The Preparation of Binuclear and Polynuclear Methyl Complexes of Palladium as Catalyst Precursors in Phenylacetylene polymerization

DECLARATION

I declare that “**The Preparation of Binuclear and Polynuclear Methyl Complexes of Palladium as Catalyst Precursors in Phenylacetylene polymerization**” is my own work and that all sources I have used or quoted have been indicated and acknowledged by means of references.

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Johannes Mlandu Sibanyoni

DEDICATED TO THE

SIBANYONI FAMILY

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Abstract

Bifunctional ligands of the type *N,N'*-{1, n}-alkanediyl-*bis*(pyridinyl-2-methanimine) {n = 5, 8, 9, 10, 12}(**L1-L5**) and Dendritic ligands (**L6-L7**) were synthesized and fully characterized by ^{1}H-NMR, ^{13}C-NMR and IR spectroscopy. Binuclear palladium-methylchloride complexes **C1-C5** and multinuclear palladium-methylchloride complexes **C6-C7** were formed by reacting the formed ligands with (COD)Pd(CH_3)Cl. The formed complexes were fully characterized by ^{1}H-NMR, ^{13}C-NMR and IR spectroscopy, Electron Spray Ionization Spectroscopy and elemental analysis.

Some of the synthesized complexes were evaluated as catalyst precursors for phenylacetylene polymerization activated with $AgBF_4$, $AgBPh_4$ and $NaB(Ar_f)_4$ under varying reaction conditions (solvent ratio, catalyst type, catalyst/monomer ratio, reaction time and nature of counterion). The cationic palladium-methyl catalyst precursors **C1a-C5a** were found to be active catalysts for phenylacetylene polymerization. When the two metal centers are far removed from each other, higher molecular weight polyphenylacetylene are obtained in high yields. Stabilizing solvents were found to give lower molecular weight products indicating a competitive effect between the monomer and the solvent for the active vacant site during polymerization.

The obtained polyphenylacetylene were analyzed by ^{1}H-NMR, ^{13}C-NMR and IR spectroscopy and gel permeation chromatography (GPC). The NMR results indicates the formed product contain *cis*-transoidal polyphenylacetylene in all the reaction conditions. High monomer conversions in most reactions were obtained and GPC results indicate that the obtained products are oligomers and polymers depending on the reaction conditions.

Conference Contributions

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4 **Cape Organometallic Symposium (COS)**; Cape Town, South Africa (**2005**).

5 **Cape Organometallic Symposium** (COS); Cape Town, South Africa (**2004**).

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ABBREVIATIONS

bpy	bipyridine
bian	*bis*(aryl)acenaphthene
COD	Cycloocta-1,5-diene
DAB	Diaminobutane
DEE	Diethyl ether
DMSO	Dimethyl sulphoxide
ESI-MS	Electron Spray Ionization-Mass spectroscopy
GPC	Gel permeation chromatography
Ind	Indenyl
MA	Methylacrylate
MMA	Methyl metacrylate
MAO	Methylaluminoxane
MMAO	Modified Methyaluminoxane
Mp	Melting point
PA	Phenylacetylene
PPA	Polyphenylacetylene
THF	Tetrahydrofuran
(PBB)	*tris*(2,2,2-perfluorobiphenyl)borane
(PNB)	*tris*(2-perfluoronapthyl)borane
^{1}H-NMR	Proton nuclei magnetic resonance
^{13}C-NMR	Carbon nuclei magnetic resonance

Chapter 1

Transition metal catalyzed polymerization of unsaturated hydrocarbons, copolymerization and terpolymerization with CO and other vinylic monomer types: Current status.

1.1 General Introduction

The application of transition metal complexes as catalysts in C-C bond formation has attracted much interest over the last couple of decades. The reason for this is the novelty of the chemistry involved, as proven in numerous examples of their practical applications [1]. Different kinds of inorganic and organometallic compounds are used as catalysts in a vast number of chemical reactions. Some of the important processes catalyzed by transition-metals include hydrogenation of alkenes (Wilkinson's catalyst), [2] Hydroformylation (Cobalt and Rhodium catalysts) [3] and alkene oxidation (Wacker process) [4].

Catalytic application of transition metals in olefin polymerization has been used on an industrial scale for several years. Some of these catalysts, particularly group 4 metallocenes [5] are currently utilized by the polymer industry. The range of catalysts has expanded beyond the early transition metals [6], as shown by the recently reported homogeneous chromium, iron, cobalt, and palladium systems [7-10]. The use of late transition metal catalysts in polymerization had previously been considered unsuitable due to the short chain products formed as a result of the high rate of chain termination steps [11-12]. The discovery of late transition metal catalysts that are able to produce high molecular weight polymers using palladium and nickel for ethylene and higher olefin polymerization stimulated a lot of interest in their application [11]**.** This can be seen by the number of publications and patents filed by different groups in recent years [13].

The strong propensity of late transition metal catalysts to undergo β-hydrogen elimination had largely relegated this class of catalysts to applications in oligomerization processes [10]. Homogeneous late transition metal catalysts, particularly nickel catalysts for ethylene oligomerization have been widely used to convert ethylene into value-added α-olefins. The latter are used as co-monomers to synthesize linear low density polyethylene. They are also used in the production of lubricants, plasticizers, surfactants and detergents [13].

Carefully tuning the ligands of metal complexes can vary product composition from oligomers to polymers [13]. The ability of cationic Ni(II) and Pd(II) α-diimine catalyst precursors to form polymers is the result of the steric bulk of the α-diimine ligands. The bulky aryl-ortho substituents on the α-diimine ligand located at the axial coordination sites efficiently retard the rate of chain transfer relative to chain propagation. When α-diimine ligands lacking bulky aryl-ortho substituents are used, the resulting catalyst system can produce oligomers starting from ethylene [14].

A very important application of C-C bond formation using organometallic catalysts is the polymerization of olefins and the closely related oligomerization of olefins. Both processes will be discussed in more detail in the following sections.

1.2 Late transition metal complexes as alkene polymerization catalysts

Palladium and Nickel α-Diimine catalysts

The polymerization of ethylene by late transition metal-catalysts has received considerable attention since Brookhart *et al.* first reported this. These workers developed a family of cationic Pd(II) and Ni(II) α-diimine catalysts for the polymerization of ethylene, α-olefins and cyclic olefins as well as the copolymerization of nonpolar olefins with a variety of functionalized olefins [7].

The key features of this catalyst system are:

1) Highly electrophilic metal centers (e.g. Palladium and Nickel)

2) Use of bulky α-diimine ligands and

3) Use of noncoordinating counterions.

The electrophilicity of late transition metal centers, help in the high rate of olefin coordination. The use of sterically bulky ligands favors insertion over chain transfer while, the use of a noncoordinating counterion provides an accessible coordination site for the incoming monomer.

1.2.1 α-Diimine catalyst precursor of late transition metal complexes

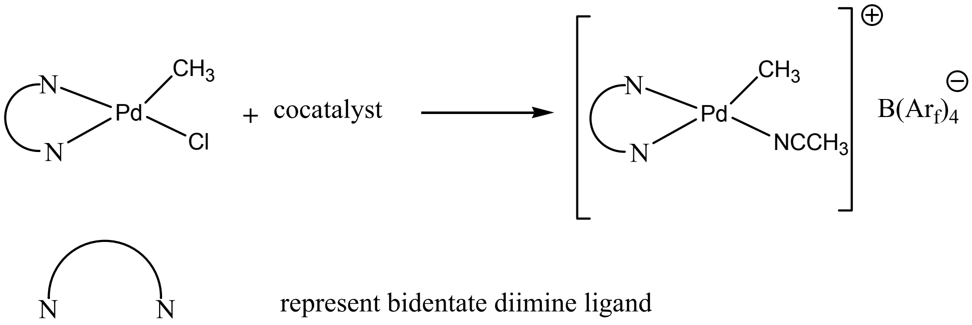
The synthesis of cationic α-diimine complexes of palladium and nickel are well developed [7]. In order to create active complexes, it's important to realize that the counterion is potentially a Lewis-base, thus competing with the monomer for coordination to the vacant coordination site. Cationic complexes which are active for olefin polymerization have been successfully synthesized by the introduction of very weak coordinating anions. Late transition metal halides can be reacted with a variety of abstracting anions [e.g. BF_4^-, PF_6^-, $(B\{Ar_f\}_4)^-$ (Ar_f = 3,5$\{CF_3\}_2C_6H_3$), $B(C_6F_5)_4^-$, $MeB(C_6F_5)_3^-$, MAO, MMAO] that are noncoordinating to yield a cationic organometallic species [15]. Recently, more sterically demanding but weaker coordinating anions for example *tris*(2,2,2-perfluorobiphenyl)borane (PBB) or *tris*(2-perfluoronapthyl)borane (PNB) have been described [16]. The obtained cationic alkyl metal complexes are very strong electrophiles and consequently very sensitive to air and moisture. They are typically stabilized by the addition of Lewis-bases or by close contact with the counterion. Both of the aforementioned processes can lead to situations were the vacant site is occupied. In most cases the Lewis-base stabilization is inevitably connected with the synthetic route of the cationic generation. The stabilizing ligand must be weak enough in order to be replaced by the monomer under polymerization conditions [15-17].

It is generally agreed that the catalytic active species in the late transition metal catalyst for olefin polymerization, is a coordinatively unsaturated cationic alkyl complex of the form $[L_nMRR']^{n+}$ Scheme1 below (L = stabilizing ligand which remains bound to the metal center over the course of the catalytic reaction, M = transition metal or rare earth metal, R'= aryl, alkoxide, R = initiating group or polymer chain). This species is generated by the reaction of a transition metal complex (halide, alkoxide, alkyl, aryl) with a main group organometallic compound (generally an organoaluminum or organoboron) referred to as co-catalyst.

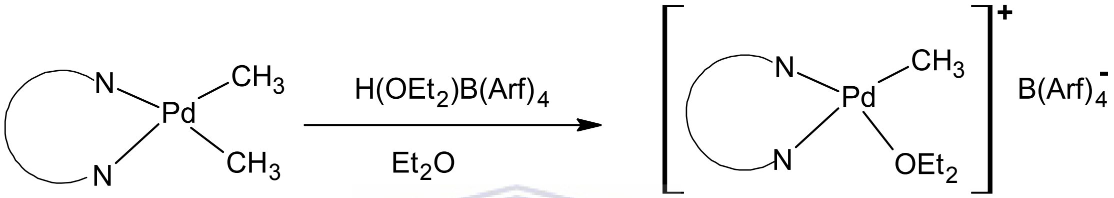
Scheme 1.1: formation of the catalytic active species, (R = Alkyl or aryl; R'= aryl, alkoxide; X^- = cocatalyst-counterion or halide).

The reaction shown in Scheme 1.2 illustrates chlorine abstraction with $NaB(Ar_f)_4$. The resulting complex is stabilized by a relatively weak donor ligand such as acetonitrile. The acetonitrile complexes are stable and easily handled precursors for use in preparative-scale polymerization. Attempts to make palladium-ether adducts by chloride abstraction with $NaB(Ar_f)_4$ resulted in the formation of the chlorine bridged dimer $\{[(N\text{-}N)\,PdCH_3]_2\text{-}\mu\text{-}Cl\}\,B(Ar_f)_4$ [13].

A more successful route towards the cationic palladium and the nickel-ether complexes is through protonation of the nickel and the palladium dimethyl precursors with $H(OEt_2)B(Ar_f)_4$ in the presence of diethyl ether as illustrated in Scheme 1.3.



Scheme 1.2: Palladium-acetonitrile adduct formation by chloride abstraction with $NaB(Ar_f)_4$ in the presence of acetonitrile.



Scheme 1.3: Protonation of palladium-dimethyl with $H(OEt_2)B(Ar_f)_4$ in the presence of Et_2O.

The ether ligand is extremely labile, making this type of catalyst precursor ideal for low-temperature ^{1}H-NMR mechanistic studies. The protonation of the dimethyl complex in the presence of an olefin to yield the olefin adduct has been successful only at low temperature [18]. In a typical preparative scale polymerization with a nickel α-diimine derived catalyst, a rapidly stirred suspension of the nickel dibromo complex in toluene solvent, is saturated with ethylene and activated by methylaluminoxane (MAO). The nature of the product can be varied from oligomers to high polymers, by varying the catalyst structure and the polymerization conditions [7,13,19]. Under a given set of conditions, polymers obtained using nickel α-diimine catalysts are generally less branched than polymers derived from their palladium analogues. Introducing bulky groups as substituents on the aryl ring of the α-diimine leads to an increase in the catalytic activity on the late transition metal complexes towards olefin oligomerization/polymerization. The conjugation of the aryl-ring with its substituents decreases the net charge on the active metal center and reduces its activity as the final result [20].

A number of factors determine the rate of chain propagation relative to the rate of chain transfer. In addition, there are also several factors which influence the molecular weight of the oligomeric products. These factors includes; the kind of metal used and its oxidation state; electronic properties and steric bulk of the ligands attached to the metal, reaction temperature, pressure, monomer concentration and the nature of the solvent used [21].

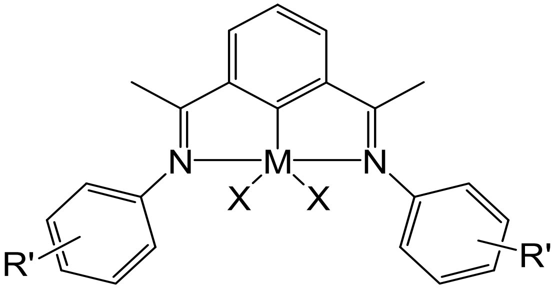
The easily varied steric and electronic properties of the ligands are important features of the α-diimine catalyst systems. The synthesis of α-diimine ligands with heteroatom backbone substituents synthesized from bis-(imidoylchloride) precursors has been reported. The backbone of the ligand was varied enabling the preparation of a number of different ligands with independent control over the steric and electronic effects at the metal center [22].

A unique feature of late transition metal catalyst systems based on Ni (II) and Pd (II) is the ability to produce polyolefins with very different microstructures relative to those produced using early transition metal catalysts [23]. Employing α-diimine complexes bearing bulky aryl-groups as illustrated in Figure 1.1, polymerization of ethylene results in the production of branched polyethylenes with few branches while polymerization of other α-olefins which upon chain migration yields branches in the polymer chain [10,25]. Fewer branches in poly(α-olefins) arise due to the fact that 2,1 insertion is more favored than 1,2 insertion of the α-olefin, followed by chain walking of the 2,1 inserted olefin to form a primary metal-alkyl bond. The latter then undergoes further alkene insertion [24].

1.2.2 Ethylene polymerization

In the search for appropriate late transition metal complexes that are cheap and readily available for olefin and higher-olefin polymerization activity, Brookhart *et al*. [26] and Gibson *et al.* [10] reported almost simultaneously the use of 2,6 *bis*(imino)pyridine iron (II) complexes (**a** in Figure 1.1) as ethylene polymerization catalysts after their activation with MAO. These catalysts exhibit exceptionally high activities, equivalent to or even higher than those observed with metallocene catalysts based on early transition metals, producing strictly linear high molecular weight polyethylene [10,25]. The key feature of this catalyst is the steric bulk provided by the *ortho*-substituents on the imine-aryl groups [25-26]. It was found that increasing the size of the *ortho*-substituents (methyl vs. isopropyl) of the aryl-imine ligand resulted in an increased degree of polymerization (positioning the *ortho* substituents above and below the plane as in Figure 1a, thus blocking the axial coordination site). On the other hand complexes with only one *ortho*-substituent on each aryl-group produce oligomers with unsaturated end groups (the sign of a dominant β-Hydride chain transfer process) [27]. It has been proposed that the steric protection around the metal center retard β-hydride transfer, thus favoring the chain growth [25-26]. This has been confirmed by theoretical studies [28].

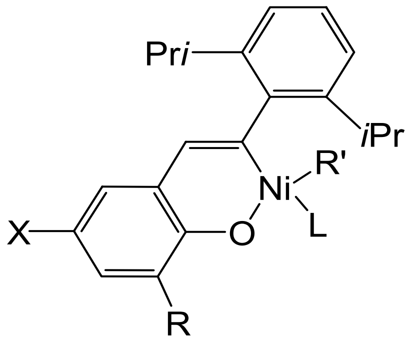
Brookhart and Gibson tridentate catalyst



M = Fe, Co
X = Cl
R = 2,6-^{i}Pr; 2,6-^{t}Bu

(a)

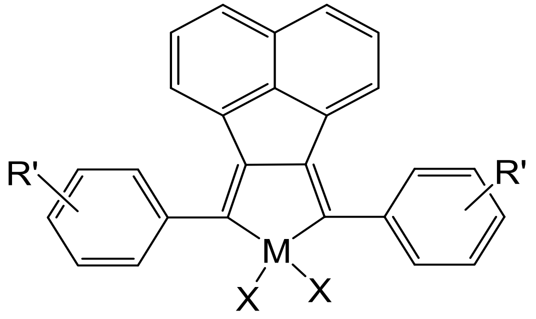
Grubbs, Mecking catalyst



R' = Ph, CH_3
R = H, ^{t}Bu, 9-Phenanthenyl
X = I, NO_2
L = PPh_3, CH_3CN

(b)

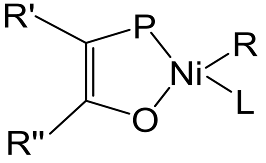
Brookhart's catalyst



M = Ni, Pd
X = Cl
R' = 2,6-^{i}Pr; 2,6-^{t}Bu

(c)

Keim and Klaubunde catalyst



R = H, CH_3
R' = Ph, CH_3
R'' = H, Ph
L = PR_3

(d)

Figure 1.1: Late transition metal catalysts for the oligomerization and polymerization of olefins.

In the work reported by Blom *et al.* [29], they used the Brookhart-Gibson catalyst in Figure 2, modified with dendritic wedges at the *para*-position of the imine-aryl ligand**.** In this way they obtained a catalyst with the active centre at the core of the dendrimer. They employed the catalysts in ethylene oligomerization and found no correlation between the activity of the complexes and the size of the dendritic wedges on the ligand. It was found that the dendritic wedges do not interfere sterically with the cationic metal centre. Similar results were also found in other work reported by these authors [30].

Ethylene polymerization reported by Laine *et al*. [31] shows that the dominating factor in controlling the molecular weight besides the reaction conditions was the steric bulk of the ligand. Structural analysis by ^{13}C-NMR spectroscopy of the different polymers obtained indicates that decreasing the steric bulk in the aryl-ring by replacing the isopropyl groups with methyls in the 2 and 6-positions gives more linear polymers. This was also seen in the case of using the diazabutane ligand system [7,32].

The effect of solvent on the polymerization reaction of ethylene was found to be significant. Thus for example using $[Pd(CH_3)(NCCH_3)(\textit{iso}\text{-DAB})][PF_6]$ as catalyst and trifluoroethanol (TFE) as solvent yielded reaction rates twice that obtained using CH_2Cl_2 as solvent even after prolong reaction time. The analysis of the products obtained from polymerization in the two different solvents showed that, in CH_2Cl_2 a bimodal weight distribution for the polyethylene synthesized while in TFE, the polymers show monomodal distribution curves.

High molecular weight polyethylene is obtained in TFE showing that the chain transfer process is retarded [33].

1.2.3 Copolymerization of Ethylene and α-Olefins

The development of new methods for the synthesis of polyolefins of well-defined molecular weight, stereochemistry and comonomer composition continues to be an important frontier in the field of polymer synthesis. Early transition metal catalysts have been developed that give precise control over polymer stereochemistry but these are unable to polymerize functionalized alkenes [34]. In contrast, late transition metal catalysts are more tolerant of functional groups. However, they generally produce amorphous atactic polymers [13].

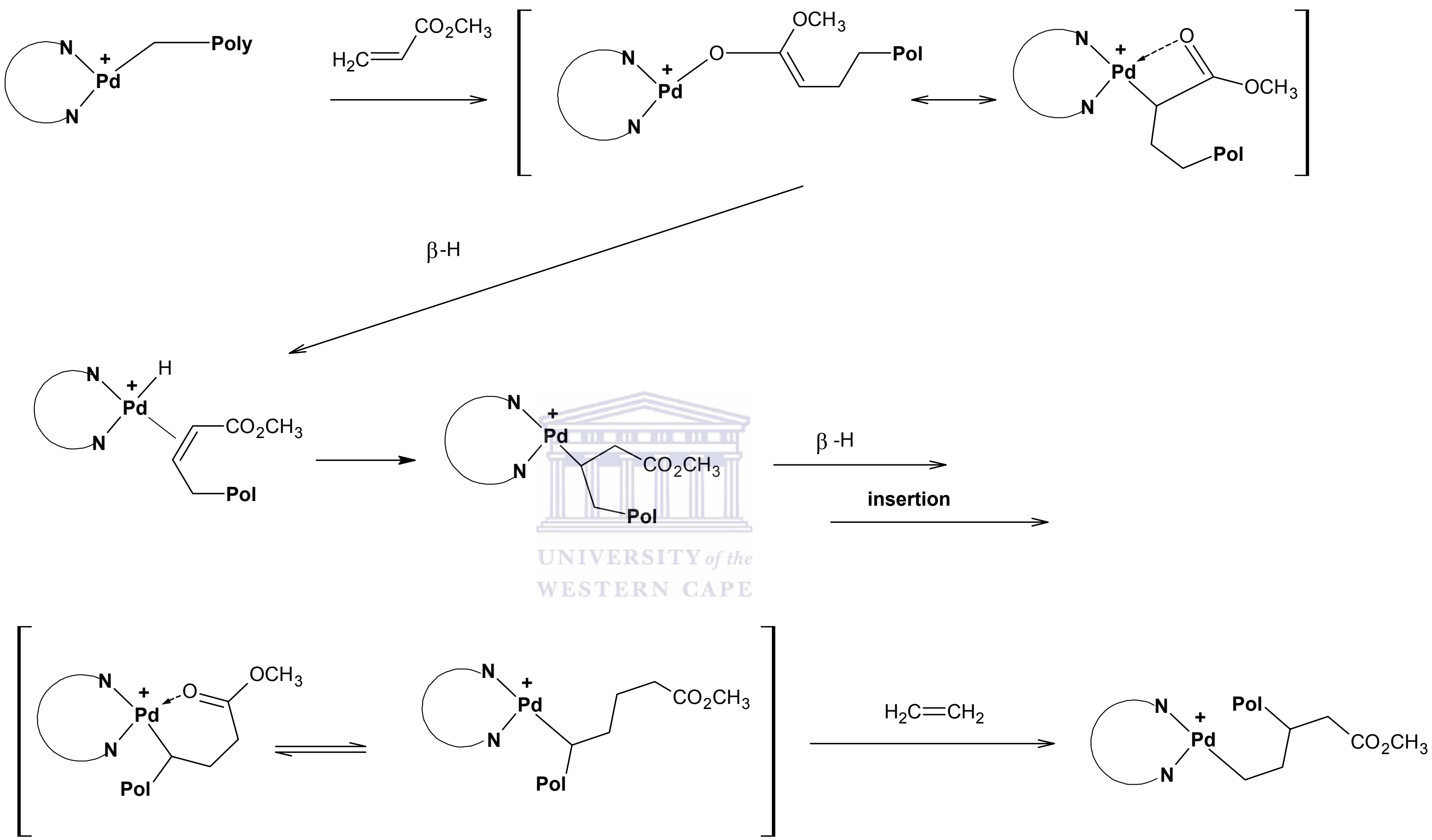
Given the promise of Ni(II) and Pd(II) α-diimine catalysts originally reported by Brookhart *et al.* [7,13], chiral ligands have been designed in an attempt to promote isotacticity in these polymers. These catalysts generally produce amorphous polymers during polymerization. At low temperatures the growing chain end can induce syndiotactic enchainment in the case of propylene [35].

Polyolefins with a high-density of functional groups along the polymer backbone are of great interest because of their many desirable properties [36]. These are mostly synthesized by the copolymerization of ethylene and polar monomers. Introduction of polar groups along the polymer backbone can yield materials with advantageous properties such as adhesion on polar surfaces, improved barrier properties, and solvent resistance [37].

Industrial production of such materials is carried out via radical-initiated copolymerization of ethylene and polar vinyl monomers at very high temperatures and pressures [38]. Although a number of papers have been published in which transition metal-catalyzed copolymerization of ethylene and α-olefins with polar monomers are reported, polymerization rates are much lower than industrial homo-polyolefin production [39]. The currently used radical processes provide little control over the polymer microstructure and molecular weight.

Amongst the various polymerization procedures, late transition metal-catalyzed routes are particularly attractive because of the potential ability to (a) control polymer tacticity and chirality, and (b) incorporate both polar and nonpolar monomers into the polymer chains [40]. Unfortunately, most transition metal-based olefin polymerization systems are not very tolerant of the functionalities present in polar monomers, especially if the functionality is close to the C=C bond [41]. In particular early transition metals are highly oxophilic resulting in the inhibition of polymerization by oxygen-containing functionalities in the monomer**.** Even with late transition metals, inhibition of polymerization due to coordination of functionalities in the monomer or the polymer chain can occur and does occur [42]. The functional group tolerance of cationic palladium α-diimine catalysts permits the copolymerization of ethylene with functionalized olefins such as acrylates. Polymerization intermediates were spectroscopically observed and identified using low-temperature NMR mechanistic studies. According to Brookhart *et al.* acrylate insertion proceeds in a 2,1-mode, yielding a C-bound enolate intermediate in which the carbonyl oxygen binds to the palladium. This transient intermediate rearranges into a more stable six-membered chelate structure, defined as the catalyst resting-state from which further ethylene insertion will take place. The isomerization from a four- to six-membered chelate explains the isolation of the ester functionality at a chain/branch end (Scheme 1.4). Later, Drent *et al.* [40] reported the random copolymerization of various acrylates with ethylene, producing linear polymers in which acrylate units are incorporated into the polyethylene backbone via a coordination/insertion mechanism. MAO activated nickel complexes have been shown to be efficient catalysts for the copolymerization of ethylene and MMA, leading to a high incorporation of methacrylate units (up to 81%), whereas methylmethacrylate (MAO) activated 2,6-*bis*(imino)pyridine iron(II) complexes were found to be unsuccessful in achieving the copolymerization. Instead, only blends of homopolymers were recovered [43].

A common understanding is that the palladium species employed are cationic and therefore relatively electrophilic. One of the reasons why cationic metal species are employed for polymerizations is that they usually have weakly bound solvent molecule(s) in place of more strongly coordinating anion(s). This allows greater accessibility to the metal centre for the incoming monomer. However, the high electrophilicity of the cationic metal centre also causes stronger binding of any functionality that may be present either in the monomer or in the growing polymer chain. It is clear from the above description that a metal catalyst for the homo- and copolymerization of polar monomers should have one or more weakly bound ligands that are easily displaced by the incoming monomer and, at the same time, be neutral to reduce the electrophilicity of the metal centre. One such complex, Pd(L)(CH_3CN)(C_6F_5)(Br) (L = monodentate phosphine or amine), appears to be the first known metal species to catalyze the homopolymerization of acrylate esters through an insertion mechanism [41].



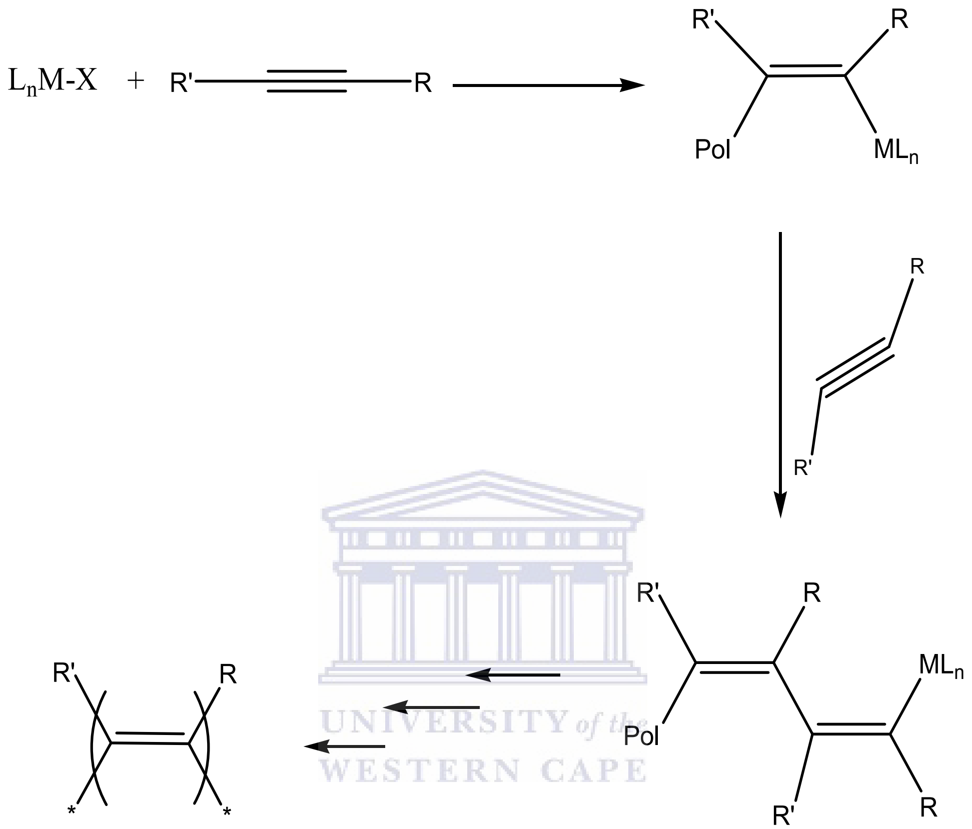
Scheme 1.4: ethylene/methylacrylate copolymerization mechanism with cationic palladium catalyst [41].

The 2,1-insertion of methyl acrylate into the Pd–C_6F_5 bond in the parent compound, Pd(L)(CH_3CN)(C_6F_5)(Br), occurs but is followed by rapid β-hydrogen abstraction to yield CH(CO_2Me)=CHC_6F_5, along with the precipitation of metallic palladium. However, when 1 equiv of a monodentate phosphine or amine was added to Pd(CH_3CN)$_2$(C_6F_5)(Br) along with excess methyl acrylate, there was no precipitation of metallic palladium, and the formation of poly(methyl acrylate) occurred. Evidently, the presence of the ligand suppresses β-hydrogen abstraction in favour of further monomer insertions [43].

1.3 Alkynes polymerization

The transition metal catalyzed oligomerization of alkynes is among the most extensively studied reactions in organometallic chemistry, beginning with the work of Reppe *et al.* [44] in the 1940's and continuing to the present day. Alkynes are highly reactive towards transition metals; the difficulty in this area is to control the reactivity so that a single major product is formed.

The number of reported catalysts for polymerization of acetylenes can be divided into two types: metathesis- or insertion polymerization catalysis are classified on the basis of their polymerization mechanism. The former mechanism is probably the more common and is illustrated in Scheme 1.5. Since the insertion process proceeds with *cis*-stereochemistry, the resulting (σ-vinyl) metal complex has no appropriate group (e.g. H) *cis* to it, to allow β-H elimination to occur and to shorten the sequence (as occurs in the case of olefin polymerization). Hence insertion of alkynes into a σ-vinyl complex generates another σ-vinyl complex. Any reagent that can intercept the σ-vinyl metal complex (e.g. hydrogen source), can stop oligomerization/polymerization [45].



Scheme 1.5: Alkyne insertion via vinyl metal complex [48].

The synthesis of highly π-conjugated organic polymers is of high interest in the polymer industry, this has been shown by the number of papers published. Polyacetylene is a (structural) conjugated organic polymer; however, its intractable nature has made its characterization quite difficult. The first successful polyacetylene film was produce in 1971 by Shirakawa and Ikeda from acetylene monomer using a Ziegler-Natta catalyst [46]. Over the past few decades, several methods have been introduced which allow the synthesis of a polymer that can be subsequently transformed into large molecular weight fragments that can limit the processing of these polymers [47-48].

The use of WCl_6 and $MoCl_5$ to produce high-molecular weight polyacetylene opened new interest in the use of this type of monomer in polymerization reactions. Since then, various types of transition metal catalysts have been reported for the polymerization of acetylenes [49-50].

A number of studies have been carried out with various kinds of monosubstituted (terminal) or disubstituted (internal) acetylenes, among which phenylacetylene is the most studied, by using a number of catalytic systems. This was in order to develop new polyconjugated polymeric systems especially in view of their potential applications.

Phenylacetylene is an aromatic molecule with an unsaturated side group and is commonly used as a precursor for the synthesis of the polymer, poly(phenylacetylene) [$(\text{-RCCH-})_n$ where R = phenyl]. The polymer is stable in air, soluble in most organic solvents, and has many interesting properties such as non-linear optical properties, potential use in semiconductors, electrophotographic materials, photoreceptors, and chemical sensor devices [51]. Poly(phenylacetylene) is commonly synthesized using a variety of catalytic methods. The catalysts often used in poly(phenylacetylene) synthesis include Ziegler-Natta type catalysts, transition metal halides and metal carbonyls, ionic catalysts and free radicals [50]. The use of cationic Pd(II) compound $[Pd(CH_3CN)]_4(BF_4)_2$ has been found to be versatile for the polymerization of acetylenes and olefins under mild reaction conditions. In many cases moderately high molecular weight poly(phenylacetylene), M_n = 9000 are obtained [52]. The infrared spectrum (KBr) of the obtained polymer shows bands at 1595 cm^{-1}, indicating the presence of polyconjugated –C=C– bonds. The strong bands appearing at 755 cm^{-1} and 695 cm^{-1} correspond to the out of plane deformation of monosubstituted benzenes. In addition, a band at 960 cm^{-1} indicates a *trans*-configuration around the –C=C– bond. When $CHCl_3$ instead of CH_3CN was used as a solvent, a slightly different polymer exhibiting infrared bands at both 910 cm^{-1} and 870 cm^{-1} was obtained. The latter band can be ascribed to the *cis*-configuration around the –C=C– bands. Thus, the stereo-structure of the poly(phenylacetylene) obtained appears to be solvent dependent, in acetonitrile predominantly *trans* polymers are obtained while *cis*-tran*s* mixtures resulted in chloroform. The ^{1}H-NMR spectrum of poly(phenylacetylene) exhibit only a broad featureless absorption between 7.55 ppm and 6.5 ppm.

Li *et al.* [53] reported high molecular weight poly(phenylacetylene) using $[(P\text{-}P)Pd(CH_3)(NCCH_3)]^+OTf^-$ and $[(P\text{-}P)Pd(NCCH_3)_2]_2^+(OTf)_2^-$ generated *in situ* from $(P\text{-}P)Pd(CH_3)(Cl)$ and $(P\text{-}P)PdCl_2$ {(P-P) = dppe, dippf, dppf}. Solvent free polymerization of phenylacetylene catalyzed by nickelocene has also been reported [54]. The product obtained consists of mixture of cyclotrimers, linear oligomers and *trans*-cisoidal poly(phenylacetylene). In solution nickelocene and $[(\eta\text{-}Cp)Ni]_2$ (PhC≡CH) catalyze acetylenes in the presence of an aromatic heterocyclic amine (e.g. pyridine) or $AlBr_3$ [55]. The treatment of phenylacetylene with nickelocene (115 °C, 6 hours) in the absence of solvent resulted in 92% conversion with the final reaction mixture containing 50% polymer. The reaction was unaffected by the presence of the radical scavenger (2,6-di-*tert*-butyl-4-methylphenol). Lower conversions (26%) are observed at 65 °C over 24 hours. The reaction yields a mixture of products. In addition the product mixture has lower amounts of cyclotrimers. Polymerization of internal acetylenes ($MeSiC\equiv CSiMe$, $PhC\equiv CSiMe_3$, $PhC\equiv CPh$) in solvent free systems could not be initiated using nickelocene or other (cyclopentadienyl)nickel catalyst [55].

Four major isomeric structures exist for polyacetylene (Figure 1.2); the *cis* and *trans* isomers can be observed by solid-state ^{13}C-NMR [56]. Previous reports indicate that the thermodynamically favoured *trans*-polyacetylene can be obtained by heating the polymer.

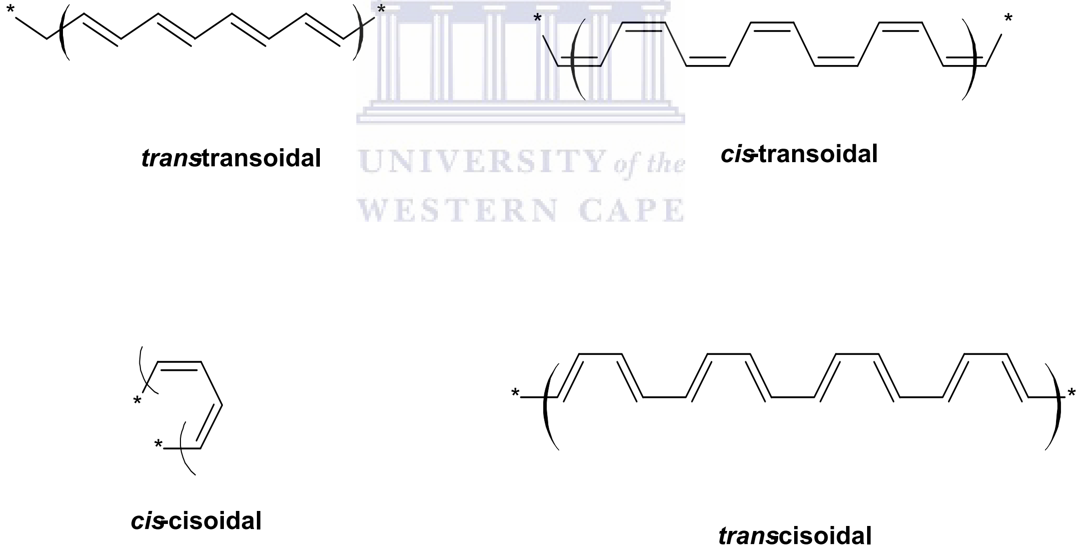


Figure 1.2: Poly(acetylene) isomers.

1.3.1 Polymerization and copolymerization of other alkyne derivatives

The polymerization of disubstituted acetylenes by late transition metal catalysts like Ni and Pd would open a possible route to the copolymerization of acetylene with other monomer types. The polymerization of cyclooctyne using Ni, Pd and Rh catalysts has been reported [57]. Palladium catalysts afford polymer in good yields as compared to the nickel catalysts. The use of $[(nbd)RhCl]_2$-Et_3N catalysts for the polymerization of cyclooctyne gave polymers in good yields. This catalyst is known to be inactive for the polymerization of disubstituted acetylenes. The Et_3N promotes the dissociation of the dimeric Rh complex to provide a cationic complex which behaves as the active species. The synthesized polymers of cyclooctyne were found to be insoluble in organic solvents for all the catalysts used [58]. High molecular weight copolymers of cyclooctyne and phenylacetylene ($M_n = 31700$) were obtained using $[(nbd)RhCl]_2$ with feed ratio of 40:60 for cyclooctyne: phenylacetylene. Copolymerization of phenylacetylene and CO reported by Liaw *et al*. [59] resulted in low yields and copolymers which are insoluble. High activity was observed when using bidentate nitrogen ligands and protic solvents (such as CH_3OH). The use of protic solvents serves as both co-initiator and chain transfer agent in the palladium complexes, which forms a palladium methoxy species.

Phenylacetylenes bearing non-polar groups are usually polymerized in the presence of WCl_6 and disubstituted acetylenes with $TaCl_5$. Masuda *et al*. carried out the polymerization of several arylacetylenes bearing bulky condensed aromatic rings obtaining polymers with molecular weights up to 1.4×10^5 g/mol depending on the structure of the monomer. The obtained polymers were found to be highly conjugated despite enhanced steric effects. The position of the acetylene bond in the aromatic ring significantly influences the reactivity of the monomer towards polymerization due to steric and electronic effects.

1.3.2 Aqueous polymerization of alkynes

Conducting catalytic processes in aqueous media is an attractive way of obtaining important chemicals due to the low environmental impact and the lowering of the operating cost associated with the expensive process of product separation from the reaction mixture or solvent removal and its subsequent recycling. Polyacetylenes are interesting polymeric materials, because of their chemical and physical properties [60]. Palladium complexes of the type **1-3** (Figure 1.3) have been tested as catalysts in the polymerization of phenylacetylene in water. Initially, the stability of the complexes in water was verified by stirring a suspension of the complex in distilled water and boiling the mixture for 24 hours under nitrogen atmosphere. The Pd: monomer ratio was kept constant for all reactions and fixed at 1:100. In a typical catalytic test, when phenylacetylene was added to a vigorously stirred suspension of the complex in water, after a variable induction period, the mixture started to darken [61].

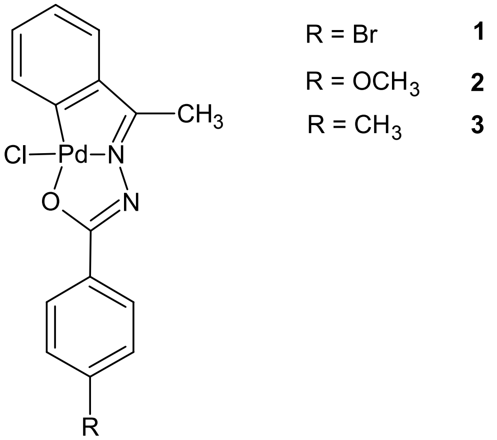


Figure 1.3: Catalysts used in emulsion polymerization of alkynes.

1.4 Styrene polymerization

Various catalyst systems have been explored for the polymerization of styrene especially those based on late transition metal complexes [13]. Bidentate nitrogen ligands have mainly been used, although hemilabile (P-N) ligands have also shown activity. For example cationic η^3-allylnickel complexes alone or those modified by phosphine and phosphite ligands were found to be active for low molecular weight polymerization of styrene by a simple cationic mechanism [62]. Neutral allylnickel complexes alone or those activated by addition of electron-poor additives as well as homogeneous organometallic catalysts in combination with methylaluminoxane {e.g., $Ni(acac)_2/MAO$} are known to produce non-stereospecific polystyrene via the coordination mechanism [63].

More recently**,** a series of neutral nickel and palladium σ-acetylide complexes [$M(C{\equiv}CR')_2(PR_3)_2$](M = Ni, Pd; R = Ph, CH_2OH, CH_2OOCH_3, CH_2OOCPh; R' = Ph, Bu) have been found to be efficient initiators for styrene polymerization in $CHCl_3$ [64]. Among these complexes $Ni(C{\equiv}CPh)_2(PBu_3)(NBP)$ shows the highest catalytic activity. The use of chlorinated solvents has been favored for homogenous styrene polymerization. However, the catalyst type used by Sun *et al.* [65] showed little activity in highly polar solvents containing N, O and S, such as (1,4-Dioxane, THF and DMSO). Similarly low activity was observed in the non-polar solvent (toluene). It was however found that at elevated temperatures and long reaction times, the yields were high when employing chlorinated solvents.

The mechanism of styrene polymerization has been probed; first hydroquinone which is known to be an inhibitor for radical-polymerization was added to the reaction mixture prior to the initiation of styrene polymerization, in the second setup hydroquinone was added into the system after the polymerization had been started. In the former reaction, it was found that the polymerization had stopped completely and no polymer was obtained after 24 hours, while in the latter case, it was found that the reaction completely stopped after the addition of the initiator. This indicates that in chlorinated solvents, styrene polymerization using $Ni(C{\equiv}CPh)_2(PBu_3)(NBP)$ catalyst proceeds via a radical mechanism. This is possibly due to the homolytic activation of the carbon-chlorine bond of the solvent via a single electron redox reaction between Ni(II) and Ni(III) [66].

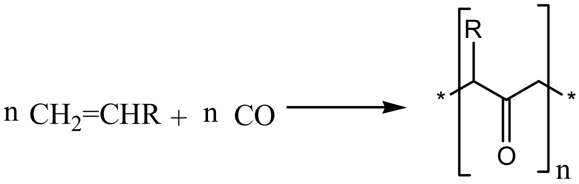
Mixtures of oligostyrene and polystyrene are obtained when using $(Ind)Ni(PPh_3)(Cl)$ and $NaBPh_4$ to polymerize styrene at 80 °C over 24-48 hours [76]. Cationic complexes $[(\eta^3: \eta^1\text{-}Ind(CH_2)_2N\{CH_3\}_2)Ni(PR_3)][BPh_4]$(R = Ph (**1**), CH_3 (**2**), Cy (**3**) can catalyze this reaction in the absence of an initiator. Styrene polymerization by **1** requires heating the reaction to 80 °C; this was attributed to the difficulty of displacing the chelating $N(CH_3)_2$ moiety by styrene. The pre-catalyst with the more labile $P(CH_3)_3$ and PCy_3 ligands were found to catalyze styrene at room temperature with high levels of catalytic activity. High molecular weight products were obtained at high reaction temperatures [68].

1.5 Copolymerization and Terpolymerization of vinylic olefins with CO and /or amines.

1.5.1 Olefin /CO copolymers.

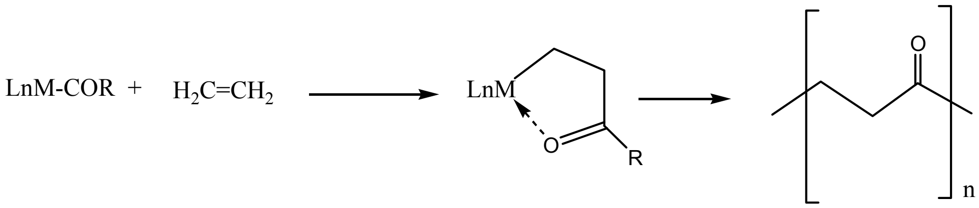
Synthetic organic reactions involving carbonylation of alkenes, are typically catalyzed by complexes of late transition metals such as Ni, Pd and Rh [10,69-71].

These reactions involve activation of the CO molecule by transition metal complexes as the key step. CO coordinates to the metal centre, giving the metal-carbonyl intermediates, followed by migratory insertion of the alkene into the metal-acyl bond which proceeds smoothly to afford the polyketones composed of alternating insertion of olefin and CO monomer units as shown in Scheme 1.6.



Scheme 1.6: Co-polymerization of α-olefin and carbon monoxide.

Cationic complexes with non-coordinating anions ensure the presence of accessible coordination sites and chelating ligands cause *cis*-coordination of the monomer thus enabling migratory insertion reactions to take place. The complete absence of a double ethylene insertion is remarkable because ethylene insertion into a Pd-alkyl species is exothermic**.** CO insertion into the Pd-acyl bond is thermodynamically not favored. Alkene insertion in the Pd-alkyl bond is much slower than the CO insertion, although it is possible [72]. The observation of strict alternating insertion between the two monomer types is remarkable considering cationic palladium(II) complexes dimerizes ethene to butenes [73]. Even high ethene-CO ratios produce exclusively error-free polyketones until all CO is consumed [74]. The perfect alternation is attributed to CO being kinetically favored over C_2H_4, despite the thermodynamic preference for pure olefin polymerization [75].



Scheme 1.7: Alternating insertion of olefin into the metal-acyl bond.

In the insertion mechanism for the co-polymerization of olefin and CO, the formed ketone coordinates to the metal through the oxygen (Scheme 1.7). The interaction between the metal and oxygen is very weak and the coordinated oxygen is easily displaced by the incoming CO allowing the copolymerization to proceed. This seems to help to perfect the alternation. The process is more cost effective and the products obtained are environmentally friendly (being more readily degradable) [40,76].

The palladium(II) catalyzed alternating copolymerization of alkenes with carbon monoxide is of great interest due to low monomer cost, photodegradation of copolymers, and the presence of carbonyl groups in the polymer backbone that lend themselves to further functionalization. One of the advantages for using late transition metals, such as palladium, as catalyst is that they are not likely to be poisoned or deactivated by the presence of oxygen, nitrogen or halogen, functionalities, either in the solvent or in the substrate [77].

The metal catalyzed non-alternating copolymerization of ethene and CO could open new areas of research for this type of material [78]. A family of [O-P] ligand modified palladium catalysts co-activate ethene and CO to generate high molecular weight non-alternating copolymer with low activities compared to the classical dppp-based cationic palladium systems. High steric hindrance in the [O-P] ligands leads to an increased amount of ethene being incorporated into the copolymer. The multiple ethene insertions are thought to be facilitated by stereoelectronic destabilization of the neutral complex to an extent that C_2H_4 can effectively compete with CO for the next insertion. The degree of non-alternation (observed by $^{13}C\ \{^1H\}$ NMR analysis) can be tuned by reaction temperature, C_2H_4 and CO concentrations and the ancillary ligands present [78].

Low molecular weight polyketones obtained from CO and styrene are isolated when using palladium catalysts stabilized by a chelating diphosphine ligand. The effective copolymerization of styrene and its analogues with CO using palladium catalysts requires the use of (N-N) chelating ligands [79-80]. Using a phosphine modified catalyst, it was found that β-H elimination prevailed over chain propagation due to higher electron density on the metal in the palladium-phosphine catalysts. It has been suggested that the (diphosphine) Pd-styryl intermediate formed in the initial steps of CO/styrene copolymerization are strongly stabilized by π-benzylic coordination (Figure 1.4) to inhibit CO insertion. The termination process via β-H elimination becomes the favored reaction and oligoketones are formed instead of polyketones. The downside of this type of polymerization is that CO/styrene copolymer yields are very low and of too low molecular weights for industrial application [81].

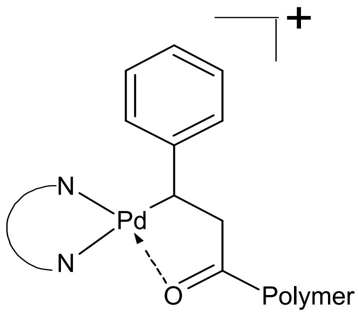


Figure 1.4: π-benzylic intermediate formed after a 2,1 insertion of styrene into a Pd-acyl bond.

Styrene/CO copolymers have been produced at low pressures of CO (1 or 4 Bar) in only few cases. The copolymers obtained are characterized by chemoregularity, i.e. perfect alternation of carbon monoxide and styrene, and by regioregularity, i.e. head-to-tail placement of the styrene monomeric units. The latter being a consequence of the secondary migratory insertion of styrene units into the palladium-acyl bond of the catalytic system [82]. The stereochemical control of the copolymer has been ascribed to chiralilty of the polymer chain end, whereas in the case of the *iso*tactic-specific catalyst, it has been ascribed to the chirality of the ligands [83]. The reactions are usually performed in methanol solution. Different co-catalyst and co-reagents (e.g. oxidant) may be required depending on whether an *in-situ* generated catalytic system or preformed complexes are being used [84]. The Brookhart group has reported a catalytic system that can produce a stereochemical product which depends on the ligand type used [85]. Consiglio *et al.* also showed that the regiochemistry of the polyketones can be strictly controlled by the use of a (N-N) ligand that gives a regioregular copolymer, while (P-N) ligands give regio-irregular products [86]. The common feature in all these nitrogen-containing ligands is the sp^2 character of the coordinating nitrogen.

The use of [Pd(bpy)](PF_6) was found to promote CO/styrene copolymerization in fluorinated solvents such as (2,2,2 trifluoroethanol) TFE, with the copolymer obtained in high yields without decomposition of the catalyst precursor to palladium metal. In this type of solvent, unlike in methanol, the catalyst precursor was found to be active after 48 hours of the reaction and gave copolymerization activity of 17 kg CP/g Pd. In addition, the high product yields did not need large amounts of oxidants [87].

Nowadays Pd(II) complexes are the best choice for producing alternating copolymers of carbon monoxide with ethylene, propylene or styrene. They may also be used for the polymerization of unsaturated substrates such as alkenes substituted with polar groups, strained alkenes, alkynes, carbonates and amides [87-88]**.** However, the commercialization of polyketones still raises many questions. The most important is the instability of the palladium-catalyst, which decomposes to palladium metal during the catalytic process and the copolymer workup. Therefore, the search for active catalyst in this process remains of interest.

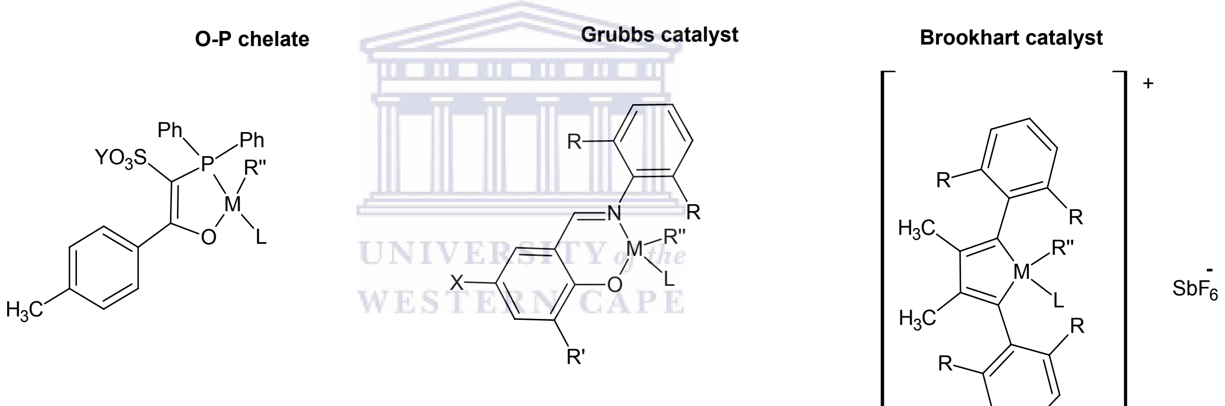
1.6 Emulsion polymerization of vinylic olefins

Emulsion polymerization of olefinic monomers is an important and versatile process. Usually the polymerization of the monomer by a water-soluble free-radical initiator takes place in a mixture of water and surfactant. Polymer latexes are obtained, i.e. stable aqueous dispersions of surfactant-stabilized polymer microparticles with a size range of 50 to 1000 nanometers in diameter. Latexes find a variety of applications, e.g. in paints and coatings. They can also be used as carriers for drugs and catalysts.

To date, polymer latexes are produced industrially by free radical processes exclusively. Transition metal catalyzed coordination polymerization in aqueous media has received little attention since the early transition metal catalysts (Ziegler-catalysts and metallocenes) used commercially for polyolefin productions are extremely sensitive to moisture [89]. Carrying out such polymerization reactions in water is a highly attractive goal, however, as many polymer microstructures are not available by other means than catalytic coordination polymerization. Recently, novel catalysts based on late transition metals have been considered for catalytic transformation in aqueous media due to their low oxophilicity. This is illustrated by the commercial application of aqueous bi-phasic catalysts in the Ruhrchemie-Rhone-Poulenc process for propylene hydroformylation [90]. The coordination polymerization of simple olefins in emulsion mixtures has only recently begun to attract interest. Soula *et al.* [91] and Wang *et al.* [92] have reported coordination polymerization of ethylene in aqueous emulsion or suspension by neutral nickel(II)salicylaldiminato complex, cationic palladium diimine complex [93] and the O-P chelating neutral Ni(II) complex [8], to form semi crystalline, linear polyethylene.

Catalysts of type [**a** and **b** Figure 1.5] are active in water for hours. Using water-soluble derivatives (**a** in Figure 1.5**)** in the presence of a surfactant, stable polymer latexes of linear polyethylene can be obtained. The material obtained has a relatively low molecular weight, around (M_w = 3000 g /mol at M_w/M_n = 2 to 3). However, by using complexes of type **c** in Figure 1.5, polyethylenes with high molecular weights (M_w = 4 x 10^5 g / mol at M_w/M_n = 2 to 4) are also accessible in aqueous polymerizations [94]. By copolymerization with norbornene, the crystallinity of these polymers can be adjusted.

Preliminary NMR studies at low temperature using the catalyst in **d** Fig 1.5 show that the water ligand (R = ^{i}Pr, L = H_2O) is displaced completely upon addition of ethylene. The hydrolysis of the M-R” bond to release a hydrocarbon H-R” and the formation of a M-OH hydroxyl bond is another possible side reaction. This is a similar process to the reverse of the C-H activation process that has been observed for palladium(II) complexes.



a) Y = Na^+ (hydrophilic)

c

b) Y = $H_{33}C_{16}N(CH_3)_3$ (lipophilic)

d

M = Ni, Pd
L = H_20, C_2H_4
R = CH_3, ^{i}Pr
R' = H, ^{t}Bu
R'' = CH_3, Ph, ^{i}Pr, CF_3
X = H, NO_2

Figure 1.5: Catalysts for emulsion polymerization of olefins.

Using cationic Pd(II) α-diimine complexes, ethylene can be polymerized in aqueous suspension. Remarkably, the reaction continues at a constantly high rate for >16 hours, without any apparent deactivation of the catalyst by water. However, this high stability is only due to an 'encapsulation' of the catalyst in the hydrophobic polymer, which prevents access of water. By contrast to the Ni(II) catalyzed polymerizations, the resulting ethylene homopolymer is a rubbery, amorphous material. This reaction also serves as an example to study fundamental aspects of aqueous coordination polymerization of simple olefinic monomers [89-94].

1.7 Summary and conclusion.

Catalysis by soluble metal complexes has been practiced in industry for several years in a number of processes. The unique features of these catalysts are high activity and selectivity at mild operating conditions, ability to activate commercially available and cheap substrates such as CO and olefins, and the plausible characterization of intermediates at molecular level. While the industrial importance of homogeneous catalysis was realized several decades ago, it is only in recent years that the true potential of homogeneous catalysis has become evident with widely expanding applications for the synthesis of fine chemicals, specialty chemicals and pharmaceuticals. The performance of homogeneous catalysis depends on the type of metal, ligands, promoters and co-catalysts and in most cases the selectivity is one of the most important issues. The main drawback of homogeneous catalysis is the separation of the catalyst and products, which is often a tedious task involving precipitation of the catalyst.

The motivation for further research into the application of homogeneous catalysis is that it is a key tool for the selective synthesis of certain organic compounds especially optical active compounds with applications as drugs, pesticides, insecticides and food additives. The recent development of new metal complexes, ligands and variety of tandem reactions indicates a strong potential of homogeneous catalysis in new synthetic routes and economical processes for a wide variety of fine, speciality and pharmaceutical products. Efforts to develop new, active and selective metal complexes catalysts with industrially feasible separation strategy are most desirable.

1.8 Aim and Scope of this thesis

Considering the afore-going discussion, the present study was focused on the development of binuclear and multinuclear catalyst for use in vinylic monomer oligomerization and polymerization. The main objective was to develop new homogeneous catalysts systems with hopefully improved activity, selectivity and stability.

The following objectives were identified to form part of the present work.

- To develop synthetic routes to methylchloro complexes of palladium using bifunctional and polyfunctional ligands.
- Activation of methyl chloride complexes with either $NaB(Ar_f)_4$ or Ag-salts to produce cationic intermediates
- Evaluation of cationic species in the oligomerization/polymerization of phenylacetylene using the synthesized palladium-methyl complexes under homogeneous conditions.

The thesis is presented in the following chapters, a summary of which is given below:

Chapters 1 briefly reviews the literature on transition metal catalyzed polymerization of olefins, copolymerization and terpolymerization with CO and other monomer types. Palladium, nickel and other late transition metal complexes generally used for such reactions are reviewed in this section. Emphasis has been placed on recent developments in polymerization chemistry such as new catalyst types, ligands and various reaction mechanisms.

Chapter 2 presents a detailed description of the synthesis and characterization of novel binuclear and polynuclear palladium-methyl complexes containing nitrogen ligands. The palladium-methylchloride complexes of the bifunctional ligands of the type *N,N'*{1, n}-alkanediyl-*bis*(pyridinyl-2-methanimine) {n = 5, 8, 9, 10, 12} (**C1-C5**) and their palladium-methylchloride complexes of the dendritic ligands of the type poly(propyleneimine)-DAB-(pyridinyl-2-methanimine)$_4$, poly(propyleneimine)-DAB-(pyridinyl-2-methanimine)$_8$ were prepared (**C6-C7**). The complexes were fully characterized using FTIR, ^{1}H-NMR, mass spectroscopy (ESI-MS) and elemental analysis. The palladium-methylchloride complexes will be evaluated as catalyst precursors in phenylacetylene polymerization reactions.

Chapter 3 reports on the preliminary studies on phenylacetylene oligomerization/polymerization using Pd(II)-methyl complexes prepared in Chapter 2.

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Chapter 2

Synthesis and characterization of bifunctional, polyfunctional ligands and their palladium-methyl complexes.

2.1 Introduction

The chemistry of binuclear palladium(II) complexes has attracted considerable interest over the years [1]. Isolation of allylpalladium and *ortho*-palladated complexes in the 1960's gave a new impetus to the development of binuclear palladium complexes owing to their relevance in organic transformations. The field has become multidisciplinary in nature encompassing areas such as organic synthesis, catalysis, material-science, photo-physical chemistry, chemotherapy, and other areas of applications [2].

In particular, binuclear models of metallo-proteins have received great attention [3-4] and a variety of new homo- [5] and hetero-binuclear [6] complexes have been synthesized. In the design of these compounds, the choice of the ligand system is of prime importance [7]. When the two metal centres are incorporated in close proximity, the complexes have the potential of catalyzing the reaction either more efficiently or with different chemo-, regio-, or stereo-selectivity than those of the corresponding mononuclear complexes due to cooperation of the two metals in the transition state of the catalytic reaction [8]. An example of an excellent binuclear catalyst which exhibits higher regio-selectivity and reactivity than those of related mononuclear systems by bimetallic cooperation is the dirhodium system reported by Stanley *et al.* [9] for the hydroformylation of α-olefins.

Binuclear organometallic compounds are interesting in view of the expectation that their reactivity in synthesis and catalysis may differ significantly from that of analogous mononuclear catalysts [10]. Additional oxidation states might also be accessible to binuclear complexes as a result of stabilization via metal-metal interactions [11]. Interaction between closely adjacent metal centers might cause increased reaction rates or transformation rates not possible with mononuclear species [12]. In particular, the distance between the two metal centers and their orientation to each other may be important for catalytic performance [13].

In the systems studied so far, ligands are often either highly flexible or rigid: in the latter case, the two metal centers are in a fixed orientation relative to each other. It is envisaged that, when the distance between two metal ions is fixed, this might lead to optimum cooperation of the two metal centers in the transition state of a catalytic reaction.

Wang *et al*. [14] reported bifunctional salicylaldiminate ligands bridged by an alkanediyl or benzyl linker in between the two salicylaldiminato groups. The synthesized bifunctional ligands were complexed with $Ni(PPh_3)_2(Ph)(Cl)$ to obtain the desired binuclear complexes. The binuclear complexes were tested as catalysts for ethylene polymerization and could not be used as a single component catalysts for ethylene polymerization compared to the mononuclear Grubbs salicylaldiminato of nickel catalysts. The salicyladiminato mononuclear catalyst was found to be active for ethylene polymerization in the absence of any cocatalyst [15]. From this, it was evident that the binuclear catalysts reported by Wang *et al*. operates differently from the salicyladiminato mononuclear nickel catalysts type. The binuclear nickel catalyst bridged by a benzyl linker was found to be inactive for ethylene polymerization when activated with MAO, while the alkanediyl bridge binuclear nickel complexes were found to be active for ethylene polymerization when activated with MAO giving polymers with molecular weight (M_w) of M_w 44 x 10^5 g/mol.

The control of steric and electronic properties of the catalytically active metal centre is a fundamental problem in catalyst design. As part of a general study of ligands devoted towards olefin polymerization catalysts, we became interested in the possibility of influencing the electronic characteristic of potentially active metal centres by connecting it to a second metal complex via linkers capable of allowing electronic interaction, as shown by Figure 2.1. The ***Z*** in Figure 2.1 may represent any linker type between the two metals centers. We became interested in complexes of this type having *bis*(pyridinyl-2-methanimine) ligands separated by an alkanediyl chain linker between the two pyridinyl rings.

Figure 2.1: Structural illustration of binuclear catalyst type.

Over the last few decades, an increased effort has been devoted to the design of ligands and metal complexes aimed at homogeneous catalytic conversions. The designs have primarily been focused on the ligands since the reactivity, selectivity, and stability of transition metal compounds in homogeneous catalytic reactions are highly dependent on the ligand environment. Complementary approaches to ligand design have been developed, which rely on the (i) insight and sometimes the knowledge of the reaction mechanism, (ii) molecular modeling, (iii) fast screening methods and (iv) serendipity. The latter appears to play an important role in the discovery of new ligands and catalysts as reported in the open and patent literature.

The rigidity and the bulk imposed by the nitrogen ligands have been the subject of many studies, especially the class of rigid α-diimine ligands such as *bis*(aryl)acenaphthene (*bian*) [16]. The palladium *(bian*) system allowed for the first time the isolation of alternating CO/alkenes oligomerization [17] and they are very selective homogeneous catalysts for *cis*-hydrogenation of alkynes [18]. Most of the reported catalysts contain *N,N*-symmetrical or *N,N'*-unsymmetrical related donor ligands. Unsymmetrical *N,N'*-pyridinyl-2-methanimine type compounds have been used as catalysts in ethylene polymerization reactions catalyzed by group 10 metals [19]. The α-diimine ligand compounds combine good π-acceptor and α-donor properties and as a result can stabilize low and high oxidation state transition metals [20]. Thus transition metals with α-diimines can adapt to a catalytic cycle containing an oxidative addition/reduction elimination sequence. Another advantage of these types of ligands is the facile tunability of their electronic and steric properties. In the literature, there have been few reports on the use of [(*N,N'*-(alkanediyl)*bis*(pyridinyl-2-methanimine)*bis*metal] compounds as polymerization catalyst for olefins and copolymerization reactions [16, 20].

In the search for catalysts with a high concentration of active sites, the use of metallodendrimers has also gained interest in the past years. A considerable number of dendritic macromolecules containing transition metals at their core, branches, or periphery of the dendrimer have been prepared for use in metal-based catalysis, including oligomerization and polymerization (Figure 2.2).

$PdCl_2$ or $Pd(Cl)(CH_3)$ anchored at the periphery of the dendrimer by bidentate chelating ligands has been reported [21-22]. The advantage of using metallodendrimer catalysts is their facile removal from the reaction mixture, providing a recyclable property to the dendritic catalysts.

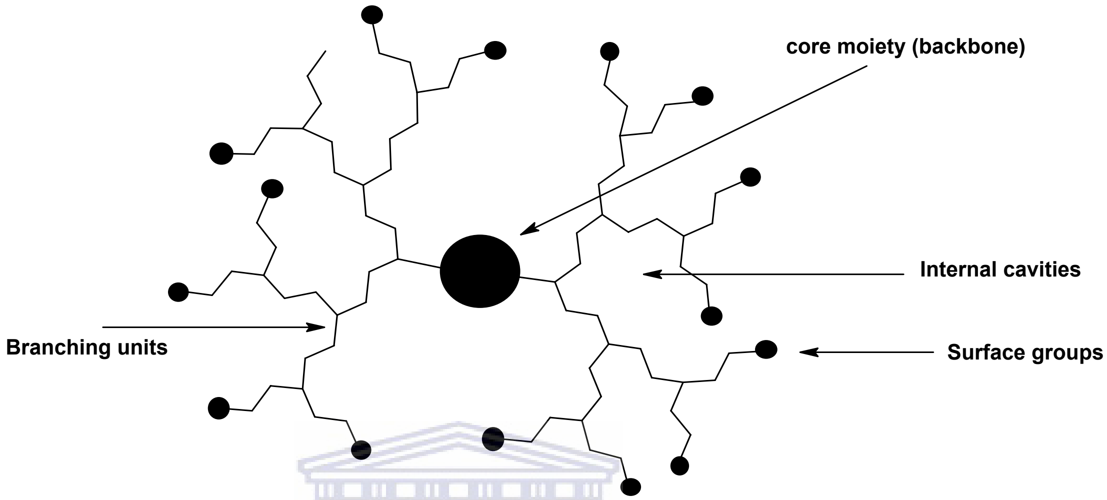


Figure 2.2: Structural illustration of dendrimeric ligands [21].

Palladium as catalyst

Several palladium (II) systems, either prepared *in situ* or presynthesized complexes have been reported to catalyze a number of reactions homogeneously. *In situ* generated systems, widely investigated are composed of palladium (II) salts with diphosphine (P-P) or dinitrogen (N-N) chelating ancillary ligands [23]. In a catalytic system based on preformed complexes, the palladium compounds always bear at least one molecule of diphosphine or dinitrogen in the coordination site. The other two coordination sites can be occupied either by anionic or neutral ligands.

The preparation of cationic complexes $[(COD)Pd(CH_3)(X)]$ (X = weakly or non-coordinating anion)] starting from the neutral complexes $[(COD)Pd(CH_3)(Cl)]$

by halide abstraction in the presence of a weakly coordinating ligand has been reported to be a versatile synthetic route. Preparation of the neutral starting compound, [(COD)Pd(CH_3)(Cl)] starting from [(COD)Pd(Cl_2)] with a slight excess of $SnMe_4$ by selective monoalkylation has been reported [24]. The COD ligands can be replaced by a variety of bindentate ligands L-L, to yield the [(L-L)Pd(CH_3)(Cl)].

Late transition metal catalyst based on cationic complexes containing multidenate ligands have been recently found to be of great interest in olefin polymerization. Such catalyst can be highly active and allow the homopolymerization of ethylene to high molecular weight products [23].

This chapter reports on the synthesis of a variety of [*N,N'*{1,n}-alkanediyl-*bis*(pyridinyl-2-methanimine) {n = 5, 8-10, 12}] ligands (**L1-L5**) and their palladium-methyl complexes (**C1-C5**). Dendritic ligands of the type poly(propyleneimine)-DAB-(pyridinyl-2-methanimine)$_4$ (**L6**), poly(propyleneimine)-DAB-(pyridinyl-2-methanimine)$_8$ (**L7**) and their palladium-methyl complexes have also been synthesized in this section (**C6-C7**). The obtained ligands and complexes were characterized by different spectroscopic techniques.

2.2 Results and discussion

2.2.1 Synthesis and characterization of bifunctional ligands (L1-L5)

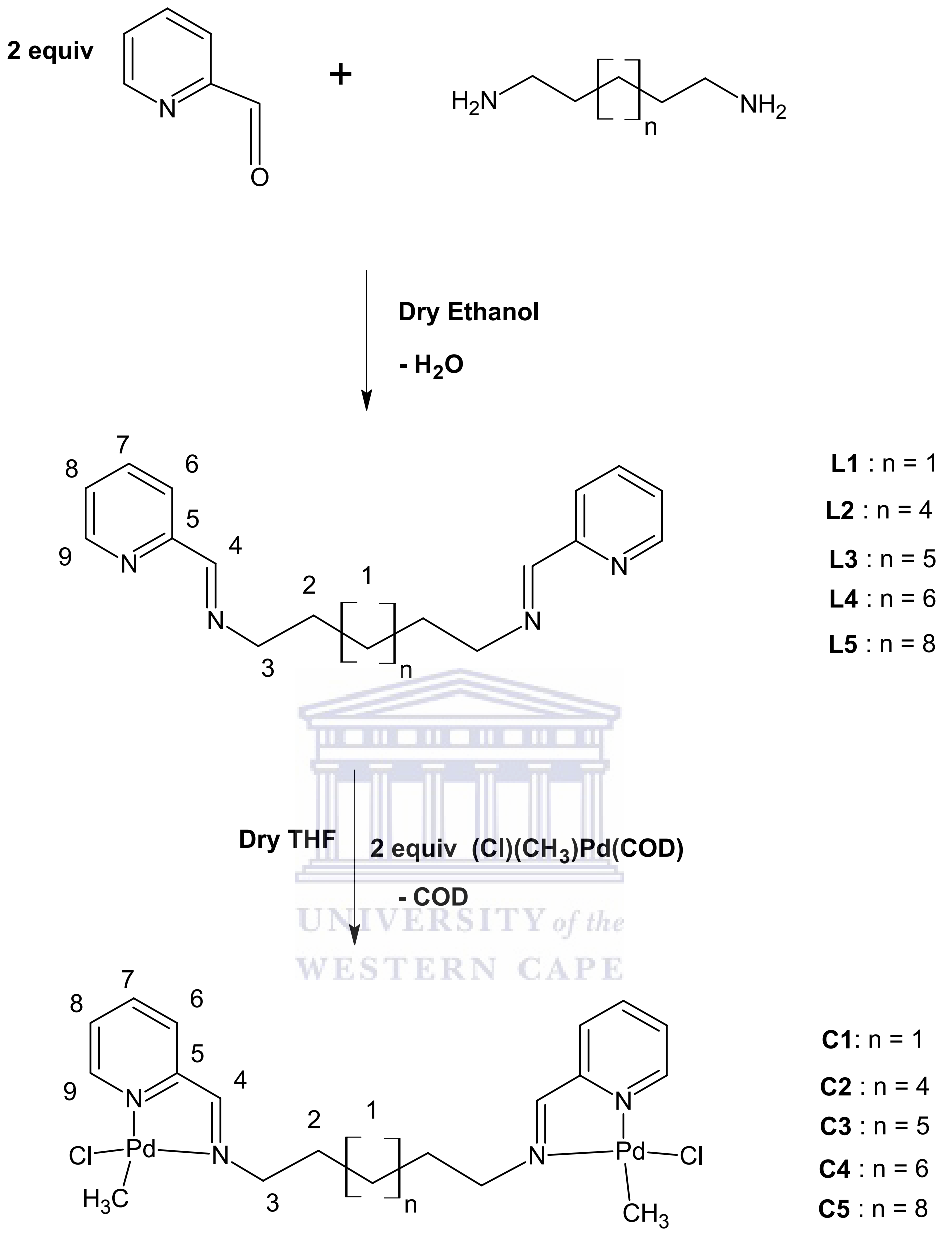
The synthesis of bifunctional [*N,N'*{1,n}-alkanediyl-*bis*(pyridinyl-2-methanimine)] ligands (**L1-L5**) with different carbon chain length (n = 5, 8-10,

12) linkers between the imine nitrogens, was achieved by a Schiff-base condensation reaction of pyridine-2-carboxaldehyde and with the appropriate diamines in a 2:1 ratio as shown in Scheme 2.1 [20,25]. Schiff-base condensation reactions were achieved by stirring the reaction mixtures for 24 hours at room temperature in anhydrous ethanol and in the presence of anhydrous $MgSO_4$ to remove the water formed in the reaction. Recrystallization of the synthesized ligands from dichloromethane and hexane resulted in the formation of the products as air-stable yellow solids (in moderate-high yields 62-80%) except for **L1** which was isolated as an orange oil in (74% yield). All the ligands were found to be soluble in a number of solvents (e.g. dichloromethane, tetrahydrofuran, diethylether and chloroform). The obtained ligands where characterized by ^{1}H-NMR, ^{13}C-NMR spectroscopy and IR spectroscopy. The NMR and IR data confirmed the formation of the ligands. The Schiff-base condensation of analogous compounds starting from ketones is reported to be less successful (giving low yields) requiring more severe reaction conditions (refluxing the reaction) and prolonged reaction time [26].

2.2.1.1. ^{1}H-NMR

Full ^{1}H-NMR details for **L5** is given in Figure 2.3. Table 2.1, show the ^{1}H-NMR of **L1-L4** which showed the same spectral pattern as **L5**. The ^{1}H-NMR spectra showed the azomethine proton (-N=C*H*-) resonance at approximately δ = 8.36 ppm as a sharp singlet. The signal for 9-H_{pyr} proton of the pyridine ring was observed as a doublet at ~δ = 8.63 ppm, which was slightly downfield from the azomethine signal while the signal for 6-H_{pyr} proton was observed as a doublet ~δ = 7.86 ppm. The 7-H_{pyr} protons and 8-H_{pyr} proton are observed as triplets (~δ = 7.73 and 7.25 ppm).

A triplet at 3.62 ppm and broad multiplets at 1.68 ppm and 1.27 ppm were observed in the ligand spectra respectively. The triplet was assigned to the protons of the terminal methylene group (-NC$\boldsymbol{H}_2$-) attached to the azomethine nitrogen while the multiplet at 1.68 ppm was assigned to protons adjacent to terminal methylene (-NCH$_2$C$\boldsymbol{H}_2$-). The other methylene protons of the alkanediyl linker (-NCH$_2$CH$_2$C$\boldsymbol{H}_2$-) were observed at 1.27 ppm. These assignments were similar to those reported for analogous system [20, 27-28].



Scheme 2.1: Synthesis of bifunctional ligands and their *bis*(methylchloride-palladium) complexes.

2.2.1.2. ^{13}C-NMR results

The ^{13}C-NMR chemical shifts for the synthesized ligands are shown in Table 2.2. The alkanediyl chain carbons (**C**$_1$-**C**$_3$) were observed around (~δ = 25.02 - 61.54 ppm) with the carbon of methylene attached to the azomethine (**C**$_3$) appearing at ~δ = 61.54 ppm while the other methylene carbons appears upfield of **C$_3$**. The carbons of the pyridine ring (**C**$_5$-**C**$_9$) were observed to appear in the region 121.19-149.30 ppm in the ^{13}C-NMR spectra. The azomethine carbon (**C**$_4$) signal appears appear downfield at ~δ = 161 ppm. The ^{13}C-NMR data show that the structures of the obtained ligands is symmetrical is evidenced by the fact that the two pyridine units were equivalent. These assignments were compared to the reported analogous compounds [20, 27-28].

2.2.1.3 IR spectroscopy results

Using IR spectroscopy to follow the reaction, the ligand formation was seen by the disappearance of the carbonyl band (1700 cm^{-1}) of the starting aldehyde that had condensed with the starting diamine (3418 cm^{-1}) forming a pyridinyl-2-methanimine (see Figure 2.4). The characteristic absorption band at 1640 cm^{-1} denoted the formation of the –C=N- bond, while the absorption bands at 1586, 1566, 1464 cm^{-1} and 1436 cm^{-1} are characteristic of the pyridine structure. The band at 1586 cm^{-1} appears especially when the pyridine is conjugated with other groups (C=N) by π-π conjugation. The ligand spectra showed a band at 3048-3082 cm^{-1} corresponding to unsaturated -CH of the pyridine, while the bands appearing at 2850-3012 cm^{-1} correspond to the saturated C-H of the aliphatic group. The IR spectra of the ligands do not show any bands around 1700 cm^{-1} corresponding to the starting aldehyde, indicating that the condensation reaction of the aldehyde with the amine was successful [20, 27-28].

2.2.2 Synthesis and characterization of binuclear palladium-methylchloride complexes (C1-C5)

The binuclear palladium-methylchloride complexes (**C1-C5)** were isolated in good yields as air-stable yellow solids by displacement of the weakly coordinating ligand, cyclo-1,5-octadiene (COD) from the [(COD)Pd(CH_3)(Cl)] precursor with the corresponding ligands **L1-L5** as shown in Scheme 2.1. The reaction proceeded smoothly at ambient temperature in tetrahydrofuran. In all cases complex formation started within 10 minutes, which could be observed by the precipitation of the product, but stirring was continued for 4 hours to maximize the product yields. This reaction procedure was based on the published method for the preparation of binuclear-$PdCl_2$ complexes [20].

Washing of the product with dry diethyl ether or dry hexane afforded complexes **C1-C5** as air-stable yellow-brown solids. The complexes were insoluble in most common organic solvents and found to be soluble only in dimethylsulphoxide (DMSO) and 1,2-dichloroethane. The complexes were characterized by ^{1}H-NMR spectroscopy, IR spectroscopy, electron spray ionization mass spectrometry (ESI-MS) and elemental analysis.

Table 2.1: ^{1}H-NMR spectral data for the ligands in $CDCl_3$. **L1-L5**.

	δ (ppm)							
Ligands	**1-H**	**2-H**	**3-H**	**8-H_{pyr}**	**7-H_{pyr}**	**6-H_{pyr}**	**4-$H_{N=CH-}$**	**9-H_{pyr}**
L1	1.46 (m, 2H)	1.76 (m, 4H)	3.69 (t, 4H, $^3J_{HH}$ = 7.0 Hz)	7.25 (t, 2H, $^3J_{HH}$ = 3.8 Hz)	7.73 (t, 2H, $^3J_{HH}$ = 7.6 Hz)	7.99 (d, 2H, $^3J_{HH}$ = 7.8 Hz)	8.37 (s, 2H)	8.64 (d, 2H, $^3J_{HH}$ = 3.8 Hz)
L2	1.27 (m, 8H)	1.68 (m, 4H)	3.62 (t, 4H, $^3J_{HH}$ = 7.0 Hz)	7.25 (t, 2H, $^3J_{HH}$ = 4.8 Hz)	7.73 (t, 2H, $^3J_{HH}$ = 7.6 Hz)	7.96 (d, 2H, $^3J_{HH}$ = 8.2 Hz)	8.33 (s, 2H)	8.61 (d, 2H, $^3J_{HH}$ = 3.0 Hz)
L3	1.32 (m, 10H)	1.70 (m, 4H)	3.65 (t, 4H, $^3J_{HH}$ = 7.0 Hz)	7.25 (t, 2H, $^3J_{HH}$ = 4.0 Hz)	7.73 (t, 2H, $^3J_{HH}$ = 7.8 Hz)	7.96 (d, 2H, $^3J_{HH}$ = 7.8 Hz)	8.36 (s, 2H)	8.62 (d, 2H, $^3J_{HH}$ = 4.0 Hz)
L4	1.29 (m, 12H)	1.69 (m, 4H)	3.65 (t, 4H, $^3J_{HH}$ = 7.0 Hz)	7.25 (t, 2H, $^3J_{HH}$ = 3.8 Hz)	7.73 (t, 2H, $^3J_{HH}$ = 7.0 Hz)	7.99 (d, 2H, $^3J_{HH}$ = 8.2 Hz)	8.35 (s, 2H)	8.67 (d, 2H, $^3J_{HH}$ = 4.6 Hz)
L5	1.23 (m, 16H)	1.67 (m, 4H)	3.62 (t, 4H, $^3J_{HH}$ = 7.0 Hz)	7.23 (t, 2H, $^3J_{HH}$ = 4.0 Hz)	7.69 (t, 2H, $^3J_{HH}$ = 7.8 Hz)	7.93 (d, 2H, $^3J_{HH}$ = 7.6 Hz)	8.33 (s, 2H)	8.69 (d, 2H, $^3J_{HH}$ = 4.4 Hz)

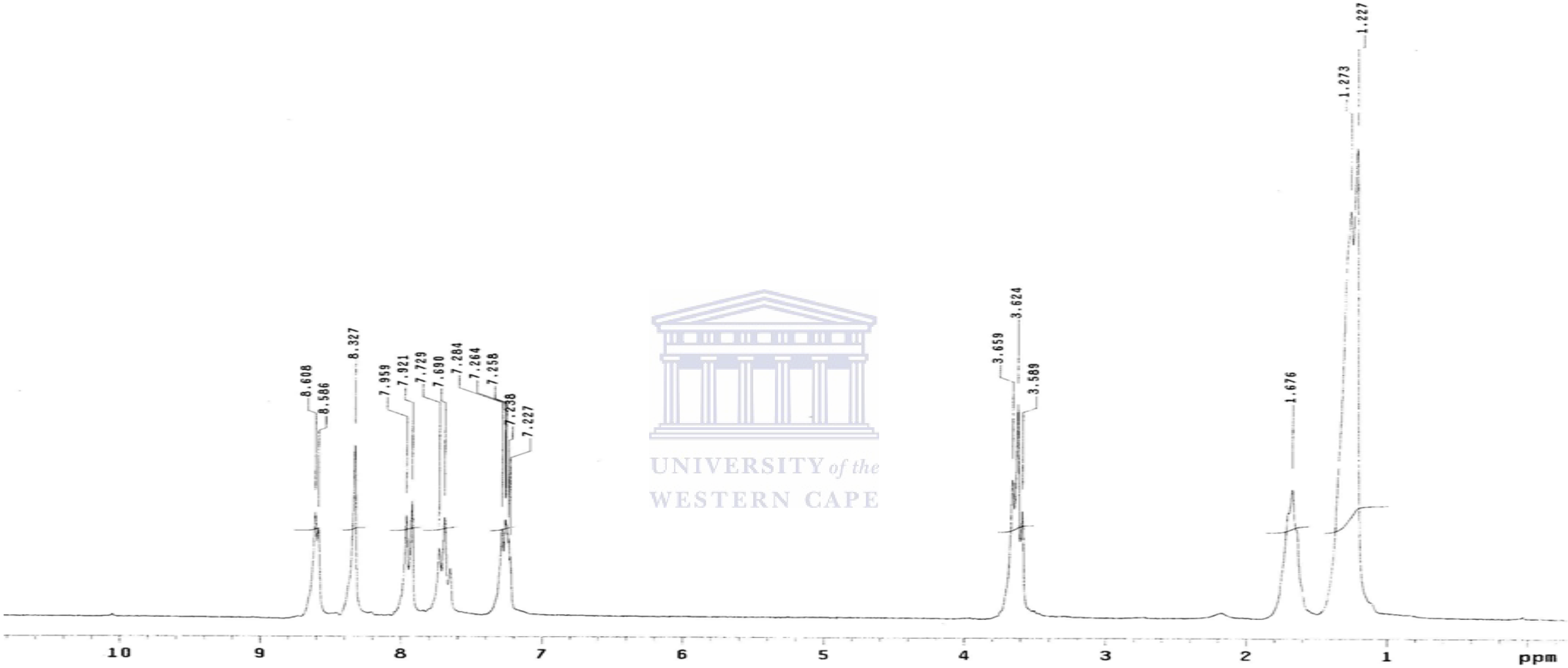


Figure 2.3: ^{1}H-NMR ($CDCl_3$); *N, N'*-(1, 8-dodecanediyl)*bis*(pyridinyl-2- methanimine) **L5**.

Table 2.2: ^{13}C-NMR spectral data for the ligands in $CDCl_3$. **L1-L5**

	δ (ppm)								
Compound	**C_1**	**C_2**	**C_3**	**C_4**	**C_5**	**C_6**	**C_7**	**C_8**	**C_9**
L1	25.02	30.42	61.32	161.77	154.56	121.19	136.49	124.57	149.33
L2	29.33	30.67	61.54	161.66	154.53	121.16	136.49	124.55	149.37
L3	29.33	30.65	61.54	161.63	154.68	121.15	136.47	124.53	149.36
L4	28.99	30.19	61.05	161.14	154.27	120.65	135.97	124.02	148.88
L5	29.52	30.67	61.15	161.60	154.69	121.13	134.61	124.51	149.70

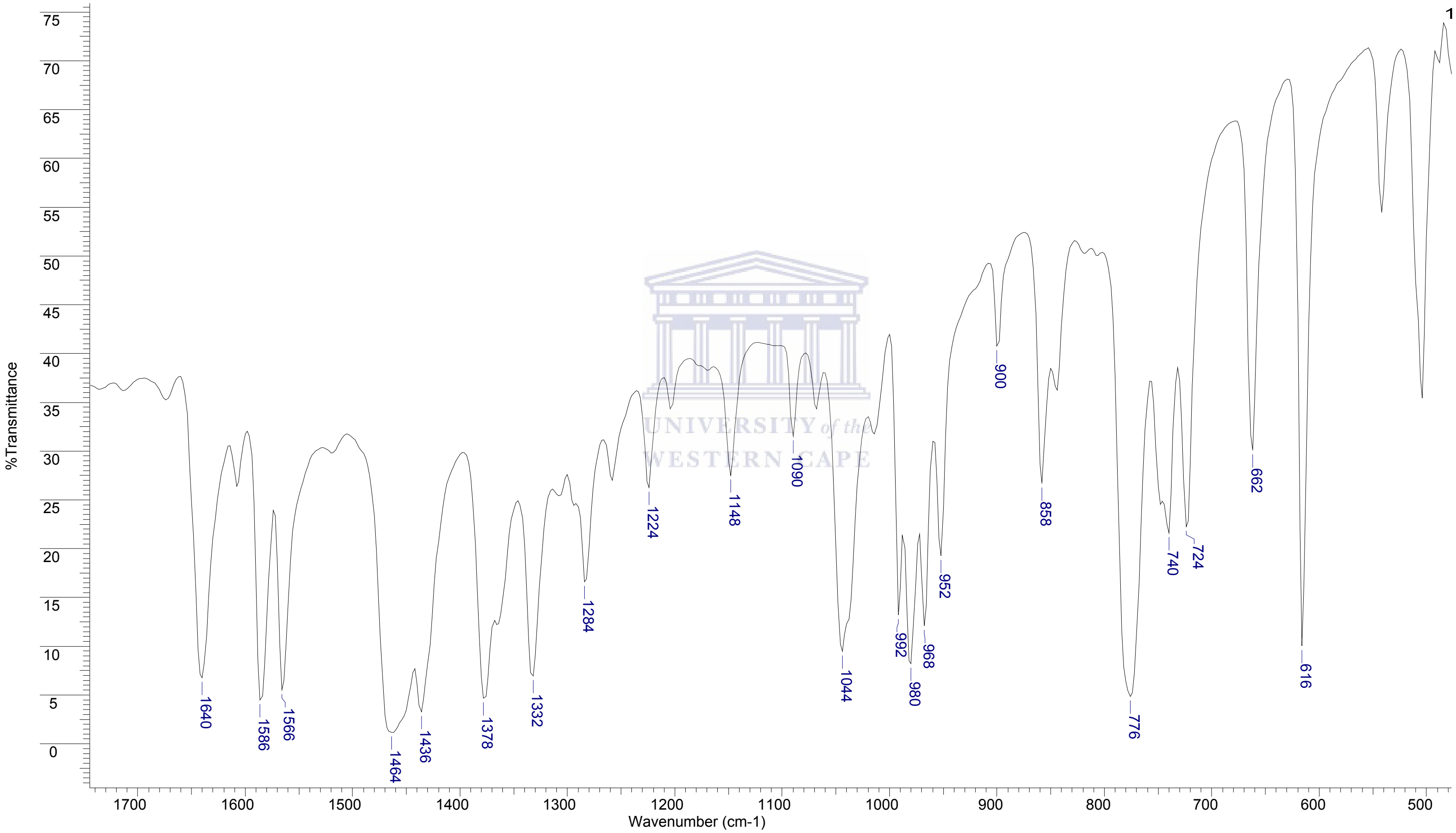


Figure 2.4: IR (NaCl Nujol); *N,N'*-(1,8-dodecanediyl)*bis*(pyridinyl-2-methanimine) **L5**.

Metallation of the ligand with palladium was evidenced from the NMR, IR and ESI-MS data of the complexes. From the data obtained using the above-mentioned analysis methods, complex formation were consistent with the general formula $Pd_2(Cl_2)_2(CH_3)_2$(**L**) for the binuclear complexes, where **L** represent the ligand **L1-L5**.

2.2.2.1 IR spectroscopy results

IR spectra of **C5** is shown in Figure 2.5 and the spectra of **C1-C4** showing similar absorption bands, for **C5** (see Figure 2.5) the spectrum show a single medium-strong absorption band at 1590 cm^{-1}, together with a much weaker band at 1566 cm^{-1}indicating the C=C and C=N bands of the pyridinyl-2-methanimine. These bands show clear shift to lower frequencies when compared to the IR spectra of the uncomplexed ligands which shows three intense absorptions bands in the range 1566-1652 cm^{-1}. The disappearance/overlap of C=N and C=C vibrations has been reported to result from infrared inactive of C=N vibration on bonding of the ligand to the metal [20, 29].

2.2.2.2 ^{1}H-NMR results

All the ^{1}H-NMR spectra of the complexes where recorded in DMSO-d_6 and the proton numbering employed is shown in Scheme 2.1.

The ^{1}H-NMR spectrumof **C5** is shown in Figure 2.6 and the chemical shifts of **C1-C4** showing the same spectral pattern as C5 with their chemical shifts tabulated (see Table 2.3), **C1-C5** showed similar characteristics for all the bifunctional ligands (**L1-L5**) used. The proton signals of the pyridinyl-2-methanimine was observed to be shifted downfield (0.08 ppm) and the alkanediyl protons was upfield shifted in the ^{1}H-NMR spectra of the complexes (**C1-C5)** in comparison with those of uncomplexed ligands **L1-L5**. The general understanding is that proton and carbon resonances of pyridinyl-2-methanimine shift to lower fields on complexing the metal to the ligand. This is a result of the lowering in electron density of the *N,N'* ligands on complexation. Such shifts thus confirm coordination of the pyridinyl-2-methanimine ligand to the palladium metal center [20,28-29]. The most notable effect upon coordination of the ligand to the metal is the change in the chemical shift of azomethine proton (-N=C***H***-), which shift in all the complexes.

The ^{1}H-NMR spectra of **C1-C5** show one set of protons corresponding to the pyridinyl-2-methanimine moieties of the ligand in the range ~δ (7.60-8.76) ppm. A triplet around 7.60 ppm corresponding to protons (8-H_{pyr}) and another triplet around 8.22 ppm corresponding to protons (7-H_{pyr}) were observed. The signal for the 6-H_{pyr} appeared as a doublet ~ δ (7.98) ppm. There was a positional change between the 7-H_{pyr} and the 6-H_{pyr} chemical shift of the complexes compared to the uncomplexed ligands spectra. The signal for the 9-H_{pyr} proton overlaped with that of the azomethine proton (-N=C***H***-) resulting in an apparent broad singlet around δ (8.76) ppm.

The signals for the aliphatic protons of **C1-C5** were shifted upfield compared to those of the alkanediyl protons of uncomplexed ligands. The terminal methylene protons (=NC$\boldsymbol{H}_2$-) bonded to the azomethine nitrogen appeared at ~3.62 ppm as triplet and a broad peak at 1.68 ppm corresponding to the $=NCH_2C\boldsymbol{H}_2$- protons. The peak at ~1.27 ppm appeared as a sharp singlet thus corresponding to the $=NCH_2CH_2C\boldsymbol{H}_2$- protons.

In all the complexes (**C1-C5)**, the methyl groups bonded to the palladium centres at the two ends of the complex was observed to be equivalent giving a singlet at ~δ 0.63 ppm, indicating that the two ends of the complexes were symmetrical. In the starting material [(COD)Pd(CH_3)(Cl)], the methyl signal appeared around 1.00 ppm. The appearance of the palladium-methyl signal in all the complexes at lower frequency (~0.63 ppm) indicated strong interaction of the palladium-methyl with the alkanediyl chain [19, 25]. In a number of reported papers, complexes of pyridinyl-2-methanimne and palladium-methylchloride it was observed that the signal for the 9-H_{pyr} has been reported to appear downfield due to strong deshielding effect of the chlorine when in the same proximity to the 9-H_{pyr} [8].

2.2.2.3 ESI-MS spectrometry

The positive ion electron spray-mass spectra (ESI^+-MS) were recorded in THF solution for the complexes and exhibited fragments after the loss of chloride anion $[M-Cl]^+$. ESI-mass spectra of **C1-C5** did not show any peaks corresponding to the molecular ion. The fragmentation pattern of **C1-C5** show sequential loss of the chloride anion followed by methyl anion at either end of the chain. No signals of concerted loss of two chlorides or two methyls anion were detected in the mass spectra of the complexes.

In the ESI spectrum of **C5** shown in Figure 2.7, a peak at 657.0 m/z was detected corresponding to the molecular ion minus one chloride $[M-Cl]^+$. Peak at m/z 641corresponds to the molecular ion having lost the methyl and chloride $[M-(CH_3 + Cl)]^+$. The peak at m/z 626 corresponds to the molecular ion having lost one chloride and two methyls $[M-(CH_3)_2 + Cl]^+$ and peak at 606 m/z show the molecular ion having lost two chlorides and one methyl $[M-CH_3 + Cl_2]^+$. The peak at m/z 591 show the lost of two methyls and two chlorides from the molecular ion $[M-Cl_2 + (CH_3)_2]^+$ and the peak at m/z 378 corresponding to the remaining ligand after removal of the metal centres and its associated methyls group and chlorides.

The fragmentation patterns of **C1-C5** agree closely with the expected spectrum and clearly confirmed the formation of the complexes.

2.2.3 Synthesis and characterization of dendritic ligands (L6-L7).

The functionalized dendritic ligands **L6-L7** were prepared by Schiff-base condensation of pyridine-2-carboxaldehyde with DAB-$(NH_2)_4$ and DAB-$(NH_2)_8$ in 4:1 and 8:1 mole ratio respectively as shown in Scheme 2.2 and Scheme 2.3. The reaction mixture was stirred in toluene for 2 days under nitrogen atmosphere with the water formed removed by anhydrous $MgSO_4$. Copious washing of the ligands with water is required to remove excess traces of unreacted pyridine-2-carboxaldehyde and DAB-$(NH_2)_4$ or DAB-$(NH_2)_8$. The dendritic ligands were isolated as air-stable orange oils in high yields 73% and 78%, respectively and characterized by ^{1}H-NMR and IR spectroscopy methods. The obtained spectroscopic data, showed that the ligands were successfully synthesized.

2.2.3.1 IR spectroscopy results

Evidence of condensation of the amine and the aldehyde from the IR spectra (see Figure 2.8) was seen by the disappearance of carbonyl group (1700 cm^{-1}) from the starting aldehyde and amines band (~3418 cm-1) of the starting DAB-$(NH_2)_4$ and DAB-$(NH_2)_8$ with the appearance of three medium-strong absorption bands (ν = 1585-1436 cm^{-1}) similar to **L1-L5** corresponding to $\nu_{C=C}$ and $\nu_{C=N}$ of the pyridinyl-2-methanimine absorption bands. This indicated that the condensation of the dendritic polyamines and the aldehyde was successful to form the imine.

2.2.3.2 ^{1}H-NMR results

Evidence of Schiff-base condensation of the respective dendritic polyamines with pyridine-2-carboxaldehyde was clearly seen by the absence of -C***H***$_2$NH$_2$**-** signal adjacent to the –NH$_2$ of the starting dendritic polyamines with the appearance of a new downfield signal due to the imine (H-6, -N=C***H***-, ~8.36 ppm). The condensation of the amine with the pyridine-2-aldehyde was also seen by the disappearance of aldehyde peak (10 ppm) from the starting aldehyde. The dendritic ligands **L6-L7** ^{1}H-NMR show the same spectral pattern. For all the dendritic ligands, the ^{1}H-NMR spectra shown in Table 2.3 showed the azomethine proton (-N=C*H*-) resonance at approximately δ = 8.36 ppm as a sharp singlet. The proton numbering for **L6** and **L7** is shown in Schemes 2.2 and 2.3. For **L6** (see Figure 2.9), the signal for proton 10-

H$_{pyr}$ of the pyridine ring was observed as a doublet at ~δ = 8.62 ppm, which was slightly downfield from the azomethine signal while the signal for proton 7-H$_{pyr}$ was observed as a doublet ~δ = 7.95 ppm. The protons 8-H$_{pyr}$ and 9-H$_{pyr}$ were observed as triplets at ~δ = 7.70 and 7.27 ppm, respectively. Ligand **L6** shows the following peaks in the aliphatic region of the ^{1}H-NMR spectrum. A singlet and triplet appearing at 1.44, 1.84 ppm corresponding to the methylene protons (H-1, -NCH$_2$C$\boldsymbol{H}_2$-) and (H-2, -NC$\boldsymbol{H}_2$-) of the core moiety. The multiplet at 2.49 ppm was assigned to the methylene (H-3, -NC$\boldsymbol{H}_2$-) at the branching N with the methylene attached to the azomethine nitrogen appearing as triplet at 3.64 ppm. The dendritic ligand **L7** show the same NMR spectral features as **L6**.

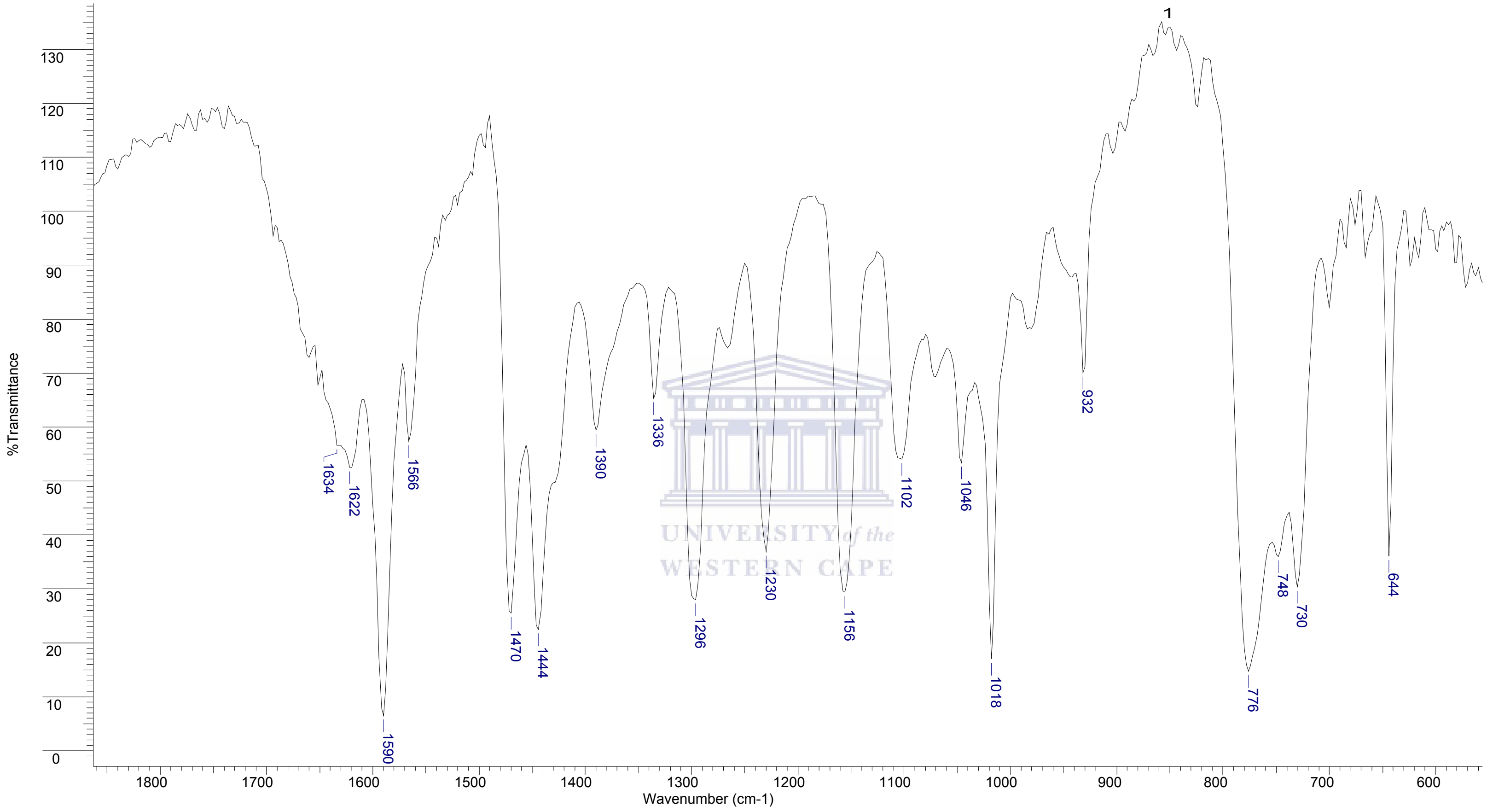


Figure 2.5: IR (KBr pellets); [*N,N'*-{μ-1,8}-dodecanediyl*bis*{(pyridinyl-2-methanimine)palladium-methylchloride}] **C5**.

Table 2.3: ^{1}H-NMR spectral data for the binuclear complexes in DMSO-d_6. **C1-C5**

δ (ppm)

Compound	**Pd-CH$_3$**	**1-H**	**2-H**	**3-H**	**8-H$_{pyr}$**	**6-H$_{pyr}$**	**7-H$_{pyr}$**	**9-H$_{pyr}$ + 4-H$_{N=CH}$**
C1	0.47 (s, 6H)	0.82 (br s, 2H)	1.66 (br s, 4H)	2.85 (t, 4H, $^{3}J_{HH}$ =7.6 Hz)	6.98 (t, 2H, $^{3}J_{HH}$ = 6.2 Hz)	7.17 (t, 2H, $^{3}J_{HH}$ =7.2 Hz)	7.42 (d, 2H, $^{3}J_{HH}$ =8.0 Hz)	7.91 (br s, 4H)
C2	0.67 (s, 6H)	1.32 (br s, 8H)	1.66 (br s, 4H)	3.69 (t, 4H, $^{3}J_{HH}$ =7.0 Hz)	7.82 (t, 2H, $^{3}J_{HH}$ =6.2 Hz)	7.98 (t, 2H, $^{3}J_{HH}$ =7.8 Hz)	8.22 (d, 2H, $^{3}J_{HH}$ =7.8 Hz)	8.76 (br s, 4H)
C3	0.69 (s, 6H)	1.23 (br s, 10H)	1.78 (br s, 4H)	3.81 (t, 4H, $^{3}J_{HH}$ =6.2 Hz)	7.82 (t, 2H, $^{3}J_{HH}$ =6.2 Hz)	8.08 (t, 2H, $^{3}J_{HH}$ =7.8 Hz)	8.21 (d, 2H, $^{3}J_{HH}$ =7.8 Hz)	8.76 (br s, 4H)
C4	0.63 (s, 6H)	1.46 (br s, 12H)	1.65 (br s, 4H)	3.75 (t, 4H, $^{3}J_{HH}$ =7.0 Hz)	7.31 (t, 2H, $^{3}J_{HH}$ =6.2 Hz)	7.98(t, 2H, $^{3}J_{HH}$ =7.4 Hz)	8.22 (d, 2H, $^{3}J_{HH}$ =7.8 Hz)	8.76 (br s, 4H)
C5	0.68 (s, 6H)	1.32 (br s, 16H)	1.66 (br s, 4H)	3.69 (t, 4H, $^{3}J_{HH}$ =7.4 Hz)	7.82 (t, 2H, $^{3}J_{HH}$ =5.8 Hz)	8.01 (t, 2H, $^{3}J_{HH}$ =7.4 Hz)	8.22 (d, 2H, $^{3}J_{HH}$ =7.4 Hz)	8.76 (br s, 4H)

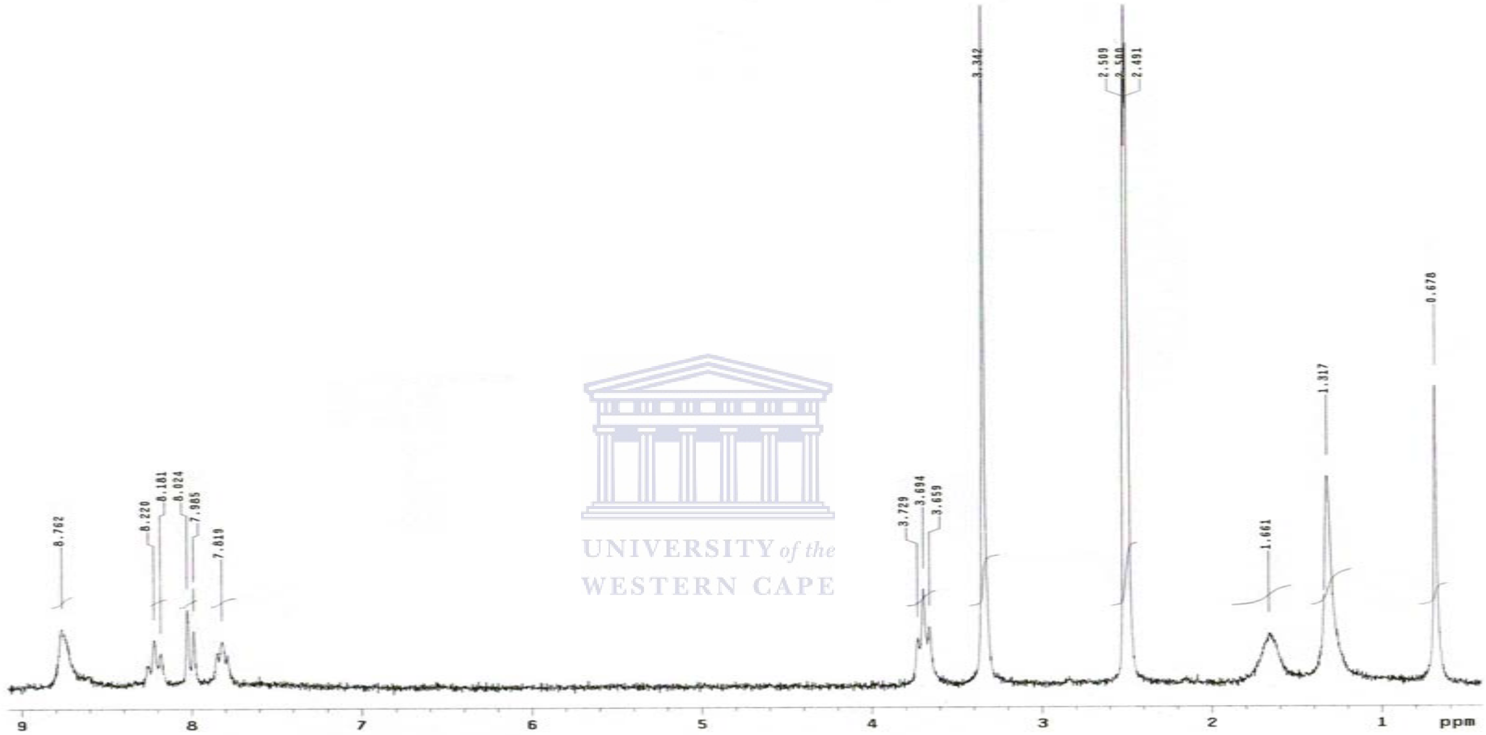


Figure 2.6: ^{1}H-NMR (DMSO-d_6); [*N,N'*-(1,8-dodecanediyl-*bis*{(pyridinyl-2-methanimine)palladium-methylchloride}] **C5**.

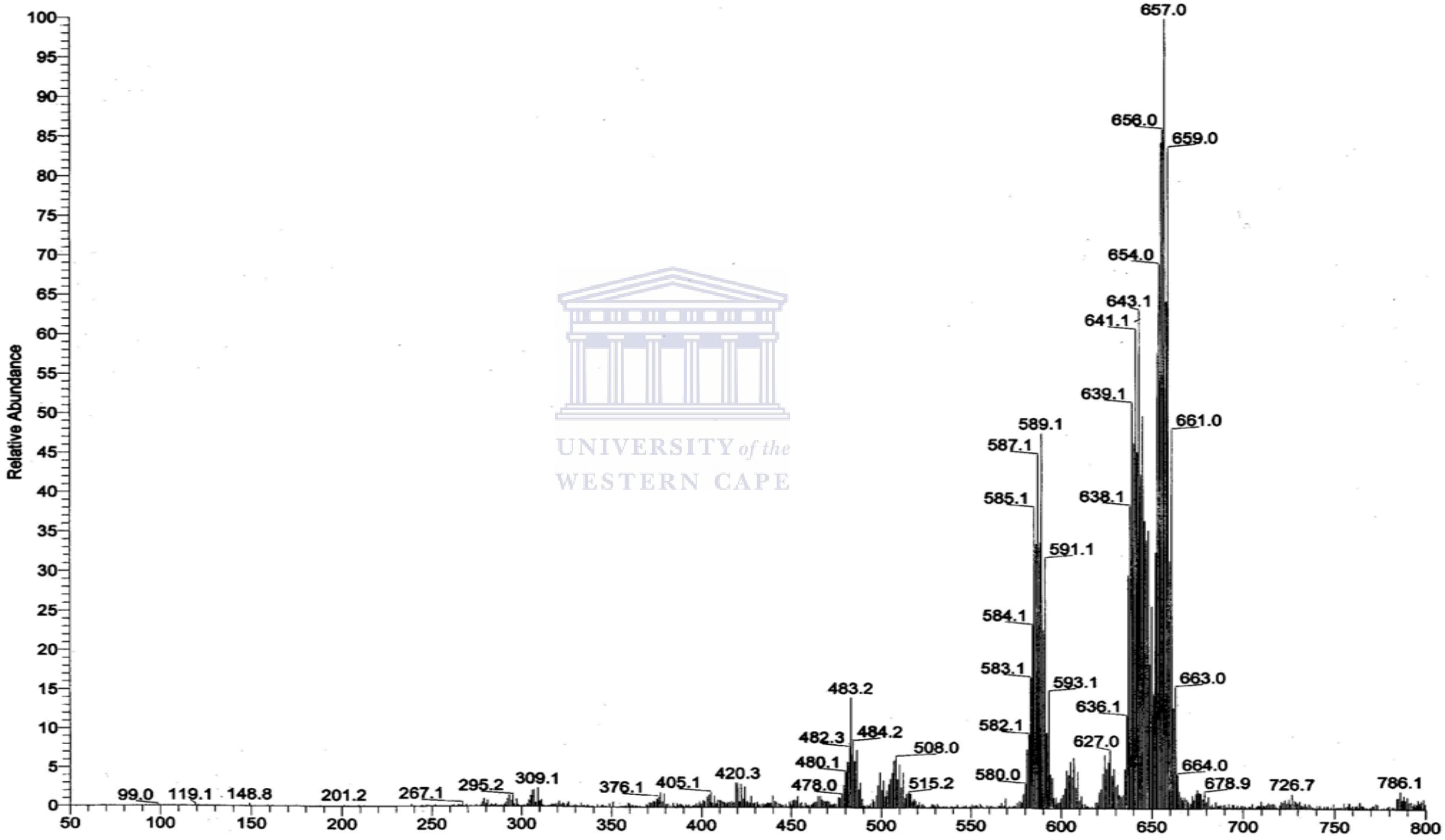
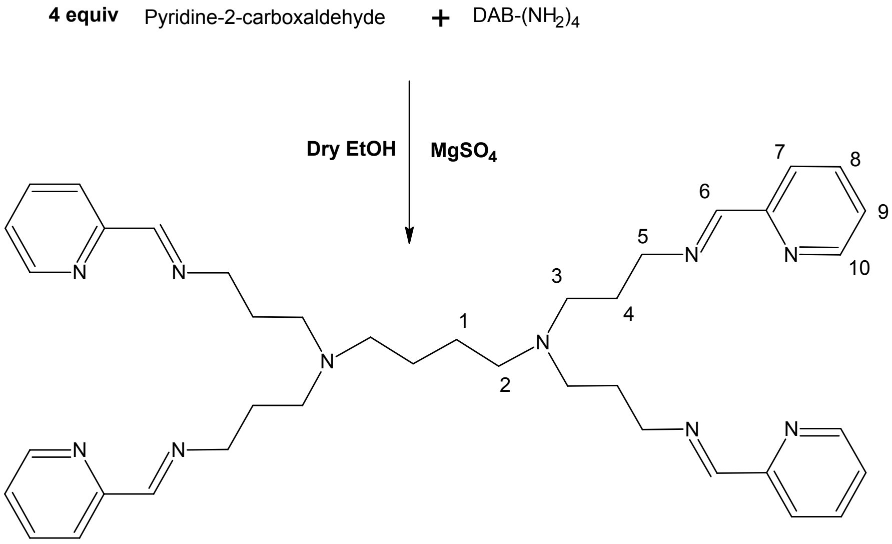
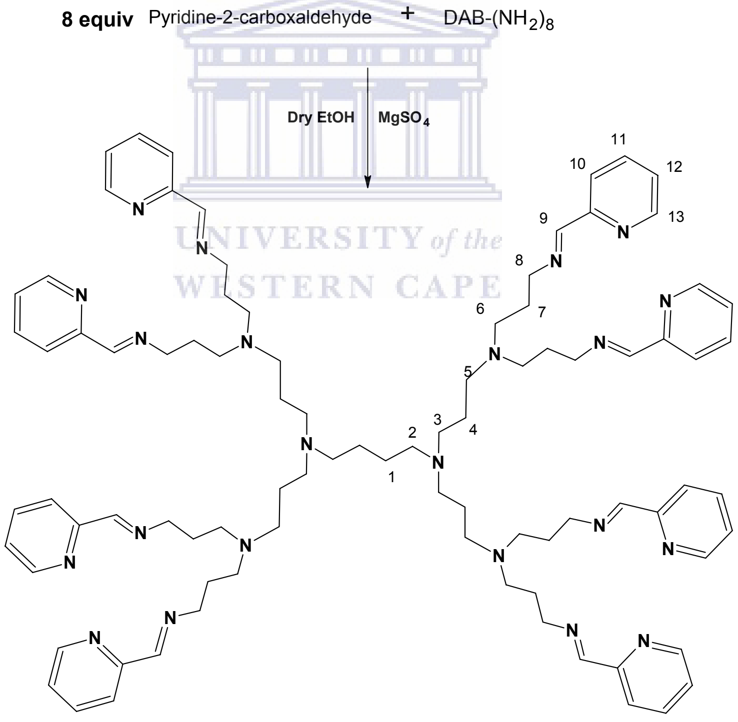


Figure 2.7: ESI-MS spectra**;** [*N*,*N'*{1,12}-dodecanediyl-*bis*{(pyridinyl-2-methanimine)palladium-methylchloride}] **C5**.



Scheme 2.2: Poly(propylenimine)-DAB-(pyridinylimine)$_4$ ligand synthesis **L6**.



Scheme 2.3: Poly(propylenimine)-DAB-(pyridinylimine)$_8$ ligand synthesis **(L7)**.

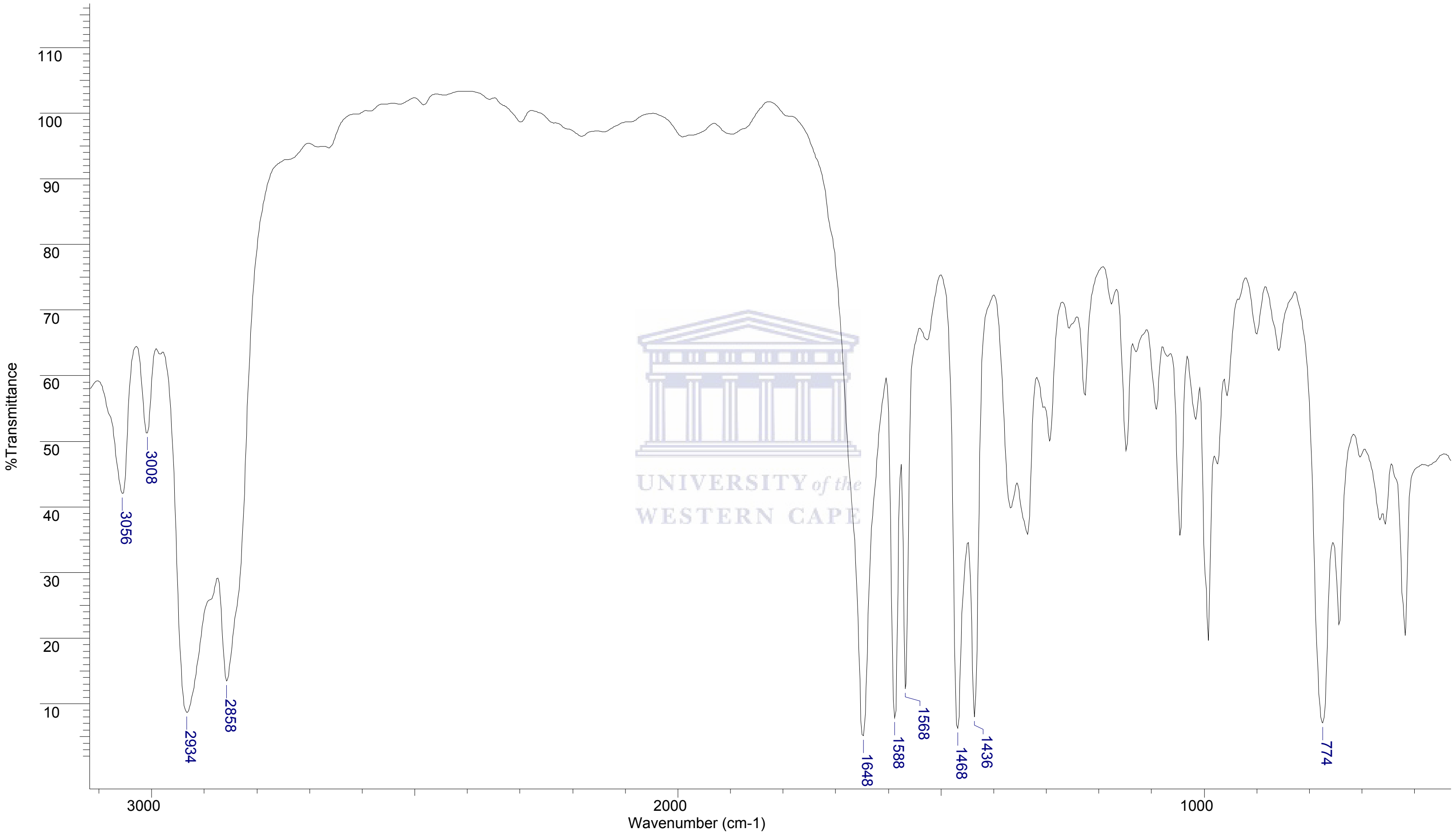


Figure 2.8: IR (Nujoll); Poly(propylenimine) DAB-(pyridinyl-2-methanimine)$_4$ ligand **L6**.

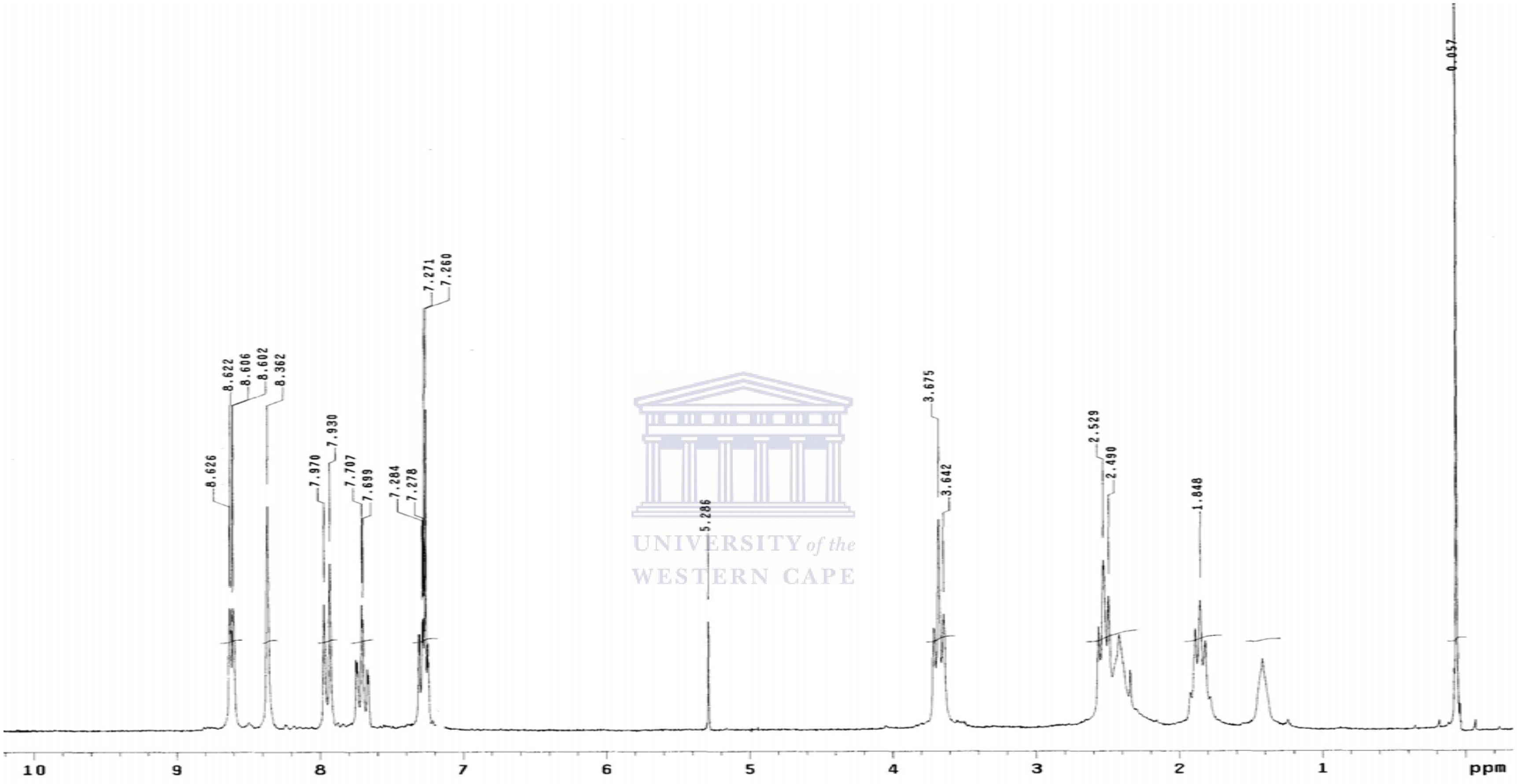


Figure 2.9: ^{1}H-NMR ($CDCl_3$); Poly(propylenimine)-DAB-(pyridinyl-2-methanimine)$_4$ ligand **L6**.

2.2.4 Synthesis and characterization of dendritic palladium-methyl complexes (C6-C7).

The metallodendrimer complexes **C6-C7** were synthesized by reacting **L6-L7** with [(COD)Pd(CH_3)(Cl)] in tetrahydrofuran under nitrogen atmosphere as shown in Scheme 2.4 and Scheme 2.5. In all cases complex formation started within 10 minutes of stirring, which could be observed by the precipitation of the product. Stirring was however continued for 4 hours to maximize the product yield. The product was obtained in high yield as yellow-brown air-stable solids that are only soluble in 1,2 dichloroethane and DMSO [28]. The obtained complexes **C6-C7** were characterized by ^{1}H-NMR, IR, and elemental analysis.

2.2.4.1 ^{1}H-NMR results

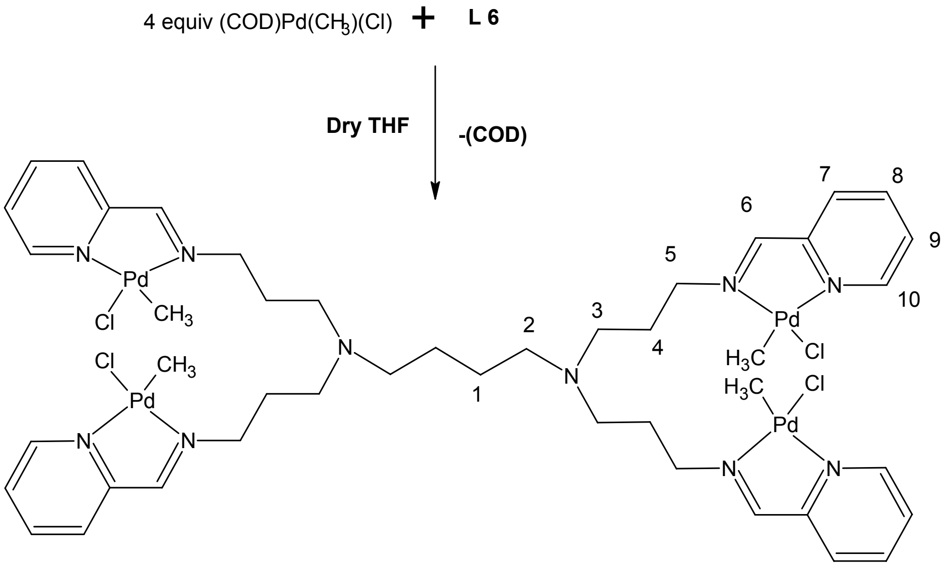
The ^{1}H-NMR spectra of the complexes showed broad peaks compared to their corresponding ligands. The complexes **C6-C7** showed the same NMR spectral trends as **C1-C5**. The peaks due to the pyridine ring are shifted to lower chemical shift values, the same trend as observed for the binuclear complexes **(C1-C5)**.

The ^{1}H-NMR spectra of **C6-C7** (see Figure 2.10) show only one set of protons corresponding to the pyridinyl-2-methanimine moieties of the ligand ~ 7.80 ppm. A triplet around 7.78 ppm corresponding to two protons (9-H_{pyr}) and another triplet δ (8.18) ppm corresponding to two protons (8-H_{pyr}) are observed. The proton 7-H_{pyr} for the pyridine ring appears as a doublet ~ 8.01 ppm. There is a positional change between the 8-H_{pyr} and the 7-H_{pyr} chemical shift of the complexes compare to the uncomplexed ligands spectra. The signal for the 10-H_{pyr} proton overlaps with that of the azomethine proton (-N=C***H***-) resulting in an apparent broad singlet around δ 8.78 ppm.

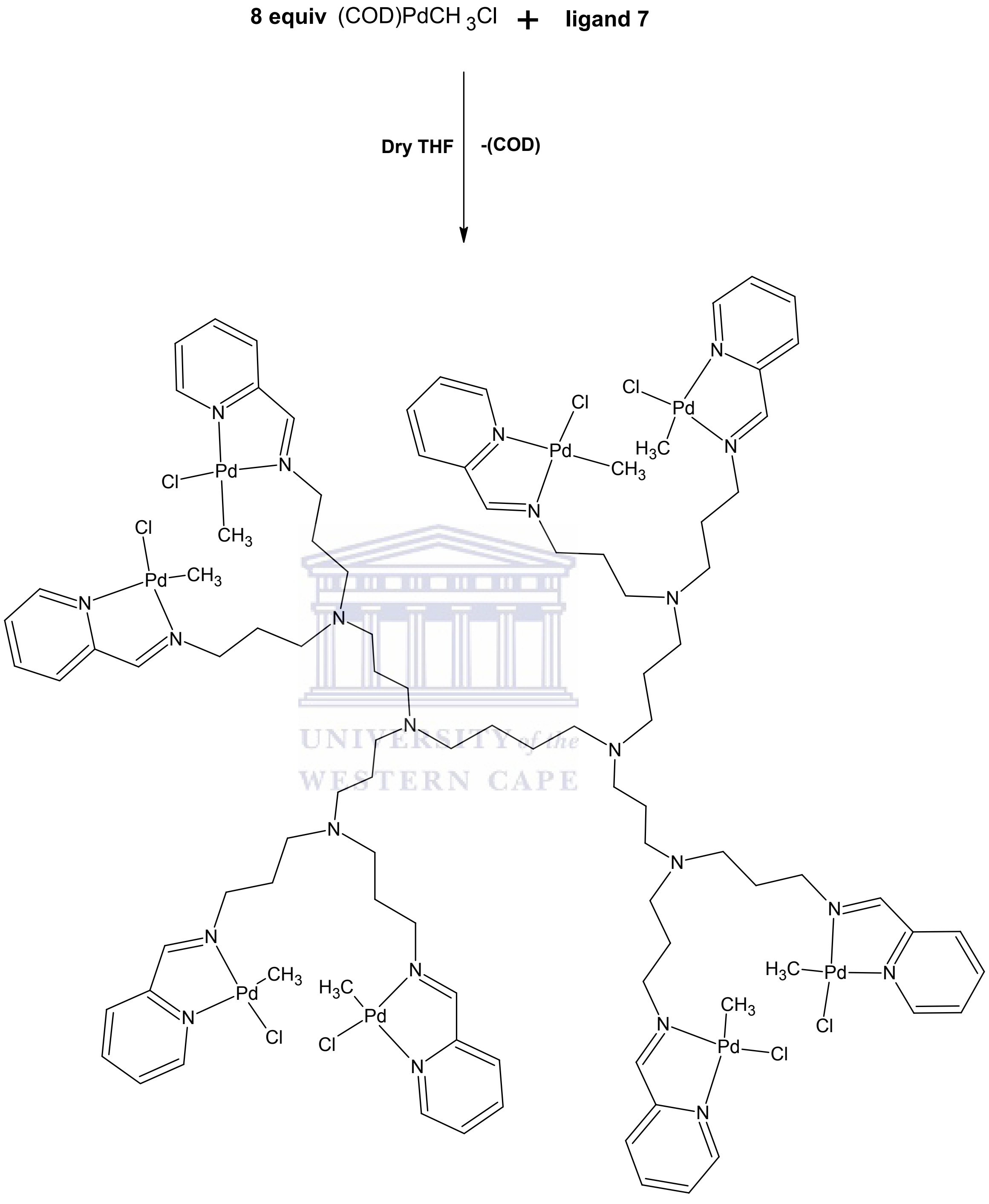
The methylene protons of the core moiety are observed as a broad singlet and a multiplet at ~δ 1.03 and δ 1.79 ppm respectively whilst the methylenes at branching N are observed as multiplet ~ δ 2.51 ppm. The methylene proton adjacent to azomethine nitrogen appear as a broad singlet ~ δ 3.72 ppm of the core moiety.

2.2.4.2 IR spectroscopy results

The IR spectra for **C6-C7** showed the same characteristic absorption bands as observed in **C1-C5** IR spectra. The IR spectra (see Figure 2.11) show a single medium-strong absorption band at 1588 cm^{-1}, together with a much weaker band at 1566 cm^{-1} indicating the presence of C=C and C=N bands. These bands show a clear shift to lower frequency when compared to the IR spectra of the uncomplexed ligands, which shows three intense absorptions bands in the range 1566-1652 cm^{-1} [20,28].



Scheme 2.4: Tetranuclear palladium-methylchloride complex **C6**.



Scheme2.5: Polynuclear palladium-methylchloride complex **C7**.

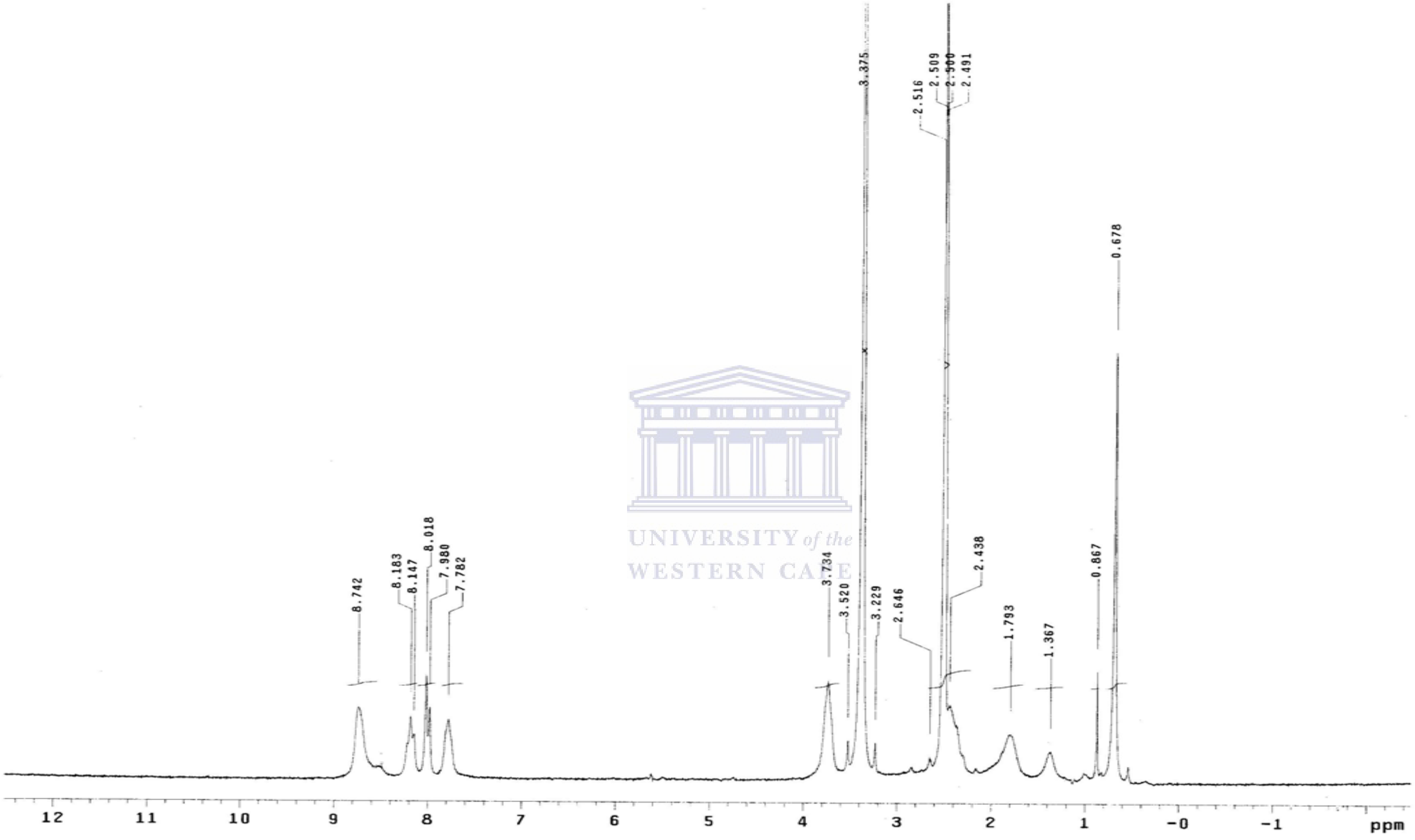


Figure 2.10: ^{1}H-NMR (DMSO, d_6); Poly(propylene)-DAB-(pyridinyl-2-methanimine)$_4$*tetra*(palladium-chloromethyl), complex **C6**.

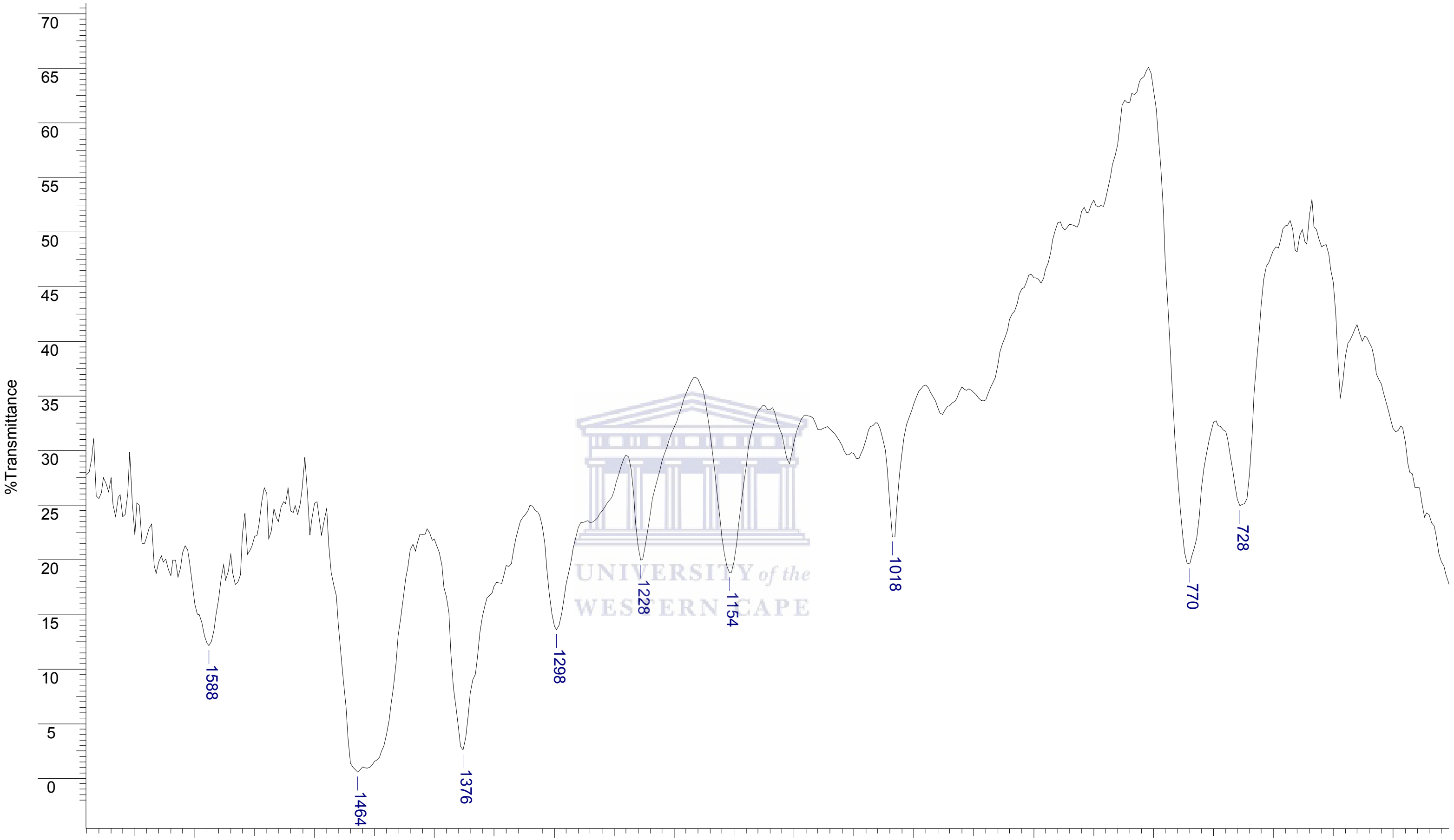


Figure 2.11: IR (KBr pellets) Poly(propylene)DAB-(pyridinyl-2-methanimine)$_4$*tetra*(palladium-chloromethyl) complex **C6**.

2.3 Conclusion

Five bifunctional and two dendritic pyridinal-imine ligands have been prepared and fully characterized. The ligands were also successfully used to prepare a range of new binuclear methyl chloride complexes of palladium in which the metal centers are separated by hydrocarbyl linker of various carbon lengths. In addition, two new metallodendrimers of palladium were prepared and characterized. The new complexes are stable in the solid state and can be stored for long periods at room temperature.

2.4 Experimental Section

General Methods: All manipulations and reactions involving air-sensitive compounds were performed under a positive pressure of nitrogen using Schlenk tube techniques. Dry, degassed solvents were obtained by distillation over appropriate drying agents. Dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN) and chloroform ($CHCl_3$) were distilled from phosphorus pentoxide (*di*-P_2O_5) and CaH_2 granules respectively, methanol from magnesium turnings, diethyl ether (DEE), toluene and tetrahydrofuran (THF) from sodium-benzophenone ketyl.

Materials: Palladium(II)dichloride-hydrate ($PdCl_2.xH_2O$) was purchased from Next Chemica (South Africa), pyridine-2-carboxaldehyde (99%), tetramethyltin $(CH_3)_4Sn$, magnesium sulfate (anhydrous $MgSO_4$), cycloocta-1,5-diene (COD), 1,12-diaminododecane, 1,10-diaminodecane, 1,9-diaminononane, 1,8-diaminooctane, 1,5-diaminopentane were all purchased from Sigma-Aldrich. DAB-4-$(NH_2)_4$ (**G1**) and DAB-8-$(NH_2)_8$ (**G2**) from SyMO-Chem/Holland. All the reagents were used as received unless stated otherwise.

(1,5-cyclooctadiene)palladium(II)dichloride, $(COD)PdCl_2$ [29], (1,5-cyclooctadiene)palladium(II)methylchloride, $(COD)Pd(Cl)(CH_3)$ [29], the bifunctional ligands (**L1-L5**) [20] and the dendritic ligands (**L5-L6**) [28] were prepared using the literature procedures.

Instrumentation

IR spectra were recorded as Nujol mulls as neat films on NaCl plates or KBr pellets (solids) using a Perkin-Elmer, Paragon 1000 PC FTIR spectrometer. Proton (^1H) NMR spectra were recorded on a Varian Gemini-2000 spectrometer (at 200 MHz). Chemical shifts are reported in δ units (ppm) referenced to the residual protons of deuterated solvents as internal reference relative to $SiMe_4$ (δ 0.00 ppm). The ^1H-NMR splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), and br (broad). The $^{13}C\ \{^1H\}$-NMR spectra were recorded on a Varian Gemini-2000 spectrometer (at 50.3 MHz). Melting points were recorded on a Leitz Microscope Hot Stage 350. Elemental analyses were performed at the Microanalytic laboratory at University of Cape Town, South Africa and Electron Spray Ionization-Mass spectroscopy (ESI-MS) analyses were performed at the Chemistry Department of University of Botswana.

2.5 Preparation of Bifunctional ligands

2.5.1 *N,N'-{1,5}-pentanediyl-bis(pyridinyl-2-methanimine)* (L1)

In a Schlenk tube filled with dry ethanol (40 ml) under nitrogen atmosphere, 1,5 diamino-pentane (1.98 g, 19.50 mmol) was added whilst stirring giving a light-orange colour solution. Pyridine-2-carboxaldehyde (4.17 g, 39.0 mmol) was added to the formed solution giving an orange solution. The resulting solution was stirred for 5 minutes followed by the addition of anhydrous magnesium sulphate (~3 g, $MgSO_4$) giving a light-orange solution. The solution was stirred for 24 hours under nitrogen atmosphere after which it was filtered to remove the $MgSO_4$. The solvent was removed from the filtrate under high vacuum and the orange oily residue was dissolved in 10 ml dichloromethane and washed with (4 x 40ml) distilled water. The organic layers were combined and dried over 3 g of anhydrous $MgSO_4$ and filtered. The filtrate was evaporated under high vacuum with the product obtained as an orange oil, yield (4.02 g, 74%). IR bands (NaCl plates as neat oil), (1568, 1588, 1648) cm^{-1}, ν (C=C) and ν (C=N).

2.5.2 *N,N'{1,8}-octanediyl-bis(pyridinyl-2-methanimine)* (L2)

This compound was prepared in a similar manner to **L1** with the workup being different. The yellow solution was filtered to remove $MgSO_4$ and the filtrate volume was reduced to ~5 ml after which 10 ml diethylether was added to precipitate the pale-yellow solid product. The solution was allowed to stand in the fridge for 2 days to precipitate more of the solid product. The product was obtained as a pale yellow solid (1,54 g; 73%). IR bands (KBr pellet), (1566, 1586, 1640) cm^{-1}, ν (C=C) and ν (C=N).

2.5.3 *N,N'-{1,9}-nonanediyl-bis(pyridinyl-2-methanimine)* (L3)

This compound was prepared in a similar manner to **L2** by reacting 1,9 diamino-nonane (0.96 g, 6.05 mmol) and pyridine-2-carboxaldehyde (1.29 g, 12.1 mmol). The product obtained as a pale yellow solid (1.18 g, 62 %). IR bands (KBr pellet), (1566, 1586, 1652) cm^{-1}, ν (C=C) and ν (C=N).

2.5.4 *N,N'-{1,10}-decanediyl-bis(pyridinyl-2-methanimine)* (L4)

This compound was prepared in a similar manner to **L2** by reacting 1,10 diamino-decane (1.21 g, 7.02 mmol) and pyridine-2-carboxaldehyde (1.48 g, 14.00 mmol). The product obtained as a yellow solid (1.78 g, 79%). IR bands (KBr pellet), (1568, 1588, 1648) cm^{-1}, ν (C=C) and ν (C=N).

2.5.5 *N,N'-{1,12}-dodecanediyl-bis{(pyridinyl-2-methanimine)* (L5)

This compound was prepared in a similar manner to **L2** by reacting 1,12 diamino-dodecane (5.01 g, 25.0 mmol) and pyridine-2-carboxaldehyde (5.35 g, 50.0 mmol). The product obtained as pale yellow solid (6.90 g, 80%). IR bands (KBr pellet), (1566, 1586, 1652) cm^{-1}, ν (C=C) and ν (C=N).

2.6. Preparation of Bifunctional complexes

2.6.1

N,N'-(1,5-pentanediyl)bis{(pyridinyl-2-methanimine)palladium-methylchloride} (C1)

In a Schlenk tube having dry THF (60 ml) under nitrogen atmosphere, (COD)Pd(CH$_3$)(Cl) (0.38 g, 1.40 mmol) was introduced under nitrogen atmosphere whilst stirring giving a cream-white solution. **L1** (0.19 g, 0.70 mmol) was added into the stirring solution giving an orange-yellow solution. The reaction mixture was stirred for 5 hours under nitrogen after which the solvent volume was reduced to ~5 ml. 10 ml hexane was added and the solution left in the fridge for 2-days to allow precipitation of the solid. The product was obtained as a yellow solid (0.27 g, 64%). Mp = 142-144 °C. IR (KBr): 1620 cm^{-1}(w), 1590 cm^{-1}(s), ν (C=N). Elemental analysis for $C_{19}H_{26}N_4Cl_2Pd_2$ (598.1 g/mol): calculated; C, 38.0; H, 4.35. N, 9.36. Found: C, 37.69; H, 4.26; N, 8.26%. ESI-MS: 598 $[M]^+$; 563 $[M\text{-}Cl]^+$; 548 $[M\text{-}(CH_3 + Cl)]^+$; 497 $[M\text{-}\{(CH_3)_2 + Cl_2\}]^+$; 284 $[M\text{-}\{Pd_2 + (CH_3)_2 + Cl_2\}]^+$.

2.6.2 *N,N'-(1,8-octanediyl)bis{(pyridinyl-2-methanimine)palladium-methylchloride}* (C2)

This complex was prepared in a similar manner to **C1** using **L2** (0.07 g, 0.24 mmol) and (COD)Pd(CH_3)(Cl) (0.139 g, 0.526 mmol). The product was obtained as yellow solid, yield (0.11 g, 66%). Mp = 183-185 °C. IR bands (KBr): 1620 cm^{-1} (w), 1592 cm^{-1}(s), ν (C=N). Elemental analysis for $C_{22}H_{32}N_4Cl_2Pd_2$ + 0.5 THF (653.74 g/mol): calculated, C, 42.87; H, 5.35; N, 8.34. Found: C, 42.76; H, 5.14; N, 8.08%. ESI-MS: 636 $[M]^+$; 600 $[M\text{-}Cl]^+$; 549 $[M\text{-}(CH_3 + Cl)]^+$; 535 $[M\text{-}\{(CH_3)_2 + Cl_2\}]^+$; 322 $[M\text{-}\{(Pd_2) + (CH_3)_2 + Cl_2\}]^+$.

2.6.3 *N,N'-(1,9-nonanediyl)bis{(pyridinyl-2-methanimine)palladium-methylchloride}* (C3)

This complex was prepared in a similar manner to **C1** using **L3** (0.12 g, 0.35 mmol) and (COD)Pd(CH_3)(Cl) (0.19 g, 0.70 mmol). The product was obtained as yellow solid, yield (0.16 g, 71%). Mp = 186-88 °C. IR bands (KBr pellet), 1622 cm^{-1}(w), 1590 cm^{-1}(s), ν (C=N). Elemental analysis for $C_{23}H_{34}N_4Cl_2Pd_2$ (649.04 g/mol), calculated: C, 42.48; H, 5.23; N, 8.62.Found: C, 42.76; H, 5.14; N, 8.08 %. ESI-MS: 650 $[M]^+$; 615 $[M-Cl]^+$; 599 $[M-(CH_3 + Cl)]^+$; 549 $[M-\{(CH_3)_2 + Cl_2\}]^+$; 336 $[M-\{(Pd_2) + (CH_3)_2 + Cl_2\}]^+$.

2.6.4 *N,N'-(1,10-decanediyl)bis{(pyridinyl-2-methanimine)palladium-methylchloride}* (C4)

This complex was prepared in similar manner to **C1** using **L4** (0.22 g, 0.70 mmol) and (COD)Pd(CH_3)(Cl) (0.37 g, 1.40 mmol). The product was obtained as yellow solid, yield (0.302 g, 64%). Mp = 194-196 °C. IR bands (KBr pellet): 1620 cm^{-1}(w), 1592 cm^{-1}(s), ν (C=N). Elemental analysis for $C_{24}H_{36}N_4Cl_2Pd_2$ (663.04g/mol): calculated, C, 42.47; H, 5.42; N, 8.45. Found: C, 41.19; H, 5.45; N, 5.91%. ESI-MS: 663 $[M]^+$; 628 $[M-Cl]^+$; 613 $[M-(CH_3 + Cl)]^+$; 562 $[M-\{(CH_3)_2 + Cl_2\}]^+$; 349 $[M-\{(Pd_2) + (CH_3)_2 + Cl_2\}]^+$.

2.6.5 *N,N'-(1,12-dodecanediyl)bis{(pyridinyl-2-methanimine)palladium-methylchloride}* (C5)

This complex was prepared in a similar manner to **C1** using **L5** (0.24 g, 0.70 mmol) and (COD)Pd(CH_3)(Cl) (0.093 g, 0.35 mmol). The product was obtained as yellow solid, yield (0.36 g, 74%). Mp = 232-234 °C. IR bands (KBr pellet): 1622 cm^{-1}(w), 1594 cm^{-1}(s), ν (C=N). Elemental analysis for $C_{26}H_{40}N_4Cl_2Pd_2$: (691.8g/mol): calculated, C, 45.22; H, 5.78; N, 8.10. Found: C, 45.41; H, 6.01; N, 7.66 %. ESI-MS:

692 $[M]^+$; 657.0 $[M\text{-}Cl]^+$; 642 $[M\text{-}(CH_3 + Cl)]^+$; 591 $[M\text{-}\{(CH_3)_2 + Cl_2\}]^+$; 378 $[M\text{-}\{(Pd_2) + (CH_3)_2 + Cl_2\}]^+$.

2.7 Preparation of dendritic ligands

2.7.1 *Tetrafunctional dendrimeric ligand* (L6)

In a Schlenk tube under nitrogen atmosphere, dendrimer DAB-$(NH_2)_4$ (Generation 1) (0.513 g, 1.62 mmol) was dissolved in dry toluene (50 ml). A solution of pyridine-2-carboxaldehyde (0.07 g, 6.48 mmol) dissolved in toluene (5 ml) was syringed into the Schlenk tube containing a DAB-$(NH_2)_4$ solution. The mixture had a yellow colour. Anhydrous magnesium sulfate ($MgSO_4$) 1 gram was added into the solution to remove any water released during the reaction. The reaction was allowed to stir at room temperature under nitrogen for 2 days.

After two days the mixture was filtered by gravity to remove magnesium sulfate ($MgSO_4$) which was washed with freshly dried toluene. The yellow filtrate was evaporated on a rotatory evaporator at 50 ^oC. A yellow oil was obtained and dissolved in CH_2Cl_2 (10 ml) then washed with water (4 x 50 ml). After washing, the organic layer was collected and dried over anhydrous $MgSO_4$ and then filtered. Solvent from the filtrate was removed on rotatory evaporator yielding an orange-yellow oily product, yield (0.74g, 73%). ^1H NMR ($CDCl_3$): $\delta = 1.44$ (br s, 4H, -$NCH_2C\boldsymbol{H}_2$-), 1.84 (t, 8H, $^3J_{HH} = 6.6$ Hz, -$NCH_2C\boldsymbol{H}_2$-), 2.49 (m, 12H,-$NC\boldsymbol{H}_2$-), 3.64 (t, 8H, $^3J_{HH} = 5.8$ Hz, $NC\boldsymbol{H}_2$-), 7.27 (t, 4H, $^3J_{HH} = 5.8$ Hz, 9-H_{Pyr}), 7.69 (t, 4H, $^3J_{HH} = 7.4$ Hz, 8-H_{Pyr}), 7.97 (d, 4H, $^3J_{HH} = 6.8$ Hz, 7-H_{pyr}), 8.36 (s, 4H, -N=C$\boldsymbol{H}$-), 8.62 (d, 4H,

$^{3}J_{HH}$ = 4.0 Hz, 10-H$_{Pyr}$). IR bands (neat oil, NaCl plates): ν (C=C) = 1592 cm^{-1}; very strong absorption band at 1647.8 and 1565.9 cm^{-1}ν (C=N).

2.7.2 *Polyfunctional dendrimeric ligand* (L7)

This compound was prepared in similar manner to **L6** by reacting the dendrimer-DAB-(NH$_2$)$_8$ (Generation 2) (0.512 g, 0.81 mmol) and pyridine-2-carboxaldehyde (0.69 g, 6.48 mmol). The product was obtained as an orange-yellow oil, yield 78%. ^{1}H NMR (CDCl$_3$): δ = 1.45 (s, 4H, -NCH$_2$C$\boldsymbol{H}_2$-), 1. 84 (t, 24H, $^{3}J_{HH}$ = -NCH$_2$C$\boldsymbol{H}_2$-), 2.51 (m, 4H, -NC$\boldsymbol{H}_2$-), 3.66 (t, 48H, $^{3}J_{HH}$ = NC$\boldsymbol{H}_2$-), 7.26 (t, 4H, $^{3}J_{HH}$ = 12-H$_{Pyr}$), 7.70 (t, 4H, $^{3}J_{HH}$ = 11-H$_{Pyr}$), 7.93 (d, 4H, $^{3}J_{HH}$ = 10-H$_{pyr}$), 8.58 (s, 8H, -N=C$\boldsymbol{H}$-), 8.62 (d, 4H, $^{3}J_{HH}$ = 13H$_{Pyr}$). Selected IR bands (neat oil, NaCl plates): very strong absorption band at 1647.8 and 1565.9 cm^{-1} ν (C=N).

2.8 Preparation of dendritic complexes

2.8.1 *Tretranuclear palladium-methylchloride complex* (C6)

In a Schlenk tube containing dry THF (60 ml) under nitrogen atmosphere, (COD)Pd(CH$_3$)(Cl) (0.37 g, 1.40 mmol) was introduced under nitrogen whilst stirring giving a cream-white solution. (**L6**) (0.24 g, 0.35 mmol) was added into the stirring solution giving a yellow-coloured solution. The reaction mixture was stirred for 6 hours under nitrogen and the solvent volume reduced to about 5 ml. Hexane (10 ml) was added and the solution left in the fridge for 2 days to precipitate the product. The light brown solid was collected by gravity filtration (0.30 g, 68%).^{1}H-NMR (DMSO-*d*$_6$): δ 0.68 (s, 12H, Pd-C$\boldsymbol{H}_3$), 1.37 (br s, 4H,-NC$\boldsymbol{H}_2$-), 1.79 (br s, 4H, -NCH$_2$C$\boldsymbol{H}_2$-), 2.51 (m, 12H, -NC$\boldsymbol{H}_2$-), 3.73 (br s, 8H, =NC$\boldsymbol{H}_2$-), 7.78 (br s, 4H, $^{3}J_{HH}$ 9-H$_{pyr}$), 8.01 (d,

$^3J_{HH}$ = 7.6 Hz, 4H, 7-H$_{pyr}$), 8.18 (t, 4H, $^3J_{HH}$ = 7.2 Hz, 8-H$_{pyr}$), 8. 74 (br s, 8H, 10-H$_{pyr}$ overlapping with -N=C***H***-). Mp = 181-183 °C. IR bands (KBr pellet), 1566 cm^{-1}(w), 1588 cm^{-1}(s), ν (C=N). Elemental analysis for $C_{44}H_{64}N_{10}Cl_4Pd_4$: + THF (1446.44 g/mol): calculated, C, 39.82; H, 4.97; N, 9.67. Found: C, 39.69; H, 5.11; N, 10.16 %. ESI-MS: 651 $[M]^{2+}$; 616 $[M\text{-}Cl]^{2+}$; 601 $[M\text{-}\{CH_3 + Cl\}]^{2+}$; 550 $[M\text{-}\{(CH_3)_2 + Cl_2\}]^{2+}$; 337 $[M\text{-}\{Pd_2 + (CH_3)_2 + Cl_2\}]^{2+}$.

2.8.2 *Polynuclear palladium-methylchloride complex* (C7)

This complex was prepared in a similar manner to **C6** using **L7** (0.21 g, 0.14 mmol) and (COD)Pd(CH_3)(Cl) (0.31 g, 1.12 mmol) in a 1:8 ratio. The product was obtained as a brown solid, yield (0.44 g, 87 %). Mp = 257-259 °C. ^{1}H-NMR (DMSO-d_6): δ 0.54 (s, 24H, Pd-C***H***$_3$), 1.03 (br s, 4H,-NCH$_2$C***H***$_2$-); 1.79 (br s, 4H, -NC***H***$_2$-), 2.51 (m, 12H, -NC***H***$_2$-), 3.72 (s, 16H, =NC***H***$_2$-), 7.81 (br d, 8H, 9-H$_{pyr}$), 8.01 (br d, 8H, 7-H$_{pyr}$), 8.21 (br d, 8H, 8-H$_{pyr}$), 8. 78 (br s, 16H, 10-H$_{pyr}$ overlapping with -N=C***H***-). IR bands (KBr pellet), 1566 cm^{-1}(w), 1591 cm^{-1} (s), ν(C=N). Elemental analysis for $C_{96}H_{144}N_{22}Cl_8Pd_8$: + 4 THF(2885.30 g/mol): calculated, C, 44.36; H, 5.51; N, 10.16. Found: C, 45.71; H, 5.16; N, 10.28%. ESI-MS: 685 $[M]^{4+}$; 649 $[M\text{-}Cl]^{4+}$; 635 $[M\text{-}\{CH_3 + Cl\}]^{4+}$; 584 $[M\text{-}\{(CH_3)_2 + Cl_2\}]^{4+}$; 372 $[M\text{-}\{Pd_2 + (CH_3)_2 + Cl_2\}]^{4+}$.

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Chapter 3

Binuclear palladium-methylchloride complexes of the type [$Pd_2(CH_3)_2(Cl)_2$(*N,N*'{1,n}-alkanediyl)*bis*(pyridinyl-2-methanimine) (n = 5, 8-10, 12)] as catalyst precursors for phenylacetylene transformation.

3.1 Introduction

The use of mononuclear late transition metal complexes having pyridinyl-imine ligands as olefin polymerization catalysts is well documented [1]. The use of binuclear complexes as olefin polymerization catalysts has been reported recently [2], however, there have been no reports on the use of binuclear palladium-methyl complexes as phenylacetylene polymerization catalysts. The prepared binuclear palladium-methyl complexes discussed in Chapter 2 were evaluated as catalyst precursors for phenylacetylene polymerization.

Transition metal complexes prepared as catalysts for olefin polymerization can be tuned by altering a number of components in the system. The choice of ligand can impact on the properties of the complex as a result of variable electronic and steric factors. In addition the choice of metal can also affect certain qualities of the complex [3].

A number of transition metal catalysts from group 4-10 have been previously reported and used as catalysts for the polymerization of substituted acetylenes [4]. For example rhodium complexes of the type {[Rh(C≡CC_6H_5)(2,5-norbornadiene)(P$(C_6H_5)_3)_2$] and [Rh(norbornadiene)(OCH_3)]$_2$ used with an equivalent amount of a bidentate phosphine of the type [($Ph_2P(CH_2)_xPPh_2$)(x = 1-4)]} have been successfully applied in the polymerization of substituted acetylenes. The stability of the catalyst in a number of solvents, its functional group tolerance and the precise control of the stereochemistry of the propagation have been key features for the use of Rh(I) catalysts in acetylene polymerization [5].

The use of palladium complexes [e.g. $Pd(CH_3CN)_4][BF_4]_2$ as polymerization catalysts for phenylacetylene giving polymer of molecular weight, $M_w = 9000$ has also been reported [6]. Masuda *et al*. reported the synthesis of semi-conducting polyphenylacetylene (PPA) using $[Ni(\eta^3\text{-allyl})(\eta^4\text{-1,5 COD})][PF_6]$ as polymerization catalyst [5]. These authors reported that, depending on the reaction conditions, the proportion of *cis/trans* polymers changes. In addition the conductivity of the polymer also changes. Douglas *et al*. reported the use of $[(Ph_3P)_2Ni(CO)_2]$ as catalyst for the polymerization of phenylacetylene in the absence of solvent giving mixtures of linear polymer and/or oligomers and cyclotrimers [7]. The same authors reported the use of nickelocene in solvent-free conditions to catalyze phenylacetylene giving cyclotrimers and linear polyenes with no tetramers [8].

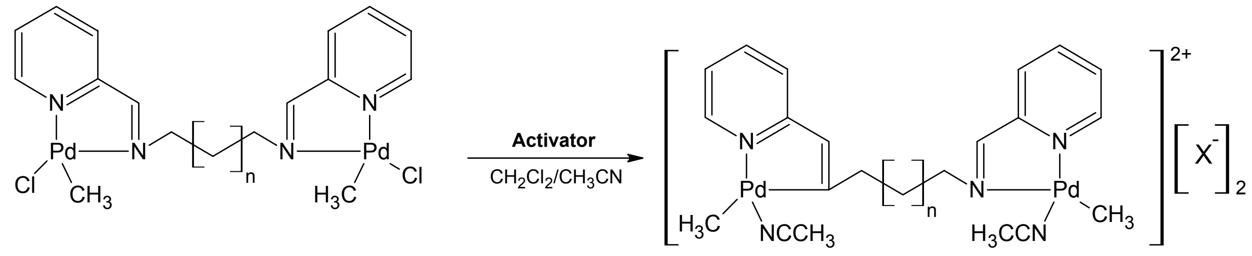
Electrically conducting organic polymers constitute an interesting class of material for various technological applications. The synthesis of such material from acetylene (leading to polymer with π-conjugated carbon-carbon double bonds) produces satisfactory conducting properties. Polyphenylacetylene shows chemical and physical properties that are intermediate to substituted polyacetylenes. Its colour can vary from red-brown to yellow, its soluble in common organic solvents such as toluene, dichloromethane, acetone and is air stable displaying semi-conducting properties (10^{-10} $S.cm^{-1}$) that is 10^8 times more conducting than polystyrene [9-11].

In this chapter preliminary studies on the use of the synthesized binuclear palladium-methylchloride complexes of the type $[Pd_2(CH_3)_2(Cl)_2$(*N,N'*{1,n}-alkanediyl)*bis*(pyridinyl-2-methanimine) (n = 5, 8-10, 12)] as catalyst precursors for phenylacetylene transformation is reported. A range of reaction conditions (solvent ratio, catalyst type, catalyst/monomer ratio, reaction time and nature of counterion) are reported here.

3.2 Results and discussion

3.2.1. Activation of catalyst precursors {$Pd_2(CH_3)_2(Cl)_2$(N,N'{1,n}-alkanediyl)bis(pyridinyl-2-methanimine) (n = 5, 8-10, 12)]}.

The active catalysts **C1a-C5a** were generated by the abstraction of the chloride atoms with either silver salts ($AgBF_4$, $AgBPh_4$) or $NaB(Ar_f)_4$ in a CH_2Cl_2-CH_3CN solvent mixture. This solvent mixture allows weak coordination of the acetonitrile to the vacant coordination site to stabilize the active catalyst precursors as shown in Scheme 3.1 Attempts to use other types of weakly coordinating ligands (Et_2O, THF, methylacrylate {MA}) to stabilize the active catalyst at room temperature were unsuccessful leading to precipitation of metallic palladium. Et_2O however at -78°C was able to stabilize the active catalysts. Attempts to isolate the activated catalysts **C1a-C5a** were also unsuccessful since the active catalysts were found to be air- and moisture-sensitive decomposing to palladium metal even when stored at low temperatures. Activated catalysts containing bindentate N-donors ligands such as bipyridine or related α-diimine ligands have previously been reported to be stable in solution and in some cases their X-ray crystal structures have been reported [12].



C1a, n = 3

C2a, n = 6

C3a, n = 7

C4a, n = 8

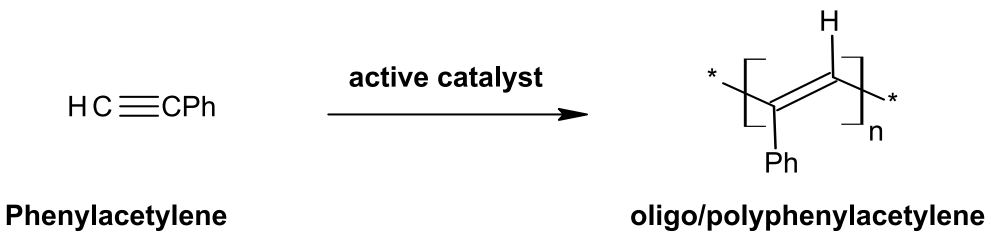
C5a, n = 10

X = BF_4^-, $B(Ar_f)_4^-$, BPh_4^-

Scheme 3.1: Preparation of active catalyst precursors **C1a-C5a**.

3.2.2. Phenylacetylene oligomerization/polymerization catalyzed by active catalysts, {$Pd_2(CH_3)_2(NCCH_3)_2$(N,N'{1, n}-alkanediyl)bis(pyridinyl-2-methanimine) (n = 5, 8-10, 12)][X]}.

Phenylacetylene oligomerization/polymerization was performed in (9:1 and 3:1) CH_2Cl_2-CH_3CN solvent mixtures with the activation of catalyst precursors with either silver salts ($AgBF_4$ and $AgPh_4$) or $NaB(Ar_f)_4$) as shown in Scheme 3.1. In experiments where single solvent systems were used, the active catalysts were first generated in the CH_2Cl_2-CH_3CN (1:1) solvent mixture followed by removal of the solvents under vacuum before addition of the single solvent. The active catalysts were stabilized by the residual CH_3CN from the CH_2Cl_2-CH_3CN solvent mixture that was used to generate the active catalyst. The residual CH_3CN was displaced by the phenylacetylene monomer during the reaction.



Scheme 3.2: Phenylacetylene transformation using the active catalysts **C1a-C5a**.

All reactions were performed with active catalyst-monomer ratio of 1:50 in CH_2Cl_2-CH_3CN solvent mixture of different ratios or in single solvent systems (CH_3CN, THF, CH_2Cl_2 and toluene) unless stated otherwise. After addition of monomer to the activated complex (see Scheme 3.2), the reaction mixture was stirred for the desired reaction time and then quenched by adding 10 ml acidified methanol. The solvent was removed on a rotary evaporator and the product residue recrystallized from CH_2Cl_2 and methanol giving brown-dark brown solids with low to high yields (16% - 99%). The products were characterized by ^1H and ^{13}C-NMR as well as IR spectroscopy and gel permeation chromatography (GPC). The obtained PPA was soluble in common organic solvents like CH_2Cl_2, CH_3CN, CH_3Cl, THF and acetone. In all the reactions the yields were calculated based on the polymer residue isolated after solvent removal.

3.2.2.1 Effect of solvent composition

The results of phenylacetylene polymerization using solvent mixture of CH_2Cl_2-CH_3CN (9:1 and 3:1 ratio) activated with $AgBF_4$ and $AgBPh_4$ are shown in Table 3.1. The solvent ratio was seen to affect the catalytic activity. When the reactions were performed using a 3:1 solvent mixture of CH_2Cl_2-CH_3CN high monomer conversions were obtained. Similar reactions were performed using catalysts **C1-C5** activated with $AgBF_4$ in 9:1 solvent mixture of CH_2Cl_2-CH_3CN over 24 hour reaction time. The results are shown in Figure 3.1 and Table 3.1 (entries 1, 5, 9, 13, 17). For all catalysts except **C1a** low molecular weight products ranging between 570-680 were obtained in moderate to high yields (entries 1, 5, 9, 13). The products also exhibited narrow polydispersity indices (PDI) between 1.05-1.14. **C1a** (entry 17) on the other hand produced high molecular weight polymer (M_w = 17884). However, in this case, the yield was low and the PDI slightly higher. In all experiments where a 9:1 solvent mixture of CH_2Cl_2-CH_3CN was used, it was observed that an increase in the reaction time also led to an increase in the monomer conversion.

Reactions carried out over 24h in 3:1 solvent mixtures of CH_2Cl_2-CH_3CN using catalysts **C2a**, **C4a** and **C5a** gave relatively high molecular weight polymers with M_w varying between 20500-28150. Once again the yields obtained were high. In addition the PDI values were slightly higher than those obtained in reactions carried out in a 9:1 solvent mixture. **C1a** and **C3a** on the other hand gave low molecular weight products (M_w = 673 and 714) in low yields. Increasing the reaction time for reactions in 3:1 solvent mixtures of CH_2Cl_2-CH_3CN to 48 hours resulted in increased polymer yields. There was also an increase in monomer conversion (see Figure 3.2), from the results obtained it appears that a decrease in the CH_3CN concentration resulted in a decrease in monomer conversion as well as low M_w polymer. This might be due to the fact that the lower CH_3CN concentration resulted in lower stability of the catalyst decreasing its life-time and hence its overall activity. Figure 3.3 shows the results for monomer conversion in 3:1 solvent mixtures of CH_2Cl_2-CH_3CN activated with $AgBF_4$ over 24 and 48 hours. The results shown in Figure 3.3 indicates that, as the time is increased the monomer conversion also increases.

C2 and **C5** activated by $AgBPh_4$ also catalyzed the polymerization of phenylacetylene. Results for these reactions are shown in Table 3.1. The products were obtained in varying yields over different reaction times. **C2** shows consistently high monomer conversion irrespective of the solvent mixtures used. From the results shown in Figure 3.4 it was observed that there was little difference in the monomer conversion when the reactions were done over a longer reaction time.

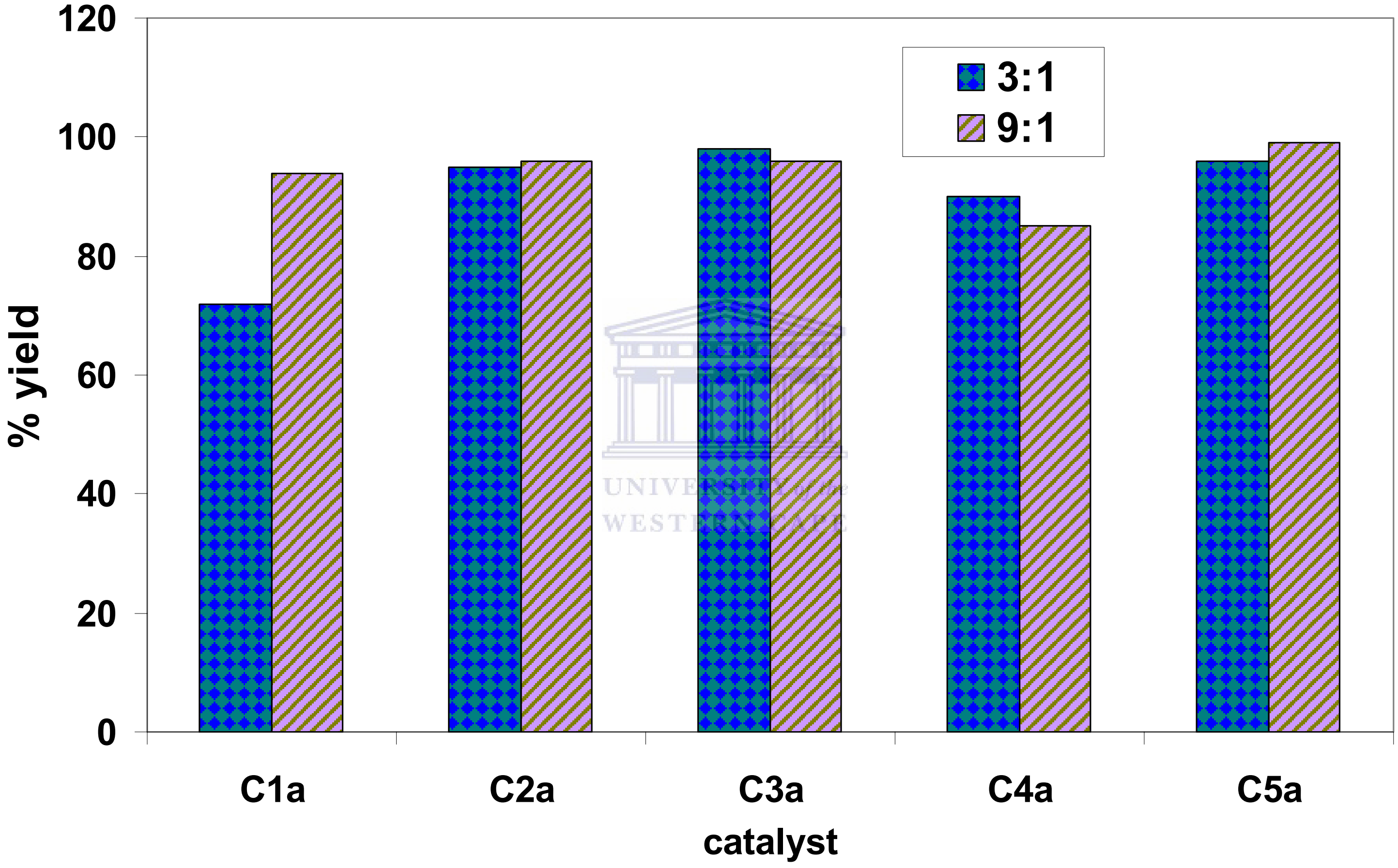


Figure 3.1: Monomer conversion in 3:1 and 9:1 solvent mixtures of CH_2Cl_2-CH_3CN (24h reaction time, $AgBF_4$ as activator).

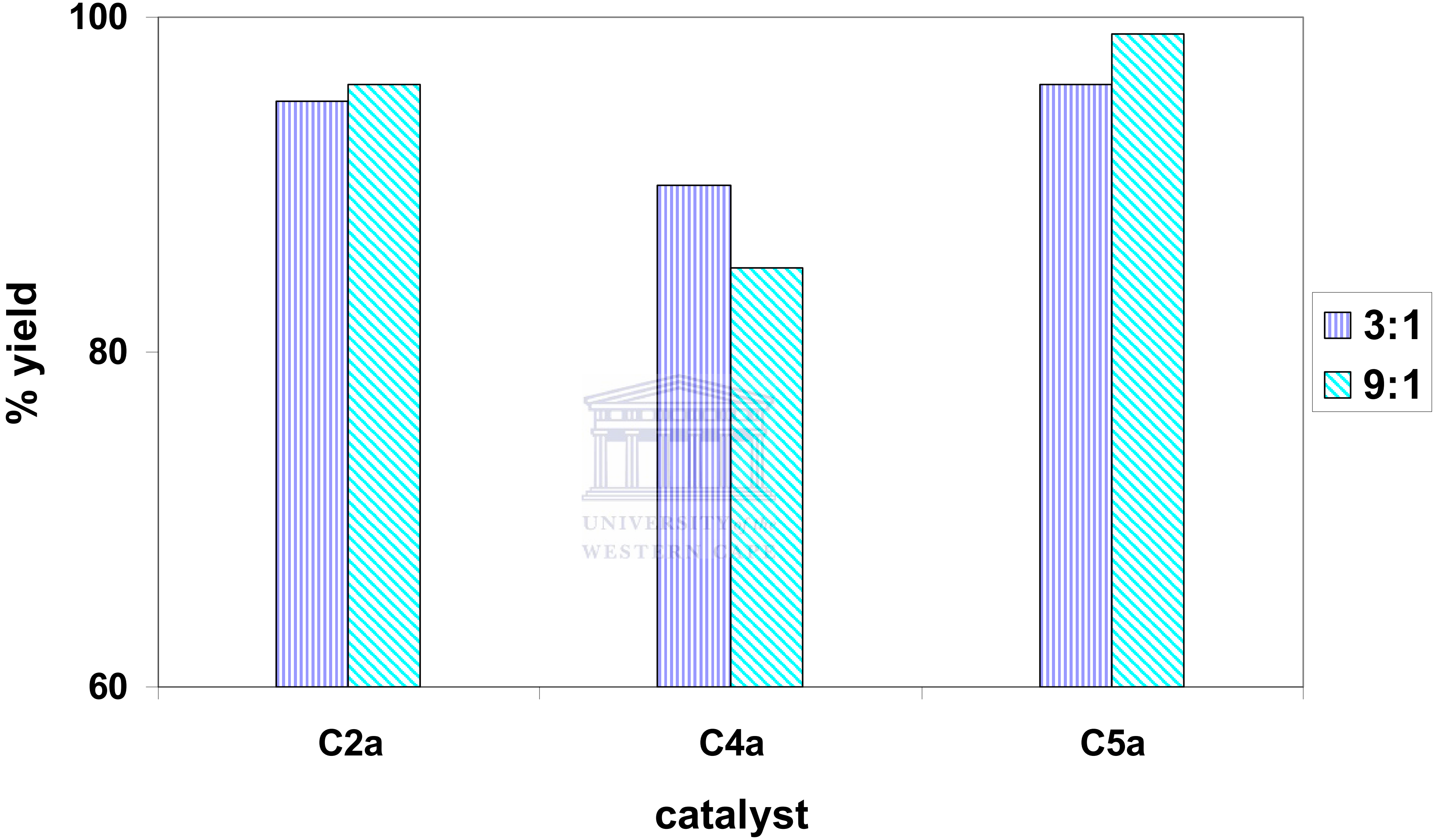


Figure 3.2: Monomer conversion in 3:1 and 9:1 solvent mixture of CH_2Cl_2-CH_3CN (48h reaction time, $AgBF_4$ as activator).

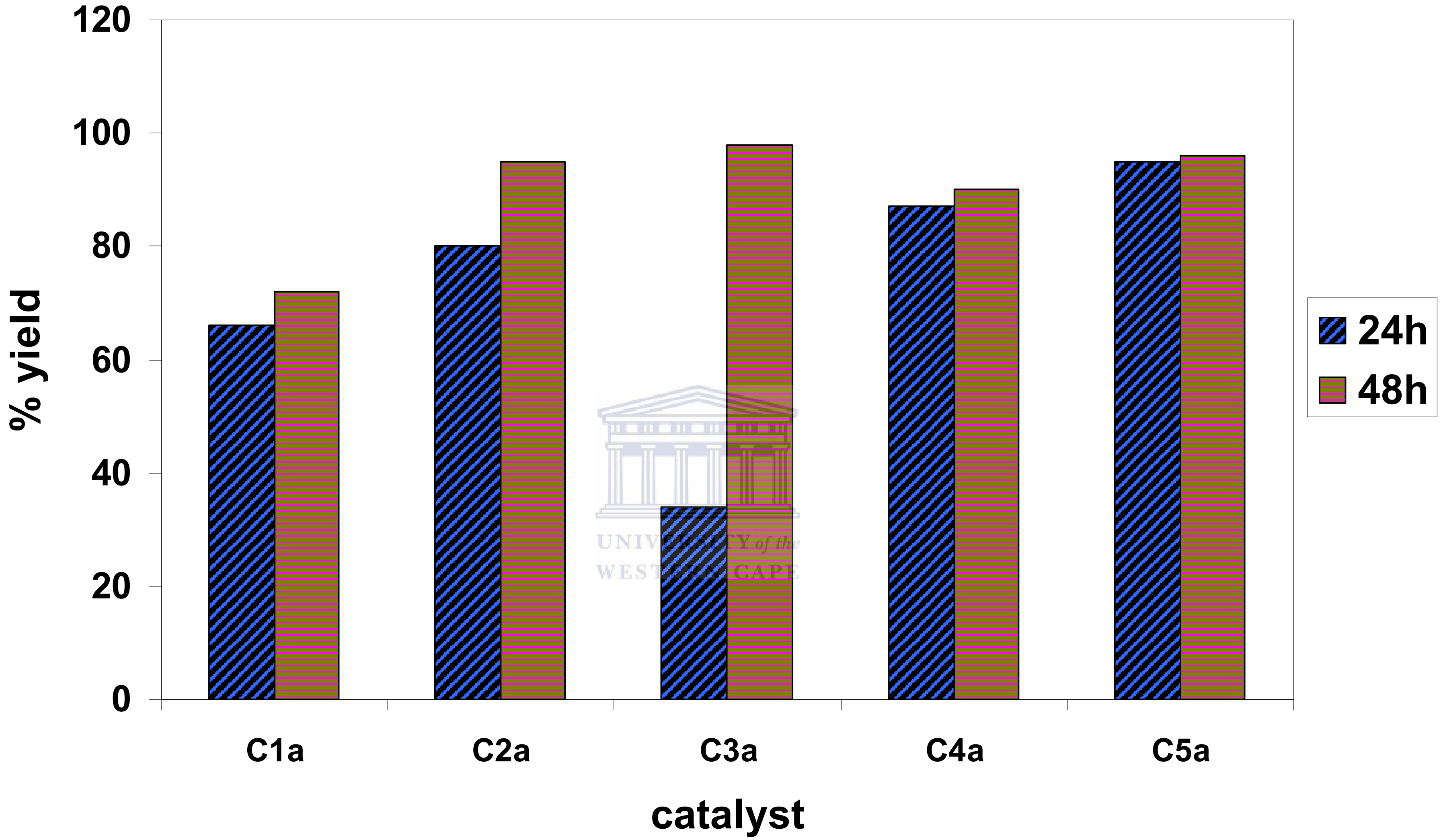


Figure 3.3: Effect of time on monomer conversion in 3:1 solvent mixture of CH_2Cl_2-CH_3CN ($AgBF_4$ as activator).

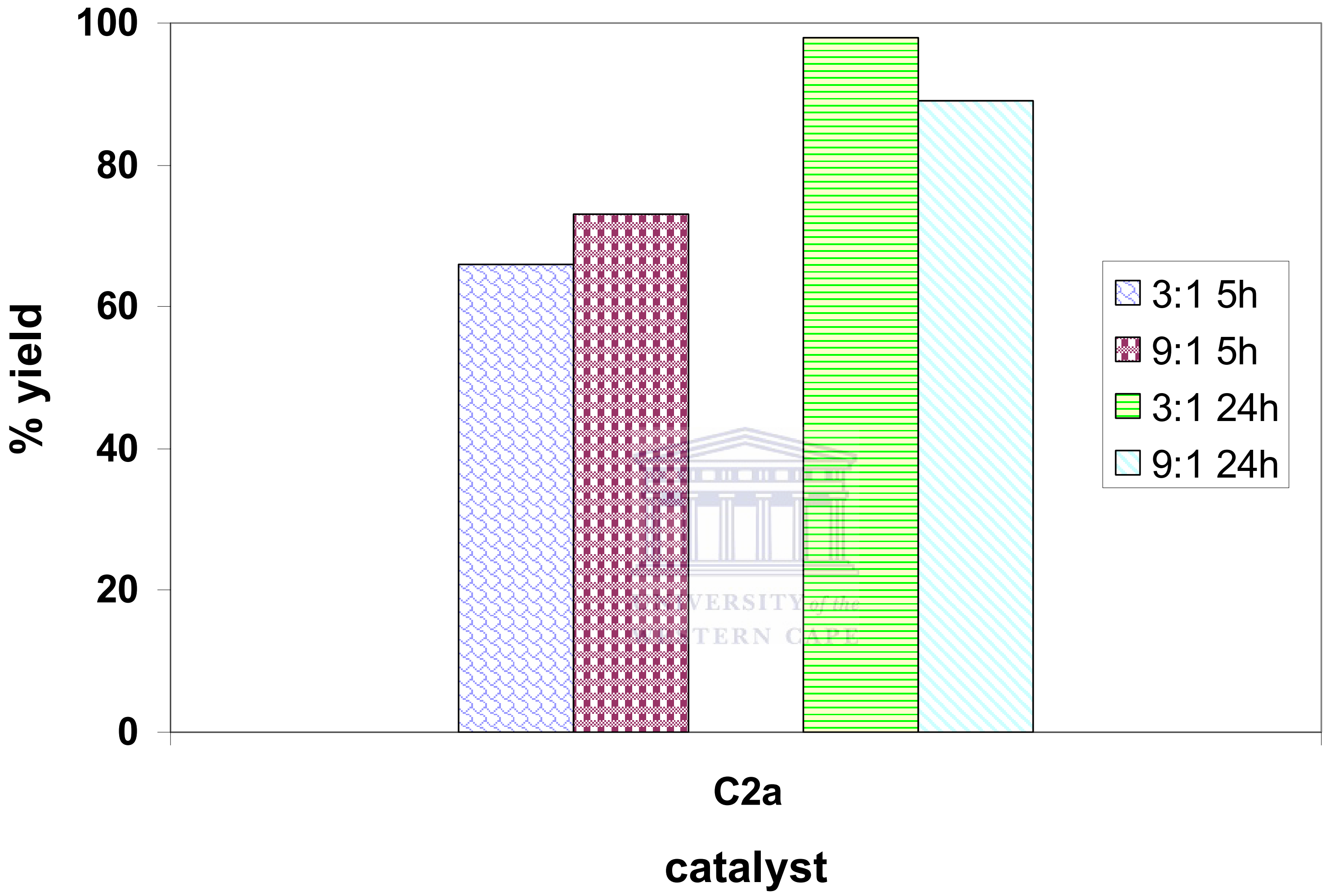


Figure 3.4; Solvent mixture (3:1 and 9:1 CH_2Cl_2-CH_3CN) effect on **C2a** using $AgBPh_4$ as activator over varying reaction time (5h and 24h).

Solutions with high concentrations of coordinating solvent (3:1 solvent mixtures of CH_2Cl_2-CH_3CN) give low monomer conversion because of high level of competition for the coordination site in the active catalyst and this resulted in the insertion rate of the monomer to be slow leading to low monomer conversions. This can be seen in reactions performed in 9:1 solvent mixtures of CH_2Cl_2-CH_3CN with low concentration of coordinating solvent giving high monomer conversions because of lower competition for the vacant coordination site.

Polymerization of PA in a single solvent was investigated in acetonitrile, toluene, dichloromethane and tetrahydrofuran in order to evaluate the influence of the solvent polarity on the reaction. Table 3.2 shows the conversion results obtained for the reactions performed with different solvents under same reaction conditions. Using activated catalyst, **C4a** in various solvents, the resulting products were obtained as brown-dark brown solids in yields moderate to high yields. Reactions performed in coordinating solvents such as THF and CH_3CN gave very high yields (Table 3.2, entries 30, 31) compared to CH_2Cl_2 and toluene which gave yields of 58% and 83% respectively (Table 3.2, entries 29 and 32). Reactions in toluene gave higher molecular weight products ($M_w \sim 69297$) while low molecular weight products were obtained with CH_2Cl_2 ($M_w = 916$). The presence of coordinating solvents like CH_3CN and THF during polymerization are crucial to the stabilization of the cationic active catalysts before coordination of PA take place. However if the coordinating solvent is present in excess, then it would be difficult for the monomer to displace the solvent, rather leads to chain termination (low Mw).

Table 3.1: Phenylacetylene polymerization catalyzed by **C1a-C5a**[a]

Run	Catalyst	Reaction time (h)	Solvent ratio (CH_2Cl_2-CH_3CN)	Yield (%)	M_n	M_w	PDI
1	**C5a**	24	9:1	75	520	570	1.09
2	**C5a**	48	9:1	99	14040	24650	1.75
3	**C5a**	24	3:1	95	15600	28150	1.36
4	**C5a**	48	3:1	96	18364	29812	1.56
5	**C4a**	24	9:1	82	693	742	1.43
6	**C4a**	48	9:1	85	10860	17784	1.63
7	**C4a**	24	3:1	87	13373	25199	1.88
8	**C4a**	48	3:1	90	637	708	1.11
9	**C3a**	24	9:1	52	591	621	1.05
10	**C3a**	48	9:1	96	8314	17131	1.58
11	**C3a**	24	3:1	34	604	714	1.18
12	**C3a**	48	3:1	98	15683	21352	1.48
13	**C2a**	24	9:1	60	580	680	1.14
14	**C2a**	48	9:1	96	570	640	1.11
15	**C2a**	24	3:1	80	11020	20500	1.84
16	**C2a**	48	3:1	95	520	616	1.19
17	**C1a**	24	9:1	50	13978	17884	1.28
18	**C1a**	48	9:1	94	16218	20341	1.73
19	**C1a**	24	3:1	66	587	673	1.14
20	**C1a**	48	3:1	72	606	676	1.11
21	**C5a**	5	9:1	77	377	409	1.08
22	**C5a**	24	9:1	97	349	371	1.06
23	**C5a**	5	3:1	20	387	463	1.04
24	**C5a**	24	3:1	26	474	504	1.06
25	**C2a**	5	9:1	73	497	536	1.06
26	**C2a**	24	9:1	89	583	613	1.26
27	**C2a**	5	3:1	66	517	555	1.07
28	**C2a**	24	3:1	98	528	1461	2.76

[a]All the reactions were performed in 10 ml total solvent mixture at room temperature: n_{Pd} = 36.40 µmol; n_{PA} = 1.82 mmol; PA/ Pd = 50:1; activator = $AgBF_4$ (entries 1-20) and $AgBPh_4$ (entries 21-28). [b]Yield determined gravimetrical based on recrystallized residue amount. [c]Molecular weight GPC data were determined at room temperature.

Table 3.2: Single solvent effect on phenylacetylene polymerization.

Entry	Catalyst	Ratio	Reaction time (h)	solvent	Yield (%)	M_n	M_w	PDI
29	**C5a**	1:50	5	Toluene	83	38865	69297	1.79
30	**C5a**	1:50	5	CH_3CN	99	315	318	1.00
31	**C5a**	1:50	5	THF	99	387	427	1.10
32	**C5a**	1:50	5	DCM	58	711	916	1.28

[a]All the reactions were performed in 10 ml total solvent mixture at room temperature: n_{Pd} = 36.40 μmol; n_{PA} = 1.82 mmol; PA/ Pd = 50:1; activator = $AgBF_4$.[b]Yield determined gravimetrical based on recrystallized residue amount. [c]Molecular weight GPC data were determined at room temperature.

3.2.2.2 Effect of activator on phenylacetylene polymerization

The effect of the nature of the counterion of the cationic catalyst, **C5a** on PA polymerization was also evaluated. The results are shown in Table 3.3 and when solvent mixtures rich in acetonitrile was used, it was found that the small and weakly coordinating anion BF_4^- gave higher monomer conversion. $NaB(Ar_f)_4$ when it was used it gave lower monomer conversions. It thus appears that the weakly coordinating BF_4^- ion is more easily displaced by the incoming monomer than the $NaB(Ar_f)_4$ that has a bulky anion Thus in the case of BF_4^- systems the rate of polymerization is higher than in the case for $NaB(Arf)_4$.

In solvent mixtures containing lower levels of CH_3CN, (9:1, CH_2Cl_2-CH_3CN), the $NaB(Ar_f)_4$ system tended to give lower monomer conversion, while both AgBF4 and $AgBPh_4$ give moderate to high conversions.

Table 3.3: Activator effect on polymerization catalyzed by **C5a**.

Entry	Catalyst	Solvent ratio (CH_2Cl_2-CH_3CN)	Reaction time (h)	Activator	Yield (%)	M_n	M_w	PDI
33	**C5a**	3:1	5 hrs	$AgBF_4$	91	600	667	1.11
34	**C5a**	3:1	24 hrs	$AgBF_4$	95	15600	28150	1.36
35	**C5a**	3:1	5 hrs	$AgBPh_4$	20	387	463	1.04
36	**C5a**	3:1	24 hrs	$AgBPh_4$	26	474	504	1.06
37	**C5a**	3:1	5 hrs	$NaB(Ar_f)_4$	16	311	314	1.00
38	**C5a**	3:1	24 hrs	$NaB(Ar_f)_4$	30	357	370	1.14
39	**C5a**	9:1	5 hrs	$AgBF_4$	45	8840	14070	1.59
40	**C5a**	9:1	24 hrs	$AgBF_4$	75	520	570	1.09
41	**C5a**	9:1	5 hrs	$AgBPh_4$	77	377	409	1.08
42	**C5a**	9:1	24 hrs	$AgBPh_4$	97	349	371	1.06
43	**C5a**	9:1	5 hrs	$NaB(Ar_f)_4$	40	314	316	1.00
44	**C5a**	9:1	24 hrs	$NaB(Ar_f)_4$	47	362	397	1.09

[a] All the reactions were performed in 10 ml total solvent mixture at room temperature: n_{Pd} = 36.40 μmol; n_{PA} = 1.82 mmol; PA/ Pd = 50:1;.[b] Yield determined gravimetrical based on recrystallized residue amount. [c] Molecular weight GPC data were determined at room temperature.

3.2.2.3 Effect of phenylacetylene to palladium ratio on polymerization efficiency.

The effect of phenylacetylene to palladium ratio was probed using **C5** activated with $AgBF_4$ and the results are shown in Table 3.4. From the results it can be seen that the conversion of PA decreased with an increase in the PA:Pd ratio. The highest conversion were obtained at PA to Pd ratio of 50: 1giving high molecular weight polyphenylacetylene.

Table 3.4: Effect of PA:Pd ratio on polymerization efficiency.

Entry	Complex	Reaction time (h)	Solvent ratio	Yield (%)	PA: Pd	M_n	M_w	PDI
45	**C5a**	24	3:1	95	50:1	15600	28150	1.36
46	**C5a**	24	3:1	59	136:1	527	593	1.13
47	**C5a**	24	3:1	34	565:1	306	309	1.01

[a]All the reactions were performed in 10 ml total solvent mixture at room temperature: Activator = $AgBF_4$.[b]Yield determined gravimetrical based on recrystallized residue amount. [c]Molecular weight GPC data were determined at room temperature.

Low PDI values are obtained when the molecular weight is low while the PDI values increase with increasing molecular weights. The PDI values for most of the obtained products were less than 2.0 indicating that active species of uniform nature were present in the reaction. This compares well with the reported rhodium catalyzed PPA production which also show PDI values of less than 2.0 [13].

3.2.3. Determination of polymers stereochemistry

3.2.3.1. IR results

Figure 3.5 shows a representative IR spectrum (KBr pellet) of the obtained polyphenylacetylene. Products obtained form other reactions showed similar IR spectra. Four absorption bands due to the monosubstituted phenyl group were observed in the region ~1700-2000 cm^{-1}. This observation indicated that the polymer has an alternating double bond structure (–C=CPh). The spectrum also showed bands at ~1596 cm^{-1} indicating the presence of polyconjugated –C=C– bonds. The strong absorption bands at ~758 cm^{-1} and ~694 cm^{-1} corresponded to the monosubstituted phenyl out of plane bending. Absorption bands at ~742 cm^{-1}, ~842 cm^{-1}, 890 cm^{-1} and ~914 cm^{-1}, indicated the *cis*-configuration around the –C=C– bonds. The absorptions at 742, 890 cm^{-1} were characteristic of the *cis* structure in polyphenylacetylene. Therefore, the obtained products were considered to be linear oligomer/polymer with a *cis*-transoidal polyene structure. Kern *et al*. [14] explained the absences of bands at 742 and 890 cm^{-1} in the product containing *cis* isomer as due to the coiling of the unsaturated chain, i.e the partial rotation about the C-C bonds that relaxes the proton-ring interaction occurring in the *cis*-transoidal planar form.

3.2.3.2. Oligo/polyphenylacetylene characterization using NMR.

^{1}H-NMR results

In the ^{1}H-NMR spectra for the obtained polymers shown in figure 3.6, the ≡CH signal observed at around 3 ppm in the starting phenylacetylene was absent with a new singlet corresponding to the vinyl hydrogen appearing in the range 5.88-5.98 ppm. The ^{1}H-NMR spectra for all the obtained products showed the following peaks in their ^{1}H-NMR spectra (see Figure 3.6); a sharp singlet at ~ 5.85 ppm for the vinylic proton (-C=C*H*-) in addition to a broad singlet at ~ 6.64 ppm (o-H_{Ph}) and a multiplet at ~ 6.94 ppm (m-H_{Ph} and p-H_{Ph}) for the proton of the phenyl rings. This pattern is reported to be characteristic of a head-to-tail insertion mechanism of the phenylacetylene monomer giving *cis*-transoidal PPA [15-17].

Solvent removal at moderate high temperature from the solution of the polymer products was accompanied by a change in the nature of the polymer. Such heating leads to isomerization form *cis*-transoidal to *trans*-cisoidal configurations. This is evident from the changes in the NMR spectrum, specifically the signal associated with the four aromatic protons centered at 6.94 ppm which shifted towards 7.12 ppm. The peak at 5.85 ppm corresponding to the *cis*-transoidal disappeared with a new peak at

7.61 ppm resembling the peak from thermal isomerization of the *cis*-transoidal giving a *trans*-cisoidal PPA when the solvent product is removed under high temperature.

^{13}C-NMR results

The peak at 129 ppm in the ^{13}C-NMR is attributed to the *C*H group of the vinylene units in the main chain of the polymer and the signal at 140 ppm is attributed to the quaternary main chain carbon. The signals from the benzene ring are at 139, 137, 127 (*C*H of C_6H_4), and 120 ppm (quaternary *C* of C_6H_4) [18-19].

Two mechanistic pathways for PA polymerization are known, namely metathesis and coordination/insertion of the alkyne into a metal-alkyl bond. The latter can be deduced from the NMR spectroscopy, if the active catalyst contains a metal-alkyl bond. The ^{1}H-NMR spectra of the polymer and oligomer isolated showed an alkyl peak at 1.25 ppm indicative that the reaction proceeds via an insertion mechanism. The proposed reaction mechanism occurs by initial π-coordination of PA to the Pd-methyl followed by insertion of PA into the Pd-CH_3 bond giving chain growth. A similar mechanistic route is known for the reaction of acetylene with other cationic palladium (II) methyl complexes [20].

3.3 Conclusion

The binuclear cationic palladium-methyl catalyst precursors **C1a-C5a** were found to be active catalysts for phenylacetylene polymerization. When the two metal centres are far removed from each other, higher molecular weight polyphenylacetylene were obtained in high yields. Coordinating solvents were found to give lower molecular weight products indicating a competitive effect between the monomer and the solvent for the active vacant site during polymerization. The investigation of stereochemistry of the obtained polyphenylacetylene showed that the binuclear complexes give *cis*-transoidal products.

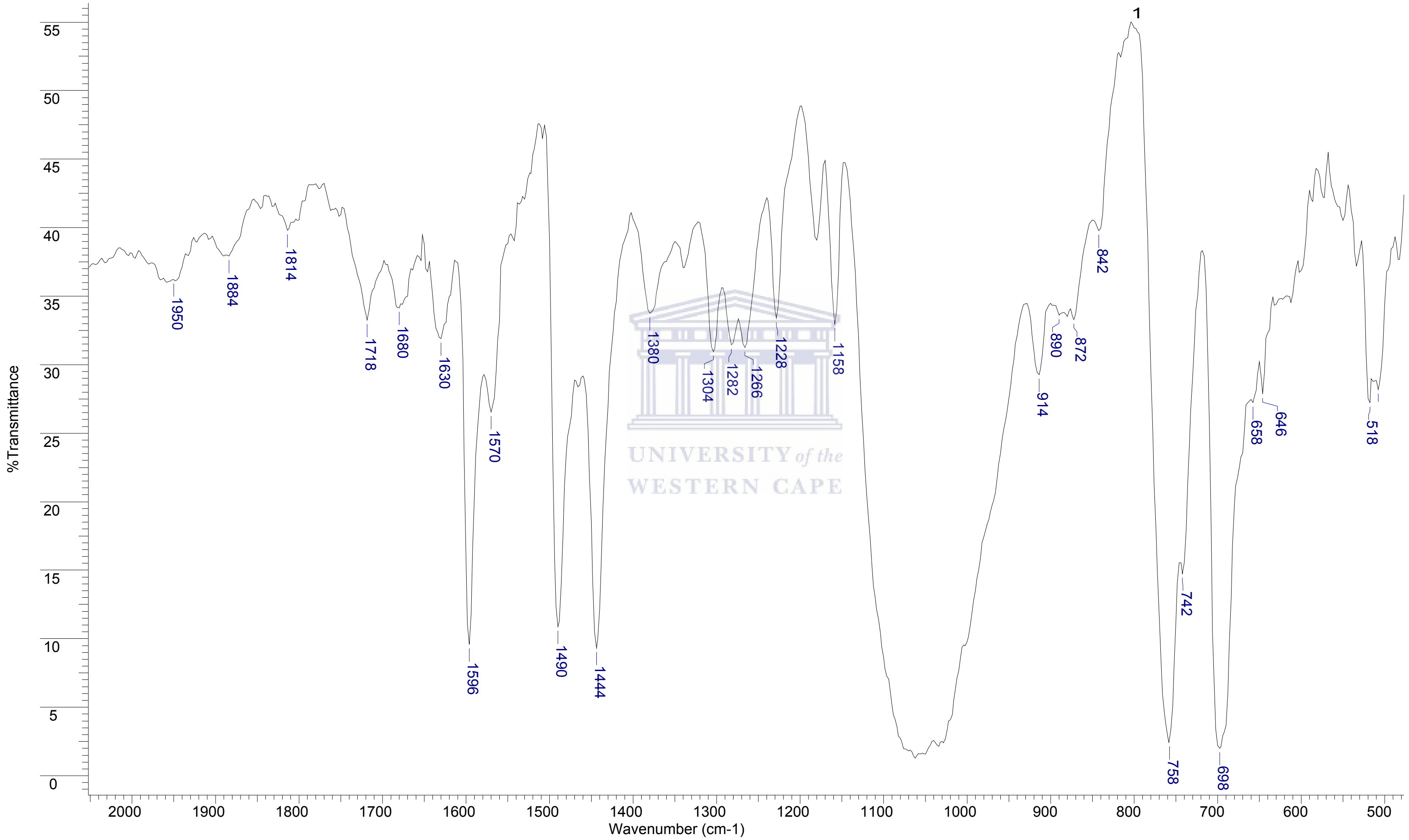


Figure 3.5: IR (KBr pellet) of Polyphenylacetylene.

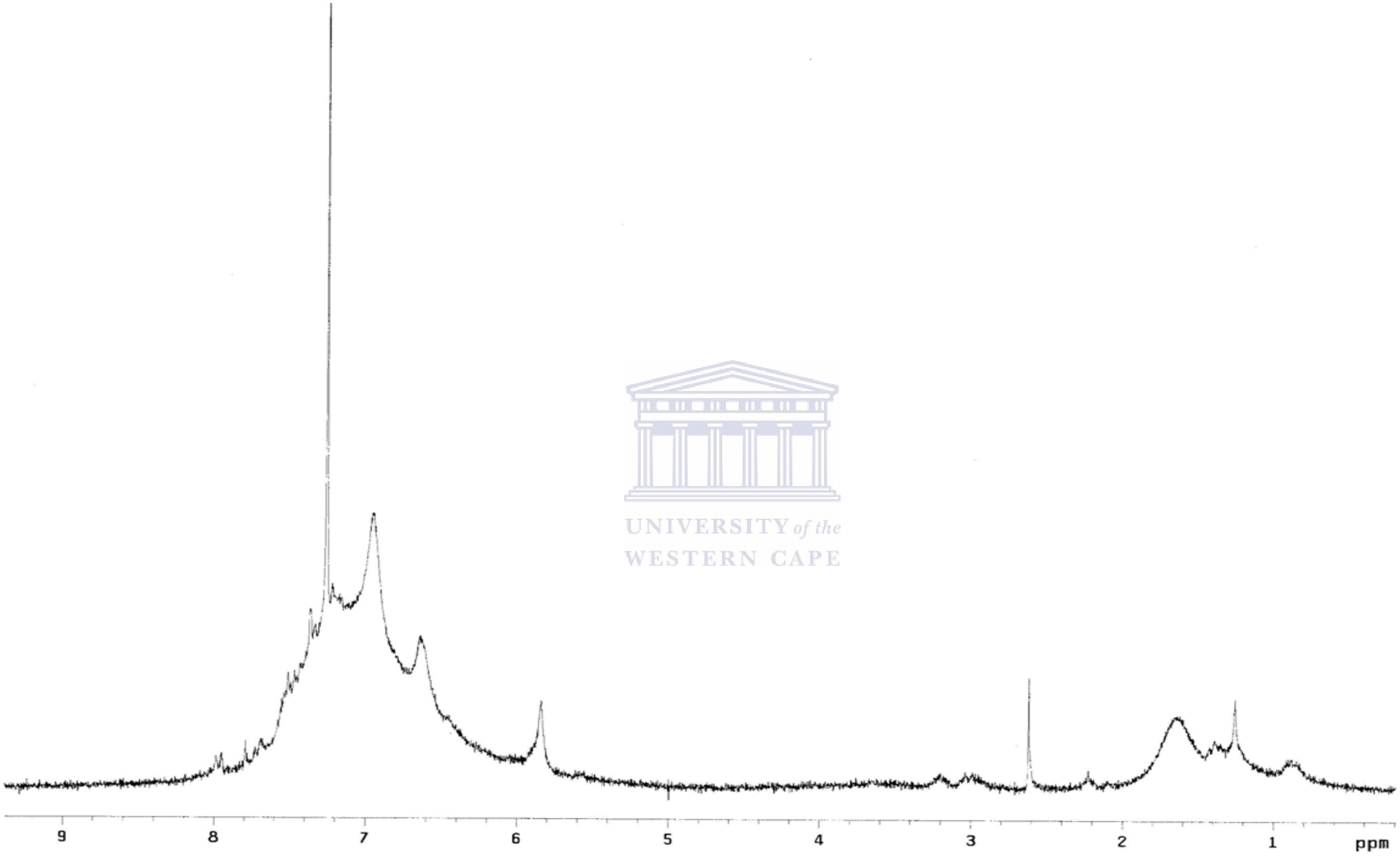


Figure 3.6: ^{1}H-NMR of *cis*-transoidal oligo/ polyphenylacetyene using mixed solvents.

3.4 Experimental Section

3.4.1 Materials and Instruments

General Methods: All manipulations and reactions involving air-sensitive compounds were performed under a positive pressure of nitrogen using Schlenk line techniques. Dry degassed solvents were obtained by distillation over appropriate drying agents. Dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN) were distilled from phosphorus pentoxide (*di*-P_2O_5) and CaH_2 granules. Diethyl ether (DEE), toluene and tetrahydrofuran (THF) were dried over sodium-benzophenone ketyl.

Materials: All the reagents, silver salts ($AgBF_4$ and $AgBPh_4$) and phenylacetylene were purchased from Sigma-Aldrich, sodium *tetrakis*[(3.5-trifluoromethyl)phenyl]borate $NaB(Ar_f)_4$ from Boulder Scientific Company. All the chemicals were used as received unless otherwise stated.

Instrumentation: IR spectra were recorded as KBr pellets (solids) for all the polymeric materials on a Perkin-Elmer, Paragon 1000 PC FTIR spectrometer. ^{1}H-NMR spectra were recorded on a Varian Gemini-2000 spectrometer (at 200 MHz). Chemical shifts are reported in δ units (ppm) referenced to the residual protons of deuterated solvents as internal reference relative to $SiMe_4$ (δ 0.00 ppm). The ^{1}H-NMR splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), and br (broad). The ^{13}C {^{1}H}-NMR spectra were recorded on Varian Gemini-2000 spectrometer (at 50.3 MHz).

The number-average molecular weight (Mn), weight average molecular weights (Mw) and polydispersity (Mw/Mn) of polymers were determined by gel permeation chromatography (GPC) (THF, 30 °C, rate = 1.0 cc/min) with PL mixed-column using polystyrene standards. GPC analyses were performed at the University of the Western Cape. The polymer yields were determined gravimetrically based on the amounts polymer residue isolated after solvent removal.

3.4.2 Phenylacetylene transformation procedure

3.4.2.1. General procedure for phenylacetylene transformation using (N,N'{1, n}-alkanediyl)bis(pyridinyl-2-methanimine)bis(PdCH$_3$X) {n = 5, 8, 9, 10, 12} in solvent mixture of CH$_2$Cl$_2$-CH$_3$CN

In a typical phenylacetylene transformation procedure (Table1, entry 1), a Schlenk tube with **C5** (0.050g, 36.40 μmol) catalyst precursor and magnetic stirrer-bar was vacuumed and then flushed under nitrogen atmosphere for 10 minutes. $AgBF_4$ dissolved in 2 ml of a 1:1 dry dichloromethane-acetonitrile mixture was syringed into the Schlenk tube under nitrogen. Dry dichloromethane (8 ml) was introduced into the Schlenk tube for a final composition 9:1 (10 ml total solvent volume) and the solution was stirred under nitrogen atmosphere for 20 minutes. A cream-white precipitate of AgCl was formed after activation of the catalysts precursor. The precipitate was allowed to settle and the filtrate was cannula transferred into another clean Schlenk tube equipped with a magnetic stirrer-bar. The active catalyst precursor **C5a** was reacted with 0.21 ml (1.82 mmol, 50 equiv.) of phenylacetylene. During the first 10 minutes of the reaction, the solution gave a light orange colour which turned into a dark brown coloured solution after 30 minutes of stirring. At the end of reaction time the reaction was deactivated with 10 ml acidified methanol and the solvent removed under high vacuum. The obtained brown residue was recrystallized with 1:1 mixture of dry dichloromethane and dry ethanol (20 ml) giving brown PPA.

The transformation of phenylacetylene catalyzed by **C1a-C4a** in a solvent mixture CH_2Cl_2-CH_3CN of 9:1 and 3:1 activated with $AgBF_4$ were performed using the same procedure as aforementioned experiment.

The polymerization results shown in Table 3.2 were performed as the aforementioned experimental procedure with the complexes activated with $AgBPh_4$.

3.4.2.2 Polymerization of phenylacetylene catalyzed by (N,N'{1, n}-alkanediyl-N)bis(pyridinyl-2-methanimine)bis(PdCH$_3$X) {n = 5, 8, 9, 10, 12} in a neat solvent (THF, Toluene, CH$_3$CN)

In a typical reaction, **C5** (0.050g, 36.40 µmol) was reacted with $AgBF_4$ in 10 ml solvent mixture of 1:1 CH_2Cl_2-CH_3CN. The reaction was stirred for 30 minutes with AgCl precipitated as cream white solid. The resulting filtrate was cannula transferred into another Schlenk tube equipped with magnetic stirrer bar. The solvent was removed from the filtrate under high vacuum and the pure solvent (10 ml) was added to the residue. Phenylacetylene (0.21 ml, 1.82 mmol, 50 equiv) was added to the formed solution giving an orange mixture that changed to a dark brown solution after 30 minutes of stirring. The reaction was stirred for 5 hours at room temperature and the reaction quenched by 10 ml acidified methanol. The solvent was removed on a rotary evaporator and the residue recrystallized by 10 ml: 10 ml dichloromethane and ethanol with the solvent removed on a rotary evaporator to obtain the PPA product

All the other reactions using neat solvent where performed using the aforementioned reaction procedure and the same spectroscopic results were obtained.

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