Synthesis of non-water-soluble and water-soluble Pd(II) complexes as catalysts for methoxycarbonylation reaction of olefins

By

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DECLARATION

I**, Ntombizonke Precious Ngubane** declare that the thesis titled 'Synthesis of non-water- soluble and water soluble Pd(II) complexes as catalysts for methoxycarbonylation reaction of olefins' is my authentic work and has never been presented for an award of any degree at any institution. All other sources used have been acknowledged through references.

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DEDICATIONS

To

My mother Gertrude Ngubane and my siblings

ABSTRACT

The treatments of (E)-2-(((2-methoxyethyl)imino)methyl)phenol (**L1H**), (E)-2-(((2-hydroxyethyl)imino)methyl)phenol (**L2H**) (E)-3,5-di-tert-butyl-2-(((2-hydroxyethyl)imino)methyl)phenol (**L3H**) with $Pd(OAc)_2$ afforded the corresponding palladium complexes [Pd(**L1**)$_2$] (**Pd1**), [Pd(**L2**)$_2$] (**Pd2**) and [Pd(**L3**)$_2$) (**Pd3**) respectively in excellent yields. Successful formation of these structures was confirmed by the use of ^{1}H-NMR, ^{13}C-NMR, FT-IR, ESI-MS and X-ray crystallography. In addition, reactions of water-soluble sodium 4-hydroxy-3-(((2-methoxyethyl)imino)methyl)benzenesulfonate (**L4H**), sodium 4-hydroxy-3-(((2-hydroxyethyl)imino)methyl)benzenesulfonate (**L5H**) and sodium (E)-3-(((2-(dimethylamino)ethyl)imino)methyl)-4-hydroxybenzenesulfonate (**L6H**) with $Pd(OAc)_2$ gave the respective water-soluble palladium complexes [Pd(**L4**)$_2$] (**Pd4**), [Pd(**L5**)$_2$] (**Pd5**) and [Pd(**L6**)$_2$] (**Pd6**) in moderate yields. Molecular structures of complexes **Pd1** and **Pd3** confirmed the formation of N^O bis(chelated) square planar complexes. All the palladium complexes (**Pd1**-**Pd6**) were found to be active in the methoxycarbonylation of 1-hexene, achieving percentage yields of up to 90% and regio-selectivity of up to 78% in favor of linear esters. The performance of the catalysts was found to be dependent on their architecture, due to electronic and steric parameters of the complexes. For instance, **Pd1** with methoxy substituent gave higher activity compared to **Pd2** with electron withdrawing pendant arm. On the other hand, **Pd3** exhibited higher compositions of linear ester as in comparison to other complexes. The observed results due to the steric encumbrance noted in **Pd3**.

Similarly, the type of acid promoter, and amount of phosphine used influenced the reactivity and selectivity of the catalysts both at higher and lower ratios. For instance, high phosphine

ratios were observed to favour linear esters due to steric hindrance factors. Branched esters were notably favoured as the chain length was increased. Whereas diminished activities were observed at lower amount of acid due to the formation of palladium black. Moreover, different olefin substrates were investigated using the most active **Pd4** complex, the results revealed varied catalytic performance, which is a clear indication of the dependance of activity on the identity of the alkene. The water-soluble catalysts (**Pd4-Pd6)** were observed to have lower catalytic activity compared to the non-water soluble analogues. However, enhanced catalytic performance was noted in biphasic media. The complexes could be recycled up to four runs with minimal loss of activity and change in regio-selectivity.

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I would like to convey my warmest gratitude to the people mentioned below. Their help is one thing I will forever cherish. Through difficult and happy times, they stood with me and encouraged to be a better version of myself. When I felt like quitting due to difficulties of the journey, they kept me motivated and they strongly believed in me.

- I would like to thank God Almighty for how powerful he has been in my life. I got this golden opportunity from him and I believe that everything I have is because of Him. Thank you, Father.

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List of Abbreviations

SHOP-Shell higher olefin Process

BASF- Badische Anilin- und SodaFabrik

PTSA- p -toluene sulfonic acid

TOF-Turn over frequency

TON-Turn over number

NMR-Nuclear Magnetic resonance

ppm- part per million

FT-IR-Fourier Transform Infrared

XRD-X-ray diffraction

ESI-Electrospray Ionization

MHz-Megahertz

GC-MS- Gas chromatography –mass spectrophotometer

LC-MS- Liquid chromatography-mass spectrophotometer

PPh_3- triphenylphosphine

$Pd(OAc)_2$-palladium acetate

L-ligand

HCl- Hydrochloric acid

m/z -mass to charge ratio

BAILs- Bronsted acid ionic liquids

IL-Ionic liquids

TFE-2,2,2-trifluoroethanol

$scCO_2$- supercritical carbon monoxide

MMA- methyl-methylacrylate

Chapter 1

Background Information on heterogeneous and homogeneous systems in catalysis

1.1 Introduction

Catalysis can be divided into two main categories namely; heterogeneous and homogeneous system. Each type of system has its own merits and demerits. One of the merits of homogenous systems is that they enable good selectivity with respect to chemoselectivity, regioselectivity and stereoselectivity, whereas heterogeneous catalysts are known to have poor selectivity [1]. Moreover, the active catalytic site for homogeneous catalyst is easily accessible which makes them highly active as opposed to heterogeneous [2, 3]. However, it has been established that homogenous suffer from major disadvantage, which is the difficulty in separation of the products from the reaction mixture which leads to tough catalyst recovery and recycling [4]. Heterogenous are advantageous and have been employed for over decades in industries due to easy separation of products from the reaction media since reactants and products are in different phases. Heterogenous are preferred also for their thermal stability [3]. However, the major drawback for is that it not as selective as the homogenous [5]. Even though this is appreciated in industry, developments of systems that combine advantages of both homogeneous and heterogeneous systems are intensively investigated. This phenomenon is referred to as heterogenising a homogeneous system. Therefore, the main endeavor for current research is to develop more active and selective atom economic, environmental benign and recyclable catalytic systems [3]. **Table 1.1** lists some of the differences between homogeneous and heterogeneous systems.

Table 1.1: Homogeneous vs heterogeneous systems [3, 6]

Property	**Homogeneous system**	**Heterogeneous system**
Form	soluble metal complexes	metals, usually supported
Catalyst recovery	difficult and expensive	easy and cheap
Thermal stability	Poor	good
Availability of active site	well defined active sites	poor active sites
Selectivity	excellent (single active site)	poor (multiple active sites)
Product separation	Difficult	simple

1.2 Methods of heterogenisation of homogeneous catalysts

1.2.1 Use of support systems

Heterogenisation of homogeneous catalytic systems can be defined as the modification of homogeneous catalysts in order to be able to form multiple phases for easy separation of products from the reaction mixture [7]. There are several ways of achieving this, for instance, the use of solid supports which can be incorporated into the catalysts. Such supports include clay, silica, alumina [8], zeolites, dendrimers [9, 10] as well as magnetic nanoparticles [11, 12]. Immobilization of the system by supports can be achieved by directly immobilizing the homogeneous catalyst or by impregnating the support with a metal linker [13]. **Figure 1.1** depicts one of the mobilization strategies by a metal linker.

For supported catalyst, the performance solely depends on the size, structure and in the composition of the catalyst particle.

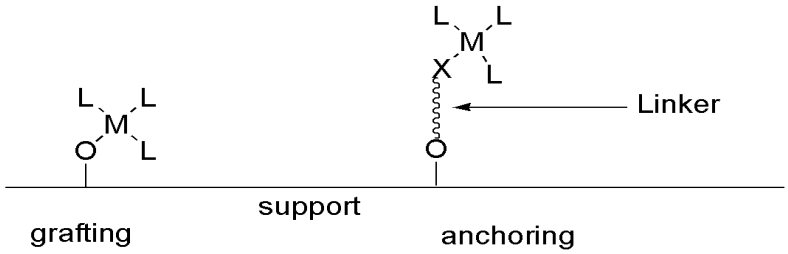


Figure 1.1: Immobilization of a complex by grafting and anchoring technique [13].

1.2.2 Silica supports

Supported metal catalysts particularly noble metals supported on SiO_2, have attracted considerable attention due to the importance of the silica–metal interface in heterogeneous catalysis [14] (**Figure 1.2**). The silica support is used because of the silanol groups present on its surface, which makes it very easy for the complex to bind. Moreover, the use of silica supports is advantageous because it leads to enhanced accessibility of active sites in the catalyst in comparison to other supports [8]. Furthermore, immobilizing metal complexes on mesoporous silica is one notable approach, owing to its chemical and thermal stability properties, not neglecting its lower cost and availability [15, 16].

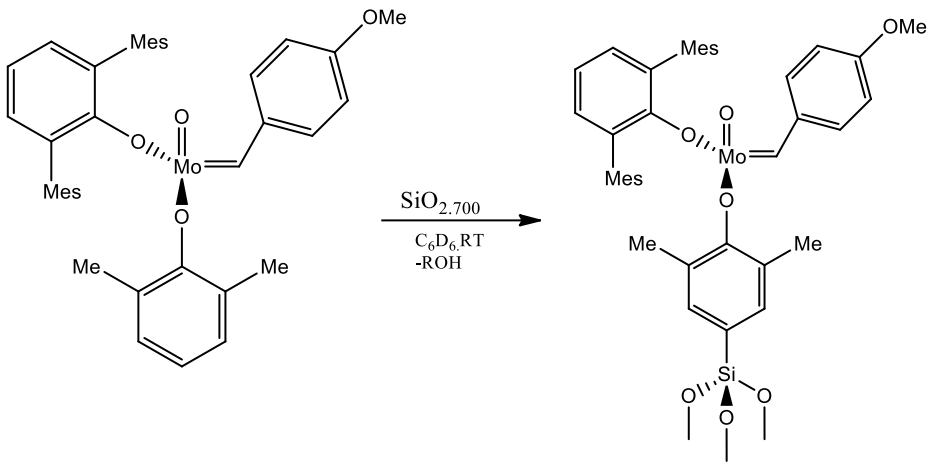


Figure 1.2: Example of silica supported Mo Oxo complex for methathesis of olefins [17].

1.2.3. Clay supports

Clays are naturally occurring layered type of silicates with crystalline properties. They are broad, easily obtained and cheap chemical substances, which are appreciated due to their lack of harmful effect on the environment. They can be defined as alterable materials that catalyzes and act and also acts as supports for a wide spectrum of chemical reactions including organic reactions which means they can both act as catalysts in organic reactions and catalyst supports in metal complexes [18 another reff]. Owing to their malleable nature, they can be molded to in to any shape so as to suit researchers needs to promote diverse chemical reaction However natural clay has limited specific surface area, therefore utility and effectiveness is restricted as support for catalysts [15].

1.2.4 Nanoparticles and magnetic nanoparticles as supports

Magnetic nanoparticles (MNPs) have extensively been used as alternative catalyst supports. This is due to their high surface area resulting in high catalyst loading capacity, high dispersion,

outstanding stability properties, and most importantly it allows facile catalyst recycling [19]. Nanoparticles can also be used as supports but it is much more advantageous to employ magnetic supports due to easy recovery from the reaction mixture using magnetic separation [15, 20]. Magnetic separation allows the recovery of catalysts from liquid-phase reactions much easier than cross-flow filtration or centrifugation techniques used for separation non -magnetic. In addition, the magnetic properties of the particles are stable enough to withstand most chemical environments, except for those that are acidic or corrosive. As the catalysts are usually immobilized on the surface of the magnetic nanoparticles (MNP), easy access of reactants to the active sites can also be achieved [19]. One of the most promising MNP supports is superparamagnetic iron oxide (Fe_3O_4) as depicted in **Figure 1. 3**. The notable merits of Fe_3O_4 MNPs are effortless synthesis, ready accessibility, high surface, minimum toxicity and low costs. Therefore, Fe_3O_4 MNPs are considered as ideal supports for the heterogenization of homogeneous catalyst. However, the unavoidable agglomeration of nanoparticles may inhibit their practical application as catalyst supports [20].

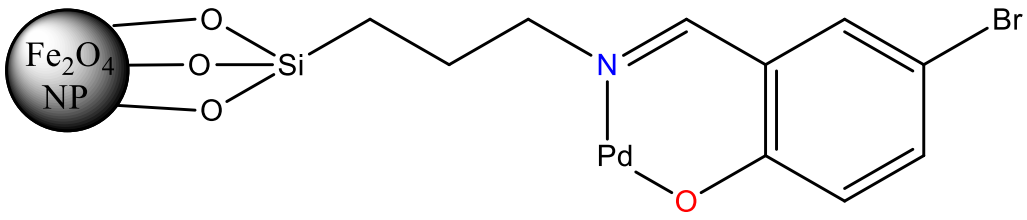


Figure 1.3: Magnetic nanoparticles supported Pd complex used for Heck and Suzuki reactions [20].

1.2.5. Polymer supports

Polymers are mostly microporous (i.e. having pore size < 2nm) activated carbons that have been extensively used as catalyst supports because of their high surface areas and pore sizes that are comparable to small molecules. Their heterogeneous structure and chemical nature however, limits their potential for chemo-selective processes. Thus, a variety of newer classes of micro and meso-porous (2-50 nm) materials such as porous organic polymers (POPs) have been constructed from catalytically active, molecular building blocks and then employed for chemical catalysis, often with high selectivity[14, 21]. Polymers offers many advantages over other supports because they can be easily functionalized (**Figure 1.4**). However, they have a principal disadvantage of poor heat transferability and poor mechanic properties which hinders them from being used in stirred reactor since they break down [14].

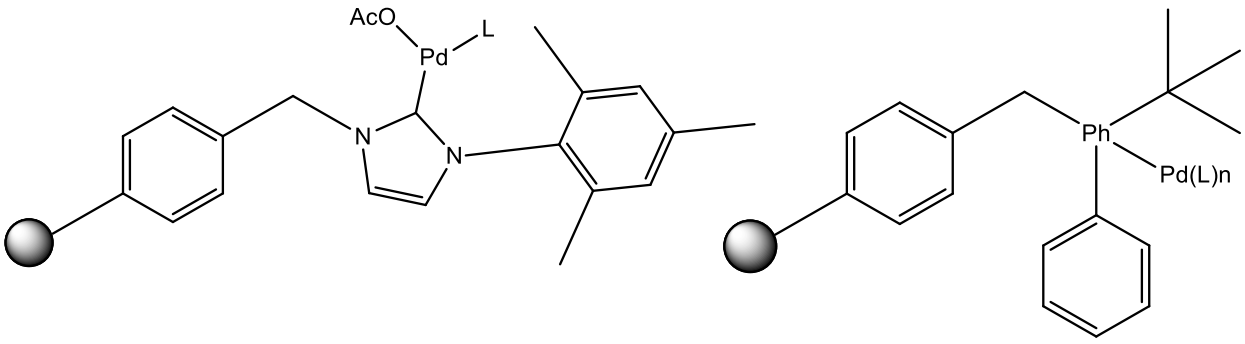


Figure 1.4: Polymer supported Pd catalyst for Suzuki reactions [22].

1.2.6 Biphasic system/ multiphase system

The system is termed biphasic since it consists of two immiscible phases; usually an aqueous phase (i.e. water) in which the catalyst dissolves in and the organic phase containing the substrate as

depicted in **Figure 1.5**. The catalytic process occurs upon heating and vigorously stirring to allow interfacial interaction between the phases [2, 15]. When the reaction is complete, the immobilized aqueous phase (catalyst) and organic phase (containing the product) are allowed to settle and are separated easily by decantation [23, 24]

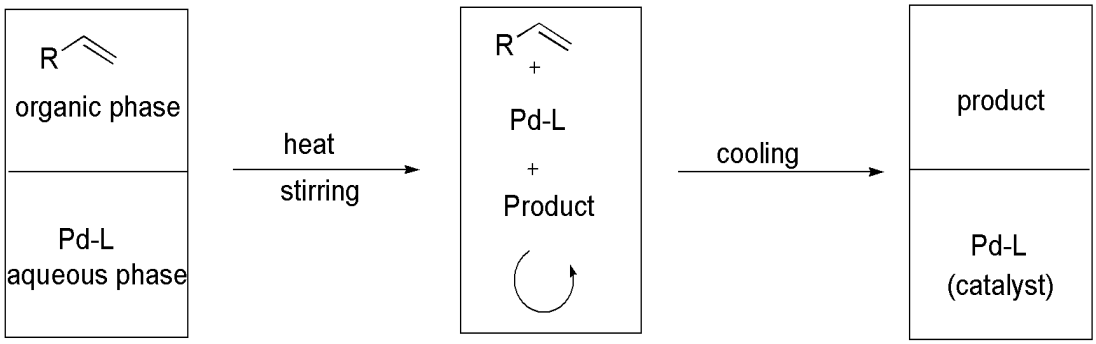


Figure 1.5: Schematic diagram of a multiphase/biphasic system [23].

The fundamental concept of two-phase catalysis was first realized industrially in the "SHELL Higher Olefins Process" (SHOP) which was designed by W. Keim *et al*. [15, 25] (**Figure 1. 6**). In this process ethylene is polymerized at temperatures of 80-120°C and pressure of 70-140 bar, in a polar phase of 1,4-butanediol which consist of homogeneous organonickel catalyst to afford oligomers with chains of $C_{4\text{-}20\alpha}$ olefins. 1,4 Butanediol was treated as catalyst phase, whereas the nickel catalyst was modified with a diol soluble phosphine R_2PCH_2COOH. Since ethylene has high solubility in butanediol while higher olefins are insoluble, therefore, the products readily separates from the catalyst phase due to their immiscibility. To the present time, the idea of biphasic catalysis has drawn so much attention and has turned out to be a more promising route for developing catalysts with high activity, selectivity and reusability [26-28].

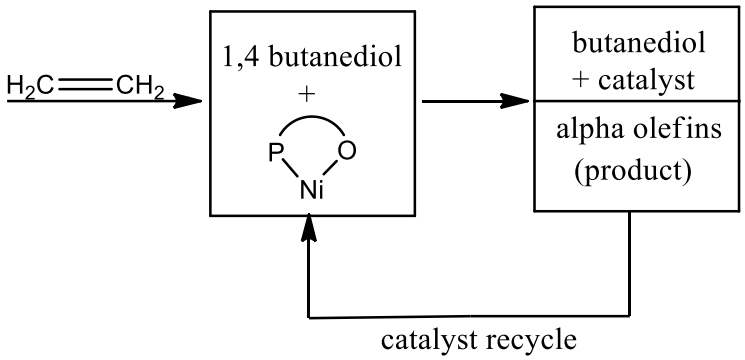


Figure 1.6: First multiphase catalytic process by Keim *et al.* [6, 25].

There are number of investigated combination of solvents used to a generate biphasic environment. Such solvents include supercritical carbon dioxide ($scCO_2$), supercritical solvents, ionic liquids (IL), perfluorinated solvents, water and two immiscible organic liquids [23, 27, 29-31]. However, water is the most preferred solvent from the economical perspective, owing to the number of advantages it offers as a reaction medium. For instance, water is known to have high polarity and it is easily removed from most substrate and nonpolar organic solvents. Moreover, it has high availability, nonflammable, nonhazardous, nontoxic, odourless [32]. Hence, its safe to work with as opposed to other solvents. Nonetheless, organometallic complexes exhibit poor solubility in water. For this reason, it is very vital to design ligands that will lead to complete solubility of the complex in water to establish immobilization of the catalyst. Polar groups are considered to be advantageous in terms of activity, selectivity and strong enhancement of solubility, thus, prevents catalyst transfer to the organic phase after the completion of the reaction [29]. Thus, tailoring the ligands with more polar substituents is vital for this of system.

1.2.6.1 Classes of water-soluble ligands containing polar substituents

Water-soluble ligands possess characteristics which enables them to dissolve in water (polar compounds). Some of these types of ligands are referred to as surfactants (molecules bearing hydrophilic heads and hydrophilic tails). Such ligands are fine-tuned by incorporating the following substituents: sulfonate (SO_3H, SO_3A^+), carboxylate (COOH or COO^-A^+), ammonium (NR_3^+), phosphonium (PR_3^+) or hydroxyl groups (OH) which induces solubilization in water [24] (**Figure 1.7**).

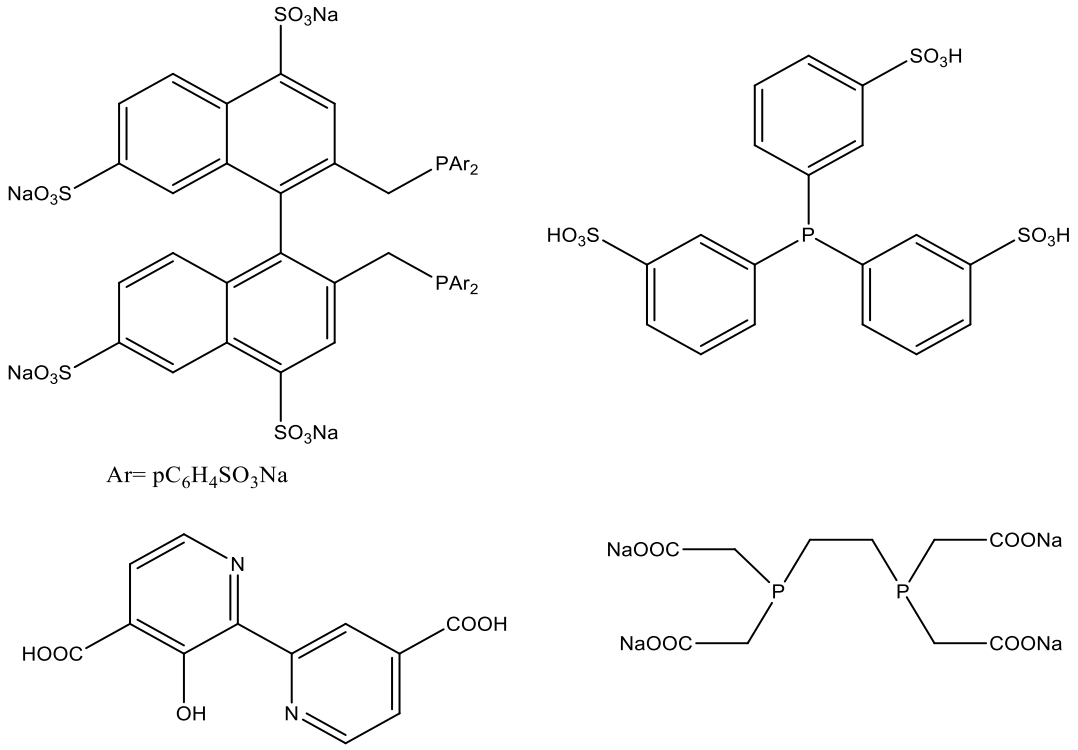


Figure 1.7: Examples of water- soluble ligands

1.2.6.2 Limitations of using water in biphasic media

Despite the merits of using water as a reaction medium. There is a limitation of water solubility of organic substrates. For instance, the solubility of alkenes are progressively reduced as the chain

length increases; therefore, the reaction is rapid for short-chain olefins (**Figure 1.8**). Thus, co-solvents may be required to enhance the solubility when investigating olefin transformation reactions [33].

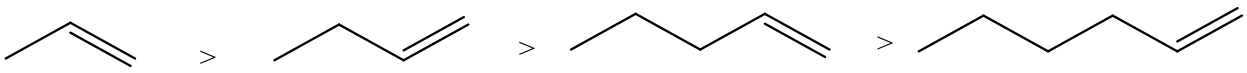
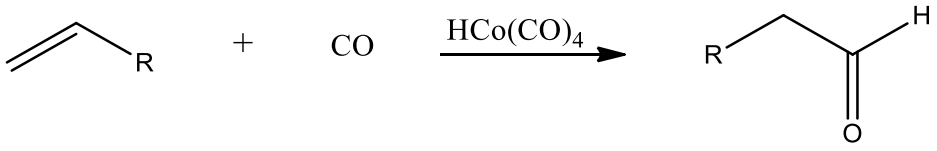


Figure 1.8: Decrease in solubility of alkene in aqueous and organic medium

1.3 Transition metal catalyzed carbonylation reactions

Carbonylation reactions are type of reactions that entails the insertion of a carbonyl carbon into a substrate, i.e .olefin, alcohol, amines or other molecules in the presence of a catalyst [34, 35]. The first well established carbonylation was discovered by Roelen many years ago. He investigated the mechanism of cobalt-catalyzed Fischer Tropsch for the synthesis of hydrocarbons from carbon monoxide and alkene [36] (**Scheme 1.1**).

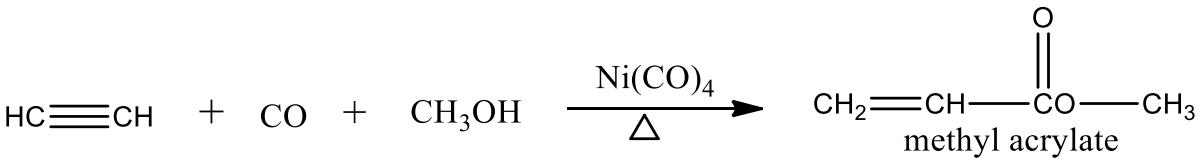


Scheme 1.1: First carbonylation process by Otto Roelen using cobalt catalyst [34].

Reppe and co-workers at BASF then extended Roelene's work by probing the carbonylation reaction using a nickel metal-catalyst. Since then, any reaction in which carbon monoxide substrate

is incorporated into an organic molecule in the presence of an alcohol and acid promoter is referred as carbonylation reaction.

In the study, they discovered a reaction of acetylene, carbon monoxide, and water to form acrylic acid, using [$Ni(CO)_4$] as a catalyst [37] (**Scheme 1.2**). This lead to more developments of the use of transitional metal complexes in the synthesis of organic compounds due to the success of this process. Thus, transition metal-catalyzed olefin transformation has become a useful tool for the conversion of bulk chemicals to fine chemicals [34, 38].

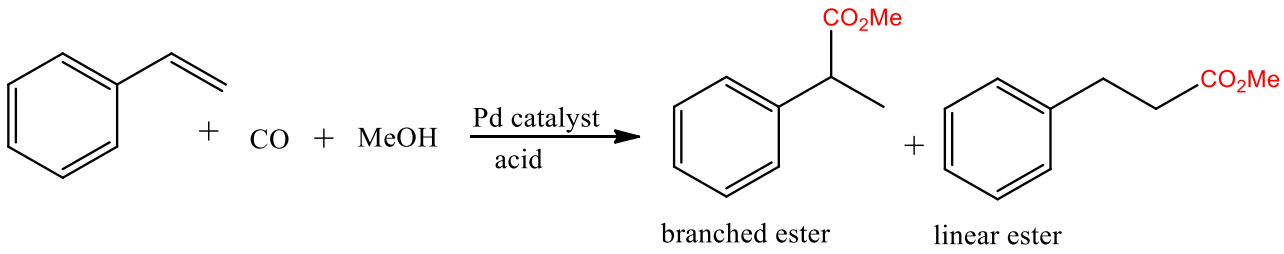


Scheme 1.2: Carbonylation of acetylene by Walter and co-workers [37].

Carbonylation reactions are extensively favored by metal complexes such as nickel, ruthenium, cobalt, rhodium, platinum palladium due to the fact that metal complexes displays good catalytic activities because of their strong electronic and steric properties especially phosphine containing complexes [39]. Although carbonylation reactions are favored by the previously mentioned transition metals, palladium catalysts have been extensively used since they require mild reaction conditions such as low pressure and low temperature compared to the other metals. There are various types of useful carbonylation reactions namely; hydroformylation [32, 40], hydrocarboxylation [41] and hydroesterification usually known as methoxycarbonylation [42].

1.3.1. Methoxycarbonylation reactions

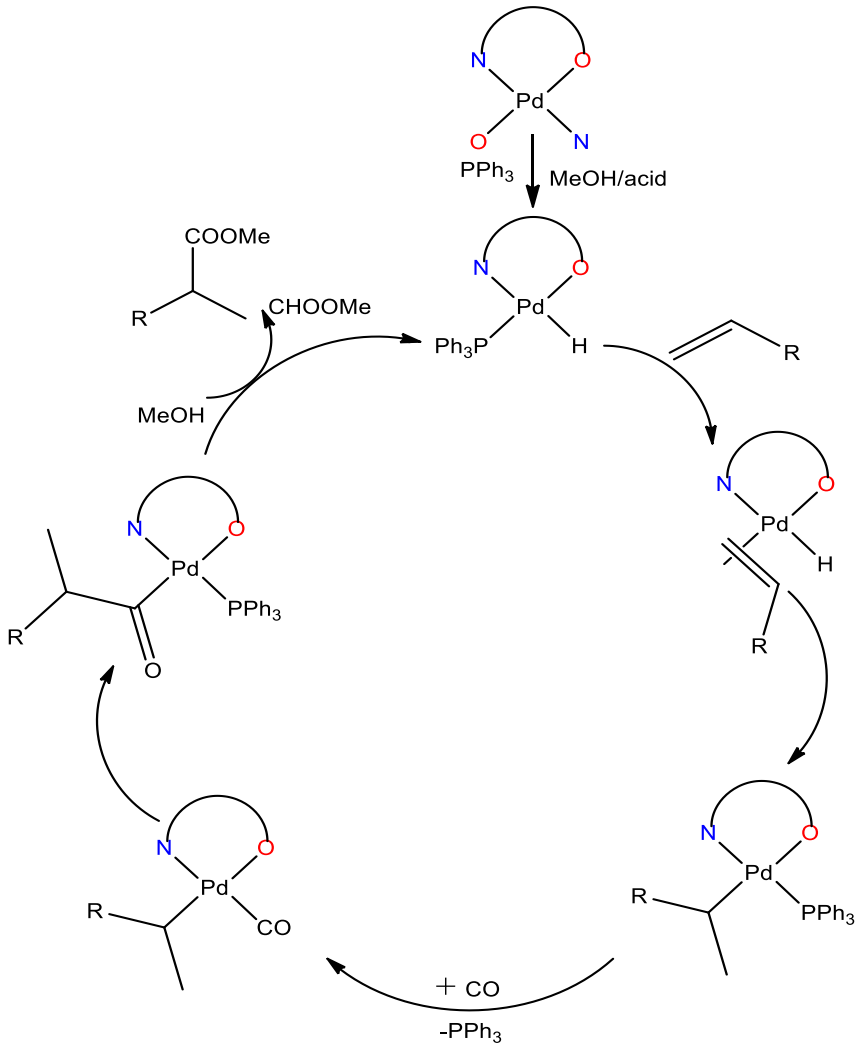
Methoxycarbonylation is a type of reaction whereby a substrate, for instance olefin or alcohol is converted into either a branched or linear ester (**Scheme 1.3**). This reaction involves five components namely: metal-catalyst, an alcohol, carbon monoxide, acid promoter and the substrate. The selectivity between these isomers solely depends mainly on the nature of the complex and the reaction conditions employed [43, 44].



Scheme 1.3: Methoxycarbonylation of styrene using a Pd catalyst.

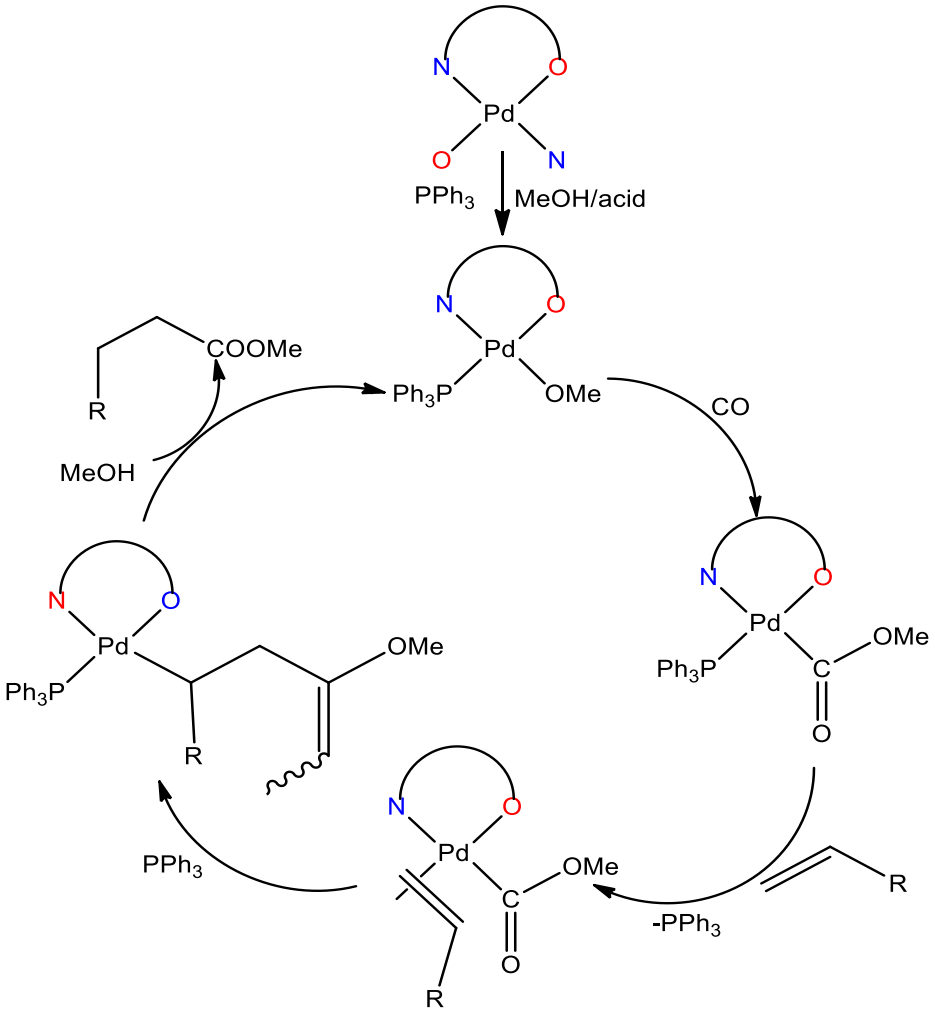
1.3.1.2 Plausible mechanisms of methoxycarbonylation of olefins

There are two possible proposed mechanisms, namely, hydride mechanism (Pd-H) and carbomethoxy mechanism (Pd-OMe) [45, 49]. However, according to literature, the hydride cycle is considered to be the most likely mechanism to occur as all intermediates can be observed with NMR spectroscopy [45, 50-52]. This cycle is initiated by the formation of the Pd-H active species, which allows the bonding of a substrate to form a Pd-substrate species (**Scheme 1.5**), followed by insertion of the carbon monoxide group to form a Pd-acyl intermediate. The ester is then produced upon nucleophilic attack of the Pd-acyl intermediate by the alcohol reagent [45, 49].



Scheme 1.4: Methoxycarbonylation of alkene via the Hydride mechanism [45, 49].

Contrary to the hydride mechanism, the carbomethoxy is prompted by the formation of Pd-acyloxy complex (Pd-OMe), followed by carbon monoxide insertion as shown in **Scheme 1.5**. A substrate is then inserted to form a Pd-alkyl intermediate which is followed by protonolysis of the metal-alkyl bond which results into a formation of the ester and the regeneration of active palladium species, as shown in **Scheme 1.5**. Similarity in both mechanisms is observed in the production of branched or linear products controlled by the 1.2 or 2.1 substrate insertion [38, 52].



Scheme 1.5: Methoxycarbonylation of alkene via the carboalkoxy cycle [45, 49].

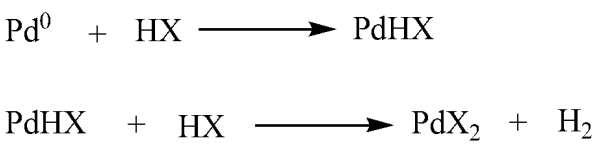
1.3.1.3 Role of an alcohol reagent/solvent

Alcohol is the most essential component of this type of reaction, it is used in the last stage of the reaction cycle (**Scheme 1.5** and **1.6**), where the ultimate ester product formed is released and the catalytically active species is generated via reductive elimination [45]. For an efficient reaction, the type of solvent used should not be bulky or complex because longer- chained alcohols can slow down the rate of the reaction or stop the reaction due to the introduced steric hindrance [43].

Therefore, the preferred alcohol is methanol. Another role played by this component is being a solvent, it is involved in the increase of the solubility between the substrate, catalyst and the products. However, co-solvent can be introduced into the system in cases where methanol can turn out to be poor solvent. Thus, a co-solvent can be used in cases where the reaction temperature required is greater than the boiling point of the primary alcohol being used for the carbonylation. [46].

1.3.1.4 Role of acid promotor

Palladium complexes are known to exist in two oxidation states of +2 and 0, (believed to be the active state and palladium black non active states respectively). Literature studies has established that without the presence of a stabilizer, the palladium complex tend to decompose and form palladium black (**Scheme 1.4**). Thus, the role of the co-catalyst is stabilize the Pd catalyst and to generate the catalytically active species [38, 47].



Scheme 1.5: Activation of palladium catalyst by an acid promoter [38].

Different types of acids can be used for this type of reaction. For instance, Brønsted acids and Lewis acids have been employed as promoters in the methoxycarbonylation reactions, however, different olefins afford varied catalytic activities orders for numerous acids. For example, in one study it was observed that in the methoxycarbonylation of styrene, the activity varied in such

order; HCl< trifluoroacetic acid< trimethanesulfonic acid< methanesulfonic acid, whereas for propene, the order is HCl<PTSA, <sulfuric acid< trifluoromethanesulfonic acid [38]. This trend is believed to be associated with different coordinating abilities and strengths of the counter ions [48].

1.3.2 Commercial and industrial significance of methoxycarbonylation of alkenes

Methoxycarbonylation of olefins is perceived to be one of the principal tools mainly used to produce useful linear and branched ester functional groups. Branched esters specifically are used as precursors for non-steroidal anti-inflammatory drugs such as ibuprofen and naproxen [53, 54] (**Figure 1.9**).

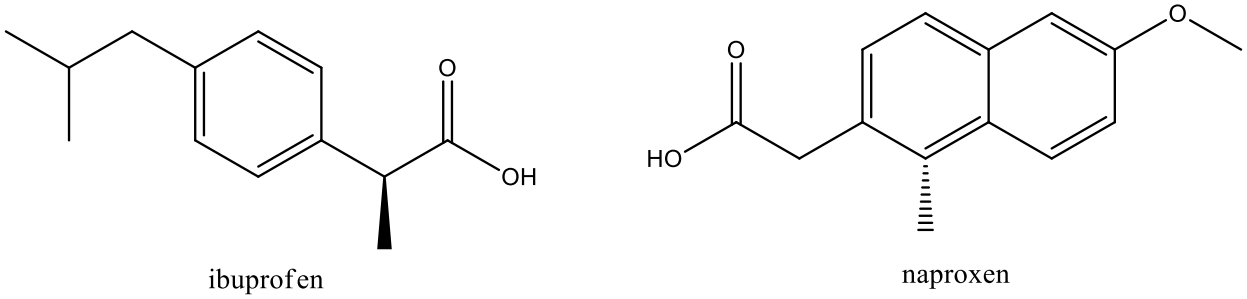


Figure 1.9: Structures of pharmaceutical drugs delivered from branched esters [54].

On the other hand, alkyl aliphatic or aliphatic esters are mainly used in industrial applications such in the production of food colorants [57], detergents, fragrances and surfactants [54] shown in **Figure 1.10**. Moreover, methoxycarbonylation of propyne produces a small molecule feedstock referred to as methyl methacrylate (MMA). This compound is crucial in industry since its polymeric form, poly(methylacrylate) is featured in medical sutures, cosmetics, coatings, packaging and transportation [55, 56].

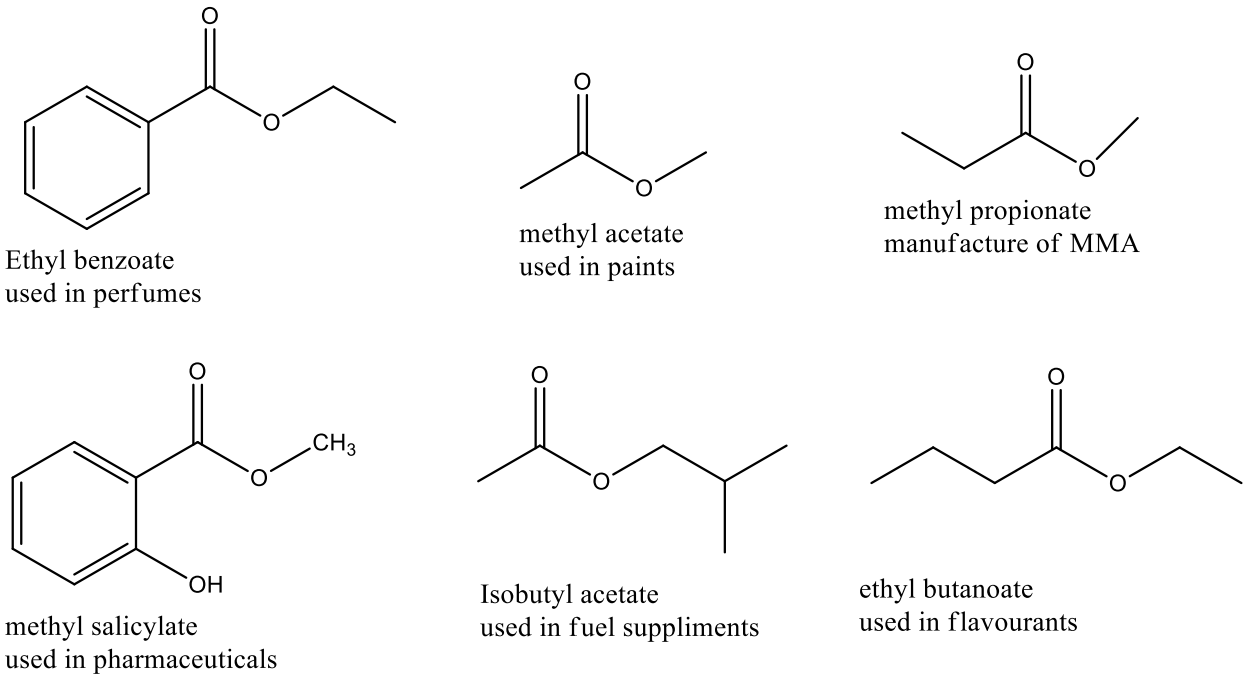


Figure 1.10: Examples of linear esters and their applications [57].

Chapter 2 gives a detailed literature review of the previously investigated Pd (II) complexes in the methoxycarbonylation reaction of olefins using both homogeneous and biphasic catalytic systems. The influence of different donor ligands and reaction conditions employed in methoxycarbonylation employed are also discussed.

1.4 References

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Chapter 2

Literature review on homogeneous and water-soluble Pd(II) complexes as catalysts in the methoxycarbonylation of alkenes

2.1 Introduction

Research on palladium catalyzed methoxycarbonylation reactions of olefins has gained momentum over the last few years. It is one of the most investigated catalyzed carbonylation reactions. Pd(II) complexes are appreciated for methoxycarbonylation reactions, owing to their high activity, thermal stability and superior selectivity properties they exhibit [1-3]. For instance, literature studies reveal that under low pressure of CO and moderate temperatures, some palladium catalysts afford excellent conversions of up to of 80%, as well as percentage compositions of up to 80% in favour of linear ester products [4-8].

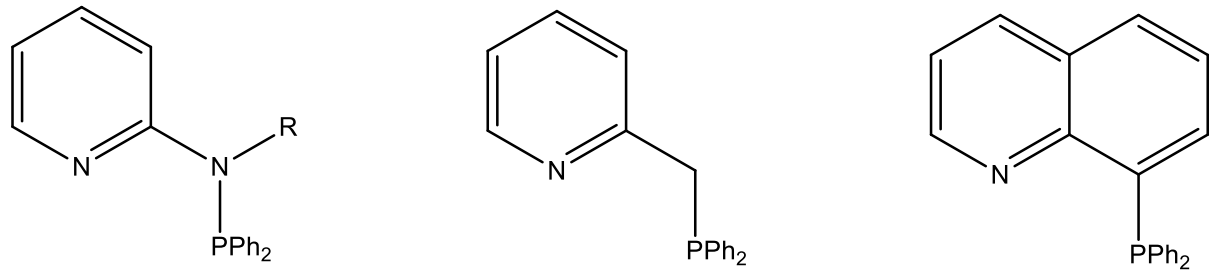
The reactivity of the catalysts are in most cases influenced by the architecture of the complex. For example, the combination of hard and soft donor sites in the same ligand motif results in good ligand candidates for catalytic reactions, due to the ability of these ligands to acts as hemi-labile ligands which results in enhanced activity and selectivity and good stability to the catalyst and catalytic intermediate formed during the methoxycarbonylation cycle [9, 10]. Moreover, the denticity of the ligand plays a huge role towards the composition of linear or branched esters, for example, monodentate ligands are believed to favor the formation of branched esters whereas bidentate ligands lead to more formation of linear esters. However, the ligand electronic may have profound effect on the regio-selectivity [11, 12].

Apart from complex structure, the reactivity and selectivity of the catalyst can be easily influenced by the reaction conditions employed [12-16]. For instance, the identity and the amount of phosphine [4, 5, 13], type of acid promoter [13, 17] and solvent system used can lead to either enhanced or reduced activity [15]. Nevertheless, different types of substrates have been observed to afford varied conversions and regio-selectivities due to electronic and steric factors. For example, the activity decreases with an increase in chain length, and longer chained olefins favours branched esters over linear esters due to high possibility of isomerization [6, 16-19]. This section reviews previously reported Pd(II) complexes used as catalysts in the methoxycarbonylation of olefins under both homogeneous and biphasic conditions.

2.2 Different ligand architecture used in palladium based complexes for methoxycarbonylation reactions

2.2.1 P^N- donor chelated Pd(II) complexes

Mixed P,N-donor ligands are one of the most important heterobidentate chelates that have been employed in various catalytic transformations [7, 10, 20, 21]. It is believed that the π-acceptor character of the phosphorus donor aids in the stability of the metal center in low oxidation states, while the nitrogen σ-donor ability enables easy susceptibility of the metal for oxidation addition reactions to occur. Thus, such an intermediate with combined abilities, stabilizes the oxidation state generated during the catalytic cycle [22]. Aguirre and co-workers investigated this type of system for methoxycarbonylation of olefins. The system they employed included Pd(II) complexes formed by treatment of $Pd(Cl)_2$ with 2-[(diphenylphosphino)methyl], pyridine (Ph_2PCH_2py) and 2-[diphenylphosphino methyl] pryridine (Ph_2PCH_2py) and 2-[diphenylphosphino] quinoline (Ph_2Pqn) based chelates to afford complex **A**, **B**, **C** and **D** respectively [7] shown in **Figure 2.1**.



R=H :Ph_2PNHpy **A**

R= Me:$Ph_2PNMepy$ **B**

Ph_2PCH_2py **C**

Ph_2Pqn **D**

Figure 0.1: P^N donor ligand system investigated by Pedro and colleagues [7].

From their results, it was apparent that their system was active in transforming olefins to ester product, with complex **A** being the most reactive. For example, for styrene conversions of 99% with complete region-selectvivity of up to 98% in favour of branched isomers was observed for complex **A** in the presence of *p*-toulenesulfonic acid and PPh_3. Moreover, it was deduced that the replacement of the ligand in complex **D** with diphenylphosphino, phenylamine (Ph_2PNHPh) and 2-(diphenylphosphinoamino methyl) pyridine ($Ph_2PNMepy$) significantly lowered the activity, indicating the importance of the presence of the pyridine and N-H functionalities in enhancing the activity. One notable observation discussed was that the identity of the substrate significantly influenced the catalytic activity. For instance, under similar reaction conditions complex **A** showed a remarkable conversion of 99% for styrene, whereas conversions of 19% and 43% were realized for cyclohexene and 1-hexene respectively. On the other hand, a decline in catalytic activity was observed for complex **C** and **D** when styrene was used as substrate.

Another P^N based Pd(II) complexes were investigated by Abarca and colleagues. They designed 2-diphenylphosphino pyrimidine and 2-diphenylphosphinoaniline ligand based Pd(II) complexes

(Figure 2.2) and employed them in the methoxycarbonylation of styrene in an aim to gain insight in selectivity and regioselectivity of the complexes. Under similar reaction conditions, it was established that **A** and **B** afforded chemoselectivity of 71% and 82% towards the formation of the ester species respectively. In addition, regioselectivty of 75% and 82% in favor of branched isomers was observed. Noteworthy to mention is that complex **C** and **D,** anionic complexes generated from **A** and **B** respectively showed enhanced chemo-selectivity of 99% and 93% with an excellent composition of 97% and 96% respectively in favor of branched ester species [13].

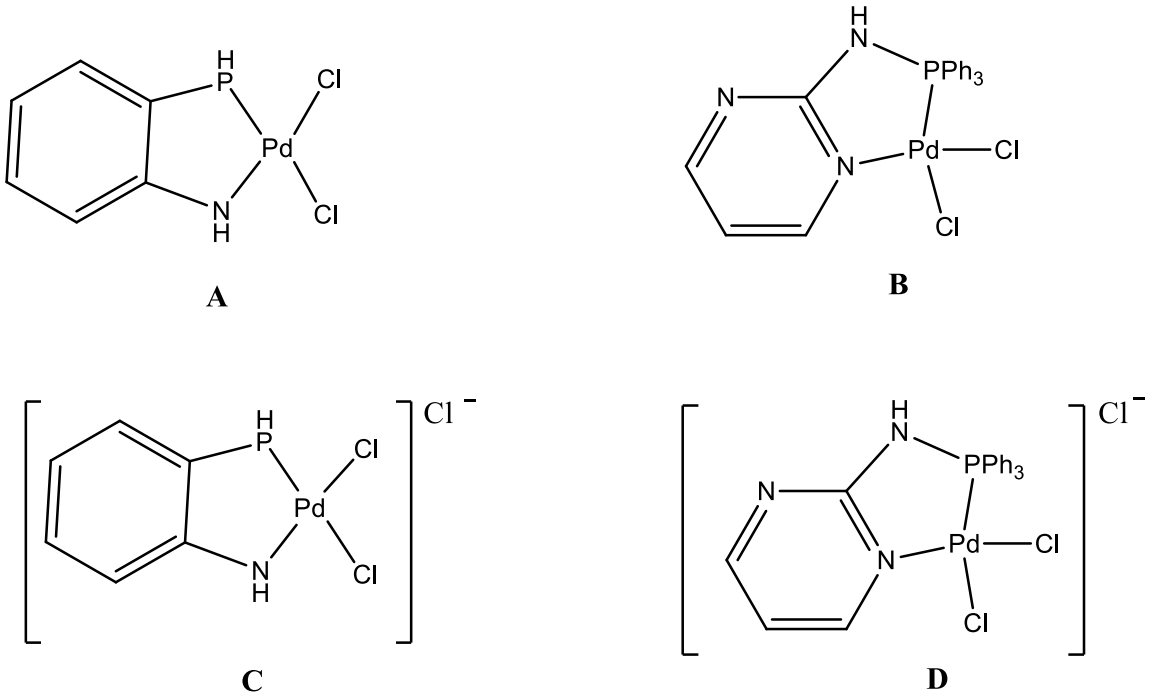


Figure 0.2: P^N anchored Pd (II) complex by Abarca *et al* [13].

2.1.2 P^P-donor chelated Pd(II) complexes

In another study, Zolezzi *et al.* [14] investigated P^P ligands chelated with palladium. The Pd(II) complexes containing phosphine donor ligands derived from naphthyl (diphenyl) phosphine (**Figure 2.3)**. In their experiment, they performed the methoxycarbonylation of styrene,

methylstyrene, n-hexene and cyclohexene. Both complexes **Pd1** and **Pd2** (**Figure 2.3**), respectively afforded conversions of 93% and 99% for styrene substrate and selectivity of 93% and 92% towards branched esters. Notably, substituting chloride groups present in complex **Pd1** with trifluoromethanesulfonate moieties to afford complex **Pd2** revealed no significant variations in the catalytic activity apart form a slight increase in styrene conversions from 93% to 97 %. Catalytic conversion further proved to be dependent upon the substrate identity. For instance, both complexes exhibited moderate conversions of 40% to 60% which were realized for methylstyrene, n-hexene and cyclohexene whereas excellent conversions of 97% in 6 h for styrene, under similar reaction conditions.

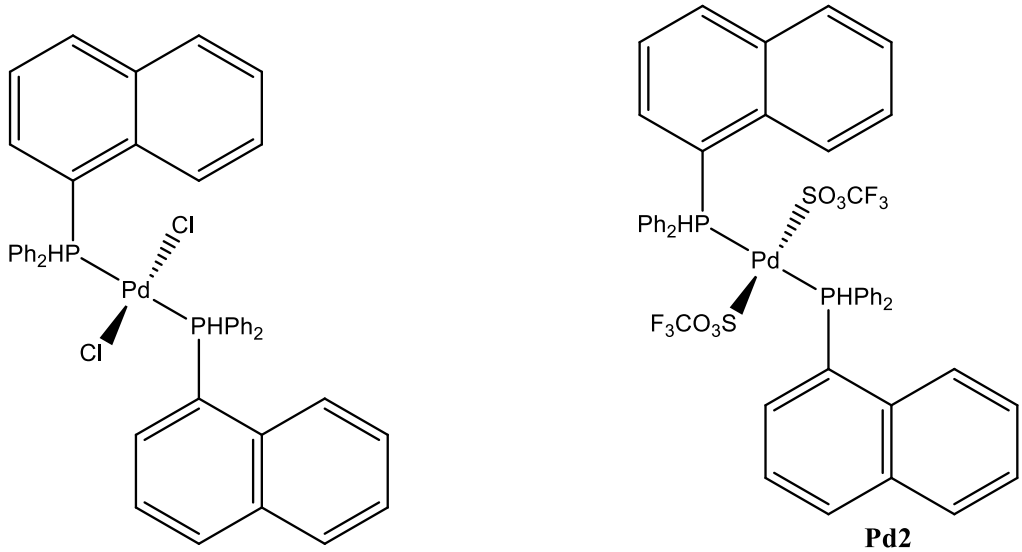
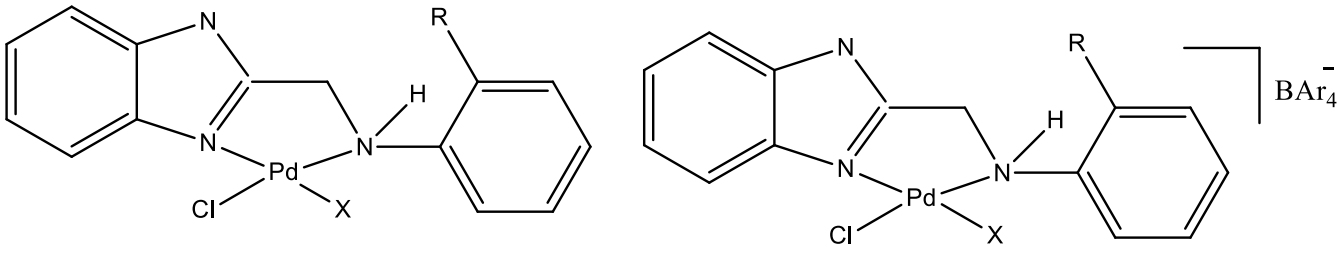


Figure 0.3: P^P donor Pd (II) complexes by Zolezzi *et al.* [14].

2.2.3 N^N-donor chelated Pd(II) complexes

Homobidentate N^N- donor ligands is another class of ligands investigated for in methoxycarbonylation of olefins. Tshabalala *et al.* [17] designed the N^N phenoxy based ligands

and probed them in methoxycarbonylation of different substrates. It was observed that fine tuning the ligands has an influence on the performance of the catalytic activity of the complex. For example, complex **D** bearing a methoxy species in the phenyl ring afforded high activity (86%) as opposed to that of complex **E** (26%) which bears a bromide substituent on the same position. This was believed to be due to the electron donating effect of OCH_3, which increases the stability of the complex. On the other hand, complex **B** bearing Pd-Me was observed to have enhanced activity of 80% compared to that of complex **A** containing Pd-Cl. A feasible explanation for this observation is the ease of CO insertion into the Pd-Me. [23, 24].



R=OCH_3, X= Cl (**A**)
R= OCH_3, X= Me (**B**)
R= Br, X= Me (**C**)

R= OCH_3, X= Me (**D**)
R= Br, X= Me (**E**)

Figure 0.4: N^N chelated Pd(II) complexes investigated by Tshabalala *et al*. [17]

In another study an N^N-donor system was reported by Zulu *et al.* using (pyridyl) imine-based ligands [23]. The designed complexes (**A**-**D**) shown in **Figure 2.5**, exhibited varied catalytic activities in methoxycarbonylation of 1-hexene. For example, complex **A** afforded conversion of 91% whereas complex **B**, **C** and **D** gave catalytic activities of 62%, 58% and 40% respectively under similar reaction conditions. The higher conversion observed for complex **A** is believed to

be influenced by the presence of the electron-donating group, which causes an overall increase in the rate of coordination of the substrate to the active palladium complex. Another feasible explanation for the observed high activity could be the ease of formation of Pd-H species from the dichloride atom. The investigated complexes did not show any direct effect in terms of regioselectivity since percentage compositions for linear esters was observed to be between 60-65% in all cases.

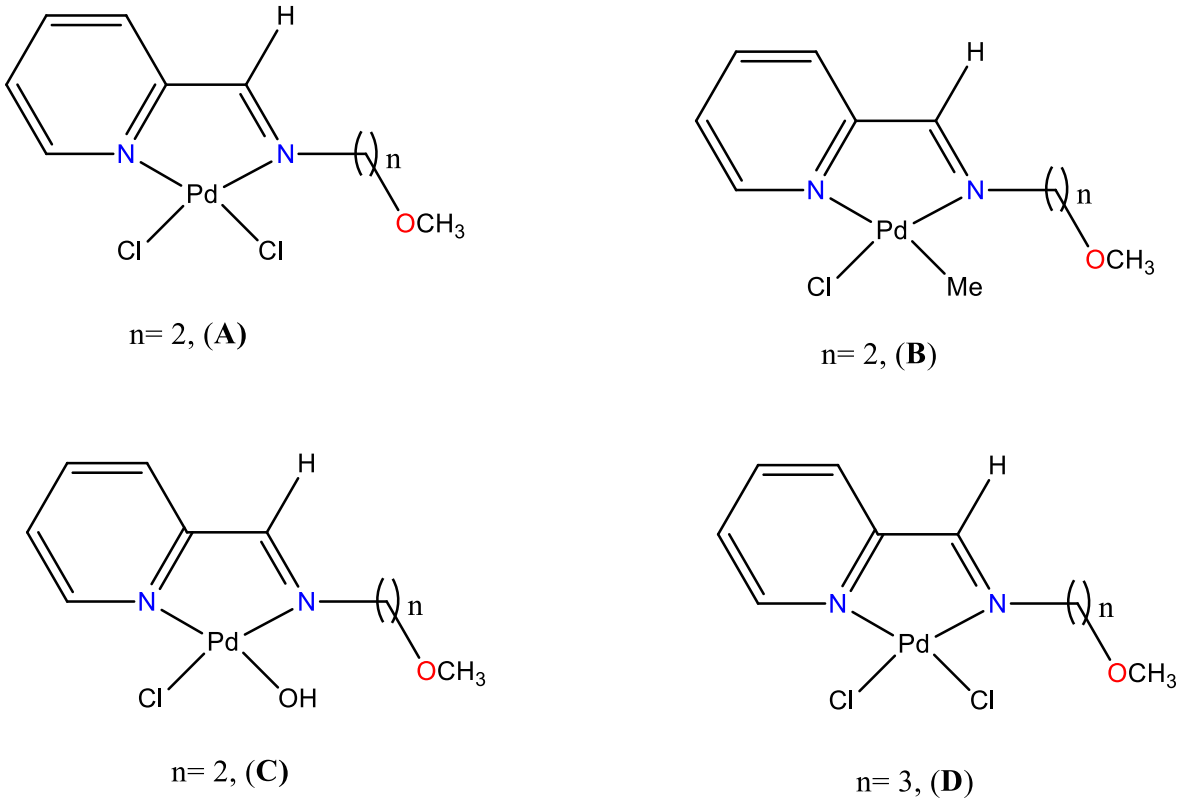
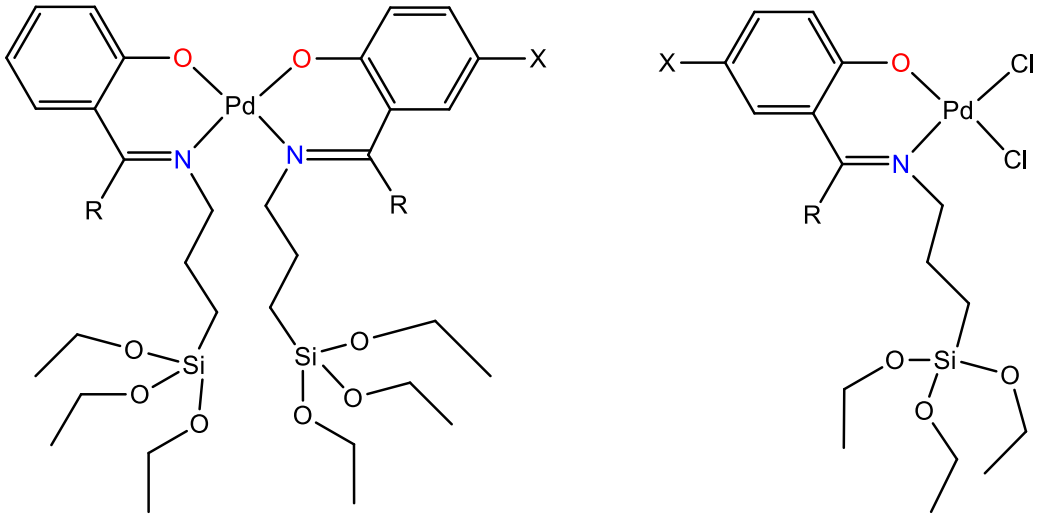


Figure 0.5: N^N donor Pd (II) complexes by Zethu *et al.* [23]

2.2.4 N^O donor based Pd(II) complexes

Akiri & Ojwach [16] applied (phenoxy)imine ligands based Pd(II) complexes with alkoxysilane groups and probed them in the methoxycarbonyaltion of 1-hexene **(Figure 2.6)**. For these

complexes, moderate to good conversions of 64-85% were realized. It was discovered that bis(chelated) complexes **A** and **B** afforded higher catalytic activities of 85% and 84% relative to the mono chelated complexes **C** and **D** (61% and 65%). This behavior can be explained by the increased stability afforded by the bischelation in complex **A** and **B,** resulting in decomposition of the catalyst. Another plausible reason could be the decreased electrophilicity around the metal center caused by the presence of anionic ligands, which are likely to be electron deficient. In their study, they also investigated the effect of substrate identity on the catalytic activity. From their results recorded, the substrate significantly influences the activity and selectivity. For instance, 1-hexene afforded higher conversions compared to 1-heptene, 1-octene, 1-nonene and 1-decene, hence an increase in chain length leads to a decline in activity due to the increased steric hindrance and higher electron density. Both the factors can hinder the substrate form coordinating to the metal center [19]. Noteworthy to mention that the longer-chained olefins gave more branched ester products due to the possibility of high number of possible isomers [19].



R= CH_3, X= H (**A**)
R= H, X= CH_3 (**B**)

R= CH_3, X= H (**C**)
R= H, X= CH_3 (**D**)

Figure 0.6: N^O Pd(II) complexes probed by Akiri *et al.*[16]

2.2.5 N^N, N^O and S donor Pd(II) complexes

In a study conducted by Kumar and Darkwa [24] tridentate N, N, O and S palladium complexes were was investigated for the methoxycarbonylation of alkenes **(Figure 2.7)**. In this system, it was observed that neutral complexes (**1a-4a**) together with palladium salts (**3c** and **4c**) exhibited no activity in the absence of PPh_3 in the methoxycarbonylation reaction of 1- hexene. However, good to excellent conversions (65% -94%) for **1a-4a**, **3c** and **4c** were realized after the addition of PPh_3. In terms of regioselectivity, percentage compositions of 60 -63% in favor of linear esters was observed. Interestingly, palladium salts (**1b-4b**) were catalytic active in the absence of PPh_3 under the same reaction conditions, although the conversions were observed to be low to moderate (28% -66%). This behavior was explained to be associated with minimum stability of the complex with PPh_3 present as the ligand structure. Interestingly, the activity elevated to excellent conversion of 95% upon addition of PPh_3 species for the palladium salts with an increase in regioselectivity of

10% towards linear esters. This trend observed was believed to be due to the extra stability caused by the added PPh_3 species. The nature of the alkene was observed to have profound effect on the performance of the catalyst. For instance, longer chained alkenes resulted in lower activity compared to short-chain alkenes. Moreover, increasing the chain length leads to increased percentage compositions towards branched alkenes as observed in literature.

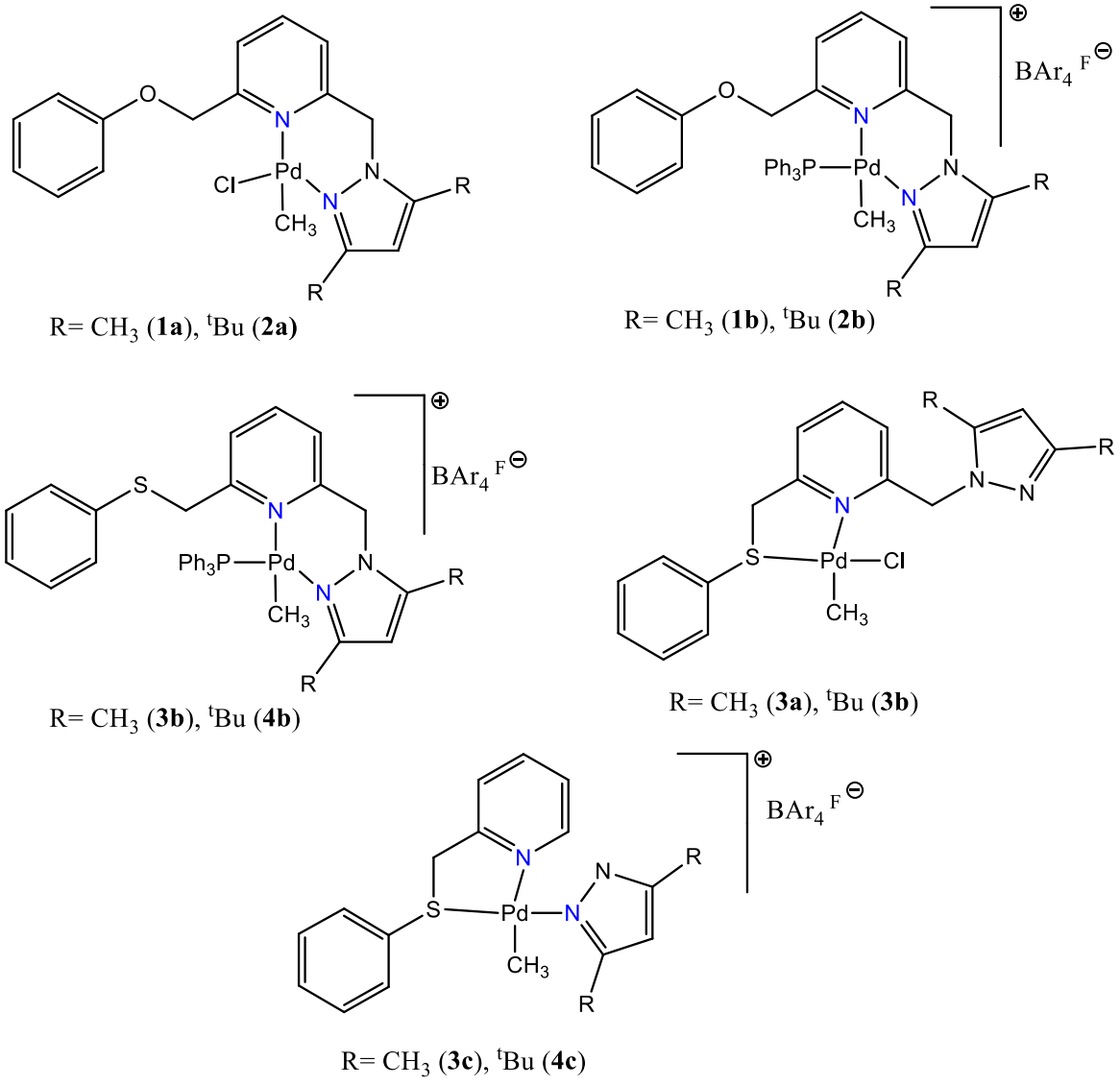


Figure 0.7: Palladium (II) complexes investigated by Kumar and Darkwa [24].

2.3 Multiphase methoxycarbonylation reactions using Pd(II) complexes

The fundamental of the multiphase or biphasic system entails the presence of two immiscible phases, where one phase contains the catalyst and the other contains the substrate. The reaction occurs during the vigorous stirring and heating at the interface between the two solvents. After the reaction is complete, the two phases can be easily separated. This allows easy reusability of the catalyst due to the facile separation of the two layers [27-29]. Few approaches employed for methoxycarbonylation reactions using biphasic media are discussed below.

2.3.1 Polyol phase employed in the methoxycarbonylation of 1-hexene

In one study conducted by Pruvost and coworkers [30], palladium catalyzed methoxycarbonylation of alkenes was conducted using polyol phases. A polyol is an organic compound that contains multiple hydroxyl groups. Polyols are hydrophilic and essentially insoluble in apolar or organic solvents. Thus, their biphasic media consisted of ethylene glycol which immobilizes the catalyst and apolar phase containing the products. The layers can be easily decanted at ambient temperatures. The ligand system they used was cationic triarylphosphines (**L1**, **L2**, **L3**) and sulphonated **TPPTS** which are insoluble in the catalytic phase.

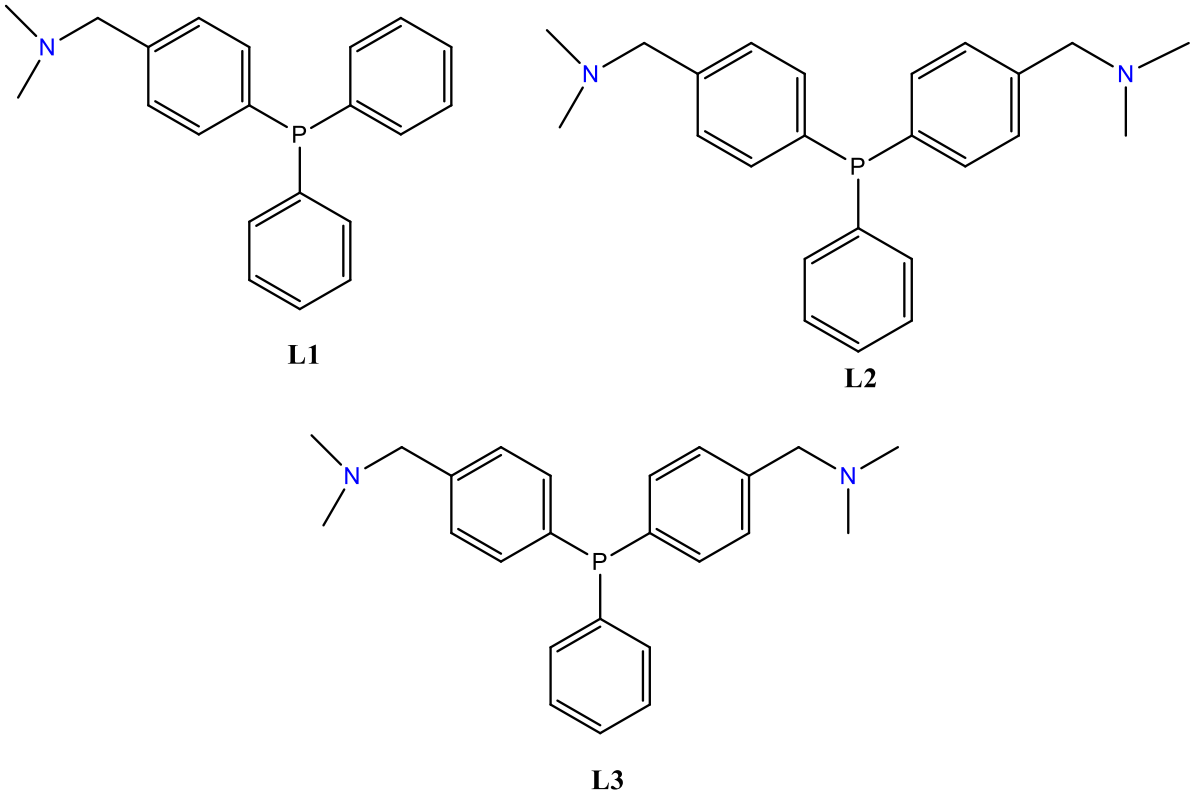


Figure 0.8: Phosphorus based ligands investigated by Pruvost and co-workers [25].

In this study, it was observed that **L1** bearing one dimethylamino moiety, afforded higher 1-octene conversions (99%) relative to that of **L2** and **L3** (70 and 30% respectively), when PTSA was used as the acid promotor. The variation in activity could be attributed to the number of dimethylamino substituent present in each ligand, which is believed to cause less or marked amphiphilic character of the phosphine. Therefore, the most ionic phosphine results in better mobilization of the catalyst in the polar phase. The use of TPPS afforded activity between those of **L2** and **L3**, however, high regioselectivity of 45% in favor of linear esters. The combination effect of acid promotor and solvent system was investigated, and optimum conversions were realized when PTSA and toluene was used. Moreover, the selectivity for monoesters was observed to be higher (70%) when **L3** was used compared to the 37% observed for **L2.**

2.3.2 Use of water-soluble ligands

Water soluble ligands are type of ligands bearing hydrophilic moieties such as sulfonates, carboxylates, ammonium, phosphonium and hydroxyl groups. Ligands incorporated with such species therefore allows them to be soluble in water to form aqueous phase and organic phase depending on the type of solvent system employed. Schimdt and his co-workers demonstrated a systematic approach for the application of palladium(II) catalyzed methoxycarbonylation of a longer chained 1-dodecene substrate using the previously designed water-soluble SulfoxantPhos ligand shown in **Figure 2.9**. Their system consisted of methanol (containing 1-dodecene) and the immobilized aqueous catalyst phase [26].

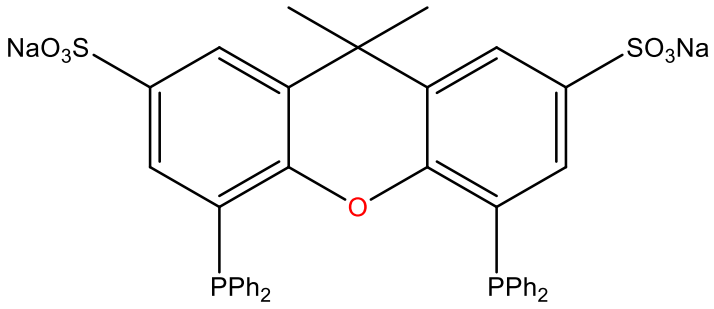


Figure 0.9: SulfoxantPhos ligand probed in methoxycarbonylation of 1-dodecene [26]

The water soluble Pd (II) complex designed was found to be active in methoxycarbonylation of 1-dodecene substrate. It was deduced that reactivity of the catalyst increased with an increased in catalyst loading. For instance, catalyst concentrations of 0.04 mmol 0.08 mmol and 0.16 mmol resulted in conversions of 79%, 94% and 97% respectively, with no profound effect in terms of regioselectivity. Since the complexes were hydrophilic in nature, they then probe biphasic environment using water. In their experiment, varied amount of water content used in

methoxycarbonylation of 1-dodecene. Noteworthy to mention that when methanol was used as a solvent at 0% of water, high catalytic activity of 97% was observed with high catalyst leaching of 4.6 ppm. However, 5% addition of water to the polar phase lead (methanol and water) lead to a slight decline in activity of 95% with catalyst leaching of 1.0 ppm. The decline in activity in the presence of 5% of water was rationalized by the decrease in solubility of 1-dodecene and carbon monoxide in the polar phase which leads to reduction of the reaction rate.

They then investigated the reusability of their palladium catalyst. The biphasic system chosen was composed of methanol as polar phase and 1-docene/octane as nonpolar phase. Surprisingly, the conversion of 35% for the first run was significantly lower that the following runs (>55). The plausible explanation is due to the induction period for the formation of active catalyst species, which occurred, only for the initial run. However, the activity increased slightly from the second run to the fourth run whereas the regioselectivity remained constant in every run. It was concluded from these results that the behavior observed is an indication of the high stability of the complex during the recycling process.

Jayasree *et al*. [27] probed carbonylation reaction of olefins and alcohol using palladium (II) complex bearing a chelating anionic N^O ligand in aqueous/organic biphasic medium. The designed complex (**Figure 2.10**) was found to be highly soluble in polar solvents and slight soluble in less polar solvents. Methoxycarbonylation of aliphatic and aryl substituted terminal olefins using complex **1** revealed excellent conversion of 83% to 97% and regioselectivity of 55% to 75% towards the branched ester under the same reaction conditions. The experiments were conducted using LiCl as a co-catalyst. Unsuprisingly, the regioselectivity towards branched esters was found

to be higher for a short-chain olefin relative to a longer chain, for instance, 1- hexene afforded selectivity of 75% whereas dodecane gave 70% selectivity in favor of branched esters. The reusability of complex was investigated by carrying out using fresh styrene substrate. According to their observations, their catalyst exhibited complete conversions with no profound change in regioselectivity and thus found to be highly active and ecomically attractive towards methoxycarbonylation reactions.

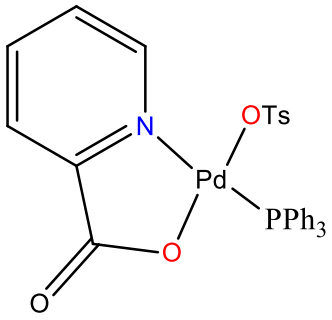


Figure 0.10: Water-soluble N^O ligand investigated by Jayasree *et al.* [27]

2.3.3 Use of Ionic liquids

Ionic liquids can be described as salts that are completely composed of ions with melting points below 100 °C [33]. These ionic liquids can be employed in methoxycarbonylation reactions as substitutes for the traditional organic acid promoters. Acid promoters are required to preserve the catalytic activity by forming Pd active species and to stabilise the intermediate cation Pd (II) species formed during the catalytic cycle to prevent the formation of palladium black. Thus, the use of ionic liquids as a reaction media in liquid biphasic reaction is considered a greener approach owing to the low vapour pressure, good thermal stability and tuneable solubility properties they exhibit. In one study reported by Eduardo *et al.*[34], Bronsted acid ionic liquids (BAILs) solvent were employed as acid promoter and phase separable reaction media in methoxycarbonylation

reaction of ethylene using phosphine based palladium. Their system consisted of BAILs and MeOH as a solvent, thus, achieving the immobilization of the catalyst in the ionic liquid phase.

According to their results, conversions of 95-99% were realised when six BAILs (**Figure 2.11**) were used. Moreover, selectivity of greater than 99% achieved in favour of methyl propionate. Noteworthy to mention that one recycling experiment conducted using BAIL (**3**) showed reuse was possible up to 15 cycles with no loss in performance.

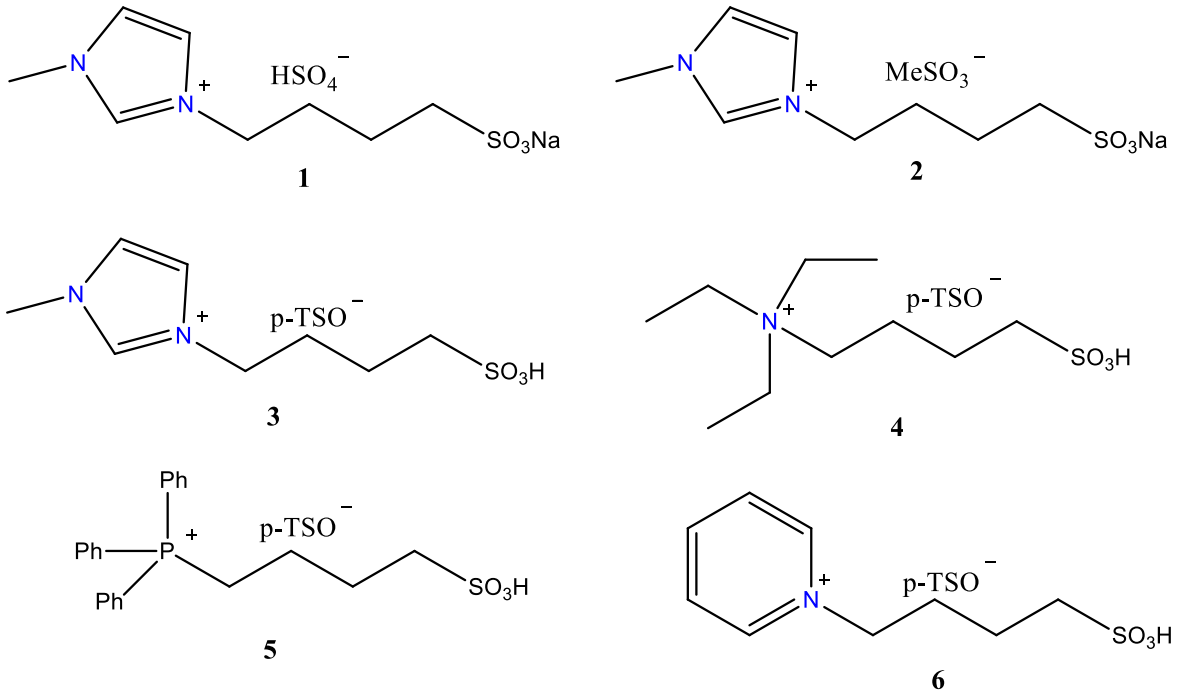
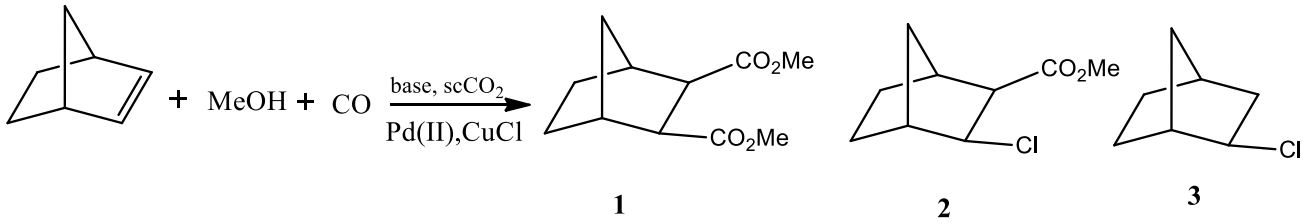


Figure 0.11: Bronsted acid ionic liquids used in methoxycarbonylation of ethylene [34].

2.3.4 Supercritical CO_2 in methoxycarbonylation reactions

The use of supercritical carbon dioxide ($scCO_2$) is another technique that offers biphasic medium in the reaction mixture. The employment of $scCO_2$ as a reaction medium is considered to be environmentally benign, owing to its non-toxicity and non-flammability. Moreover, it is economically attractive due to its ready availability and inexpensiveness. Worthy to mention that low viscosity of scCO2 and high solubility of gases in scCO2 environments enables facile diffusion gases and transport of gases across the interfaces compared to the conventional solution conditions [35]. The use of scCO2 in methoxycarbonylation using Pd catalyst was first reported by Jing *et al* [36]. In their study, three Pd (II) catalyst, $PdCl_2$, $PdCL_2(PhCN)_2$ and $PdCl_2(MeCN)_2$ were investigated in methoxycarbonylation of norbornene. However, three products, cis-exodiester, cis-exo-β-chloride ester and exo-chloronorbornene were detected (**Scheme 2.1**).

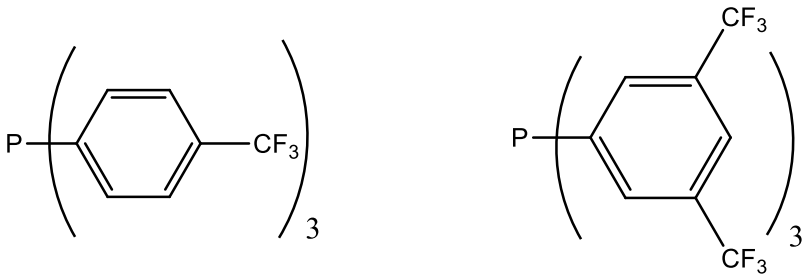


Scheme 0.1: Methoxycarbonylation of norbornene using $scCO_2$ by Jing and co-workers [36]

From their results, conversions of 96-100% were realised and regioselectivity of 21-62% were observed in favour of the targeted diester products (**1**) when using MeOH as a base. Worthy to mention that enhance selectivity was observed when the pressure of $scCO_2$ was 13 MPa, whereas a decline in activity was noted at 8 MPa. In their experiment, the effect of different types of bases was also evaluated. Excellent selectivity of 97% towards the diester product was realised when

$PdCl_2$, Et_3N was used. Unfortunately, no experiment was conducted for the recyclability of their catalysts.

Another study was reported by Estorach *et al*. [36] where linear alkenes were converted to their respective esters using insitu system of $PdCl_2(PhCN)_2$/**1** and PdCl2$(PhCN)_2$/**2** in $scCO_2$ in the presence of MeOH.



1 **2**

Figure 0.12: Phosphine ligands used in methoxycarbonylation of linear alkenes using $scCO_2$ [36].

For their system they deduced that the best condition of pressure and temperature for hydroesterification of 1-hexene were 30 atm of carbon monoxide pressure, 90° C and 120 atm of total pressure using $PdCl_2(PhCN)_2$/**2**, since the highest conversions of 67% and regioselectivity of 45% towards linear esters were recorded under these conditions. However, when 1-octene was used as a substrate conversion of 25 % and percentage compositions of 86% in favour of linear esters were recorded. They also investigated the use of other alcohols and found that no activity was observed when trifluoroethanol (TFE) and EtOH were used. As expected, diminished activity was noted for higher chained alkenes. For instance, conversion of 12% and 5% were realised for 1-hexadecene and 1-dodecene respectively.

2.4.1 Problem statement

Palladium catalyzed methoxycarbonylation is perceived as one of the most important olefin transformation reactions due to the production of many useful ester product used both domestically and industrially. For instance, branched esters products are used in the manufacturing of pharmaceutical drugs whereas linear esters are involved in the synthesis of detergents, perfumes, drugs and solvents. However, developments of environmentally benign systems for the production of these esters remains vital due to sustainability. There are few recyclable, active and selective complexes designed for methoxycarbonylation reactions. Moreover, N^O based Pd (II) complexes were evaluated and found to be the most active for methoxycarbonylation reaction. Therefore, the driving force behind this study is the design of active and selective Pd complexes and their recyclable analogues.

2.4.2 Rationale of the study

Homogeneous systems are still pursued in methoxycarbonylation reactions. However, forming a hybrid of the two systems is vital in order to obtain highly active systems with good selectivity and facile separation of the products to allow for recyclability. One way of achieving this is through the use of a biphasic media system whereby a catalyst is immobilized in the aqueous phase and the substrate in the organic phase. Therefore, tailoring of the ligand motif to afford water-soluble complexes which are easily recycled upon completion of the reaction is of interest in this present day.

2.4.3 Aim of the project

- The aim of this research project was to design active, selective and recyclable homogeneous Pd(II) complexes to be used for methoxycarbonylation of olefins.

2.4.4 Specific objectives of the study

1. To synthesize and characterize non-water soluble and water- soluble Schiff base ligands and their respective Pd(II) complexes.
2. Perform methoxycarbonylation reactions using the synthesized Pd(II) complexes and optimize reaction conditions.
3. Investigate the catalytic performance of water-soluble Pd(II) complexes in a biphasic system.
4. Investigate the reusability of the water -soluble Pd(II) complexes.

2.5 References

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Chapter 3

Synthesis and characterization of Schiff base ligands and their palladium(II) complexes

3.1 Introduction

Schiff base ligands are organic compounds possessing the azomethine group (-HC=N-) that results from the condensation of an amine with an aldehydes or ketone. These compounds can be considered as sub-class of imines, being either secondary ketimines or secondary aldimines depending on their structure [1, 2]. The Schiff base ligands are one of the most widely used ligands due to the ease of formation and remarkable versatility. They have therefore played an important role in the development of coordination chemistry as they readily form stable complexes with most transition metals [3]. Schiff bases are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations and therefore considered to be good chelating agents [4]. Amongst all the catalytic transformations reactions, carbonylation reaction is one of the reactions in which Schiff bases are used as chelating agents [5]. Catalytic carbonylation of organic substrates is a very promising and clean route for the synthesis of carbonyl compounds such as carboxylic acids, esters, ketones, amides, and amino acids. Even though many carbonylation catalysts have emerged in the past few decades, the search for new catalysts and processes continues due to economic and environmental demands, for instance, catalyst systems that adhere to the stipulated twelve principles of green chemistry are much sought-after [6, 7].

Carbonylation reactions are highly favored by metal complexes such as nickel, ruthenium, cobalt, rhodium, platinum and palladium. This is due to that these metals display good catalytic activities

which is attributed by their strong electronic and steric properties. This is observed especially for phosphine containing complexes. However, palladium complexes are the most widely used catalysts in methoxycarbonylation reactions of olefins, owing to their stability, high activity and selectivity [8].

A series of Pd(II) complexes with a variety of ligand donor atom has been reported in literature as mentioned in the previous chapter, these complexes include either same donor ligands or heterobidentate ligands for example the P^P ligands reported by Zolezzi *et al.* [9], P^O ligands reported by Ardene *et al.* [10], P^N ligands report by Aguirre *et.al.* [11], N^N ligands reported by Tshabalala *et al.* [12], N^O ligands reported by Akiri & Ojwach [13], as well as tridentate ligands such as N^N^X (X= O or S) ligands reported by Karma *et al.* [14]. However, the synthesis and characterization of transition metal complexes of Schiff bases containing nitrogen and oxygen donor atoms has an increased significance in the recent past mainly because of the great activity it possesses as opposed to other donor ligands. Moreover, water-soluble complexes employed for methoxycarbonylation of olefins are very few in literature, such systems have been reported by Schimdt *et al.* [15]. Therefore, herein, we report the successful synthesis of N^O donor ligands and their corresponding homogeneous and water-soluble Pd(II) complexes by the use of ^{1}H-NMR, ^{13}C-NMR, LC-MS, elemental analysis and X-ray chrystalography.

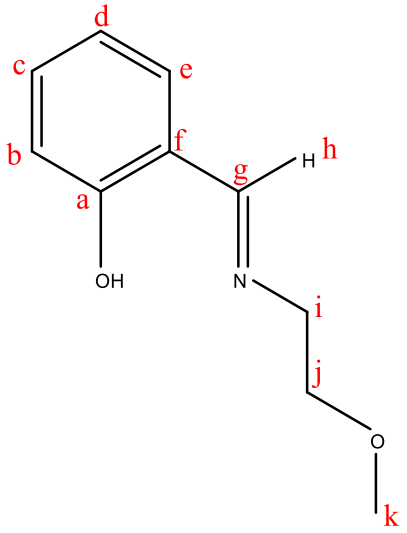
3.2 Experimental section and methods

3.2.1 General instrumentation and materials

All the reagents and solvents used below were purchased from Sigma Aldrich and were dried following relevant methods. Methanol was dried over 3Å molecular sieves overnight followed by distillation, whereas acetone, diethyl ether was died via distillation using calcium hydride, dichloromethane was dried over P_2O_5 and distilled prior use. The chemicals, chloroform ($CDCl_3$), aniline (≥ 99%), ethanolamine (≥ 99%), 3.5 ditertbutyl-2-hydroxybenzaldehyde, N,N-diethylenediamine (≥ 99%), N,N dimethylenediamine (≥ 99%), 2-methoxyethylamine (99%), salicylaldehyde (98%), palladium (II) acetate (98%) and sodium carbonate anhydrous (98%) were purchased from Sigma Aldrich and used without further purification. All ^{1}H NMR and ^{13}C NMR (100 MHz) spectra were collected on a 400 MHz Bruker Ultra shield NMR spectrometer using deuterated solvents, i.e. either $CDCl_3$ or DMSO-d_6. The infrared spectra were collected on an Agilent Technologies, Cary 630 ART-FTIR and Perkin Elmer Spectrometer 100. Mass spectrometric data collection was performed using an LC Premier micro-mass Spectrometer model LCMS-2020. The X-ray crystallographic measurements were performed on a Bruker APEX-II CCD diffractometer fitted with a low temperature device operating at temperature of 100(2) K.

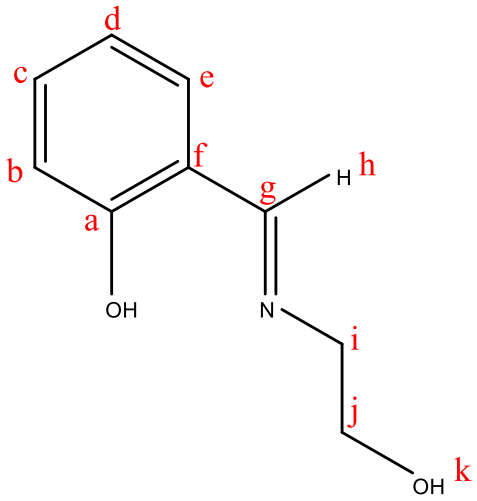
3.2.2 Synthesis of non water -soluble Schiff base ligands (L1H- L3H)

*3.2.2.1 2-[(2-Methoxyethylimino) methyl)] phenol (**L1H**)*



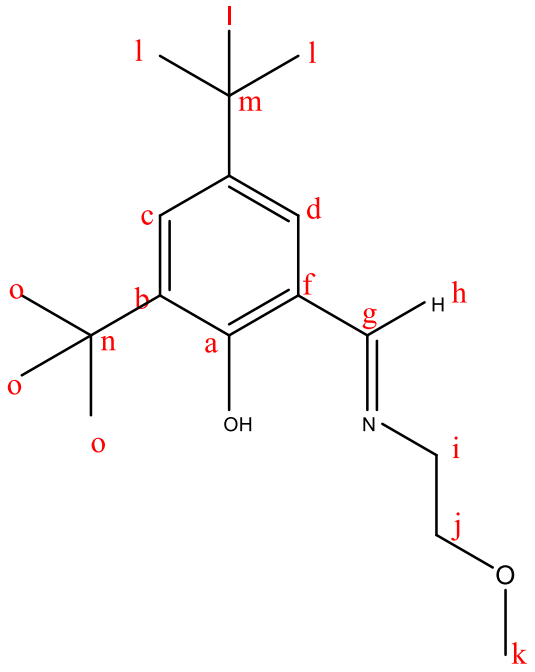
A mixture of salicylaldehyde (3.45 g, 28 mmol) and methanol (20 ml) was added to a solution of 2-methoxyethylamine (2.12 g, 28 mmol) and methanol (10 ml), the solution was then stirred for 24h at ambient temperature. Upon completion of a reaction, the solvent was removed *via* the *vacuo* to afford a yellow oily product obtained without further purification. Yield = 5.20 g (98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 3.38 (s, 3H, H_k), 3.67 (t, 2H, $^{3}J_{HH}$ = 6.5, H_j), 3.77 (t, 2H, $^{3}J_{HH}$ = 6.6, H_i), 6.98 (d, 1H, $^{3}J_{HH}$ = 8.0, H_d), 7.28 (t, 1H, $^{3}J_{HH}$ = 8.2, H_b), 7.33 (m, 2H, H_c, H_e), 8.37 (s, 1H, H_h). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 58.97 (C_k), 59.10 (C_i), 71.87 (C_j), 117.0 (C_b), 118.51 (C_d), 118.83 (C_f), 131.36 (C_e), 132.22 (C_c), 161.22 (C_a), 166.33 (C_g). HRMS-ESI [M-H^{+}]: m/z cal: 180.1025; found: 180.1022. ATR-IR ν_{max}/ cm^{-1}: $\nu_{(C=N)}$ = 1631.

*3.2.2.2 2-(2-hydroxyethylimino) methyl) phenol (**L2H**)*



L2H was synthesized following the procedure described for **L1H** using salicylaldehyde (3.45 g, 28 mmol) and 2-amino ethanol (1.72 g, 28 mmol) giving a pure reddish oily product obtained without further purification. Yield = 4.59 g (88%). ^{1}H NMR (400MHz, $CDCl_3$): δ_H (ppm) 3.72 (t, 2H, $^{3}J_{HH}$ = 6.2, H_i), 3.87 (t, 2H, $^{3}J_{HH}$ = 6.8, H_j), 6.98 (d, 1H, $^{3}J_{HH}$ = 8.0, H_d), 7.28 (t, 1H, $^{3}J_{HH}$ = 8.0, H_b), 7.32 (m, 2H, H_c, H_e), 8.34 (s, 1H, H_d). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 61.42 (C_j), 61.95(C_i), 117.0 (C_b), 118.556 (C_d), 118.61(C_f), 131.50 (C_e), 132.52 (C_c), 161.55 (C_a), 166.81(C_g). HRMS-ESI $[M+H]^+$: m/z cal: 166.0866; found: 166.0863. ATR-IR ν_{max}/ cm^{-1}: $\nu_{(C=N)}$ = 1629.

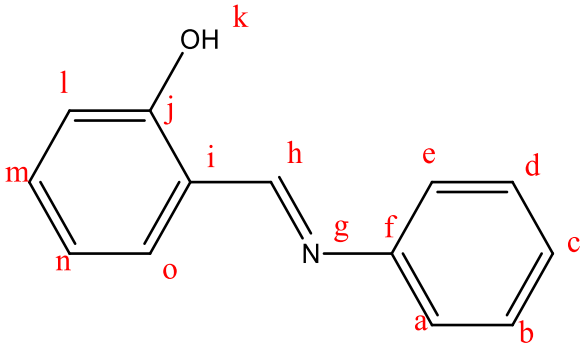
*3.2.2.4 2-(2-methoxyethylimino) methyl)-3,5-di-tert-butylphenol (**L3H**)*



L3H was synthesized following the procedure described for **L1H** using 3,5-di-tert-butyl-2-hydroxybenzaldehyde (2.06 g, 8.8 mmol) and 2-methoxyethylamine (0.66 g, 8.8 mmol) to afford a yellow oily product. Yield = 2.20 g (81%). ^{1}H NMR (400MHz, $CDCl_3$): δ_H (ppm) 1.35 (s, 9H, H_o). 1.49 (s, 9H, H_l), 3.41 (s, 3H, H_k) 3.72 (t, 2H, $^{3}J_{HH}$ = 6.4, H_j) 3.80 (t, 2H,$^{3}J_{HH}$ = 6.7, H_i) 7.13 (d, 1H, $^{4}J_{HH}$ = 8.0, H_b) 7.42 (d, 1H, $^{4}J_{HH}$ = 7.9, H_d), 8.41 (s, 1H, H_h). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 29.47 (C_o), 31.52 (C_l), 34.13 (C_n), 35.03 (C_m), 58.97 (C_k), 59.09 (C_i), 72.3 (C_j), 117.91 (C_b), 125.99 (C_d), 126.88 (C_f), 136.65 (C_c), 139.99 (C_e), 158.13(C_a), 167.44 (C_g). HRMS-ESI $[M^+-H]^+$: m/z cal: 292.2284; found: 292.2282. ATR-IR ν_{max}/ cm^{-1}: $\nu_{(C=N)}$ = 1631.

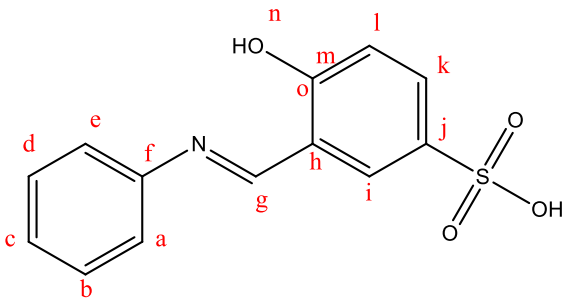
3.2.3 Synthesis of water-soluble Schiff base ligands (L4H - L6H)

*3.2.3.1 (E)-2-((phenylimino) methyl) phenol (**S1**)*



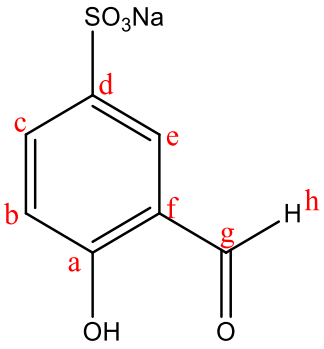
To a solution of salicylaldehyde (5.03 g, 41.10 mmol) in methanol (50.00 ml) was added aniline (3.75 ml, 41.10 mmol) and the mixture was stirred for 1.5 h to give a yellow solution. To the yellow solution, distilled water was added dropwise till the solution turned milky for some seconds before becoming translucent. The mixture was then cooled to 0° and the yellow crystalline solid filtered and washed with 5.00 ml of water followed by similar amount of methanol. The resulting solid was dried to give (E)-2-((phenylimino) methyl) phenol as a crystalline yellow product. Yield= 7.93 g (98 %). ^{1}H NMR (400 MHz, DMSO): δ_H (ppm); 5.40 (s, 1H, H_k), 7.06 (m, 3H, H_c ,H_l, H_n), 7.48 (m, 5H, Ha, H_b, H_d, H_e, H_m), 7.66 (d, 1H, $H_{o,}$), 8.8 (s,1H, H_h). ^{13}C NMR (100 MHz, $CDCl_{3,}$ δ ppm): 117. 8 (C_l), 120.6 (C_i), 121.4 (C_n), 122.7 (C_a,C_e), 127.2 (C_c), 130.8 (C_b, C_d),132.5 (C_m,C_o), 152,4 (C_f), 160,7 (C_h), 161.7 (C_j). ATR-IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ = 3345, $\nu_{(C=N)}$ = 1634.

*3.2.3.1 (E)-4-hydroxy-3-((phenylimino)methyl)benzenesulfonic acid (**S2**)*



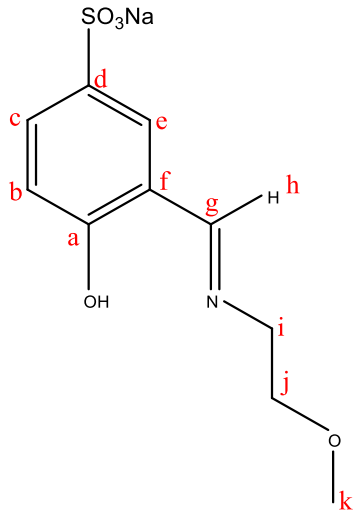
To 98% concentrated H_2SO_4 (10 ml) was added (E)-2-((phenylimino) methyl) phenol (3.50 g, 17.70 mmol) with stirring. The mixture was then heated at 103° C. for 3h. The hot solution was then transferred into a beaker containing 90.00 ml of ice water, producing a yellow solid instantly. The yellow suspension was then heated to obtain a clear orange solution. The resulting product was then filtered, and the filtrate was cooled to room temperature to obtain light yellow crystals, which was then washed with 5.00 ml of cold water. Yield = 3.75 g (75%).^{1}H NMR (400 MHz, DMSO): δ_H (ppm); 5.35 (s, 1H, H_h), 7.05 (t, 1H, $^{3}J_{HH}$= 8.0 Hz), 7.30 (d, 1H, $^{3}J_{HH}$= 2.5Hz), 7.48 (m, 4H, H), 8.12 (s, 1H, H), 8.87 (s, 1H, H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 117.2 (C_c,), 122.5 (C_a, C_e), 124.2 (C_h), 125.2 (C_c), 130.7 (C_b, C_d), 135,5 (C_i), 138.4 (C_j), 152.2 (C_f), 160. (C_g), 164. (C_o). ATR-IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ = 3410, $\nu_{(C=N)}$ = 1623.

3.1.3.2 3-Formyl-4-hydroxybenzensulfonic acid sodium salt ***(S3)***



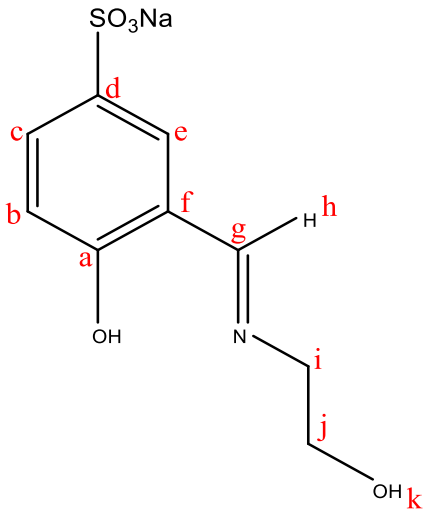
In a flask containing 10.00 ml of water, and **S2** (1.49, 5.40 mmol) and Na_2CO_3 (0.60 g, 5.70 mmol) were added. The mixture was the heated to boiling for approximately 2h while replenishing the water to maintain the total volume of 10.00 ml. The resulting solution was then cooled to 25°C and 6.00 ml of glacial acetic acid added followed by 6.00 ml of ethanol the mixture kept in an ice bath for 15 h to obtain light yellow crystals which were then washed with ethanol and dried *in vacuo*. Yield = 0.9045 g (85 %).^{1}H NMR (400 MHz, DMSO): δ_H (ppm); 6.94 (d, 1H, $^{3}J_{HH}$= 8.0, H_b) 7.72 (dd, 1H, $^{3}J_{HH}$= 6.0, $^{4}J_{HH}$ = 2.3, H_c), 7.90 (d, 1H, $^{4}J_{HH}$= 2.2, H_e), 10.27 (s, 1H, H_h). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 117.10 (C_b), 121.52 (C_e), 126.76 (C_f), 134.19 (C_c), 140.27 (C_d), 161.47 (C_a), 191.90 (C_g). ATR-IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ = 3422, $\nu_{(C=N)}$ = 1653.

*3.2.3.3 Sodium-4-hydroxy-3-((2-methoxyethylimino) methyl) benzenesulfonate (**L4H**)*



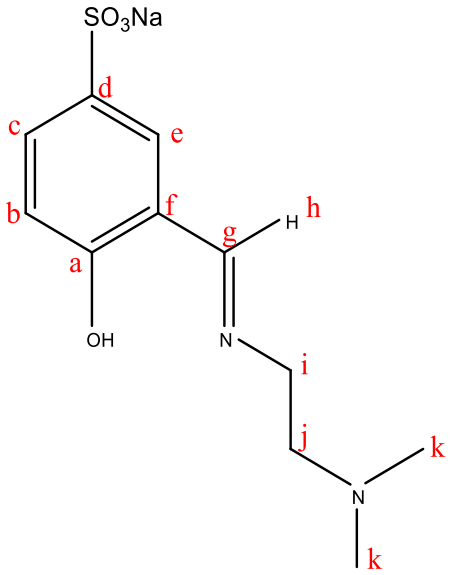
A solution of 3-formyl-4-hydroxybenzenesulfonate (**S3**) (1.83g, 0.8 mmol) and methanol (10ml), 2-methoxyethanamine (0.062 g, 0.8 mmol) was added, the reaction mixture was refluxed for 24 h at ambient temperature. After the reaction was complete, the solvent was removed in *vacuo* to afford a yellow solid, further rinsed with methanol and dried in oven. Yield = 0.153 g (68%). ^{1}H NMR (400MHz, DMSO): δ_H (ppm) 3.29 (s, 3H, H_k), 3.61 (t, 2H, $^{3}J_{HH}$ = 6.0, H_j) 3.78 (t, 2H, $^{3}J_{HH}$ = 6.4, H_i), 6.79 (d, 1H, $^{3}J_{HH}$ = 8.0, H_b), 7.54 (dd, 1H, $^{3}J_{HH}$ = 6.7, $^{4}J_{HH}$ = 2.2, H_c), 7.69 (d, 1H, $^{4}J_{HH}$ = 8.0, H_e), 8.59 (s, 1H, H_h). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 57.81 (C_k), 58.46 (C_i), 71.71 (C_j), 116.31 (C_b), 117.46 (C_e) 129.32 (C_f), 130.46 (C_c), 139.57 (C_d), 161.87 (C_a), 167.30 (C_g). MS-ESI: m/z (%) = 258 $[M\text{-}Na]^+$, 100 %). IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ = 3410, $\nu_{(C=N)}$ = 1611.

*3.2.3.4 . Sodium-4-hydroxy-3-((2-hydroxyethylimino) methyl) benzenesulfonate (**L5H**)*



L5H was synthesized following the procedure described for **L4,** using **S3** (0.27 g, 1.00 mmol) and ethanolamine (0.09 g, 1.00 mmol), dried using nitrogen . Yield = 0.15 g (55%). ^{1}H NMR (400MHz, DMSO): δ_H (ppm) 3.66 (s, 4H, H_i, H_j), 4.79 (s, 1H, H_k) 6.79 (d, 1H, $^{3}J_{HH}$ = 8.0, H_b), 7.54 (dd, 1H, $^{3}J_{HH}$ = 6.0, $^{4}J_{HH}$ = 2.2, H_c), 7.69 (d, 1H, $^{4}J_{HH}$ = 7.9, H_e), 8.59 (s, 1H, H_h). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 47.18 (C_j), 53.30 (C_i), 56.24 (C_b), 116.67 (C_e), 117.23(C_f), 129.35 (C_c), 136.48(C_d), 162.91 (C_a), 166.63(C_g). MS-ESI: m/z (%) = 244 ([M-Na]$^{+}$, 100 %). ATR-IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ = 3410, $\nu_{(C=N)}$ = 1628.

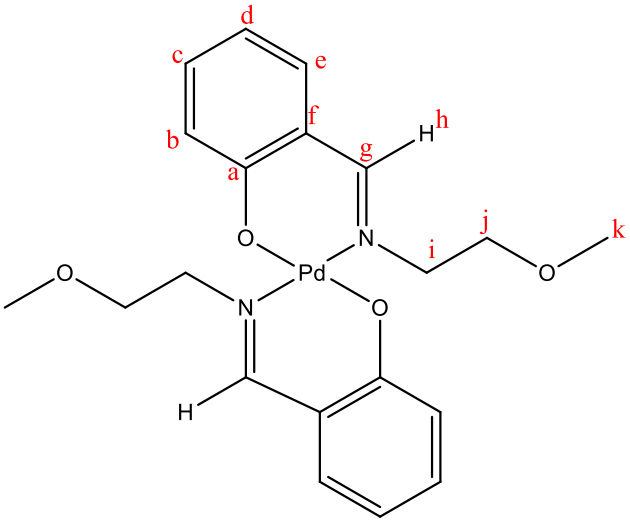
*3.2.3.5. Sodium-3-((2-(dimethylamino)ethylimino)methyl)-4-hydroxybenzenesulfonate (**L6H**)*



L6H was synthesized following the procedure described for **L4H**, using **S3** (0.29 g, 1.29 mmol) and N, N dimethylethylenediamine (0. 15 g, 1.29 mmol). Yield = 0.25 g (65%). ^{1}H NMR (400MHz, DMSO): δ_H (ppm) 0.93 (t, 6H, $^{3}J_{HH}$ = 6.0 H_k), 2.66 (t, 2H, $^{3}J_{HH}$ = 6.0, H_j), 3.63 (t, 2H, $^{3}J_{HH}$ = 6.0, H_i), 6.794 (d, 1H, $^{3}J_{HH}$ = 8.0, H_b), 7.54 (dd, 1H, $^{3}J_{HH}$ = 6.4, $^{4}J_{HH}$ = 2.5, H_c), 7.69 (d, 1H, $^{4}J_{HH}$ = 7.8, H_e), 8.59 (s, 1H, H_h). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 47.18 (C_k), 53.30 (C_i), 56.24 (C_j), 116.67 (C_b), 117.24 (C_e), 129.35 (C_f), 130.48 (C_c), 138 (C_d), 162.90 (C_a), 166.64 (C_g). MS-ESI: m/z (%) = 295 ($[M+H]^+$, 100 %).IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ = 3400, $\nu_{(C=N)}$ = 1625.

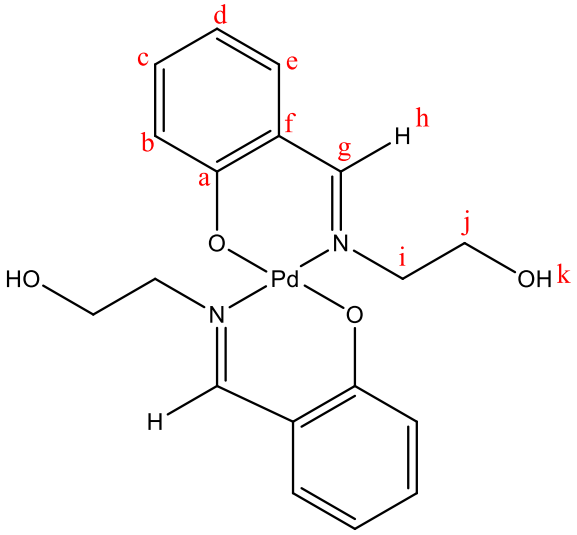
3.2.4 Synthesis of non- water soluble Pd (II) complexes

*3.2.4.1 [Pd (**L1**)$_2$] (**Pd1**)*



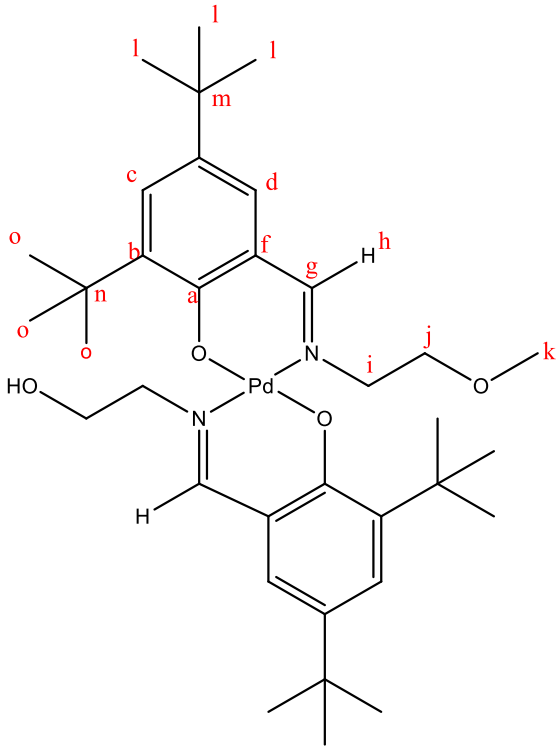
A methanol solution of **L1H** (0.34, 1.80 mmol) (10 ml) was added to a methanol solution of $Pd(OAc)_2$ (0.21g, 0.90 mmol) (10 ml), the mixture was then refluxed for 24 h at 65°C. A precipitate formed after 8hrs. Upon completion of the reaction the precipitate was then filtered, rinsed with methanol (5 ml) and left to dry overnight to afford a yellowish solid. Yield = 0.42 g (47%). ^{1}H NMR (400MHz, $CDCl_3$): δ_H (ppm): 3.39 (s, 3H, H_k), 3.76 (t, 2H, $^3J_{HH}$ = 6.2, H_i), 3.92 (t, 2H, $^3J_{HH}$ = 6.8, H_j), 6.63 (t, 1H, $^3J_{HH}$ = 7.88, H_b), 6.86 (d, 1H, $^3J_{HH}$ = 8.0, H_d), 7.29 (m, 2H, H_c, H_e), 7.71 (s, 1H, H_h). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 57.78 (C_k), 59.01 (C_i), 72.43 (C_j), 114.99 (C_b), 120.09 (C_d), 120.20, (C_f) 134.49 (C_e), 134,58 (C_c), (163.41 (C_a), 164.25 (C_g). ATR-IR ν_{max}/ cm^{-1}: $\nu_{(C=N)}$ = 1615. MS-ESI m/z (%) 463 (M^+, 100), 485 (M^++Na^+). Anal. calcd for $C_{20}H_{24}N_2O_4Pd$: C,51.90; H, 5.23; N, 6.05. Found: C, 51.94; H, 5.26; N, 6.05.

*3.2.4.2 [Pd (**L2**)$_2$] (**Pd2**)*



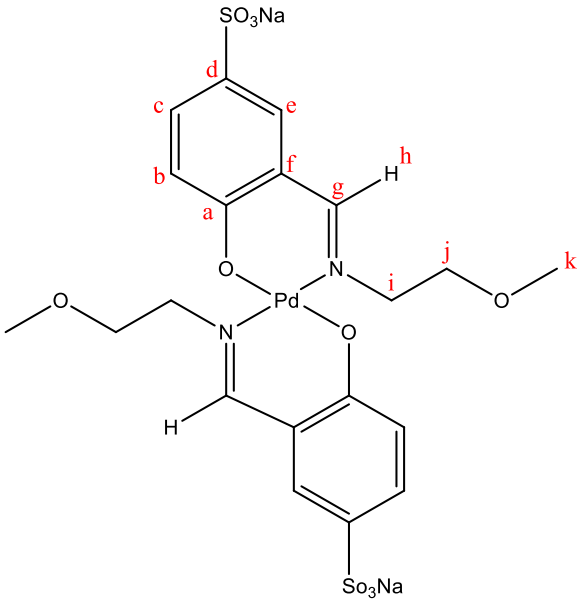
Pd2 was synthesized following the same procedure described for **Pd1**, using **L2H** (0.28 g, 0.82 mmol) and $Pd(OAc)_2$ (0.19 g, 0.41 mmol) to afford a green solid. Yield= 0.39 (71%). ^{1}H NMR (400MHz, $CDCl_3$): δ_H (ppm): 3.73 (t, 2H, $^3J_{HH}$ = 5.00, H_i), 3.78 (t, 2H, $^3J_{HH}$ = 6.00, H_j), 4.77 (t, 1H, $^3J_{HH}$ = 5.20, H_k), 6.60 (t, 1H, $^3J_{HH}$ = 8.0, H_b), 6.78 (d, 1H, $^3J_{HH}$ = 8.2, H_d), 7.25 (t, 1H, $^3J_{HH}$ = 8.1, H_c), 7.39 (d, 1H, $^3J_{HH}$ = 8.0, H_e), 7.92 (s, 1H, H_h). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 59.83 (C_i), 61.30 (C_j), 115.21 (C_b), 120.22 (C_d), 120.54 (C_f), 134.78 (C_e), 135.09 (C_c), 163.84 (C_a), 164.04 (C_g). IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ = 3245, $\nu_{(C=N)}$ = 1603. MS-ESI m/z (%) 457 (M^+Na, 51). Anal. calcd for $C_{18}H_{20}N_20_4Pd$: C,9.72; H,4.64; N, 6.44. found: C,49.52; H, 4.57; H, 6.66.

*3.2.4.3 [Pd (**L3**)$_2$] (**Pd3**)*



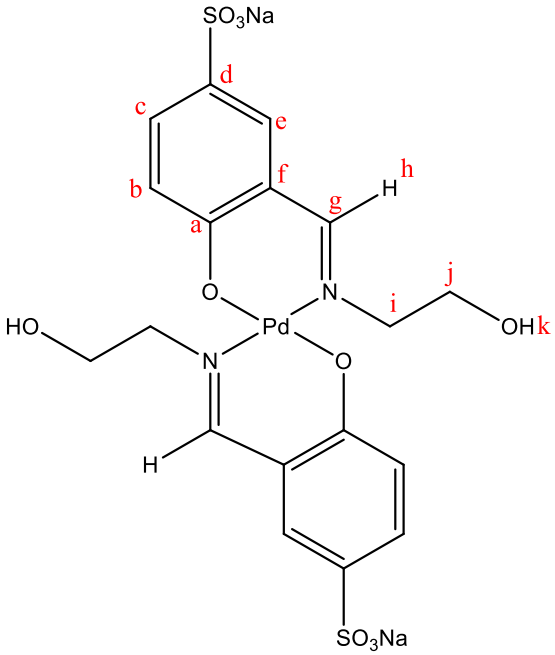
Pd3 was synthesized following the same procedure described for **Pd1,** using **L3H** (0.39 g, 1.3 mmol) and $Pd(OAc)_2$ (0.15 g, 0.65 mmol) to afford an orange solid without any purification. Yield = 0.47 g (67%). ^{1}H NMR (400MHz, $CDCl_3$): δ_H (ppm): 1.29 (s, 9H, H_o), 1.39 (s, 9H, H_l), 3.48 (s, 3H, H_k), 4.10 (t, 2H, $^3J_{HH}$ = 6.3, H_i), 4.00 (t, 2H, $^3J_{HH}$ = 6.9, H_j), 7.02 (d, 1H, $^3J_{HH}$ = 8.2, H_d), 7.38 (d, 1H, $^3J_{HH}$ = 7.2, H_b), 7.60 (s, 1H, H_h). ^{13}CNMR (100 MHz, $CDCl_3$, δ ppm): 29.31(C_o), 31.34 (C_l), 33.76 (C_n), 35.36 (C_m), 58.29 (C_i), 59.20 (C_j), 72.88 (C_k), 120.82 (C_b), 120.99 (C_d), 128.42 (C_f), 129.73 (C_c), 138.49 (C_e), 162.06 (C_a), 164.21 (C_g). ATR-IR ν_{max}/ cm^{-1}: $\nu_{(C=N)}$ = 1621. MS-ESI m/z (%) 687 ([M]$^+$, 100), 709 (M^++Na^+). Anal. calcd for $C_{36}H_{56}N_20_4Pd$: C, 62.91; H, 8.21; N, 4.08. Found: C, 62.92; H, 9.18; N, 4.23.

*3.2.5.1 [Pd (**L4**)$_2$] (**Pd4**)*



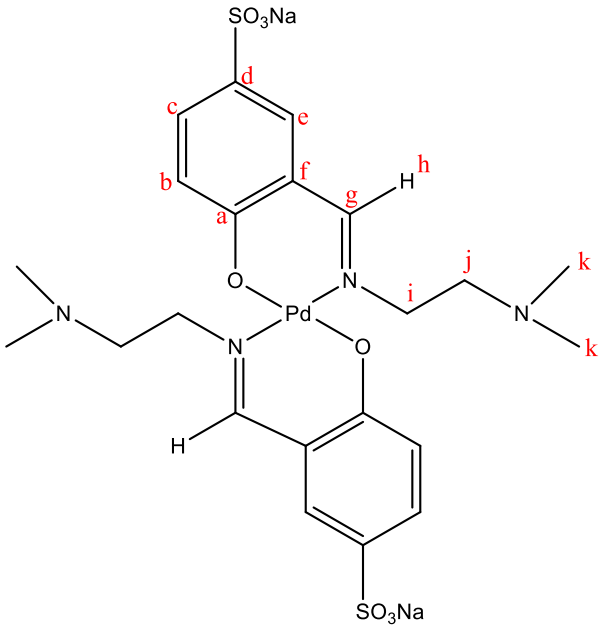
To a solution of **L4H** (0.06 g, 19 mmol) in methanol (10 ml), $Pd(OAc)_2$ (0.02 g, 9.5 mmol) was added, the mixture was stirred for 48 h at ambient temperature under nitrogen. The solvent was removed under vacuum to afford a green solid. Yield = 0.02 g (40%). ^{1}H NMR (400MHz, DMSO): δ_H (ppm) 3.28 (s, 3H, H_k), 3.63 (t, 2H,$^3J_{HH}$ = 8.2 Hz, H_i), 3.86 (t, 2H, $^3J_{HH}$ = 8.0 Hz, H_j), 6.68 (d, 1H, $^3J_{HH}$= 8.0 Hz, H_b), 7.47 (dd, 1H, $^3J_{HH}$= 7.5 Hz, $^4J_{HH}$ = 2.0 Hz, H_c), 7.63 (d, 1H, $^4J_{HH}$= 2.10 Hz, H_e), 7.99 (s, 1H, H_h).^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 59.83 (C_i), 61.30 (C_j), 72.02 (C_k), 115.21 (C_b), 120.22 (C_f), 120.54 (C_d), 134.78 (C_c), 135.09 (C_e), 163.84 (C_g), 164.04 (C_a). ATR-IRν_{max}/ cm^{-1}: $\nu_{(C=N)}$ =1624. MS-ESI m/z (%) 689 (M^++Na^+). Anal. calcd for $C_{20}H_{22}N_2Na_2O_{10}PdS_2$:C, 36.02; H, 3.32; N, 4.20. Found: C, 36.29; H, 3.14; N, 4.09.

*3.2.5.2 [Pd (**L5**)$_2$] (**Pd5**)*



Pd5 was synthesized following the procedure described for **Pd4** using **L5H** (0.11 g, 40 mmol) and $Pd(OAc)_2$ (0.04 g, 20 mmol). Yield = 0.26 g (78%). ^{1}H NMR (400MHz, DMSO): δ_H (ppm) 3.45 (s, 1H, H_k), 3.65 (t, 2H,$^3J_{HH}$ = 4 Hz, H_i), 3.75 (t, 2H, $^3J_{HH}$ = 6.0 Hz, H_j), 4.77 (d, 1H, $^3J_{HH}$= 7.0 Hz, H_b), 7.46 (dd, 1H, $^3J_{HH}$= 6.0 Hz, $^4J_{HH}$ = 2.0 Hz, H_c), 7.63 (d, 1H, $^4J_{HH}$ = 8.0 Hz, H_e), 8.3 (s, 1H, H_h). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 59.69 (C_j), 52.30 (C_i), 118.79 (C_c), 119.19 (C_e), 132 (C_f), 132.58 (C_c), 136.15 (C_d), 163.86 (C_a), 164.18 (C_g). ATR-IR ν_{max}/ cm^{-1}: $\nu_{(C=N)}$ = 1621. MS-ESI m/z (%) 661 (M^++ Na^++H^+, 100). Anal. Calcd for $C_{18}H_{18}N_2Na_2O_{10}PdS$: C,33.84; H, 2.84; N, 4.38. Found: C, 32.65; H, 2.34; N, 4.84

*3.2.5.3 [Pd (**L6**)$_2$]* (**Pd6**)



Pd6 was synthesized following the procedure described for **Pd4**, using **L6H** (0.04 g, 0.13 mmol) and Pd(OAc)$_2$ (0.015 g, 0.065 mmol). Yield= 0.29 g (65%). ^{1}H NMR (400MHz, DMSO): δ_H (ppm) 2.28 (s, 1H, H$_k$), 2.60 (t, 2H,$^3J_{HH}$ = 6.7 Hz, H$_j$), 3.63 (t, 2H, $^3J_{HH}$ = 6.7 Hz, H$_i$), 6.70 (d, 1H, $^3J_{HH}$= 7.20 Hz, H$_b$), 7.80 (dd, 1H, $^3J_{HH}$= 6.7 Hz, $^4J_{HH}$ = 2.0 Hz, H$_c$), 7.95 (d, 1H, $^4J_{HH}$ = 1.8 Hz, H$_e$), 8.30 (s, 1H, H$_h$). ^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 46.73 (C$_k$), 52.67 (C$_i$), 66.88 (C$_j$),116, 98 (C$_b$), 118.43 (C$_b$), 124,50 (C$_f$), 131.14 (C$_c$), 138.12 (C$_d$), 161,25 (C$_g$), 165.52 (C$_a$). ATR-IR ν_{max}/ cm^{-1}: $\nu_{(C=N)}$ =1625, $\nu_{(C-N)}$ = 1616. MS-ESI m/z (%) 671 (M^+-Na^+, 60). Anal. Calcd for $C_{22}H_{28}N_4Na_2O_8PdS_2$: C,38.13; H,4.07; N,8.08. Found: C, 37.65; H ,7.34; N, 8.99.

3.2.6 General procedure for the methoxycarbonylation reactions

The methoxycarbonylation catalytic reactions were carried out in a stainless-steel autoclave equipped with a temperature control unit and a sample valve where the sample is purged. In a typical experiment, complex **Pd1** (37.29 mg, 0.08 mmol), HCl (0.025 ml), 1-hexene (2 ml, 16.00 mmol) and PPh_3 (0.04 g, 0.16 mmol) were dissolved in a mixture of toluene (30 ml) and methanol (30 ml). The reactor was then evacuated and the catalytic solution delivered into the reactor through a cannula and purged three times with CO, set to the reaction temperature and pressure and then the reaction stirred at 500 rpm. At the end of the reaction time, the reactor was cooled to room temperature, excess CO vented off and samples drawn and filtered using micro-filter prior to GC analysis to determine the percentage conversion of the substrate to the products.

3.2.7 General procedure for GC analysis

The GC analyses was using a Varian CP-3800 gas chromatograph fitted with flame ionization detector and run under the standard chromatography conditions of; 25 m (1.2 mm film thickness) CP-Sil 19 capillary column, injector temperature 250°C, oven program 50°C for 4 minutes, rising to 200 °C at 20 °C/min and holding at 200°C, nitrogen carrier column gas 5. GC-MS analyses were run under the following standard chromatography conditions: -25 m CPSil 19 capillary column, 1.2 mm film thickness, Helium carrier column gas 5 psi, injector temperature 250 ˚C, oven program 50 ˚C for 4 minutes rising to 200 ˚C at 20 ˚C/ min and holding at 200 ˚C. For determination of conversion and percentage yield, samples were filtered by micro-filter prior being subjected to GC analysis, 0.2 ml of ethylbenzene was used as an internal standard in a total sample volume of 1.8 ml and GC–MS was used for the identity of the ester products, whereas the linear and branched esters were assigned using commercial linear methyl heptanoate standard

sample. The percentage yield was calculated using equation 1 and 2 [16] , using the R factor extrapolated to be 0.4412. whereas the Turn over frequency (TOF) and Turn over number (TON) was calculated using equation 3 and 4 respectively.

Equation 1: R.F = $\frac{Ax}{Ais} \times \frac{Cis}{Cx}$

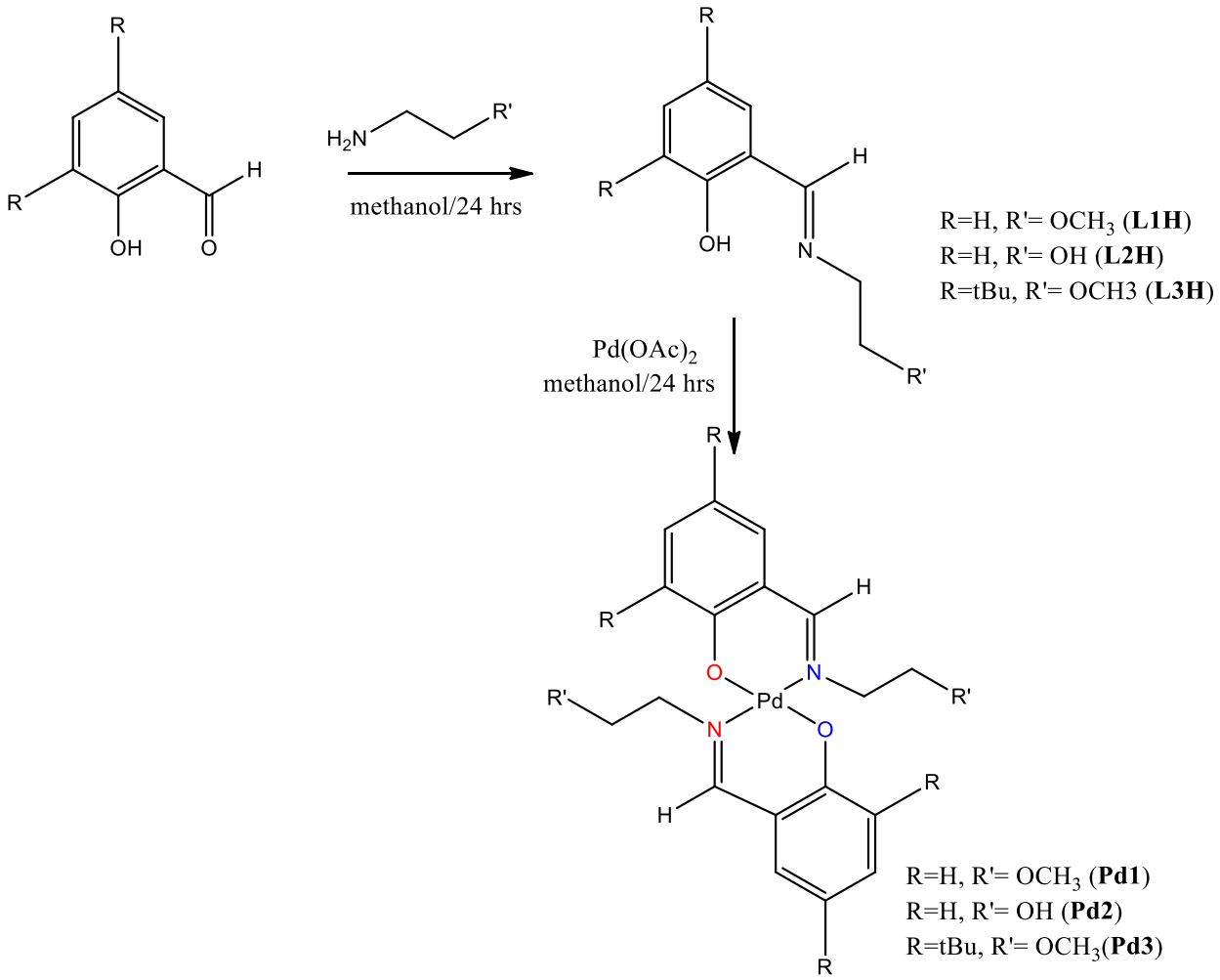
Equation 2: Cx = $\frac{Ax}{Ais} \times \frac{Cis}{RF}$

Where Ax, Ais, Cis and Cx = peak area of analyte, peak area of internal standard, concentration of internal standard and concentration of the analyte respectively.

3.3 Results and discussion

3.3.1 Synthesis of Schiff base ligands and their complexes

The Schiff base ligands (**L1H-L3H**) were synthesized *via* a condensation reaction of salicylaldehyde and the corresponding amine: methoxylamine, (**L1H**) 2-amino ethanol (**L2H**). In addition, 3,5 ditertbutylsalicylaldehyde was also reacted with methoxylamine to afford **L3H** (**Scheme 3.1**)**.** The non -water soluble ligands were synthesized according to previously reported literature methods [17, 18] and were obtained in excellent yield (81-85%). Pd(II) complexes (**Pd1-Pd4**) were synthesized according to a modified procedure [19] with low to good yield (40-76%). Characterization of all the compounds involved using ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopy, HRMS-ESI and X ray crystallography for **Pd1** and **Pd3**.

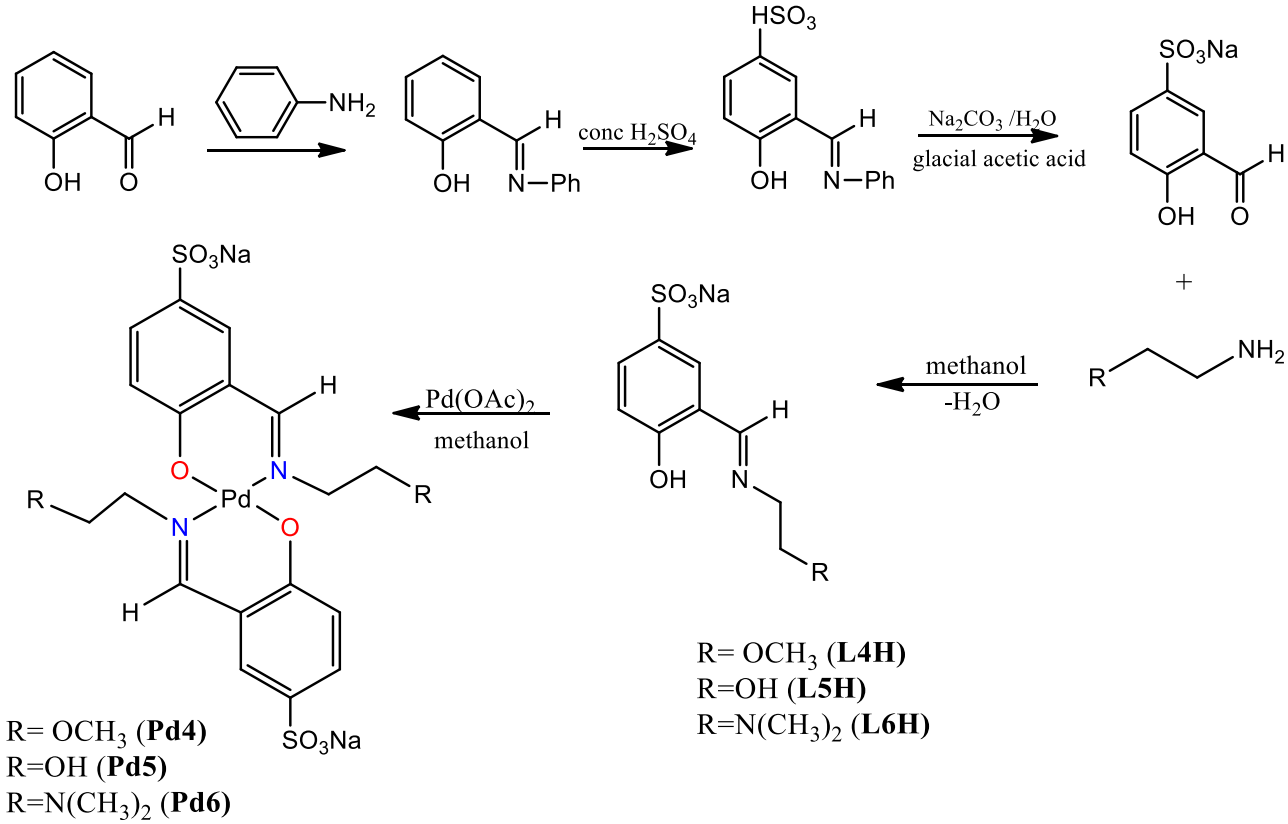


Scheme 2.1: Synthetic route of Schiff base ligands (**L1H-L3H**) and their corresponding Pd (II) complexes (**Pd1-Pd3**)

3.3.2 Synthesis of water- soluble Schiff base ligands and their corresponding complexes

The synthesis of water soluble ligands (**L4H-L6H**) was carried out following a previously reported procedure [20].These ligand are also prepared via a condensation reaction using 3-Formyl-4-hydroxybenzensulfonic acid sodium salt (**S3**) and the respective amine: 2-methoxyethylanaline, 2-amino ethanol and 1,2-ethanediamine to afford **L4H**, **L5H** and **L6H** respectively. (**Scheme 3.2)**. Treatments of water-soluble Schiff base with $Pd(OAc)_2$ gave Pd (II)

complexes (**Pd4-Pd6**) in low to moderate yield (39- 66%). The compounds were indeed found to display excellent solubility in water at ambient temperatures and were characterized 2by ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopy, HRMS-ESI and Elemental Analysis.



Scheme 2.2: Synthesis of water-soluble Schiff base ligands (**L4H-L6H**) and their corresponding Pd (II) complexes (**Pd4-Pd6**).

The ^{1}H NMR spectra of the ligands (**L1H-L6H**) were obtained using DMSO and their synthesis were confirmed. For instance, a signature peak observed at 8.34-8.54 ppm was realized for all the ligands synthesized, this signal was assigned to the proton of the azomethine group (H-C=N), thus this validates the replacement of the carbonyl (C=O) specie with the imine bond (C=N), these

chemical shifts recorded are comparable with those reported by Abbasi *et al.* [21] and Hager *et al*.[20]. Both aliphatic and aromatic signals expected for these types of compounds were observed, methylene proton present in the pendant groups were observed to resonate at the lower end of the spectra (2-3 ppm). **L1H** and **L2H** showed four aromatic peaks whereas **L3H** only showed two proton peaks because of the t-butyl substituents in the third and fifth position. On the other hand water-soluble Schiff bases only revealed three aromatic proton signals due to the incorporation of the sulfonate moiety in ortho position with the hydroxyl species. Moreover, two set of doublets with coupling constants of 8.2 Hz and 6.4 Hz respectively were realized. Similar observation are reported by Hager *et al.* [20] and Dauchy *et al.* [22].

^{1}H NMR spectra of the complexes (**Pd1**-**Pd6**) revealed an overall upfield shift of the azomethine proton from 8 ppm - 7ppm. For instance, while the imine proton resonated at 8.37 ppm in **L1H**, the corresponding complex **Pd1** has the same proton shifting upfield to 7.71 ppm (**Figure 3.1)**. The significance shift of this peak is a clear indication of the successful coordination of the ligand to the palladium metal centre. This trend is also observed in similar N^O bischelated Pd(II) complexes reported by Akiri & Ojwach [13].

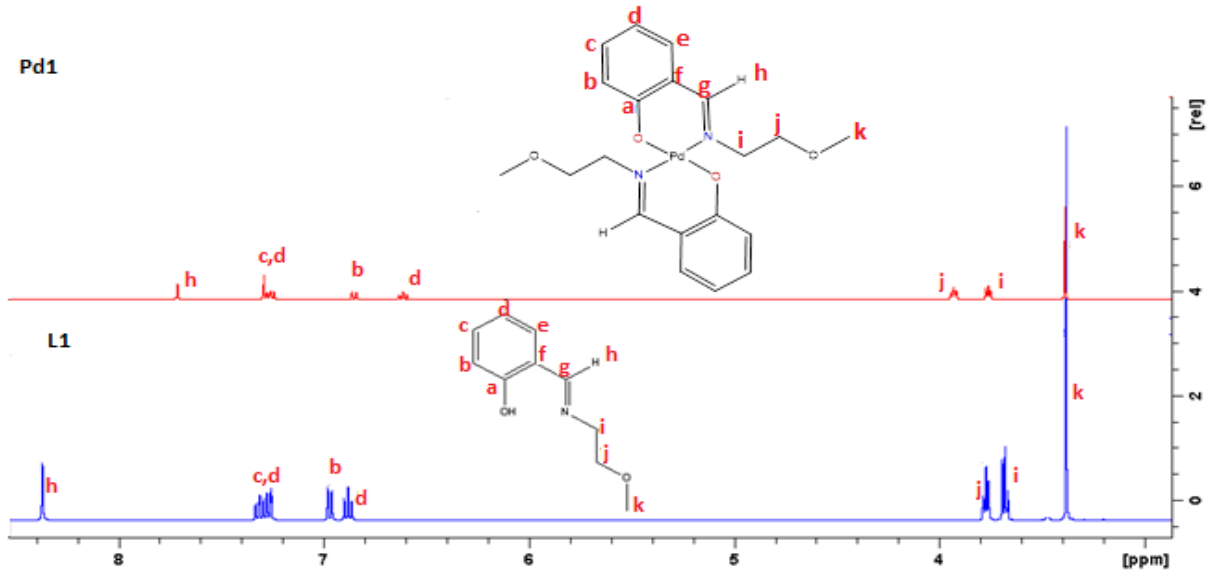


Figure 2.1: Overlay ^{1}H NMR spectra of **L1H** and **Pd1** showing an upfield shift of the aldimine proton peak labelled (h) at 8.4 ppm and 7.8 ppm for the ligand and complex respectively

^{13}C NMR data were consistent with the ^{1}H NMR data, all the number of signals observed were in correspondence with the number of carbons present in the structures. Two distinctive signals attributed to imine carbon (C=N) and carbonyl carbon(C=O) were observed to resonate in the downfield region for Schiff base ligands 161 ppm and 166 ppm respectively (**Figure 3.2**). However, in the ^{13}C NMR of the complexes, the imine carbon and carbonyl carbon were observed to shift to 166 and 164 ppm respectively. This significant change is also a validation of a successful coordination of the ligand with the palladium center.

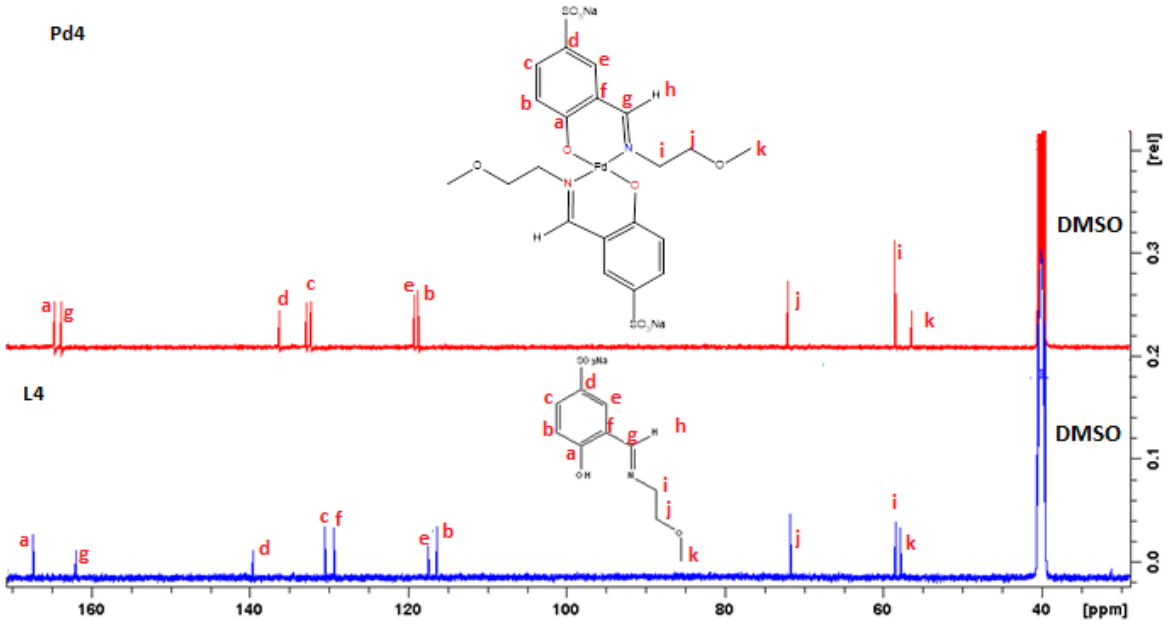


Figure 2.2: Overlay ^{13}C NMR spectra of L4H and Pd4 showing carbonyl carbon shift from 164 ppm to 162 ppm (a) and imine carbon (g) shift 161 ppm to 162 ppm respectively.

For further elucidation of the structures, FT-IR spectra of the Schiff base ligands (**L1H-L6H**) were recorded and they revealed the most characteristic absorption band ν(C=N) observed in the region range of 1625 cm^{-1}-1651 cm^{-1} (**Table 3.2**). This observation is in agreement with formation of azomethine functionality observed in the ^{1}H NMR and ^{13}C NMR spectra. However, the ν(C=N) signal was observed to stretch at slightly lower frequency for complexes, for instance, in the spectrum of **L1H,** the ν(C=N) band appeared at 1630 cm^{-1} compared to its respective complex **Pd1** (1610 cm^{-1}). This trend has been observed upon complexation of Pd complexes reported in literature studies [22, 23]. Looking at our ligand architecture, it is expected that an ν(OH) broad band associated to the phenol moiety should appear in the range of 3000 -3800 cm^{-1},surprisingly, this was not the case for all the ligands. For instance, the broad band only appeared for water-

soluble Schiff bases (**L4H-L6H**). This occurrence is due to the ability of Schiff bases to exist in zwitterionic form, caused by intramolecular strength of N-H-O hydrogen bond. Similar trend is observed and explained by Król-Starzomska *et al.* [25] and Hernandez *et al.* [26] (**Figure 3.3**).

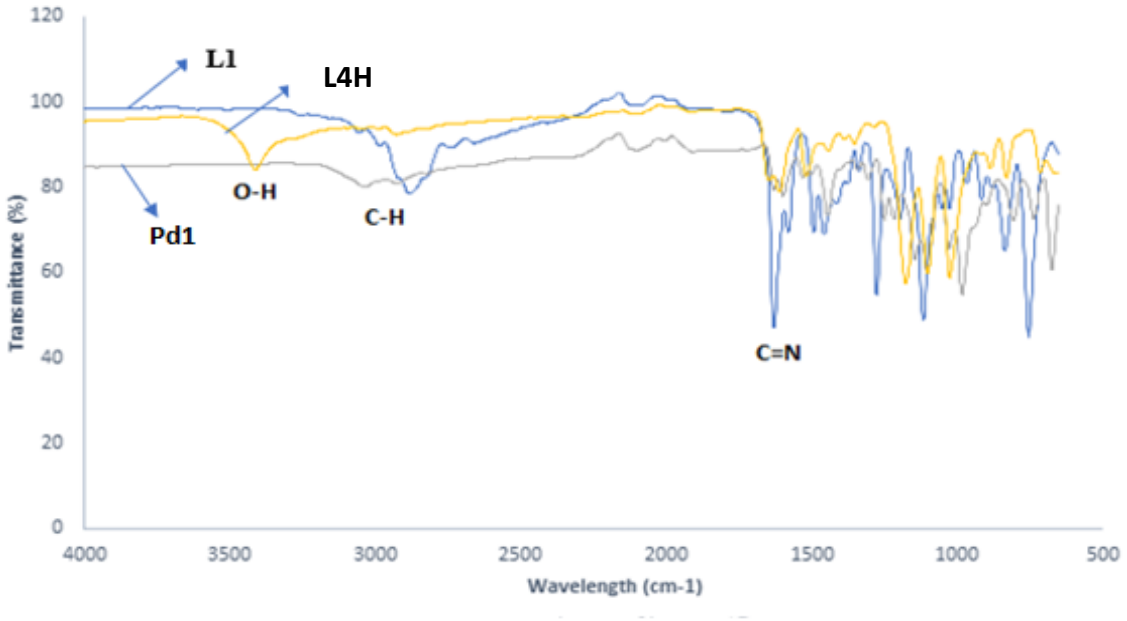


Figure 2.3: Overlay FT-IR spectra of **L1H**, **L4H** and **Pd1** showing the appearance and disappearance of ν (C=N) and ν (OH) band at 1651 cm-1 and 3400 cm-1 respectively.

Table 2.1: Hydroxy and imine stretches observed for the Schiff base ligands and their corresponding Pd(II) complexes

Schiff base ligand	OH (ν cm^{-1})	C=N(ν cm^{-1})	Complex	OH (ν cm^{-1})	C=N (ν cm^{-1})
L1H	absent	1630	**Pd1**	absent	1613
L2H	3346	1628	**Pd2**	3123	1634
L3H	absent	1628	**Pd3**	absent	1620
L4H	3410	1624	**Pd4**	absent	1623
L5H	3450	1625	**Pd5**	3145	1615
L6H	3350	1622	**Pd6**	absent	1625

Mass spectral data was obtained to further verify identity of the ligands and their respective Pd(II) complexes, the positive ion mass spectra of the compounds showed molecular ion peaks of the cations along with various peaks corresponding to the molecular fragments and comparable to the theoretical mass distribution patterns. For instance, ESI-MS of ligand **L1H (**Mw =179**)** showed a base peak $[M]^+$ at *m/z* =179 corresponding to the molecular mass of the compound in addition to another resonating at m/z= 180 which is associated to the $[M+H]^+$, furthermore, mass spectrum of **Pd1** (Mw = 463) revealed a base peak at m/z= 463 (and a molecular ion peak at m/z= 485 attributed to $[M+Na]^+$ fragment. Noteworthy to mention that the peak distribution patterns of complexes are similar to that of theoretical isotopic mass distribution patterns. Most intriguing was the trend observed for the water-soluble Schiff bases, where only the negative ion mode mass spectral data was observed, for instance **L4H** (Mw= 281) revealed m/z= 258 [M-

Na]$^{+}$fragmentation while its corresponding **Pd4** exhibited a peak at m/z= 644. Noteworthy to mention that the ESI-MS for water soluble Schiff bases and complex were all obtained in negative mode

The data observed for **L4H** and **Pd4** indicates that the Na cation was fragmentated during the ionization. Similar trends were observed for **L5H** and **L6H** and their corresponding complexes.

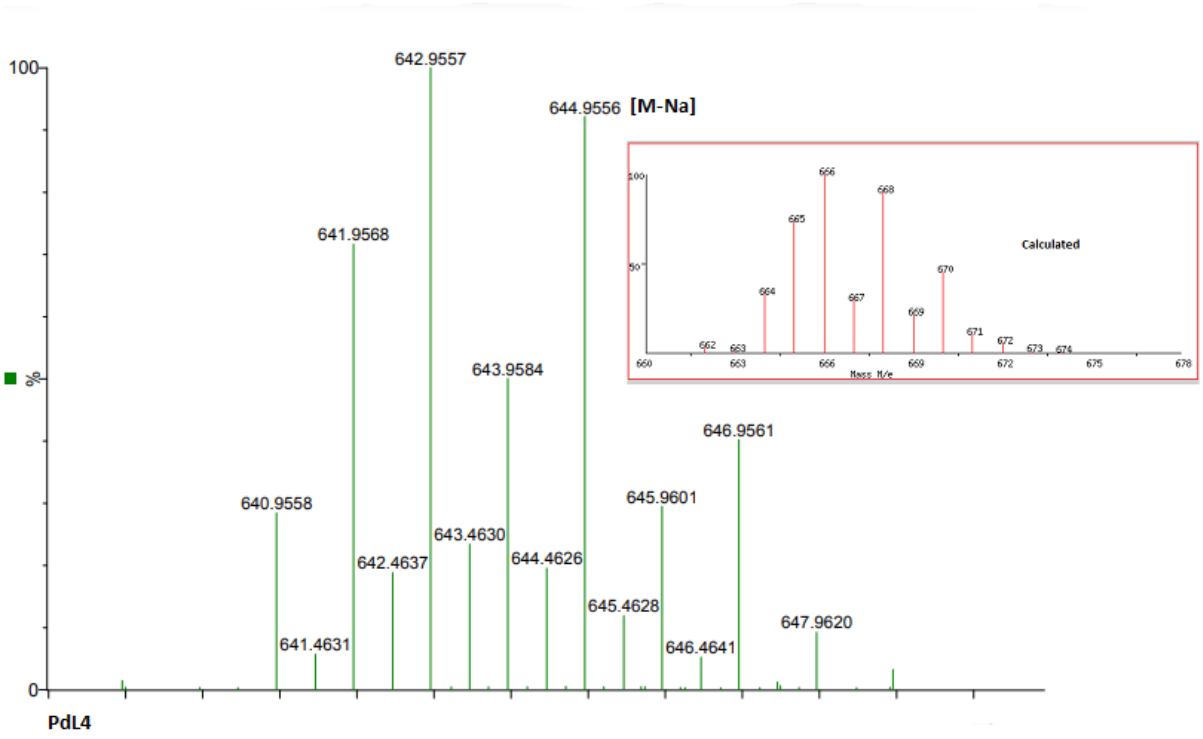


Figure 2.4: An overlaid mass spectra of ligand **Pd4** showing [M-Na] fragmentation at 644.95 m/z and the theoretical molecular mass of 666.95 m/z and its corresponding distribution patterns.

Table 2.2: Mass spectral data for Schiff base ligands and Pd(II) complexes

Schiff base Ligands	Molecular mass	m/z (amu)	Complexes	Molecular mass	m/z (amu)
L1H	179.09	180.1025 $[M+H]^+$	**Pd1**	462.08	484 $[M+Na]^+$
L2H	165.08	166.0863 $[M+H]^+$	**Pd2**	434.05	473$[M+Na]^+$
L3H	291.22	292.2282 $[M+H]^+$	**Pd3**	686.33	709 $[M+ Na]^+$
L4H	281.03	258 $[M-Na]^+$	**Pd4**	665.95	644$[M-Na]^+$
L5H	267.02	244$[M-Na]^+$	**Pd5**	639.92	617$[M-Na]^+$
L6H	294.07	295$[M+H]^+$	**Pd6**	692.02	714$[M+Na]^+$

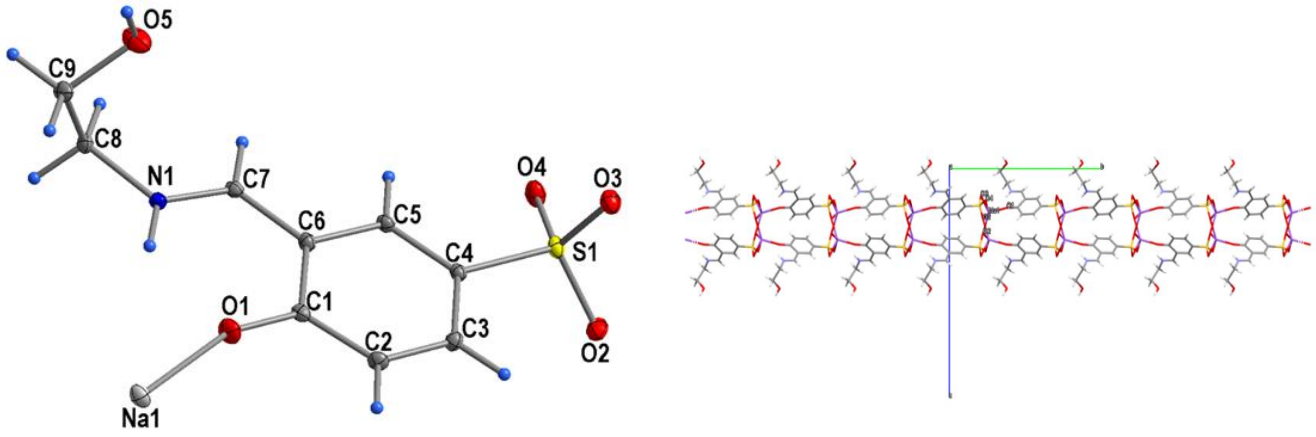
3.3.2 Single crystal structure determination

In an aim to verify the proposed coordination modes of the bis(chelated) N^O Pd(II) homogeneous complexes, single crystal structures suitable X-ray analysis for **Pd1** and **Pd3** (Figure 3.5 and 3.6) were obtained by slow diffusion of hexane in CH_2Cl_2 solutions of the complexes at room temperature. In addition, crystal structures of the new water-soluble Schiff base ligands **L4H** and **L6H** were obtained. Crystallographic data and structural refinement parameters are shown in **Table 2.3**.

Table 2.4: Selected crystal data for **L4H** and **L6H** ,**Pd1** and **Pd4**

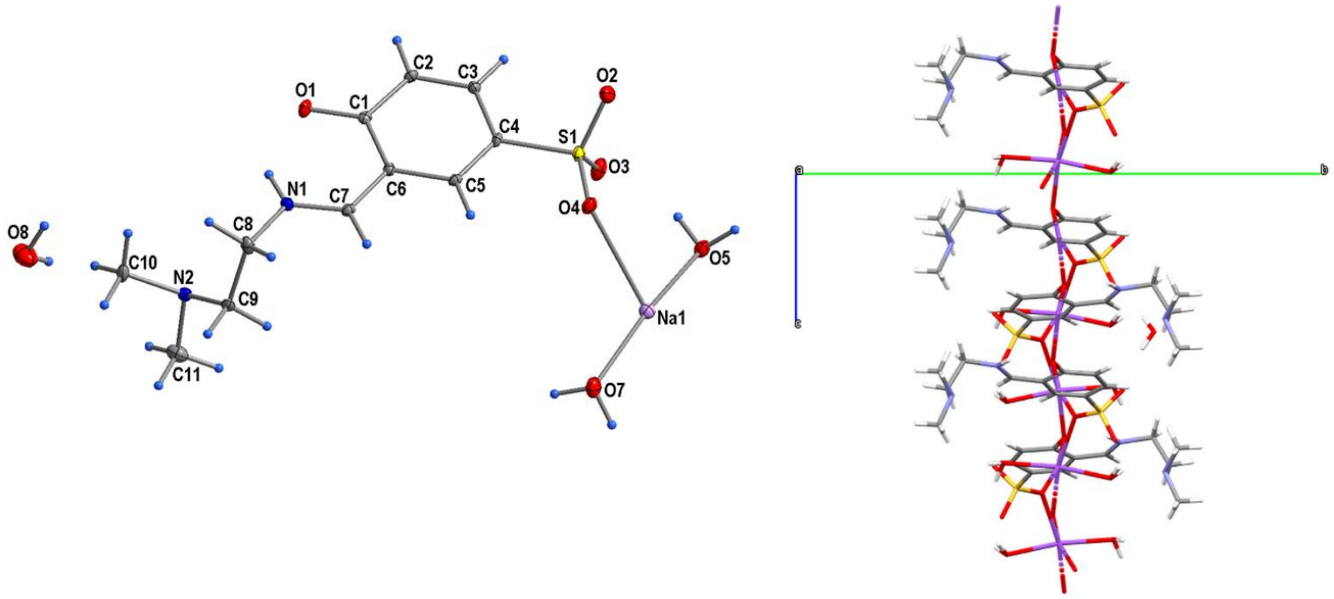
Parameter	**L4**	**L6**	**Pd1**	**Pd3**
Empirical formula	C_{10} $H_{0.12}$ N_0 Na O_2 S	C_{11} H_{21} N_2 Na O_7 S	C_{13} H_{12} $N_{0.25}$ $O_{0.25}$ $Pd_{0.50}$	C_{36} H_{56} N_2 O_4 Pd
Formula weight	207.28	348.35	228.93	687.22
Temperature	100(2) K	103(2) K	100(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Crystal system	*Pbca*	*Cc*	$P2_1/c$	$P2_1/c$
Unit cell dimension	a = 5.7992(3) Å α = 90° b =17.8850(11) Å β = 90°(2) c =22.5730(14) Å γ = 90°.	a = 10.1508(6) Å α = 90°. b = 23.0284(15)Å β = 106.555(2)° c = 6.9911(4) Å γ = 90°.	a = 9.0195(6)Å α= 90° b = 9.8714(6) Å β= 98.454(3)°. c = 10.6886(7) Å γ = 90°	a = 14.2175 (5)Å α = 90° b = 10.4771 (4) Å β = 102.076° (2) c = 25.2304 (10) Å γ = 90°
Volume	2341.2 (2) $Å^3$	1566.47(17) $Å^3$	941.32(11) $Å^3$	3675 (2) $Å^3$
Z	8	4	4	4
Density (calculated)	1.322 Mg/m^3	1.477 Mg/m^3	1.615 Mg/m^3	1.242 Mg/m^3
Absorption coefficient	0.283 mm^{-1}	0.269 mm^{-1}	0.999 mm^{-1}	0.542 mm^{-1}
Crystal size	0.205 x 0.056 x 0.052 mm^3	0.563 x 0.320 x 0.060 mm^3	0.800 x 0.420 x 0.360 mm^3	0.800 x 0.420x 0.360 mm^3
Theta range for data collection	1.804 to 26.709°.	1.769 to 26.635°.	2.283 to 28.987°.	1.523 to 26.694°
Index ranges	-7<=h<=5, -22<=k<=22, -28<=l<=28	-12<=h<=12, -28<=k<=28, -8<=l<=7	-12<=h<=12, -13<=k<=13, -14<=l<=14	-17<=h<=17, -13<=k<=13, -31<=l<=27
Independent reflections	3061 [R(int) = 0.0238]	3061 [R(int) = 0.0238]	2465 [R(int) = 0.0203]	7620 [R(int) = 0.0240]
Completeness to theta	99.9 %	99.0 %	99.0 %	92. 0 %
Goodness-of-fit on F^2	1.081	1.402	1.006	0.896

Both structures confirmed the formation of ligands and are zwitterionic influenced by intramolecular N-H--O hydrogen bonding between the amino N(1)—H and phenolic oxygen O(1). For compound **L4H**, the anion was stabilized by a Na cation. In fact, its asymmetric unit consists of Na^{+} and $L4^{-}$ cations and anions. The Na centre is five coordinate and has a distorted square pyramidal geometry in which the phenolic O atom occupies the apex while sulphonate O atoms occupy the other coordination sites as the base of the pyramid. The bond angle around the Na center range between 58 and 149°. The asymmetric unit of the solvated **L6H** on the other hand contains the Na cation, **L6**H anion two coordinated water molecules and an uncoordinated water molecule. In its structure, the Na centre is six coordinate resulting in a distorted octahedral geometry with the two coordinating water molecules occupying the axial positions while the equatorial positions are occupied by two phenolic O atoms from two separate **L6H** ligands and two sulphonate O atoms from two separate **L6H** ligands. The bond angle around the Na center range between 79.16 and 171.59°. A similar trend was also noted by Ozlem and co-workers [27]



(a) (b)

Figure 2.5: Single crystal structure of anionic Schiff base ligand **L4H** (a), showing sodium ion coordinated to the phenolic oxygen atom and coordination polymer (b).



(a) (b)

Figure 2.6: Single crystal structure of Schiff base **L6H** (a), showing two H_2O molecules coordinated to Na ion and one free H_2O molecule and its coordination polymer

In the crystal packing of **L4H**, O_2 bridges two Na centers while kind of terminally coordinated to the Na center. This results in alternating anion cation strips in a rope ladder-like formation in the crystallographic *b* direction. These ladders are connected to adjacent ones and form polymeric network parallel to the *ab* face. In the crystal packing of **L6H**, only O4 and O1 from two different ligands bridge two Na centers. This is done in an alternating manner such that the alternating anion-cation networks are formed parallel to the *ac* face of the unit cell. O5 and O7 are terminally coordinated as they do not participate in the coordination polymer formation. In both structures the entire lattice is held through other interactions.

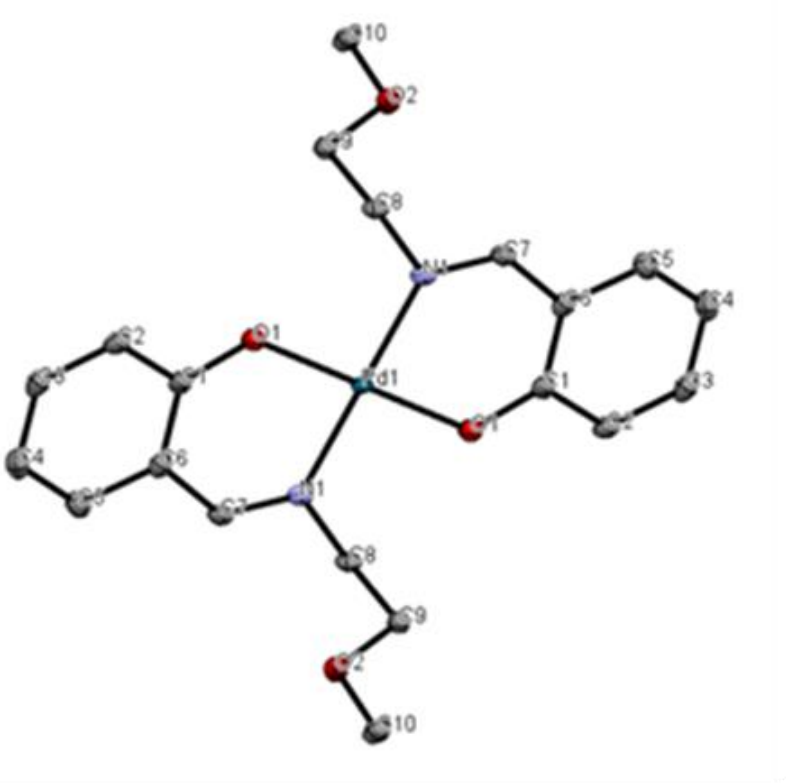


Figure 2.7: Single crystal structures of **Pd1** showing C2 axis of symmetry (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Pd-N, 2.0257; Pd-N, 2.0258; Pd-O, 1.9795; Pd-O, 1.9799; O-Pd-O, 180.0; N-Pd -N, 180.0; O-Pd-N, 92.44; O-Pd-N, 87.56; O-Pd-N, 91.55.

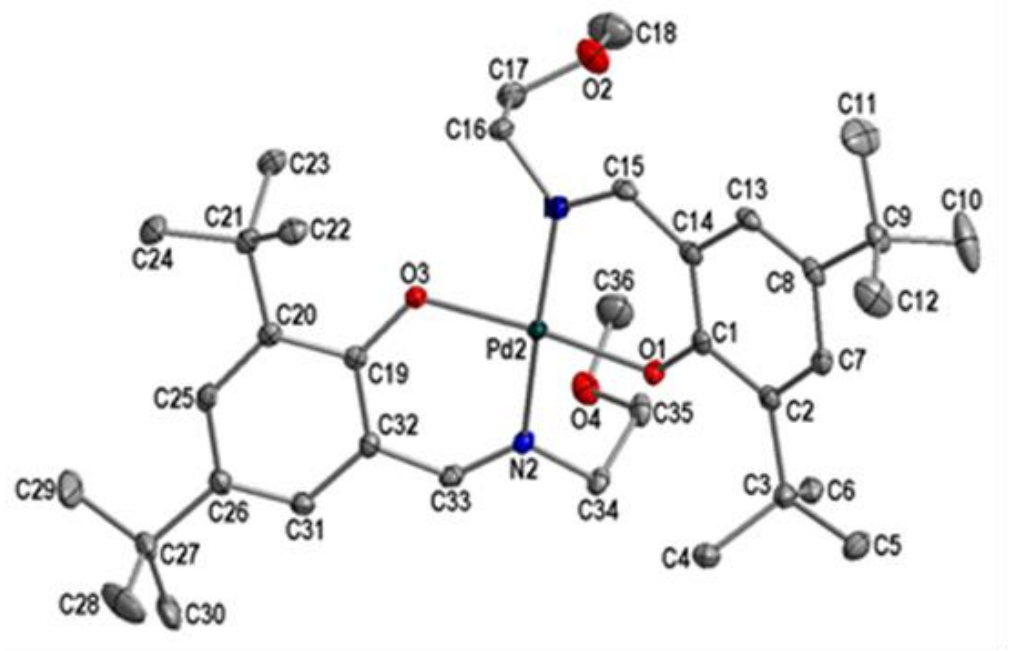


Figure 2.8: Single crystal structures of Pd3 showing C2 axis of symmetry (H atoms for clarity).Selected bond lengths (Å) and angles (°): Pd(2)-O(1), 1.9976; Pd(2)-O(3), 2.0003; Pd(2)-N(2), 2.0037; Pd(2)-N(1), 2.0120; O(1)-Pd-O(3), 173.10; N(2)-Pd-N(1), 171.35; O(1)-Pd-N(2), 88.15; O(3)-Pd-N(2), 91.20; O(1)-Pd-(N), 89.86

The solid-state structures of **Pd1** revealed that the symmetry unit possess one half a molecule of the complex, the other half is generated by C_2 axis whereby the Pd ion is situated at the center. The molecular structures of **Pd1** and **Pd3** confirmed the formation of mononuclear complexes in which the Schiff base **L1H**, **L3H** adopt a bidentate coordination mode to the palladium centre, in a bis(chelated) fashion through the deprotonated phenolic oxygen atom and the imino nitrogen atom. The observed bite angles and bond lengths exhibited by the structures indicates square planar geometry for both complexes points to the square planar. For instance, **Pd1** shows bite angles for O(1)-Pd(1)-N(1) and O(1)-Pd(1)-N(2) of 92,44° and 87,56° respectively, while **Pd3** displayed

bite angles for O(1)-Pd-N(1) and O(3)-Pd-N(2) of 88.15 and 91.20 respectively. In addition, it is worthy to mention that dihedral angles of O(3)-Pd-O(1) and N(1)-Pd-N(2) were respectively found to be 173.10° and 171. 35° for **Pd3**, showing minimal deviation from the ideal angle of 180°. This clearly shows that **Pd3** possesses higher level of distortion as opposed to **Pd1**, owing to the steric demand of **L3** induced by the presence of the t-butyl substituents. **Pd1** average bond length of Pd-O and Pd- N_{imine} distances of 1.9795Å and 2.0257Å respectively are similar to those of related complexes [28, 29]. However, Pd-O(1) (1.9976 Å) and Pd-O(1) (2.003 Å) bond distance for **Pd3** were found to be slightly longer than those of similar compounds of 1.982 Å whereas Pd-N_{imine} bond lengths were within the range observed in related complexes [29]. The longer bond distance observed for Pd-O may be due to the electronic effect exhibited by the alky substituents present in **L3H**, even though they are remotely located from the Pd atom.

3.4 Conclusions

Non-water-soluble and water-soluble Schiff base ligands (**L1H**-**L6H**) were successfully synthesized and fully characterized by spectroscopic techniques. Reactions of Schiff base ligands (**L1H**-**L6H**) with $Pd(OAc)_2$ gave **Pd1**-**Pd6** in moderate to good yields (53-67%). Single crystal structures of **L4H** and **L6H** obtained revealed the expected molecular structures showing successful coordination of sulfonate moiety. Molecular structures of **Pd1** and **Pd3** showed the expected bis(chelation) of the N^O donor ligands to the palladium centers. Both structures were observed to have a distorted square planar geometry, with **Pd3** bearing sterically demanding butyl groups which resulted in more distortion.

3.5 References

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Chapter 4

Investigation of water-soluble and non-water soluble N^O palladium(II) complexes as catalysts in methoxycarbonylation of alkenes

4.1 Introduction

Methoxycarbonylation of olefins is a clean pathway for the synthesis of carboxylic acid functional groups such as esters. The esters are then further utilized in the manufacture of industrial and domestic products such as detergents, cosmetic and pharmaceuticals. For example, branched esters are extensively used in the production of anti -inflammatory drugs namely; ibuprofen and naproxen [1, 2], whereas alkyl aliphatic or aliphatic esters are mainly used for solvents, food colorants, detergents, fragrances and surfactants [3, 4]. The use of transition- metal complexes in catalytic systems has advanced over the past years, however, the search for more effective systems continues to be of high importance since researchers are still evaluating different chemical properties of different complexes in attempt to obtain best catalytic systems.

To date, palladium complexes bearing different ligand architecture has been discovered to be worthy for methoxycarbonylation reactions, owing to the observed thermal stability, high activity and superior selectivity they exhibit [5-7]. Literature studies has shown that homobidentate complexes results in appreciable activities, however, heterobidentate complexes leads to enhanced activity due to increased robustness. The selectivity is believed to mainly influenced by the denticity of the complex, for instance, bidentate complexes tend to favor the formation of less sterically demanding linear esters meanwhile monodentate favours branched esters [7-11].

However, the reaction conditions employed and substrates investigated can lead to varied regioselectivity [12-16].

In attempt to bridge a gap between homogeneous and heterogeneous systems, developments of systems with easy separation of the products has over the last years. Researchers have investigated several approaches in combining the strengths of these type of systems. For instance, immobilization of a catalyst on solid support, which involves modification of the ligand or the catalyst precursor [17-21]. Another approach is liquid/liquid or multiphase system, whereby a catalyst is immobilized on the other phase while the products rest on the second phase [22, 23]. The biphasic media can be achieved by incorporating water-soluble groups such as sulfonates, carboxylate, ammonium or phosphonium species on the ligand motif [24]. This type of system is the most attractive not only because it enables easy recyclability, but also due the use of water as a solvent.

In this Chapter, we report an investigation on N^O- donor non-water-soluble and water-soluble palladium(II) complexes as catalysts in the methoxycarbonylation of olefins. Details on the effects of catalyst structure, reaction condition, nature of substrate and recycling studies are discussed.

4.2 Experimental section

4.2.1 General procedure for methoxycarbonylation reactions

The catalytic methoxycarbonylation reactions were carried out in a stainless-steel autoclave equipped with temperature control unit and a sample valve. All the reagents and solvents used below were purchased from Sigma Aldrich and were dried following relevant methods. Methanol was dried over 3Å molecular sieves overnight followed by distillation, whereas acetone, diethyl ether was dried via distillation using calcium hydride, dichloromethane was dried over P_2O_5 and distilled prior use. The chemicals, 1-hexene (99%) , methyl heptanoate (98%), and ethyl benzoate (98%) were obtained from Sigma Aldrich and used without further purification. In a typical experiment, **Pd1** (0.03 g, 0.08 mmol), PPh_3 (0.04 g, 0.16 mmol), HCl (0.02 mL, 0.80 mmol) and 1-hexene (2.00 ml, 15.89 mmol) were dissolved in methanol (20 ml) and toluene (20 ml). The reactor was evacuated the solution was introduced to the reactor via cannula. The reactor was then purged three times with carbon monoxide gas set at required pressure and temperature and stirred at 50 rpm. Upon completion of the reaction, the reactor was then allowed to cool to room temperature, excess CO gas was vented off and the samples were filtered via micro filter and drawn for GC analysis. The major esters products methyl heptanoate and methyl hexanoate were identified using GC and GC-MS techniques as depicted in Figure 4.2, whereby m/z peak ratios of 145 were realized, with linear ester (methyl heptanoate) eluting at a retention time of 10.47 min followed by that of branched ester (2-methylhexanoate) at 11.68 min. (0.2 ml) of ethyl benzoate

was used as the internal standard and the percentage of 1-hexene converted to esters was determined from GC conversion by comparing areas of products versus substrate, whereas the percentage yield was calculated using the R factor extrapolated to be 0.4421, which was obtained from the calibration curve of internal standard versus concentration of analyte. The GC-MS analyses were run under the following standard chromatograph conditions: -25 m CPSil 19 capillary column, 1.2 mm film thickness, Helium carrier column gas 5 psi injector temperature 250°C, oven program 50°C for 4 minutes rising to 200°C at 20°C/min and holding at 200°C.

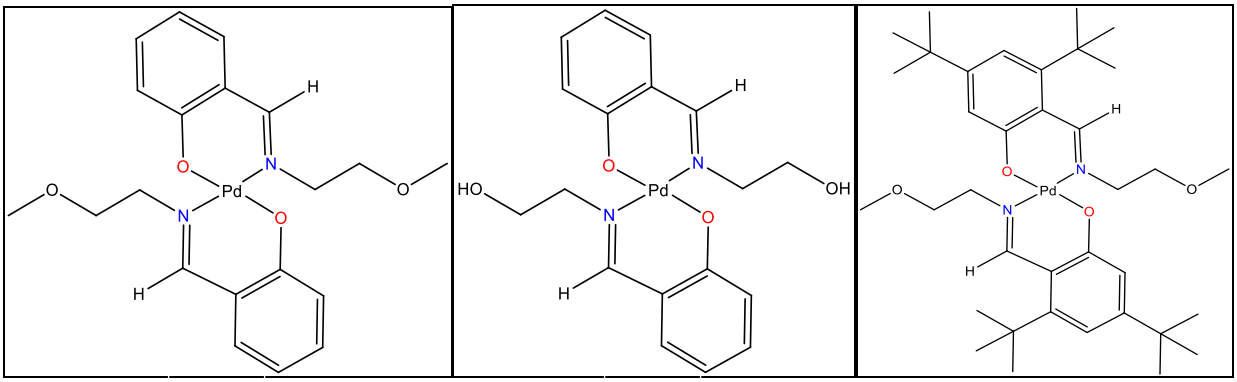
4.2.2 Recycling experiments in biphasic methoxycarbonylation reactions

The recycling of the water-soluble **Pd1** was carried out by a simple decantation process. In a typical reaction using **Pd1**, upon completion of the reaction, the reaction mixture is allowed to cool at ambient temperatures, excess carbon dioxide gas is vented, and the reaction mixture is then transferred into a measuring cylinder. The mixture was allowed to stand in order to allow separation of the phase, the aqueous phase containing the catalyst was decanted from the organic phase (containing the products and unreacted substrate) and then reintroduced into the reactor, followed by an addition of fresh 1-hexene substrate, PPh_3, HCl and methanol. The reaction was then set for another run.

4.3 Results and discussion

4.3.1 Preliminary investigation of complex Pd1 as a catalyst in the methoxycarbonylation of 1-hexene

In attempt to probe the N^O donor palladium complexes (**Pd1-Pd6**) prepared in Chapter 3 (**Figure 4.1**), in the methoxycarbonylation of olefins, we initially used complex **Pd1** and 1-hexene as a model substrate (Scheme 4.1). The following conditions were employed: 1-hexene:PPh_3:HCl:Pd ratios of 200:2:10:1 at 60 bar and 90 °C; solvent: toluene (20 ml) and methanol (20 ml). Under the given - reaction conditions, **Pd1** afforded good conversions and yield of 74% and 70% respectively, with regioselectivity of 58% in favor of the linear esters (Table 4.1, entry 1). The TOF was calculated using the percentage yield and the number of moles catalyst, the TON was calculated using the TOF and the complete time of the reaction.



Pd1 **Pd2** **Pd3**

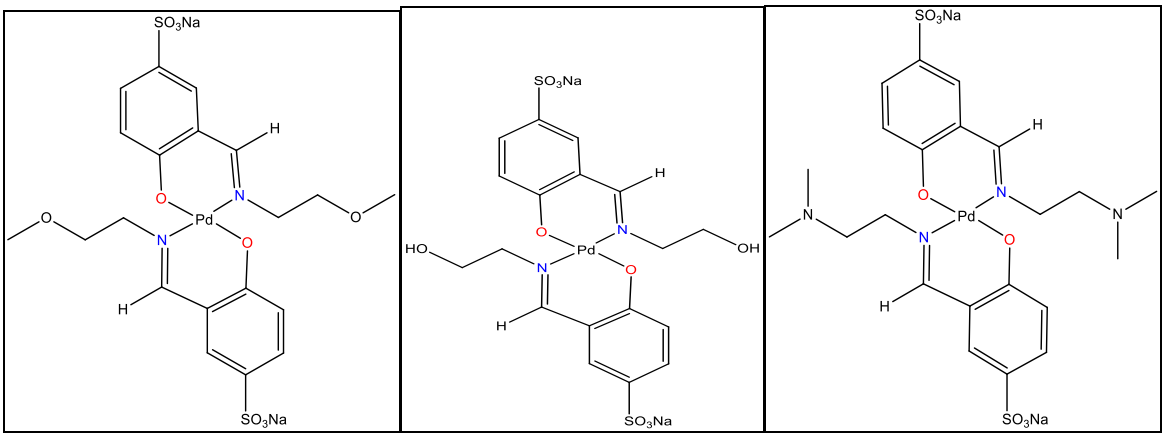
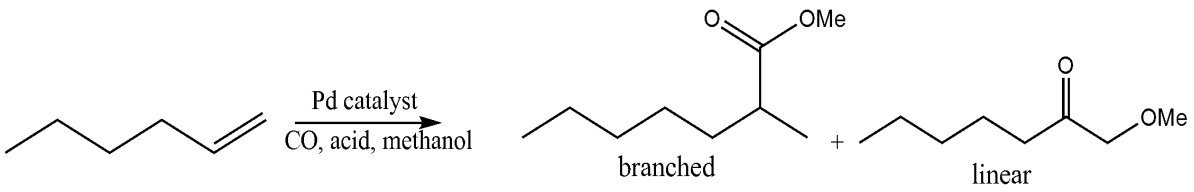


Figure 0.1: Non-water soluble and water soluble Pd(II) complexes investigated in the study.



Scheme 0.1: Methoxycarbonylation of 1-hexene by Pd(II) pre-catalysts to give branched and linear esters as major products.

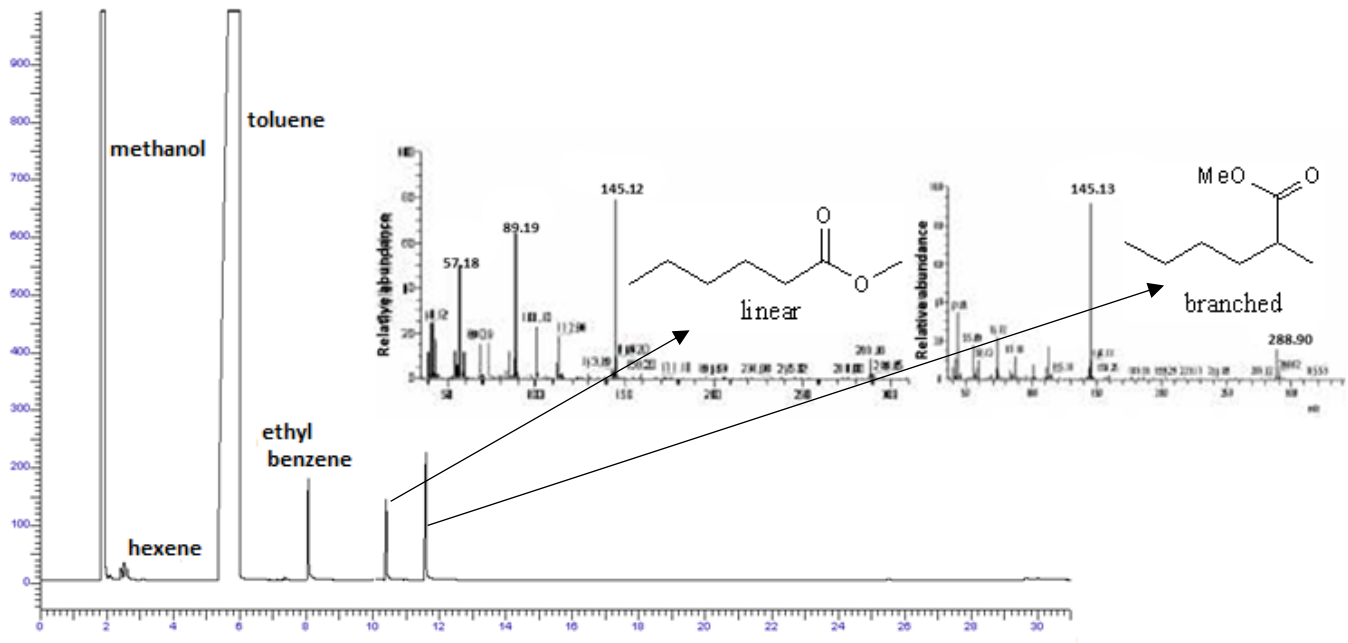


Figure 0.2: Overlaid GC and GC-MS spectra showing conversion of 1-hexene to linear and branched major ester products using complex **Pd1** under the following reaction conditions:1-hexene: PPh_3:HCl:C1 of molar ratios 200:2:10:1 at 60 bar and 90° C.

Table 0.1: Preliminary and optimization data in the methoxycarbonylation of 1-hexene.

Entry	Catalyst	[Pd]: [PPh_3]: [HCl]	Conv (%)[b]	Yield[c]	b/l (%)[d]	TOF (h^{-1})
1	**Pd1**	1:2:10	74	70	42:58	6.17
2	**Pd1**	1:4:10	78	75	38:62	6.25
3	**Pd1**	1:6:10	84	81	31:69	7.00
4	**Pd1**	1:8:10	65	61	28:72	5.42
4	**Pd1**	1:6:20	93	89	30:70	7.50
5	**Pd1**	1:6:5	54	50	33:67	4.35
6	**Pd1**	1:6: 20 PTSA	68	65	34:56	5.67
7	**Pd1**	1:6:30 PTSA	90	87	30:70	7.80
8	**Pd1**	1:6:40 PTSA	55	51	28:72	6.55

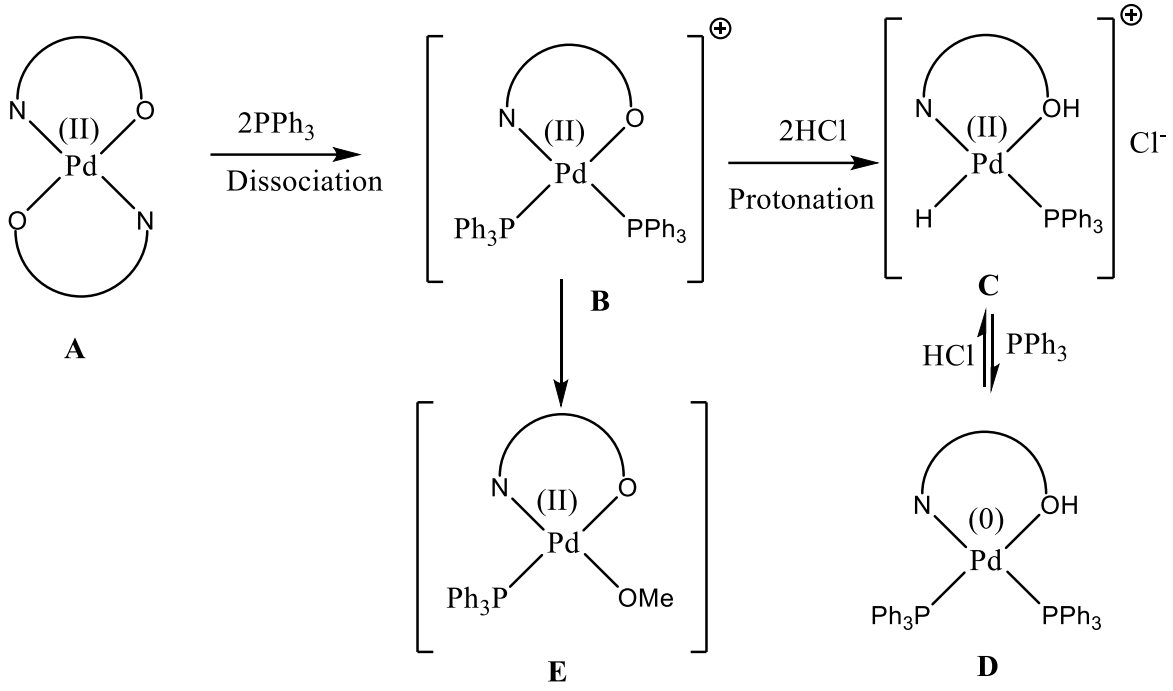
[a]Reaction conditions: Pressure: 60 bar, Temp: 90 °C; Time: 24 h, Acid; HCl, Solvent: methanol 20 ml and toluene 20 ml; [Pd]:[hexene] ratio; 1:200; [b]Amount of hexene substrate consumed as determined by the use internal standard and GC assuming 100 % mass balance; [c]Amount of esters produced as determined using ethyl heptanoate as internal standard and GC; [d]Molar ratio between branched and linear ester determined using commercial authentic samples and GC.

4.3.2 Optimization of methoxycarbonylation reaction of 1-hexene as substrate using complex Pd1

4.3.2.1 Effect of PPh_3 additives and PPh_3/Pd ratio in the methoxycarbonylation of 1-hexene

After establishing the ability of **Pd1** to catalyse the methoxycarbonylation of 1-hexene, we then found it prudent to optimize the reaction parameters in order to improve the catalytic activity and regioselectivity in this reaction. It is evident from literature reports that the amount of phosphine additives play a significant role the methoxycarbonylation of olefins [25]. Therefore, in an aim to probe the effect of the concentration of PPh_3 in the catalytic activity of **Pd1**, we varied the PPh_3/**Pd1** ratio from 2 to 6 (Table 4.1, entry 1- 3). From the data recorded, the conversion was noted to increase from 74% to 85% respectively. However, when the PPh_3/**Pd1** ratio was further increased to 8, the conversion was observed to decrease drastically to 65% (Table 4.1, entry 4). The increased in reactivity of **Pd1** observed at PPh_3/**Pd1** ratio of up to 6 can be rationalized by the enhanced stability rendered by the PPh_3, in limiting the decomposition of the active catalyst to Pd(0), since PPh_3 species are believed to form more stable and active intermediate species [17, 25-27]. Whereas lower catalytic activities reported at higher PPh_3/**Pd1** ratio of 8 may be associated with the competition between the PPh_3 ligand and the substrate for the active site. This has net the effect of limited access of the olefin substrate to the active site, consistent with the lower percentage conversions observed [28, 29]. Similar results were reported in the methoxycarbonylation of acetylene, However, the best optimum catalytic performance was observed at PPh_3/Pd lower ratio of 2 [30,31]. Whereas in our case, the higher PPh_3/Pd optimum ratio of 6 could be due to the bis(chelated) nature of our complexes, hence higher amounts of PPh_3 required to displace the coordinated ligand units as shown in the proposed mechanism (**Scheme 4.2**).

In any catalytic reactions, it is very vital to design catalysts that afford both excellent substrate conversion and product selectivity [32-34]. We thus only examined the regioselectivity towards the formation of either linear or branched esters, on changing the PPh_3/**Pd1** ratio. In our recorded data, it can be observed that increasing the PPh_3/Pd ratio led to profound effect in percentage compositions. For instance, compositions of 58% towards linear esters were realized at PPh_3/**Pd1** ratio of 2, whereas composition of 73% was realized at PPh_3/**Pd1** ratio of 8 (Table 4.1, entry 1 and 4). This observed trend may be associated to the fact that at lower PPh_3 ratios, only one PPh_3 specie was coordinated to the metal center, whereas at higher ratios there were two molecules of PPh_3 coordinated to the Pd intermediate. Moreover, the hydride species only comes in upon the reaction between species **B** and **HCl** to displace one PPh_3 unit and form **C**. Thus, there is increased steric encumbrance around the metal at high PPh_3 concentrations, which led to more production of the less sterically demanding esters, and less preference to the sterically hindered branched esters [13]. Similar trends were observed for N^O and N^N Pd (II) complexes reported by Tshabalala *et al.*[16], using hexene, Akiri & Ojwach using 1-hexene [35] and Kumar & Darkwa [36].



Scheme 4.2: Proposed mechanism of activation and stabilization of complex **Pd4** in the presence of PPh_3 species and HCl/PTSA.

4.3.2.2 Investigation of the role of the nature of the acid promotor

The nature of the acid-promoter is another important factor in the methoxycarbonylation reactions since it aids in the regeneration of the Pd-H active species [19]. Moreover, literature reports clearly indicates that different types of acids results in varied catalytic activities, owing to their dissimilar coordinating abilities and degree of stabilization of the Pd(II) active species [26, 29-31]. Therefore, in an effort to scrutinize the influence of the nature of acids in the catalytic performance of complex **Pd1**, we performed experiments using HCl and PTSA as acid promotors. Our results clearly revealed the dependence of catalytic activity on the type of acid used. For instance, at HCl/**Pd1** ratio of 20 a remarkable percentage yield of 89% was achieved, while at the same PTSA/Pd ratio of 20, only 65% percentage yield was realized (Table 4.1, entries 4 *vs* 6). The lower activity

observed for PTSA can be associated with the weak coordinating abilities exhibited by TsO^- anions, which is consistent with previous literature findings [3]. Upon establishing that the identity of the acid promotor affects the catalytic behavior of complex **Pd1,** we then varied the HCl/**Pd1** ratio from 5 to 20. As expected, a diminished percentage yield of 50% was realized at the HCl/**Pd1** ratio of 5 (Table 4.1, entry 5). The trend observed is a clear indication insufficiency in the amount of the acid to stabilize the catalytically active species up to a 24 h period. In addition, palladium black traces were observed after the completion of the reaction, which further points to catalyst decomposition due to lack of stability [26, 32-34]. Furthermore, NMR stability kinetics was performed while mimicking the reaction conditions. The imine proton was monitored for a period of 9 hours and it was observed in all the spectra, indicating that the catalysts do not hydrolyze in the presence of the acid as shown in **Figure 4.3**.

Considering the safety appeal of PTSA, due to its ability to operate under milder conditions compared to the more hazardous HCl acid, we also optimized the concentrations of PTSA. To our delight, a good percentage yield of 87% was realized at the PTSA/Pd ratio of 30 (Table 4.1, entry 7). The enhanced activity observed at this ratio of 30 further points to the importance of having a sufficient amount of the acid promotor to stabilize the active Pd species since the role of the acid promoter is to form the Pd-H species and also stabilize the Pd intermediates formed during the reaction[28] as shown in **Scheme 4.2**. When a unit of PPh_3 is eliminated from the cycle, there is a possibility of the tosylate coordinating to the palladium center hence inhibiting the expected coordination of the substrate to the palladium center, hence a lower activity.

[29,30]. On the other hand, lower catalytic activities reported at higher the PTSA/Pd ratio of 40 may be associated with the competition for the active species between the substrate and coordinating OTs^- anion, hence, there is limitation of incoming olefin for the active site. Another plausible reason could be catalyst decomposition via ligand hydrolysis [20, 35, 36]. No notable change was observed in terms of regio-selectivity.

4.3.2.3 Evaluation on the exact role of PPh_3 and PTSA in the methoxycarbonylation reactions through insitu NMR techniques.

After establishing the profound effects that PPh_3 and PTSA has in the methoxycarbonylation of 1-hexene substrate. We were then intrigued to further inspect and gain insight on the exact role these play in governing the activity. Thus, *insitu* ^{1}H NMR and ^{31}P NMR were used in an aim track the formation of any possible active species and the stability of the complex during a 9 h period. We conducted an *insitu* ^{1}H NMR spectroscopy using the optimum conditions Pd1/PPh_3/PTSA ratio of 1:6:30. Thus, aiming to establish if there is any hydrolysis of the **Pd1** complex upon the addition of PTSA, we examined the switch on the imine proton signal resonating at 7.92 ppm Interestingly, no notable change was observed in the peak of interest during the 9 h period (Figure 3). Moreover, no azomethine peak nor aldehyde peak was noted at 8.42 ppm and 9.81 ppm present in **L1H**. Thus, this further points to the stability of our **Pd1** complex in acidic media since no ligand dissociation was observed.

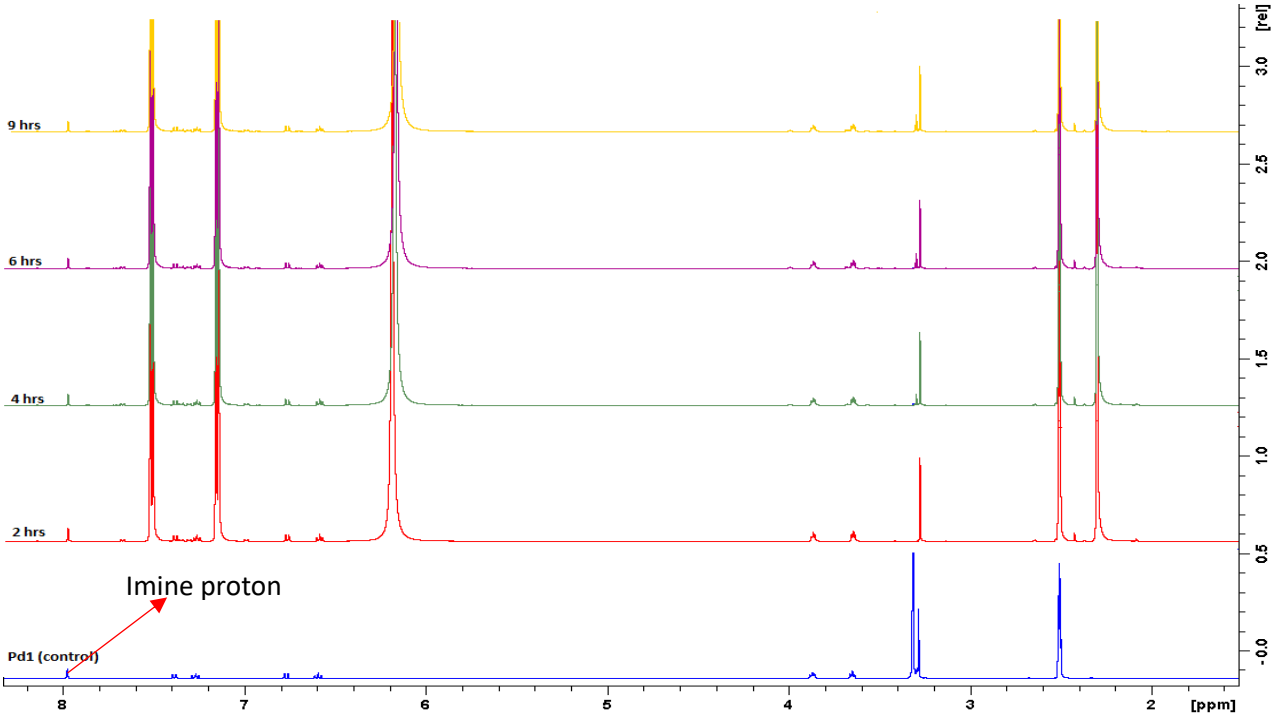


Figure 4.3: ^{1}H NMR of complex **Pd1** in the presence of PTSA and PPh_3 showing the stability of the complex in acid media over the 9 h period.

4.3.2.4 Control experiment studies and role of ligand in the methoxycarbonylation reactions

Previous literature reports have displayed varied conversions by *in situ* palladium salts and precursor and their complexes [35, 41, 42]. We therefore sought to gain an in depth insight on the effects of the isolated complexes and the coordinated ligands on the methoxycarbonylation reactions of 1-hexene. Thus, various control experiments were carried out in the absence of the acid promotor, palladium complex and PPh_3 to determine their roles in controlling the reactions. To determine the role the coordinated ligands in the isolated complexes, we performed in situ reactions using $Pd(OAc)_2$ and ligand **L1H** (Table 4.2).. From the data, the use of $Pd(OAc)_2/PPh_3$/HCl and $Pd(OAc)_2/PPh_3$/PTSA *in situ* generated systems afforded lower yield of

8% and 4% respectively, when compared to the percentage yield of 68% obtained for the **Pd1**/PPh_3/PTSA system (Table 4.2, entries 1-3). These conducted experiments clearly show the significance of the isolated palladium complexes (**Pd1**-**Pd6**) in promoting the methoxycarbonylation of 1-hexene. To further evaluate the role of the coordinated ligand (discrete Pd coordination complexes), *in situ* experiments using $Pd(OAc)_2$/**L1H**/PPh_3/HCl and $Pd(OAc)_2$/**L1H**/PPh_3/PTSA were also conducted (Table 4.2, entries 4 and 5). From our results, the addition of **L1H** appears to have slightly enhanced the catalytic activities, giving percentage yields of 43% and 26% respectively. These percentage yields recorded for the *in situ* systems were thus far much lower than the value of 87% afforded by the complex **Pd1**. These data therefore affirm the importance of the ligand motif/isolated complexes, in promoting the methoxycarbonylation reactions [28, 43].

Table 0.2: Control experiments and influence of ligand data

Entry	Catalyst system	Conv (%) [b]	Yield[c]	b/l (%)[d]	TOF (h^{-1})
1	Pd1 1:6:20	68	65	34:56	5.67
2	$Pd(OAc)_2/PPh_3/HCl$ 1:6:20	11	8	29:71	0.92
3	$Pd(OAc)_2/PPh_3/PTSA$ 1:6:20	8	4	31:69	0.67
4[e]	$Pd(OAc)_2/PPh_3/HCl$ 1:6:20	46	43	28:72	3.83
5[f]	$Pd(OAc)_2/PPh_3/PTSA$ 1:6:20	30	26	34:66	3.25

[a]Reaction conditions: Pressure: 60 bar, Temp: 90 °C; Time: 24 h, Acid; PTSA/HCl, Solvent: methanol 30 ml and toluene 30 ml; [Pd]: [PPh_3]: [Acid]: [1-hexene] = 1:6:20:200; [b]Amount of hexene substrate consumed as determined by the use internal standard and GC; [c]Amount of esters produced as determined using ethyl benzene as internal standard and GC; [d]Molar ratio between branched and linear ester determined using commercial authentic samples and GC. [e,f] Reactions with ligand **L1H**.

4.3.3 Investigating the effect of structure in the methoxycarbonylation of 1-hexene

The ligand motif plays a huge role in the catalyst's behaviour, therefore, tuning the electronic and steric properties of the ligands can lead to adjusted activity and selectivity. One of the main objectives of this study was to determine the influence of complex architecture/ligand motif (**Pd1-Pd6**) in controlling the catalytic activity and selectivity in the methoxycarbonylation of 1-hexene. From the data in Table 4.3, it was evident that there was profound effect of the complex structure. For example, complex **Pd1,** bearing the methoxy pendant arm (OCH_3), afforded higher percentage conversion of 87%, compared to yields of 72% observed for **Pd2,** containing the hydroxyl remote moiety (**Table 4.3, entry 1** and **2**). The higher catalytic activity recorded for complex **Pd1** may be associated with the better donor ability of the methoxy group, thus enhancing the stability of resultant active species and due that This was due to that the designed system exhibited hemilability [44]. On the other hand, **Pd3** bearing methoxy group was observed to results in lower catalytic activity of 69% than **Pd1** of 87% **(**Table 4.3, entry 3). The diminished activity observed for **Pd3** can be rationalised by the low solubility of the complex in methanol and toluene solvents, moreover, palladium metal traces were observed upon completion of the reaction indicating partial decomposition of the catalyst. In terms of regio-selectivity, we also noted the dependence of the preference towards either the linear or branched esters on complex structure. For instance, percentage compositions of 70% and 78% of linear esters were obtained for complexes **Pd1** and **Pd3** respectively. This trend is also consistent with the greater steric contribution from the *tert*-butyl groups (in **Pd3**) resulting in the formation of the less sterically demanding linear ester products [36, 45]. The regioselectivity data thus supports the catalytic activity trends observed.

Comparison of the **Pd1**-**Pd3** and **Pd4**-**Pd6** complexes allowed us to draw comparisons between the non water- and water-soluble -complexes under similar conditions (methanol/toluene solvent system). According to our recorded data, lower percentage yields were observed for the water-soluble complexes (44%-57%), compared to the non-water soluble catalysts of 65%-87% (**Table 4.3**). One plausible reason for the diminished conversions observed for water-soluble complexes is minimal solubility of the catalysts in toluene/methanol solvent system. The next section thus deals with the biphasic catalysis of these water-soluble complexes and subsequent recycling studies.

Table 0.3: Effect of complex structure in the methoxycarbonylation of 1-hexene

Entry	Catalyst	Conv. (%)[b]	Yield[c]	b/l (%)[d]	TOF (h^{-1})	TON
1	**Pd1**	90	87	30:70	7.80	174
2	**Pd2**	72	69	28:72	7.00	138
3	**Pd3**	68	65	22:78	6.45	130
4	**Pd4**	59	57	30:70	6.77	114
5	**Pd5**	47	44	29:71	5.25	88
6	**Pd6**	60	56	31:69	6.21	112

[a]Reaction conditions: Pressure: 60 bar, Temp: 90 °C; Time: 24 h, Acid; PTSA, Solvent: methanol 30 ml and toluene 30 ml; [Pd]: [PPh_3]: [PTSA]: [1-hexene] = 1:6:30:200; [b]Amount of hexene substrate consumed as determined by the use internal standard and GC; [c]Amount of esters produced as determined using ethyl benzene as internal standard and GC; [d]Molar ratio between branched and linear ester determined using commercial authentic samples and GC.

4.3.4 Investigating the effect of substrate in methoxycarbonylation reactions

Previous literature studies revealed varied conversions for every substrate used under the same reaction conditions [16, 35, 46, 47]. Thus, it is apparent that the catalytic activity and regioselectivity is greatly influenced by the identity of the substrate. Therefore, the following series of experiments were conducted to investigate how the change in nature of olefin would affect the reactivity of **Pd2**. From the data obtained, it was noted that increasing the chain length of the substrate significantly decreased the activity. For instance, **Pd2** afforded 72% conversion for 1-hexene substrate, while conversions of 56% and 42% were realized for 1-octene and 1-decene respectively (**Fig 4.2**). The trend on the data observed can be influenced by two factors i.e. chain length and steric hindrance. Hence the longer the substrate chain, the higher the steric hindrance. The second factor is attributed to the increased electron density [48]. Therefore, both the factors limit access for the substrates to the active site. In addition, regioselectivity was also noted to alter upon an increase in carbon chain length. According to our results, branched esters were notably favored by high chain length, for example 1-decene produced high composition of branched esters (60%) relative to that of low chained 1-hexene substrate (30%). This occurrence is believed to be attributed to the high number of possible isomers present in longer chain alkenes as opposed to shorter chain alkenes [48].

Further investigations were carried out in an attempt to establish the effect of internal olefins in the methoxycarbonylation reactions, since the position of the double bond is believed to have profound effect to both substrate conversion and regioselectivity of products. We therefore investigated trans-2-hexene and trans-4-octene as models of internal olefins. From the data recorded, we observed that internal olefins resulted in lower conversions. For instance, good to moderate activities of 72% and 56% were realized for 1-hexene and 1-octene respectively, whereas

reduction in activities to 33% and 26% were recorded for trans-2-hexene and trans-4-octene respectively as depicted in Figure 4.3. The low reactivity observed for internal alkenes can be associated with slow binding affinity of the olefin to the Pd center due to their sterically hindered nature [5, 49]. With respect to regioselectivity, a switch in percentage composition towards linear esters was noted for internal substrates in comparison to terminal substrates , for example, trans-2-hexene exhibited high percentage composition of 70% in favor of branched esters, while 30% of branched esters was recoded for 1-hexene. This behavior is believed to be influenced by the high double bond isomerization observed for internal olefins [[50-52]. Additionally, when the olefin substrate was changed to styrene, high reactivity of 98% was achieved (Figure 4.3). Higher conversions of styrene to produce methyl 2-phenylpropanoate and methyl 3-phenylpropanoate are commonly observed and can be linked to the more reactive benzylic Pd(II) intermediate in comparison with the alkyl Pd(II) intermediate formed during the catalytic cycle [14, 41, 53]. In terms of regioselectivity, percentage composition of 78% in favor of branched esters was realized. High selectivity observed for styrene can be associated with the presence of monodentate phosphine ligand, hence such complexes tend to provide high percentage composition in favor of branched esters, however, the selectivity of styrene can vary upon the reaction condition used [11, 28, 36, 54, 55].

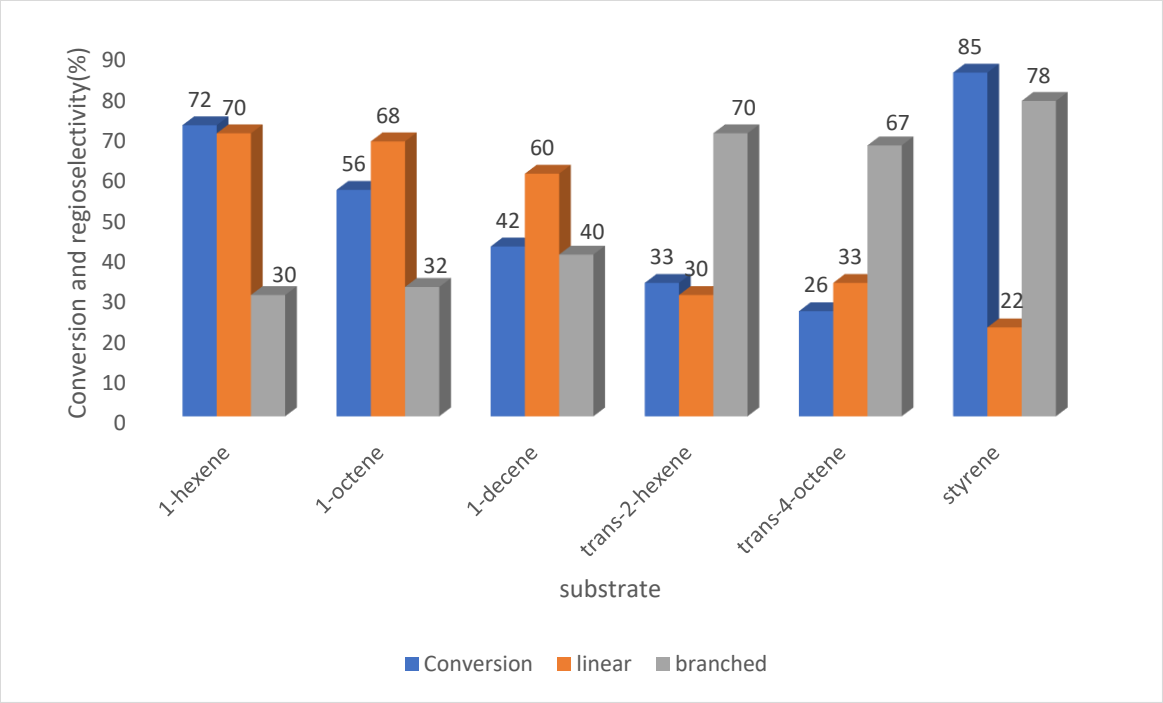


Figure 0.3: Conversions and regioselectivity of different substrates using complex **Pd2**. Reaction conditions: time, 24 h; 60 bar; temp, 90 °C; solvent; toluene (20 ml), methanol (20 ml).

*4.3.5 Biphasic methoxycarbonylation of 1-hexene using water-soluble complexes **Pd4-Pd6***

One of the major thrusts of this research was to design recyclable water-soluble catalysts in the methoxycarbonylation reactions of olefins under biphasic conditions. This investigation is influenced by the limited number of biphasic systems reported in literature [56-59], the water-soluble complexes (**Pd4-Pd6**) were used the methoxycarbonylation to catalyse 1-hexene using a water/methanol/ toluene solvent system (Table 4.4). In order to establish the optimum solvent ratio and water content, we varied the percentage of water in the system from 0% to 20%. From the data, it is clear that addition of water to the system generally increased the catalytic activities of the complexes. For example, using complex **Pd1**, 0% and 10% water content in the methanol/water fraction afforded percentage yields of 59% and 86% respectively (Table 4.3, entries 1 and 3). The

higher catalytic activities upon addition of water may be associated with increased solubility of the complexes in the aqueous phase. In addition, Pd(0) deposits were observed in the single phase medium, whereas no traces of the catalysts were observed in the biphasic system. These remains observed were due to the catalyst particle that did not dissolve. " This is consistent with the minimal solubility observed for **Pd4** in the absence of water [23, 60]. However, a further increase in the water content to 6 ml (20%) resulted in a drastic decline in percentage yield of product to 23% (Table 4.4, entry 4). The decline in catalytic activity may be attributed to the lower solubility of 1-hexene and carbon monoxide at higher volumes of water. For example, the solubility of CO in water is known to be 0.03 mol/L whereas it is 0.28 mol/L in pure methanol [61]. Another plausible reason could be catalyst decomposition since palladium black traces were observed after the completion of the reaction. Complexes **Pd5** and **Pd6** showed similar trends, giving percentage yield and conversion of 74% and 78% respectively. Notably, no significant change was observed in terms of regioselectivity (Table 4.4, entries 5-6).

Table 0.4: Biphasic catalysis data using different compositions of water

Entry	Catalyst	H_2O (ml)	Conv (%)[b]	Yield[c]	b/l (%)[d]
1	**Pd4**	0	59	57	30:70
2	**Pd4**	2	83	80	30:70
3	**Pd4**	4	86	84	29:71
4	**Pd4**	6	23	20	33:67
5	**Pd5**	4	78	74	29:71
6	**Pd6**	4	80	78	30:70

[a]Reaction conditions: Pressure: 60 bar, Temp: 90 °C; Time: 24 h, Acid; PTSA, Solvent: varying methanol volume, toluene 30 ml; [Pd]:[hexene] ratio; 1:200; [b]Amount of hexene substrate consumed as determined by the use internal standard and GC; [c]Amount of esters produced as determined using ethyl benzene as internal standard and GC; [d]Molar ratio between branched and linear ester determined using commercial authentic samples and GC.

4.3.6 Catalyst recycling under biphasic conditions

Upon establishing the viability of the water-soluble Pd (II) analogues **(Pd4-Pd6**) to catalyse the methoxycarbonylation of 1-hexene under multiphase media, we then turned our focus to the recycling of the catalysts. The optimum biphasic reaction conditions established are: 60 bar; temp, 90 °C; solvent; toluene (20 ml), methanol (16 ml), 10% water (4 ml) at [Pd]:[hexene] ratio of

1:200. Under these conditions, effective phase separation occurred within 1 h. The aqueous layer (containing the catalyst) was carefully decanted from the organic phase (containing the product) and added to the reactor, followed by a fresh substrate, acid and PPh_3 [60]. From the recorded data, it is apparent that **Pd1** retained its catalytic activity over the four cycles (Figure 4.4 and Table 4.4). For instance, the decrease in catalyst activity was realised to be between 6%- 19% with the highest TOF of 7.12 h^{-1}. The product distribution however remained unchanged since 69 %-71% of the linear esters was produced. This is important as it points to the stability and retention of the integrity of the active species in the subsequent runs.

Table 0.5: Recycling experiments using water-soluble Pd4 complex

Entry	**Run**	**Conv (%)[b]**	**Yield[c]**	**b/l (%)[d]**	**TOF (h^{-1})**	**TON**
1	1	86	85	30:70	7.12	170
2	2	80	78	29:71	7.00	312
3	3	70	68	32:69	6.88	408
4	4	65	62	30:70	6.56	496
5[e]	5	88	87	30:70	7.24	174

[a]Reaction conditions: time, 24 h; 60 bar; temp, 90 °C; solvent; toluene (20 ml), methanol (16 ml), water (4 ml). [Pd]:[hexene] ratio; 1:200; [b]Amount of hexene substrate consumed as determined by the use internal standard and GC; [c]Amount of esters produced as determined using ethyl benzene

as internal standard and GC; [d]Molar ratio between branched and linear ester determined using commercial authentic samples and GC. [e]hot filtration experiment

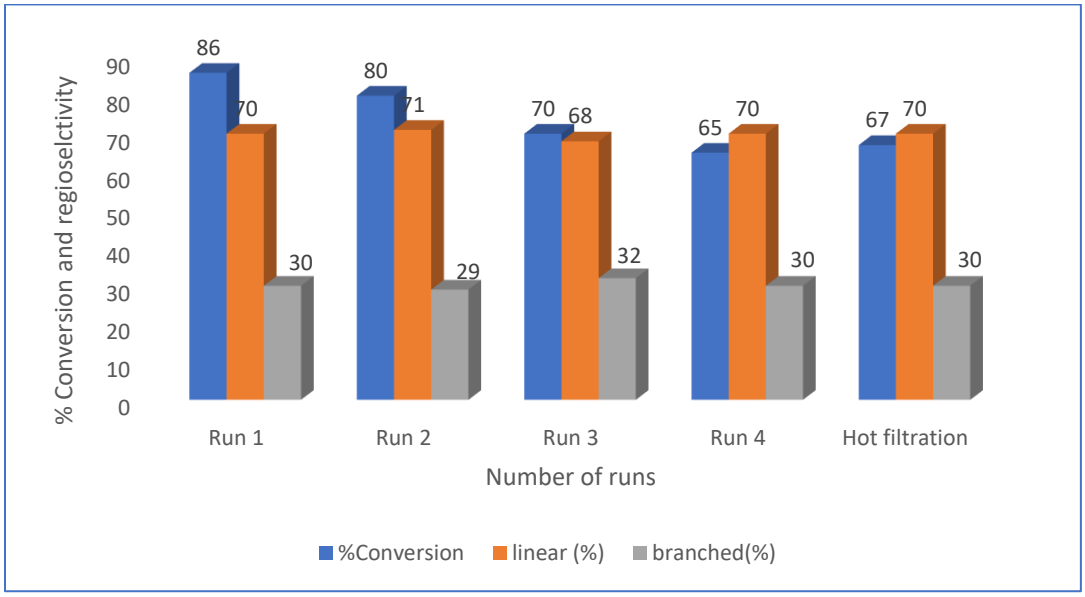


Figure 0.4: Percentage conversion of methoxycarbonylation of 1-hexene using **Pd4**, at different cycles. Reaction conditions: time, 24 hrs; 60 bar; temp, 90 °C; solvent; toluene (20 ml), methanol (16 ml), water (4 ml).

In attempts to gain deep insight to the source of the observed reduction in catalytic activities during the recycling experiments, we investigated the possibility of leaching using hot filtration test (**Figure 4.4**) since leaching usually reduces catalytic activities. Thus, this experiment was done to determine if leaching was indeed the cause of subsequent runs. This was done by running the reaction for 12 h and we separated the aqueous phase which contains the active catalyst. While the organic phase (containing substrate/products) was reintroduced into the reactor and the reaction

continued for another 12 h. Substrate conversion was observed to be 35% within the first 12 h, whereas it was only 37% for the next 12 h (Table 4.4 entry 5). This phenomenon points to minimal catalyst leaching to the organic phase. Thus, catalyst degradation may also be a contributing factor to the diminished conversion after each cycle.

4.4 Conclusions

This research clearly demonstrated the ability of our designed water-soluble and non-water soluble Pd(II) complexes to catalyze the methoxycarbonylation of 1-hexene substrate in excellent percentage yields of 70%-93% and selectivity of 23%-75% in favor of linear esters. The ligand motif was observed to have a significant effect on the performance of the complex, due to the varied strength of electron donating groups present in each complex architecture. For instance, **Pd1** and **Pd4** bearing electron-donating ligands, demonstrated enhanced substrate conversions as opposed to other catalysts**.** On the other hand, **Pd3** showed high percentage composition towards linear ester product due to its bulkiness. In addition, **Pd2** was investigated for different olefins and it was proved that both the catalytic activity and regioselectivity is dependent on the substrate identity, where longer chain and internal alkenes achieved less conversions with lower percentage compositions of the linear esters. Separately, water-soluble complexes were active in the biphasic methoxycarbonylation of 1-hexene and showed comparable catalytic performance to the non-water soluble catalysts. Significantly, the recycling experiments conducted showed that the water soluble catalysts could be recycled up to four times, with minimal loss in activity and minor leaching of the active species to the organic phase was established.

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Chapter 5

General concluding remarks and potential future developments

5.1 General conclusions

In summary, this thesis focused on the design, synthesis and application of non-water soluble and water soluble N^O Pd(II) complexes as recyclable catalysts in the methoxycarbonylation of olefins. Characterization of the synthesized complexes included the use of ^{1}H NMR, ^{13}C NMR, FT-IR, ESI-MS and Xray crystallography for **Pd1** and **Pd3**. Single crystal structures of complexes **Pd1** and **Pd3** established the formation of bis(chelated) square planar neutral compounds, containing anionic ligands.

All complexes formed active catalysts in the methoxycarbonylation of 1-hexene However, Pd (II) complexes bearing electron donating ligands **Pd1** and **Pd4** were found to be more stable which resulted in enhanced catalyst performance compared to those with no electron donating strength as shown in **Table 4.1**. In addition, the acid promotor and PPh_3 additives were found to have profound effect on the performance of the catalyst. *In situ* generated experiments afforded lower yields when compared to the yields obtained for complexes. The activity and regio-selectivity was observed to be dependent on the type of substrate used, decline in activity was noted upon an increase in chain length, whereas branched esters were notably favored by long chain length. On the other hand, when comparing the reactivity of internal versus terminal olefins, reductions in activity for internal olefins was observed due to their sterically hindered nature. Water soluble Pd(II) analogues were observed to be more active in biphasic media, due to the increased solubility, and was controlled by the amount of water added. These complexes had the ability to be recycled

up to four times with minimal loss of catalytic activity with no change in regioselectivity. Hot filtration test ran displayed possible minimal leaching of the active catalyst species under biphasic environment.

5.2 Future prospects and recommendations

One of the main thrusts of the project was the design of an active catalyst that possesses the merits of both homogeneous and heterogeneous systems. Thus, the aim was successfully met since the water-soluble complexes demonstrated the ability of catalyzing 1-hexene in biphasic media. Moreover, our complexes were able to be recycled in 4 consecutive cycles with minimal activity loss. Informed by literature, such systems are adored because they are environmentally benign and economically attractive. However, there are limited reports of biphasic systems in methoxycarbonylation reactions. Therefore, in the next research, we aim to generate and probe more highly active, selective and recyclable Pd(II) catalysts in the methoxycarbonylation of olefins using more electron donating species for more enhanced stability of the of the bis (chelated) complexes (**Pd1**-**Pd3**). On the other hand, we are intrigued to incorporate another type of water soluble species into the ligand to give catalytical active, selective and recyclable Pd(II) complexes with a water soluble phosphine moiety which will enhanced the stability of the complex since phosphine species leads to increased intermediates.(**Pd4**-**Pd6**).

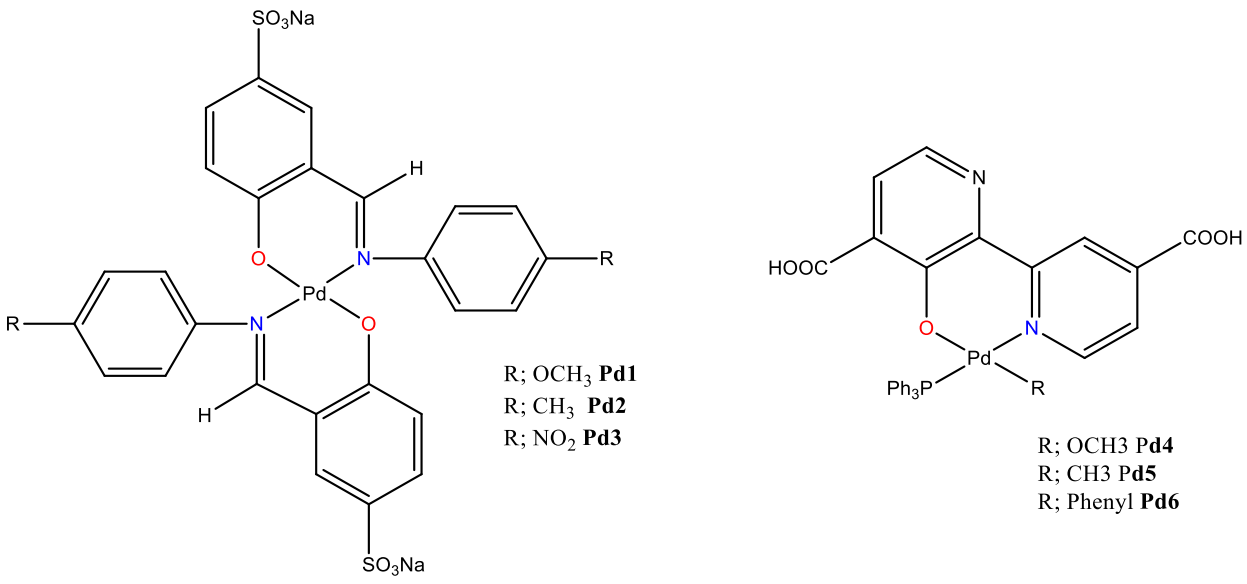

Figure 3.1: Proposed water-soluble Pd (II) complexes for methoxycarbonylation of olefins.