Design of (phenoxy)imine palladium complexes as homogeneous and immobilized catalysts for methoxycarbonylation of olefins

By

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Supervisor: Professor Stephen Ojwach

DECLARATION

I, Saphan Owino Akiri hereby declare that the project "**design of (phenoxy)imine palladium complexes as homogeneous and immobilized catalysts for methoxycarbonylation of olefins"** is my own work and all other sources used have been sufficiently acknowledged through complete references.

Name: Saphan Owino Akiri

Signature…………………………….. Date…………………………………….

As University Supervisor; I approve the dissertation for examination.

Supervisor: Professor Stephen Ojwach

Signature………………………………

DECLARATION 1: PLAGIARISM

I, Saphan Owino Akiri, declare that:

1. The research reported in this dissertation, is my original work, except where otherwise acknowledged or indicated, is my own original work.
2. This dissertation has never been submitted in part or full for any examination or degree to any other university.
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This dissertation is basically a collection of data and material, prepared by myself, presented orally or as posters at conferences or published as journal articles whereas in some instances, additional material has been included.

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DECLARATION 2: CONFERENCE CONTRIBUTIONS

Part of the research reported here have been presented in the following conferences as indicated.

1. Saphan O. Akiri & Stephen O. Ojwach, DST-NRF Centre of Excellence in Catalysis: Centre for Catalysis Research Conference (November 2016), Champagne sports resort; Drakensburg, KwaZulu-Natal. Oral presentation. Design of nitrogen-donor palladium complexes as homogeneous and immobilized catalysts for methoxycarbonylation of olefins.

2. Saphan O. Akiri & Stephen O. Ojwach, DST-NRF Centre of Excellence in Catalysis: Centre for Catalysis Research Conference (November 2017), Pilanesburg, North West. Oral presentation. Design of nitrogen-donor palladium complexes as homogeneous and immobilized catalysts for methoxycarbonylation of olefins.

3. Saphan O. Akiri & Stephen O. Ojwach, Catalysis South Africa Conference (CATSA) (November 2017) Pilanesburg, North West. Poster presentation. Design of nitrogen-donor palladium complexes as homogeneous and immobilized catalysts for methoxycarbonylation of olefins.

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CHAPTER THREE:_Synthesis and characterization of (phenoxy)imine ligands and their homogeneous palladium (II) complexes for methoxycarbonylation of olefins

ABSTRACT

This dissertation focuses on the syntheses of mixed nitrogen and oxygen-donor (phenoxy)imine ligands, their palladium(II) complexes and applications of the complexes as catalysts in the methoxycarbonylation of olefins. In this research, Schiff bases (2-phenyl-2-((3(triethoxysilyl)propyl)imino)ethanol) **(L1)** and (4-methyl-2-((3(triethoxysilyl)propyl)imino)methyl)phenol) (**L2)**, and immobilized ligands **L1**-MCM-41 (**L3**), and **L2**-MCM-41 (**L4**) were synthesized. The synthesized ligands were further reacted with palladium(II) acetate and palladium acetonitrile dichloride to synthesize complexes [Pd (**L1**)$_2$] (**C1**), [Pd (**L2**)$_2$] (**C2**), [Pd (**L1**)(Cl_2)] (**C3**), [Pd (**L2**)(Cl_2)] (**C4**). The immobilized complexes, [Pd (**L1**)$_2$]-MCM 41] (**C5**) and [Pd (**L2**)$_2$]-MCM 41(**C6**) were prepared through convergent synthetic route while [Pd (**L1**)(Cl_2)]-MCM 41] (**C7**) and [Pd (**L2**)(Cl_2)]-MCM 41] (**C8**) were synthesized *via* sequential route . Complexes **C1-C4** were characterized using ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR, Fourier transform infrared spectroscopy (FT-IR), mass spectrometry and elemental analysis, while **C5-C8** were characterized using FT-IR, Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA).

Generally, all the homogeneous and immobilized catalysts showed catalytic activities from 59% to 85% under similar reaction conditions. The immobilized systems showed less catalytic activities than their respective homogeneous systems. The structures of the complexes played a role in their catalytic activities as the bischelated complexes **C1**, **C2, C5** and **C6** showed significantly higher activities than their corresponding monochelated **C3**, **C4, C7** and **C8**. For example bischelated **C2** gave an activity of 78% compared to the monochelated **C4** (60%) which bears a similar ligand motif. However, the structures of the complexes did not have significant effects on the selectivity of the products formed. Nature of the olefin used also affected the catalytic activities since the reactivities decreased with increase in the olefinic chain length while reaction conditions such as temperature, catalyst concentration, time, and carbon monoxide pressure also had profound effect on activity. However, they did not have effect on selectivity apart from the reaction time. Different solvent combinations displayed effects on catalytic activity as a combination of methanol and toluene resulted in the highest catalytic activity whereas a combination of methanol and dimethylformamide gave no activity. Acid promoters contributed significantly in the activities of the complexes; while hydrochloric acid gave the highest catalytic activities in the homogeneous systems, there was no activity observed for the immobilized catalysts. On the other hand, the use of para-toulenesulfonic (p-TsOH) acid showed catalytic activities with both the homogeneous and the immobilized systems. The type of phosphine group also influenced both the catalytic activity and regioselectivity in the methoxycarbonylation reactions. The immobilized catalysts were recycled up to four times without loss of appreciable catalytic activity while hot filtration showed insignificant catalytic activity of the filtrate indicating lack leaching. The analysis of the spent catalyst using TEM, SEM and EDX showed slight changes in the morphology of the catalysts.

ACKNOWLEDGEMENTS

Firstly I would like to thank my God for his guidance through every other obstacle which crossed my path during this research. I would also like to appreciate my supervisor, Professor Stephen Ojwach for the excellent supportive ideas and guidance throughout the project. I am grateful to the DST-NRF Centre of Excellence in Catalysis for the financial support throughout this research. My appreciation also goes to the members of the Catalysis research group at the University of KwaZulu-Natal, Pietermaritzburg campus for their unending support during this study. I would also like to appreciate the technical team at the University of KwaZulu-Natal, Pietermaritzburg campus for their analytical support techniques. Lastly I would like to appreciate my family members, my mum, Rose Akiri, brothers and sisters for their invaluable moral and spiritual support. A special thanks in this regard to my wife, Naomy Nthenya, for standing tall for me in every situation during this project.

DEDICATION

Dedicated to all my family members.

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ABBREVIATIONS

APTES	(3-aminipropyl)triethoxy silane
BASF	Baden Aniline and Soda Factory
Dppe	1,2-bis(diphenylphosphino)ethane
EADC	Ethyl aluminium dichloride
EDX	Energy-dispersive X-ray spectroscopy
ESI	Electrospray Ionization
FT-IR	Fourier transform infrared spectroscopy
GC	Gas chromatography
HRMS	High-resolution mass spectrometry
LC	Liquid chromatography
MHz	Megahertz
MNP	Magnetic nanoparticles
MS	Mass spectrometry
MSA	Methane sulfonic acid
NMR	Nuclear magnetic resonance
NU	Nucleophile
PPM	Parts per million
PPMA	poly-methyl methacrylate
PVC	Polyvinylchloride
RPM	Rotation per minute
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis

CHAPTER ONE

An introduction to homogeneous and immobilized catalysts for olefin transformation reactions

1.1 Introduction

Homogeneous catalysts are known to possess a number of advantages over their heterogeneous counterparts. The homogeneous catalysts are powerful tools for chemical synthesis enabling the control of reactivity with stereoselectivity, chemoselectivity and regioselectivity [1]. They have all their catalytic sites accessible and an advantage of the ease of understanding the reaction mechanisms involved [2]. Despite the merits, homogeneous catalysts suffer from some drawbacks including the difficulty in separating the catalyst from the product mixture, subsequent catalyst recovery and recycling [3].

Even though there are notable advantages of homogeneous catalysts such as superior selectivity, heterogeneous catalyst systems have been used for decades because of their ease of separation and recycling. However, heterogeneous system have disadvantages too, for example, poor selectivity compared to their homogeneous counterpart systems [4]. There have been advances in developing alternative solutions to the problems faced by the two catalytic systems. The goal of such developments is to have a hybrid system with the desirable qualities of both heterogeneous and homogeneous catalytic systems. By combining the strengths of both systems, a hybrid system is developed where the active catalytic site would remain homogeneous in nature hence a good selectivity as well as ease of separation, regeneration and recycling of the resulting catalyst [5]. Such a process of taking a homogeneous catalyst and making it to be insoluble in the reaction mixture using different supports such as inorganic,

organic and magnetic supports, commonly known as heterogenization, has received a lot of attention in catalyst design and development [6].

1.2 Methods of heterogenization of homogeneous catalysts

There are two major methods that have been used to heterogenize the homogeneous catalysts, namely, the use of biphasic catalysis [7] and immobilization of homogeneous catalysts on insoluble solid supports [8].

1.2.1 Biphasic catalytic systems

The biphasic catalytic system is composed of two different phases; a catalytic phase which contains the dissolved catalysts and the product phase [8]. Two immiscible solvents are usually used, for example, water and an organic solvent. The catalyst dissolves in the more polar solvent, normally water while the reactant and the product dissolve in the organic phase. Since most organic compounds and water are immiscible, the reaction usually proceeds in both phases with high rate mixing to create more contact between the substrate and the catalysts. The product is then decanted after the reaction to leave the catalyst in aqueous phase [2]. The formation of the liquid-liquid biphasic system results from the different intermolecular forces of the two chosen liquids, the selection of the catalyst phase is therefore based on the solvent properties of the product phase at high activity [9]. Figure 1.1 shows an example of a biphasic system containing an organic solvent and an ionic liquid.

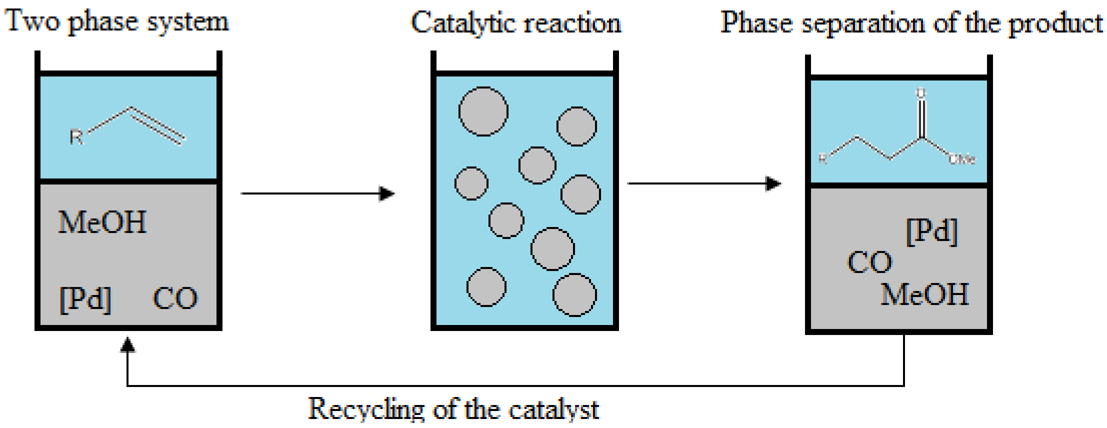


Figure 1.1: A biphasic system for methoxycarbonylation of 1- dodecene [10]

1.2.2 Immobilization methods

A range of materials have been applied as solid supports to immobilize homogeneous catalysts. Such materials are often divided into three main categories: organic supports which include dendrimers, [11] polymers [12] and rigid (fluoro) - organic backbones [13], inorganic supports, for example silica, clay and alumina [14], and the use of magnetic nanoparticles [15]. There are various ways of immobilizing homogeneous ligands on the supports, mainly, the covalent tethering and non-covalent method [16]. The covalent method is more common where a silica support is used because of the silanol groups present on its surface which offer reactive sites where covalent bonding with silane group functionalized catalysts can occur [16].

1.2.2.1 Covalent tethering

Covalent tethering technique is one of the most favoured method in the immobilization of homogeneous complexes [16]. One of the covalent techniques is the use of ordered mesoporous silica which has a surface containing the silanol groups. The silanol groups makes it easy to bind metal complexes to the silica support through covalent bonding [16]. Two synthetic approaches have been used in binding of complexes onto the silica support, i.e. convergent and sequential methods. In the convergent route (Figure 1.2), used by Standfest-Hauser and co-workers [17], a ligand is first functionalised so that at one end it contains a triethoxy-silyl or trimethoxy group which is later bonded to the silanol groups of the support. The metal atom is then coordinated to the ligand to form the immobilized complex.

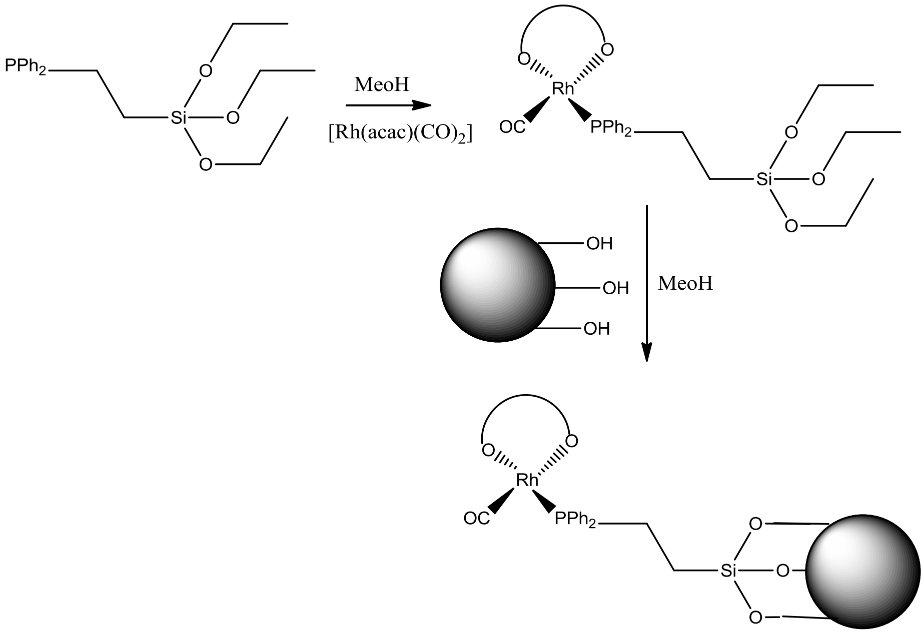


Figure 1.2: Convergent immobilization used by Standfest-Hauser and co-workers in 1-hexene hydroformylation and arene hydrogenation [17].

In the sequential method, a carbon tether is first bonded to the silica support (Figure 1.3). This is followed by the attachment of the Schiff base and finally the attachment to the metal centre. As opposed to the convergent method, there is difficulty in characterisation of the immobilized complex formed using the sequential route since there is uncertainty whether it is the target catalyst or a by-product that has been bonded to the silica support [11]. Despite such a drawback, the sequential synthesis method has been widely used due to the enormous synthetic effort required in the preparation of precursors in the convergent method [18-22].

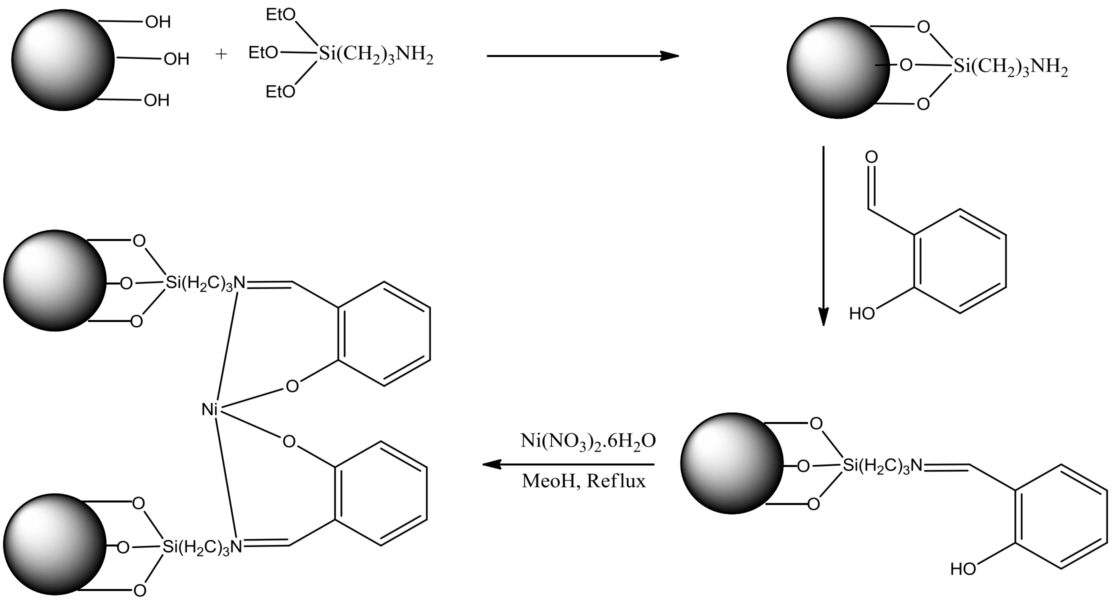


Figure 1.3: Sequential immobilization used by Bhunia and Koner in the epoxidation of olefins [18].

1.2.2.2 Non-covalent interaction

Immobilization of catalyst has also been carried out through the non-covalent method apart from covalent tethering approach. There are several non-covalent methods in literature which have been used for the immobilization of catalysts [16, 23-24].

1.2.2.2.1 Adsorption

Adsorption method can sometimes involve purely the use of weak van der Waals forces. Where the forces act to join the catalyst and the solid support. Due to the fact that these interactions are weak, leaching into the reaction medium is common place. In an effort to minimize leaching, such systems are commonly modified so that the catalyst and the solid support can enable hydrogen bonding. The adsorption method is mostly used to immobilize enzymes onto solid supports [23].

1.2.2.2.2 Electrostatic interaction

Electrostatic interaction method uses the advantage that most porous solids have the ability to behave as ion exchangers. Some of the porous solids ever used as ion exchangers include zeolites, ordered mesoporous silicates, zeolites, and layered materials such as hydrotalcites and clays [16]. The porous materials offer relatively facile mechanisms for the immobilization of complexes and metal cations. Leaching is greatly reduced in this method as compared to adsorption method [24]. Figure 1.4 shows an example of immobilization of a complex through electrostatic interaction.

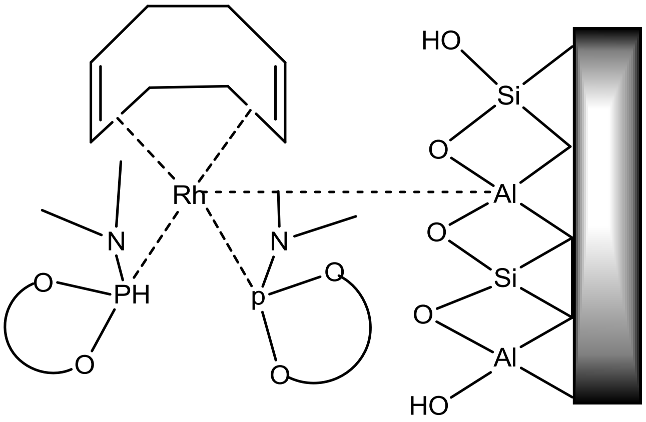


Figure 1.4: Immobilization by electrostatic interaction method [23].

1.2.2.2.3 Encapsulation

In encapsulation method, an interaction between the support and the catalyst is not required and therefore, it is the only method which tries to mimic catalysis reactions which are homogeneous in nature since other methods require ligand modification which leads to catalyst change [25]. The support material chosen for encapsulation must have pores which are smaller in size than the catalyst so as to eliminate catalyst loss into the solution during the process. There are generally three techniques used in encapsulation [25]. The first technique involves assembling the catalyst within the pores which is usually employed if the support must maintain stability in the reaction conditions applied. The side reactions should be avoided and therefore the chemical method for preparing the catalyst must be crucially investigated. The second technique involves assembling the support around the catalyst which is considered if the catalyst must maintain stability when exposed to the synthetic conditions of that particular support [26]. The choice of the method depends on the stability and how easy it is to synthesize the catalyst. In a case where the catalyst is easy to make, then assembling the catalyst within pores of the support is used. On the other hand, if the catalyst is harder to make, then assembling the support around the catalyst is the route chosen [26]. The third method is the use of sol-gel support [27]. This is a process which is majorly applied in the fields of ceramics, material science and bioengineering [28-29]. It is carried out by first synthesizing materials from polymers. Precursors such as metal alkoxides like ($Si(OEt)_4$) are normally used for the process.

Olefin transformation reactions are known to be important processes in the production of industrial feedstocks. The next section discusses some of the olefin transformation reactions catalysed by transition metal complexes.

1.3 Transition metal catalysed olefin transformation reactions.

There are a number of olefin transformation reactions which are important in chemistry and chemical technology since they have been used as paths of synthesizing a wide range of materials that are utilized as intermediates in many applications and as end products themselves [30]. Examples of the olefin transformation reactions include the following: metathesis [30], polymerization [4], hydrogenation [31], oxidation (epoxidation) [32] and carbonylation [33]. Figure 1.5 shows some of the olefin transformation reactions.

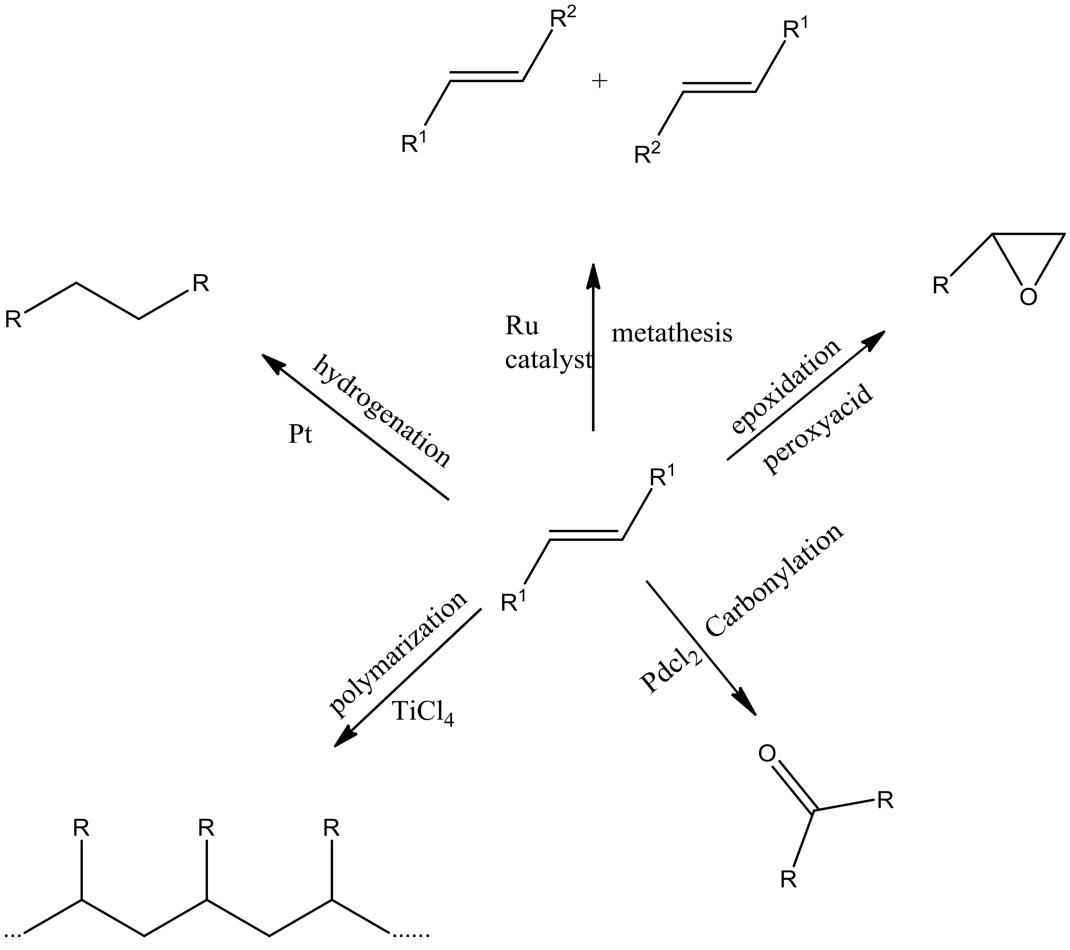


Figure 1.5: Some of the olefin transformation reactions catalysed by transition metal catalysts.

Considering the many olefin transformation reactions and the vast uses of the products obtained thereof, it is of a great concern that such transformation processes are carried out feasibly [34]. The olefin transformation reactions summarised in Figure 1.5 lead to formation of important products used both industrially and domestically. Some of the olefin transformation reactions, products formed and some applications of the products are listed in Table 1.1.

Table 1.1: A summary of some olefin transformation reactions products and their uses

Reaction	**Products**	**Applications**
Hydrogenation	Alkanes	Cooking and heating fuels [35]
Hydroformylation	Aldehydes	Adjuvants and immunoeffectors [36]
Oxidation	Epoxides	Reacted with amines to forma epoxy glues and structural material [37]
Polymerization	Polyolefins	Manufacturing of water pipe, plumbing fittings, synthetic floor tiles [38]
Metathesis	Higher olefins	Manufacture of pharmaceutical drugs [39]
Carbonylation (methoxycarbonylation)	Esters,	Preparation of cosmetics and perfumes.

1.4 Methoxycarbonylation reactions

Carbonylation reaction entails the insertion of the carbonyl group (C=O), usually obtained directly from carbon(II) oxide, together with or without other moieties into substrates such as olefins, amines, alcohols, the nitro groups or substituted aromatic derivatives of these groups [40]. During his time at BASF, Walter Reppe introduced the word carbonylation to explain a range of reactions he discovered from the year 1938 and subsequent years [41]. From that time, reactions where carbon monoxide, in the presence of a catalyst, solely or together with other compounds such as alcohols, amines or water is chemically added to an organic molecule has come to be known as carbonylation [40].The carbonylation reactions are normally favoured by the transition metal complexes of ruthenium, nickel, cobalt, rhodium, platinum, iridium, and palladium. Carbonylation reactions are quite a number, including but not limited to the synthesis of carboxylic acid (hydrocarboxylation) [42], aldehydes (hydroformylation) [43] and esters (hydroesterification) which is commonly referred to as methoxycarbonylation when an alcohol reagent used is methanol [44] or alkoxycarbonylation in general terms. Even though many substrates have been used in carbonylation, olefins in particular have been widely used for many carbonylation transformation reactions (Figure1.6).

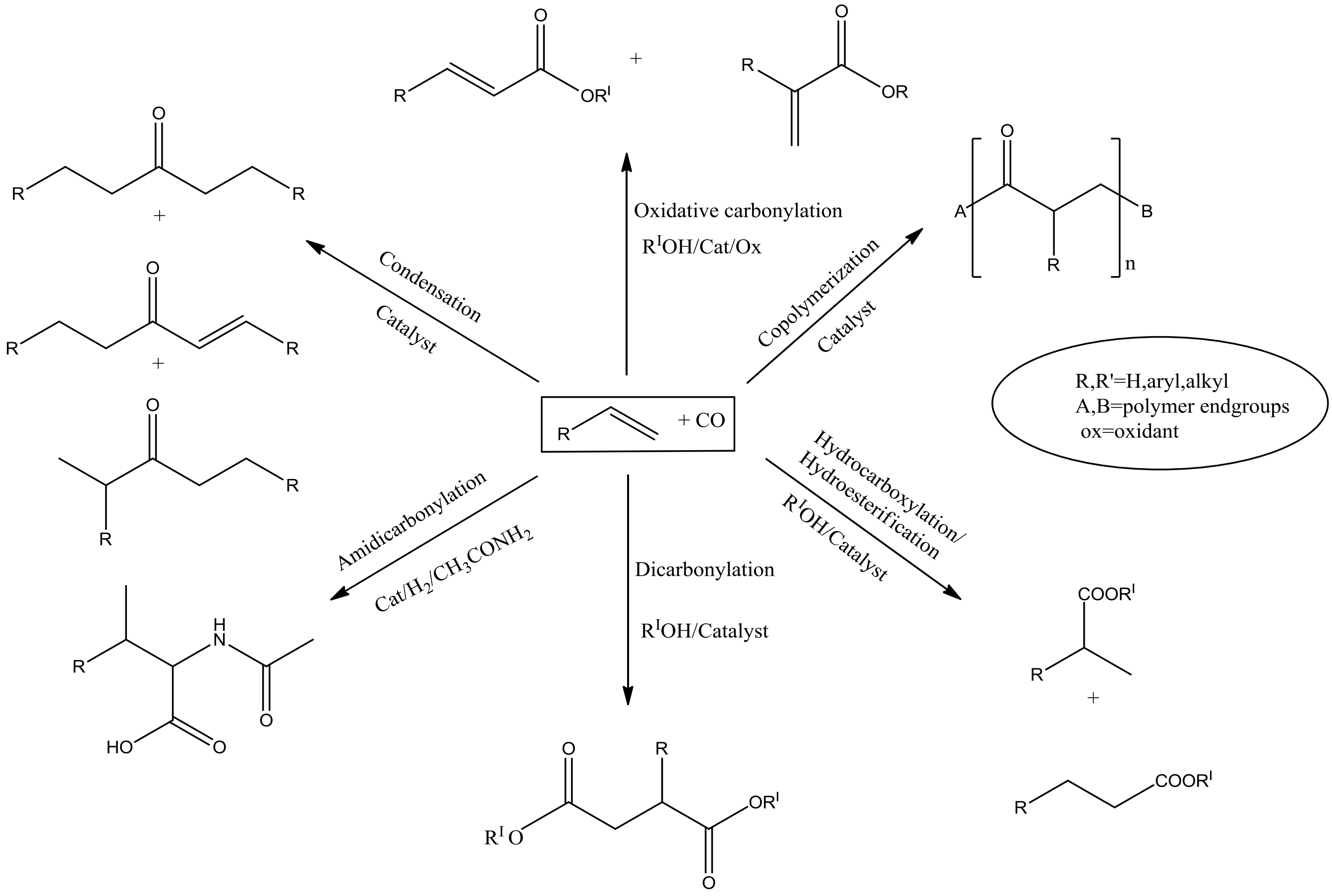
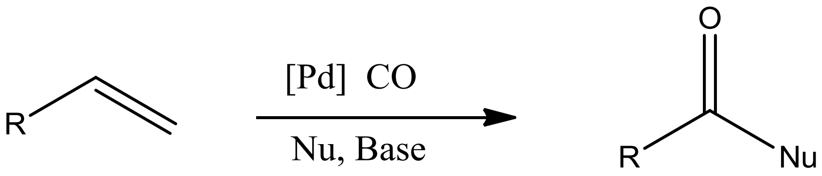


Figure 1.6: Various carbonylation reactions of olefins [45].

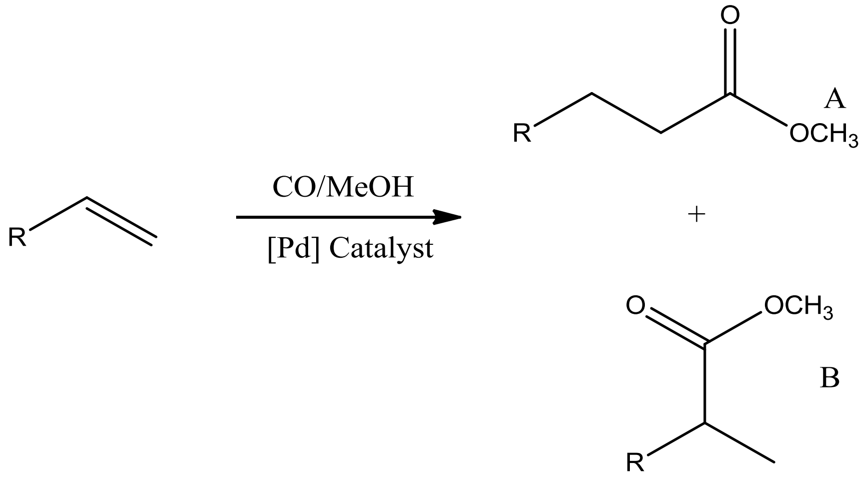
The palladium metal catalysts have been used effectively for a range of carbonylation reactions due to the fact that the reactions proceed at relatively lower pressures and temperatures than with many other metal catalysts [46]. The palladium(II) catalysed carbonylation reactions in the presence of an acid or a base, nucleophile and carbon dioxide can be used to synthesize acids, aldehydes, amides, halides and esters (Scheme 1.1). The kind of the resulting functional group resulting in a carbonylation reaction majorly depends on the nucleophile used.



Nu= $R^{I}R^{II}N$, H, OR^{I}

Scheme 1.1: Schematic representation of carbonylation reaction (R^{I} = Methyl, R^{II} =ethyl)

This research focuses on methoxycarbonylation as a type of carbonylation reaction with a bias to olefin substrates and therefore the next section deals with methoxycarbonylation of olefins, the significance of the various components of a typical methoxycarbonylation catalytic system and significance of methoxycarbonylation. Methoxycarbonylation is a type of carbonylation reaction where by a substrate, for example, an olefin, alcohol or a halide is converted to ester products. The ester product is formed through reductive elimination of an intermediate via methanolysis using a metal catalyst (most cases palladium), methanol, carbon monoxide, and an acid promoter [47]. The methoxycarbonylation reaction can give a branched and/or straight chained ester isomer depending on the reaction conditions and the catalyst structure [48] (Scheme 1.2).



Scheme 1.2: Methoxycarbonylation of an olefin yielding branched and linear products.

1.4.1 The catalytic system for methoxycarbonylation of olefins

Palladium(II) catalysts have been successfully and extensively used as a catalyst in the methoxycarbonylation of olefins [48,55]. The palladium precursor can have an oxidation state of +2 or 0, even though it has not been well established [49]. In the case where there is no stabilizer, the palladium metal usually forms an inactive or a less active binuclear species or forms palladium black which precipitates out of the solution and therefore rendering the catalyst inactive. The components such as the co-catalyst and the ligand thus contribute in the catalytic activity and stabilization of the catalyst [50].

1.4.2 The role of acid promoter

The acid promoter, also known as the acid co-catalyst has been proven to play a major role of stabilizing the catalyst and regenerating the active catalyst in methoxycarbonylation reactions [51]. Brønsted acids have been used as promoters in the methoxycarbonylation reactions while different olefin substrates have produced varied catalytic activities orders for a number of acids. For example, in the methoxycarbonylation of styrene, the activity increased in the order, hydrochloric acid< trifluoroacetic acid< trifluoromethanesulfonic acid< methanesulfonic acid<

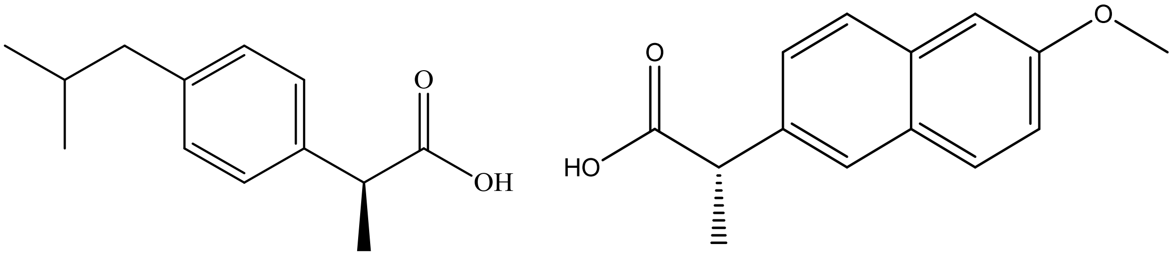
p-toulenesulfonic acid [49]. For propene, the order differed slightly, increasing from hydrochloric acid< p-toulenesulfonic acid < sulphuric acid< trifluoromethanesulfonic acid [49]. Even though the substrate used has a significant part in determining the promoter which would give more reactivity, a good reactivity also requires a strong acidity ($pK_a<2$) with weak co-ordinating power [47]. Apart from the use of traditional Brønsted acids as promoters in the methoxycarbonylation of olefins, Lewis acids have also been used, for example Al $(OTf)_3$, $AlMe_3$ [51].

1.4.3 Role of alcohol as a solvent and reagent

An alcohol is another important component of the methoxycarbonylation setup since it is used in the last stage of the reaction cycle where the ultimate ester product formed is released and the active species are regenerated in the reductive elimination step. Methanol is more commonly used, even though, other alcohols like ethanol can be used instead of methanol to give ethyl esters instead of methyl esters but complications arise since the more complex the alcohol, the slower the reaction due to increased steric hindrance [47]. Apart from taking part in the reaction, alcohol also acts as a solvent as it contributes to increased solubility of the substrate, catalyst and the products, but co-solvents are used in cases where methanol turns out to be a poor solvent [52]. Co-solvents are also used in cases where the reaction temperature is greater than the primary alcohol solvent’s boiling point. However, care must be taken concerning the polarity of the co-solvent since solvents which increase the value of the polarity of the reaction mixture are likely to lower the catalytic activity [53].

1.5 Industrial significance of methoxycarbonylation of olefins

Appreciable interest in the branched esters, particularly in the pharmaceutical industry has been in existence for years. They are used as precursors for valuable types of non-steroidal anti-inflammatory drugs such as naproxen and ibuprofen [44, 54] shown in Figure 1.7.

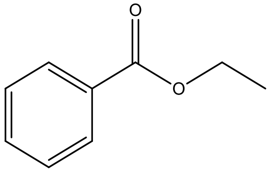
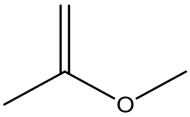
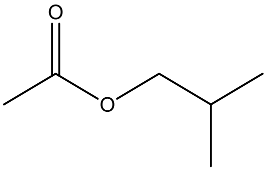
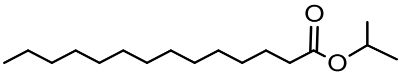
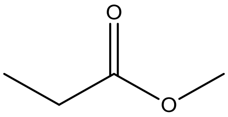


(S)-ibuprofen (S)-naproxen

Figure 1.7: Some methoxycarbonylation of olefins products.

The aliphatic ester products of methoxycarbonylation of olefins are important in the production of surfactants, detergents and as essential oils, cosmetics, solvents, food flavours, monomers for vast bulk polymers and potential and promising fuel supplements [54]. Methoxycarbonylation is also among the most useful chemical processes in the manufacturing of poly-methyl methacrylate (PMMA), a greatly sought after transparent thermoplastic which is applied in many other areas. For example, in electronics, energy and coating [44]. The methoxycarbonylation of ethene results in methyl propionate, an intermediate in the production of methyl methacrylate (MMA) which is the monomer used in the manufacture of the poly-methyl methacrylate (PMMA) [55]. Table 1.2 shows a summary of some ester products and their applications.

Table 1.2: Some ester products and their uses.

Ester product	Structure	Application
Ethyl benzoate		Manufacture of perfumes
Methyl acetate		Solvents in paints and glues
Isobutyl acetate		Fuel supplement
Isopropyl myristate		Cosmetics
Methyl propionate		Manufacture of poly-methyl methacrylate

The next chapter reviews the design and development of palladium(II) complexes as catalysts in the methoxycarbonylation reactions in both homogenous and immobilized catalyst systems. The specific focus is given to ligand design and its influence in catalytic activity and selectivity.

1.6 References

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CHAPTER TWO

Literature review of palladium(II) complexes as homogeneous and immobilized catalysts for methoxycarbonylation reactions

2.1 Introduction.

Palladium(II) catalysts have drawn a lot of interest in the methoxycarbonylation of olefins because of their better catalytic activities [1]. Based on the reaction conditions coupled with the catalytic system used, a considerably greater regioselectivity towards either linear or branched esters may be achieved through the use of palladium(II) catalysts [2-5]. A number of reports have a considerable range of palladium(II) catalysts composed of various ligand designs which show activities and selectivities towards the methoxycarbonylation of olefins like styrene, 1-hexene [6], cyclohexene, methyl styrene [7] and ethene [8] under different reaction conditions. Varied selectivities towards the branched products have also been achieved using the palladium(II) complexes with phosphine stabilizer and an acid promoter such as p-toulenesulfonic acid [9]. Using the palladium(II) catalyst alone without any phosphine stabilizer and an acid promoter results in the formation inactive complex of palladium(0). It has been proposed that promoters help facilitate the generation of a palladium-hydride intermediate and reactivating the palladium(0) group through the addition of triphenyl phosphine by oxidative addition of the acid and therefore, explaining their importance [7]. In the following section, possible mechanisms involved in the methoxycarbonylation are also discussed.

2.2 Proposed mechanism for methoxycarbonylation of olefins

Like other catalytic reactions with different proposed mechanisms, methoxycarbonylation of olefins catalysed by palladium(II) has been suggested to proceed through two likely mechanisms, namely: carbomethoxy and hydride mechanisms (Figure 2.1). However most studies in literature have suggested the hydride mechanism [10-14].

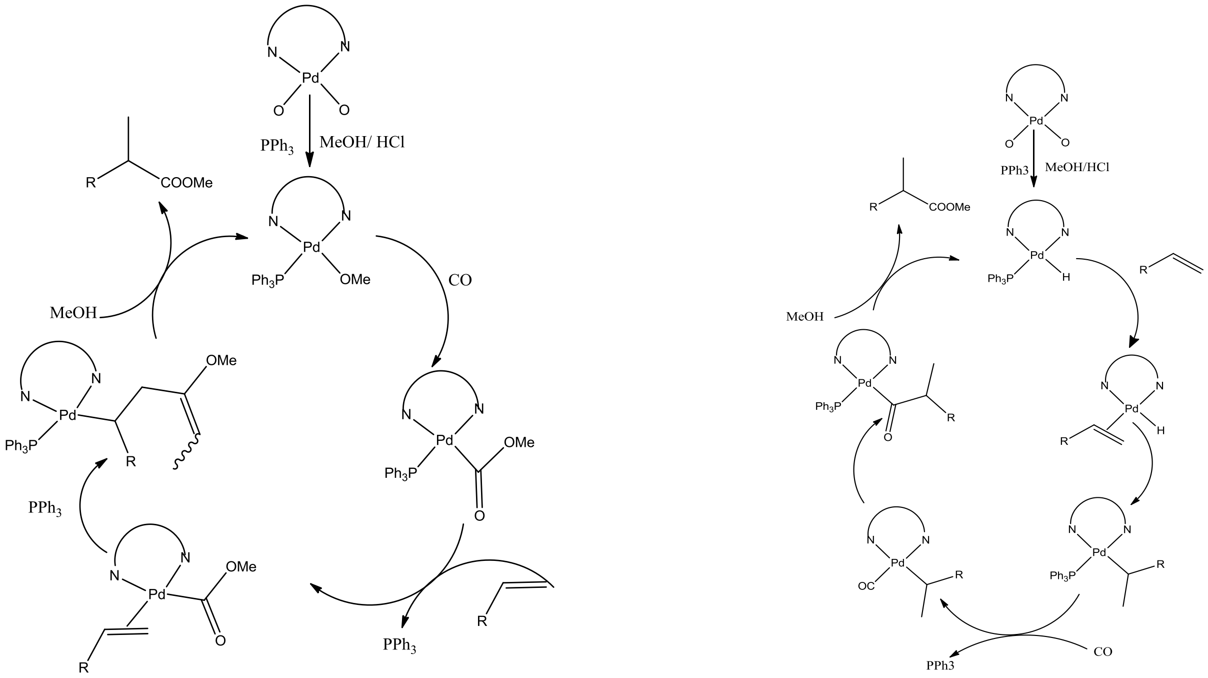


Figure 2.1: Proposed mechanism for palladium(II) catalysed methoxycarbonylation of olefins [8].

In the carbomethoxy mechanism, the whole process is triggered via the creation of Pd-OMe bond which is hydrochloric acid facilitated. The migratory insertion of carbon monoxide to the Pd-OMe then follows giving an ester before the olefin coordination [8]. In hydride mechanism as opposed to carbomethoxy, a Pd-H bond and not the Pd-OMe bond creation occurs in the activation stage. Substrate coordination then follows and afterwards carbon monoxide coordination and migratory insertion resulting to a coordinated ketone ester. The generation of Pd-H active species proceeds via methanolysis. There is a similarity in both mechanisms in that the formation of branched or linear product is directed by the 1, 2 or 2, 1 substrate insertions where either the olefin is inserted into the Pd-OMe or Pd-H species [9, 13]. The PPh_3 performs a function of majorly stabilizing the 14-electron species when Pd-OMe or Pd-H active groups are formed [8].

2.3 Catalytic systems used for methoxycarbonylation

2.3.1 P^P donor catalytic systems

Palladium(II) complexes formed from diphosphine ligands have been reported to give active catalysts in the methoxycarbonylation of olefins [7, 15-16]. For example, de la Fuente *et al.* [14], reported palladium(II) complexes of *cis*-1, 2- bis (di-tertbutyl-phosphinomethyl) carbocyclic ligands as catalysts (Figure. 2.2) in methoxycarbonylation of ethene.

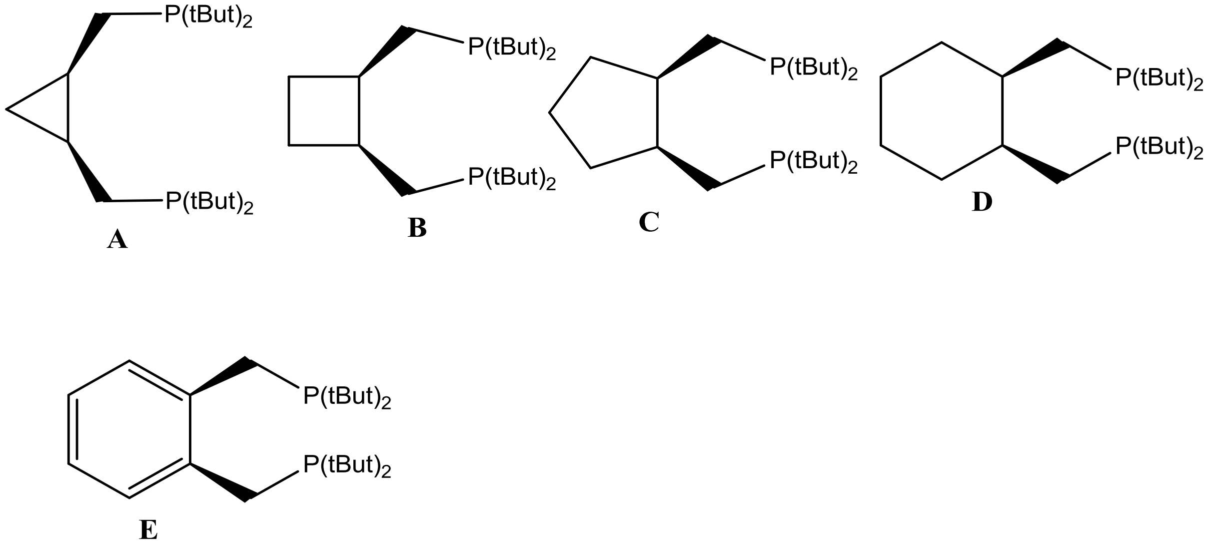


Figure 2.2: P, P- donor systems used by de la Fuente *et al.*, in the methoxycarbonylation of ethane to methyl propanoate [11].

By varying the size of the cyclic backbone, the catalytic activity of the system also changed. For example, palladium(II) catalysts synthesized from **A**, **B** and **D** with three, four and six membered rings in the ligand backbone were found to be more active the **E**, a five-membered ring ligand backbone catalytic system. Palladium(II) catalysts from **A**, **B** and **D** were similarly found to be more active than **C**, a five membered ring as **E**, though with no double bonds. The literature failed to report any established catalytic activity trend obtained as far as ring size is concerned and thus there is no clear correlation between catalyst performance and the flexibility in the chelate ring [6].

Another P^P donor palladium(II) systems for methoxycarbonylation of olefins has also been reported by Zolezzi *et al.* [7] where they used palladium(II) complexes containing phosphine donor ligands derived from naphthyl(diphenyl)phosphine (Figure 2.3). These palladium(II) complexes under mild conditions of pressure and temperature show higher catalytic activities in the methoxycarbonylation of styrene (93%) than cyclohexene (47%) and n-hexene (61%). The catalytic activities of the complexes are dependent on the substrate used, for example, complex **A** (Figure 2.3) show high activity in the methoxycarbonylation of styrene, giving a conversion of 93% and selectivity of 92% towards the branched ester within 6 h at catalyst to substrate ratio of 1:400 (TOF = 62 h^{-1}). On the other hand, the same catalyst exhibits moderate conversions of 40% to 61% for n-hexene, α-methylstyrene and cyclohexene under similar reaction conditions. Replacing the chlorides at the metal center with the trifluromethanesulfonates to give complex **B** does not confer any significant difference in their catalytic activities and selectivities. A slight increase in the conversion of styrene from 93% to 97% was observed. However, the selectivity towards the branched isomer remained largely the same (92% and 93%).

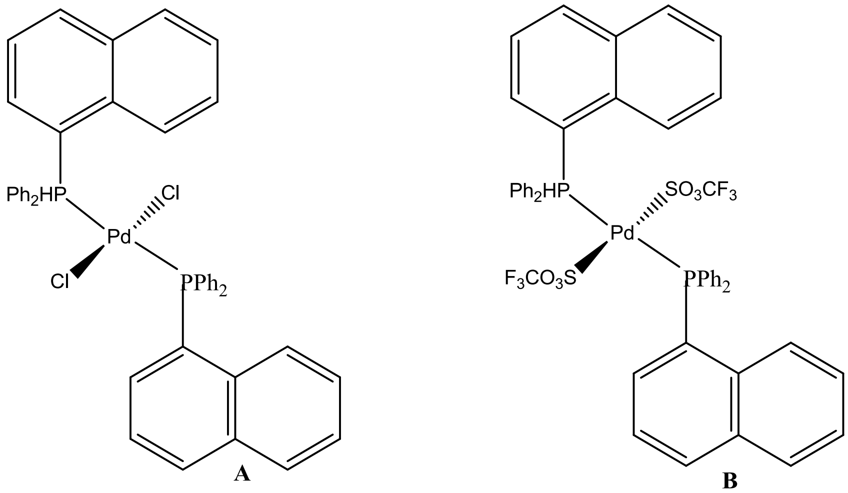


Figure 2.3: The P^P donor systems reported by Zolezzi *et al.*, used in the methoxycarbonylation of styrene n-hexene, α-methylstyrene and cyclohexene [7].

Bianchini *et al.,* [17] applied palladium(II) complexes anchored on 1, 1-bis (diphenylphosphino) octamethylferrocene (dppomf), 1, 1-bis (diphenylphosphino) ferrocene (dppf), 1, 1-bis (diphenylphosphino)osmocene (dppo) and 1, 1-bis (diphenylphosphino) ruthenocene (dppr) ligands (Figure 2.4) in the methoxycarbonylation of styrene. The 1, 1-bis (diphenylphosphino) metallocene palladium(II) complexes in the presence of TsOH give active and selective catalysts for the methoxycarbonylation of styrene, resulting in predominantly the linear isomer, methyl 3-phenylpropanoate. With respect to catalytic activity, catalyst **C** displays the highest turnover frequency (TOF) of 334 mol of products per mole of catalyst. Changing the metallocene metal from Ru, Fe and Os or substituting cyclopentadienyl ligands with methyl cyclopentadienyl ligands did not appreciably change chemoselectivity nor regioselectivity [17]. The activity of the catalysts also increases with increase in temperature. For example, catalyst **C** gives a conversion of 31% and 73% at 80 ^{o}C and 100 ^{o}C respectively with higher catalytic activity at a higher temperature indicative of thermal stability of the catalyst.

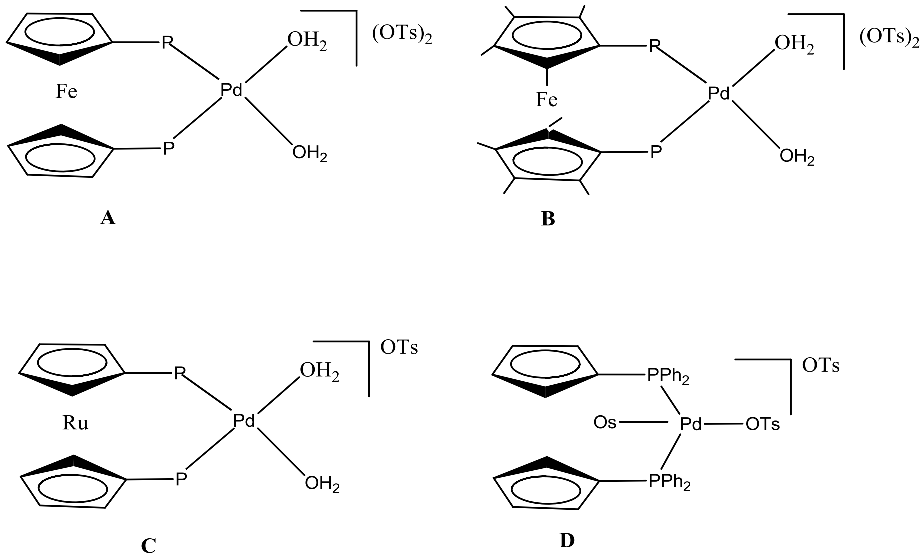
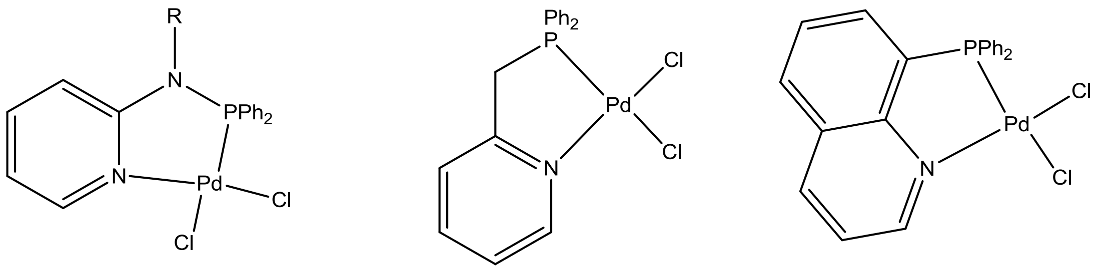


Figure 2.4: The P^P donor systems used by Bianchini *et al.,* in the methoxycarbonylation of styrene [17].

2.3.2 P^N donor Palladium(II) catalytic systems

Heterobidentate P, N donor ligands are a class of ligands which have a lot of importance in various catalytic transformations [18]. Pedro *et al.,* [6] employed P, N donor palladium(II) systems for the methoxycarbonylation of olefins. The systems investigated in the methoxycarbonylation of the olefins include palladium(II) complexes bearing, 2-(diphenylphosphinoamino) pyridine (Ph_2PNHpy), 2-[(diphenylphosphino) methyl] pyridine (Ph_2PCH_2py), and 2-(diphenylphosphino) quinoline (Ph_2Pqn) (Figure 2.5).



Ph$_2$Pqn

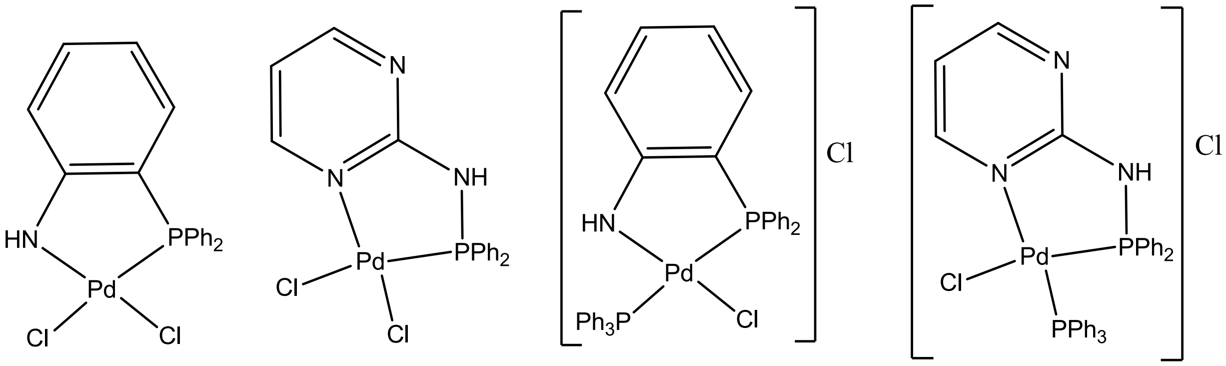
R=H; Ph$_2$PNHpy **A** Ph$_2$PCH$_2$py **C** **D**

R=Me: Ph$_2$PNMepy **B**

Figure 2.5: P, N donor systems used by Pedro *et al.,* in the methoxycarbonylation of olefins [3].

The use of complex **A** [PdCl (PPh$_3$)(Ph$_2$PNHpy)]Cl, promotes the conversion of olefins to ester products with ranges of activities, chemoselectivities and regioselectivities. The nature of the olefin substrate influences the catalytic activities of the complexes. For example, complex **A,** is more efficient in the methoxycarbonylation of styrene than cyclohexene and 1-hexene. Under similar conditions of catalyst concentration, pressure and temperature, complex **A** gives conversions of 99 % for styrene but only 19% for cyclohexene and 43% for 1-hexene in 24h. Comparatively, complexes **C,** and **D** display lower catalytic activities in the methoxycarbonylation of styrene than complexes **A** and **B**. Replacement of the ligand in complex **D** with (diphenylphosphino), phenylamine (Ph$_2$PNHPh), or 2-(diphenylphosphinoaminomethyl) pyridine (Ph$_2$PNMepy) also significantly reduces the catalytic activities of the complexes, indicating that both the presence of the pyridine fragment as well as the NH group, are essential in achieving high catalytic activities [6].

Abarca *et al.,* also reported the use of palladium(II) complexes bearing P, N donor ligand for methoxycarbonylation of styrene. They used palladium(II) complexes bearing (2-diphenylphosphino) pyrimidine and 2-diphenylphosphinoaniline ligands (Figure 2.6) to achieve different chemoselectivities and regioselectivities depending on the catalyst structure. Under similar reaction conditions, neutral complexes **A** and **B** (Figure 2.6) give chemoselectivities of 71% and 75% respectively towards the ester products with regioselectivities of 75% and 82% towards the branched isomer products in 6 h. The cationic complexes **C** and **D** generated from **A** and **B** respectively afford improved ester products formation. Complex **C** and **D** afford chemoselectivities of 99% and 93% with regioselectivities of 97% and 96% respectively towards the branched products [19]. Complexes **A** - **D** therefore have remarkable regio-and chemoselectivities in the methoxycarbonylation of styrene. However, **B** and **D** perform slightly better than **A** and **C** respectively due to the presence of pyridine fragment [19].

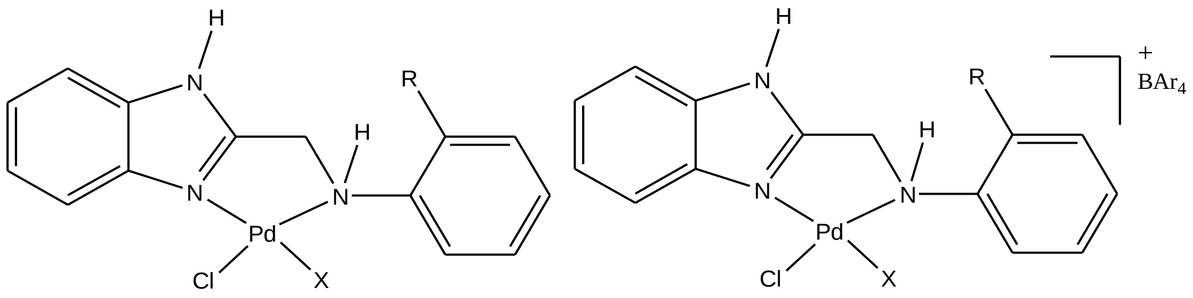


A **B** **C** **D**

Figure 2.6: P, N donor systems used by Abarca *et al.*, in the methoxycarbonylation of styrene [19].

2.3.3 N^N donor catalyst systems

Multidentate N^N donor ligand systems represent another group which have been used recently to in the methoxycarbonylation of olefins. In one such report, Tshabalala *et al.* [20] used palladium(II) complexes with N^N ligand backbone in the methoxycarbonylation of olefins (Figure 2.7).



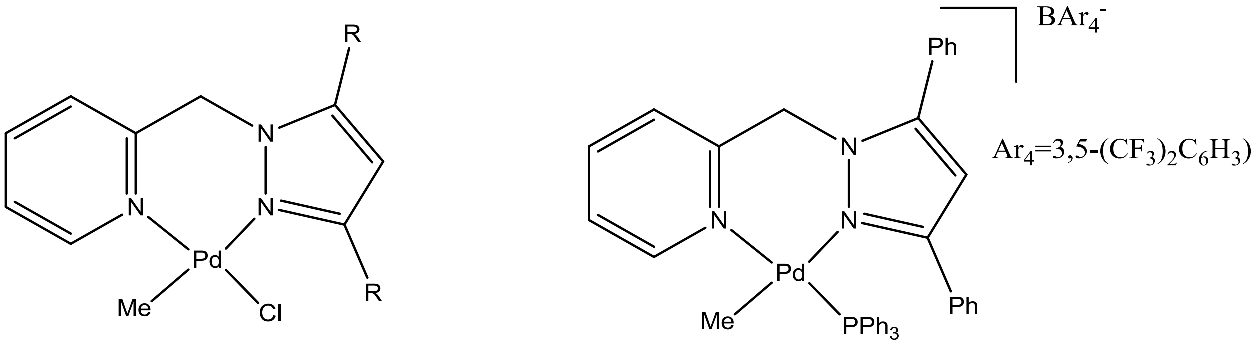
R=OCH$_{3,}$ X=Cl - **A**
R=OCH$_{3,}$ X=Me-**B**
R= Br, X=Me -**C**

R=OCH3, X= Me **- D**
R=Br, X= Me **-E**
Ar$_4$=3,5-(CF$_3$)$_2$C$_6$H$_3$)

Figure 2.7: N, N donor systems used by Tshabalala *et al.*, in the methoxycarbonylation of olefins to yield ester products [20].

In terms of their catalytic activity, the structure of the complex plays a major role, for example complex **D** whose system bears a methoxy on the phenyl ring is more active than complex **E** whose system has a bromide on the same spot. This is due to the electron donating effect of OCH$_3$ group. The Pd-Cl/Me bond on the complex structure also has an effect on the activity. For example, complex **A** bearing Pd-Cl bond and Complex **B** bearing the Pd-Me bond give conversions of 52% and 80% respectively under comparable conditions. The behaviour is attributed to the ease of CO insertion into the Pd-Me compared to Pd-Cl bond which must be activated by methanol solvent [15]. The addition of PPh$_3$ influences regioselectivity, for instance, the addition of PPh$_3$ to complex **E** results in a decrease of the branched ester from 68% to 40% which is largely attributed to steric hindrance from the bulky PPh$_3$. The best result is obtained by complex **D** where a conversion of 49% of hexene to the products is achieved after 12 h [20].

Alam *et al.* also employed (pyrazolylmethyl) pyridine palladium(II) complexes bearing N^N donor ligands in the methoxycarbonylation of olefins (Figure 2.8). The structures of the complexes have influence on their catalytic activities. For example, in the methoxycarbonylation of 1-octene, complex **A** which contains the CH_3 moiety on the pyrazolyl ring affords a conversion of 63% compared to a conversion of 77% for complex **B** which bears phenyl substituents. The nature of the complexes however do not have a bearing on the regioselectivity of the esters. Formation of branched esters is however boosted in the absence of triphenyl phosphine due to the reduced steric hindrance around the palladium(II) coordination sphere and hence promoting chain migration/isomerization of the coordinated olefins [22-24]. Varying the reaction temperatures also affect the catalytic activities. For example the activity of complex **B** drops from a conversion of 77% to 24% when the temperature varies from 90 ^{o}C to 60 ^{o}C respectively. On the other hand, the change in temperature does not appreciably alter the regioselectivities.



R=Me, **A**
R= Ph, **B**

C

Figure 2.8: (Pyrazolylmethyl) pyridine palladium(II) complexes applied by Alam *et al.* in the methoxycarbonylation of different olefins [21].

2.3.4 Immobilized catalyst systems

In an effort to overcome the difficulty of recyclability and reuse of homogeneous catalyst, there have been a number of reports concerning the immobilization of homogeneous catalysts on different supports and their application in a wide range of transition metal catalyzed reactions including olefin transformation reactions [25-33]. Some of the support materials which have been widely used include, silica, clay and polymer supports. Even though the immobilized catalyst systems have been used in many olefin transformation reactions, it is surprising that methoxycarbonylation has had fewer reports. The next section captures some of these rare instances where supported palladium(II) systems have been applied in the methoxycarbonylation reactions.

2.3.4.1 Clay supported catalysts

Crocker and Herold reported using palladium(II) derivatives which were intercalated in different forms of clay for the methoxycarbonylation of ethylene [34]. They used palladium(II) derivatives [Pd (PPh) (NCMe)][BF] and $Pd(NO_2)_2.3H_2O$ intercalated montmorillonite. The $[Pd (PPh_3)_3 (NCMe)]^{2+}$ complex supported on montmorillonite results in a more active catalyst than $[Pd(OH_2)_4]^{2+}$ complex supported on a similar montmorillonite.

Other clay supports of high Brønsted acidity were examined giving different results. For example, proton-exchanged montmorillonite and montmorillonite exchanged with Al^{3+} or Cr^{3+}. The high Brønsted acidity materials, due to their less polarizing effect as compared to the Na^+ ion afford moderate activities of 60-70 turnovers h^{-1} in the methoxycarbonylation of ethylene when used as support for $[Pd(PPh_3)_3 (NCMe)]^{2+}$. They also investigated the effects of catalyst loading, temperature and catalyst recycling on the activity of the catalyst. Temperature values of between 100-120 ^oC yield best results, even though the paper does not report the results from these optimum temperature conditions. Changing the catalytic loading has different effects on the activities of the catalysts. Catalyst $[Pd(OH_2)_4]^{2+}$ supported on potassium montmorillonite shows an increase in turnover rate per active site when the catalytic loading is reduced. As an example, loadings of 1.0% and 0.3 % gives a TOF of 60 h^{-1} and 90 h^{-1} respectively, while under comparable conditions, $[Pd(PPh_3)_3(NCMe)]^{2+}$ affords a constant TOF of 115 h^{-1}. The $[Pd(PPh_3)_3(NCMe)]^{2+}$ supported on potassium montmorillonite was recycled with no activity loss in cases where recycling was done under inert atmosphere.

2.3.4.2 Polymer supported palladium(II) catalysts

Wan *et al.*, reported the use of polymer-supported PVP-Pd-Ni-PPh_3 bimetallic catalyst obtained *in situ* from PVC-$PdCl_2$, $NiCl_2$ and PPh_3 for methoxycarbonylation of styrene under mild reaction conditions [35]. $PdCl_2$ shows no catalytic activity, but on addition of PPh_3 in a ratio of 5:1 to palladium(II), the conversion and the selectivity towards the branched ester becomes 42% and 82% respectively after 10 h. The $PdCl_2$ –4$NiCl_2$ –5PPh_3 catalyst exhibits a conversion of 76% and selectivity of 95% even though $NiCl_2$ by itself shows no activity. The polymer- supported PVP–$PdCl_2$ –4$NiCl_2$ –5PPh_3 catalyst gives a conversion of 99% and a selectivity of 95% towards the branched product under the same reaction conditions [35]. To determine the effect of changing the amount of PPh_3 to catalytic activity and selectivity, PVP–$PdCl_2$ –4$NiCl_2$ –*n*PPh_3 catalytic system was examined. The best result is obtained when Pd: PPh_3 is 1:1. The best catalyst, PVP–$PdCl_2$ –4$NiCl_2$ –PPh_3 exhibits no catalytic activity at 20 ^oC and very low catalytic activity at 40^0C while the catalytic activity increases as the temperature rises with the best results realised at an optimum temperature of 80 ^oC [35]. The PVP–$PdCl_2$ –4$NiCl_2$ –PPh_3 is the most active, affording a conversion of 100% and selectivity of 99% towards the branched ester in 10 h at CO pressure of 2.1 MPa and temperature of 80 ^oC [35].

Chen *et al.* [36] managed to heterogenize their homogeneous catalysts through the immobilization of the complexes on the surface of polymer support. They synthesized a porous 2-vinyl-functional diphenyl-2 pyridylphosphine (2V-P, N) polymer (POL-2V-P, N) which were used as support in the immobilization of palladium(II) complexes.

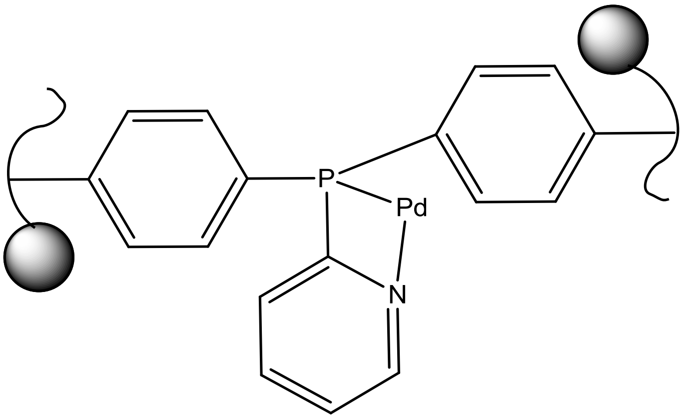


Figure 2.9: Pd/POL-2V-P, N catalyst system by Chen *et al.* in the methoxycarbonylation of acetylene [36].

The immobilized systems display high catalytic activities for the methoxycarbonylation of acetylene to produce methyl acrylate. In comparing the activity of homogeneous Pd-N, P catalyst and the immobilized Pd/POL-2V-P, N catalyst under the similar conditions, the Pd/POL-2V-P, N affords a TOF of 2983.3 h^{-1}, higher than that of the corresponding homogenous catalyst which gives a TOF of 1238.8 h^{-1}. This is due to the fact that the Pd species of the Pd/POL-2V-P, N catalyst is coordinated with the exposed nitrogen and phosphorus atoms of the POL-2V-P, N, therefore, the catalytic active species of both catalysts are Pd/N, P complex [36]. However, for the immobilized catalyst, the active species is located on the surface of the POL-2V-P, N support, whereas in the homogeneous catalyst it is a soluble species in the reaction mixture. The excellent activity of the Pd/POL-2V-P, N could have been from the high surface area and large pore volume of the POL-2V-P, N polymer allowing the substrates more access to the active metal site [36]. The immobilized catalyst Pd/POL-2V-P, N is recycled and reused three times. The activity after the third cycle (78%) is higher than the first cycle where the conversion is at 72%. Such an observation is attributed to catalytic activation in the third cycle.

2.3.4.3 Magnetic nanoparticles support

Apart from other methods of immobilization which in most cases require filtration and centrifugation for catalyst recovery, magnetic supports provide an alternative route. The magnetic nanoparticles with high stability, large surface area, superparamagnetic properties, high reactivity and facile preparation have in recent years come up as robust supports which could be isolated by simply using an external magnetic field [37-40].

Duta *et al.* reported palladium(II) catalyst supported on magnetic nanoparticles modified with aminofuctionalized dihydro-imidazolium groups for alkoxycarbonylation of aryl bromides (MNP-Im-NH_2-Pd). The MNP-Im-NH2-Pd catalyst was tested in the methoxycarbonylation of various aryl bromides. The methoxycarbonylation of 4-bromoacetophenone, 4-bromoanisole and 4-bromotoluene gives comparable activities of about 90% indicating that the presence of electron-withdrawing or electron donating groups has no significant effect on the catalytic activity. Catalyst MNP-Im-NH2-Pd also affords a range of activities when different bases are used. In the methoxycarbonylation of bromobenzene, in the presence of triethylamine a yield of 90% of methyl benzoate is achieved while inorganic bases like Cs_2CO_3 and K_2CO_3 afford yields of 75% and 80% respectively.

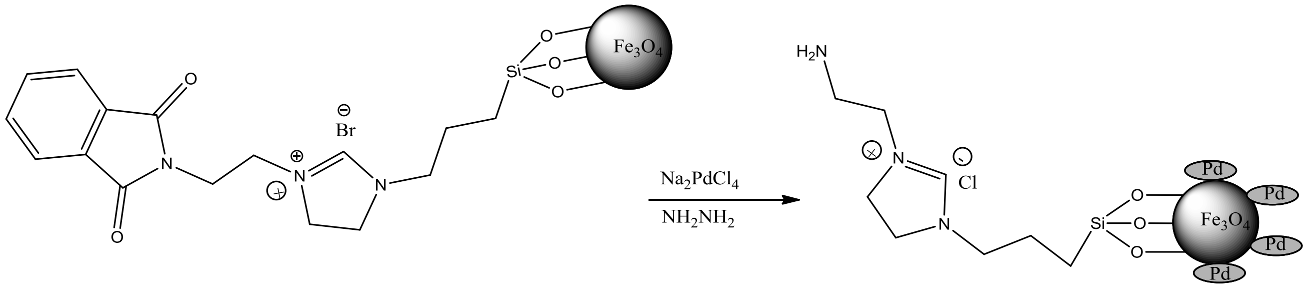
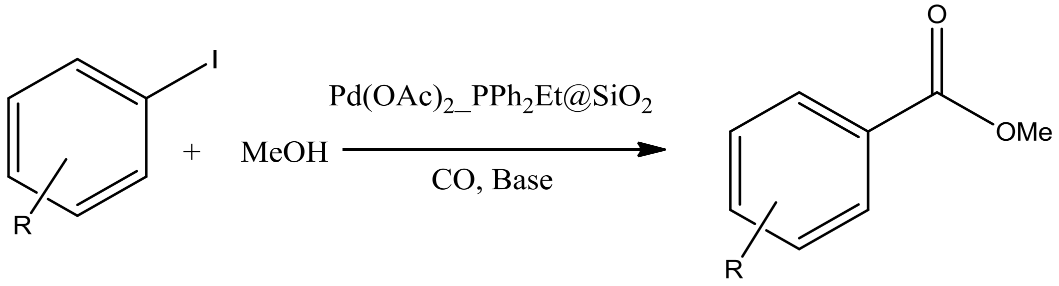


Figure 2.10: Palladium(II) nanoparticles catalyst supported on magnetic nanoparticles used by Duta *et al.* [41].

2.3.4.4 Silica supported systems

Even though the research on the heterogenization of the homogeneous catalysts systems has been going on for years, there are currently few reports about silica supported systems for the methoxycarbonylation of olefins. This section therefore reviews some of the few systems reported.

Mane *et al.* reported the use of palladium(II) phosphine complexes supported on silica (2-diphenylphosphinoethyl functionalized silica) for the alkoxycarbonylation of aryl iodides to yield aromatic esters (Figure 2.11). They used two catalysts; $PdCl_2$_PPh_2Et@SiO_2 (**A**) and Pd $(OAc)_2$_PPh_2Et@SiO_2 (**B**) in the methoxycarbonylation of various aryl iodides. For both catalysts, a decrease in catalytic loading leads to a lower catalytic activity, for instance, 0.6 mol% of catalyst **A** affords a conversion of 100% of iodobenzene while a lower loading of 0.4 mol% gives 93% and a reduced chemoselectivity of 85% down from 99% of methyl benzoate under similar reaction conditions [42]. Higher reaction times results into higher catalytic activities, as an example, increasing the reaction time from 1 h to 2 h raises conversion from 93% to 100% while at the same time improving chemoselectivity from 87% to 99% [42]. Catalyst **A** similarly affords higher conversion at increased temperatures, for instance, at a temperature of 100 °C, the catalyst converts 100% of the substrate with a chemoselectivity of 99% while the catalytic activity drops drastically to 75% with a chemoselectivity of 73% when the temperature is lowered to 70 °C. Under the optimized conditions, catalyst **A** was recovered and recycled five times without a notable activity loss since run 1 gives a conversion of 99% while run 5 displays a 95% conversion [42].



R=H, Me. OMe, NH_2,
COMe, NO_2, CN

Figure 2.11: Methoxycarbonylation of Aryl iodides to yield benzoate esters [42].

Another silica supported palladium(II) catalysts for the alkoxycarbonylation of aryl iodides was reported by Khedkar *et al.* [43]. The group used palladium(II) phosphine free catalysts supported on silica, Aerosil 300 (Figure 2.12). They used different solvents apart from the alcohol to determine the solvent effects on the activity of the catalysts. Reactions in toluene affords the highest activity (90%) while DMF and 1, 4-dioxane gives 56% and 62% respectively [43]. The variations in the CO pressure also produces varied results where the best conversion (90%) is achieved at a pressure of 1 MPa. Lowering the CO pressure to 0.5 MPa reduces the conversion to 80%. The recyclability studies shows that the catalyst is recyclable and active up to four cycles in the methoxycarbonylation of iodobenzene. The first run gives a chemoselectivity of 96% while the fourth run affords a 90% chemoselectivity [43].

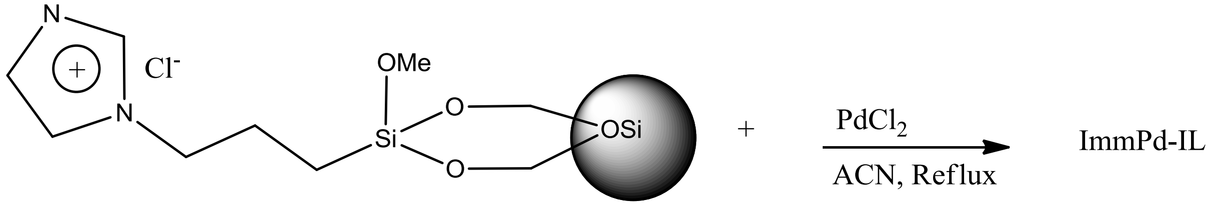


Figure 2.12: Synthesis of silica supported catalyst (ImmPd-IL) by Khedkar *et al.* [43].

2.4.1 Problem statement

Homogeneous catalysts have various advantages one of which is possessing active site but it is difficult to recovery the catalysts, heterogeneous catalysts on the other hand has strengths which are missing in homogeneous catalysis in that the heterogeneous catalysts are easy and cheap to recover in addition to having good thermal stability. Creating a bridge between homogeneous and heterogeneous catalysis has been a key challenge in chemical industry, i.e. combining the advantages of both catalytic systems to come up with a hybrid system for methoxycarbonylation of olefins. Higher olefins have limited uses in real life and therefore, there is a need to transform them to other useful products such as esters, carboxylic acids.

2.4.2 Justification of the study

The methoxycarbonylation reaction constitutes a part of important organic reactions in the transformation of olefins to produce many useful products domestically and industrially like detergents, cosmetics and pharmaceuticals [44-46]. For decades, palladium(II)-catalysts have drawn a lot of interest in the methoxycarbonylation of olefins because of better catalytic activities [9]. It is therefore important to design not only selective and active catalysts, but also recyclable systems for ease of separation from the reaction mixture for efficient and cost-effective industrial applications.

2.4.3 Aim of the project

The overall aim of this research project was to design active, selective and recyclable catalysts in the methoxycarbonylation of higher olefins.

2.4.4 Specific objectives of the project

To achieve the above aim, the following objectives have been arrived at:

i. To synthesize and characterize mixed nitrogen – oxygen donor ligands and their palladium(II) complexes.
ii. To immobilize and characterize homogeneous complexes.
iii. To test both systems for the activity in methoxycarbonylation of olefins.
iv. To optimize the reaction conditions of the methoxycarbonylation catalysis.

The next chapter dwells on the synthesis and characterization of ligands and homogeneous complexes and their catalytic application in the methoxycarbonylation of olefins.

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CHAPTER THREE

Synthesis and characterization of (phenoxy)imine ligands and their homogeneous palladium (II) complexes for methoxycarbonylation of olefins

3.1 Introduction

Metal complexes containing nitrogen donor ligands have been used in catalysis for many years and are pivotal in coordination chemistry in general (Sunatsuki, Motoda, & Matsumoto, 2002)[1]. Synthesis of Schiff base ligands including their coordination to metal centres have been studied for many years since Hugo Schiff reported on the condensation between an aldehyde and an amine leading to a Schiff base ligand in 1864 [2]. Depending on the choice of the aldehyde and amine, these condensation reactions can proceed under a number of reaction conditions and in different solvents [3]. Schiff bases can also be formed by condensation of a ketone and an amine but it is less efficient due to increased steric hindrance in ketones [4]. Schiff base metal complexes have many applications in chemical catalysis, such as in olefin polymerization [5, 6, 7], epoxidation reactions [8, 9], Suzuki cross-coupling reactions [10], oxidation reactions [11], and methoxycarbonylation reactions [12-20] among other applications.

Over the last years, a range of palladium(II) complexes with different structures have been used in homogeneous methoxycarbonylation of olefins as discussed partly in literature review in chapter two. Depending on the aims of different studies, different researchers designed their catalyst systems to get varied catalytic activities and selectivities, in the methoxycarbonylation of olefins [12-20]. The palladium(II) complexes have been applied widely in the methoxycarbonylation catalysis because of their selectivity and catalytic activity [12-22]. Examples of the palladium(II) complex systems reported to have been used in the methoxycarbonylation of olefins include, P^P donor systems reported by De La Fuente *et al.*

[13], Bianchini *et al.* [16] and Zolezzi *et al.* [21]. P^N donor palladium(II) complexes have been reported by Pedro *et al.* [22] and Abarca *et al.* [18], while N^N donor systems have been reported by Alam *et al.* [19] and Tshabalala *et al.* [20].

In this chapter, we report the synthesis and characterisation of (phenoxy) imine ligands, and their palladium(II) metal complexes using (3-aminopropyl) triethoxy silane (APTES). We also report the catalytic application of the homogeneous mixed nitrogen - oxygen palladium (II) complexes in the methoxycarbonylation of olefins. The effect of substrate chain length, catalyst structure design, temperature, pressure, solvent, nature of acid promoter and the type of phosphine applied have been explored and the results are therefore reported in this chapter.

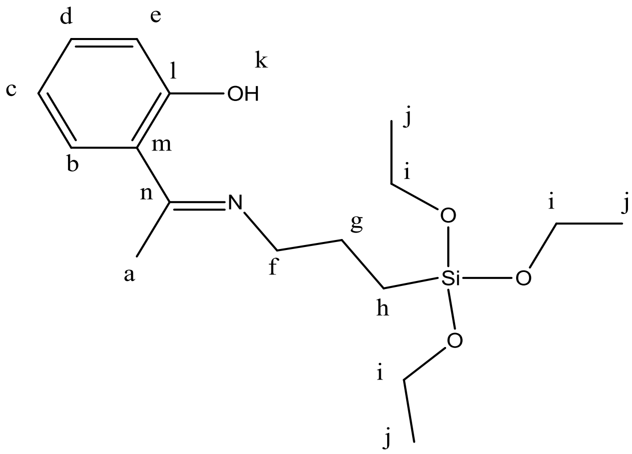
3.2 Experimental section and methods

3.2.1 General instrumentation and materials

The synthesis of the compounds was performed under pure nitrogen atmosphere and moisture free conditions using standard Schlenk techniques. All solvents purchased from Merck were of analytical grade and were dried before use. Toluene was dried over sodium wire and benzophenone, methanol dried by heating over magnesium activated with iodine. Dichloromethane was dried over phosphorus pentoxide under nitrogen and stored in molecular sieves before use, DMF was dried over calcium oxide, while chlorobenzene was dried over phosphorus pentoxide [23]. The reagents (3-aminopropyl) triethoxy silane (purity 99%), 2-hydroxyacetophenone (purity, 98%), 2-hydroxy-5-methylbenzaldehyde (purity, 98%), palladium(II) dichloride, palladium (II) acetate, C_6-C_{10} olefins, hydrochloric acid, p-TsOH, PPh_3, dppe, $P(Cy)_3$ were bought from Sigma-Aldrich and were used as received without further purification. The ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Ultrashield 400 (^1H NMR 400 MHz, $^{13}C\{^1H\}$ NMR 100 MHz) spectrometer in $CDCl_3$ solution at room temperature. The chemical shift values (δ) were referenced to the residual proton and carbon signals at 7.24 and 77.0 ppm, respectively of the $CDCl_3$ NMR solvent. The infrared spectra were recorded on a Perkin-Elmer Spectrum 100 in the 4000–400 cm^{-1} range. Mass spectral analyses were carried out using LC premier micromass.

3.2.2 Synthesis of (phenoxy)imine ligands and palladium(II) complexes

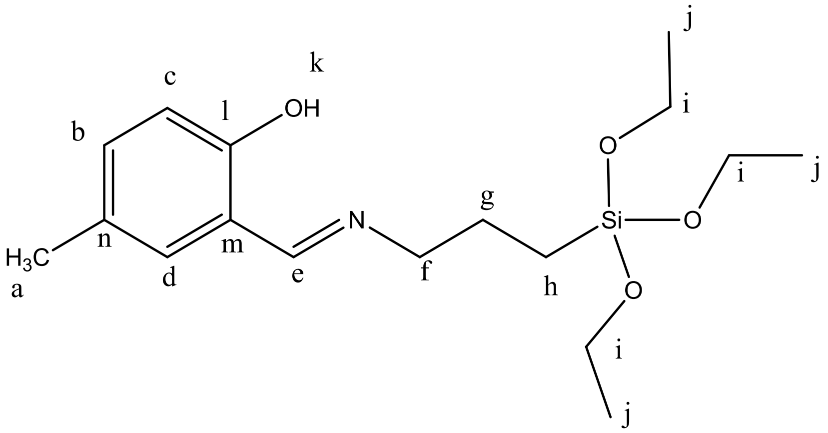
*3.2.2.1 Synthesis of 2-phenyl-2-((3-(triethoxysilyl)propyl)imino) ethanol (**L1**)*



A solution of 2-hydroxyacetophenone (1.36 g, 10.00 mmol) in toluene (25 ml) was refluxed using Dean-Stark apparatus for 3 h followed by addition of a solution of (3-aminopropyl) triethoxy silane (APTES) (2.21 g, 10.00 mmol) in toluene (15 ml) and the mixture further refluxed for 24 h. At the end of the reaction, the organic solvent was evaporated under vacuum to give **L1** as a yellow oil. Yield =3.20 g (94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.79 (t, 2H, J = 8.4 H$_z$, H$_h$) , 1.26 (t, 9H, $^3J_{HH}$ = 7.2 Hz, H $_j$), 1.91 (m, 2H, H$_g$), 2.38 (s, 2H, H$_a$) , 3.60 (t, 2H, $^3J_{HH}$ = 7.2 Hz, H$_f$) , 3.86 (q, 6H, $^3J_{HH}$ = 7.2 Hz, H $_i$), 6.76 (d, 1H, $^3J_{HH}$ = 7.2 Hz, H$_b$) 7.02 (d, 2H, $^3J_{HH}$ = 8.4 Hz, H$_e$), 7.28 (dt, 1 H, $^3J_{HH}$ =7.2 Hz, H$_c$) 7.52 (d, 1H, $^3J_{HH}$ = 8.0 Hz, H$_d$). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 171.46 (C$_n$), 165.24 (C$_l$), 132.56 (C$_d$), 129.03 (C$_b$), 127.95 (C$_m$), 119.20 (C$_c$), 116.48 (C$_e$), 58.45 (C$_i$), 51.41 (C$_f$), 23.94 (C$_a$), 18.31 (C$_j$), 14.14 (C$_g$)

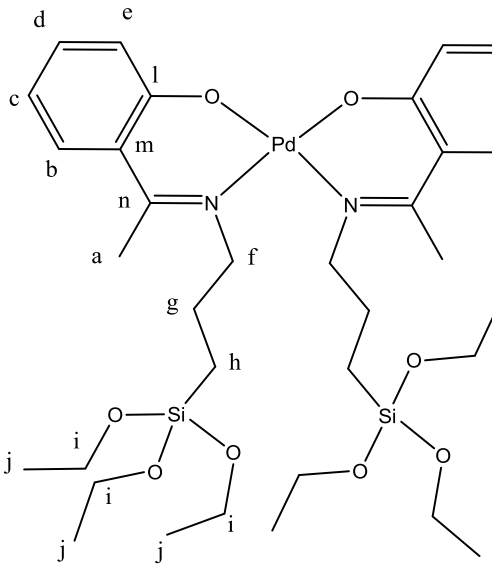
8.19 (C_h). MS (ESI) m/z (%) 255 (M^+, 100). HRMS-ESI ([M^+-H^+]): m/z calc: 339.5; found: 340.0. IR ν_{max}/cm^{-1}: $\nu_{(OH)}$ = 2973, $\nu_{(C=N)}$ = 1615, $\nu_{(Si\text{-}O)}$ = 1071.

*3.2.2.2 Synthesis of 4-methyl-2-(((3-(triethoxysilyl)propyl)imino)methyl)phenol (**L2**)*



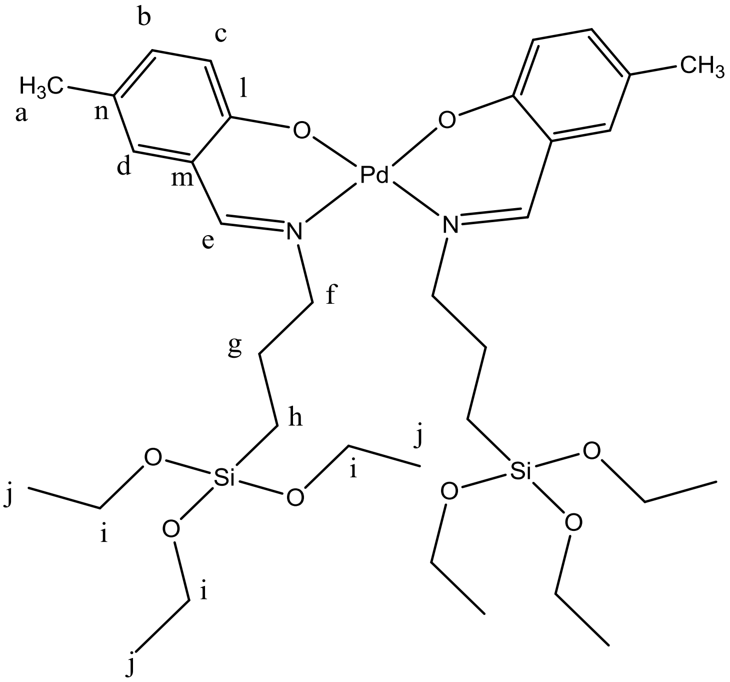
To a solution of 2-hydroxy-5-methylbenzaldehyde (0.82g, 6.00 mmol) in dichloromethane (30 ml), a solution of (3-aminopropyl) triethoxy silane (APTES) (1.33g, 6.00 mmol) in dichloromethane (10 ml) was added in drops and stirred for 12 h. The organic solvent was the evaporated under vacuum to obtain **L2** as a yellow oil. Yield= 1.54 g (75%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.71 (t, 2H, $^3J_{HH}$ = 8.0 Hz, H_h), 1.26 (t, 9H, $^3J_{HH}$ = 4.0 Hz, H_j), 1.90 (m, 2H, H_g), 2.31 (s, 3H, H_a), 3.70 (t, 2H, $^3J_{HH}$ = 8.0 Hz, H_f), 3.86 (q, 6H, $^3J_{HH}$ = 8.0 Hz, H_i), 6.88 (d, 1H, $^3J_{HH}$ = 8.0 Hz, H_b), 7.05 (s, 1H, H_d), 7.13 (d, 1H, $^3J_{HH}$ = 8.0 Hz, H_c), 8.31 (s, 1H, H_e). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 164.75 (C_l), 159.07 (C_e), 132.70 (C_b), 131.17 (C_n), 127.37 (C_d), 118.49 (C_m), 116.71 (C_c), 62.12 (C_f), 58.40 (C_i), 24.40 (C_a), 20.30 (C_g), 18.30 (C_j), 7.96 (C_h). MS (ESI) m/z (%) 454 (M^+, 100). HRMS-ESI ([M^+-H^+]): m/z calc: 339.5; found: 341.0. IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ = 2974, $\nu_{(C=N)}$ = 1634, $\nu_{(Si\text{-}O)}$ = 1073.

*3.2.2.3 Synthesis of [Pd (**L1**)$_2$] (**C1**)*



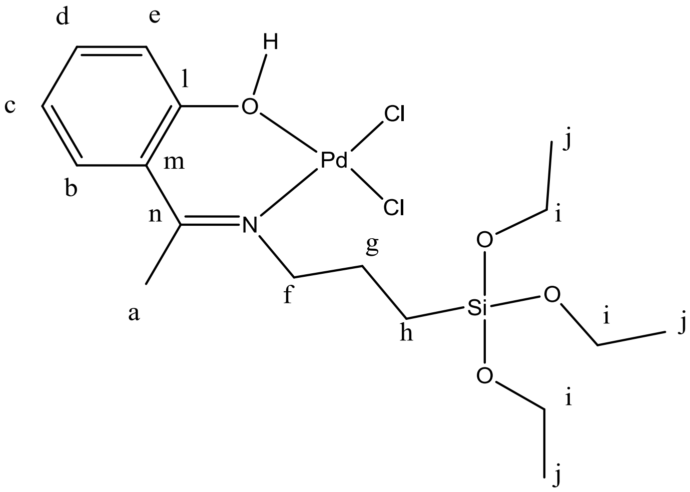
To a solution of **L1** (0.34 g, 1.00 mmol) in methanol (20 ml), Pd (OAc)$_2$ (0.11 g, 0.50 mmol) dissolved in methanol (15 ml) was added and the mixture refluxed under nitrogen for 8 h. The organic solvent was then reduced under vacuum and the resulting mixture filtered, washed with methanol and recrystallized from CH$_2$Cl$_2$-hexane mixture to afford **C1** as a yellow powder. Yield = 0.40g (79%). ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 0.79 (t, 4H, $^3J_{HH}$ = 8.0 Hz, H_h), 1.22 (t, 18H, $^3J_{HH}$ = 8.0 Hz, H_j) , 2.02 (m, 4H, H_g) , 2.45 (s, 4H, H_a), 3.80 (q, 16H, $^3J_{HH}$ = 8.0 Hz, $H_{f,i}$), 6.58 (t, 2H, $^3J_{HH}$ = 8.0 Hz, H_c), 6.87 (d, 2H, $^3J_{HH}$ = 8.0 Hz, H_b), 7.11 (t, 4H, $^3J_{HH}$ = 8.0 Hz, H_d),7.37 (d, 2H, $^3J_{HH}$ = 8.0 Hz, H_e). ^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 183.93 (C_n), 166.82 (C_l), 132.43 (C_d), 131.23 (C_b), 128.68 (C_m), 118.92 (C_c), 115.15 (C_e), 58.42 (C_i), 54.47 (C_f), 26.61 (C_a), 23.57 (C_j), 18.30 (C_g) 7.85 (C_h). Anal.calcd for $C_{34}H_{5}6N_{2}O_{8}PdSi_{2}.$ CH$_2$Cl$_2$: C, 48.41; H, 6.73; N, 3.23. Found: C, 48.58; H, 6.73; N, 10.16. IR ν_{max}/ cm^{-1}: $\nu_{(C=N)}$ = 1655, $\nu_{(Si-O)}$ = 1098.

*3.2.2.4 Synthesis of [Pd (**L2**)$_2$] (**C2**)*



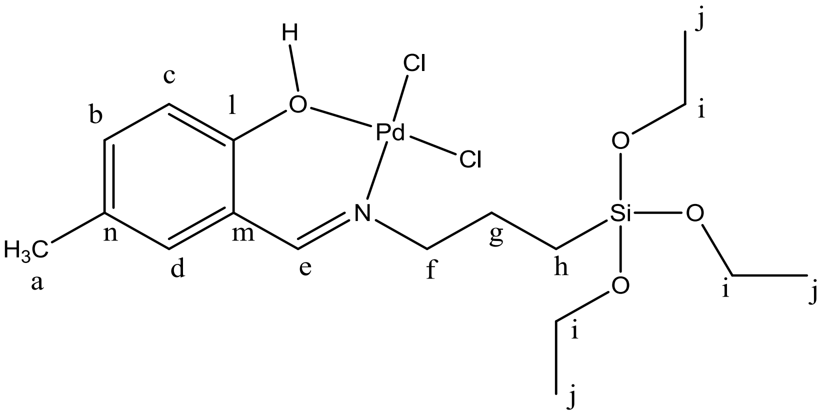
Complex **C2** was synthesized by following the procedure described for **C1** using Pd (OAc)$_2$ (0.14 g, 0.64 mmol) and **L2** (0.43 g, 1.28 mmol) in dichloromethane (20 ml). Yield = 0.05 g (87%). ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 0.69 (t, 4H, $^3J_{HH}$ = 8.0 Hz, H$_h$), 1.20 (t, 18H, $^3J_{HH}$ = 8.0 Hz, H$_j$), 1.90 (m, 4H, H$_g$), 2.24 (s, 6H, H$_a$), 3.71 (t, 4H, $^3J_{HH}$ = 8.0 Hz, H$_f$), 3.80 (q, 12H, $^3J_{HH}$ = 8.0 Hz, H$_i$), 6.78 (d, 2H, $^3J_{HH}$ = 8.0 Hz, H$_c$), 6.95 (s, 2H, H$_d$), 7.05 (d, 2H, $^3J_{HH}$ = 8.4 Hz, H$_b$),7.60 (s, 2H, H$_a$), ^{13}C NMR (100 MHz, CDCl$_3$, δ ppm): 190.36 (C$_e$), 162.76 (C$_l$), 161.67 (C$_b$), 135.83 (C$_n$), 133.17 (C$_d$), 123.45 (C$_m$), 120.02 (C$_c$), 60.71 (C$_f$), 58.43 (C$_i$), 25.60 (C$_a$), 19.96 (C$_j$), 18.27 (C$_g$), 7.56 (C$_h$). Anal.calcd for $C_{34}H_{56}N_2O_8PdSi_2$. CH_2Cl_2 : C, 48.92; H, 6.80; N, 3.27. Found: C, 48.96; H, 6.11; N, 9.54. IR ν_{max}/ cm^{-1}: $\nu_{(C=N)}$ = 1621, $\nu_{(Si\text{-}O)}$ = 1085.]

*3.2.2.5 Synthesis of [Pd (**L1**)(Cl_2)] (**C3**)*



To a solution of [Pd(NCMe) Cl_2] (0.30 g, 1.20 mmol) in dichloromethane (20 ml) a solution of **L1** (0.41 g, 1.20 mmol) in dichloromethane (10 ml) was added. The resulting orange solution was then stirred under nitrogen for 24 h. The solution was concentrated in vacuum and hexane (10 ml) added to precipitate **C3** as an orange solid. Yield= 0.25 g (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.52 (t, 2H, J = 8.0 H_z, H_h) , 1.27 (t, 9H, $^3J_{HH}$ = 8.0 Hz, H_j), 2.27 (s, 2H, H_a) , 3.27 (m, 2H, H_g),3.74 (t, 2H, $^3J_{HH}$ = 8.0 Hz, H_f) , 3.85 (m, 6H, H_i), 7.02 (d, 1H, $^3J_{HH}$ = 7.2 Hz, H_b) 7.21 (d, 2H, $^3J_{HH}$ = 8.4 Hz, H_e), 7.46 (t, 1 H, $^3J_{HH}$ =7.2 Hz, H_c) 7.55 (d, 1H, $^3J_{HH}$ = 8.0 Hz, H_d). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 181.60 (C_n), 164.42 (C_l), 131.23 (C_d), 129.41 (C_b), 126.60 (C_m), 117.50 (C_c), 113.22 (C_e), 56.92 (C_i), 52.84 (C_f), 24.74 (C_a), 21.82 (C_j), 18.12 (C_g) 7.66 (C_h). Anal.calcd for $C_{17}H_{29}Cl_2NO_4PdSi$. 0.5 CH_2Cl_2, C, 37.58; H, 5.41; N, 2.50. Found: C, 37.55; H, 5.34; N, 2.65. IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ = 2993, $\nu_{(C=N)}$ = 1650, $\nu_{(Si\text{-}O)}$ = 1080.

*3.2.2.6 Synthesis of [Pd (**L2**)(Cl_2)] (**C4**)*



Complex **C4** was synthesized by following the procedure described for **C3** using **L2** (0.20 g, 0.60 mmol and [Pd(NCMe) Cl_2] (0.15 g, 0.60 mmol). Yield= 0.13g (65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.70 (t, 2H, J = 8.0 H_z, H_h) , 1.21 (t, 9H, $^3J_{HH}$ = 8.0 Hz, H_j), 1.92 (m, 2H, H_g),2.03 (s, 2H, H_a) , 3.74 (t, 2H, $^3J_{HH}$ = 8.0 Hz, H_f) , 3.82 (m, 6H, H_i), 6.80 (d, 1H, $^3J_{HH}$ = 8.0 Hz, H_c) 6.90 (d, 2H, $^3J_{HH}$ = 8.4 Hz, H_b), 7.05 (t, 1 H, $^3J_{HH}$ =7.2 Hz, H_d) 7.06 (s, 2H, H_e). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 186.42 (C_e), 161.64 (C_l), 159.62 (C_b), 134.80 (C_n), 132.34 (C_d), 122.54 (C_m), 118.32 (C_c), 61.56 (C_f), 57.48 (C_i), 22.80 (C_a), 20.44 (C_j), 18.86(C_g), 7.46 (C_h). Anal.calcd for $C_{17}H_{29}Cl_2NO_4PdSi.CH_2Cl_2$, C, 35.93; H, 5.19; N, 2.33. Found: C, 35.85; H, 5.25; N, 2.28. IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ = 2998, $\nu_{(C=N)}$ = 1651, $\nu_{(Si-O)}$ = 1083.

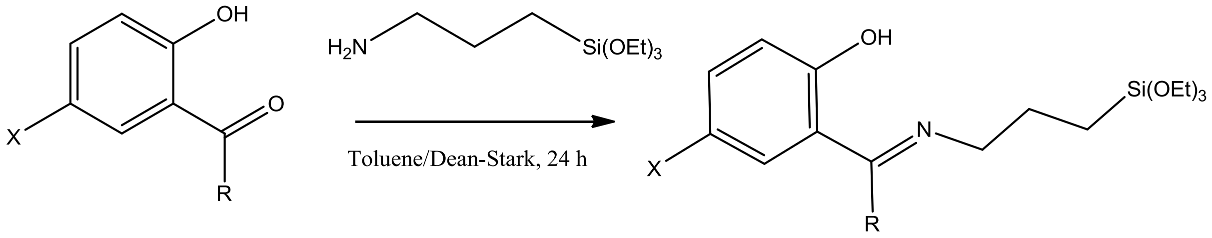
3.2.3 General procedure for the methoxycarbonylation reactions

The methoxycarbonylation catalytic reactions were carried out in a stainless steel autoclave equipped with a temperature control unit and a sample valve. In a typical experiment, complex **C2** (62.60 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 (50 ml) and methanol (50 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. 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 psi whereas Shimadzu GC-MS QP2010 equipped with a quadrupole mass detector was used for GC-MS analyses.

3.3 Results and discussion

3.3.1 Synthesis of (phenoxy)imine ligands and their palladium (II) complexes

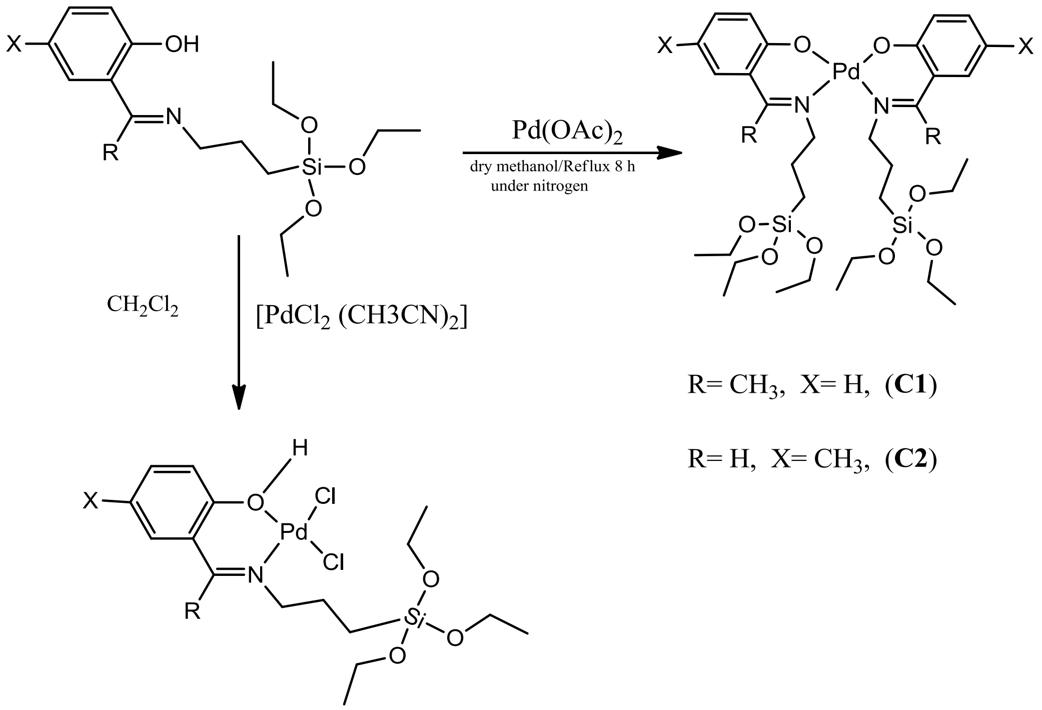
The (phenoxy)imine ligands (**L1** and **L2)** were synthesized by condensation of 2-hydroxyacetophenone and 2-hydroxy-5-methylbenzaldehyde respectively with (3-aminopropyl) triethoxy silane (Scheme 3.1) in good yields (75%-94%) according to modified previously reported procedure [24]. Complexes **C1- C4** were synthesized from their respective ligands **L1** and **L2** (Scheme 3.2) according to modified previously reported procedure [25] in good yields. All the compounds were characterised using ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopy, mass spectroscopy, HRMS-ESI and elemental analyses.



R= CH_3, X= H (**L1**)

R=H, X= CH_3 (**L2**)

Scheme 3.1: Synthesis of (phenoxy)imine ligands.



R= CH_3, X= H, (**C1**)

R= H, X= CH_3, (**C2**)

R= CH_3, X= H, (**C3**)
R= H, X= CH_3, (**C4**)

Scheme 3.2: Synthesis of palladium (II) complexes of **L1** and **L2** showing the effect of palladium precursor on the structures

The ^{1}H NMR spectra of the ligands confirmed their syntheses. For example, the CH_2 protons close to nitrogen atom in ligand **L1** (Figure 3.1) were observed at 3.59 ppm, shifting from 2.53 ppm in APTES due to formation of C=N bond. This value is comparable to a similar compound reported by Murphy *et al.* at 3.58 ppm [26]. The CH_3 group attached to the imine bond also shifted to 2.37 ppm from 3.06 ppm observed in the spectrum of the aldehyde, indicating the successful formation of **L1.**

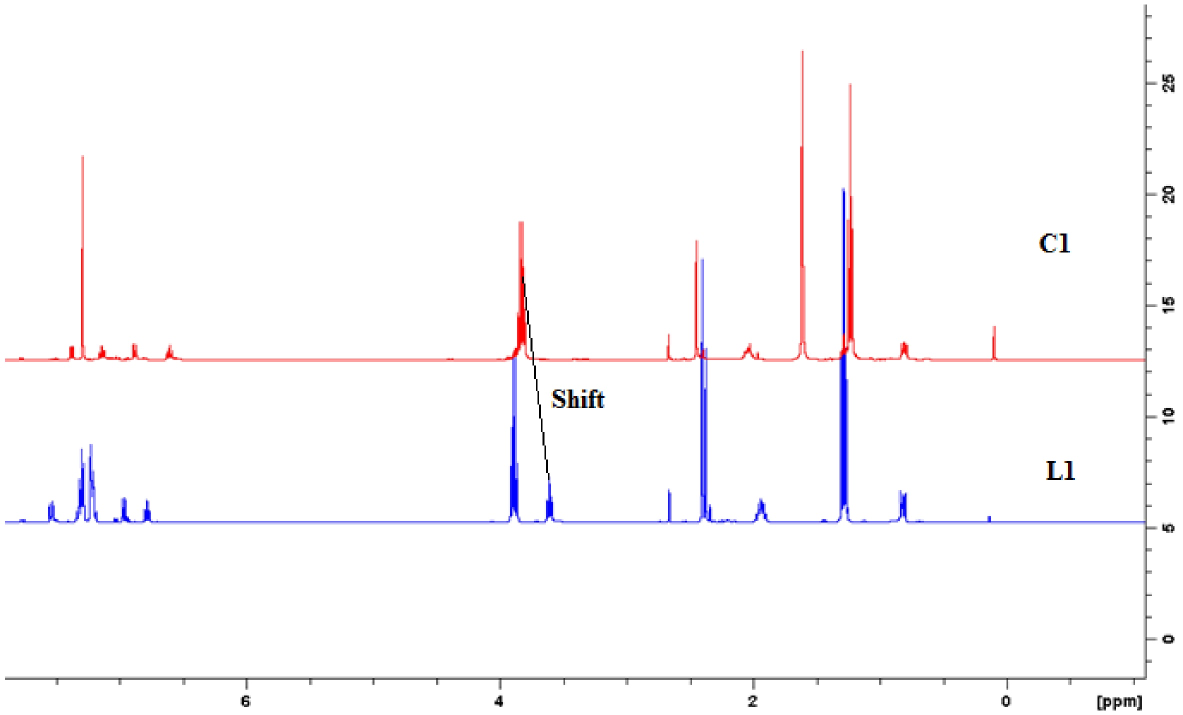


Figure 3.1: ^{1}H NMR spectra of **L1** and **C1** in $CDCl_3$ showing downfield shift of imine methylene group

The palladium(II) complexes for the homogeneous system were similarly characterized by the ^{1}H NMR spectroscopy and the peaks in the spectra were consistent with the expected compounds. For example, in the spectrum of complex **C1** (Figure 3.1) the methylene group close to the imine bond was observed at 3.80 ppm, relative to 3.59 ppm in the respective ligand **L1**. This was indicative of the successful formation of the palladium(II) complex.

^{13}C NMR spectrum of Schiff's base ligand **L2 (**Figure 3.2) showed diagnostic signals of imine carbon at 159.07 ppm, which shifted to 190. 36 ppm for **C2** indicating successful complexation, consistent with previous observations of Singh *et al.* of 160.08 ppm [27]. The carbon atom bonded to silica was recorded up field at 7.95 ppm; in good agreement with observations of Murphy *et al.*, who observed the peak of a similar compound at 8.2 ppm [26].

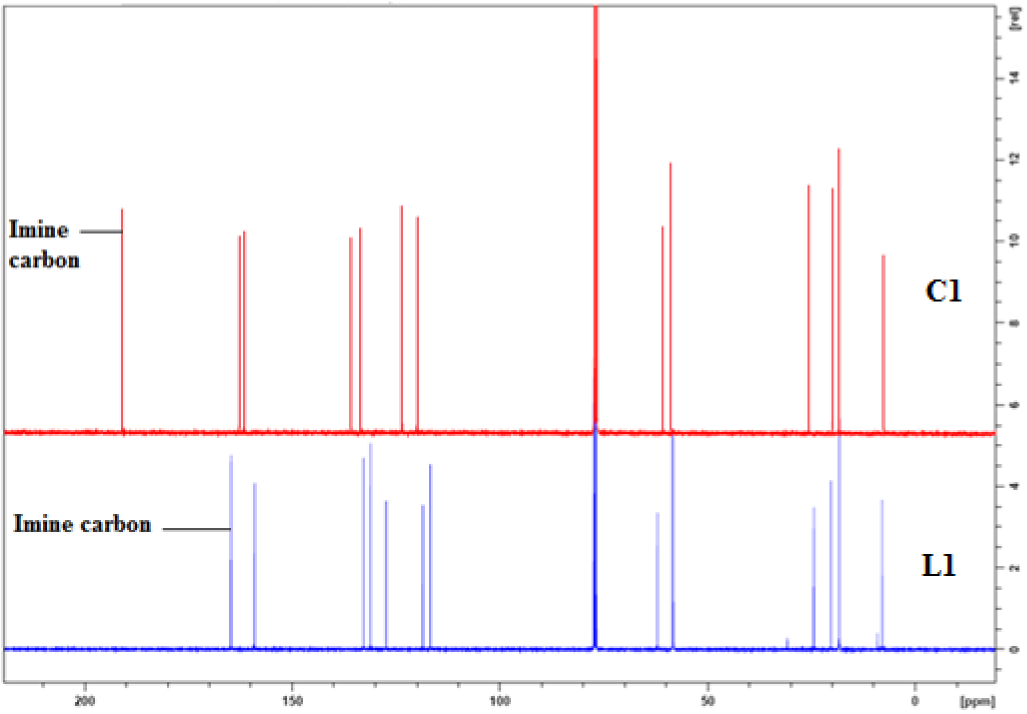


Figure 3.2: ^{13}C NMR spectra of **L1** and **C1** in $CDCl_3$ showing a downfield shift of imine carbon from 171.46 ppm in **L1** to 183.93 ppm in **C1**.

Another useful technique which was used in the establishment of compounds formed is the FT-IR (Table 3.1). The FT-IR spectra of all the ligands showed a sharp band in the region of 1600-1656 cm^{-1} assigned to $\nu_{(C=N)}$ bond which confirmed the formation of the ligands [28]. The spectra of the complexes also confirmed their formation. For instance, the $\nu_{(C=N)}$ bond for complex **C2** was observed at 1621 cm^{-1} compared to its respective ligand **L2** (1634 cm^{-1}) (Figure 3.3). The $\nu_{(C=N)}$ values were consistent with typical $\nu_{(C=N)}$ stretching frequencies (1600-1690 cm^{-1}) of ligands and palladium(II) complexes reported for similar compounds [28].

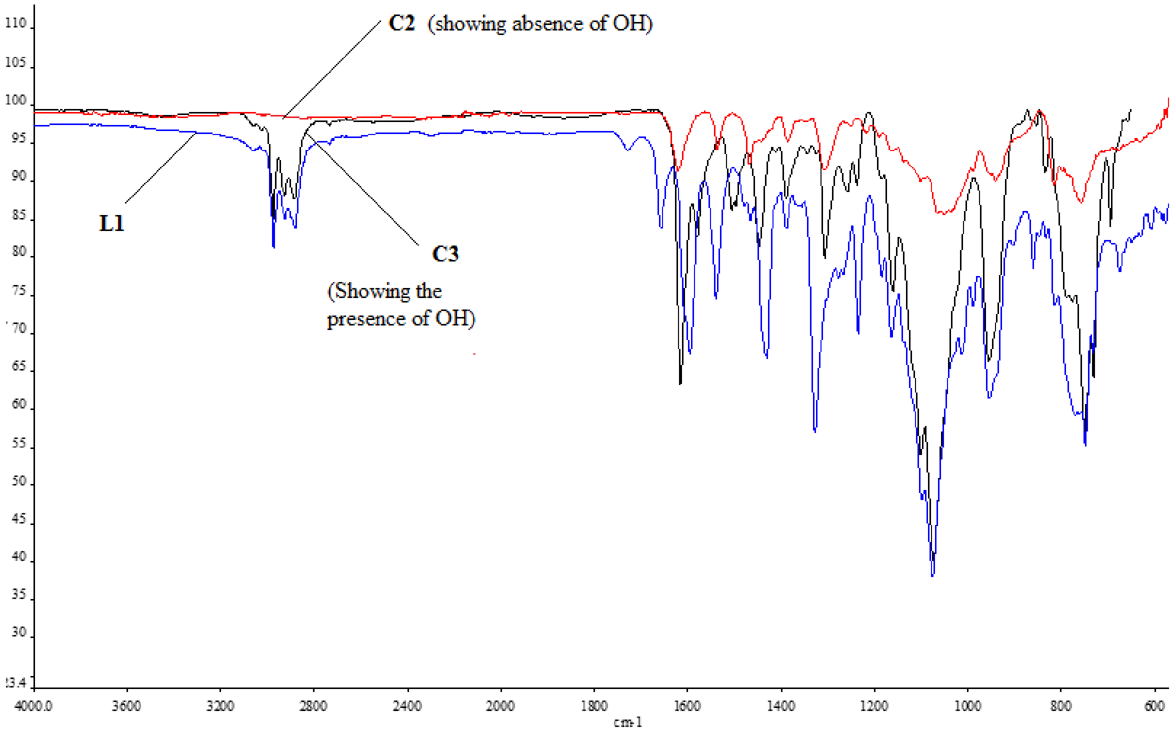


Figure 3.3: An overlaid Infrared spectra of **L1** and corresponding complexes **C2** and **C3**

The absorption bands observed in the regions of 1071-1075 cm^{-1} for (phenoxy)imine ligands (**L1** and **L2**) was assigned to the stretching vibration of Si-O [27]. In all ligands, the OH stretching vibrations were observed around 2944-3072 cm^{-1}. It is noteworthy to mention the absence of the OH stretching vibrations values in **C1** and **C2** but its presence in both **C3** and **C4** confirming their proposed structures (Scheme 3.2). This could be largely attributed to the different metal sources employed. The palladium(II) acetate precursor used in the synthesis of complexes **C1** and **C2** results in the deprotonation of **L1** and **L2** to form anionic ligands (loss of acetic acid); while for complexes **C3** and **C4** , the [Pd(NCMe)$_2$Cl$_2$] used results in no such deprotonation since NCMe leaving group is neutral.

Table 3.1.: FT-IR data for ligands and their complexes.

IR ν (cm-1)	**L1**	**C1**	**C3**	**L2**	**C2**	**C4**
ν(OH)	2973	-	2993	2974	-	2998
ν(C=N)	1615	1655	1650	1634	1621	1628
ν(C=C)	1579	1595	1587	1590	1568	1570
ν(Si-O)	1071	1098	1080	1073	1085	1083

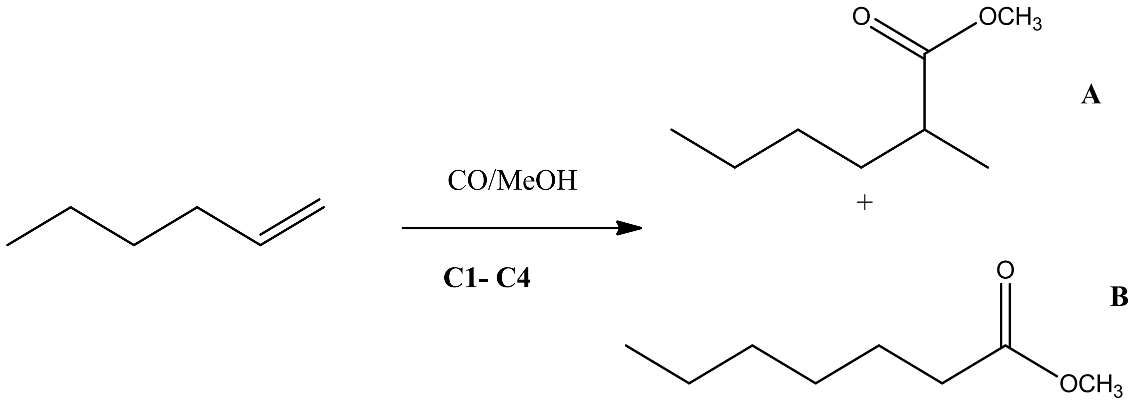
The mass spectrum of ligand **L1** (339.50 g/mol) showed the molecular ion peak at *m/z* = 339 attributed to the molecular mass of ligand. On further fragmentation a base peak at *m/z* = 255 was observed for a compound with molecular formula $C_{11}H_{14}NO_4Si$. The positive ionisation spectra (ESI (+)) of complex **C1** (782.26 g/mol) showed a molecular ion peak at *m/z* = 805.27, attributed to the (M^++Na) fragment. Table 3.2 shows a summary of the mass spectral data of the selected ligands and their palladium(II) complexes.

Table 3.2: Selected mass spectral data for ligands and their palladium(II) complexes

Compound	**Molar mass (g/mol)**	***m/z* (amu)**
L1	339.19	362.09 (M^++Na)
L2	339.19	362.17 (M^++Na)
C1	782.26	805.27 (M^++Na)
C2	782.26	782.46 (M^+)

*3.3.2 Preliminary screening of homogeneous palladium (II) complexes **C1-C4** in methoxycarbonylation of olefins*

The preliminary catalytic studies of complexes **C1-C4** for the methoxycarbonylation of 1-hexene were carried out at a CO pressure of 60 bar, temperature of 90 °C and [Pd]:[1-hexene]:[HCl]= 1:200:10. The major products formed as identified by GC-MS and gas chromatography were 2-methylhexanoate (branched product **A)** and methyl heptanoate (linear product **B**) (Scheme 3.3). Figure 3.4 shows the spectra obtained from the GC-MS and GC for 1-hexene and the corresponding ester products.



Scheme 3.3: Main products resulting from the methoxycarbonylation of 1-hexene

The addition of triphenyl phosphine (PPh_3) was observed to have a great influence in the catalytic activities. From literature, it is reported that PPh_3 elevates the stability of the catalyst by lowering the decomposition of the active palladium(II) species to palladium(0) [29, 30]. In the absence of PPh_3, we observed an extensive decomposition of the catalyst resulting into inactivity while when PPh_3 was used, the same catalyst (**C2**) was able to give a conversion of 85 % (Table 3.4. entries 6 and 7). To ascertain whether products could be obtained without the palladium(II) complexes, a reaction was performed under similar reaction conditions without a catalyst and no activity was observed (Table 3.3, entry 1), hence highlighting the important roles of both the PPh_3 and the palladium(II) complexes. The subsequent sections discuss the influence of complex structure and reaction conditions on the catalytic activities and selectivities.

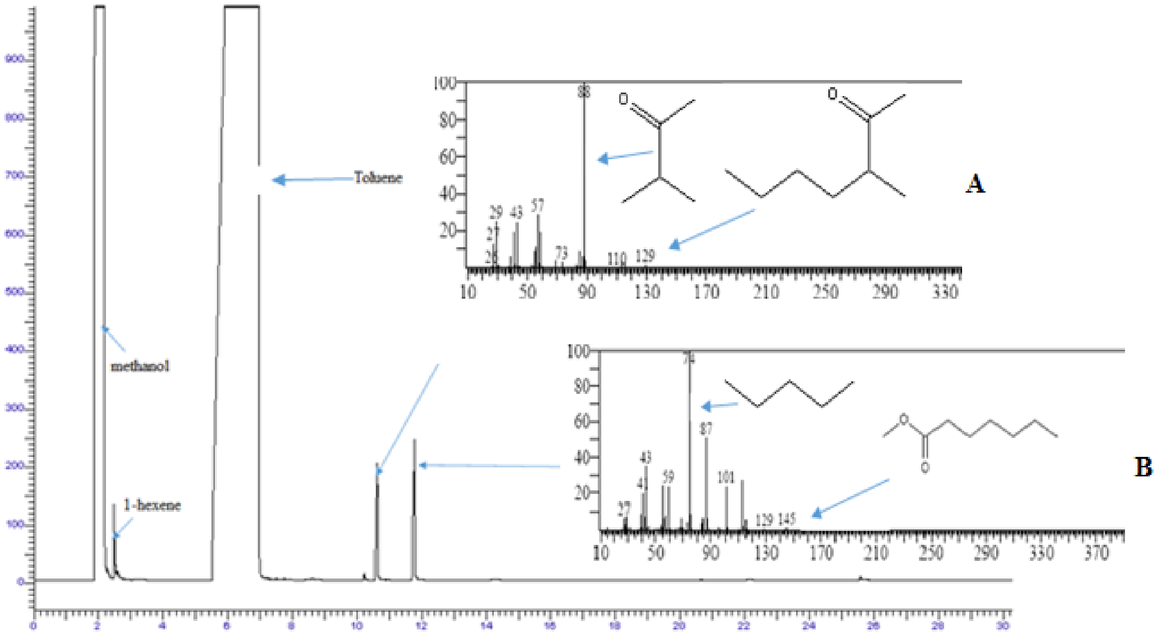


Figure 3.4: GC and GC-Ms spectra of products (A and B, branched and linear products respectively) extracted from 1-hexene using **C2** (0.06 mmol), temperature; 90°C; time 24 h ; Pd/1-hexene ratio, 200:1, Pd/ HCl ratio; 1:10; solvent: toluene (50 ml) and methanol (50 ml); P(CO) = 60 bar

3.3.2.1 The effect of complex structure on methoxycarbonylation of 1-hexene

The catalytic activities of complexes **C1-C4** in the methoxycarbonylation of 1-hexene were performed to determine the influence of complex structure on the performance of the catalyst. The catalytic behaviour of **C1** and **C2** were comparable (TOF of 7.0 h^{-1} and 7.1 h^{-1}) (Table 3.3, entries 2 and 3) as well as **C3** and **C4** (TOF of 5.0 h^{-1} and 5.4 h^{-1}) due to the pairs of **C1**/**C2**, and **C3**/**C4** having similar structures even though the pairs have different ligand units. The nature of ligand motif therefore, did not have a bearing on the catalytic activities of these complexes. The double chelated complexes **C1** and **C2** were more active than the mono-chelated **C3** and **C4**. The double chelation in **C1** and **C2** contributed to enhanced stability leading to higher catalytic activities [31]. The structure of the complexes had no significant effect on the regioselectivity of the methoxycarbonylation reactions. All complexes resulted in more linear products than the branched esters indicating that the steric hindrance effects were not significant possibly due to lack of close proximity of any groups to the metal centre [29].

Table 3.3: The effect of catalyst structure in the methoxycarbonylation of 1-hexene using **C1-C4**$^{\mathbf{a}}$**.**

Entry	Catalyst	[Pd]:[1-hex]	Conv(%)^{b}	l/b(%)^{c}	TOF (mol. sub/mol. Pd. h^{-1})
1	**-**	0:200	0	-	-
2	**C1**	1:200	84	58/42	7.0
3	**C2**	1:200	85	61/39	7.1
4	**C3**	1:200	61	65/35	5.0
5	**C4**	1:200	65	60/40	5.4

Reaction conditions: Pressure: 60 bar, Temp: 90 °C, Time: 24 h, Acid; HCl, Solvent: methanol 50 ml and toluene 50 ml; [Pd]:[HCl]:[hexene] ratio; 1:10:200; ^{b}% of hexene converted to esters; ^{c} Molar ratio between branched and linear ester.

3.3.2.2 The effect of acid promoter on methoxycarbonylation of 1-hexene

The effect of different acid promoters, p-TsOH, HCl, EADC, $AlMe_3$ and MSA on the catalytic performance of complex **C2** were investigated using 1-hexene as the substrate (Table 3.4). The catalytic results showed that HCl gave the highest activity while $AlMe_3$ gave the lowest activity (85% and 9%) respectively. The result obtained can be connected to the strength and coordinating abilities of the acids to aid in stabilizing the active Pd (II) species [13-14].

Table 3.4: The effect of acid promoter and phosphines in the methoxycarbonylation of 1-hexene using complex **C2**[a]

Entry	Acid promoter	Phosphine derivative	Pd:P	Conv(%)[b]	l/b (%)[c]	TOF
6	HCl	PPh_3	1:2	85	63/37	7.1
7	HCl	PPh_3	1:0	0	-	-
8	p-TsOH	PPh_3	1:2	80	67/33	6.6
9	p-TsOH	PPh_3	1:2	78[d]	65/35	6.5
10	p-TsOH	PPh_3	1:2	60[e]	64/36	4.5
11	p-TsOH	PPh_3	1:2	62[f]	62/38	5.2
12	EADC	PPh_3	1:2	63	60/40	5.2
13	$AlMe_3$	PPh_3	1:2	9	23/77	0.8
14	MSA	PPh_3	1:2	75	68/32	6.3
15	HCl	$P(Cy)_3$	1:2	61	49/51	5.1
16	HCl	Dppe	1:2	< 1%	-	-

Reaction conditions: Pressure: 60 bar, temp: 90 °C, Solvent: methanol 50 ml and toluene 50 ml; [Pd]:[acid]:[hexene] ratio; 1:10:200; [b]% of hexene converted to esters; [c] Molar ratio between branched and linear ester. [d, e] and [f]: conversions for **C1**, **C3** and **C4** respectively. TOF (mol. sub/mol. Pd. h^{-1}).

Tang *et al.*, reported the methoxycarbonylation of acetylene and obtained an order of reactivity decreasing from p-toluene sulfonic acid> methanesulfonic acid> sulphuric acid> trifluoromethane sulfonic acid> hydrochloric acid> p-aminobenzenesulfonic acid> acetic acid [32]. They found p-toluene sulfonic acid to be having a superior activity than hydrochloric acid which was attributed to the stronger coordinating power of the chloride ions to the palladium (II) center and thus barring the coordination of other molecules like the CO [32].

From our observation, hydrochloric showed a superior activity compared to p-toluene sulfonic acid suggesting that the activities were dependent on the strength of the acids and not the coordination ability. The hydrochloric acid having a more negative logarithmic acid dissociation constant (pK_a) of -7 is stronger compared to that of p-toluene sulfonic acid (-2.8) and methanesulfonic acid (-2.6). Previous reports in our research group gave no activity with p-toluene sulfonic [19-20] but complexes **C1-C4** showed a notable activity with p-TsOH. The Lewis acid EADC showed higher activity than $AlMe_3$ due to its stronger Lewis acidity. An order of increasing activity $AlMe_3$< EADC< MSA< p-TsOH<HCl was thus established in the methoxycarbonylation of 1-hexene. All the acid promoters yielded more linear products than the branched products (over 60 %) except for $AlMe_3$ which yielded more branched products (77%) possibly due to lower steric bulk in comparison to the other promoters, therefore favouring the more sterically demanding branched products [20].

3.3.2.3 The effect of phosphine derivatives on methoxycarbonylation of 1-hexene

To establish the effect of phosphine derivatives on the methoxycarbonylation of 1-hexene, PPh_3 $P(Cy)_3$ and 1,2- bis(diphenylphosphino) ethane (dppe) were studied. The activities afforded in the presence of different phosphine derivatives can be connected to steric effects and basicity of the derivatives. For example the more basic $P(Cy)_3$ gave a lower activity (61%) than PPh_3 (85%) under similar reaction conditions due to the fact that its superior electron donating ability makes the palladium(II) center to be less electrophilic and hence reduced substrate coordination. However, the use of dppe showed no catalytic activity possibly due to its chelating nature and therefore completely blocking the substrate from accessing the palladium(II) catalyst vacant coordination site [33]. The PPh_3 (cone angle of 145^0) also yielded more linear product (61%) than the more bulky $P(Cy)_3$ PPh_3 (cone angle of 170^0) (49%) contrasting expectations where more bulky phosphine are expected to yield more linear products [29]. An indication that catalytic selectivity might have been influenced by other factors (not clear to us) other than that steric hindrance caused by the phosphine stabilizers.

3.3.2.4 The Effect of reaction conditions in methoxycarbonylation reactions

In an effort to optimize the catalytic conditions, the influence of reaction conditions like temperature, gas pressure, catalyst concentration, reaction time, nature of solvent and solvent ratios were scrutinized using complex **C2** and 1-hexene. It was evident that when the reaction temperature was decreased from 90 ^{o}C to 60 ^{o}C the catalytic activity of complex **C2** dropped from 85% to 51% (Table 3.5 entries 18 and 26). However, lowering of temperature had no effect on the regioselectivities of the ester products. Alam *et al.* observed a similar trend, where lowering reaction temperatures from 90 ^{o}C to 60 ^{o}C lowered their catalyst's activity from 77% to 24 % while there was no notable change in regioselectivity [20]. Higher catalytic activities at higher temperatures indicated appreciable stability of the catalysts. Similarly, the pressure of carbon monoxide gas had a notable effect on the catalytic activity. For instance, higher pressures of 60 bar afforded a higher catalytic activity (85%) (Table 3.5, entry 18) while at reduced pressure of 40 bar, a lower activity of 60 % was observed (Table 3.5. entry 25). The higher activity might have been due to a faster CO insertion at higher pressures [19]. However change in carbon monoxide pressure did not have an appreciable effect on the selectivity of the ester products formed.

Table 3.5: The effect of reaction conditions in the methoxycarbonylation of 1-hexene using **C2**[a].

Entry	Solvent (ration)	CO pressure (Bar)	Temp (°C)	Time (H)	[Pd]:[1-hex]	Conv(%)[b]	l/b(%)[c]	TOF
18	Toluene-MeOH(1:1)	60	90	24	1:200	85	63/37	7.1
19	Toluene-MeOH(9:1)	60	90	24	1:200	84	62/38	7.0
20	Toluene-MeOH(1:9)	60	90	24	1:200	60	63/37	4.5
21	DMF-MeOH (1:1)	60	90	24	1:200	< 1%	-	-
22	ClBz-MeOH (1:1)	60	90	24	1:200	52	58/42	4.3
23	Toluene-MeOH(1:1)	60	90	12	1:200	33	66/34	5.5
24	Toluene-MeOH(1:1)	60	90	36	1:200	89	60/40	4.9
25	Toluene-MeOH(1:1)	40	90	24	1:200	60	64/36	4.5
26	Toluene-MeOH(1:1)	60	60	24	1:200	51	61/39	4.3
27	Toluene-MeOH(1:1)	60	90	24	1:100	86	63/37	3.6
28	Toluene-MeOH(1:1)	60	90	24	1:400	27	68/32	4.5

Reaction conditions: [Pd]: [PPh_3]: [HCl acid]: [hexene]; 1:2:10: 200, [b]% of hexene converted to esters; [c] Molar ratio between branched and linear ester. TOF (mol. sub/mol. Pd h^{-1})

Another parameter which has been shown to have influence on a catalyst activity is catalyst concentration. It was observed that at lower catalyst concentration of 1:400, lower catalytic activity (TOF of 4.5 h^{-1}) was observed than at higher concentration of 1:200 (Table 3.5, entries 18 and 28). Increasing the catalyst concentration to 1:100 however led to the drop in TOF. Previous studies have shown that at relatively higher concentrations of palladium (II) catalyst, TOF may drop due to modification of active sites from initial palladium(II) complex [34]. We also investigated the influence of time on the activity and regioselectivity of **C2** by changing the reaction time from 12 h to 36 h. After 12 h a TOF of 5.5 h^{-1} was afforded (Table 3.5, entry

23) while a TOF of 4.9 h^{-1} was obtained after a reaction time of 36 h, suggesting that the catalyst was more active in the first 12 h than the last 12 h. An observation which could be explained by a possible catalyst deactivation with increased time of reaction [35]. Optimum reaction time was 24 h where a TOF of 7.1 h^{-1} was achieved. Increasing reaction time also led to the formation of more branched products. For example, after 12 h and 36 h, the branched ester products formed was 34% and 40% respectively. The observation could be due to increased isomerization of the substrate before methoxycarbonylation with time since more isomerization may occur with increased reaction time and therefore leading to more branched esters [20].

Having used toluene as a co-solvent in earlier reactions, we explored what effects other solvents and solvent ratios could have in the catalytic activity and selectivity. Chlorobenzene gave a lower yield compared to toluene (Table 3.5, entry 18 vs 22). The catalytic activity has been proven to be dependent on the polarity and respective dielectric constants of the solvents used [32]. A mixture of methanol and chlorobenzene resulted in a higher dielectric constant and hence higher polarity leading to lower activity. A mixture of DMF and methanol afforded no activity, possibly due to a far much greater resulting dielectric constant. Solvents of a dielectric constant of 20 and below are the once suitable for methoxycarbonylation [32], whereas DMF has a dielectric constant of 36.71 making it unsuitable. Another reason could be that DMF is a strongly coordinating solvent and coordinates to the palladium(II) centre more strongly and therefore blocking the substrate from accessing the metal centre. Solvent ratios also proved to show significant effects on the catalytic activity. A methanol: toluene volume ratio of 9:1 resulted into a lower catalytic activity compared to a ratio of 1:9 (Table 3.5, entries 19 and 20). The observation made could be due to the fact that at a methanol: toluene volume ratio of 9:1 the reaction mixture’s polarity is increased leading to lower activity. Another reason could be that methanol offers more competition for the active sites with the substrate. The less polar reaction mixture (methanol: toluene volume ratio of 1:9) resulted into more branching due to decreased Pd-ligand dissociation to aid in the Pd-H addition to the olefin to yield more linear products [38].

3.3.2.5 Effect of olefin substrate in methoxycarbonylation reactions

Complex **C2**, was applied in the study of the influence of olefins such as 1-hexene, 1-heptene, 1-octene, and 1-decene on the methoxycarbonylation reactions. It was evident that the catalytic activity was greatly affected by the carbon chain length of the olefin used. To demonstrate, in the presence of 1-hexene, a relatively higher activity of 85% was achieved while a conversion of only 35 % was achieved for 1-decene. The decrease in catalytic activity with increase in olefin chain length could be as a result of greater steric hindrance and lower reactivity of the higher olefins, a trend which has been observed in our research group [19-20] as well as by Pruvost *et al.* [36].

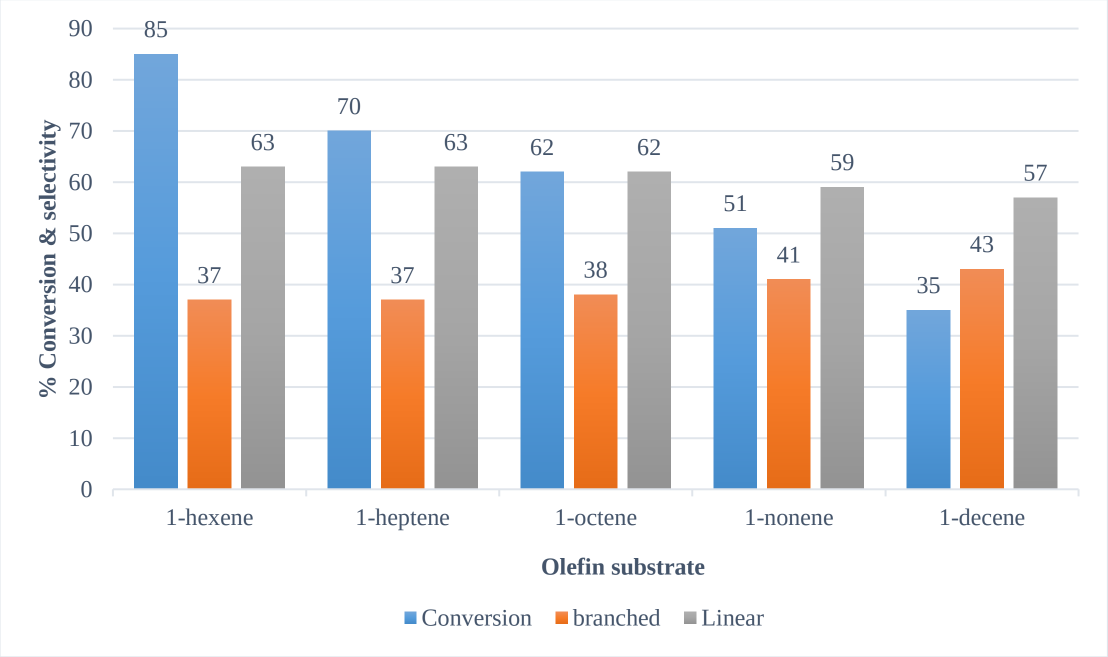


Figure 3.5: The effect of olefin substrate in the methoxycarbonylation using **C2**

The increase in the olefin chain length also led to the formation of more branched products, as an example, 1-heptene afforded 37% of the branched ester product while 1-decene gave 43% under similar reaction conditions (Table 3.6, entries 29 and 32). The observation could be as a result of a possible higher number of isomers with increase in olefin chain length [19-20, 36].

3.4 Conclusions

In conclusion, two (phenoxy)imine ligands (**L1** and **L2**) were synthesized and characterized by the ^1H and ^{13}C NMR techniques, mass spectrometry, FT-IR and high resolution mass spectrometry. The reactions of the (phenoxy)imine ligands with either $[PdCl_2(CH_3CN)_2]$ or Pd $(OAc)_2$ resulted in respective palladium(II) homogeneous complexes (**C1**-**C4**) in appreciable yields. All the resulting complexes were found to be active in the methoxycarbonylation of olefins where the nature of the catalyst structure was found to have an effect on activity. The double chelation in **C1** and **C2** led to better catalytic stability and therefore leading to higher activities than **C3** and **C4** which had single chelates. The complex structures did not however have an effect on regioselectivity. Strength of acids dictated their catalytic activities where the use of stronger HCl acid as a promoter resulted into significantly higher activity compared to other acid promoters such as p-TsOH and EADC. Reaction conditions such higher pressure, catalytic concentration and temperatures resulted into higher catalytic activities but no significant effects on regioselectivities. Triphenyl phosphine as a phosphine stabilizer gave the highest activity. The next chapter deals with the synthesis of the immobilized complexes of these systems and their catalytic application in the methoxycarbonylation of olefins under heterogeneous conditions.

3.5 References

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CHAPTER FOUR

Synthesis and characterization of immobilized (phenoxy)imine ligands and their Immobilized palladium(II) complexes for methoxycarbonylation of olefins

4.1 Introduction

Homogeneous catalysts have been used in the industry for many years because of their selectivity as well as the ease of understanding the mechanism involved [1]. However, they suffer from difficulty in separating the catalyst from the product mixture and recycling of the catalyst. Heterogeneous catalysts on the other hand can easily be recovered and reused, but they suffer from poor selectivity, leading to the challenge of creating a bridge between the homogeneous and heterogeneous catalysts [2-3]. The heterogenization of the homogeneous catalysts through various methods to promote the creation of hybrid catalytic systems which exploit the strengths of both heterogeneous and homogeneous catalysts such as selectivity and recovery has been an area of study for some time now [4-5]. Considering the advantages that come with immobilized catalysts, it is no surprise that notable interest in this field has been shown in both academic and industry in the last few decades [3].

To date, the major methods of heterogenizing the homogenous catalysts that exist include, the immobilization of homogeneous catalysts on insoluble solid supports, magnetic nanoparticles [6] and the use of water soluble catalysts or the biphasic catalysis [7]. The currently favoured approach is immobilization using the mesoporous silica which has attracted interest for a long time [8-9]. Silica supported catalysts have been applied widely in organic transformation reactions due to the fact that silica possesses incredible chemical and thermal stability in addition to having a more rigid structure as opposed to other solid supports such as organic supports. It can therefore be used effectively at low and high pressures and temperatures [10].

Some of the silica supported catalysts include, Oxo-vanadium(IV) silica supported catalysts applied in the bromination of aromatic compounds by Bhunia *et al.* [11], palladium(II) silica supported catalysts reported by Okubo *et al.* in heck coupling reactions [12] and palladium(II) silica supported catalysts in the alkoxycarbonylation of aryl iodides reported by Khedkar *et al.* [13].

This chapter focuses on an attempt to take on the key challenge of creating a bridge between homogeneous and heterogeneous catalysts through the immobilization method by using silica (MCM-41) as the supporting material and applying the synthesized complexes in the methoxycarbonylation of olefins. We report synthesis and characterisation of immobilized (phenoxy)imine ligands, and their silica supported palladium(II) metal complexes based on (3-aminopropyl) triethoxy silane (APTES) amine. The catalytic activity, recovery and reuse of the immobilized complexes in the methoxycarbonylation of olefins were studied. The effect of substrate chain length, catalyst structure, catalyst loading, temperature, pressure, solvent, nature of acid promoter and the type of phosphine derivatives used have been explored and the results are therefore reported in the next sections.

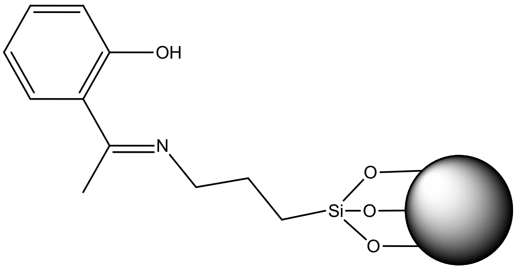
4.2 Experimental section and methods

4.2.1 General instrumentation and materials

All solvents purchased from Merck were of analytical grade and were dried before use. Toluene was dried over sodium wire and benzophenone, methanol were dried by heating over magnesium activated with iodine. Dichloromethane was dried over phosphorus pentoxide under nitrogen and stored in molecular sieves before use, DMF was dried over calcium oxide, and chlorobenzene was dried over phosphorus pentoxide. The reagents palladium dichloride, palladium (II) acetate, C_6-C_{10} olefins, hydrochloric acid, p-TsOH, PPh_3 , $P(Cy)_3$, Dppe, EADC,MSA,MCM-41 were purchased from Sigma-Aldrich and were used as received without a further purification. The infrared spectra were recorded on a Perkin-Elmer Spectrum 100 in the 4000–400 cm^{-1} range. The TEM images were taken using a transmission electron microscope (JEOL JEM, 1400 model) operating at 200kV accelerating voltage. All the samples were sonicated in ethanol and placed on carbon-coated copper grids. The morphology of the surfaces and particles sizes were studied using scanning electron microscope of ZEISS EVO LS15 model operating at an accelerating voltage of 20kV while the elemental contents of the immobilized complexes were analysed using an Oxford make EDX detector. The thermogravimetric analysis was done in a thermogravimetric analyser (TGA 4000 model) with the samples (5-12 mg) weight placed in ceramic pan and heated within the temperature range of 50 ^{o}C - 800^{0}C at a 40 ^{o}C/ min heating rate under nitrogen flow.

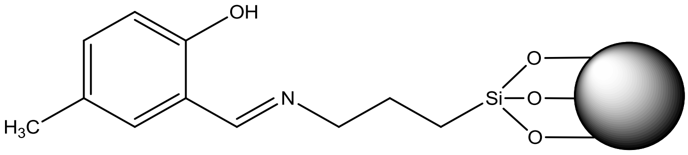
4.3 Synthesis of (phenoxy)imine immobilized ligands and their palladium(II) complexes

*4.3.1 Synthesis of **L1**-MCM 41 (**L3**)*



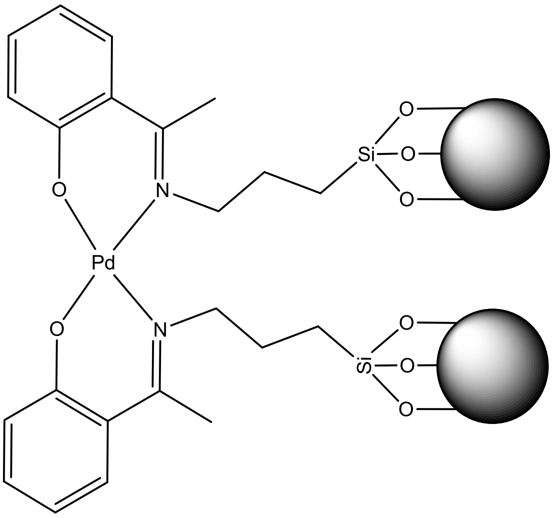
To a suspension of MCM41 (0.25 g) in toluene (50 ml), **L1 (**0.50 g, 1.47 mmol) was added and the mixture sonicated for 25 min. The reaction mixture was then heated at 90 °C for 14 h. After the reaction period, the crude product was filtered and the resulting precipitate washed with ethanol and toluene to give a yellow precipitate which was then dried in an oven for 12 h at 110 °C to give **L3** as yellow powder. Yield= 0.61 g (87%). IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ = 2944, $\nu_{(C=N)}$ = 1614, $\nu_{(Si\text{-}O\text{-}Si)}$ = 1061.

*4.3.2. Synthesis of **L2**-MCM 41 (**L4**)*



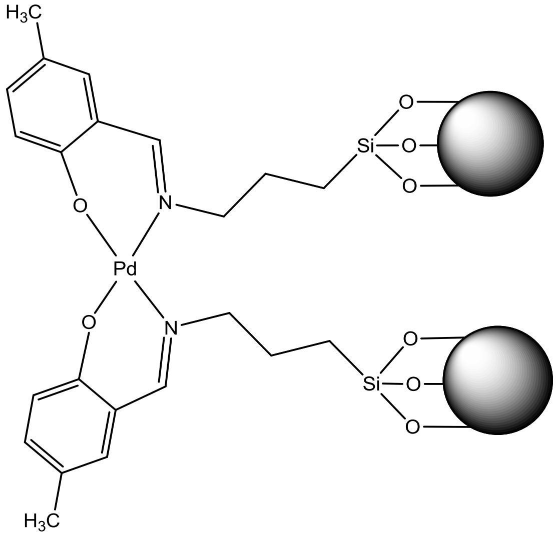
L4 was synthesized following the procedure reported for **L3** by using MCM-41 (0.20 g) and **L2** (0.40 g, 1.18 mmol). Yield 0.47 g (84 %) IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ = 3072, $\nu_{(C=N)}$ = 1611, $\nu_{(C=C)}$ = 1547, $\nu_{(Si\text{-}O\text{-}Si)}$ = 1031.

*4.3.3 Synthesis of [**C1-MCM-41**)] (**C5**)*



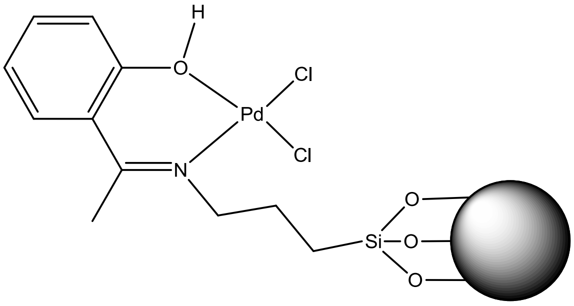
A solution of complex **C1** (0.15 g, 0.19 mmol) in toluene (10 ml) was added to MCM- 41 (1.35 g) in toluene (10 ml). The mixture was then refluxed for 24 h to give a yellow mixture. The solid was filtered off and then washed with dry dichloromethane to remove unreacted material. The resulting yellow product was dried under vacuum to give a light yellow powder. Yield, 1.35 g. IR $\nu_{\max}$/ cm^{-1}: $\nu_{(C=N)}$ = 1648, $\nu_{(Si\text{-}O\text{-}Si)}$ = 1055.

*4.3.4 Synthesis of [**C2**-MCM-41] (**C6**)*



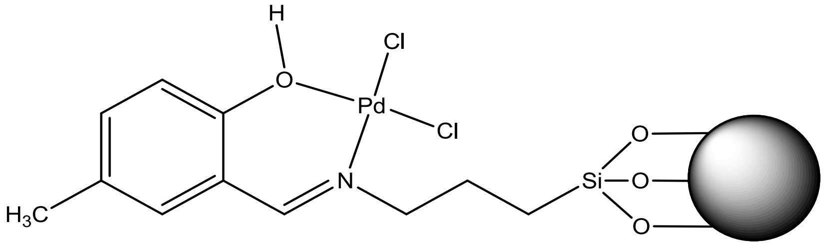
C6 was synthesized using the same procedure as **C5** using complex **C2** (0.15 g, 0.19 mmol), MCM- 41 (1.35 g). Yield, 1.32 g. IR ν_{max}/ cm^{-1}: $\nu_{(C=N)}$ = 1625, $\nu_{(Si\text{-}O\text{-}Si)}$ = 1054.

*4.3.5 Synthesis of [Pd (**L3**) (Cl₂)] (**C7**)*



To of a solution of [$PdCl_2$ (CH_3CN)$_2$] (0.10 g ,0.39 mmol) in ethanol (20ml) , **L3** (0.10 g) was added and refluxed overnight. The brown precipitate obtained was washed with ethanol, dichloromethane, ether and dried in oven at 110 °C. Yield: 0.13 g. IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ =2998, $\nu_{(C=N)}$ =1622, $\nu_{(C=C)}$ =1536, ν (Si-O-Si) = 1055.

*4.3.6 Synthesis of [Pd (**L4**) (Cl_2)] (**C8**)*



Complex **C8** was synthesized following the same procedure as **C7** by using [$PdCl_2$ (CH_3CN)$_2$] (0.10 g ,0.39 mmol) and **L4** (0.10 g) Yield: 0.11 g. IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ =2996, $\nu_{(C=N)}$ =1652, $\nu_{(C=C)}$ =1547, $\nu_{(Si\text{-}O\text{-}Si)}$ = 1058.

4.3.7 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. As an example of the reactions done, complex **C5** (0.5 % mol [Pd]), p-TsOH (0.14 g), 1-hexene (2 ml, 16.00 mmol) and PPh_3 (0.04 g, 0.16 mmol) were mixed in toluene (50 ml) and methanol (50 ml). The mixture was then introduced into the reactor and purged three times with CO, set at the required temperature and pressure and then the reaction stirred at 500 rpm. By the end of any single reaction the reactor was cooled and the CO vented and a sample extracted from the reaction mixture 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 psi.

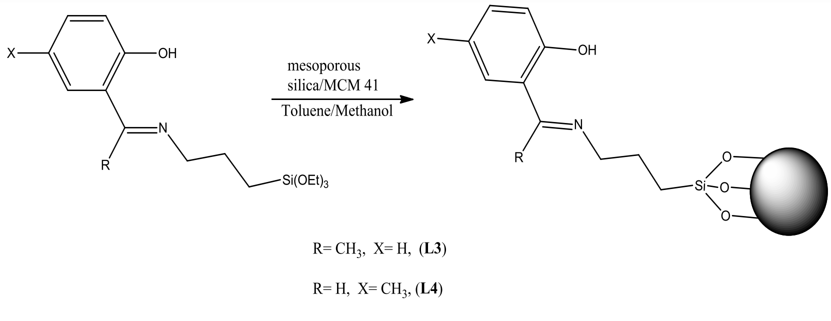
4.3.8 General procedure for catalyst recycling

After the complexion of a catalytic reaction, the reaction mixture was centrifuged at 8500 RPM for 10 minutes. The supernatant liquid was the carefully removed to leave the catalyst as a solid which was then reintroduced into the reactor together with a new set of other reagents and the recycled catalyst reused for three more runs. The GC-MS was used to determine the identity of the resulting ester products and their molecular weights. The linear and branched esters were assigned using the standard authentic samples.

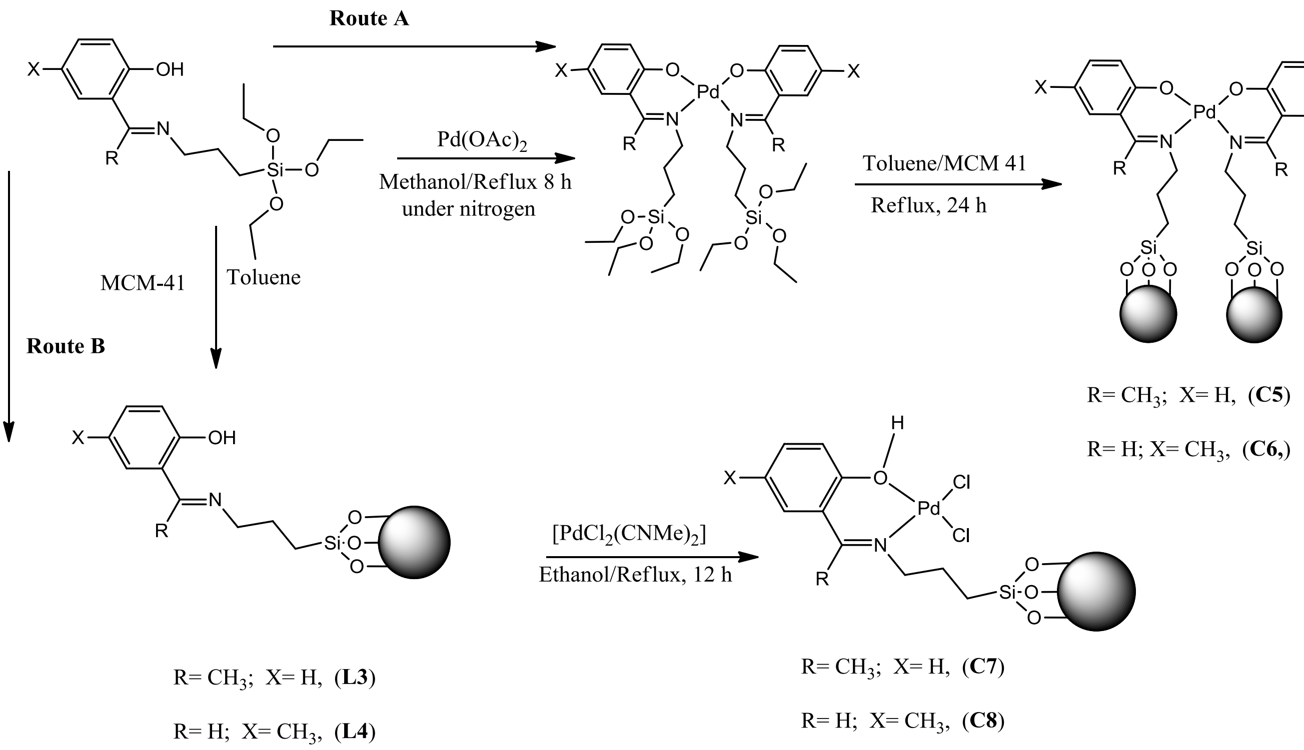
4.4 Results and discussion

4.4.1 Synthesis of immobilized (phenoxy)imine ligands and their palladium(II)complexes

Immobilized ligands **L3** and **L4** were synthesized from ligands **L1** and **L2** respectively through their reactions with MCM-41 according to Scheme 4.1 in good yields. Immobilized complexes **C5** and **C6** were synthesized from **C1** and **C2** respectively using the convergent immobilization method. Prior attempts to prepare **C1** and **C2** *via* the sequential route did not materialize and only led to the decomposition of palladium(II) acetate precursor. On the other hand, compounds **C7** and **C8** were synthesized from reactions of pre-immobilized ligands **L3** and **L4** respectively with [PdCl$_2$ (CH$_3$CN)$_2$] *via* the sequential route as shown in Scheme 4.2 in good yields. Characterization of all the new compounds was done using FT-IR, mass spectrometry, TGA, TEM and SEM-EDX.



Scheme 4.1: Grafting of the (phenoxy)imine ligands.



*Scheme 4.2: Synthesis of immobilized palladium complexes (**C5-C8**) via convergent (A) and sequential (B) routes.*

The FT-IR absorption bands were observed at 1031-1061 cm^{-1} with high intensity coupled with the disappearance of medium bands for CH_2 and CH_3 (attached to the Si-O bond). In addition, bending vibrations between 1306 and 1365 cm^{-1} assigned to the Si-O-Si bonds of the MCM-41 support confirmed successful isolation of the immobilized ligands **L3** and **L4** [14]. The disappearance of the bands in the regions of 1085-1098 cm^{-1} (stretching vibration of Si-O) from the homogeneous complexes **C1** **a**nd **C2** upon addition of MCM-41 to give **C5** and **C6** confirmed the formation of the immobilized complexes. In addition, the FT-IR spectra confirmed successful complexation of **L3** and **L4** to yield **C7** and **C8** respectively (Figure 4.1). For instance, the $\nu_{(C=N)}$ bond for complex **C8** was observed at 1652 cm^{-1} compared to its respective ligand **L4** recorded at 1611 cm^{-1} (Table 4.1) This established coordination of the nitrogen to the palladium(II) centre as previously reported for silica supported catalysts with the similar group observed at 1643 for the ligand and 1632 for the respective complex by Bhunia *et al.* [15]. The presence of the OH group in complexes **C7** and **C8** support their respective proposed structures, and the presence of neutral ligands **L3** and **L4**.

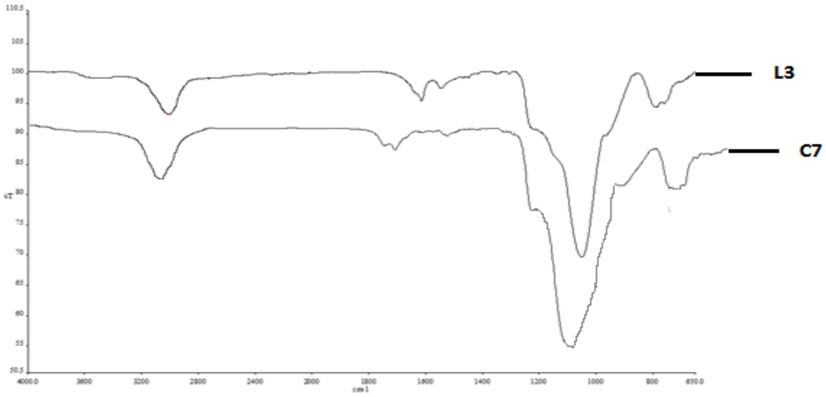


Figure 4.1: An overlaid Infrared spectra of **L3** and corresponding complex **C7**

Table 4.1: FT-IR data for immobilized ligands and their Palladium (II) complexes.

IR ν *(cm-1)*	**L3**	**C7**	**L4**	**C8**
OH	2944	2998	3072	2996
C=N	1614	1622	1611	1652
Si-O-Si	1061	1055	1031	1051

To determine the morphology and particle size of the immobilized ligands **L3** and **L4** and complexes **C5 - C8,** SEM was used for characterization. Figure 4.2 shows the SEM image of ligand **L4** and corresponding immobilized complex **C8** as containing agglomeration of particles of different morphology from each other, suggesting successful complexation of the immobilized ligand. Particles of different shapes and sizes were observed. For example, complex **C8** had some spherical particles having diameters ranging from 1.163 µm to 3.642 µm, similar compounds reported by Polshettiwar and Molnár had diameters ranging from hundreds of nanometres up to a micrometres [16].

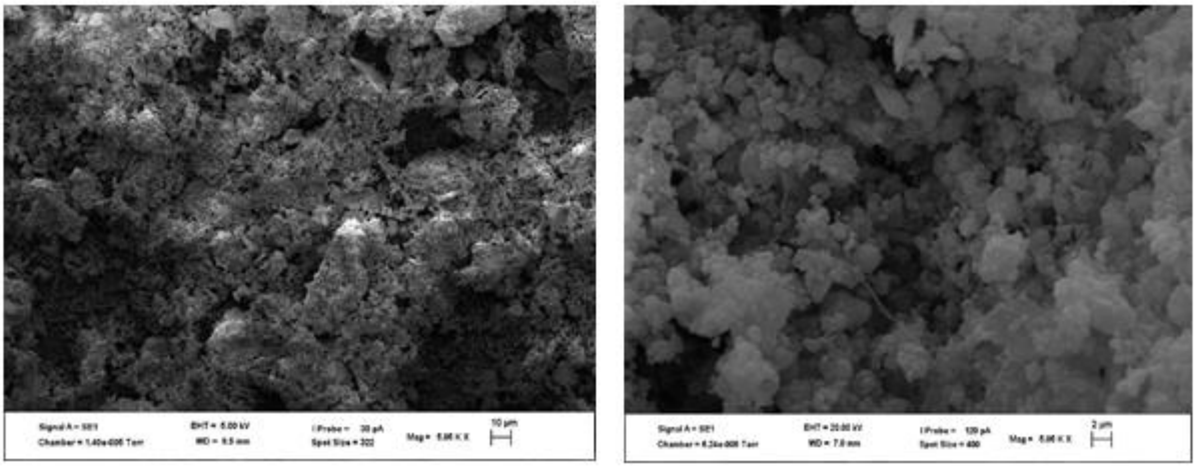


Figure 4.2: SEM image of ligand **L4** and the correspomding immobilized complex **C8** showing different morphologies

To investigate the palladium content in the complexes **C5**-**C8**, the complexes were analysed using the Energy Dispersive X-ray Spectroscopy (EDX) recorded at random surface points for qualitative analysis. For example, the analysis of complex **C8** produced an EDX image (Figure 4.3) showing the elemental percentages as C (18.67), N (10.18), O (47.14), Cl (7.18), Pd (2.82), and Si (14.12) with weight percentages of palladium(II) as 14.48 (Table 3.3) translating to palladium content of 1.36 mmol/g. EDX values for the elemental and weight percentages were recorded as averages of three difference areas and is therefore a true representation of the compositions. The presence of palladium(II) peak in **C8** indicated that the immobilized complex was successfully synthesized from **L4**. Table 4.2 shows the EDX data of the immobilized complex **C5**-**C8**. The EDX also revealed the presence of higher palladium content in both **C7** and **C8** than **C5** and **C6** pointing to a possible influence of the synthetic approaches used since **C7** and **C8** were synthesized using sequential approach while convergent route was followed for **C5** and **C6** for the reasons discussed earlier.

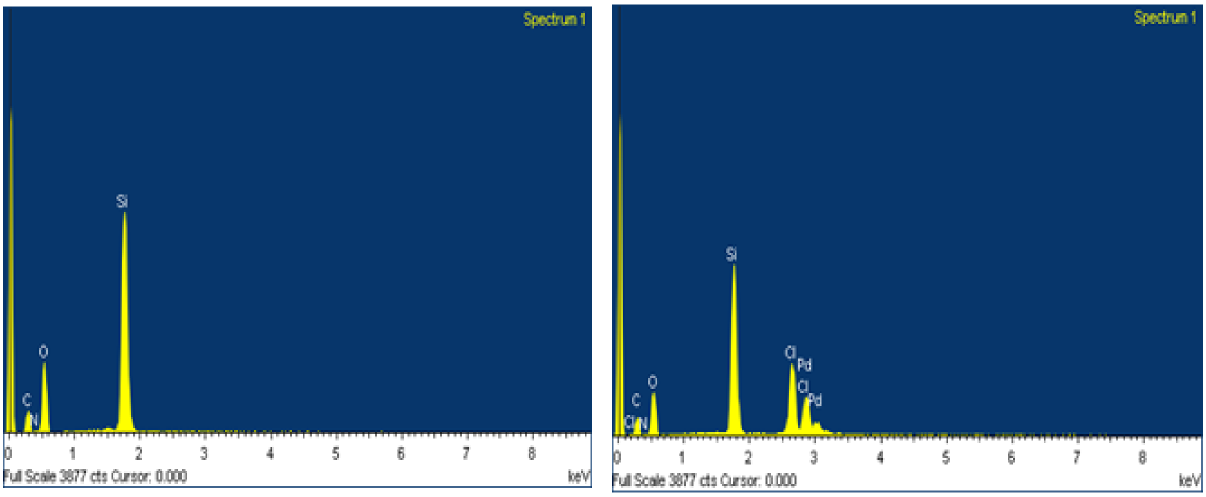


Fig 4.3: EDX spectrum of ligand **L4** and complex **C8** showing the presence of Pd signal in **C8**

Table 4.2: EDX data of showing atomic and weight percentages in **C5-C8**

Element	**C5**		**C6**		**C7**		**C8**	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
C	5.52	8.71	10.62	14.56	15.61	26.59	10.84	18.867
N	10.34	15.64	10.30	15.54	5.97	8.72	6.89	10.18
O	48.40	54.00	45.97	50.22	32.67	41.75	36.45	47.14
Si	34.26	20.38	31.26	19.38	17.98	13.09	19.03	14.02
Cl	-	-	-	-	11.73	6.77	12.30	7.28
Pd	1.47	1.26	1.85	1.32	16.04	3.08	14.48	2.82
Totals	100.00		100.00		100.00		100.00	

The TEM images of immobilized complexes displayed the morphologies with uniform size. The complexation of immobilized ligands was expected to disturb the ordered mesoporous structure to a certain degree, but TEM images showed that the mesoporous structure was retained with long-range order (Figure 4.4). This was an evidence that the complexes were anchored on the pores of mesostructured silica MCM-41 which acted as support for the synthesized catalysts [11]. The morphology also pointed to an agglomeration of particles which was agree to the SEM observations.

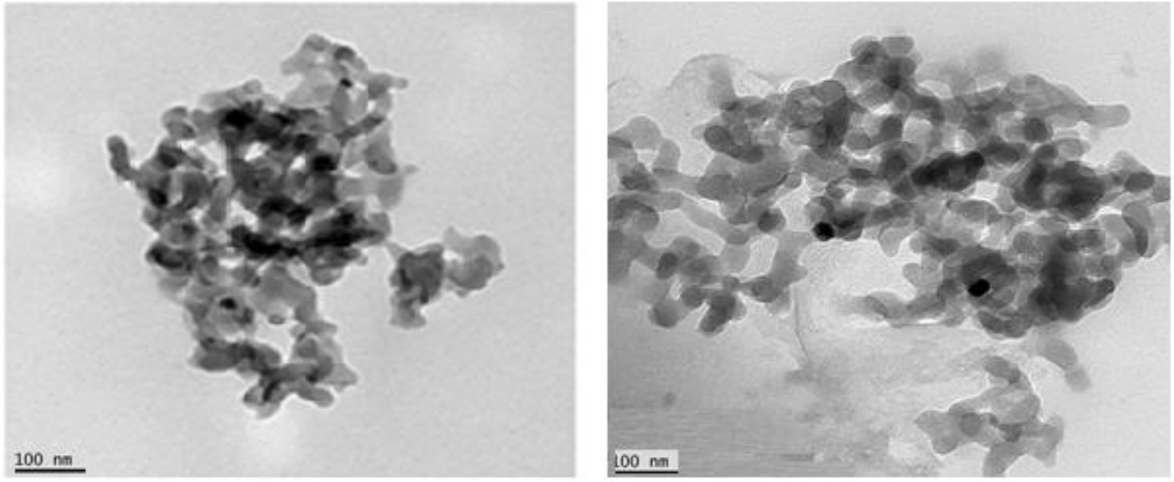


Figure 4.4: TEM images of ligand **L4** and the corresponding immobilized complex **C8**

The thermogravimetric analysis (TGA) was used to study the thermal stability of the immobized complexes **C5-C8**. All the immobilized complexes exhibited a similar decomposition pattern when heated from 50 °C to 800 °C. For instance **C5** showed three phases of thermal behavior (Figure 4.5, the intial weight loss which occurred between 50 °C and 100 °C corresponds to moisture loss [17]. The second phase of decomposition occurred between 200 °C and 500 °C and could be attributed to the loss of the immobilized ligand motif.

Thereafter the weight % remained largely constant upto 800 °C (Figure 4.5). The complexes showed a high thermal stability since even after heating to 800 °C, they all exhibited over 60% of their original weight intact (Table 4.3).

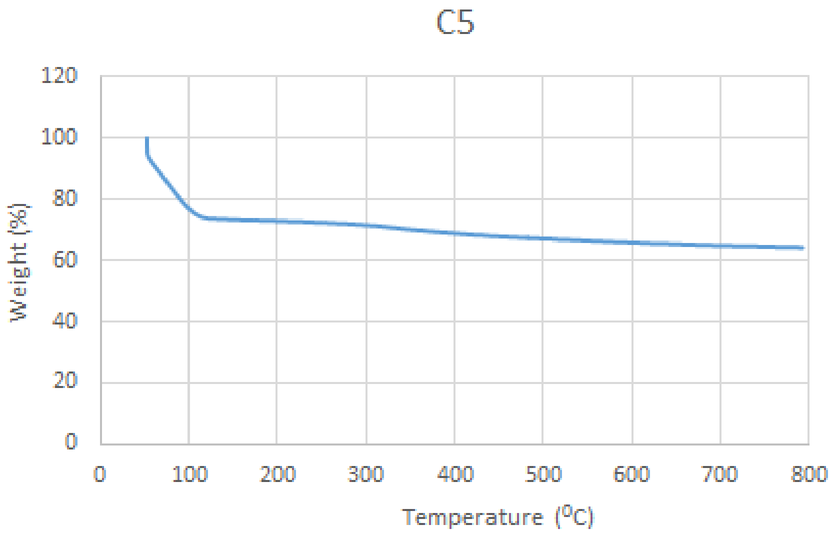


Figure 4.5: TGA graphical plot showing decomposition phases of **C5**

Table 4.3: Residual masses of the complexes after heating to 800 °C

Complex	Original mass (mg)	Residual weight (%)	Conversion (%)
C5	5.03	64	76
C6	5.47	65	78
C7	5.65	66	59
C8	10.61	62	61

4.5 Catalytic studies of the immobilized catalysts in the methoxycarbonylation of olefins

*4.5.1 Preliminary screening of immobilized palladium(II) complexes **C5-C8** in methoxycarbonylation of olefins*

Preliminary catalytic studies of complexes **C5-C8** in the methoxycarbonylation of 1-hexene were carried out at a CO pressure of 60 bar, temperature of 90 ^{o}C and 0.5 % mol palladium(II). Contrary to the results for the homogeneous systems' results discussed in chapter three, the use of hydrochloric acid as the promoter resulted in inactivity of the immobilized complexes. However, other acids like p-TsOH acid were active. The major products formed as identified by the GC-MS were 2-methylhexanoate and methyl heptanoate. The absence of a phosphine derivative led to extensive decomposition of the catalysts resulting into inactivity.

4.5.2 The effect of complex structure on methoxycarbonylation of 1-hexene

The catalytic studies on the activities and selectivities of complexes **C5-C8** in the methoxycarbonylation of 1-hexene was carried out to establish the effects of the immobilized complex structure on their performances. The structure of the complexes dictated their activity. For example, the **C5** and **C6** which are bischelated were more active than **C7** and **C8** which consist of one ligand moiety. The double chelation in **C5** and **C6** led to better catalytic stability and therefore leading to higher activity [18]. Complex **C6** was the most active, followed by **C5**, **C8** and **C7** the least reactive. The catalytic behaviour of **C5** and **C6** were comparable (TOF of 6.3 and 6.5) as well as of **C7** and **C8** (TOF of 4.9 and 5.0) due to similarity of the structures of the mentioned pairs. However, the catalyst structure did not have appreciable effect on the regioselectivity of the products formed as all the complexes afforded between 60%-63% of the linear product (Table 4.4, entries 2-5).

Table 4.4: The effect of catalyst structure in the methoxycarbonylation of 1-hexene using **C4-C8**[a].

Entry	Catalyst	[Pd]: [PPh_3]	Conv(%)[b]	l/b(%)[c]	TOF h^{-1}
1	**C5**	0	0	-	-
2	**C5**	1:2	76	60/40	6.3
3	**C6**	1:2	78	62/38	6.5
4	**C7**	1:2	59	63/37	4.9
5	**C8**	1:2	61	63/37	5.0

Reaction conditions: Pressure: 60 bar, temp: 90 °C, Time: 24 h, acid: p-TsOH, Solvent: methanol 50 ml and toluene 50 ml; 0.5 % mol Palladium(II); [b]% of hexene converted to esters; [c] Molar ratio between branched and linear ester. TOF (mol sub/mol Pd h^{-1})

4.5.3 The effect of acid promoter on the methoxycarbonylation of 1-hexene

An acid promoter has significant contribution in the methoxycarbonylation of olefins [19] and therefore the acids, hydrochloric, para-toluene sulfonic, ethyl aluminium dichloride, trimethyl aluminium and methanesulfonic acid were investigated to determine their effect on the catalytic performance using 1-hexene as the olefin substrate. As opposed to the high catalytic activities shown by the homogeneous systems with HCl as the acid promoter, the immobilized complexes, gave no catalytic activity due to a possible hydrolysis of the Si-O-Si bonds through the protonation of the siloxane oxygen [20]. The use of p-TsOH resulted into the highest activity followed by MSA and EADC while $AlMe_3$ gave no appreciable activity (Table 4.5, entries 6, 8, 9 and 10). The trend established for the acid promoters results from the strength of the acid with p-TsOH having the highest negative logarithmic acid dissociation constant of -2.8, followed by MSA, -2.6. $AlMe_3$ gave low yield due to it weak Lewis acidity nature as compared to the other acids investigated [21]. In contrast to the inactivity displayed by p-TsOH in the methoxycarbonylation reported earlier in our research group [21-23], these systems gave active catalysts upon activation with p-TsOH, hence an improvement of the previous catalysts from an industrial application perspective. The nature of the acid promoters did not however have a notable influence on the regioselectivity of the esters formed since regioselectivities of between 36-40 % of the branched products (Figure 4.6) were achieved except for $AlMe_3$ which gave predominantly branched esters (80%) possibly due to it being less bulky than the other promoters [24].

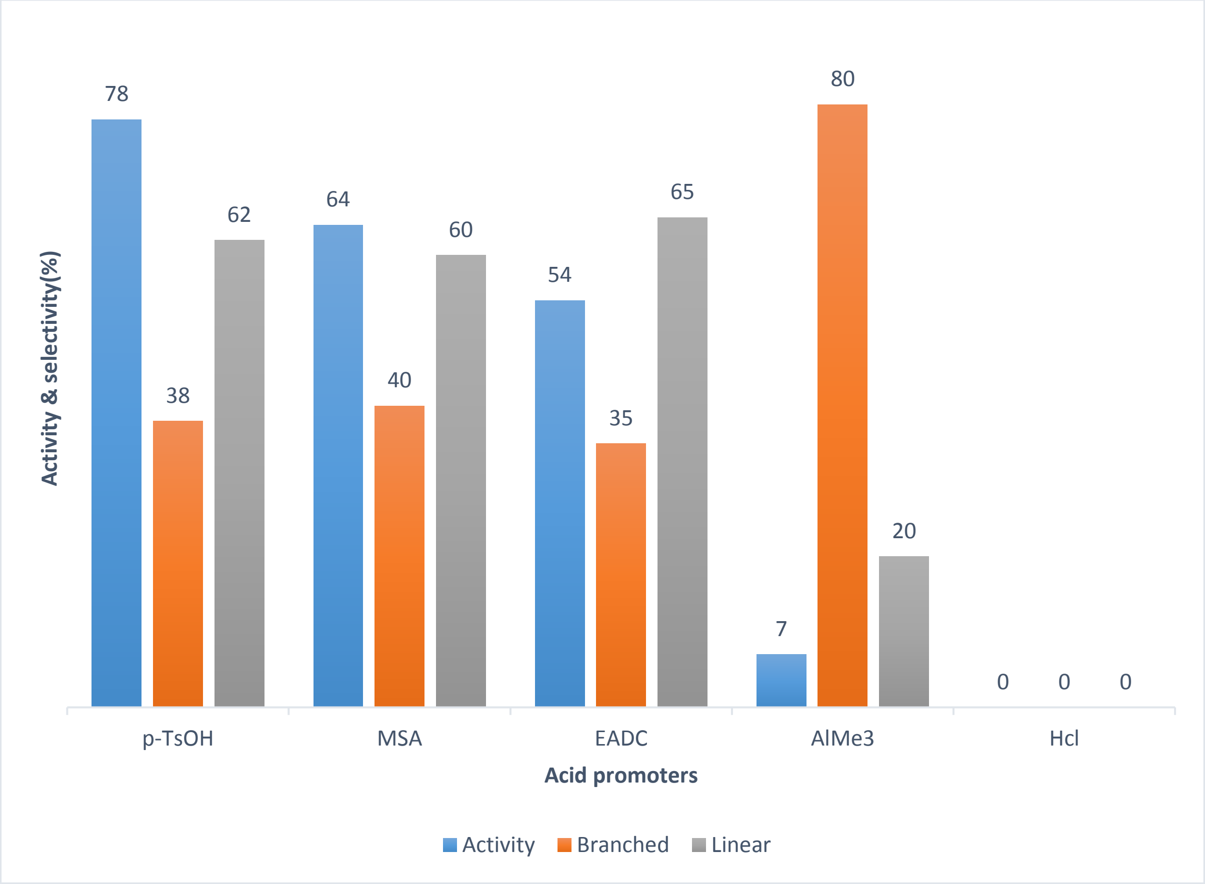


Figure 4.6: Graphical representation of effect of acid promoters showing activities and selectivities for complex **C6**

Table 4.5: The effect of acid promoter and phosphines in the methoxycarbonylation of 1-hexene using **C6**[a]

Entry	Acid promoter	Phosphine derivative	Conv(%)[b]	l/b (%)[c]	TOF h^{-1}
6	HCl	PPh_3	0	-	-
7	p-TsOH	PPh_3	78	62/38	6.5
8	EADC	PPh_3	54	64/36	4.5
9	$AlMe_3$	PPh_3	7	20/80	-
10	MSA	PPh_3	64	60/40	5.3
11	p-TsOH	$P(Cy)_3$	58	48/52	4.8
12	p-TsOH	Dppe	0	-	-

Reaction conditions: Pressure: 60 bar, temp: 90 °C, Time: 24 h, acid: p-TsOH, Solvent: methanol 50 ml and toluene 50 ml; 0.5 % mol palladium(II); [b]% of hexene converted to esters; [c] molar ratio between branched and linear ester. TOF (mol sub/mol Pd h^{-1})

4.5.4 The Effect of reaction conditions in methoxycarbonylation reactions

In optimization of the catalytic reaction conditions, the effect of carbon monoxide pressure, catalyst loading, nature of the solvent, and temperature were studied using complex **C6**. One of the factors which proved to have a bearing on the catalytic activity was temperature. Lowering the reaction temperature from 90 °C to 60 °C similarly reduced the catalytic activity from 78% to 59% due to reduction of the number of reacting particles attaining activation energy and thus less collision (Table 4.6, entries 13 vs 20). Similar observation was reported by Mane *et al.* in the methoxycarbonylation of aryl iodides using silica supported palladium(II) catalyst [25]. The pressure of carbon monoxide also had significant effect on the activity of the catalyst. Varying the pressure from 60 bar to 40 bar was accompanied with a notable decrease in the catalytic activity from 78% to 66% (Table 4.6, entries 13 vs 19) likely due to a slower insertion of CO at lower pressures [22]. Khedkar *et al.* reported a similar observation using silica supported palladium(II) complexes in the alkoxycarbonylation of aryl iodides where reducing pressure from 1 MPa to 0.5 MPa led to a reduction in activity from 90% to 80% [26].

Table 4.6: The effect of reaction conditions in the methoxycarbonylation of 1-hexene using **C6**[a].

Entry	Solvent (ration)	CO pressure (Bar)	Temp (°C)	Time (H)	Pd loading (% mol)	Conv(%)[b]	l/b(%)[c]	TOF
13	Toluene-MeOH(1:1)	60	90	24	0.5	78	62/38	6.5
14	Toluene-MeOH(9:1)	60	90	24	0.5	76	64/36	6.3
15	Toluene-MeOH(1:9)	60	90	24	0.5	75	64/36	4.3
16	DMF-MeOH (1:1)	60	90	24	0.5	0	-	-
17	ClBz -MeOH (1:1)	60	90	24	0.5	36	65/35	3.0
18	Toluene-MeOH(1:1)	60	90	12	0.5	34	66/34	5.4
19	Toluene-MeOH(1:1)	40	90	24	0.5	66	64/36	5.5
20	Toluene-MeOH(1:1)	60	60	24	0.5	59	61/39	4.9
21	Toluene-MeOH(1:1)	60	90	24	1.0	87	62/38	3.6
22	Toluene-MeOH(1:1)	60	90	24	1.5	62	61/39	1.7

Reaction conditions: [PPh_3]: [HCl acid]: 1:5: [b]% of hexene converted to esters; [c] Molar ratio between branched and linear ester, [d] percentage conversion of 1-heptene. TOF (mol sub/mol Pd h^{-1})

The effect of time was also studied using reaction times 12 h and 24 h to understand the activation and deactivation patterns of catalyst **C6**. Catalyst **C6** afforded a TOF of 5.4 h^{-1} after 12 h, and 6.5 h^{-1} after 24 h, an indication that the catalyst activity increased with time. The observation suggested that the catalyst was less active in the first 12 h than the next 12 h. An observation which could be explained by a possible catalyst activation with increased time of reaction [27]. Increased time led to the formation of more branched ester, for instance, after 12 h and 24 h, 34% and 38% the esters were produced respectively (Table 4.6 entries 13 and 18). The observation could be due to increased isomerization of the olefin substrate preceding methoxycarbonylation with time and therefore leading to more branched esters [23]. The effect of catalyst loading was also studied to ascertain the optimum catalyst concentration required for the methoxycarbonylation of 1-hexene using catalyst **C6**. Increasing loading from 0.5 mol % to 1.5 mol % was followed by a drastic decrease in TOF from 6.5 h^{-1} to 1.7 h^{-1} respectively indicating that lower loadings were more beneficial. Such an observation could be due to the formation of palladium clusters at higher loading which limits the catalyst accessibility by the olefin substrate [28].

The influence of different co-solvents were then studied by using different solvents mixtures. A mixture of chlorobenzene and methanol gave a lower activity compared to that of toluene and methanol (Table 4.6 entries 13 vs 17) due to higher polarity. The activity has been proven to be dependent on polarity of the used solvents which are in turn controlled by their respective dielectric constants [29]. Higher polarity has been proven to increase catalytic activity if the charge density in the rate determining step's transition state is bigger than that of the starting materials in the same step, otherwise it leads to decreased activity [30]. Our observation hence suggests the latter. A mixture of DMF and methanol afforded no activity, possibly due to a far much higher dielectric constant [31] and its strongly coordinating ability. Solvent ratios did not have notable effect on the activity of the catalysts. A methanol: toluene volume ratio of 9:1, 1:9 and a ratio 1:1 resulted comparable activities (Table 4.6, entries 13-15). This could be due to the fact that the immobilized catalyst was insoluble in the solvents and therefore methanol was not competing with the substrate for the active sites. The effect of the substrate chain length on the catalytic activity was studied using 1-hexene and 1-heptene. There was an evidence that the length of the chain influenced catalytic activity of **C6**. As an illustration **C6** afforded a conversion of 78 % for 1-hexene, which dropped to 63% for methoxycarbonylation of 1-heptene under similar reaction conditions (Table 4.6 entry 13 and 18).

4.5.5 Catalyst recyclability and characterization studies

To test the recyclability and reuse of the immobilized catalysts **C5-C8,** the reactions were performed under the optimized reaction conditions of temperature 90 ^{o}C, CO pressure of 60 bar, solvent mixtures of toluene and methanol (ratio 1:1), reaction time of 24 h and the use of pTsOH as the acid promoter. The immobilized catalysts were recycled up to four times without significant drop in catalytic activity. From Figure 4.7, it is evident that all the catalysts **C5**-**C8** maintained appreciable activities during the four runs. However, the increase in the number of cycles did not have an effect on the regioselectivity of the products formed. To further study if the reduced catalytic activities in the subsequent cycles were due to leaching of the active species, hot filtration test was done using catalyst **C6**. Thus, after 12 h of initial reaction with complex **C6** which gave a catalytic activity of 33 %, it was filtered from the reaction mixture and the resultant filtrate subjected to a CO pressure of 60 bar at a temperature of 90 ^{o}C for another 2 h. The catalytic activity remained largely constant, giving only a 34 % conversion. The lack of activity demonstrated using the filtrate indicated lack of leaching hence the diminished catalytic activity in the subsequent runs may be due to a possible abrasion of the catalysts during the reaction [31].

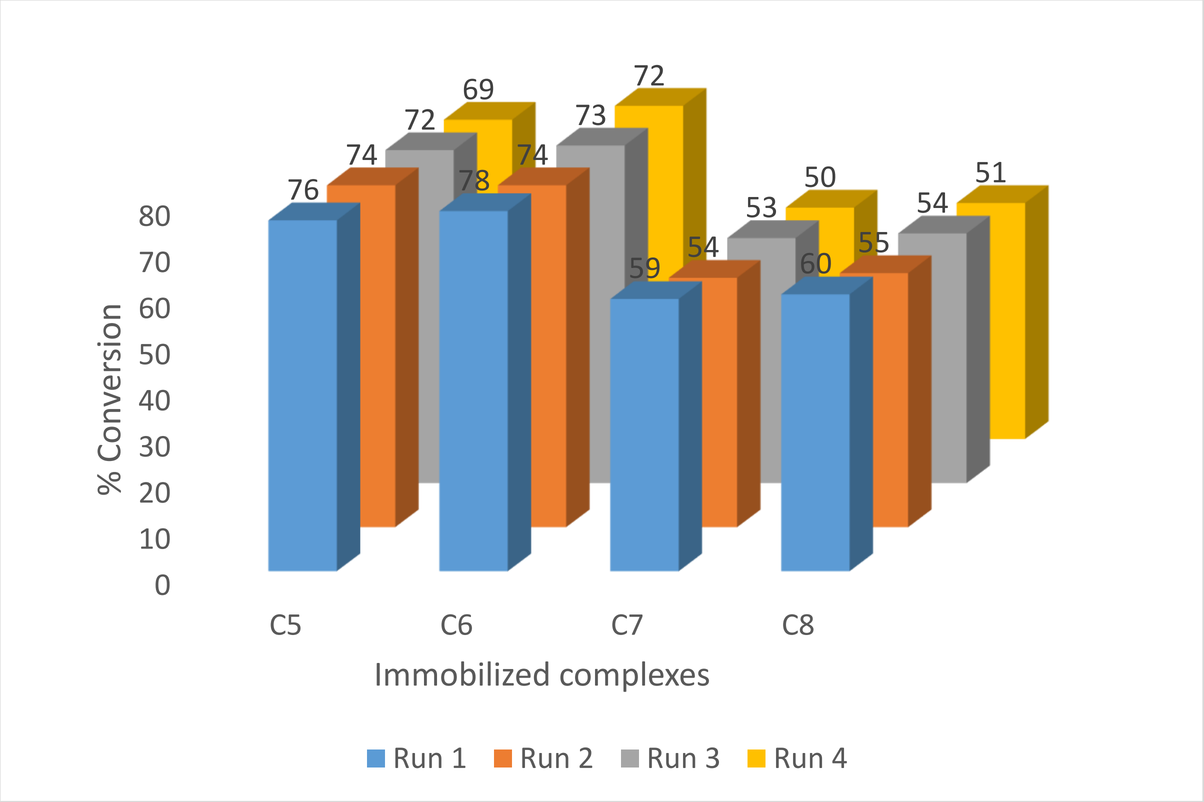
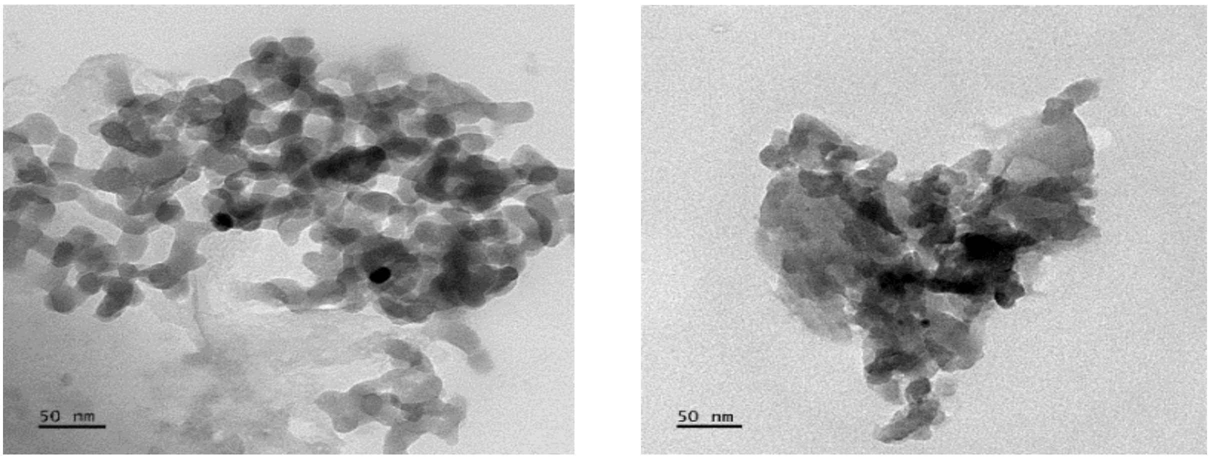
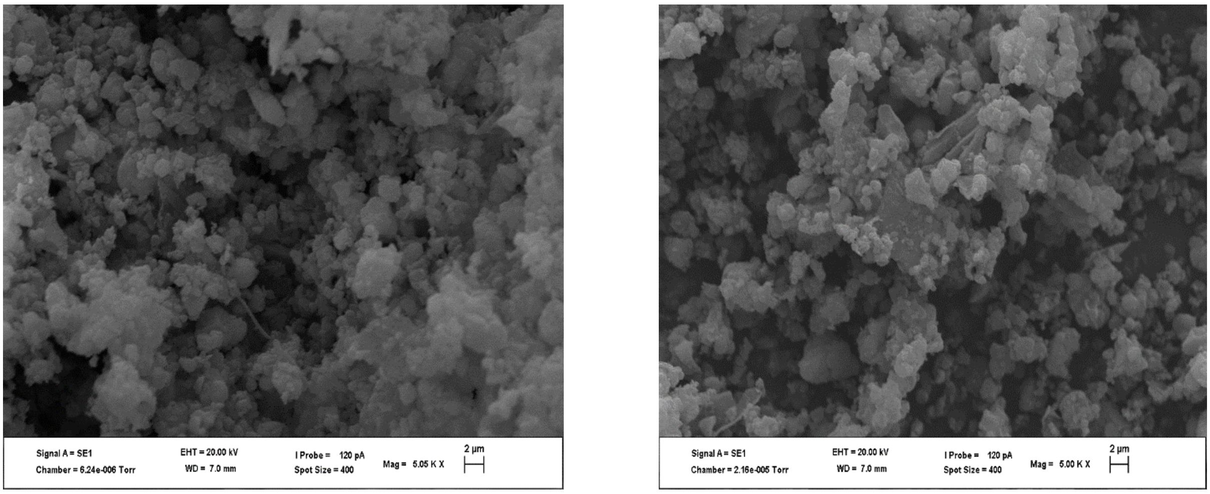


Figure 4.7: A graph showing catalytic activities of complexes **C5-C8** and their recycling.

Characterization of the used catalysts was achieved by the use of TEM and SEM-EDX to determine any changes in morphology and the palladium(II) content and if these changes may be responsible for catalytic activity loss (Figure 4.8). The TEM images of the fresh and used catalysts confirmed a slight change in the morphology of the catalysts. For example the images of complex **C8** and the corresponding used catalyst showed that the ordered mesoporous structure was partially destroyed after four runs (Figure 4.8). The SEM images similarly showed slight change in the morphology of catalyst **C8** after the fourth cycle (Figure 4.8). The EDX also confirmed a reduction of palladium content from original 1.85 % to a new value of 1.35 % pointing to a possible abrasion [31] of the catalyst during the four cycles of catalysis. Thus the damage of the ordered mesoporous structure indicated by the changes in morphology could account for the lower activities observed in the subsequent cycles.



A (Fresh catalyst) B (Recycled catalyst)



C (Fresh catalyst) D (Recycled catalyst)

Figure 4.8: TEM (A & B) and SEM images (C& D) of fresh and recycled complex **C8**.

The following chapter is a conclusion chapter giving a summary of the research reported in this dissertation and suggestions for future projects having a potential of remedying some of the problems encountered with the catalytic system applied such as regioselectivity towards a predominant isomer.

4.6 Conclusions

In conclusion, immobilized ligands **L3** and **L4** were synthesized from Schiff base ligands **L1** and **L2** respectively. The immobilized complexes **C5** and **C6** were synthesized from **C1** and **C2** respectively following a convergent synthetic route resulting in good yields whereas complexes **C7** and **C8** were synthesized *via* sequential synthetic route using ligands **L3** and **L4** respectively. The immobilized ligands and complexes were characterized using SEM-EDX, TEM, FT-IR and TGA. The bischelated complexes **C5** and **C6** were more active than the corresponding mono-chelated complexes **C7** and **C8**. The retention of significant catalytic activities up to the fourth cycle in addition to the lack of activity of the filtrate in hot filtration test established the stability of the active species and absence of leaching. The characterization of the catalysts after the fourth cycle of catalysis by TEM and SEM-EDX demonstrated a slight change in the physical and chemical nature of the catalysts which was consistent with slight decrease in the activities observed in the subsequent runs. The reaction conditions such as temperature, pressure, nature of solvent, time, acid promoter and catalyst loading all had profound effect on the catalytic activities. All the complexes showed regioselectivities towards linear esters (60-63%) with no significant change in the regioselectivity in the subsequent cycles. Increase in olefinic chain length led to lower catalytic activity.

4.7 References

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CHAPTER FIVE

Overall conclusions and future work

5.1 Concluding remarks

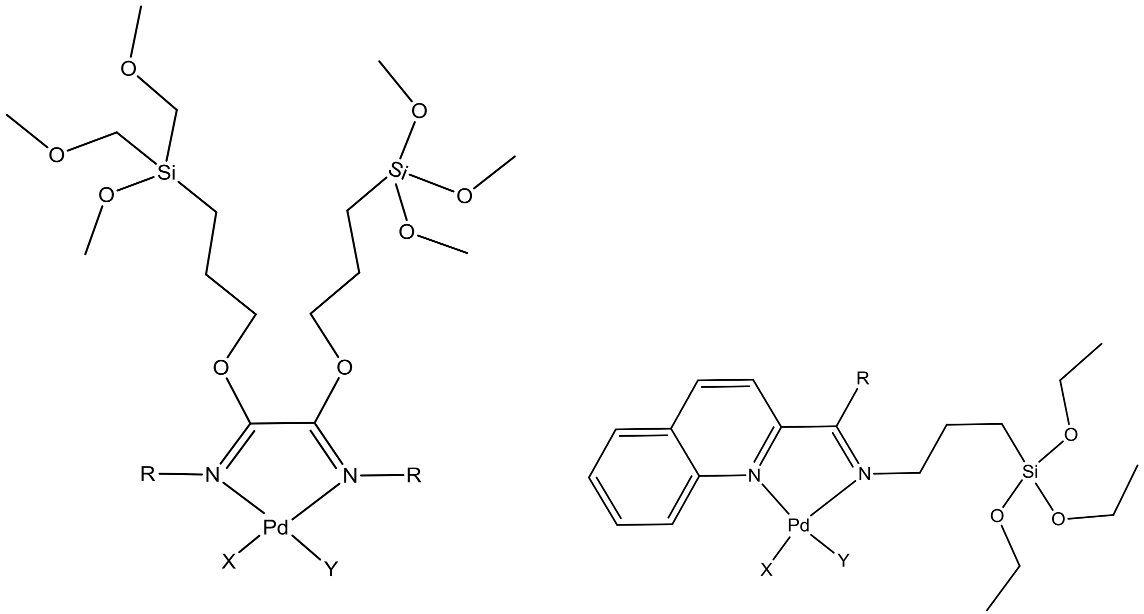
In conclusion, this dissertation reports the design of mixed nitrogen and oxygen-donor palladium(II) complexes as homogeneous and immobilized catalysts for methoxycarbonylation of olefins. The ligands **L1** and **L2** were synthesized using APTES as the stating amine, and further used to synthesize the immobilized ligands **L3** and **L4** respectively. The (phenoxy)imine palladium(II) complexes **C1** and **C2** bearing anionic ligand units were synthesized by reactions of ligands **L1** and **L2** respectively with $Pd(OAc)_2$ while **C3** and **C4** carrying neutral ligand groups were synthesized from $[PdCl_2 (CH_3CN)_2]$. Immobilized complexes (**C5-C8**) were synthesized through convergent (bischelated **C5** and **C6**) and sequential (mono-chelated **C7** and **C8**) synthetic routes. Characterization of the complexes **C1-C4** was done by ^{13}C and ^{1}H NMR, FT-IR, MS and HRMS-ESI and elemental analyses. On the other hand, the immobilized complexes **C5-C8** were characterized using FT-IR, mass spectroscopy, TGA and TEM. In addition characterization using SEM revealed particles of varied size while EDX showed palladium loadings of 1.47-16.04% where **C7** and **C8** synthesized via sequential method displaying higher palladium content. All the characterization methods established the successful formation of both sets of complexes.

In the methoxycarbonylation of olefins using the homogeneous catalysts, the bischelated complexes (**C1** & **C2**) demonstrated superior catalytic activities than mono-chelated analogues (**C3** & **C4**) under similar reaction conditions, indicating that the activity of the catalysts highly depended on their stability. The immobilized counterparts showed a similar trend. Under similar reaction conditions, catalytic activities of the homogeneous catalyst (59-78%) and their immobilized counterparts (60-80%) were comparable indicating that the immobilized catalysts retained the catalytic activities. An important observation was that using hydrochloric acid as an acid promoter was successful with the homogeneous complexes while it gave no activity of with the immobilized complexes possibly due to the hydrolysis of the Si-O-Si bonds in the immobilized complexes. The selectivities of the immobilized and homogeneous catalyst were similarly comparable under similar reaction conditions as all the complexes displayed regioselectivity towards linear ester products (60-68%). The aim of designing of immobilized catalyst which are selective, stable and easy to recover was therefore achieved. The catalysts showed higher conversions at relatively higher temperatures, pressure and increased time of reaction. The activities of the complexes were dependent on the nature of the solvents used where a mixture of toluene and methanol gave better results than a mixture of DMF and methanol and dichlorobenzene and methanol. The immobilized complexes were recycled up to four times with the catalysts largely retaining their catalytic activities.

5.2 Suggestions for future prospects

As detailed in chapter one, there are different ways of heterogenizing the homogeneous catalysts and this study explored the use of silica (MCM-41) as the anchoring material. Stability of immobilized catalysts is a major factor which may determine the suitability of their use and therefore as part of future work, other support materials like SBA-15 can be investigated in the methoxycarbonylation of olefins. The complexes also gave both linear and branched ester products in appreciable ratios but for industrial applications, it would be important to make predominantly one isomer for easier applications. This would call for the design of complexes with varied steric hindrance to regulate regioselectivity towards either linear or branched ester product. The ligand system used in this research can therefore be modified to achieve more bulky groups closer to the metal centre (Figure 5.1) which can potentially give more of the linear isomers and in targeting branched products, less bulky groups could be included.

Branched esters could also be obtained by using the internal olefins as substrates in the methoxycarbonylation of olefins.



R= Phenyl, X= Cl, Y= Me
R= CH_3, X= Cl, Y= Me
R= Phenyl, X = OAc, Y = OAc
R= CH_3, X= OAc, Y= OAc

R= Phenyl, X= Cl, Y= Me
R= Br, X= Cl, Y= Me
R= Pheny, X = OAc, Y = OAc
R= Br, X= OAc, Y= OAc

Figure 5.1: Palladium complexes bearing groups that bring different electronic and steric effects around the metal centre.