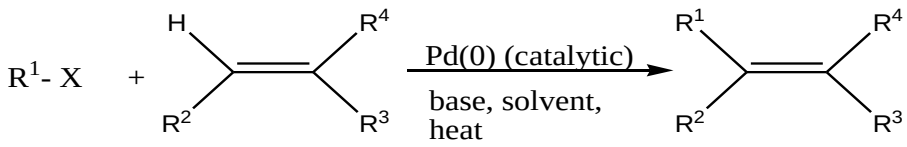
CHAPTER 3: CATALYSIS

HECK COUPLING REACTIONS

3.1 INTRODUCTION

Palladium based catalysis is a powerful tool for both common and modern organic synthesis. The best example of a catalytic processs that almost wholy uses Pd metal is Heck and Suzuki coupling reactions. The Heck reaction is a palladium-catalyzed cross coupling reaction of organyl halides to alkenes and is a very important yet somewhat unpredictable carbon-carbon bond forming process. Unlike most catalytic organic reactions, the Heck reaction is not well defined and specific for particular reagents and catalysts with optimal conditions, solvents, ligands, etc. Instead, the scope of the reaction is changing, expanding, and being improved on frequently. Therefore, fine-tuning this reaction entails thousands of variations and involves learning about palladium catalysis as a whole [1]. Among the different types of palladium-catalyzed reactions, the Heck reaction was one of the first to be developed by Mizoroki and Heck in the early 1970's.

Mizoroki and co-workers reported the reaction with aryl iodides and potassium acetate in methanol at 120 °C independently of Heck and co-workers. However, Heck and co-workers reported the reaction under more opportune laboratory conditions by reacting organyl halides with olefinic compounds in the presence of a hindered amine base and catalytic palladium to form substituted olefins. Due to the Heck reaction being a reasonably simple route to synthesize substituted unsaturated organic compounds, its application is widely used in polymerization chemistry, preparation of UV screens, pharmaceuticals, preparation of hydrocarbons, and in advanced enantioselective synthesis of natural products [1]. The Heck reaction has become one of the most useful catalytic carbon-carbon bond forming processes in organic synthesis. Scheme 3.1 shows the general Heck reaction in which aryl, benzyl and styryl halides react with olefins at high temperatures in the presence of an amine base and a catalytic amount of Pd(0) to form substituted olefins.



Scheme 3.1 General Heck reaction [1]

Kurti *et al.* reported that the Heck reaction works best for the preparation of disubstituted olefins as opposed to monosubstituted analogues and also, the electronic nature of the substituents on the olefins has a limited influence on the reaction. However, electron poor olefins tend to give higher yields. In addition, a wide variety of functional groups can be present on the olefin such as esters, ethers, carboxylic acids, nitriles, phenols, dienes, but allylic alcohols tend to rearrange [2]. An important aspect of the Heck reaction is the formed in-situ generation of the active palladium species. The active palladium catalyst can be formed in-situ from pre-catalysts such as $Pd(OAc)_2$ and $Pd(PPh_3)_4$. Usually the reaction is carried out with mono and bidentate ligands.

However, the reaction can work with or without phosphine ligands, but the phosphine ligands usually stabilize the palladium in its zero oxidation state. The utilization of phosphine ligands is the common and well-established approach that gives optimal results in a majority of cases [1]. It has also been found that the reaction rate depends on the degree of substitution of the olefinic compound. Generally, more substituted olefins progress at a slower rate than less substituted olefins. Also, the X group on the aryl or vinyl substituent has a large impact on the rate of the reaction. Typically the order of X from fastest to slowest rate is I > Br ~ OTf >> Cl. It is typically difficult in catalysis to execute a coupling reaction with an aryl or vinyl chloride and it remains a challenge to have it work as well or better than other halides. It is

also worth noting that usually unsymmetrical olefins undergo substitution at the least substituted carbon [2].

The Heck reaction has been utilized in hundreds of works and still remains a mystery as to the exact scope of the reaction. Small variations such as substrate structure, nature of the base, ligands, temperature, pressure lead to mixed results. Sometimes more sophisticated ligands for more advanced organic transformations will be unsuccessful for the simplest cases of the Heck reaction. On the other hand, much advancement has been made in its mechanistic detail and flexibility as a catalytic carbon-carbon bond forming reaction, which will be discussed below in the mechanism [1].

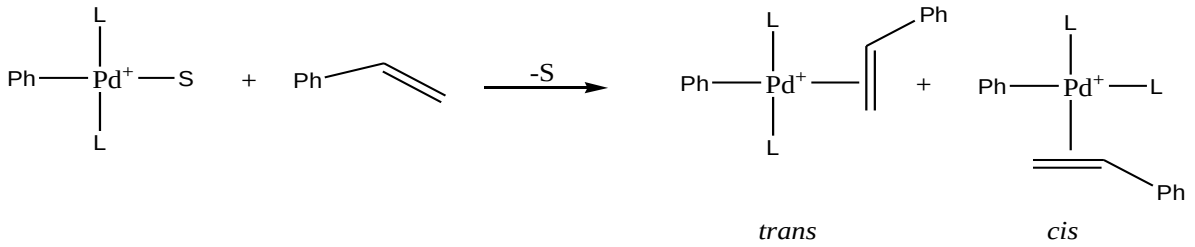
The Heck reaction is similar to the "textbook" mechanism of cross coupling reactions except that the carbon-carbon bond forming reaction is established by migratory insertion instead of reductive elimination. The process is driven by the ability of Pd(0) complexes to undergo oxidative addition with C-X bonds followed by the addition of olefinic compounds to the metal centre. In general, the reaction undergoes a cationic mechanism when X is OTf^-, OAc^-, or when Ag^+, TI^+, quaternary ammonium and phosphonium salts are used to help displacement from halides. This mechanism also predominates when chelating ligands are used for catalysis. For the Heck reaction to undergo a neutral mechanism, X is usually a strong σ-donor such as Cl, Br, or I [1].

From the mechanism (Scheme 1.12 on page 20), it is imperative to reduce Pd(II) to Pd(0) in order to generate the active species. Primary reduction is most likely accomplished by phosphine, and the reduction is assisted by hard nucleophiles. Usually the most common approach to obtain the active Pd(0) is to generate it in situ from $Pd(OAc)_2$ and PPh_3 to form Pd(0). Most likely the nucleophile attacks the coordinated phosphine via a nucleophilic

substitution of the phosphorus atom. Contrary to the belief that donor phosphines are more susceptible to oxidative oxidation, in this reaction electron-withdrawing groups on phosphine increase the rate of the reaction. Also, at high temperatures, the most likely active species is Pd nanoparticles [1]. The incorporation of an amine base has a beneficial effect in that it is involved in the primary reduction of Pd(II), but the base has no influence on the reduction rate in the presence of phosphine. However, it is notable that the Pd(0) species must have a proper coordination shell in order to undergo oxidative addition. No more than two strongly bound ligands are allowed, which leads to a restriction on the choice of ligands and their concentration in the Heck reaction [3]. The first step of the catalytic cycle is the oxidative addition to usually a 14-electron complex ($Pd(0)L_2$). The oxidative addition of C-X bonds is usually the rate determining step and proceeds through a concerted type mechanism. The *cis*-geometry is formed first, but the *trans* geometry is preferred because phosphine ligands prefer to be opposite to one another. The oxidative addition step of the Heck reaction has been investigated further by studying the kinetics of this step. The active anionic $Pd(OAc)_2$ species was measured with an amperometry at a rotating disk electrode polarized on the plateau of the oxidation wave of the Pd(0) complex. They found that the addition of PhI led to rapid decay of oxidation current, but at longer times, the oxidation current rose again. This meant that iodide ions were released into solution upon oxidative addition and the reaction proceeds through a short lived anionic pentacoordinated complex. In addition, Jutand and Amatore found that the reaction is zero order with respect to [PPh_3] and first order with respect to [$Pd(OAc)_2$]. Therefore, it was established that the oxidative addition was the rate-determining step of the Heck reaction [3].

Also, Amatore and Jutand found that the cationic complex $[PhPd(PPh_3)_2]^+[BF_4]^-$ reacts with styrene, but the reaction is slower than that with $PhPd(OAc)(PPh_3)_2$. This is because the

solvated cationic species gives a *trans*-adduct that requires isomerization to allow *syn*-insertion of the olefin into the Ph-Pd bond (Scheme 3.2). They found that the trans -$PhPd(OAc)(PPh_3)_2$ reacted slowly unless acetate ions were added, which established that $PhPd(OAc)(PPh_3)_2$ is the key reactive intermediate in Heck reactions. Its reaction with olefins is the rate-determining step of the catalytic cycle [3].



Scheme 3.2 Solvated cationic species

Migratory insertion is the product-forming step of the Heck cycle where the new C-C bond is formed. It is this step that can explain regio- and stereoselectivity as well as substrate selectivity. From the mechanistic studies, it was found that the reaction of the active intermediate is inhibited by excess phosphine, which establishes that a free coordination site is required for olefin coordination. Computational data has shown that by addition of a cationic carbene complex in the migratory insertion stage of the reaction, the degree of charge transfer from Pd to the olefin is negligible and there was no charge build-up in the transition state. This confirmed that the migratory insertion step takes place through a concerted process, not an SN2 type mechanism [4].

The stereochemistry of the product makes the Heck reaction an appealing reaction for organic synthesis. Generally, the Curtin-Hammet principle is the controlling factor for E and Z product ratio, where the *E* isomer is usually obtained unless **R** is very small [1]. However, steric and electronic factors play major role in controlling the outcome of the insertion process. Migratory insertion can place the aryl group on either carbon of the alkene.

Electronic factors can control this placement. In the case of electron deficient alkenes and styrene derivatives, the aryl group is placed on the most electrophilic β-carbon to the Ph or electron withdrawing group. With electron rich alkenes, the opposite regiochemistry is usually obtained with the aryl group α to the electron donating group, but with the aryl group still placed on the most electrophilic carbon. With neither electron rich nor electron deficient alkenes, a mixture of products can be produced with steric factors controlling the outcome [12]. Following migratory insertion, β-Hydride elimination occurs. The elimination must occur through a *syn*-coplanar geometry between the Pd and the β-hydrogen atom. The process is concerted and goes through a strong agostic interaction between the Pd and a β-hydride. After the *syn*-elimination, the PdH is scavenged by base and Pd(0) is released back into the catalytic cycle [3, 4].

3.2 GENERAL PROCEDURE FOR HECK REACTION

Under nitrogen atmosphere, iodobenzene (2.040 g, 10 mmol) and styrene (1.041, 10 mmol) were syringed into a two-necked round-bottomed flask. Triethylamine (1.020, 10 mmol) was added as a base and the mixture dissolved in 30 ml dry acetonitrile. The palladium catalyst was then added (0.02 mmol) and the mixture heated under reflux under nitrogen at 82 °C. Samples (1000 μL) were withdrawn at periodic intervals and 100 μL of toluene, the internal standard added. The consumption of iodobenzene was monitored by the GC. The product yield was obtained after the comparison with the amount of the internal standard. The converted substrate (i.e. styrene) was calculated as a percentage of the initial substrate used and thus plotted against time. After the reaction time, the reaction mixture was allowed to cool to room temperature, filtered and solvent removed under reduced pressure. After removal of the solvent, the residue was characterized by ^{1}H-NMR spectroscopy. GC analyses

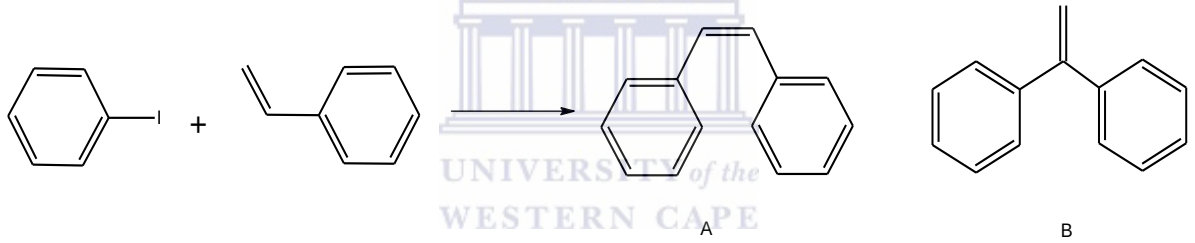
were performed on an Angilent Technologies 7890A GC system using Agilent 19091J-413: 325 °C: 30 m x 320 µm x 0.25 µm HP-5 5% Phenyl Methyl Siloxan: HP-5 column.

Oven programmed: 50 °C for 1 min, then 15 °C/min to 133 °C for 12 min, then 5 °C/min to 138 °C for 3 min, then 10 °C/min to 200 °C for 8 min. Post run temperature 40 °C.

Injection vol (1 µL), DCM vol (8 µL). Heater 250 °C, Pressure 90.389 kPa, Total flow 66 mL/min, Septum purge flow 3 mL/min. Gas saver 20 mL/min after 2 min.

3.3 RESULTS AND DISCUSSION

Evaluation of catalytic activity of dendrimeric Pd(II) complexes (C1-C5) towards Heck Coupling Reactions



Scheme 3.3 Iodobenzene conversion during arylation of styrene

The $PdCl_2(MeCN)_2$, ferrocenyliminedichloro Pd(II) complexes (**C1** and **C2**) and multinuclear [G-1/G2 DAB-dendr-(NH_2)n-1-(2-pyridyl/quinoline)-imine]dichloro Pd(II) complexes (**C3**, **C4** and **C5**) shown in figure. 3.1 in the next page, were tested as catalysts for the Heck C-C coupling reactions of iodobenzene and styrene using the literature reaction conditions [5]. These investigators used MeCN as the solvent and Et_3N as the base at a temperature of 82 °C. Our studies focused largely on the ferrocenylimine palladium complexes **C1** and **C2** as the palladium sources, although some reactions with the first-generation dendrimer palladium complexes **C3** and **C4** were also carried out. The second-generation palladium metallodendrimer complex **C5** was tested for a comparison with first-generation dendrimer

palladium complexes. Iodobenzene was chosen as the organohalide substrate, as this is the most reactive of the haloarene family. Triethylamine was used to remove the halo-acid (hydrogen iodide) formed as a by-product during the reaction. The reactions were carried out at an optimized temperature of 82 °C in acetonitrile for over a period of 24 h. Equivalent molar ratios of iodobenzene, styrene and triethylamine were used. All the complexes were found to catalyze the coupling of iodobenzene with styrene. While literature reports indicate catalyst deactivation for cyclopalladated imine catalysts at temperatures above 80 °C [6,7], only **C4** showed signs of decomposition, forming palladium black.

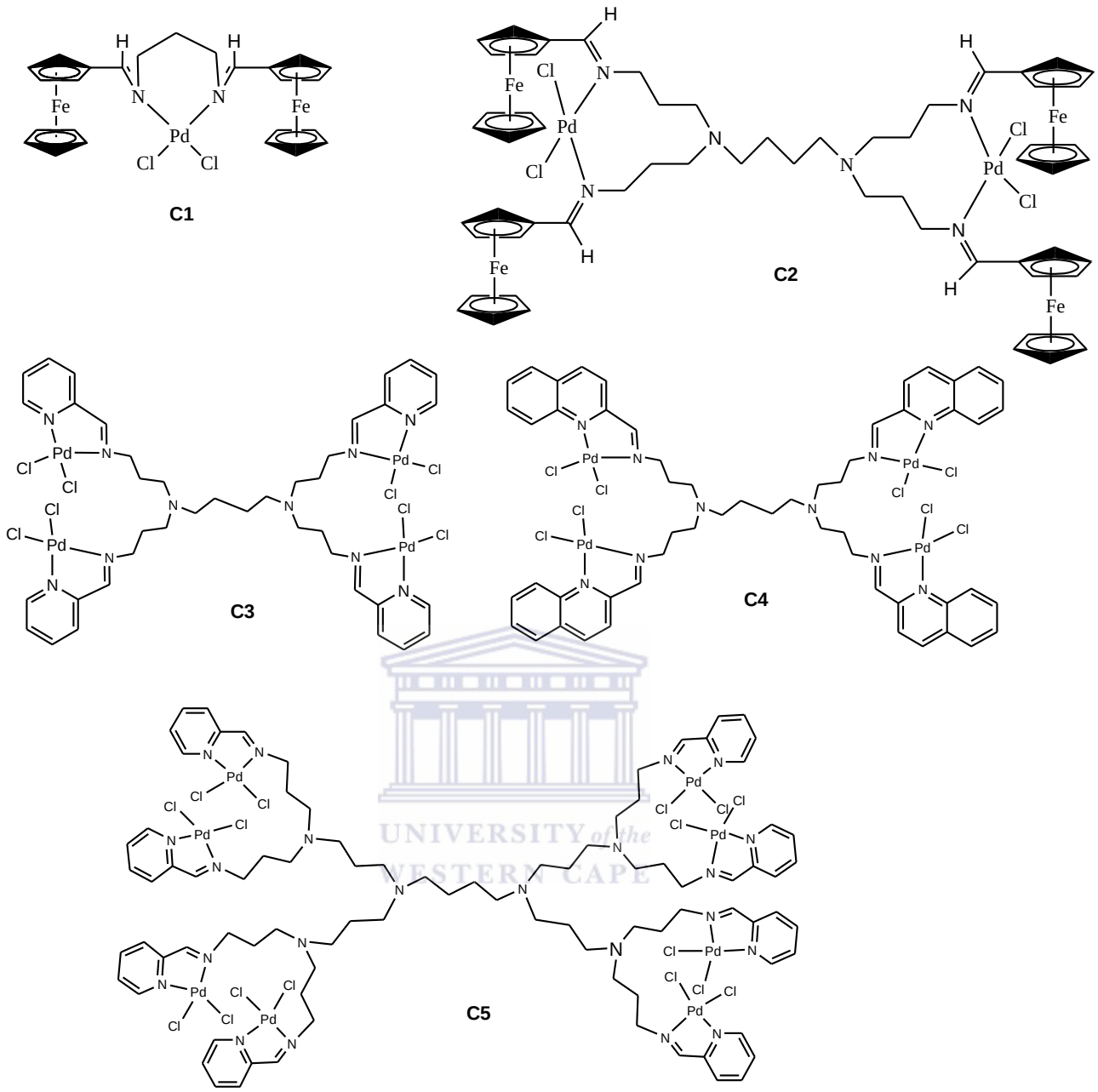


Figure 3.1 Complexes **C1 – C5**

A sample of the reaction mixture without any of the catalyst precursor present was first withdrawn. This was to determine by means of Gas Chromatography, the initial amount of iodobenzene present before commencement of the arylation reaction. After addition of the catalyst precursor, samples were withdrawn at periodic intervals and the consumption of iodobenzene was monitored by GC. Figure 3.2 gives the percentage conversion of

iodobenzene versus time using $PdCl_2(MeCN)_2$, ferrocenyliminedichloro Pd(II) complexes (**C1** and **C2**) and the multinuclear [G-1/G2 DAB-dendr-$(NH_2)_n$-1-(2-pyridyl/quinoline)-imine] dichloro Pd(II) complexes **C3**, **C4** and **C5** complexes as catalyst precursors. The conversion of iodobenzene was calculated based on toluene as an internal standard. Reactions were carried out at different catalyst concentrations.

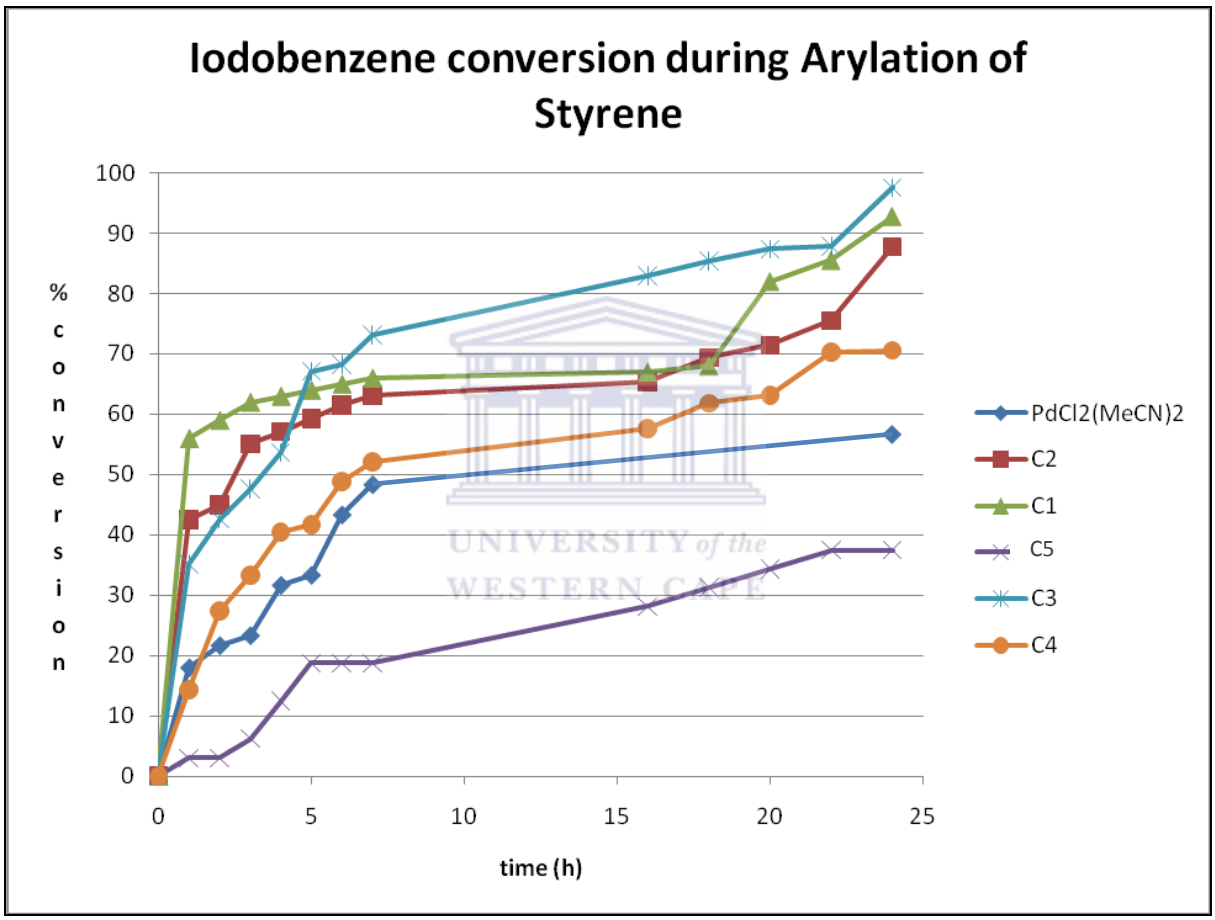


Figure 3.2 Iodobenzene conversion during arylation of styrene

All the reactions start after a short induction period of less than an hour for all the complexes, in which the initially observed orange suspension becomes a dark red solution. Catalysts **C1** – **C4** exhibited high activity as observed from the graph. Catalyst **C3**, (Figure 3.3), was the most active of all the evaluated catalysts in the arylation reaction of iodobenzene, yielding an

almost 75% conversion of the iodobenzene after only seven hours. The notably high efficiency of **C3** was attributed to the electronic effects of the coordinated pyridyl imine ligand, suggesting that pyridyl imine ligand participates in the catalytic cycle. Probably, the conversion of iodobenzene could reach 100% by prolonging the reaction time. However, ferrocenylimine-palladium complexes **C1** and **C2**, were found to be more active than complex **C4** and **C5** **(**Figure 3.2) and $Pd(MeCN)Cl_2$ yielding almost 65% iodobenzene conversion after seven hours indicating that there is a necessity for the ligands. Cyclopalladated ferrocenylimimes are very stable compounds and hence complexes **C1** and **C2** were found to be more active. As described in the literature regarding the coupling reaction mechanism, it is generally believed to consist of two parts (Scheme 3.2), which both contain three main steps: oxidative addition, insertion and reductive elimination [1]. It is reported that in the first part, the Pd–C bond in cyclopalladated ferrocenylimines undergoes rupture, thereby generating Pd(0) species. It is believed that the active catalytic species is Pd(0), rather than the Pd(II). The rupture of the Pd–C bond also releases ferrocenylimine. Due to this, the researchers proposed that the ferrocenylimine in turn coordinates the Pd(0) forming $Pd(0)L_2$, therefore stabilizing the Pd(0) catalytic core [1]. Hence the observed good catalytic power of cyclopalladated ferrocenylimine in catalyzing the coupling of vinyl halides and activated alkenes. The other reason may be due to stabilization of the catalytic core Pd(0) by ferrocenylimine coordination. This assertion is supported by others [8,9]. The $Pd(0)L_2$ reacts with iodobenzene through an oxidative addition mechanism, which results in the formation of the corresponding pentacoordinated palladium(II) species.

However, complex **C1** was actually more reactive than complex **C2**. This could be due to the fact that **C2** is much more bulky than **C1**. Complex **C1** only contains two ferrocenyl rings, i.e. four cyclopentadienyl (Cp) rings, whilst **C2** has four ferrocenyl rings, i.e. eight rings. This

means that **C2** is sterically bulky and this could be limiting the accessibility of the substrate to the catalyst's active site. Therefore, looking at the percentage conversion of the two ferrocenyl complexes, and from what we know, the Heck reaction of styrene and iodobenzene prefers the less bulky complex **C1** than the sterically bulky **C2**. A similar observation was made by Ma *et al*. [10], they investigated the Suzuki cross-coupling in a one pot borylation fashion using cylopalladated ferrocenylimine and concluded that steric hindrance had a negative effect on the synthetic reaction of symmetrical biaryls, just as other reports indicate [11,12].

During the reaction with first-generation quinoline palladium complex **C4**, partial decomposition to residual palladium metal as palladium black formation was observed. This is possibly the reason for the lower activity. Primary particles formed in solution upon reduction have a tendency to agglomerate to form larger metallic particles. Palladium is generally kept in solution as its phosphine complex, rather than precipitating out as the metal. However, for complexes **C1**, **C2**, **C3** and **C5**, no undesired formation of elemental Pd was observed. The dendrimer therefore acts as a good support and retards the tendency of the metal sites to agglomerate and precipitate from solution. Pittman and Ng [13] co-ordinated palladium(0) catalysts to polymer matrices and have shown that these resin-bound catalysts have lower levels of metal agglomeration, a phenomenon commonly observed for many homogeneous catalysts. Complex **C4** also displayed steric hindrance that is imparted by the four quinoline rings of the ligand that could hamper the reaction of the aryl halide (iodobenzene) with the metal centre catalyst thus slowing down the catalytic cycle.

A control reaction was run, using $Pd(MeCN)Cl_2$ at the same palladium concentration as for the rest of the palladium complexes used in this study. This was found to be more active than

the second-generation palladium metallodendrimer **C5** with a 58% conversion at 24 h. Again, the low activity of the second-generation palladium metallodendrimer complex **C5** might be due to the fact that it is sterically more bulky than the first generation palladium complexes thereby limiting the accessibility of the substrate to the active sites. This is a similar observation to the findings on Heck-coupling reactions of iodobenzene and styrene by Smith *et al.* [5].

By comparing the rate of consumption of iodobenzene, the catalytic activity for the series of the Pd(II) complexes may be arranged in decreasing order:

C3 > **C1** > **C2** > **C4** > **C5**

A control reaction performed with the same substrates under the same conditions, but in the absence of any palladium, revealed that the coupling reactions did not occur in the absence of the salts.

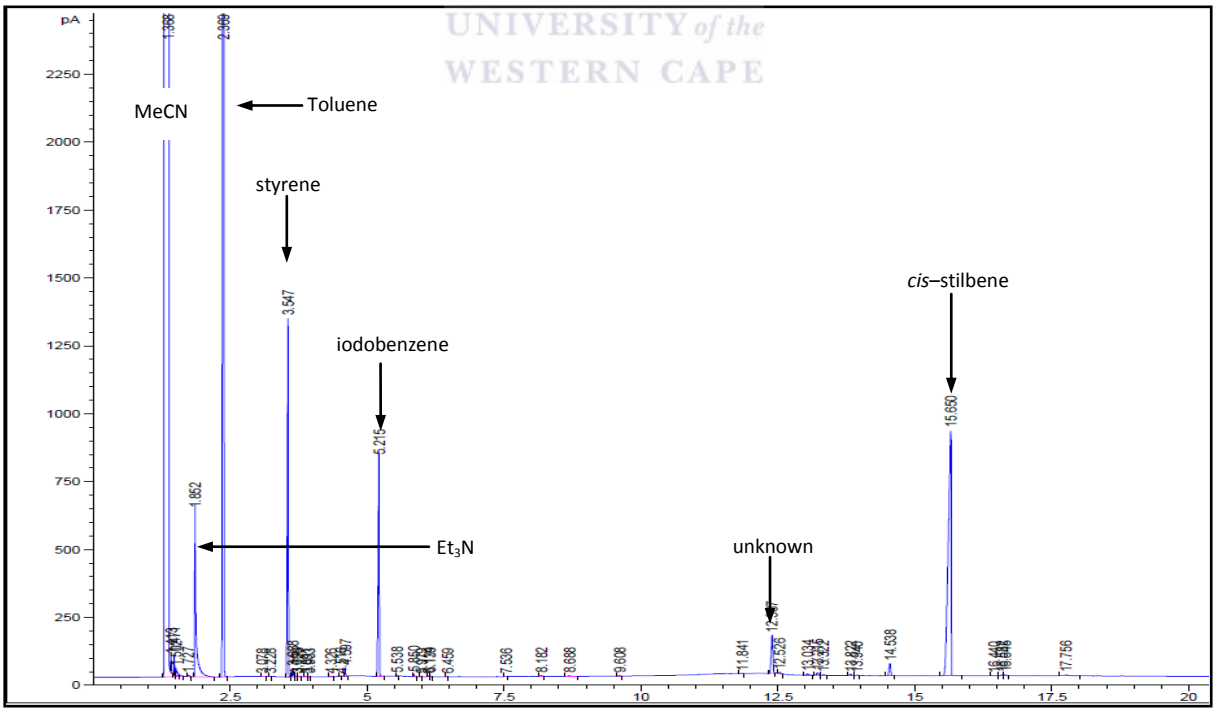


Figure. 3.3 GC-chromatogram of arylation of iodobenzene, after 24 hrs, catalysed by complex **C3**.

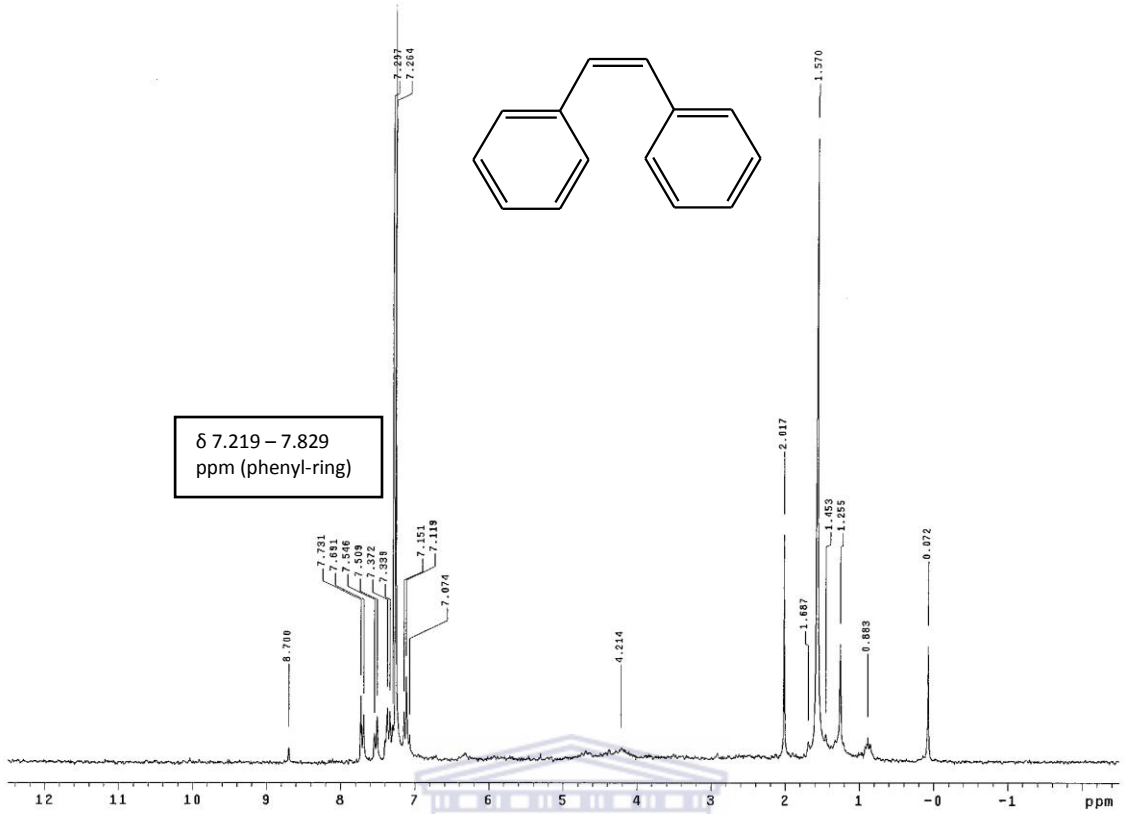


Figure. 3.4 ^{1}H NMR spectrum of crude product of arylation of iodobenzene, after 24 hrs, catalysed by complex **C3**.

The regioselectivity of the arylation of iodobenzene catalysed by the palladium complexes **C1-C5** was determined by ^{1}H NMR spectroscopy (Figure 3.4). The products obtained were filtered and dried and their ^{1}H-NMR investigated. Selectivity for the *cis*-stilbene product (compound **A**, Scheme 3.3) was observed regardless of the catalyst precursor employed. In all the ^{1}H NMR spectra, the chemical shift 8.70 ppm was obtained which could be assigned to the olefinic proton. This is the chemical shift which is characteristic of a stilbene which is one of the possible products. The aromatic protons were observed in the region 7.08 – 7.73 ppm. However, specific products identification requires the standards of all the expected products which only arrived after the experiments were complete. It would be interesting to match the complexes with the product as it is believed each should give different products due to the differences in their structures. The chromatogram (Figure 3.3) represents the arylation of

iodobenzene by **C1**. The peak at 12.39 could not be assigned as the other possible products (e.g. *trans*-stilbene, 1,1-diphenylthene) were not available. The other chromatograms are given in the Appendix.

3.4 CONCLUSION

In summary, the data reported in this work show that cyclopalladated ferrocenylimine complexes **C1** and **C2** and multinuclear [G-1/G2 DAB-dendr-(NH_2)n-1-(2-pyridyl,quinoline)-imine] dichloro Pd(II) complexes **C3** and **C4** can be used as catalysts for the Heck cross coupling reactions of iodobenzene and styrene. However, steric hindrance had a negative effect on the coupling reaction of styrene with iodobenzene. The dendritic complex **C3** generally showed a higher conversion and the reactions proceed at a faster reaction rate compared to the ferrocenylimine, G-1-DAB-dendr-(NH_2)n-1-(2-pyridyl, and the G-2 iminopyridyl-palladium complexes and the palladium precursor, Pd(MeCN)Cl_2. Steric and electronic factors played major role in controlling the outcome of the catalytic process. It was observed that if reactions were given more time, probably the conversion of iodobenzene could reach 100%. For future work, the reactions will be allowed to proceed for longer than 24 h in order to find out the optimum conversion.

Due to the unpredictable, flexible character of the Heck reaction, research is continual, and advances are still being made. However, such extensive and abundant research is done only because the Heck reaction is such a powerful carbon-carbon bond forming reaction with many uses for synthetic organic chemistry in the academic and industrial world [3].

3.5 FUTURE WORK

- More metallodendrimers, especially those based on ferrocenylimines should be synthesized and characterized by analytical techniques: IR, UV-vis and NMR spectroscopy, mass spectrometry (ESI-MS and MALDI-TOF) and elemental analysis
- The synthesized complexes will be investigated for their potential in C-C coupling reactions
- Different parameters such as temperature, catalyst loading and reaction time should be investigated in order to determine the optimum reaction conditions for the Heck C-C reactions
- The reactions should be allowed to proceed for longer period (i.e. for more than 24 hours) in order to determine the optimum conversion
- Identification tests for the GC products should be done
- Suggestion for better complex characterization

3.6 REFERENCES

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3.7 APPENDIX 1

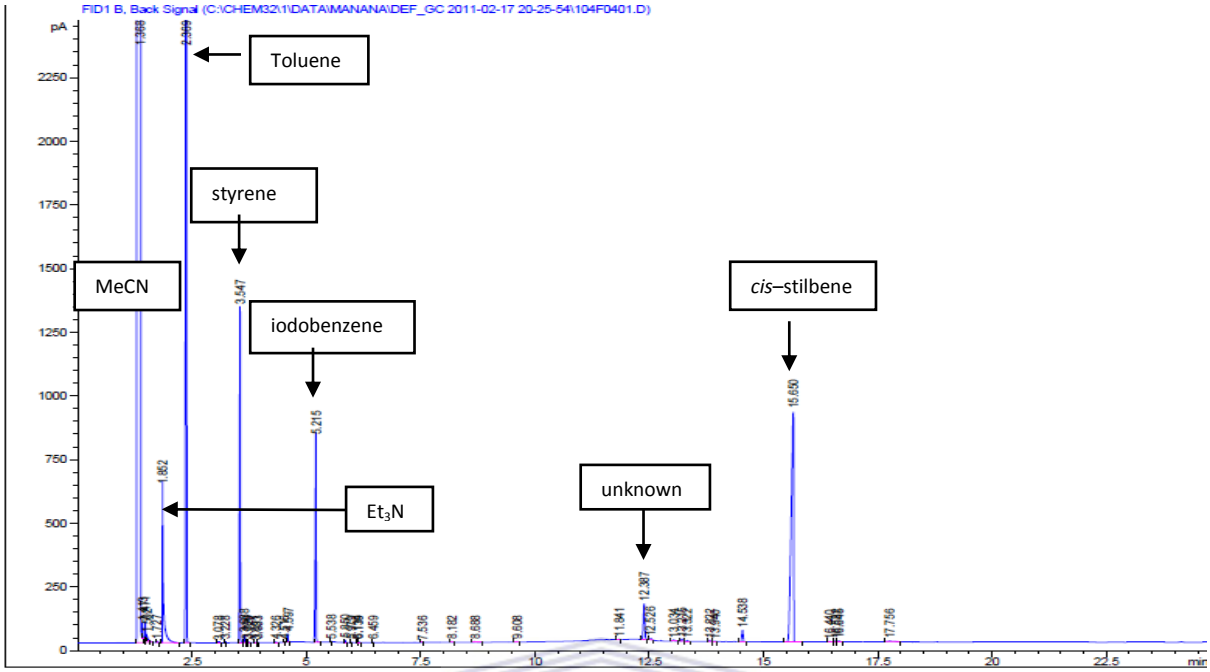

Figure A1 GC-chromatogram of arylation of iodobenzene, after 24 hrs, catalysed by complex **C2**.

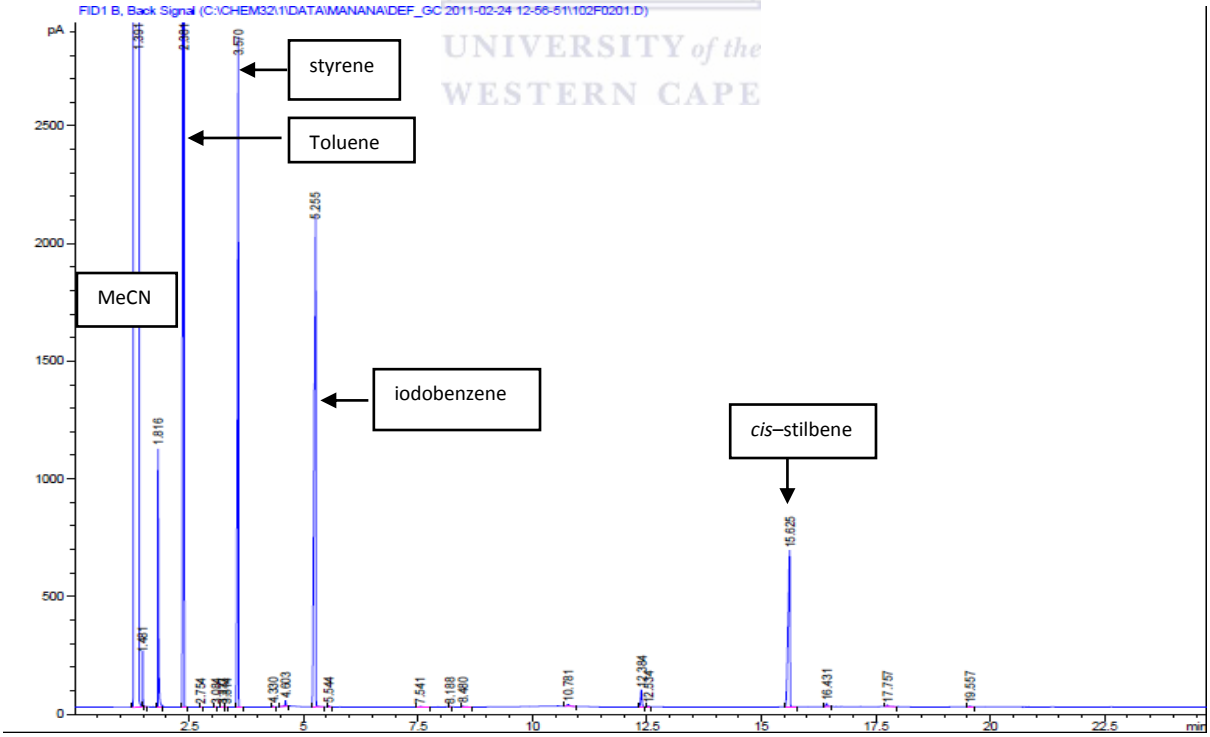

Figure A2 GC-chromatogram of arylation of iodobenzene, after 24 hrs, catalysed by complex **C3**.

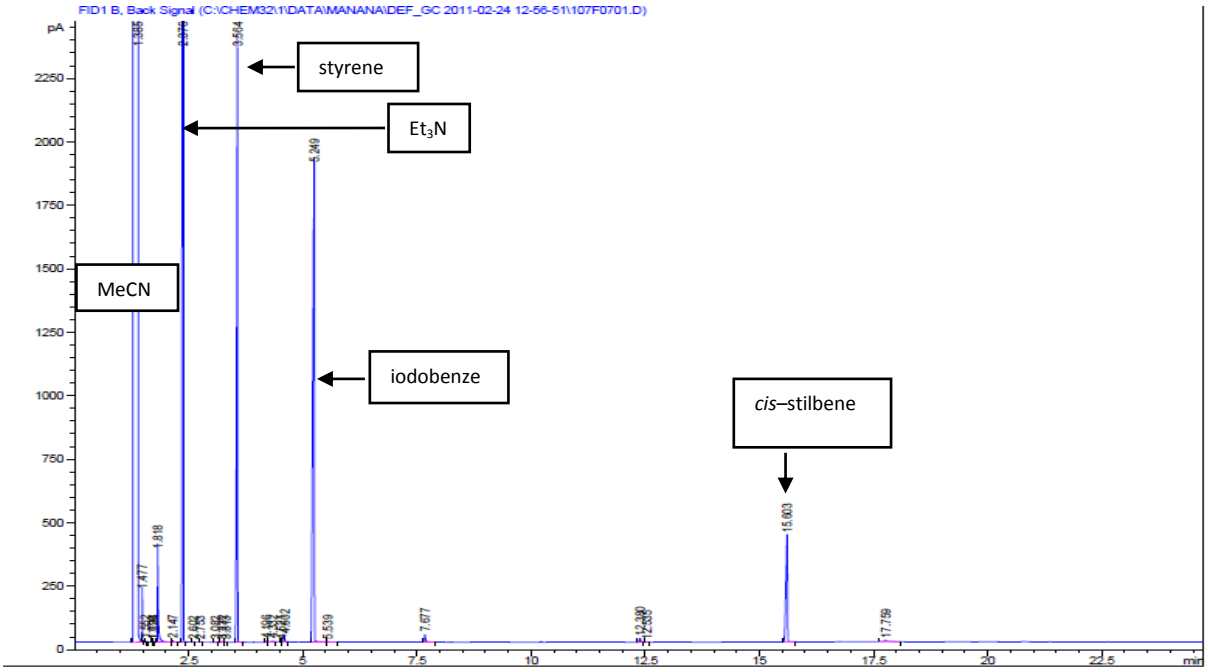

Figure A3 GC-chromatogram of arylation of iodobenzene, after 24 hrs, catalysed by complex **C4**

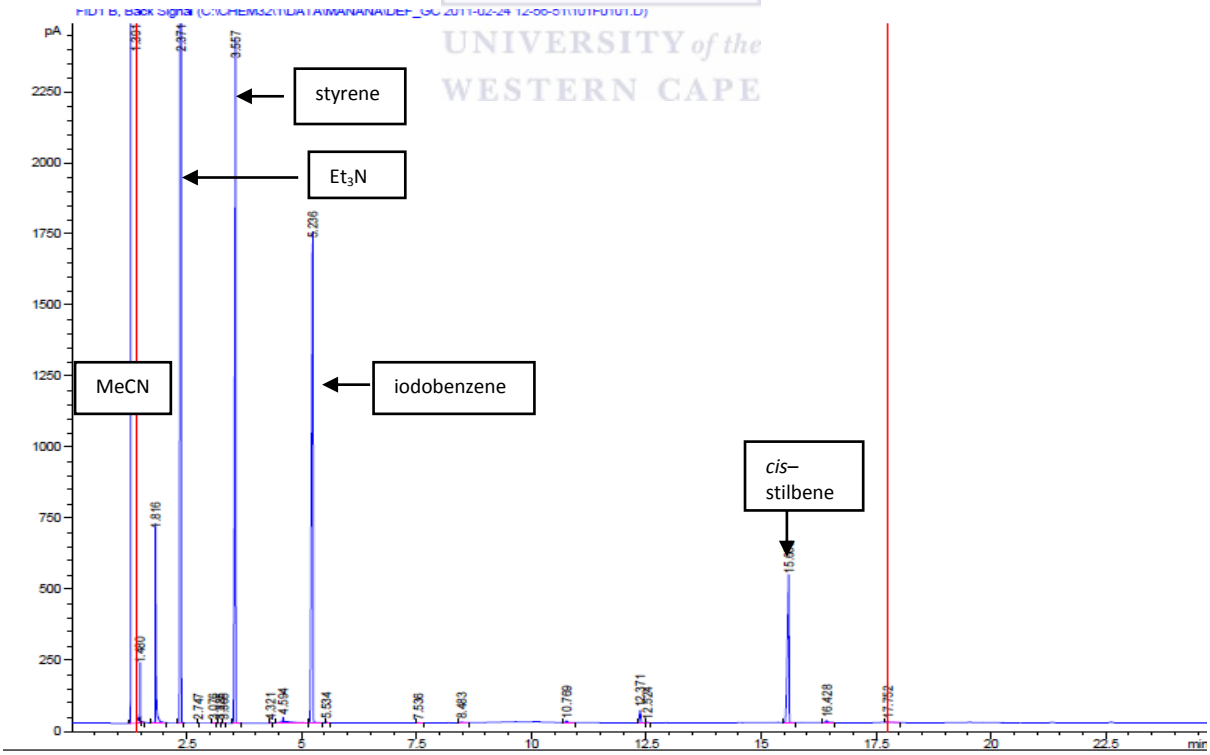

Figure A4 GC-chromatogram of arylation of iodobenzene, after 24 hrs, catalysed by complex **C5**.