**An-Najah National University** 

**Faculty of Graduate Studies** 

# Cellulose Functionalized with Amine Bidentate Ligand: Synthesis and Use as A Polymeric Support for Palladium Catalysts

By

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This Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Chemistry, Faculty of Graduate Studies, An-Najah National University, Nablus, Palestine.

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# Dedication

To my affectionate dad and mom who support me to be

the person that I always dreamed of.

To my beloved husband for being with me in every single step.

For my whole family.

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Praise and thanks to Allah, the most merciful for assisting and directing me to the right path, without his help my effort would have gone astray. Special thanks are due to my research supervisor Prof. Othman Hamed, for the opportunity to work with him in his research group. I am deeply grateful to him for his constant presence, his willingness to help at any time and his encouragement throughout this research project. I also thanks thank the thesis committee, Dr. Hisham Qarareyah, and Dr. Nisreen Alhaj for their consent to read my thesis and provide useful suggestions. I would like to take this opportunity to thank the chemistry labs supervisor Mr. Nafiz Dwikat for his assistance and support during this work.

I should never forget to thank Prof. Ismail Warad for teaching me research processes, and helping me to publish three papers -while undergraduate- in good scientific journals. أنا الموقعة أدناه مقدمة الرسالة التي تحمل عنوان:

# Cellulose Functionalized with Amine Bidentate Ligand: Synthesis and Use as A Polymeric Support for Palladium Catalysts

أقر بأن ما اشتملت عليه هذه الرسالة إنما هو نتاج جهدي الخاص، باستثنا ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يقدم من قبل لنيل أية درجة علمية أو بحث علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى.

# **Declaration:**

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student's name:	اسم الطالب:
Signature:	التوقيع:
Date:	التاريخ:

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# Cellulose Functionalized with Amine Bidentate Ligand: Synthesis and Use as A Polymeric Support for Palladium Catalysts

Bv

Oraib Nazem Ghaleb Ali Supervisor Prof. Othman Hamed

#### Abstract

Two novel polymeric palladium supported catalysts were prepared and evaluated in the oxidation of alkene and ketone. The obtained results showed that, the catalysts could be used in a lab scale or commercial scale to produce  $\alpha$ -hydroxy ketones form ketones and ketones form terminal alkenes. The polymeric material was prepared by condensation reaction of an oxidized cellulose (cellulose di-aldehyde) and 2-(2-pyridyl)ethylamine to produce cell-imine-pyridyl. Oxidized cellulose was prepared by oxidation of cellulose using sodium periodate. The polymer was characterized by FT-IR spectroscopy. The polymers then reacted with a solution of Li<sub>2</sub>PdCl<sub>4</sub> in acetonitrile to prepare the target polymeric palladium supported catalyst (cell-pyridyl-Pd(II)).

A second polymeric palladium supported (cell-picolyl-Pd(II)) catalyst was prepared in the same manner except that 2-picolylamine was used in the place of 2-(2-pyridyl)ethylamine. Hydroxylation of ketone catalyzed with cell-pyridyl-Pd(II) and cell-picolyl-Pd(II) produced  $\alpha$ -hydroxy ketone in moderate to excellent yield, while the oxidation of terminal alkene produced methyl ketone in moderate yield. So, both polymeric supported

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catalysts showed good to excellent efficiency. To enhance the solubility of the reactant, a polar aprotic solvent was chosen for the oxidation reactions in the presence of  $CuCl_2$  as a Pd(0) re-oxidant and in the presence of an acid to enhance the tautomerization of ketone to enol since the oxidation occurs on enol functional group, and the tautomerization of enol back to ketone which occurs during the oxidation of alkenes. The oxidation reactions were performed at room temperature.

# **Chapter One**

# Introduction

#### 1. Background

Transition-metal catalysts are among the most powerful tools for the synthesis of organic molecules. Over the past 70 years, inorganic and organometallic catalysts have been developed for a wide range of transformations and they are now common to all scales of productions ranging from the laboratory to the preparation of commercial production of fine chemicals and pharmaceuticals. The importance of the transition-metal catalysts has been highlighted through two novel reactions developed by the Nobel Prize winners Sharpless, Noyori, and Knowles who were honored for their asymmetric synthesis in 2001. And Chauvin, Grubbs, and Schrock who were recognized for olefin metathesis in 2005 [1-3].

Among the transition metals, palladium received a special attention by the organic chemists because of its ability to catalyze a wide range of reactions. Palladium perhaps first came to stand with commercialization of the Wacker process for the oxidation of ethene to acetaldehyde in the early 1960s as shown in figure 1.1 After that, a comprehensive survey of the uses of palladium in organic synthesis through 2000 was prepared and it covers over 3400 pages [4-7].



Figure 1.1 Equation of oxidation of ethene to acetaldehyde

### **1.1 Palladium Metal**

#### History

The chemist, William Hyde Wollastone (1766-1828) from England is the one who discovered palladium and that was in 1803 [8]. Palladium was named after the discovery of the asteroid Pallas by the astronomer Heinrich Wilhelm Olbers [9].

### **1.2 Palladium properties**

Palladium is relatively rare element with extant of one part in about  $10^{13}$  of the earth crusts. It has an atomic number of 46 on the periodic table, with face centered cubic (fcc) structure, figure 1.2. It is extracted from ores of Copper – Nickel, that is found in Canada, South Africa and Russia [10].



Figure 1.2 Unit cell of palladium face-centered cubic (fcc) structure. a, the lattice parameter, refers to the constant distance between unit cells in a crystal lattice [10]

#### **1.2.1 Physical properties**

Palladium is a silver-white metal, with a melting point of 1554 <sup>o</sup>C, which considered as the lowest melting point of B-group element, and a boiling point of 3980 <sup>o</sup>C. Palladium is also has the least density, which helps its

complexes to have their widespread use in many industrial catalytic processes. Palladium is malleable-ductile metal, which means that it capable of being hammered into thin sheets (which can have a thick of about a millionth of centimeter, same as gold), and capable of being drawn into thin wires [11]. Palladium could be spongy that can absorb hydrogen gas, in this case it absorbs up to 900 times its own volume of hydrogen gas [9,11].

#### **1.2.2 Chemical properties**

Palladium is highly resistant to corrosion. It falls in group VIII of P-Group, with electron configuration of  $d^{10}$ . It has five naturally occurring isotopes: palladium-102, palladium-105, palladium-106, palladium-108, and palladium-110. Palladium common oxidation states are 0, +2, and +4. Recently compounds with oxidation state of +6 were synthesized from three molecules of simple Pd (II) complex with two silicon atoms, as shown in Figure 1.3 [12].



Figure 1.3 Trinuclear complex with formal palladium(VII) [12]

Among the platinum group, palladium is the most reactive metal, so it has been called "the least noble" of the noble metals. Under normal conditions, it combines poorly with oxygen, but if grounded into powder it will catch fire. At room temperature, palladium does not react with most acids but will do so when mixed with most hot acids. Palladium metal also combines with fluorine and chlorine at high temperature[13].

### **1.3 Palladium Catalysts.**

The most active catalysts of transition metals are those that are unsaturated means those with an open coordination site. Palladium(II), figure 1.4, tends to adopt square-planner geometry, with two empty axial coordination sites. Palladium catalysis relevance has been recognized since 2010, through a Nobel Prize in chemistry, by Richard Heck, Ei-ichi Negishi, and Akira Suzuki [14].



Figure 1.4 Square planner electron configuration of palladium(II) [14]

Palladium complexes are one of the most widely used catalysts in the synthesis of various organic compounds worldwide. This could be related to several reasons such as: palladium catalyzes carbon-carbon bond formation; catalyze wide range of functional group transformations; specific and tolerance to many functional groups such as carbonyl and hydroxyl groups; not sensitive to moisture, or acid. More than ten industrial processes have been developed and are operated based on palladium catalyzed reactions reflects the importance of Pd catalysts commercially [15,16].

In organic synthesis, two types of palladium complexes Pd(II) and Pd(0) have been used [11]. Pd(II) usually used in stoichiometric amount and Pd(0) in catalytic amount. Pd(II) such as that in  $K_2PdCl_4$   $PdCl_2$  and  $Pd(OAc)_2$  are commercially available and widely used in oxidation of mainly alkenes. Pd(0) forms a good catalyst for hydrogenation and dehydrogenation reaction, and in petroleum cracking [8].

Palladium also makes complexes with a wide range of organic molecules ranging from phosphine to amines. Among these complexes, the most widely studied are phosphine ligands, and this include monodentate, bidentate and multidentate ligands such as for examples those shone in Figure 1.5 [17].



Figure 1.5 (a) Monodentate, (b) and (c) bidentate phosphene ligands

The use of phosphine ligands is necessary for about all homogeneous catalysis with precious metals. They are usually considered as strong

electron donors and weak acceptors. The choice of the right ligand influence on the solubility of the active species, shielding and steric properties of the catalyst, electron density at the metal atom, reactivity of the catalyst in the catalytic cycle, life time and turnover numbers of the catalyst, and enantioselectivity of the reaction with chiral ligands [18].

### **1.4 Palladium – Amine and Imine Complexes**

Imine and amine ligands contain lone pair of electrons on the nitrogen atom, which is used for the coordination with Pd(II). Catalysts containing nitrogen ligands (imines and amines) are also suitable for processes C-C cross-coupling reaction, hydrogenation, oxidation, allylic alkylation and the Heck reaction (figure 1.6). Catalysts bearing nitrogen ligands may perform even better than those with weak Lewis-base phosphorus ligands [19]. Even though the Phosphine-Palladium complex play a main role in industrial applications, nitrogen ligands catalysts are mostly of considerable interest [20].



Figure 1.6 An example of Heck reaction (coupling of arylhalide with styrene) [21].

#### **1.4.1 Synthesis of Amine and Imine ligands**

Among the important ligands for palladium are imines. Imines are not commercially available; they are usually prepared by condensation reaction between carbonyl compounds such as ketones or aldehydes and amines, an example on aromatic amines is shown in figure 1.7, the figure summarizes the synthesis of some reported imine ligands [17,22]. When imine is made by this method, water is produced as a by-product. This imine-forming reaction is reversible, so water is needed to be removed as it is formed effective method in this case is distillation, preferably azeotropic distillation, or through using a drying agent such as magnesium sulfate [23].



Figure 1.7 Schematic description of synthesis of imine ligands suitable for complexing with Pd(II) [23]

Alternative routes for the synthesis of imine ligands have been reported. In this method a Lewis acid is used as a catalyst [24]. For example when two equivalents of (1R)-(+)-camphor are refluxed with a 1,2-diamine and an excess base such as triethylamine in the presence of TiCl<sub>4</sub> for two days, the corresponding diimine is produced in a moderate yield (figure 1.8) [25].



Figure 1.8 Schematic description of condensation of (1R)-(+)-camphor with a 1,2diamine reaction

In another example condensing 2,3-butandione with chiral myrtanylamine produced imine in over 50% yield. This condensation was carried out in methanol and formic acid as catalyst, while stirring at ambient- temperature as shown in figure 1.9. Precipitation of the diimine product DMDI (N,N-bis{(-)-*cis*-myrtanyl}butylene-2,3-diimine) is the driving force in this reaction [26].



Figure 1.9 Schematic description of condensation of 2,3-butandione with chiral myrtanylamine reaction [26]

Usually, condensation of aromatic ketones or aldehydes with sterically hindered amines requires severe reaction conditions. For example, condensation of salicylaldehydes with substituted phenyl amines such as 2,6-dialkyl derivatives gave no product. However, when the reaction is carried out at 200 °C in a closed steel autoclave in the presence of the drying agent Na<sub>2</sub>SO<sub>4</sub> and a catalytic amount of formic acid (figure 1.10) imine ligands **3** and **4** were isolated in a moderate yield about 50%, while ligand **5** was isolated in only 6% yield. No increase of the yield was achieved by varying acid catalyst or solvent or by performing the reaction without solvent and at different temperatures [27].



Figure 1.10 Schematic description of condensation of aromatic ketone with sterically hindered amines

As shown above simple reaction conditions and easy product purification combined with easy availability of a wide spectrum of starting materials may give the chemist a fast entrance to imine ligands.

#### 1.4.2 Synthesis of Palladium (II) Amine and Imine Complexes

Imine transition metal complexes are often prepared in two steps: in the first step imine is synthesized followed by the synthesis of the metal-imine complex. Many complexes of imines and palladium (figure 1.11) have been reported in literature.



**Figure 1.11 Schematic description of preparation of Palladium – Imine complexes** 

Transition metal - nitrogen ligands (imines and amines) complexes have been extensively studied and suitable in catalytic processes. These include C-C cross-coupling reaction, hydrogenation, oxidation, allylic alkylation and the Heck reaction. Catalysts bearing nitrogen ligands may perform even better than those with weak Lewis-base phosphorus ligands [28]. Although phosphine transition metal complex still play the main role in industrial applications, nitrogen ligands catalysts are mostly of considerable interest [29]. Schiff-base imine ligands have played an essential role in the development of transition metal complexes for biological applications, catalysis and material science [30]. Furthermore, chiral and achiral Pd(II) complexes bearing bidentate nitrogen donors have attracted interest as catalysts for homo- and hetero- copolymerization of linear and cyclic olefins with carbon monoxide [27,31,32] and for polymerization of functionalized olefins [33].

The attractiveness of nitrogen donors is enhanced by their good availability [34]. For example, chiral and achiral multidentate ligands have been applied in transition metal-catalyzed reactions such as enantioselective C-C bond forming reactions, allylic alkylation, oxidation, reduction, and carbonylation of alkenes [35-39].

As mentioned above, late transition metal complexes with nitrogen-based ligands have found a wide range of applications in homogeneous catalysis [30].

For example, dendimeric pyridylimine-Pd(II) complexes and binuclear Pd(II) complexes with long aliphatic spacers have recently been described as effective catalyst precursors for Heck coupling [40] and ethene polymerization, respectively [41]. Moreover, palladium complexes with chiral bidentate bis(oxazoline) ligands have been found efficient in asymmetric allylic alkylation [36]. Palladium-catalyzed enantioselective transformations have recently been reviewed [42].

# **1.5 Polymer Supported Palladium Catalysts.**

Currently, there is a great interest in the development of environmentally friendly catalytic tools (Green Chemistry). Several innovative ideas related to the later subject have been already developed. Example on these is polymer supported catalysts, these kinds of catalysts offer great advantage over traditional homogenous catalysts since they afford higher activity, easy product purification, and catalyst recycling. So, after the reaction is complete, catalyst could be filtered, washed off, and reused [43-46]. In polymer supported catalysts, the active species are immobilized onto polymer surface through chemical bonds or physical interaction such as dipole –diploe or hydrogen bonds [47].

Palladium catalyst is one of the most important transition catalysts since they form the basis of many hydrocarbon oxidation catalysts [48,49]. Despite that, limited number of examples on polymer supported palladium catalysts are available in this area of research. In one example PdCl<sub>2</sub> has been supported on a styrene-divinylbenzene copolymer resin containing – dimethylaminomethyl (CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>) functionality [50,51]. This catalyst is reported to be effective in converting ethylene to vinyl acetate and acetaldehyde in the presence of dioxygen. More recently an organic quinone polymer containing sulphonic acid groups has been used to support palladium(II), yielding a catalyst effective for the conversion of ethylene to acetaldehyde [52]. Wacker-type supported catalyst has also been prepared [53] using oligo-pphenyleneterephthalamide (NHPhNHCOPhCO)<sub>n</sub>, it was used for its thermal stability. The supported catalyst was prepared by wet, impregnation of the polymer with a (water : acetic acid) solution (9:1) of  $Pd(OAc)_2$  at room temperature. After drying, the temperature of the impregnate was raised to 950°C to remove volatiles.

In another example palladium complexes were attached on resins with phosphine functional groups like those shown in Figure 1.12 and used as some heterogeneous catalysts in Heck and Suzuki-Miyaura reactions [54]. In this case the removed catalyst showed high catalytic cycles. However, these catalysts were limited to activated aryl such as ArX (X = I, Br, OTf) [55]. Several attempts were made to enhance the recyclability of the catalyst.



Figure 1.12 Polymers () with phosphene functional groups

Polymer supported with nitrogen functional group plays an important role in palladium complexes catalysis, that's because it can be clean easily and reuse many times with high activity, and without significant loss of stability or structure. Figure 1.13 shows some examples of polymer supported with nitrogen, that were attached to palladium, and used as a catalysts for C-C cross-coupling reaction [56, 57].



Figure 1.13 Polymers () with nitrogen functional groups

Preparing polymer supported Pd(II) catalysts base on natural polymers such as starch [58], chitosan [59], and cellulose could be very attractive as a green chemistry. Cellulose is a natural polymer, biodegradable and available at low cost.

#### **1.6 Cellulose**

#### **1.6.1 Cellulose structure**

A natural polymer composed of anhydroglucose repeat unit (figure 1.14) which connected respectively through  $\beta$ -1,4-glycosidic links in the configuration between C1 and C4 of adjacent units to form a polymer chain, that how cellulose could be defined. Cellulose chain consists of about 10,000 monomer units. Fibers are some bundled with bundles. Accumulates fibers group form cellulose. Cellulose can be obtained in crystalline form or in an amorphous region (less organized region).



#### Figure 1.14 Structure of cellulose

As shown in figure 1.10. Each unhydroglucopyranose repeat unit possesses three hydroxyl groups: two secondary at C2 andC3, and a primary C6 positions. All hydroxyl groups are capable of undergoing the typical reactions known for primary and secondary alcohols.

Cellulose is a safe, tasteless, and a stable polymer. It is hydrophilic, insoluble in water, nor in most organic solvents. It is biodegradable chiral polymer [60,61].

The stability of cellulose and its solubility in water is related to the presence of hydroxyl groups which allow for strong interaction between cellulose polymer chains. There are areas within the cellulose structure where the cellulose chains are in the crystalline region (high-order structure), and noncrystalline areas where cellulose chain are disordered (amprphous). Cellulose properties are derived from polymerization of glucose molecules that make up the polymer [62,63].

#### **1.6.2 Sources of cellulose**

Cellulose is one of the most abundant polymers in nature, and it can be extracted from many sources such as: Bushes: 30%, Woods: 40–50%, Bast Plants (flax): 65–70%, Cotton Fibers: >90% [64,65].

#### **1.6.2.1 Olive Industry Waste**

Olive oil production is widespread throughout the world. There is a large amount of solid and bulk waste produced by this industry.

Olive industry wastes are about 56% in the liquid phase (olive industry liquid waste (OILW)), and about 44% in the solid phase (olive industry solid waste (OISW)) [66].

Cellulose is the main substance of OISW, it is about (40-45%). Which makes it a cheap source for cellulose extraction. The waste from olive industry has a very high biological oxygen demand (BOD) 41 g/L and chemical oxygen demand (COD) 105 g/L values, it also contains highly toxic levels of poly phenols 0.038 g/L [67,68].

Perception of waste from olive oil industry are differs from one region to another. Farmers of some regions are interest in solid waste of the olive industry (OISW) with the same degree of interest in oil, while in other areas they do not care about waste at all.

Liquid waste produced from the olive industry (OILW), no one gives any attention, but constitutes a burden on the owners of contemporary olive and a concern for the environment because this disposal is a big problem in terms of effort and cost and thus the olive industry may lose the economic value through the disposal of liquid waste or sell at a low price to be used in different industries. In some areas, OISW is usually burned or left to decompose large quantities of carbon dioxide ( $CO_2$ ) are released into the atmosphere.

#### **1.6.3 Cellulose Catalytic Activity**

Natural polymer cellulose is a renewable, non-meltable, biodegradable, due to hydrogen bonding and high crystallinity it is insoluble in most solvents. Total production of cellulose, about 1011–1012 tons/year make it the most abundant natural polymer in the world [69-71].

Chemical modification of cellulose or mixing with other components can make it to be used as a green source for fabricating biodegradable and biocompatible materials with significance interesting properties [72].

Effective utilization of cellulose protects the environment as well as decreases the fossil resources crisis. Due to interesting properties of cellulose, many investigators are focused on their attention on the modification and utilization of cellulose in various applications such as drug delivery systems, removal of toxic metals and organic compounds, sensor, production of alcohol [73-76].

Cellulose can also be modified to catalysis  $H_2$  production for clean energy sources [77].

Recent work published by Yamada et al (78) showed that Palladium can be immobilized on cellulose particles (Pd/CLP) and on a cellulose-monolith (Pd/CLM). The produced composites were used as hydrogenation catalysts and their catalyst activities were evaluated. Also, both catalysts showed the ability to remove the protecting group benzyloxycarbonyl-protected from aromatic amines.

Cellulose based Pd/Co bimetallic catalyst were prepared and tested in nitrobenzene reduction by using  $H_2O/EtOH$  as solvent and NaBH<sub>4</sub> as reducing agent [79]. Modified cellulose based catalyst was used in the hydrogenation of different nitroarenes [80].

Cellulose could be a very promising polymer for support preparation due to the fact that it is available in nature in a large quantity, and excellent for sustainable carbon support production [81,82]. It has many applications within which its, structure, shape and particle size [83-87].

#### **1.7 Aims of The Thesis**

The aim of the present work is to design and develop palladium celluloseimine with nitrogen-based ligands and use them to improve existing palladium-catalyzed reactions. The reactions may include hydroxylation of ketones, and oxidation of terminal alkenes, but not limited.

Two different types of amines were chosen for this purpose:

1) 2-(2-pyridyl)ethyl amine.

2) 2-picolyl amine.

Oxidized cellulose was chosen for this work because of its uniqueness in having 2,3-diketone functionality. These carbonyls make them easy target in converting them into imine derivatives then complexed to palladium (II). Cellulose-imine could be prepared by the condensation of oxidized cellulose and 2-(2-pyridyl)ethyl amine as shown in figure 1.15, and 2-picolylamine as shown in figure 1.16. This kind of condensation is simple and effective tool for the synthesis of imine ligands. The ease of the reaction's work up and purification of the product, and the availability of the starting materials made imine ligand our first choice to attain the objective of this work. Palladium(II) then will be introduced onto the polymer chain by reacting cellulose-imine with palladium(II) chloride. The polymeric supported catalyst is novel due to the fact that each polymeric chain carries multi-catalytic sites, which are equal the double number of repeat units.



Figure 1.15 Schematic description of preparation of cell-pyridyl



Figure 1.16 Schematic description of preparation of cell-picolyl

The catalytic activity of the produced complex will be evaluated as mentioned in the previous reactions. The catalytic activity of cellulose based polyimines toward hydroxylation of ketone, and oxidation of alkenes will be studied.
# Chapter Two

### Experimental

### **General Experimental**

All reagents, solvents and chemicals used in this work were purchased from Aldrich Chemical Company and used without any further purification.

All solutions used in this work were prepared using distilled water.

Cellulose used in this study was extracted from the solid waste of the olive industry (Jeft) by a chemical process developed at our laboratories at An-Najah National University, Nablus-Palestine [88].

Shaking water bath (Daihan Labtech, 20.0 to 250.0 rpm Digital Speed Control), and pH meter (JENWAY, 3510) were used in this study.

All new compounds were characterized by FT-IR Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with the Smart Split Peaks Hemi MicroATR accessory (International Crystal Laboratories, Garfield, NJ, USA).

### 2.1 Palladium Cellulose-Imine Complexes

The complexes of this study were prepared in a three steps process. The first step involved oxidation of cellulose. Then, condensation reaction of oxidized cellulose with the amine (imine preparation). Finally, complexation of palladium (II) with the imine.

### **Oxidation of Cellulose**

A 10.00 g cellulose was placed in a 1.0 L beaker followed by addition of a 500.0 mL of distilled water. The beaker was totally covered with

Aluminum foil. Then, sodium periodate (16.00 g) was added, the mixture was stirred for 24 hours, at 35 °C. Finally, the oxidized cellulose was collected by suction filtration, and washed thoroughly with distilled water (three times, each 500.0 mL).

### 2.1.1 Determination of Aldehyde Content

To determine the aldehyde content of oxidized cellulose, a 1.00 g sample of the oxidized cellulose was placed in a 250 mL beaker and suspended in 50.0 mL of 2-propanol. The suspension was stirred for 10 minutes. Then, 10.0 mL distilled water was added. A 5% HCl solution was added dropwise until the pH of solution adjusted at 3.50, then the solution was stirred for another 30 minutes.

A 5% solution by weight of hydroxylamine hydrochloride (NH<sub>2</sub>OH.HCl) was prepared by dissolving a 1.00 g in 20.0 mL distilled water. The pH of the solution was adjusted with a 1% NaOH to 3.50.

The hydroxylamine hydrochloride 5% solution was added to the oxidized cellulose suspension and stirred for 6 hours. Finally, the mixture was titrated with 0.5 N NaOH to the end point of pH of 3.5.

## 2.1.2 Preparation of the Imine Cellulose/2-(2-Pyridyl)ethylamine (Cellpyridyl)

The reaction was performed in a one neck round bottom flask (150 mL) equipped with a magnet stirrer par and a condenser. To the flask 60.0 mL methanol was added followed by 1.00 g (6.17 mmole/AGU) of cellulose dialdehyde. Then 1.00 g (8.2 mmol) of 2-(2-pyridyl)ethylamine was added

to the suspension. Acetic acid (0.5 mL) was added to the reaction mixture as a catalyst. The reaction mixture was refluxed at 80 °C for 9 hours with stirring. At the end, the solvent evaporated, and the resident collected and washed twice with ethyl acetate.

#### **2.1.3 Preparation of the Imine Cellulose/2-Picolylamine (Cell-picolyl)**

The reaction was performed in a one neck round bottom flask (150 mL) equipped with a magnet stirrer par and a condenser. To the flask 60.0 mL was added methanol followed by 0.89 g (6.17 mmole/AGU) of cellulose dialdehyde. Then 1.00 g (8.2 mmol) of 2-picolylamine was added to the suspension. Acetic acid (0.5 mL) was added to the reaction mixture as a catalyst. The reaction mixture was refluxed at 80 °C for 9 hours with stirring. At the end, the solvent evaporated, and the resident collected and washed twice with ethyl acetate.

### 2.1.4 Preparation of Cell-pyridyl-Pd(II) Complex

Palladium(II) chloride (0.83 g, 7.83 mmole) was suspended in acetonitrile (80 mL) under nitrogen in a 150 mL round bottom flask. Cell-pyridyl (0.5 g, 1.358 mmole) was added to the suspension. The mixture was stirred in a closed system, under nitrogen pressure, for 24 hours, at 50 °C. The reaction was ended by the addition of a 50.0 mL of diethyl ether to the reaction mixture, and stirred at room temperature for an hour. Then the product was collected by suction filtration, the filtrate was evaporated, and the residue was washed with 30.0 mL of acetonitrile then a 30 mL of diethyl ether.

The prepared palladium complex was analyzed by FT-IR Spectrometer, and

DSC thermal analysis.

### 2.1.5 Preparation of Cell-picolyl-Pd(II) Complex

Palladium (II) chloride (0.83 g, 7.83 mmole) was suspended in acetonitrile (80 mL) under nitrogen in a 150 mL round bottom flask. Cell-pyridyl (0.5 g, 1.773 mmole) was added to the suspension. The mixture was stirred in a closed system, under nitrogen pressure, for 24 hours, at 50 °C. The reaction was ended by the addition of 50.0 mL of diethyl ether to the reaction mixture and stirred at room temperature for an hour. Then the product was collected by suction filtration, the filtrate was evaporated, and the residue was washed with a 30.0 mL of acetonitrile then 30.0 mL diethyl ether.

The prepared palladium complex was analyzed by FT-IR Spectrometer, and DSC thermal analysis.

# 2.2 General Procedure for the α-Hydroxylation of Cycloketones Using Cell-pyridyl-Pd(II)

a solution of CuCl<sub>2</sub> (7.7 g, 58.0 mmol) in 30 mL dioxane (40% by wt.) was prepared and placed in a round bottom flask (150 ml). 0.1 mmole sample of cell-pyridyl-Pd or cell-picolyl-Pd(II) catalyst was added followed with the addition of cycloketone (100.0 mmol). A small amount dichloroacetic acid  $C_2H_2Cl_2O_2$  (0.58 ml, 0.903 g, 7.0 mmole) was added to the reaction mixture, and the cycloketone (11.3 mmole) were added to the reaction mixture at room temperature with stirring. The reaction was stopped after 48 hrs and diluted with ether. The produced mixture was stirred at room temperature. The ether layer was separated, extracted two times with a solution of sodium bicarbonate 5% (30.0 mL), the ether layer was dried over  $Na_2SO_4$  and concentrated in vacuo.

### 2.2.1 α-Hydroxylation of Cyclohexanone Using Cell-pyridyl-Pd(II)

Cyclohexanone (1.11 g,1.0 mL, 11.3 mmole) was used to give hydroxy cyclohexanone, with a percentage yield of 72.9%, which is a liquid with yellow color, and it has a boiling point of 212.0 °C, that's give an indication that our product is not pure since it should be a colorless liquid with a boiling point of 226.3 °C [89]. Hydroxy cyclohexanone was analyzed by IR, the following peaks are shown in the FT-IR cm<sup>-1</sup> (figure 2.1): 1709.56 corresponding to C=O, 3529.53 for O-H and the peak at 1120.74 for C-O alcohol. The analysis results indicate the formation of the  $\alpha$ -hydroxy cyclohexanone.



Figure 2.1 FT-IR spectra of cyclohexanone and hydroxy cyclohexanone by cell-pyridyl-Pd(II) catalyst

### 2.2.2 α-Hydroxylation of Cyclopentanone Using Cell-pyridyl-Pd(II)

Cyclopentanone (0.95 g, 11.3 mmol) was used to give hydroxy cyclopentanone, with a percentage yield of 74.3%, which is a liquid with yellow-orange color, and it has a boiling point of 205.0 °C, that's give an indication that our product is not pure since it should be a colorless liquid with a boiling point of 210.0 °C [89]. Hydroxy cyclopentanone was analyzed by IR, the following peaks are shown in the FT-IR cm<sup>-1</sup> (figure 2.2): 1745.81 for C=O, 3504.32 corresponding to O-H, and the peak at 1120.54 corresponding to C-O alcohol. The analysis results indicate the formation of the  $\alpha$ -hydroxy cyclopentanone.



Figure 2.2 FT-IR spectra of cyclopentanone and hydroxy cyclopentanone by cellpyridyl-Pd(II) catalyst

### 2.2.3 α-Hydroxylation of Acetophenone Using Cell-pyridyl-Pd(II)

Acetophenone (1.36 g, 11.3 mmole) was used to give hydroxy acetophenone, with a percentage yield of 92.1%, which is a liquid with

orange color, and it has a boiling point of 257.0 °C, that's give an indication that our product is not pure since it should be a colorless liquid with a boiling point of 286.0 °C [89]. Hydroxy acetophenone was analyzed by IR, the following peaks are shown in the FT-IR cm<sup>-1</sup> (figure 2.3): 1684.04 for C=O, 3370 for O-H and the beak at 1121.31 corresponding to C-O alcohol. The analysis results indicate the formation of the  $\alpha$ -hydrroxy acetophenone.



Figure 2.3 FT-IR spectra of acetophenone and hydroxy acetophenone by cellpyridyl-Pd(II) catalyst

# 2.3 General Procedure for the α-Hydroxylation of Cycloketones Using Cell-picolyl-Pd(II)

Palladium (II) cell-picolyl complex (55.2 mg, 0.1 mmole) and  $C_2H_2Cl_2O_2$  (0.58 ml, 0.903 g, 7.0 mmole) were added to a solution of CuCl<sub>2</sub> (7.7 g, 58.0 mmol) in 30 mL dioxane (40 wt% in water), the cycloketone (11.3 mmole) were added with stirring at room temperature. The reaction was

interrupted after 48 hrs and diluted with ether. The produced mixture was stirred at room temperature. The ether layer was separated, extracted two times with a solution of sodium bicarbonate 5% (30.0 mL), the ether layer was dried over  $Na_2SO_4$  and concentrated in vacuo.

### 2.3.1 α-Hydroxylation of Cyclohexanone Using Cell-picolyl-Pd(II)

(1.11)g,1.0mL,11.3 Cyclohexanone mmole) was used give to hydroxycyclohexanone, with a percentage yield of 70.6%, which is a liquid with yellow color, and it has a boiling point of 217.0 °C, that's give an indication that our product is not pure since it should be a colorless liquid with a boiling point of 226.3 °C [89]. Hydroxy cyclohexanone was analyzed by IR, the following peaks are shown in the FT-IR cm<sup>-1</sup> (figure 2.4): 1709.43 for C=O, 3497.98 corresponding to O-H and the peak at 1120.74 corresponding to C-O alcohol. The analysis results indicate the formation of the  $\alpha$ -hydroxy cyclohexanone.



Figure 2.4 FT-IR spectra of cyclohexanone and hydroxy cyclohexanone by cellpicolyl-Pd(II) catalyst

### 2.3.2 a-Hydroxylation of Cyclopentanone Using Cell-picolyl-Pd(II)

Cyclopentanone (0.95)g, 11.3 mmol) was used to give hydroxycyclopentanone, with a percentage yield of 77.0%, which is a liquid with yellow-orange color, and it has a boiling point of 207.0 °C, that's give an indication that our product is not pure since it should be a colorless liquid with a boiling point of 210.0 °C [89]. Hydroxy cyclopentanone was analyzed by IR, the following peaks are shown in the FT-IR cm<sup>-1</sup> (figure 2.5): 1745.39 for C=O, 3439.08 corresponding to O-H and the peak at 1120.29 corresponding to C-O alcohol The analysis results indicate the formation of the  $\alpha$ -hydroxy cyclopentanone.



Figure 2.5 FT-IR spectra of cyclopentanone and hydroxy cyclopentanone by cellpicolyl-Pd(II) catalyst

### 2.3.3 α-Hydroxylation of Acetophenone Using Cell-picolyl-Pd(II)

Acetophenone (1.36 g, 11.3 mmole) was used to give 2-hydroxy acetophenone, with a percentage yield of 87.7%, which is a liquid with

orange color, and it has a boiling point of 255.0 °C, that's give an indication that our product doesn't pure since it should be a colorless liquid with a boiling point of 286.0 °C [89]. Hydroxy acetophenone was analyzed by IR, the following peaks are shown in the FT-IR cm<sup>-1</sup> (figure 2.6): 1683.90 for C=O, 3350 corresponding to O-H and the peak at 1121.75 corresponding to C-O alcohol. The analysis results indicate the formation of the  $\alpha$ -hydroxy acetophenone.



Figure 2.6 FT-IR spectra of acetophenone and hydroxy acetophenone by cell-picolyl-Pd(II) catalyst

# 2.4 General Procedure for the Oxidation of terminal alkene Using Cell-pyridyl-Pd(II)

Palladium cell-pyridyl complex (58.0 mg, 0.1 mmole), dichloroacetic acid  $(C_2H_2Cl_2O_2)$  (0.58 ml, 0.903 g, 7.0 mmole), and the alkene (11.3 mmole) were added to a solution of CuCl<sub>2</sub> (7.7 g, 58.0 mmol) in 30 mL dioxane (40% in water), with stirring at room temperature. The progress of the

reaction was monitored by GC and TLC. The reaction was interrupted after 48 hrs and diluted with ether. The produced mixture was stirred at room temperature. The ether layer was separated, washed two times with a solution of sodium bicarbonate 5% (30.0 mL), the ether layer was dried over  $Na_2SO_4$  and concentrated in vacuo.

### 2.4.1 Oxidation of 1-Hexene Using Cell-pyridyl-Pd(II)

1-hexene (0.9492 g, 11.3 mmole) was used to give 2-hexanone, with a percentage yield of 75.2%, which is a colorless liquid, and it has a boiling point of 120.0 °C, that's give an indication that our product is not pure since it should be a colorless liquid with a boiling point of 286.0 °C [89]. 2-Hexanone was analyzed by IR, the following peaks are shown in the FT-IR cm<sup>-1</sup> (figure 2.7): 1700.93 corresponding to C=O, and the peaks at 2853 and 2923 are corresponding to C-H. The analysis results indicate the formation of the 2-hexanone.



Figure 2.7 FT-IR spectra of 1-hexene and hydroxy 2-hexanone by cell-pyridyl-Pd(II) catalyst

### 2.4.2 Oxidation of 1-Pentene Using Cell-pyridyl-Pd(II)

1-pentene (0.791 g, 11.3 mmol) was used to give pentanone, with a percentage yield of 83.3%, which is a liquid with yellow color, and it has a boiling point of 97.0 °C, that's give an indication that our product is not pure since it should be a colorless liquid with a boiling point of 101.0 °C [89]. 2-Hexanone was analyzed by IR, the following peaks are shown in the FT-IR cm<sup>-1</sup> (figure 2.8): 1715 for C=O, and the peaks at 2962 and 2855 corresponding to C-H. The analysis results indicate the formation of the 2-pentanone.



Figure 2.8 FT-IR spectra of 1-pentene and hydroxy 2-pentanone by cell-pyridyl-Pd(II) catalyst

### 2.4.3 Oxidation of 1-Octene Using Cell-pyridyl-Pd(II)

1-octene (1.2656 g, 11.3 mmole) was used to give 2-octanone, with a percentage yield of 67.5%, which is a liquid with yellow-orange color, and it has a boiling point of 168.0 °C, that's give an indication that our product

is not pure since it should be a colorless liquid with a boiling point of 172.5.0 °C [89]. which was analyzed by IR, the following peaks are shown in the FT-IR cm<sup>-1</sup> (figure 2.9): 1712.01 for C=O, and the peaks at 2955.88 and 2926.54 corresponding to C-H. The analysis results indicate the formation of the 2-octanone.



Figure 2.9 FT-IR spectra of 1-octene and hydroxy 2-octanone by cell-pyridyl-Pd(II) catalyst

# 2.5 General Procedure for Oxidation of Terminal Alkenes Using Cell-picolyl-Pd(II)

Palladium (II) cellulose-picolyl complex (55.2 mg, 0.1 mmole), dichloroacetic acid ( $C_2H_2Cl_2O_2$ ) (0.58 ml, 0.903 g, 7.0 mmole), and the alkene (11.3 mmol) were added to a solution of CuCl<sub>2</sub> (7.7 g, 58.0 mmol) in 30 mL dioxane (40% in water), with stirring at room temperature. The reaction was interrupted after 48 hrs and diluted with ether. The produced mixture was stirred at room temperature. The ether layer was separated, washed two times with 30.0 mL of solution which contained 5% sodium

bicarbonate, then  $Na_2SO_4$  was used to dry the ether layer, and concentrated in vacuo.

### 2.5.1 Oxidation of 1-Hexene Using Cell-picolyl-Pd(II)

Hexe-1-ne (0.9492 g,1.0 mL,11.3 mmole) was used to give 2-hexanone, with a percentage yield of 71.4%, which is a colorless liquid, and it has a boiling point of 122.0 °C, that's give an indication that our product is not pure since it should be a colorless liquid with a boiling point of 128.0 °C [89]. which was identified by IR cm<sup>-1</sup> (figure 2.10): 1708 for C=O, 2962.17 and 2854.96 for C-H gave an indication of the formation of the 2-hexanone.



Figure 2.10 FT-IR spectra of 1-hexene and hydroxy 2-hexanone by cell-picolyl-Pd(II) catalyst

### 2.5.2 Oxidation of 1-Pentene Using Cell-picolyl-Pd(II)

But-1-ene (0.791 g, 11.3 mmol) was used to give 2-pentanone, with a percentage yield of 86.4%, which is a liquid with yellow color, and it has a

boiling point of 96.0 °C, that's give an indication that our product is not pure since it should be a colorless liquid with a boiling point of 101.0 °C [89]. 2-Pentanone was analyzed by IR cm<sup>-1</sup> (figure 2.11): 1742.40 for C=O, 2926.79 for C-H gave an indication of the analyzed of the 2-pentanone.



Figure 2.11 FT-IR spectra of 1-pentene and hydroxy 2-pentanone by cell-picolyl-Pd(II) catalyst

### 2.5.3 Oxidation of 1-Octene Using Cell-pyridyl-Pd(II)

Oct-1-ene (1.2656 g, 11.3 mmole) was used to give 2-octanone, with a percentage yield of 69.2%, which is a liquid with yellow-orange color, and it has a boiling point of 165.0 °C, that's give an indication that our product is not pure since it should be a colorless liquid with a boiling point of 172.5 °C [89]. which was identified by IR cm<sup>-1</sup> (figure 2.12): 1714 for C=O, 2956 and 2927 for C-H gave an indication of the formation of the 2-octanone.



Figure 2.12 FT-IR spectra of 1-octene and hydroxy 2-octanone by cell-picolyl-Pd(II) catalyst

# Chapter Three Results and Discussion

This work aimed to device a convenient method for the synthesis of hydroxylated ketones and oxidized alkenes at  $\alpha$ -position ( $\alpha$ - hydroxy ketones and ketones).  $\alpha$ -Hydroxy ketones are important precursors for the synthesis of natural products, fine chemicals like amino alcohols, and drugs as antidepressants, inhibitor of jack bean urease, and inhibitor of amyloid- $\beta$  protein [90-96]. Because of that, there is a considerable interest and there has been several reports on this topic [94]. One of the simplest approaches involves the oxidation of enolates and enol derivatives [95]. Furthermore,  $\alpha$ -hydroxy ketones are useful building units in the preparation of biologically active compounds. The isomerization of  $\alpha$ -hydroxy ketones [96]. The importance of  $\alpha$ -Hydroxy ketones leads us to describe the catalytic oxidation of ketones using two types of polymer supported Pd(II) catalysis, they are Pd(II) on cell-pyridyl ligand, and Pd(II) on cell-picolyl ligand.

### **3.1 Oxidation of Cellulose**

Sodium periodate (NaIO<sub>4</sub>) was used to oxidize cellulose into cellulose dialdehyde as shown in figure 3.1. Oxidation of cellulose by sodium periodate known as Jackson and Hudson method, optimizing the reaction conditions and amount of reagent can lead to a high yield of oxidized product [97,98].

This method involves treatment of cellulose with an aqueous solution of sodium periodate (NaIO<sub>4</sub>) in a dark system, at about room temperature. The

reaction was optimized by our group and carried out at 35 °C. The oxidation mechanism involves complexation of periodate to the vicinal hydroxyl group at  $C_2$  and  $C_3$  which leads to cleavage of  $C_2$ - $C_3$  bond and oxidation of the vicinal hydroxyl groups to create two aldehyde units per repeat unit along the cellulose chains as shown in figure 3.2.



Figure 3.1 Schematic description of cellulose oxidation with sodium periodate reagent



Figure 3.2 Schematic description of cellulose oxidation mechanism

### **3.1.1 Chemical Determination of Aldehyde Content:**

To estimate the number of carbonyl groups per cellulose repeat unit prepared in this work the aldehyde content was determined. This was done according to a published method [97], by reacting cellulose aldehyde with hydroxylamine-hydrochloride and convert it to an oxime. Then the hydrochloric acid produced from the reaction was titrated with a solution of 0.5 N sodium hydroxide until the pH value reached 3.5 (figure 3.3).



Figure 3.3 Schematic description of (a) cellulose-oxime preparation, and (b) oxime titration versus NaOH

The following equation (Eq.1) was used to determine aldehyde content:

$$[Ald] = V_{NaOH} * N_{NaOH} * 162_{g|anhydrous glucose repeat unit} / W_{OC} \qquad Eq 3.1$$

Where [Ald]: is the aldehyde content in mmol per anhydrous glucose repeat unit,  $V_{NaOH}$ : is the volume of NaOH (mL) used in the titration,  $N_{NaOH}$ : is the normality of the NaOH (eq\L) and  $W_{OC}$ : is the dry weight of oxidized cellulose (g) used in titration.

The aldehyde content according to this relationship was calculated to be about 1.83/anhydrous glucose repeat unit (about two aldehyde group per repeat unit).

### **3.1.2 FT-IR Detection of Aldehyde Content**

The FT-IR spectrum of the produced cellulose dialdehyde is presented in Figure 3.4. The figure shows an overlap IR spectrum of cellulose and oxidized cellulose. The oxidized cellulose shows peaks at 1635.64 cm<sup>-1</sup>, 1457.62, 1339.09, and 1158.04 cm<sup>-1</sup>, assigned to carbonyl of C=O of aldehyde, CH<sub>2</sub> asymmetric bending, C-O stretching, and C-O-C stretching

 $\beta$ -glycosidic linkage, respectively. The carbonyl peak appears as a weak band at 1635.64 cm<sup>-1</sup> which could be attributed the hydration and formation of acetal. The carbonyl peak is not present in the Cellulose IR spectrum.



Figure 3.4 FT-IR spectra of cellulose dialdehyde and cellulose powder

### **3.2 Preparation of Cellulose Polyimine**

The aldehyde group is a reactive precursor, can be converted to various functional group. It can be further oxidized to carboxylic groups, or reduced to primary alcohols, it also can be reacted with amine to form imine [100-102]. Reduction of imine produces amine. Due to its lone pair of electrons, imine is known to have tendency to complex with metal ions. In this study aldehyde was chosen to be converted to an imine.

The electrophilic carbon of the carbonyl group in aldehyde undergoes condensation reaction with the amine to form an imine after losing a water molecule.

### 3.2.1 Preparation of Cell-pyridyl

The reaction between dialdehyde cellulose and 2-(2-pyridyl)ethylamine is shown in figure 3.5. The first step involves a nucleophilic addition of an amine to the carbonyl group of an aldehyde to produce amino alcohol intermediate which undergoes dehydration to form an imine. A product with a very good yield about 85% was obtained.



Figure 3.5 Schematic description of conversion of cellulose dialdehyde to cellulosepyridyl

### **3.2.1.1 FT-IR Analysis of Cell-pyridyl**

The FT-IR spectrum is shown in Figure 3.6, the spectrum shows the disappearance of the aldehyde group and the development of a new peak at 1706.91 cm<sup>-1</sup> which is attributed to the imine functionality (C=N). The peaks at 1591.18 and 1568.69 cm<sup>-1</sup> confirm the presence of the aromatic pyridine ring, the peaks are corresponding to C=N and C=C of the aromatic ring.



Figure 3.6 FT-IR spectrum of cell-pyridyl

### **3.2.2 Preparation of Cell-picolyl**

The reaction of 2-picolylamine with cellulose dialdehyde is shown in figure 3.7, The first step involves a nucleophilic addition of an amine to the carbonyl group of an aldehyde to produce amino alcohol intermediate which undergoes dehydration to form an imine. A product with an excellent yield about 90% was obtained.



Figure 3.7 Schematic description of conversion of cellulose dialdehyde to cellpicolyl

### **3.2.2.1 FT-IR analysis of Cell-picolyl**

The FT-IR spectrum is shown in Figure 3.8, the spectrum shows the disappearance of the aldehyde group and the development of a new peak at 1635.34 cm<sup>-1</sup> (appear as a shoulder) which is attributed to the imine functionality. The peaks at 1614.13 and 1592.38 cm<sup>-1</sup> confirm the presence of the aromatic pyridine ring, the peaks are corresponding to C=C and C=N of the pyridine ring.



Figure 3.8 FT-IR spectrum of cell-picolyl

# **3.3 General Method for Complexation of Cellulose-imine with Palladium(II)**

Imines are compounds containing one C=N functional group, and since the cellulose polymer could handle more than one imine group the produced polymer could be called poly imine.

Polyimine shows exceptional characteristic regrading thermal stability, easily prepared, and ability to form relatively stable complexes with various transition metals such as palladium and platinum, using nitrogen free pair of electrons and metal empty orbitals. For these reasons it was chosen for this work.

Also, preparation of imine involves easy work-up and simple purification of the product, in addition to the availability of a wide group of polyamines allow us to study the effect of various factors that influence catalytic activities of cellulose polyimine supported catalyst such as steric and electronic features.

### 3.3.1 Complexation of Cell-pyridyl with Pd(II)

Cellulose-imine polymer support for Pd(II) catalytic systems used in this study to complex Pd(II) through the imine functionality, imine acts as electron donor. The polymer support affords multi-catalytic sites on the same polymeric chain, as shown in figure 3.9.

Cellulose-imine-Pd(II) catalytic preparation was carried out by reacting cellulose polyimine with Pd(II) chloride (PdCl<sub>2</sub>) in the polar aprotic solvent acetonitrile ( $C_2H_3N$ ). The product yield was 83.3%. As shown in figure 3.8 acetonitrile first complex to Pd(II) to form PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> which then undergoes ligand substitution with the imine functionality, since acetonitrile considered a labile ligand.



Figure 3.9 Schematic description of complexation of cell-pyridyl with palladium(II) chloride

### 3.3.1.1 FT-IR of Cell-pyridyl-Pd(II)

The structure of palladium cell-pyridyl complex was verified by the IR spectra, and DSC thermal analysis. IR spectrum (Fig. 3.10) shows the presence of C=N at about 1718.39 cm<sup>-1</sup>, a broad splitted peak at 1559.17 to 1574.59 cm<sup>-1</sup> corresponding to C=N and C=C of the pyridine ring. The peaks shifted and broadened compared to the un complexed Cell-Pyridyl shown in Fig 3.6.



Figure 3.10 FT-IR spectrum of cell-pyridyl-Pd(II)

### 3.3.1.2 Thermal Analysis of Cell-Pyridyl-Pd(II) by TGA

The thermogram of cell-pyridyl-Pd(II) is shown in Figure 3.11, the figure shows a big mass loss at 100 °C that extends to about 150 °C which attributed of dehydration and removal of amine group. The second mass drop is shown at 300 °C, this temperature is known for the fragmentation of cellulose, then pallidum part didn't decompose which represents about 20% of the polymer total mass.



Figure 3.11 Thermal analysis of cell-pyridyl-pd(II) using TGA

### **3.3.2** Complexation of Cell-picolyl with Pd(II)

A second cellulose-imine Pd(II) catalysts was prepared as shown before from reacting cell-picolyl with  $PdCl_2$ . The reaction is shown in figure 3.12. The yield was about 80.83%.



Figure 3.12 Schematic description of complexation of cell-picolyl with palladium(II) chloride

### 3.3.2.1 FT-IR of Cell-picolyl-Pd(II)

The structure of palladium cell-pyridyl complex was verified by the IR spectra, and DSC thermal analysis. IR spectrum (Fig. 3.13) shows the presence of C=N at about 1717.41 cm<sup>-1</sup>, a broad splitted peak at 1543.74 to

1560.33 corresponding to C=N and C=C of the pyridine ring. The peaks shifted and broadened compared to the un complexed Cell-picolyl shown in Figure 3.13.



Figure 3.13 FT-IR spectrum of cell-picolyl-Pd(II)

### 3.3.2.2 Thermal Analysis of cell-picolyl-Pd(II) by TGA

The thermogram of cell-picolyl-Pd(II) is shown in Figure 3.14, the figure shows a big mass loss at 90 °C that extends to about 100 °C which attributed of dehydration and removal of amine group. The second mass drop is shown at 160 °C, as a sign of the fragmentation of cellulose, then pallidum part didn't decompose which represents about 40% of the polymer total mass and be some amine ligand. The higher % of undecomposed mass indicate that the cell-picolyl-Pd(II) is more stable.



Figure 3.14 Thermal analysis of cell-picolyl-Pd(II) using TGA

# 3.4 α-Hydroxylation of Cycloketones Using Palladium(II) Cellulose-imine Complexes

Hydroxylation of cyclic ketones (hydroxypalladation) is considered an oxidation reaction of carbonyl. The oxidation of carbonyl by metals is well known and widely studied reactions. Many of these apparently reactions proceed through the oxidation of the enol tautomer. Hydroxypalladation of ketones was carried out in dioxane in the presence of catalytic amount of Pd(II) on cellulose polyamine (cellulose-pyridyl, or cell-picolyl) supported catalyst, re-oxidant, and small quantity of acid such as dichloroacetic acid for enolization of ketone. The produced  $\alpha$ -hydroxyketones were characterized by FT-IR spectroscopic method. The hydorxypalladation reaction was performed on the ketones: cyclohexanone, cyclopentanone and acetophenone produce 2-hydroxycyclohexanone, 2to hydroxycyclopentanone, and 2-hydroxyacetophenone, respectively. The

yield was (72.9\70.6, 74.3\77.0, 92.1\87.7)% respectively

The routes of the formation of 2-hydroxycyclohexanone, 2hydroxycyclopentanone, and 2-hydroxyacetophenone are shown in figure 3.15. As expected, hydroxylation was formed from enol which undergoes oxidation to the final product. The formation of enol occurs through tautomerization in acidic medium



Figure 3.15 Tautomerization of (a) cyclohexanone, (b) cyclopentanone, and (c) acetophenone to enol

The formation of product could be explained through the mechanism shown in figure 3.16. As shown in figure 3.15, ketone in the presence of dichloroacetic acid undergoes tautomerization to form the enol, which forms with Pd(II) the initial  $\pi$ -complex (1). The  $\pi$ -complex reacts with water by syn addition reaction to give the  $\sigma$ -complex (2). Then the  $\sigma$ complex undergoes  $\beta$ -elimination to produce cyclohex-1-en-1,2-diol which undergoes tautomerization to give the final product  $\alpha$ -hydroxycycloketone.



Figure 3.16 Schematic description of mechanism of oxidation of cyclohexanone by new catalysts

Cupric chloride was used as a re-oxidant for Pd(0) to converts Pd(0) back to the active catalytic spices Pd(II) [103].

The results are summarized in Table 3.1. As can be seen in Table 3.1, the percentage yield is good to excellent. The highest yield was obtained from acetophenone, which could be because it undergoes tautomerization faster and the enol form of acetophenone is the most stable between our ketone products [104]. The other reason could be due to the low volatility of acetophenone compared to the other cycloketones. The yields obtained from using the two catalysis are very close, cell-Pyridyl-Pd(II) gave little

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higher yields. This could be attributed to the more stable complex from pyridyl 1,4-ligand. The picolyl is considered 1,3-ligand.

Table 3.1: The results of  $\alpha$ -hydroxylation of cycloketones by the polymer supported catalysts

Starting Material	Catalyst	Product	%Yield
Cyclohexanone	Cell-pyridyl- Pd(II)	α-Hydroxy cyclohexanone	72.9
Cyclohexanone	Cell-picolyl- Pd(II)	α-Hydroxy cyclohexanone	70.6
Cyclopentanone	Cell-pyridyl- Pd(II)	α-Hydroxy cyclopentanone	74.3
Cyclopentanone	Cell-picolyl- Pd(II)	α-Hydroxy cyclopentanone	77.0
Acetophenone	Cell-pyridyl-Pd(II)	α-Hydroxy acetophenone	92.1
Acetophenone	Cell-picolyl- Pd(II)	α-Hydroxy acetophenone	87.7

### **3.4.1** α-Hydroxylation of Cyclohexanone Using Pd(II) Cellulose-imine

Hydroxylation of cyclohexanone using catalyst cell-pyridyl-Pd(II) and cellpicolyl-Pd(II) was carried out as shown before in dioxane in the presence of the re-oxidant CuCl<sub>2</sub> and small quantity of dichloroacetic acid. The first catalyst afforded 2- hydroxycyclohexanone in about 72.9 % yield, while the second one afforded it in about 70.6 % yield. Figure 3.17 summarizes the reaction. The products were characterized by FT-IR spectroscopy.



Figure 3.17 Schematic description of oxidation of hexanone to 2-hydroxy cyclohexanone by (a) Cell-pyridyl-Pd(II), (b) Cell-picolyl-Pd(II)

## 3.4.2 α-Hydroxylation of Cyclopentanone Using Palladium(II) Cellulose -imine

Hydroxylation of cyclopentanone using complex cell-pyridyl-Pd(II) or cellpicolyl-Pd(II) was carried out as before in dioxane in the presence of reoxidant CuCl<sub>2</sub> and small quantity of dichloroacetic acid. Figure 3.18 summarizes the reaction. As shown in Table 3.1, the first catalyst afforded 2-hydroxycyclopenatnone in about 74.3 % yield, and the other catalyst afforded it in about 77.0 % yield. The product was characterized by FT-IR spectroscopy.



Figure 3.18 Schematic description of oxidation of cyclopentanone to 2-hydroxy cyclopentanone by a) Cell-pyridyl-Pd(II), b) Cell-picolyl-Pd(II)

### **3.4.3** α-Hydroxylation of Acetophenone Using Palladium(II) Celluloseimine

Hydroxylation of acetophenone using catalyst Pd(II) cell-pyridyl or Pd(II) cell-picolyl was carried out as before in dioxane in the presence of reoxidant CuCl<sub>2</sub> and small quantity of dichloroacetic acid. Figure 3.19 summarizes the reaction. As shown in Table 3.1, the highest yield among all reactions was 2-hydroxyacetophenone. Pd(II) cell-pyridyl afforded 2hydroxyacetophenone in 92.1 % yield, and Pd (II) cell-picolyl afforded it in 87.7 % yield. The product was characterized by FT-IR spectroscopy.



Figure 3.19 Schematic description of oxidation of acetophenone to 2-hydroxy acetophenone by a) Cell-pyridyl-Pd(II), b) Cell-picolyl-Pd(II)

### 3.5 Oxidation of Alkenes Using Palladium(II) Cellulose-imine

Ketones have many important uses in chemical processes, such as synthesis of many organic compounds and complexes, ketones are widely used as solvents, and as preservative and hydraulic fluids in tanning. Ketones are used in medicine, especially as starting materials of some vitamins [105-107]

Oxidation of terminal alkenes by metals is well known and widely studied reactions. Oxidation of alkenes was carried out in dioxane in the presence of catalytic amount of Pd(II) on cellulose-imine (cell-pyridyl, or cell-picolyl) supported catalyst, re-oxidant, and small quantity of acid such as dichloroacetic acid. The produced ketone was characterized by FT-IR spectroscopic methods. The methyl ketones namely 2-hexanone, 2-pentanone, and 2-octanone were prepared in moderate yield from the oxidation of 1-hexene, 1-pentene, and 1-octene, respectively. The routes of the oxidation of these alkenes are shown in figure 3.20. As expected, oxidation occurs at carbon number 2 to become a carbonyl.

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Figure 3.20 Schematic description of Oxidation of (a) 1-hexene, (b) 1-pentene, and (c) 1-octene

The first step of the oxidation as shown in figure 3.21 involves coordination of the alkene to the palladium center to form a  $\pi$ -complex (1). Evidence for this step is provided by the relative sluggishness of electronpoor alkenes, which generally require higher catalyst loadings than unactivated alkenes. Hydroxypalladation then occurs to yield ether zwitterionic complex or neutral complex depending on the mode of oxidation as shown in figure 3.20. Studies employing deuterated substrates suggest that  $\beta$ -hydride elimination then occurs to afford enol complex, which re-inserts into the Pd-H bond to afford alcohol complex [108]. Computational studies support the involvement of chloride-assisted deprotonation in the subsequent step [103], which affords the product and Pd(0). Then Cu(II) oxidizes Pd(0), converts Pd(0) back to the active catalytic spices Pd(II).



Figure 3.21 Schematic description of Mechanism of oxidation of n-hexene by new catalysts

The results regarding the yield are summarized in Table 3.2. As can be seen in table 3.2, the percentage yields are good. The yield considered very attractive, since we are dealing with high volatility compounds, low insolubility and low reactivity.

Starting Material	Catalyst	Product	%Yield
1-Hexene	Cell-pyridyl-Pd(II)	2-Hexanone	75.2
1-Hexene	Cell-picolyl-Pd(II)	2-Hexanone	71.4
1-Pentene	Cell-pyridyl-Pd(II)	2-Pentanone	83.3
1-Pentene	Cell-picolyl-Pd(II)	2-Pentanone	86.4
1-Octene	Cell-pyridyl-Pd(II)	2-Octanone	67.5
1-Octene	Cell-picolyl-Pd(II)	2-Octanone	69.2

Table 3.2: The results of oxidation of n-alkenes by the new catalysts

### 3.5.1 Oxidation of 1-Hexene using Palladium(II) Cellulose-imine

Hydroxylation of 1-hexene using catalyst cell-pyridyl-Pd(II) or cellpicolyl-Pd(II) was carried and the re-oxidant CuCl<sub>2</sub> and small quantity of dichloroacetic acid. The first catalyst afforded 2-hexanone 75.2 % yield, while the second afforded 71.4 % yield. Figure 3.22 summarizes the reaction. The products were characterized by FT-IR spectroscopy.



Figure 3.22 Schematic description of oxidation of 1-hexene to 2-hexanone by a) Cell-pyridyl-Pd(II), b) Cell-picolyl-Pd(II)

### 3.5.2 Oxidation of 1-Pentene Using Palladium(II) Cellulose-imine

Hydroxylation of 1-pentene using catalyst cell-pyridyl-Pd(II) or cellpicolyl-Pd(II) was carried out as before in dioxane and the re-oxidant CuCl<sub>2</sub> and small quantity of dichloroacetic acid. The first catalyst afforded 2-pentanone 83.3 % yield, while the second afforded 86.4 % yield. Figure 3.23 summarizes the reaction. The products were characterized by FT-IR spectroscopy.



Figure 3.23 Schematic description of oxidation of 1-petene to 2-pintanone by a) Cell-pyridyl-Pd(II), b) Cell-picolyl-Pd(II)
## 3.5.3 Oxidation of 1-octene Using Palladium(II) Cellulose-imine

Hydroxylation of 1-octene using catalyst cell-pyridyl-Pd(II) or cell-picolyl-Pd(II) was carried out as before in dioxane and the re-oxidant CuCl<sub>2</sub> and small quantity of dichloroacetic acid. The first catalyst afforded 2-octanone 67.5 % yield, while the second afforded 69.2 % yield. Figure 3.24 summarizes the reaction. The products were characterized by FT-IR spectroscopy.



Figure 3.24 Schematic description of oxidation of 1-octene to 2-octanone by a) Cellpyridyl-Pd(II), b) Cell-picolyl-Pd(II)

## **3.5.4Conclusion And Suggestions For Future Work**

Two novel Pd(II) polymeric supported catalysts cell-pyridyl-Pd(II) and cell-picolyl-Pd(II) were prepared and analyzed. The polymer chosen for this work is cellulose that is a natural polymer, biodegradable, non-toxic and available at low cost. The palladium polymeric supported catalysts were identified by FT-IR and their thermal properties were studied. The polymeric supported cell-pyridyl-Pd(II) and cell-picolyl-Pd(II) were used to catalyze the hydroxylation of ketones, and oxidation of terminal alkenes to ketones. The hydroxylation process resulted in formation  $\alpha$ -hydroxyketone in good to excellent yield. While the oxidation of alkenes resulted in forming ketone in moderate yield.

The new synthetic methods could be valuable for natural product synthesis and medicinal chemistry. Based on the results obtained from this work the polymeric catalysts are preferable since they are recyclable, can be removed from the reaction mixture easily. The novelty of the developed polymeric support here is that it has multicatalytic sites, which makes them one of the very few examples in the literature wherein a polymeric support with number of catalytic sites double of the number of the repeat units.

In addition to the above accomplishment, in this work is a model and with this model we have shown that synthesis of  $\alpha$ - substituted ketone could be a catalytic process.

This process could be a base for novel method for asymmetric synthesis of  $\alpha$ -substituted ketones. This could be accomplished by replacing the achiral

imine ligands with a chiral imine or amine ligands such as R- or S-1,2diaminocyclohexane; this way instead of preparing racemic  $\alpha$ -substituted ketone, optically active  $\alpha$ -substituted ketone could be prepared.  $\alpha$ substituted ketone will be used as a starting material for drugs and natural product synthesis.

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جامعة النجاح الوطنية كلية الدراسات العليا

# سليولوز مدعم بالأمين ثنائي المنح والبلاديوم: تحضير واستخدام البوليمر كعامل مساعد في التفاعلات العضوية

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قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء في كلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين. سليولوز مدعم بالإيمين ثنائي المنح والبلاديوم: تحضير واستخدام البوليمر كعامل مساعد في التفاعلات العضوية إعداد عريب ناظم غالب علي إشراف أ.د. عثمان حامد

#### الملخص

تلعب العوامل المساعدة (الحفازات) دوراً مهماً في التفاعلات الكيميائية، ونظراً لكثرة استخدامها وارتفاع تكاليفها كان لا بد من البحث عن بديل وبأثمان زهيدة. وفي هذا المشروع كان اهتمامنا البحث عن مصادر طبيعية. والمصدر الطبيعي الذي وقع عليه الاختيار هو مادة السيليولوز؛ وذلك لاشتقاق عامل مساعد منه.

قمنا بتحضير ثنائي ألدهايد السيليولوز من خلال أكسدة السيليولوز باستخدام بيرأيودات الصوديوم، بعد ذلك قمنا بمفاعلة ثنائي ألديهايد السيليولوز مع نوعين مختلفين من الأمينات: (2(2-بيريديل)إيثيل أمين، و 2-بيكوليل أمين) لتحضير المركبين سيل-بيريديل (cell-pyridyl) و سيل-بيكوليل (cell-picolyl)، بعد ذلك تم تثبيت أيون البلاديوم (Pd<sup>+2</sup>) المحضر مسبقاً عليه. مما أدى إلى تحضير مبلمرين معقدين منه (cell-pyridyl-Pd(II), cell-picolyl-Pd(II)).

تم اختبار المبلمرات المعقدة آنفة الذكر على نوعين من التفاعلات الكيميائية المعروفة (هيدروكسيل الكيتونات الحلقية، وأكسدة الألكينات الطرفية). حيث تم تحضير كل من: ألفا-هيدروكسي سايكلوهيكسانون، ألفا- هيدروكسي سايكلوبنتانون، وألفا- هيدروكسي أسيتوفينون، من سايكلوهيكسانون، سايكلوبنتانون، وأسيتوفينون على التوالي. كما تم أيضاً تحضير 2-هيكسانون، 2-بنتانون، و2-أوكتانون، من 1-هيكسين، 1-بنتين، و1-أوكتين على التوالي، وذلك باستخدام المبلمرات المعقدة التي تم تحضيرها مسبقا في هذا المشروع. وهذه الطريقة أعطت نتائج جيدة، وذلك اعتماداً على النتائج المستخلصة من جهاز الأشعة تحت الحمراء R.