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HETEROGENIZATION OF HOMOGENEOUS CATALYSTS AND AQUEOUS BIPHASIC SYSTEMS

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Bornova-İZMİR

Rahime CAN tarafından **YÜKSEK LİSANS TEZİ** olarak sunulan **"Heterogenization of Homogeneous Catalysts and Aqueous Biphasic Systems"** başlıklı bu çalışma E. Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 08.07.2009 tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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ÖZET

HOMOJEN KATALİZÖRLERİN HETEROJENLEŞTİRİLMESİ VE SULU BİFAZİK SİSTEMLER

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08.07.2009, 77 sayfa

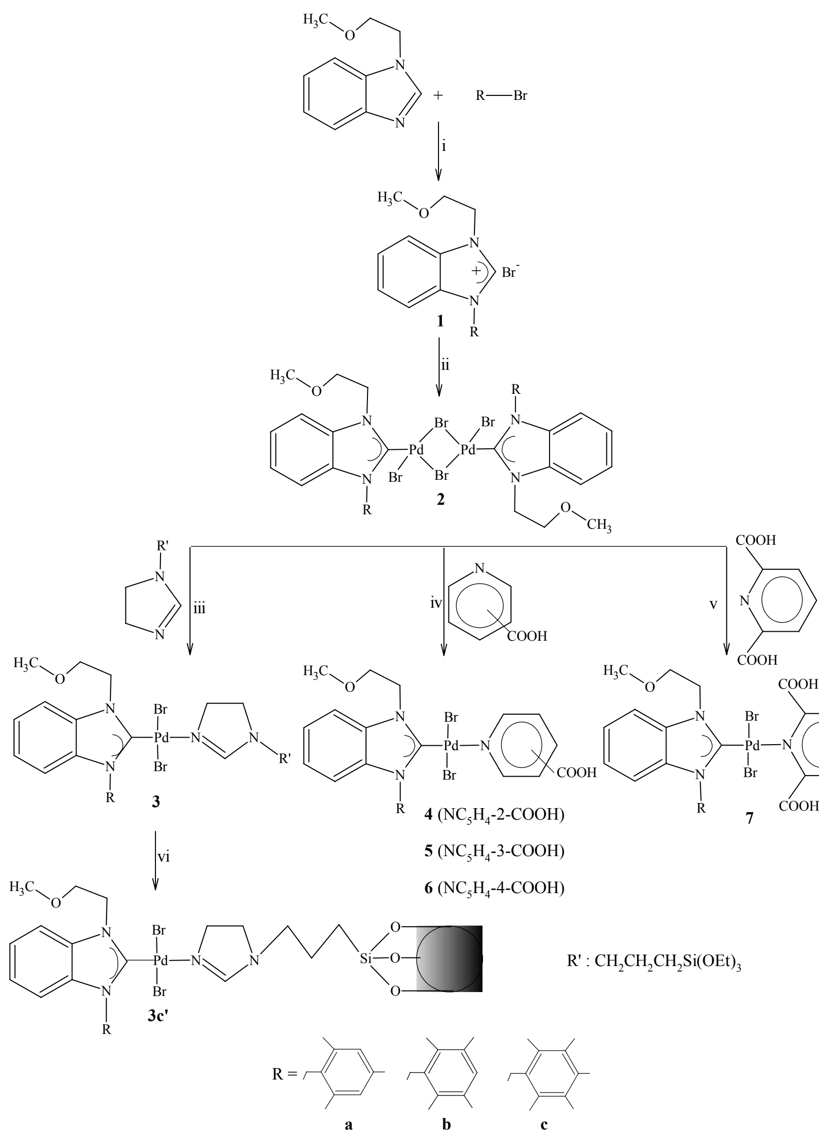
Metal-N-heterokarben (NHC) komplekslerinin homojen katalizde yaygın bir şekilde kullanılan fosfinlere alternatif olmaları, son zamanlarda büyük ilgi çekmektedir. Çünkü katalitik koşullarda (yüksek sıcaklıkta) P-C bağı kopmakta ve P atomu havanın oksijeni ile kolayca oksitlenmektedir. Buna karşın, metal-NHC kompleksleri havanın nemi ve oksijenine karşı çok kararlıdır. Dolayısıyla tepkime ortamında ligant fazlasına gerek yoktur.

Homojen katalizör tasarımında etkinliği ve seçimliliği artırmak, ürünlerden katalizörün kolay ayrılmasını sağlamak ve katalizörün ömrünü uzun tutmak temel amaçtır. Bu nedenle, bu tezde $–Si(OEt)_3$ fonksiyonel grubu ile immobilizasyon ve çözünürlük çalışmaları yapılmıştır.

Tez üç bölümden oluşmaktadır. Birinci bölümde N-heterohalkalı karben (NHC) ligantları ve onların paladyum(II) kompleksleri özetlenmiştir. Tezin ikinci bölümünde deneysel çalışmalara yer verilmiştir. Üçüncü bölümünde ise, dimerik Pd-NHC komplekslerinden (**2**) karben-imeo Pd(II) kompleksleri (**3**) ve karben-piridinkarboksilik asit Pd(II) kompleksleri (**4-7**) sentezlenerek bunların katalitik özellikleri test edilmiştir.

Sonuçta, iki farklı yöntemle: (1) $–Si(OEt)_3$ grubunu silikaya tutturarak, (2) kompleksi sulu ortama alarak homojen katalizörlerin heterojenleştirilmesi gerçekleştirilmiştir.

Anahtar kelimeler: Benzimidazolyum tuzları, N-Heterohalkalı karben, paladyum, heterojen katalizör, suda çözünür kompleksler, C-C bağ oluşumu.



Şema I: Reaktifler ve koşullar: (i) $PhCH_3$, 24 s, 110 ^{0}C; (ii) $Pd(OAc)_2$, NaBr, 90 ^{0}C, 24 s; (iii) {*N*-(3-trietoksisililpropil)-4,5-dihidroimidazol} = imeo, CH_2Cl_2, 25 ^{0}C, 24 s; (iv) Piridinkarboksilik asit, CH_2Cl_2, 25 ^{0}C, 24 s; (v) Piridin-2,6-dikarboksilik asit, DMSO, 25 ^{0}C, 24 s; (vi) Amorf silika, $CHCl_3$, 2 s.

ABSTRACT

HETEROGENIZATION OF HOMOGENEOUS CATALYSTS AND AQUEOUS BIPHASIC SYSTEMS

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Master Thesis in Chemistry

Supervisor: **Prof. Dr. Bekir ÇETİNKAYA**

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Metal-*N*-heterocyclic carbene (NHC) complexes have recently attracted considerable attention as possible alternatives for the widely used phosphine complexes in homogeneous catalysis. Because, P-C bond can be cleaved at catalytic conditions (high temperature) and P atom easily was oxidized with the oxygen of the air. In contrast, metal-NHC complexes are very stable toward moisture and oxygen. Consequently, excess ligands are not used in catalytic.

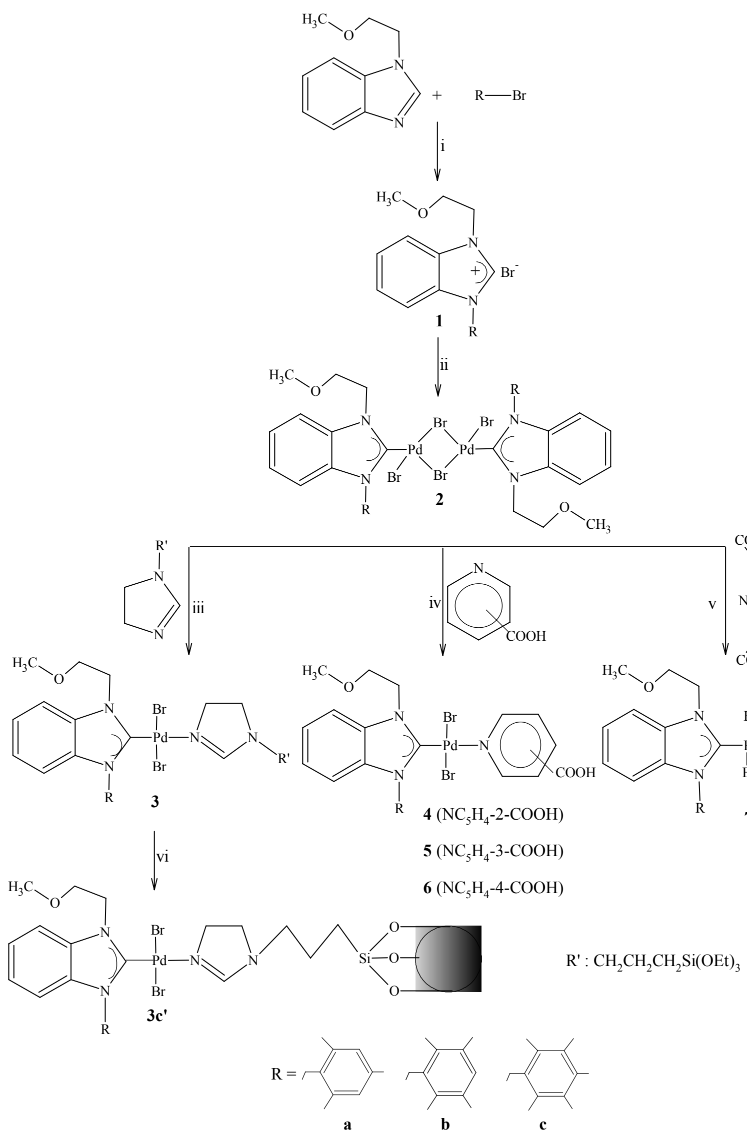
Fundamental aim in designing the new homogeneous catalyst is to increase the activity and the selectivity. Easy separation of catalyst from products and increased catalyst life is also main concern. Therefore, in this thesis immobilization via $–Si(OEt)_3$ functionality and solubilization studies were carried out.

This thesis consists of three parts. The first part is a concise review on *N*-heterocyclic carbene (NHC) ligands and their complexes. In part II the experimental details were given. In part III, from dimeric Pd-NHC complexes characterization and catalytic studies of mono carbene-mono imeo Pd(II) complexes (**3**) and

mono carbene-mono pyridinecarboxylic acid Pd(II) complexes (**4-7**).

Consequently, two different methods: (1) immobilization of $Si(OEt)_3$ to silica; (2) immobilization of complexes to water, heterogenization of homogeneous catalysts was carried out.

Keywords: Benzimidazolium salts, N-Heterocyclic carbene, palladium, heterogeneous catalyst, water soluble complexes, C-C bond formation.



Scheme I: Reagents and conditions: (i) $PhCH_3$, 24 h, reflux; (ii) $Pd(OAc)_2$, NaBr, DMSO, 90 ^{0}C, 24 h; (iii) {*N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole}, CH_2Cl_2, 25 ^{0}C, 24 h; (iv) Pyridinecarboxylic acid, CH_2Cl_2, 25 ^{0}C, 24 h; (v) Pyridine-2,6-dicarboxylic acid, DMSO, 25 ^{0}C, 24 h; (vi) Amorphous silica, $CHCl_3$, 2 h.

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ABBREVIATIONS

Abbreviations		**Explanations**
Bu	:	Butyl
Cat.	:	Catalyst
COD or cod	:	1,5-cyclooctadien
Cp*	:	Pentamethylcyclopentadien
DMAc	:	*N*,*N*-dimethylacetamide
DMF	:	*N*,*N*-Dimethylformamide
DMSO	:	Dimethylsulfoxide
E	:	Electrophyl
Ero	:	Electron-rich olefin
Et	:	Ethyl
Et_2O	:	Diethyl ether
EtOH	:	Ethyl alcohol
GC	:	Gas Chromatography
Hz	:	Hertz
Imeo	:	*N*-(3-triethoxysilylpropyl)-4,5 dihydroimidazole
IR	:	Infrared spectroscopy
L	:	Ligand
Me	:	Methyl
NHC	:	*N*-heterocyclic carbene
NMR	:	Nuclear Magnetic Resonance
Nuc	:	Nucleophyl
Ph	:	Phenyl
$PhCH_3$	:	Toluene
PPh_3	:	Triphenylphosphine
Pr	:	Propyl
η	:	Hapticity

ABBREVIATIONS (continue)

Abbreviations		Explanations
α	:	Alpha
β	:	Beta
δ	:	Delta
μ	:	Bridge ligand
Å	:	Angstrom
s	:	Singlet
d	:	Dublet
t	:	Triplet
m	:	Multiplet
q	:	Quartet
b	:	Broad

1. INTRODUCTION

A catalyst is a substance that alters the rate of a reaction without appearing in any of the products of that reaction; it may speed up or slow down a reaction. For a reversible reaction, a catalyst alters the rate at which equilibrium is attained; it does not alter the position of equilibrium (Housecroft *et al.*, 2005).

There are three important parameters that impact on both the commercial viability and the inherent greenness of a particular catalyst:

1. Selectivity - the amount of substrate converted to the desired product as a percentage of total consumed substrate (a catalyst will be of limited benefit if it also enhances the rate of by-product formation).
2. Turnover frequency - the number of moles of product produced per mole of catalyst per second (low turnover frequencies will mean large amounts of catalyst are required, resulting in higher cost and potentially more waste).
3. Turnover number - the amount of product per mole of catalyst (this is related to catalyst lifetime and hence to cost and waste) (Lancester, 2002).

1.1. Homogeneous and Heterogeneous Catalysis

Catalysts fall into two categories, homogeneous and heterogeneous, depending on their relationship to the phase of the reaction in which they are involved. A homogeneous catalyst is in the same phase as the components of the reaction that it is catalysing; a heterogeneous catalyst is in a different phase from the components of the reaction for which it is acting (Housecroft *et al.*, 2005).

If a catalyst is an insoluble solid, that is, a heterogeneous catalyst, it can easily be separated by centrifugation or filtration. In contrast, if it is a homogeneous catalyst, dissolved in the reaction medium, this presents more of a problem and offsets the major advantages of homogeneous catalysts, such as high activities and selectivities (Table 1.1). A serious shortcoming of homogeneous catalysis is the cumbersome separation of the (expensive) catalyst from reaction products and the quantitative recovery of the catalyst in an active form. Separation by distillation of reaction products from the catalyst generally leads to heavy ends which remain in the catalyst phase and eventually deactivate it. In the manufacture of pharmaceuticals quantitative separation of the catalyst is important in order to avoid contamination of the product. Consequently there have been many attempts to heterogenise homogeneous catalysts by attachment to organic or inorganic supports. However, these approaches have, generally speaking, not resulted in commercially viable processes, for a number of reasons, such as leaching of the metal, poor catalyst productivities, irreproducible activities and selectivities and degradation of the support (Sheldon, 2005).

Table 1.1 Heterogeneous vs. homogeneous catalysis

Heterogeneous	Homogeneous
Usually distinct solid phase	Same phase as reaction medium
Readily separated	Often difficult to separate
Readily regenerated and recycled	Expensive/difficult to recycle
Rates not usually as fast as homogenous	Often very high rates
May be diffusion limited	Not diffusion controlled
Quite sensitive to poisons	Usually robust to poisons
Lower selectivity	High selectivity
Long service life	Short service life
Often high-energy process	Often takes place under mild conditions
Poor mechanistic understanding	Often mechanism well understood

1.2. Recyclable Catalytic Systems

Recycling is becoming significantly more important nowadays as environmental harms increase and as resources are becoming scarcer. Chemists continue to develop new catalysts that are more efficient, robust and devise new methods to recover and reuse them. Towards this goal, the immobilization of wellknown catalysts onto supports often facilitates the recycling of these catalysts (Sommer and Weck, 2006).

There are two main approaches for the design of recyclable catalysts: running the process in a biphasic (liquid-liquid or liquid-solid) system in which the catalysts are physically bound to one of the phases; and chemically binding the catalyst to the carrier molecule possesing specific physical properties, which enables the seperation of the whole unit by methods applicable to the carrier. Both approaches have been applied already to palladium catalysis.

1.2.1. Liquid-liquid biphasic catalysis

Liquid-liquid biphasic catalysis relies on catalyst held in one of the phases, while the products accumulate in the other phase. After the reaction the phases are separated, either directly or, in the case of systems prone to emulsification, by applying various technical tricks such as passing the reaction mixture through semi-permeable membranes that allow only one phase to pass through. The simplest and most obvious example of such systems uses water as the catalyst-containing phase, although there are non-aqueous biphasic systems (Murahashi and Davies, 1996).

The main disadvantage of homogeneous catalysis is the difficulty associated with separating the catalyst from the product and solvent. Separation techniques, such as distillation, require a lot of energy and can lead to degradation of both the product and catalyst used. A possible solution to these problems is to separate the catalyst and the product into two individual and immiscible phases. Reactions may then be performed as shown in Figure 1.1 (Pinaoult and Bruce, 2003).

Before the reaction (a), the catalyst resides in the aqueous phase with the substrates being in the organic phase. During the reaction (b), the two layers are vigorously stirred, thus allowing suitable interaction of the catalyst and the substrates. Once the reaction is finished (c), the stirring is stopped and the mixture separates into two layers, one containing the product and the other the catalyst. Separation of the two phases is then carried out by simple decantation and the catalyst solution is available for immediate re-use (Pinault and Bruce, 2003).

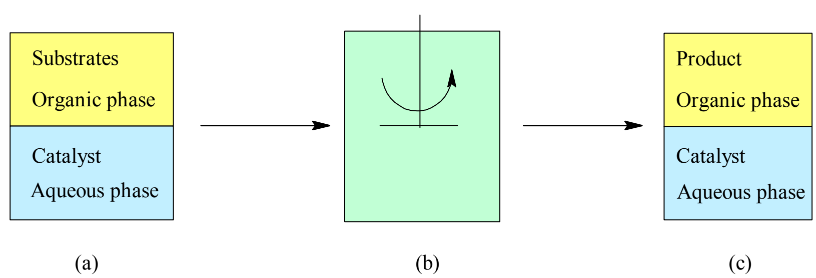


Figure 1.1 Process of biphasic catalytic reactions, (a) before the reaction, (b) emulsion formed by stirring during the reaction and (c) at the end of the reaction.

1.2.2. Catalyst Support: Silica

The selection of a carrier is based on its having certain desirable characteristics. In addition to possible chemical effects, certain physical properties are important (Satterfield, 1991):

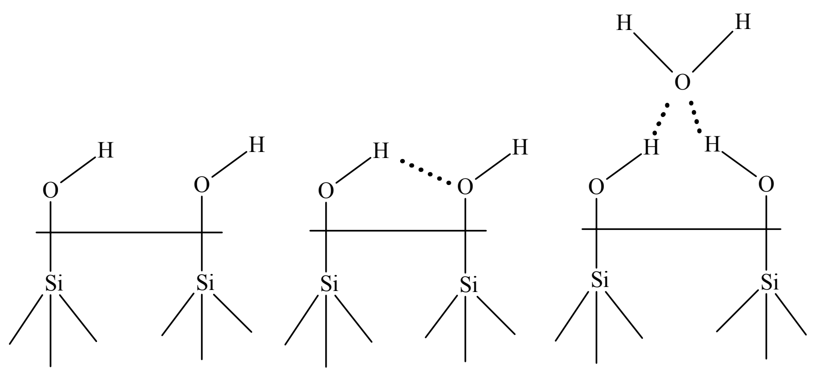
1. Inertness to undesired reactions

2. Desirable mechanical properties, including attrition resistance, hardness, and comprehensive strength
3. Stability under reaction and regeneration conditions
4. Surface area (High surface area is usually, but not always, desirable)
5. Porosity, including average pore size and pore-size distribution (high area implies fine pores but relatively small pores, such as < 2 nm may become plugged in catalyst especially if high loadings are sought)
6. Low cost

The first report on the preparation of coherent expanded aerogels was published by Kistler in 1931. He clearly showed that the inorganic gel, when dehydrated under normal conditions, collapses into a powder as a result of the disruption in the pore structure of the gel. However, when the gel was dehydrated under super-critical conditions of temperature and pressure, the liquid-vapor boundary within the pores of the gel no longer existed and the gels did not collapse on drying. Kistler described the formation of gels of silica, alumina, ferric oxide, stannic oxide, tungstic oxide, nickel oxide, and several organic materials (Gesser and Goswami, 1989). Silica gel chemistry is performed either with an inorganic precursor, like ‘‘water-glass’’ or with organic precursors such as silicon alkoxides, tetraethoxysilane (TEOS) of formula $Si(OC_2H_5)_4$ or tetramethoxysilane (TMOS) of formula $Si(OCH_3)_4$, which are usually engaged as monomers, but partially condensed silica or prepolymers (oligomers) are sometimes also used (Crudden and Allen, 2004). Silica gel is most commonly prepared by hydrolyzing an acid, generally hydrochloric acid, with a solution of “water glass” which consists of ortosilicates (Na_4SiO_4), metasilicates (Na_2SiO_3), and related compounds. It was then allowed to set and washed until the chloride was removed. As the pH is lowered, a polymerization and a condensation process takes place, which can be visualized starting with silisic acid [$Si(OH)_4$]. This polymerized with condensation of silane groups (SiOH) to form an ill-defined polymer in which the primary bonds are the siloxane type (Si-O-Si). This precipitates as a gel or as a colloid, the properties of which depend on mixing procedures, the presence of electrolytes, temperature, aging, etc. By proper control, a hydrogel consisting of small micelles that are roughly spherical is obtained. During drying, the micelles do not coalesce appreciably, particularly if the liquid is removed at above critical temperatures and pressures. Under these conditions, no interface forms that could otherwise collapse the structure by the forces of surface tension. The tiny size of the micelles and use of procedures to prevent coalescence leads to a product of high surface area. Commercial material usually has a high area, as high as about 700 m^2/g. The average pore diameter correspondingly very low typically in the range of 2.5 to 5 nm (these pores are however considerably larger than those in zeolites and are substantially greater than the most reactant molecules of interest).

By varying the manufacturing and aging procedures, silica gels can be made with considerably larger pore diameter and correspondingly lower surface area, perhaps as low as about 100 m^2/g. Silica gel is generally inert. The final dry product should be referred to strictly as a xerogel or porous silica, but the term *silica gel* is in common usage. At ambient temperature the surface consists of a layer of silanol groups (SiOH) plus the physically adsorbed water. Most of the water is removed upon drying in air at 150 to 200 °C. Silanol groups are left on the surface, and these are progressively lost with increased temperature. Some siloxane groups may also be present on the surface (Satterfiled, 1991).

A basic knowledge of the surface structure is of great help in understanding the adsorption behavior and the chemical reactivity of silica in a variety of processes. With respect to the surface of crystalline silica, it was assumed that all of the hydroxyl groups exist as a free or isolated hydroxyl groups (Figure 1.2). In contrast, the surface structure of amorphous silica is highly disordered and such a regular arrangement of hydroxyl groups cannot be expected (Unger, 1988).



isolated or free hydroxyl groups

vicinal hydroxyl groups

hydroxyl groups bond to water by hydrogen bonding

Figure 1.2 Arrangement of hydroxyl groups on a silica surface.

1.3. Carbenes

Carbenes are neutral divalent carbon compounds with general structure figure 1.3, where X and Y may be H, alkyl, aryl or heteroatoms (O, N, S, halogens). They have only six electrons in its valence shell and they have played an important role in organic chemistry (Doering and Hoffmann, 1954). Since the central carbon atom does not possess an octet of electrons, free carbenes are electron deficient and are extremely reactive. They are so reactive that some carbenes insert themselves into normally inert alkane C-H bonds or react with alkenes to form cyclopropanes, which are synthetically useful transformations.

Disubstituted carbon atoms may bind directly to a transition metal (M) producing a formal double bond between the metal and the carbon. Complexes containing these ligands are called metal-carbene complexes which have the general structure shown in Figure 1.4. Here, L_n represents all ligands expect carbene, M transition metal, X and Y same as in Figure 1.3. The first carbene complex (Figure 1.5) was reported by Fischer and Maasböl in 1964 (Fischer and Maasböl, 1964).

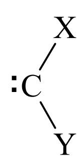


Figure 1.3 Carbene

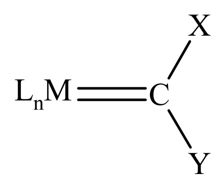


Figure 1.4 Metal-carbene complex

Ten years after the first Fischer-type carbene complex was reported, Schrock and co-workers discovered species where the substituents X and Y attached to $C_{carbene}$ were H or alkyl. Such metal-carbene complexes have since become known as Schrock-type carbene complexes or alkylidenes (Figure 1.6 shows an example of a Schrock-type carbene complex structure) (Schrock, 1974).

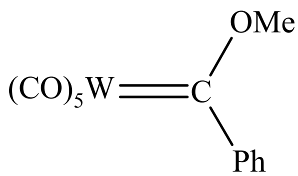


Figure 1.5 Fischer type carbene complex

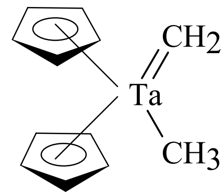
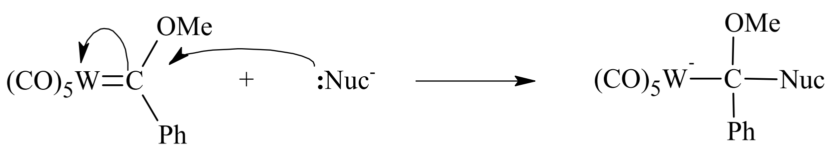


Figure 1.6 Schrock type carbene complex

The two kinds of carbene complexes differ in several ways. Fischer-type metal-carbene complexes tend to undergo an attack at $C_{carbene}$ by nucleophiles, and thus are termed electrophilic (Scheme 1.1). Schrock-type carbene complexes, on the other hand, undergo an attack by electrophiles at $C_{carbene}$, and are considered to be nucleophilic species (Scheme 1.2). Because of their chemical behaviour, Fischer-type carbene complexes are more properly called electrophilic metal-carbene complexes and Schrock-type carbenes nucleophilic metal-carbene complexes

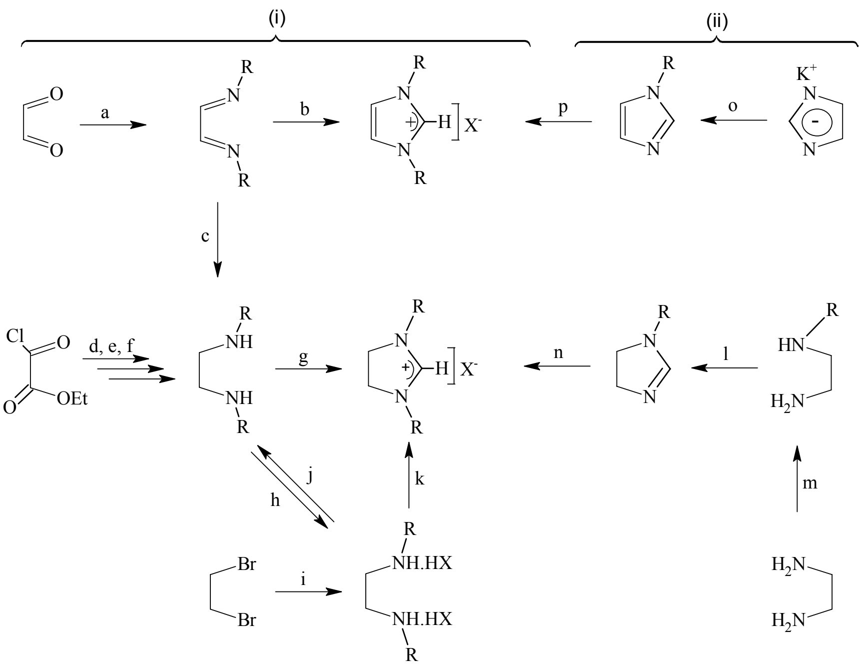


Scheme 1.1

Scheme 1.2

1.3.1. Precursors for stable carbenes

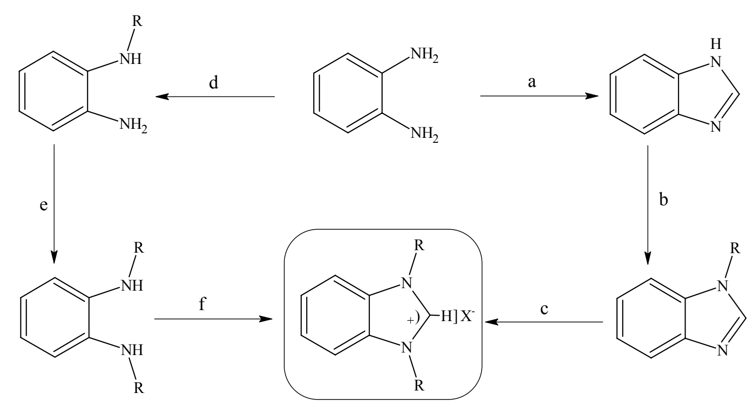
In many cases the synthesis of NHC complexes starts from *N,N*'-disubstitued azoli(ni)um salts. Imidazolium salts as precursors for imidazolin-2-ylidenes are generally accessible by two ways complementing each other: (i) a multicomponent reaction building up the heterocycle with the appropriate substituents in a one-pot reaction or (ii) quaternasition of the alkyl imidazole (Scheme 1.3).



Scheme 1.3 Pathways for synthesis of imidazol(in)ium salts. *Reagents*: (a) 2 R-NH_2; (b) $(CH_2O)_n$/HX; (c) $NaBH_4$; (d) R-NH_2; (e) R'-NH_2 or R-NH_2; (f) $LiAlH_4$; (g) $CH(OEt)_3/NH_4X$; (h) HX; (i) R-NH_2/HX; (j) NH_3; (k) $CH(OEt)_3$; (l) $Me_2NCH(OMe)_2$; (m) Li/R-X; (n) R'-X or R-X; (o) R-X; (p) R'-X or R-X.

Imidazolium salts that can be prepared by the first procedure, the alkylation of imidazole (step p), are easy to obtain and often used for metal complex synthesis. Potassium imidazolide is reacted with the first equivalent of alkyl halide in toluene to give the 1-alkylimidazole (step o). Subsequent alkylation in 3-position is achieved by addition of another equivalent of alkyl halide (step p) (Haque and Rasmussen, 1994; Grimmet, 1997).

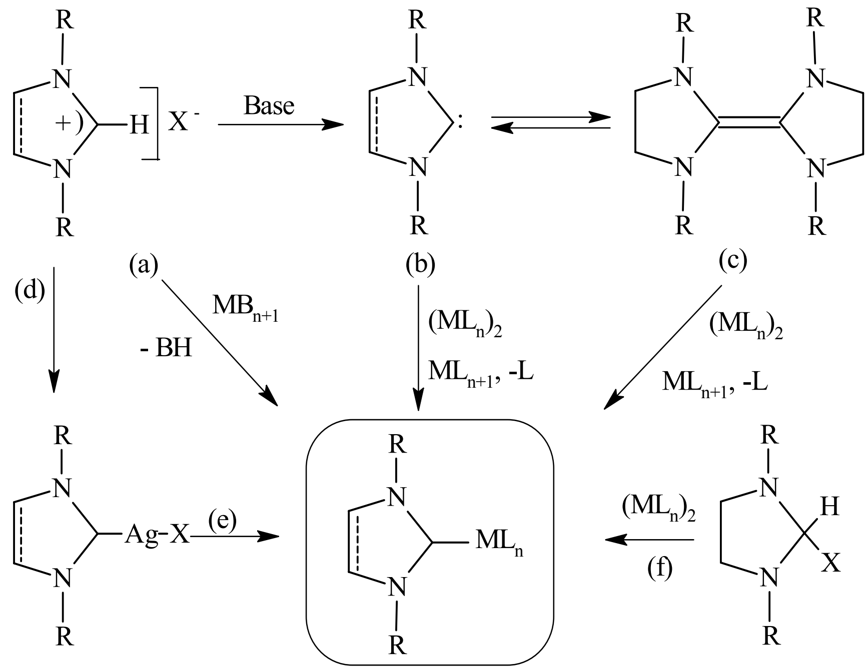
Variation of the amine allows the preparation of imidazol(in)ium salt libraries which can be diversified by using different acids or ammonium salts in order to change the anion of the imidazol(in)ium salt. The reaction of an ortho-ester, *e.g.,* $HC(OEt)_3$, with a secondary bisamine in the presence of an ammonium salt yields imidazolinium salts (Scheme 1.3) (Scholl *et al.,* 1999; Saba *et al.,* 1991). Likewise, benzimidazolium salts that can be prepared by the alkylation of benzimidazole (Scheme 1.4).



Scheme 1.4 Pathways for synthesis of benzimidazolium salts. *Reagents*: (a) HCOOH; (b) KOH/R-X; (c) R-X; (d) K_2CO_3/R-X; (e) R-X; (f) $CH(OEt)_3/NH_4X$.

1.3.2. Synthesis of transition metal-NHC complexes

Generally, four major routes were applied for the synthesis of NHC complexes: (a) the *in situ* deprotonation of ligand precursors, (b) complexation of free *N*-heterocyclic carbenes, (c) the cleavage of electron rich olefins (ero), (d) synthesis of silver–NHC complex (prepared by the direct reaction of the imidazolium precursor and Ag_2O), (e) Transmetallation from silver, (f) Thermal elimination of H-X from the C2 position (Scheme 1.5).



Scheme 1.5 Major synthetic pathways for the generation of transition metal NHC complexes.

1.4. Water as a Reaction Solvent

The best solvent is no solvent and if a solvent (diluent) is needed then water is preferred. Water is nontoxic, nonflammable, abundantly available and inexpensive. Moreover, owing to its highly polar character one can expect novel reactivities and selectivities for organometallic catalysis in water. Furthermore, this provides an opportunity to overcome a serious shortcoming of homogeneous catalysts, namely the cumbersome recovery and recycling of the catalyst. Thus, performing the reaction in an aqueous biphasic system, whereby the catalyst resides in the water phase and the product is dissolved in the organic phase, (Sheldon,

2005) allows for recovery and recycling of the catalyst by simple phase separation.

From a green chemistry viewpoint the use of water as a solvent has many advantages but also some disadvantages (Table 1.2). It is worth emphasizing that it is important to study the whole manufacturing process, not just the reaction stage. Production of a contaminated aqueous waste stream can have significant environmental and economic impacts, for example concentration of contaminated water streams by distillation is very energy intensive compared to say concentration of a propanol waste stream. The merits of replacing organic solvents by water should be viewed on a case-by-case basis; in many processes aqueous effluents are created through vessel cleaning. In these cases an aqueous reaction effluent may not pose any additional problems (Lancester, 2002).

Table 1.2 Advantages and disadvantages of using water as a solvent.

Advantages	**Disadvantages**
Non-toxic	Distillation is energy intensive
Opportunity for replacing volatile organic compounds	Contaminated waste streams may be difficult to treat
Naturally occuring	High specific heat capacity – difficult to heat or cool rapidly
Inexpensive	
Non-flammable	
High specific heat capacity - exothermic reactions can be more safely controlled	

1.5 Water Soluble NHC Complexes

L-M-(NHC) complexes (Figure 1.7) can be solubilized in water via functionalition of L, R, R' or A moiety of a complex. Polar groups such as carboxylate (-COOH, -COONa), sulfonate (-SO_3H, -SO_3Na,), ammonium groups (NR_3, $R'NR_3^+$,), hydroxyalkyl and poly-ether groups (-OH, -$(CH_2CH_2O)_n$-H), phosphonium and phosphonate (-PR_3^+, -$P(O)(OR)_2$, -$P(O)(ONa)_2$) and carbohydrates are used as hydrophilic groups.

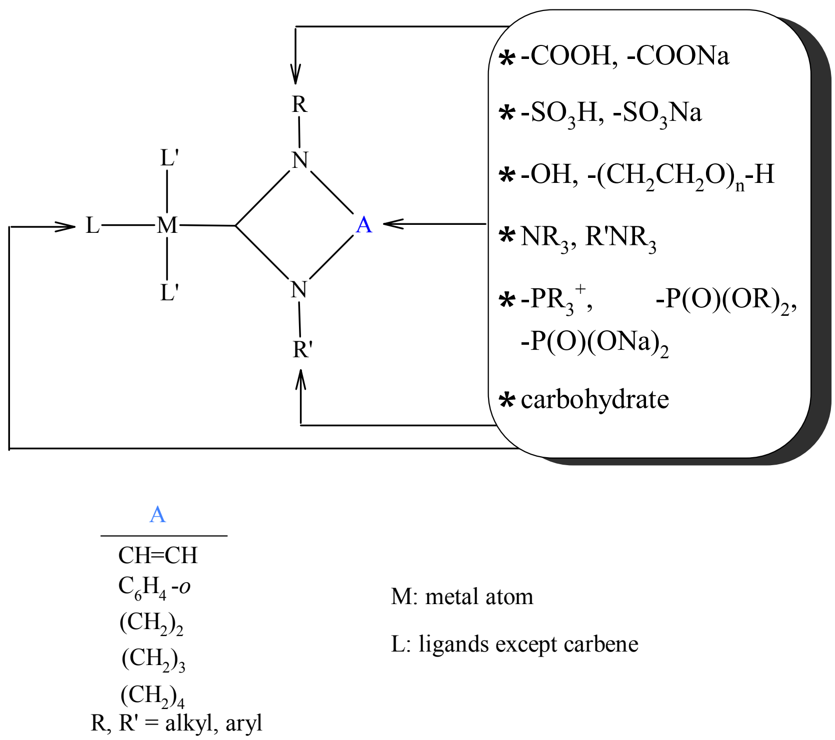


Figure 1.7

The first water-soluble imidazol-2-ylidene rhodium complex (Figure 1.8) featuring carboxylate groups on side chains has been synthesized by Herrmann et al. (Herrmann *et al.*, 1997).

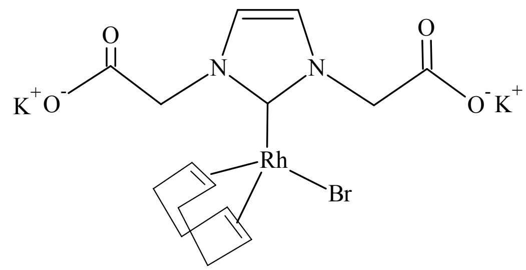
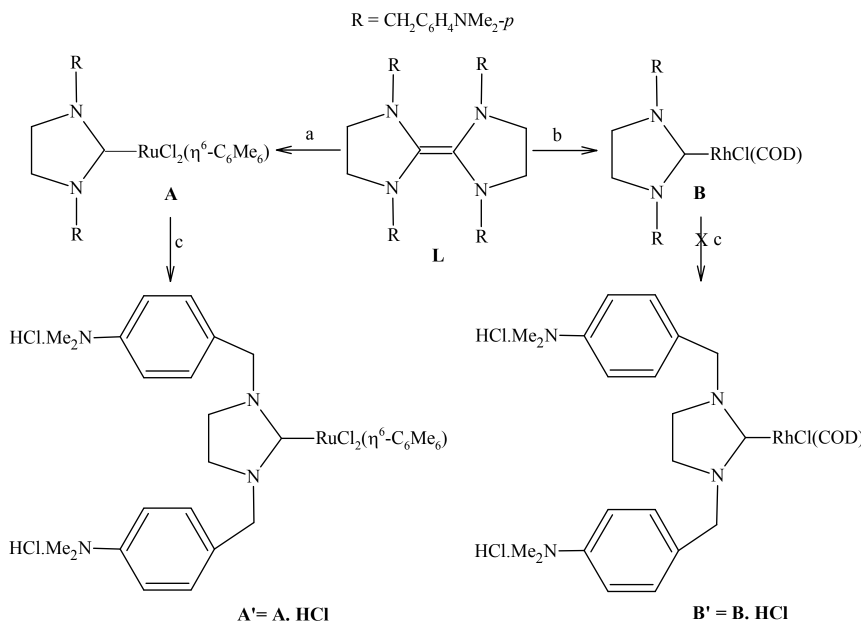


Figure 1.8

Özdemir et al. have synthesized NMe_2 functionalized imidazolin-2-ylidene metal complexes, **A** and **B** that are accessible from appropriately *N*-substituted tetraaminoalkene, **L** (Scheme 1.6). Etherial HCl readily protonates the nitrogen atoms of the -NMe_2 functionality on the carbene ligand of **A** to yield the corresponding quaternary salt **A'**. In contrast, treatment of **B** with HCl did not give the expected salt **B'**. The salt **A'** is water soluble and a more active catalyst than the neutral complexes **A** and **B** for the conversion of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran. The catalyst **A'** could be recovered by simple phase separation and the catalytic reaction was maintained for five different runs (Özdemir *et al.*, 2001).



Scheme 1.6 Synthesis of tetraaminoethene, **L** and ruthenium and rhodium complexes. *Reagents and conditions*: (a) $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$; (b) $[RhCl(COD)]_2$, PhMe, 110 ^{0}C; (c) $HCl_{(g)}$, Et_2O, 25 ^{0}C.

In 2006, Zwitterionic imidazolium salts have been synthesized bearing alkylsulfonate and alkylcarboxylate substituents and used as precursors to water-soluble metal-carbene complexes. The 1-aryl-3-(3-sulfonatopropyl)imidazolium precursors all gave bis(carbene) complexes with silver and palladium (Figure 1.9) (Shaughnessy *et al.*, 2006).

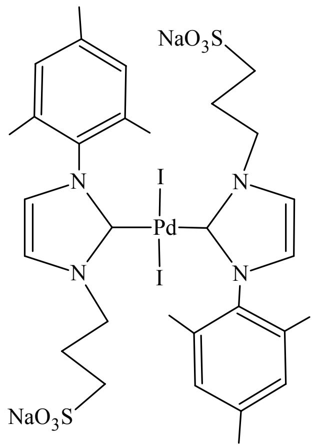


Figure 1.9

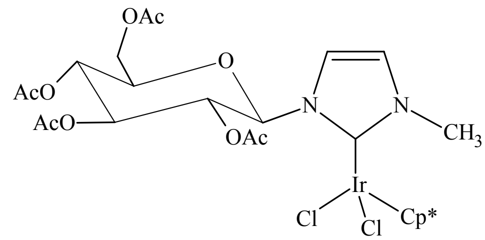


Figure 1.10

Nishioka et al. have developed a general synthesis for a saccharide-incorporated NHC ligand precursor and its NHC complexes by preparing a glucopyranoside-incorporated N-heterocyclic carbene precursor and the first examples of saccharide-incorporated NHC transition-metal complexes (Figure 1.10) (Nishioka *et al.*, 2007).

In 2007, sulfonated, water-soluble imidazolium and imidazolinium salts were synthesized and the respective Pd-complexes with *N,N′*-bis(2,6-dialkyl-4-SO_3^--phenyl)imidazol-2-ylidene and *N,N′*-bis(2,6-dialkyl-4-SO_3^--phenyl)-4,5-dihydroimidazol- 2-ylidene ligands (Figure 1.11) were applied in aqueous Suzuki coupling reactions of aryl chlorides (Plenio *et. al.*, 2007).

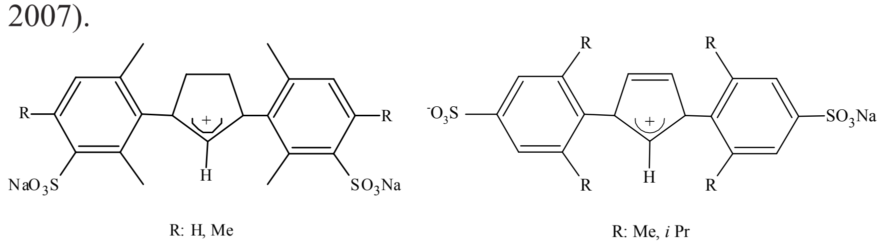


Figure 1.11

1.6. Silica Supported Pd-NHC Complexes

The support of Pd–NHC complexes is of utmost importance because of the high activity of these complexes in coupling chemistry. Coupling chemistry is vital in the synthesis of complex molecules for the drug and fine chemical industries. Supporting these complexes allows for easy removal of the toxic metal and the possibility of recycling the metal catalysts. Several groups have investigated this topic by supporting palladium complexes on a variety of supports, from poly(styrene) to clay (de Miguel, 2000; Sommer and Weck, 2007).

In 2003, Zhang et al. reported the first supported Pd–NHC catalyst trapped in silica gel (Figure 1.12) (Zhang *et al.*, 2003). The goal of their study was to support a highly active catalyst for the Suzuki coupling onto a solid support to be used in aqueous media. In this study, they synthesized a double pincer-type complex with four NHCs. The support used was either silica gel or alumina. They studied the activity of their supported catalyst towards the Suzuki transformation with a variety of reagents. By using activated and non-activated aryl bromides and chlorides as well as aryl boronic acids, they demonstrated high activities of their catalyst.

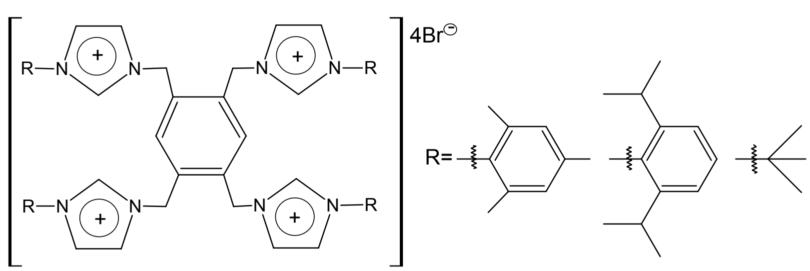


Figure 1.12 NHC precursors for Pd-complexes that have been physisorbed and trapped in silica gel as described by Zhang et al.

Two years later, Gao et al. reported the first silica coated nanoparticle supported Pd–NHC (Gao *et al.*, 2005). In this study, Gao et al. synthesized superparamagnetic maghemite (γ-Fe_2CO_3) to support the palladium complex (Figure 1.13). The small size of these nanoparticles (~11 nm) allowed them to be partially soluble in organic solvents, making them homogeneous under reaction conditions. The authors carried out Suzuki, Heck and Sonogashira reactions of common reagents. The different coupling reactions yielded close to quantitative conversions with iodo and bromo-aryls. Furthermore, the nanoparticles could be removed from the reaction vessel using a small permanent magnet. When performing recycling experiment, the conversions for each coupling reactions slightly declined after each cycle yielding 93%, 92% and 89% for the Suzuki, Heck and Sonogashira coupling respectively for the fifth cycle.

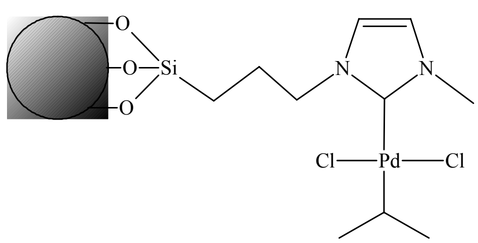


Figure 1. 13

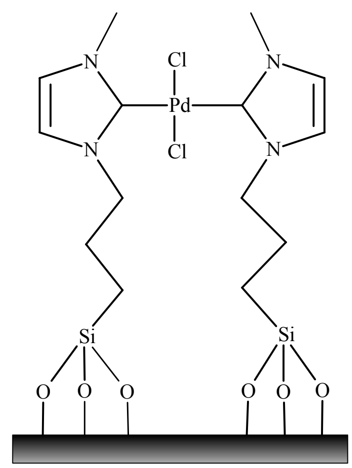


Figure 1.14

In 2006, Karimi and Enders described the immobilization of an NHC–Pd complex/ionic liquid matrix onto silica (Figure 1.14) (Karimi and Enders, 2006). They studied the activity of the catalytic system towards the Heck catalysis of aryl iodide with alkyl acrylates and showed that their catalytic system was highly active with nearly quantitative conversions for most of the Heck transformations studied. They finally recycled their catalyst three times yielding up to 89% conversions after 26 h for the third cycle.

In 2006, Pd–NHC complexes supported on insoluble supports comes from Aksın et al. who described the immobilization of an NHC–Pd complex matrix onto silica (Figure 1.15) (Aksın *et al.*, 2006) system towards the Heck catalysis of aryl iodide with alkyl acrylates and showed that their catalytic system was highly active with nearly quantitative conversions for most of the Heck transformations studied. They finally recycled their catalyst three times yielding up to 89% conversions after 26 h for the third cycle.

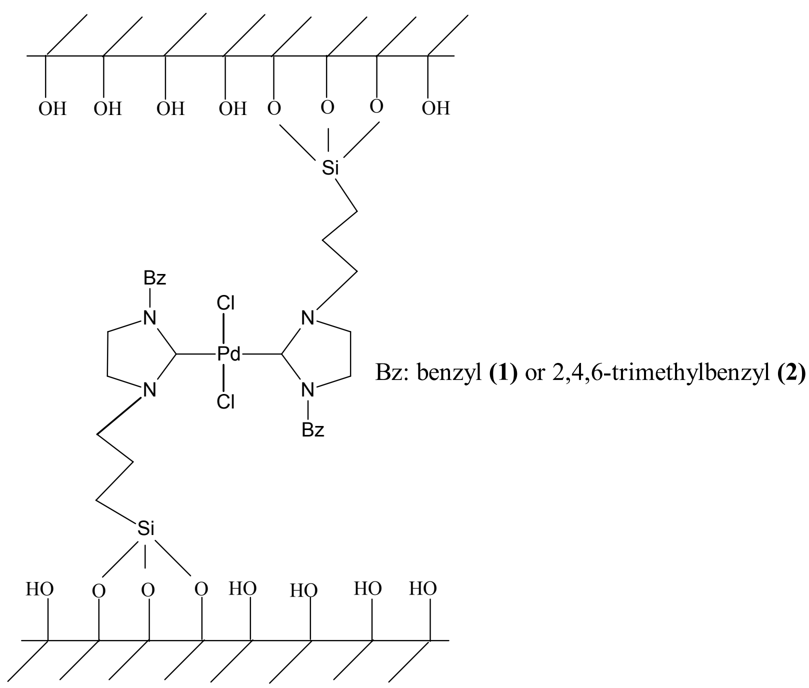


Figure 1.15

Gürbüz et al. reported the imidazole functionalised silica-Pd catalysts (Gürbüz *et al.*, 2003). A mesoporous silica-nanotube-supported 3-(4,5-dihydroimidazol-1-yl)-propyltriethoxysilane dichloropalladium(II) complex was prepared and tested for catalytic activity for Heck coupling reactions between styrene and several aryl halides. The results showed that three different morphological classes of silica xerogels were synthesised. Completely amorphous silicates were obtained in the presence of alcohols, whereas the material originating from DL-tartaric acid was silica nanotube in a morphological state. Non-porous silica sphere formation was noticed along with the nanotube formation. Figure 1.16 was found to be an active catalyst for the Heck reaction and proved to be thermally robust for high-temperature Heck olefination of aryl chlorides, bromides or iodides.

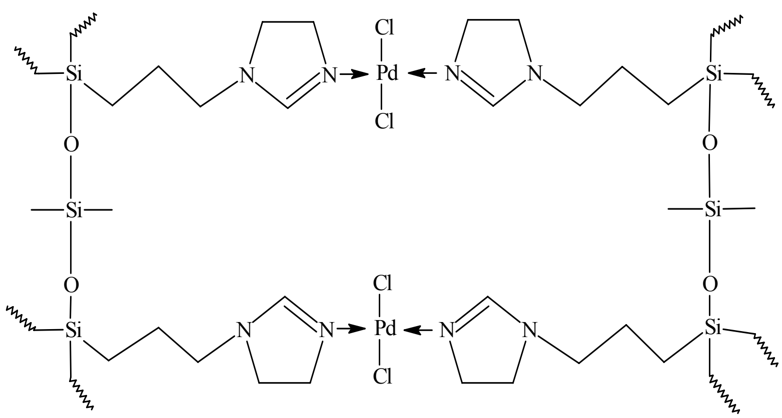
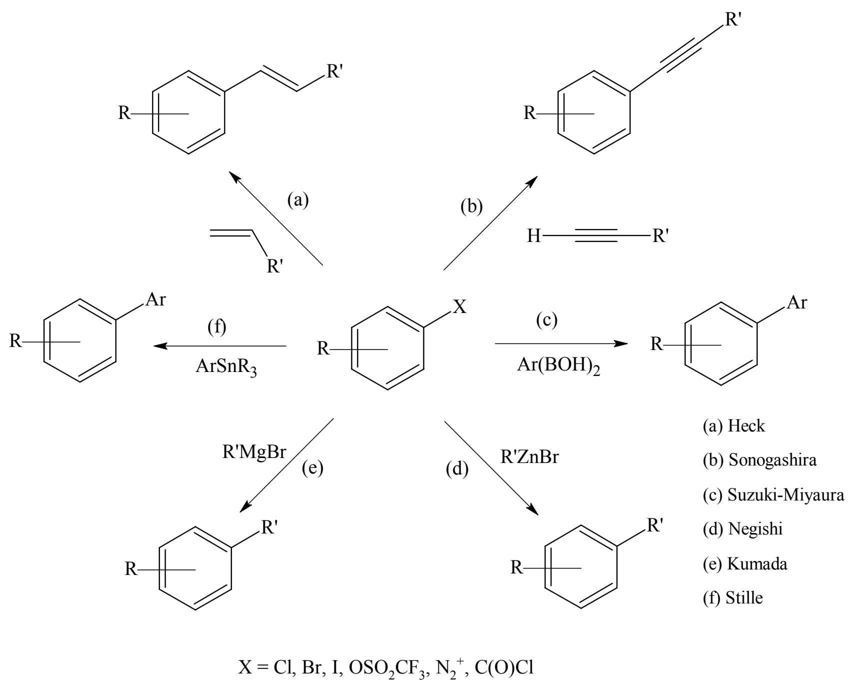


Figure 1.16

1.7. Coupling Reactions

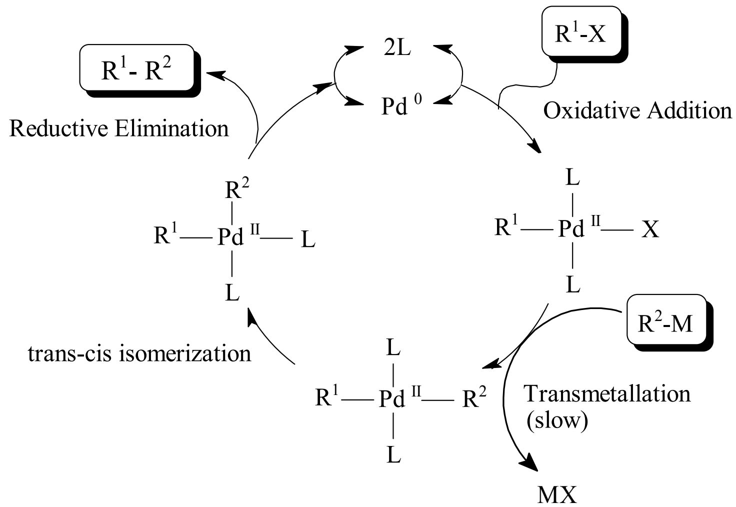
A general aim of transition metal-catalyzed organic synthesis is carbon-carbon (C-C) bond formation. In this respect, the Pd-catalyzed coupling reactions *e.g.* Heck-type reactions (a) (Heck and Nolley, 1972), the Sonogashira reaction (b) (Sonogashira *et al.,* 1975), Suzuki- Miyaura reactions (c) (Suzuki, 1985, 1994, 1999), the Negishi reaction (d) (Negishi *et al.*, 1977), Kumada-Corriu reaction (e) (Kumada *et al.*, 1972) and the Stille reaction (f) (Stille and Milstein, 1979) are available for this purpose (Scheme 1.7).



Scheme 1.7 Palladium-and nickel-catalyzed C-C bond formations.

1.7.1. Suzuki-Miyaura Reaction

Suzuki-Miyaura cross-coupling reaction which produces biaryls has proven to be the most popular in recent times. Biaryls are building blocks and subunits present in many natural products and have important applications, including use as pharmaceuticals, agrochemicals, and polymer constituents (Bringman *et al.*, 2001).
The preference for the Suzuki- Miyaura cross coupling above other Pd-catalyzed cross-coupling reactions is not incidental. The key advantages of the Suzuki-Miyaura coupling are the mild reaction conditions and the commercial availability of the diverse boronic acids that are environmentally safer than the other organometallic reagents. It is worth noting that the palladium catalysts show a broad tolerance towards various functional groups (Suzuki, 1985, 1994, 1999; Stanforth, 1998). The mechanism of the coupling reactions consists of four main steps (Scheme 1.8) (Moreno-Manas *et al.,* 1996): Oxidative addition of aryl halides to palladium species; transmetallation of aryl borate to form *trans*-diaryl palladium complex; *trans-cis* isomerization of this palladium complex; reductive elimination of the biaryl to regenerate the catalyst.



Scheme 1.8 General mechanism of Suzuki coupling reactions

Several parameters affecting the Suzuki coupling reactions are considered. These factors are; solvent effect, substitution group effect, base effect, halogen and ligand effect. Solvents are the most important parameters in organic reactions. As in general organic reactions, appropriately chosen solvent system strongly favours the cross coupling pathway. In literature, dioxan, THF, different DMF/H_2O and EtOH/H_2O ratios, toluene and benzene have been used as solvents in Suzuki coupling reactions.

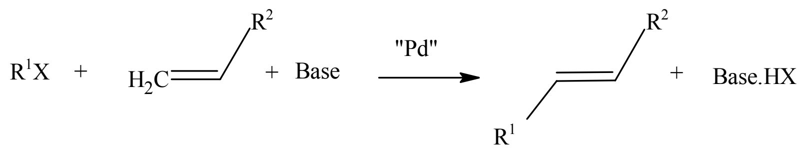
In Suzuki coupling reactions substituent are the most important to influence the activity of the reaction. These groups substantially influence the activity of aryl halide. The reaction is promoted, when electron-withdrawing groups substitute aryl halide. In Suzuki coupling reaction mechanism, first step involves carbon-halide bond cleavage. Carbon-halide bond cleaves more easily when it substitutes with electron withdrawing groups (NO_2, CF_3, CN, etc.) and thereby the reaction proceeds faster as the C-X bond is weakened. This bond will be broken easily and reaction will be faster (Scheme 1.8). In contrast, if this aryl halide group contains an electron donating substituent (CH_3, OCH_3, etc) carbon-halide bond will be stronger. So bond cleavage will be more difficult and reaction would probably proceed slower (Solomons, 2000).

The halogen type also determines the activity of aryl halide towards the Suzuki coupling reaction. The reactivity of the aryl halide component decreases drastically in the order X = I > Br > Cl and electron withdrawing substituents R are required for the chlorides to react (Suzuki, 1999; Gibson *et al.,* 2001; Bedford *et al.,* 2002). Suzuki coupling reaction proceeds via transmetallation in the presence of bases (Scheme 1.8). This procedure does not take place under neutral conditions. This is a characteristic feature of boron chemistry, which is different from that of other organometallic reagents. The most commonly used base in the Suzuki cross coupling reaction is Na_2CO_3 but this is often ineffective with sterically demanding substrates. In such instance, $Ba(OH)_2$ or K_3PO_4 has been used to generate good yields of the cross coupling products. Other bases utilized in the Suzuki cross-coupling reaction include Cs_2CO_3, K_2CO_3, KOMe, TlOH and NaOH (Kotha *et al.,* 2002).

1.7.2. Heck Reaction

The palladium-catalyzed arylation of an alkene with an organic halide was first reported by Mizoroki and Heck in the early 1970s (Mizoroki *et al.*, 1971; Heck and Nolley, 1972).

The classical Heck reaction involves bond formation between two sp^2 carbon centers by an overall substitution of a C-H bond of an alkene by R^1 from the R^1X substrate (where R^1 = aryl or vinyl; X = I, Br; R^2 = electron withdrawing or releasing group) under basic conditions. The transformation has since become known as the Heck reaction (Scheme 1.9).

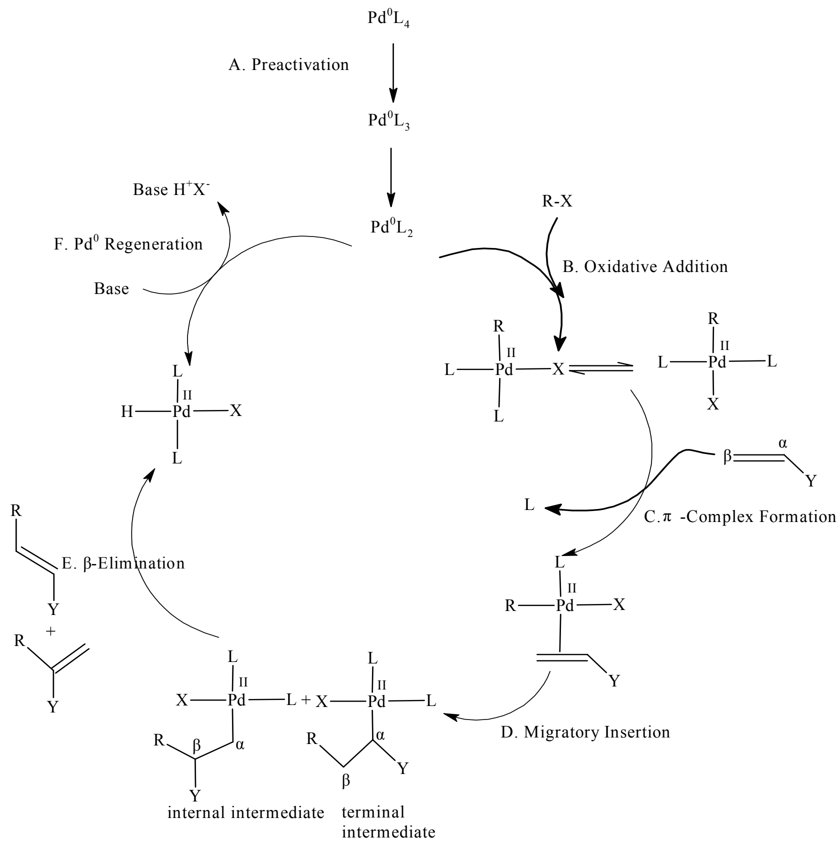


Scheme 1.9 The Mizoroki-Heck Reaction.

Since its discovery, the methodology has been found to be highly versatile and applicable to a wide range of aryl species Ar-X, where X = Cl, Br, I, OTf, OTs and N_2^+ (Whitcombe, 2001).

Advantage of this reaction is not limited to activated alkenes. The substrate can be a simple olefin (with ethylene being the most reactive one), or it can contain a variety of functional groups, such as ester, ether, carboxyl, phenolic, or cyano groups (Shibasaki and Vogl, 1999).

The mechanism outlined in Scheme 1.10, provides a general description of the steps required for catalytic olefination: The Heck Reaction involves preactivation step A which includes the reduction of Pd(II) complexes to catalytically active Pd(0) species. Thereafter, oxidation addition B of a Pd(0) catalyst to afford σ-aryl palladium(II) complexes. Coordination of an alkene and subsequent C-C bond formation by syn addition provide σ-alkyl palladium(II) intermediates which readily undergoes β-hydride elimination E to release the alkene Heck product. In order for the cycle to continue, a base is required for conversion of hydridopalladium(II) complex [$HPdXL_2$] to the active Pd(0) catalyst.



Scheme 1.10 The Mechanism of the Classical Heck Cycle

1.8. Aim of the study

Fine chemicals have a great importance and are used as a medicines, food additives, pesticides (poisons), cosmetics and dyes. Therefore, the production process of these chemicals must be environmently friendly, cheap and highly efficient under mild conditions. A chemical reaction must be effective as well as selective. Homogeneous and heterogeneous catalysts have played an important role in economic success of chemical industry. In other words, catalyst have a great role in making environment cleaner, paving the way to improve clean industrial processes which are free of side reactions. An effective and selective catalyst, provides a clean technology and minimize the operating costs by keeping the raw material sources and toxic materials at minimum level. That's why industry reactions can not be considered apart from catalysts.

Although homogeneous catalysts function at relatively mild conditions and display high activities and selectivities, they are not industrially viable because of the problems of catalyst recovery and recycling. Therefore, immobilization of the catalyst is very desirable. In order to reach this goal, we envisioned that dimeric Pd-NHC complexes can be cleaved by N-heterocycles which should bear a functional group convertible to a suitable form. Eventually, we thought $–Si(OEt)_3$ group of imeo and –COOH functionality of pyridine carboxylic acids (py-COOH) could be good choice. The influence of such heterocycles for the C-C bond formation was planned to be evaluated using standard model reactions.

Heterogenation process of homogeneous catalysts is usually carried out by immobilizing on a solid support or dissolving in water. The first method is binding the resulting complexes with $Si(OR)_3$ on polymer supported or silica supported surfaces. The second method involves incorporation of hydrophilic groups such as carboxylate (-COOH, -COONa), sulfonate ($-SO_3H$, $-SO_3Na$), ammonium groups (NR_3, $R'NR_3^+$), hydroxyalkyl and poly-ether (-OH, $-(CH_2CH_2O)_n-H$), phosphonium and phosphonate ($-PR_3^+$, $-P(O)(OR)_2$, $-P(O)(ONa)_2$) and carbohydrates.

Palladium complexes that have pyridine subtituted N-Heterocyclic Carbene (NHC) or monocarbene and monopyridine derivatives have been studied in a comprehensive manner.

However, palladium complexes containing NHC and pyridine carboxylic acids have not been synthesised.

2. EXPERIMENTAL

Reactions involving air-sensitive components were performed by using Schlenk-type flasks under argon atmosphere and high vacuum-line techniques. The glass equipment was heated under vacuum in order to remove oxygen and moisture and then they were filled with argon. The solvents were analytical grade and distilled under argon atmosphere from sodium (ethanol, toluene, diethyl ether, hexane), P_2O_5 (dichloromethane).

Reagents: Toluene, N,N-dimethylacetamide, dichloromethane, diethyl ether, hexane and ethanol (Merck), dimethyl sulphoxide (Carlo Erba). HNO_3 (Merck, 65%), HF (Merck, 40 %), $HClO_4$ (Riedel-de Haën, 65 %). Benzimidazole, 2-chloroethyl methyl ether, pyridine-4-carboxylic acid were obtained from Alfa Aesar. Pyridine-3-carboxylic acid, NaBr and pyridine-2,6-dicarboxylic acid were obtained from Merck. Pyridine-2-carboxylic acid, and $Pd(OAc)_2$ obtained from Aldrich. {*N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole} was obtained from ABCR. 2,4,6-Trimethylbenzyl bromide, 2,3,5,6-tetramethylbenzyl bromide, 2,3,4,5,6-pentamethylbenzyl bromide were prepared according to literature (van der Made, 1993). 1-(2-methoxyethyl)benzimidazole was synthesized according to literature (Özdemir *et. al.*, 2005). Silica gel (Davisil, Grade 646, 35-60 mesh, pore size 150 Å) was obtained from Aldrich.

Instruments: NMR spectra were recorded at 297 K on a Varian Mercury AS 400 at 400 MHz (^1H), 100,56 MHz (^{13}C).. The yields of C-C coupling products were determined by using Trace GC Ultra Thermo Al 3000. IR spectra were obtained by Perkin-Elmer FT-IR spectrometer. UV spectra were recorded on a Carry 100 Bio. Mixtures were heated in the Cem Mars5 Microwave.

2.1. Synthesis of benzimidazolium salts.

2.1.1. Synthesis of 1-(2,4,6-trimethylbenzyl)-3-(2-methoxyethyl)benzimidazolium bromide, 1a.

1-(2-Methoxyethyl)benzimidazole (1.76 g, 10.0 mmol) was dissolved in toluene (20 mL) and then 2,4,6-trimethylbenzyl bromide (2.13 g, 10.0 mmol) was added, the resulting solution was stirred for 2 hour at room temperature, refluxed 24 hour and cooled to 25 ^{0}C, filtered and washed with diethyl ether. The residue was crystallized from CH_2Cl_2/Et_2O. Yield: 3.5 g; 90%.

2.1.2. Synthesis of 1-(2,3,5,6-tetramethylbenzyl)-3-(2-methoxyethyl)benzimidazolium bromide, 1b (Türkmen *et al.*, 2009).

The salt **1b** was prepared in a similar manner as described for **1a** using 1-(2-methoxyethyl)benzimidazole (1.76 g, 10.0 mmol) and 2,3,5,6-tetramethylbenzyl bromide (2.27 g, 10.0 mmol). Yield: 3.9 g, 97%.

2.1.3. Synthesis of 1-(pentamethylbenzyl)-3-(2-methoxyethyl)benzimidazolium bromide, 1c (Türkmen *et al.*, 2009).

The salt **1c** was prepared in a similar manner as described for **1a** using 1-(2-methoxyethyl)benzimidazole (1.76 g, 10.0 mmol) and pentamethylbenzyl bromide (2.41 g, 10.0 mmol). Yield: 3.6 g, 87%.

2.2. Synthesis of Pd Dimers

2.2.1. Synthesis of *trans*-Dibromo(μ-dibromo)bis[1-(2,4,6-trimethylbenzyl)-3-*(*2-methoxyethyl)benzimidazole-2-ylidene]dipalladium(II), 2a.

A DMSO solution (10 mL) containing 1-(2,4,6-trimethylbenzyl)-3-(2-methoxyethyl)benzimidazolium bromide **1a** (0.389 g, 1.0 mmol), $Pd(OAc)_2$ (0.225 g, 1.0 mmol) and NaBr (0.309 g, 3.0 mmol) was stirred at 90 ^{0}C for 24 hour. The DMSO was then removed in vacuo and the remaining solid was washed with diethyl ether. The solid residue was crystallized from CH_2Cl_2/EtOH. Yield: 0.46 g, 80%.

2.2.2. Synthesis of *trans*-Dibromo(μ-dibromo)bis[1-(2,3,5,6-tetramethylbenzyl)-3-*(*2-methoxyethyl)benzimidazole-2-ylidene]dipalladium(II), 2b (Türkmen *et al.*, 2009).

The complex was prepared as described for **2a** using 1-(2,3,5,6-tetramethylbenzyl)-3-(2-methoxyethyl)benzimidazolium bromide **1b** (0.403 g, 1.0 mmol). Yield: 0.49 g, 84%.

2.2.3. Synthesis of *trans*-Dibromo(μ-dibromo)bis[1-(pentamethylbenzyl)-3-*(*2-methoxyethyl)benzimidazole-2-ylidene]dipalladium(II), 2c (Türkmen *et al.*, 2009).

The complex was prepared as described for **2a** using 1-(pentamethylbenzyl)-3-(2-methoxyethyl)benzimidazolium bromide **1c** (0.417 g, 1.0 mmol). Yield: 0.46 g, 77%.

2.3. Synthesis of (NHC)-Pd-(*N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole) Complexes

2.3.1. Synthesis of {1-(2,4,6-trimethylbenzyl)-3-(2-methoxyethyl)benzimidazole-2-ylidene}(*N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole)dibromopalladium(II), 3a.

A sample of **2a** (1.1493 g, 1.0 mmol) and *N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (imeo) (0.5488 g, 2.0 mmol) were dissolved in dichloromethane (15 mL). The mixture was stirred at ambient temperature for 24 hour. The solvent was removed in vacuo. The solid residue obtained was dissolved dichloromethane (6 mL) and hexane (30 mL) was added to the resulting solution. A bright yellow precipiate obtained was collected by filtration, which was washed with hexane (10 mL) and dried in vacuo. Yield: 1.0 g, 59%.

2.3.2. Synthesis of {1-(2,3,5,6-tetramethylbenzyl)-3-(2-methoxyethyl)benzimidazole-2-ylidene}(*N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole)dibromopalladium(II), 3b.

The complex was prepared in a similar manner as described for **3a** using **2b** (1.1773 g, 1.0 mmol) as starting material. Yield: 0.97 g, 56%.

2.3.3. Synthesis of {1-(pentamethylbenzyl)-3-(2-methoxyethyl)benzimidazole-2-ylidene}(*N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole)dibromo palladium(II), 3c.

The complex was prepared in a similar manner as described for **3a** using **2c** (1.2054 g, 1.0 mmol) as starting material. Yield: 1.0 g, 57%.

2.4. Synthesis of (NHC)-Pd-pyridine-2-carboxylic acid complexes.

2.4.1. Synthesis of {1-(2,4,6-trimethylbenzyl)-3-(2-methoxyethyl)benzimidazole-2-ylidene}(pyridine-2-carboxylic acid)dibromopalladium(II), 4a.

A sample of **2a** (1.1493 g, 1.0 mmol) and pyridine-2-carboxylic acid (0.2462 g, 2.0 mmol) were dissolved in dichloromethane (15 mL). The mixture was stirred at ambient temperature for 24 hour. The solvent was removed in vacuo. The solid residue obtained was dissolved in dichloromethane (6 mL) and hexane (30 mL) was added to the resulting solution. A bright yellow precipiate obtained was collected by filtration, washed with hexane (10 mL) and dried in vacuo. Yield: 1.09 g, 78%.

2.4.2. Synthesis of {1-(2,3,5,6-tetramethylbenzyl)-3-(2-methoxyethyl)benzimidazole-2-ylidene}(pyridine-2-carboxylic acid)dibromopalladium(II), 4b.

The complex was prepared in a similar manner as described for **4a** using **2b** (1.1773 g, 1.0 mmol) as starting material. Yield: 1.07 g, 75%.

2.4.3. Synthesis {1-(pentamethylbenzyl)-3-(2-methoxyethyl)benzimidazole-2-ylidene}(pyridine-2-carboxylic acid)dibromopalladium(II), 4c.

The complex was prepared in a similar manner as described for **4a** using **2c** (1.2054 g, 1.0 mmol) as starting material. Yield: 1.13 g, 78%.

2.5. Synthesis of (NHC)-Pd-pyridine-3-carboxylic acid complexes.

2.5.1. Synthesis of {1-(2,4,6-trimethylbenzyl)-3-(2-methoxyethyl)benzimidazole-2-ylidene}(pyridine-3-carboxylic acid)dibromopalladium(II), 5a.

A sample of **2a** (1.1493 g, 1.0 mmol) and pyridine-3-carboxylic acid (0.2462 g, 2.0 mmol) were dissolved in dichloromethane (15 mL). The mixture was stirred at ambient temperature for 24 hour. The solvent was removed in vacuo. The solid residue obtained was dissolved in dichloromethane (6 mL) and the resulting solution added dropwise to hexan (30 mL). A bright yellow precipiate obtained was collected by filtration, washed with hexan (10 mL) and dried in vacuo. Yield: 0.98 g, 70%.

2.5.2. Synthesis of {1-(2,3,5,6-tetramethylbenzyl)-3-(2-methoxyethyl)benzimidazole-2-ylidene}(pyridine-3-carboxylic acid)dibromopalladium(II), 5b.

The complex was prepared in a similar manner as described for **5a** using **2b** (1.1773 g, 1.0 mmol) as starting material. Yield: 1.14 g, 80%.

2.5.3. Synthesis of {1-(pentamethylbenzyl)-3-(2-methoxyethyl)benzimidazole-2-ylidene}(pyridine-3-carboxylic acid)dibromidepalladium(II), 5c.

The complex was prepared in a similar manner as described for **5a** using **2c** (1.2054 g, 1.0 mmol) as starting material. Yield: 1.23 g, 85%.

2.6. Synthesis of (NHC)-Pd-pyridine-4-carboxylic acid complexes.

2.6.1. Synthesis of {1-(2,4,6-trimethylbenzyl)-3-(2-methoxyethyl)benzimidazole-2-ylidene}(pyridine-4-carboxylic acid)dibromopalladium(II), 6a.

A sample of **2a** (1.1493 g, 1.0 mmol) and pyridine-4-carboxylic acid (0.2462 g, 2.0 mmol) were dissolved in dichloromethane (15 mL). The mixture was stirred at ambient temperature for 24 hour. The solvent was removed in vacuo. The solid residue obtained was dissolved in a few milliliters of dichloromethane and the resulting solution added dropwise to hexan (30 mL). A bright yellow precipiate obtained was collected by filtration, washed with hexan (10 mL) and dried in vacuo. Yield: 1.14 g, 79%.

2.6.2. Synthesis of {1-(2,3,5,6-tetramethylbenzyl)-3-(2 methoxyethyl)benzimidazole-2-ylidene}(pyridine-4-carboxylic acid)dibromopalladium(II), 6b.

The complex was prepared in a similar manner as described for **6a** using **2b** (1.1773 g, 1.0 mmol) as starting material. Yield: 1.17 g, 82%.

2.6.3. Synthesis of {1-(pentamethylbenzyl)-3-(2-methoxyethyl)benzimidazole-2-ylidene}(pyridine-4-carboxylic acid)dibromopalladium(II), 6c.

The complex was prepared in a similar manner as described for **6a** using **2c** (1.2054 g, 1.0 mmol) as starting material. Yield: 1.16 g, 80%.

2.7. Synthesis of (NHC)-Pd-pyridine-2,6-dicarboxylic acid complexes.

2.7.1. Synthesis of {1-(2,4,6-trimethylbenzyl)-3-(2-methoxyethyl)benzimidazole-2-ylidene}(pyridine-2,6-dicarboxylic acid)dibromopalladium(II), 7a.

A sample of **2a** (1.1493 g, 1.0 mmol) and pyridine-2,6-dicarboxylic acid (0.3342 g, 2.0 mmol) were dissolved in DMSO (10 mL). The mixture was stirred at ambient conditions for 24 hour. The solvent was removed in vacuo. The solid residue obtained was dissolved in ca 6 milliliters of ethanol, and to the solution was added dropwise diethyl ether (30 mL). The cream precipiate obtained was collected by filtration, washed with 10 mL of diethyl ether, and dried in vacuo. Yield: 1.22, 82%.

2.7.2. Synthesis of {1-(2,3,5,6-tetramethylbenzyl)-3-(2-methoxyethyl)benzimidazole-2-ylidene}(pyridine-2,6-dicarboxylic acid)dibromopalladium(II), 7b.

The complex was prepared in a similar manner as described for **7a** using **2b** (1.1773 g, 1.0 mmol) as starting material. Yield: 1.12 g, 74%.

2.7.3. Synthesis of {1-(pentamethylbenzyl)-3-(2-methoxyethyl)benzimidazole-2-ylidene}(pyridine-2,6-dicarboxylic acid)dibromopalladium(II), 7c.

The complex was prepared in a similar manner as described for **7a** using **2c** (1.2054 g, 1.0 mmol) as starting material. Yield: 1.09 g, 71%.

2.8. Synthesis of Amorphous Silica.

Silica (3 g) and acetic acid (50 mL, 0.01 M) were stirred for 1h in ultrasonic bath. And then was filtered off and washed with ultra pure water until a pH 7.0 was attained and dried at 200 ^{0}C in a vacuum oven.

2.9. Anchoring of Pd(NHC) complex, 3c'.

A $CHCl_3$ suspension (20 mL/g silica) which contained Pd-NHC complex of **3c** in an amount furnishing 1 wt% Pd with respect to the silica amount was added to the amorphous silica and stirred for 2 h in ultrasonic bath. After filtration, it was washed with CH_2Cl_2 and Et_2O thoroughly. ICP-MS analysis of the sample showed a palladium loading of 0.012 mmol g^{-1}.

The dissolved samples were prepared according to the microwave digestion method, which is summarized below.

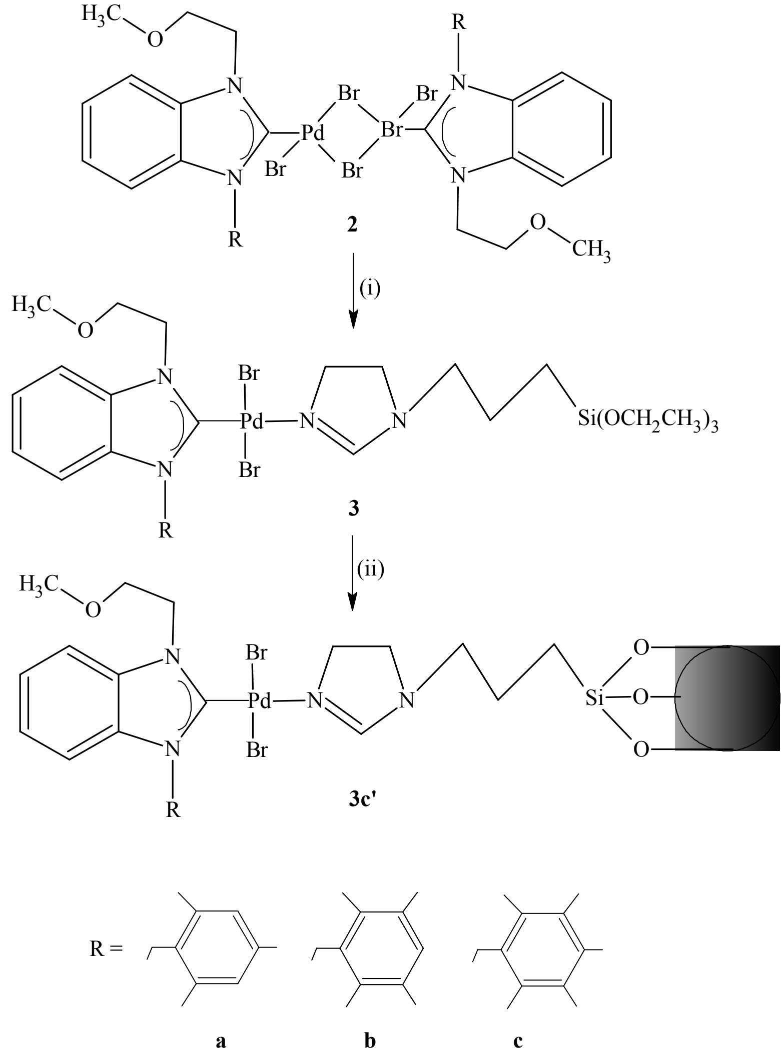
A mixture of 6 mL concentrated HNO_3, 4 mL concentrated HF and 2 mL $HClO_4$ were added over 40 mg of a compound (**3c**) and these mixtures were heated in the Cem Mars5 Microwave according to the following heating program:

Step	Time (min)	Temperature (^0C)	Microwave Power (W)
1	4	120	500
2	4	150	550
3	5	180	550
4	17	180	600

3. RESULTS and DISCUSSION

3.1. Synthesis of NHC-Pd(II)-imeo complexes, 3

Heterogeneous catalyst systems that consist of binding with covalent bond to an insoluble polymer or inorganic supports of homogeneous catalysts draw attention because of the practical advantages described in Table 1.1. Potential benefits of heterogenation are separation of the product from reaction media and purification of the catalyst for reuse. In previous studies the heterogenization were carried out by means of $Si(OR)_3$ functional groups on imidazole moiety and immobilization of silica of their palladium complexes. For example, in the Heck coupling reactions which were performed on the heterogenous systems obtained from immobilization via $–Si(OEt)_3$ gave high yield (Aksın *et al.*, 2006). In this thesis in a similar study, dimeric palladium complexes were cleaved by {*N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole} (imeo) (Scheme 3.1). Catalytic tests were carried out for the Heck reactions of the mono carbene-mono imeo palladium(II) bromide complexes (**3a-c**). Unfortunatelly, low yields has been observed. Furthermore, heterogenation process was carried out by immobilizing only one of the complexes (**3c**) with silica. The heterogenized system (**3c'**), was used as catalysts for the Heck reaction. But very low activities were observed. Therefore, immobilization in this direction was abandoned.



Scheme 3.1. Reagents and conditions: (i) *N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole, CH_2Cl_2, 25 ^{0}C, 24 h; (ii) Amorphous silica, $CHCl_3$, 25 ^{0}C, 2 h.

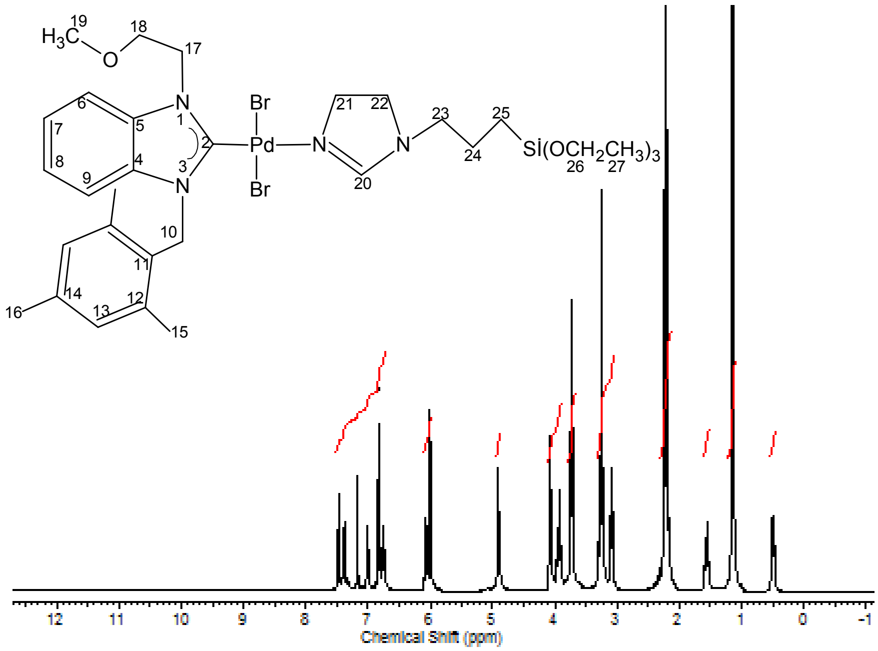


Figure 3.1 ^{1}H-NMR spectra of **3a**

Table 3.1 ^{1}H- and ^{13}C-NMR spectra of **3a**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	166.2
6, 9	6.09, 7.41 (2H, d)	8.4	111.2, 111.3
7, 8	6.78, 7.03 (2H, t)	7.8	122.5, 122.9
10	6.03 (2H, s)	-	53.98
13	6.86 (2H, s)	-	129.6
15	2.24 (6H, s)	-	21.1
16	2.27 (3H, s)	-	21.3
17	4.95 (2H, t)	5.6	50.0
18	3.30 (2H, t)	8.8	71.8
19	3.28 (3H, s)	-	59.3
20	7.50 (1H, s)	-	161.3
21	3.97 (2H, t)	7.2	51.2
22	3.12 (2H, t)	7.2	48.8
23	4.10 (2H, t)	5.6	48.2
24	1.59 (2H,m)	-	22.0
25	0.53 (2H, t)	8.0	7.6
26	3.77 (6H, q)	7.2	58.7
27	1.18 (9H, t)	7.0	18.5
4, 5, 11, 12, 14	-	-	127.8, 134.8, 136.0, 138.7, 139.2

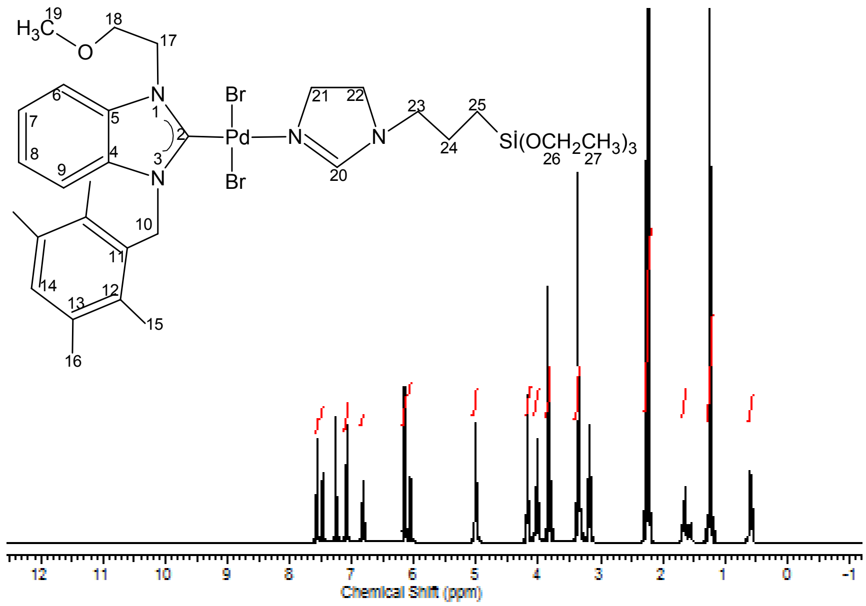


Figure 3.2 ^{1}H-NMR spectra of **3b**

Table 3.2 ^{1}H- and ^{13}C-NMR spectra of **3b**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	166.5
6, 9	6.06, 7.47 (2H, d)	8.4	111.2, 111.4
7, 8	6.82, 7.08 (2H, t)	7.8	122.3, 122.8
10	6.16 (2H, s)	-	54.0
14	7.26 (1H, s)	-	130.7
15, 16	2.23, 2.26(12H, s)	-	16.80, 20.79
17	5.01 (2H, t)	5.8	50.0
18	3.30 (2H, t)	10.0	71.9
19	3.35 (3H, s)	-	59.3
20	7.55 (1H, s)	-	161.3
21	4.03 (2H, t)	10.4	51.9
22	3.18 (2H, t)	7.0	48.9
23	4.17 (2H, t)	5.6	48.3
24	1.65 (2H,m)	-	22.1
25	0.59 (2H, t)	8.2	7.7
26	3.83 (6H, q)	7.2	58.6
27	1.24 (9H, t)	7.6	18.5
4, 5, 11, 12, 13	-	-	132.7, 134.2, 134.9, 135.4, 135.9

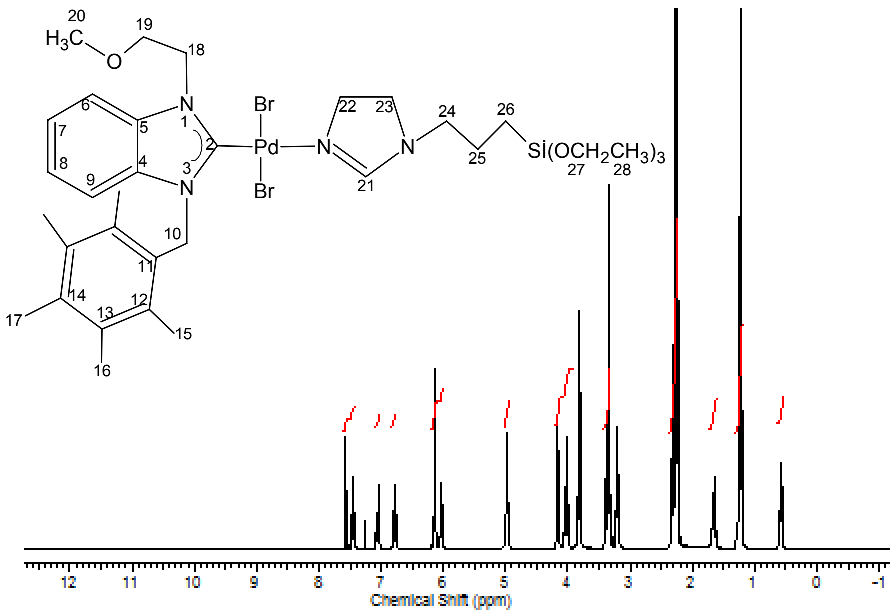


Figure 3.3 ^{1}H-NMR spectra of **3c**

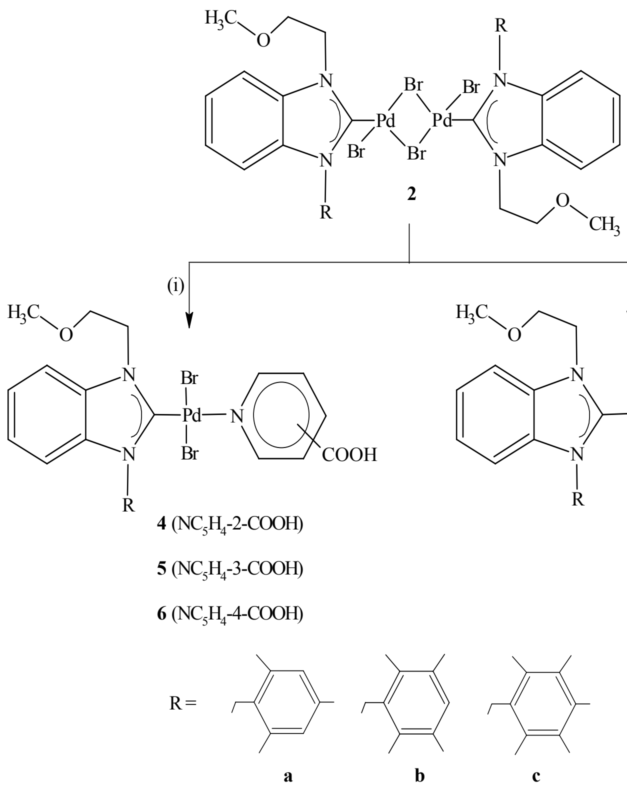
Table 3.3 ^{1}H- and ^{13}C-NMR spectra of **3c**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	166.4
6, 9	6.04, 7.45 (2H, d)	8.8	111.3, 111.4
7, 8	6.78, 7.05 (2H, t)	6.8	122.2, 122.7
10	6.14 (2H, s)	-	54.0
15, 16,17	2.25, 2.27, 2.32 (15H, s)	-	17.1, 17.5, 17.8
18	4.98 (2H, t)	5.0	50.0
19	3.37 (2H, t)	10.8	71.8
20	3.34 (3H, s)	-	59.2
21	7.57 (1H, s)	-	161.3
22	4.02 (2H, t)	6.4	52.6
23	3.19 (2H, t)	6.8	48.9
24	4.16 (2H, t)	5.0	48.3
25	1.65 (2H,m)	-	22.1
26	0.57 (2H, t)	8.0	7.7
27	3.81 (6H, qd)	6.8	58.6
28	1.23 (9H, td)	7.0	18.5
4, 5, 11, 12, 13, 14	-	-	128.1, 132.9, 134.9, 135.0, 135.9, 136.0

3.2. Synthesis of NHC-Pd(II)-Pyridinecarboxylic acid complexes, 4-7

Meanwhile, the NHC ligand is widely utilized as anchilary ligands in coordination and organometallic complexes (Peris and Crabtree, 2004; Peris *et al.*, 2007, Cavell and McGuinness, 2004; Perry and Burgess, 2003; Gade and Bellemin-Laponnaz, 2007). Recently, Organ and coworkers reported combination of Pd(NHC) with PEPPSI (PEPPSI= Pyridine Enhanced Precatalysts Preparation, Stabilization and Initiation) and successfully applied as the cross-coupling catalysts (Chass *et al.*, 2006, 2008). However, to our knowledge no pyridine derivatives containing carboxyl group, have been utilized as supporting ligand for the complexation, which will provide a straightforward approach to water-soluble NHC complexes in basic media.

The dimeric complexes of the type $[PdX_2(NHC)]_2$ can be readily prepared and cleaved by various nucleophiles to give mixed [Pd(NHC)(nuc)] complexes (Böhm *et al.*, 1999, 2001; Meyer *et al.*, 2003; Türkmen *et al.*, 2009; Huynh *et al.*, 2006, 2007, 2009; Altenhoff *et al.*, 2002, 2003, 2004; Viciu *et al.*, 2002; Jensen *et al.*, 2003; Han, 2009). Therefore, we applied this concept to the dimer **2** to obtain *trans*-$[PdBr_2(NHC)L]$ (NHC = 1,3-dialkylbenzimidazol-2-ylidene; L = pyridinecarboxylic acid) complexes of the type. Scheme 3.2 shows the synthetic routes used to prepare the desired complexes which have carboxylic acid(s) groups on different position of the pyridine ring.



Scheme 3.2. Reagents and conditions: (i) Pyridinecarboxylic acid, CH_2Cl_2, 25 ^0C, 24 h; (ii) Pyridine-2,6-dicarboxylic acid, DMSO, 25 ^0C, 24 h.

All new complexes have been isolated as yellow and air-stable solids. They are insoluble nonpolar solvents such as diethyl ether, hexane, pentane or toluene. However, **4**-**7** are soluble in DMSO, DMF, C_2H_5OH and H_2O. The complexes were characterized by their IR, NMR and UV-visible spectroscopy (Table 3.4 lists some selected data). The formation of the metal complexes were evident from the distinctive Pd-$C_{carbene}$ peak, appeared at *ca*. 160.5-163.5 ppm for **4**-**7**. These data suggest that the weakest σ-donor leads to the most upfields ^{13}C chemical shift (Huynh, 2006, 2007, 2009; Altenhoff *et al.*, 2002, 2003, 2004; Viciu *et al.*, 2002; Jensen and Sigman, 2003; Han and Huynh, 2009). The IR spectrum of displayed absorption bands due to ν(COO) at 1703-1759 cm^{-1}, and there was a broad band ν(O-H) at 3423-3722 cm^{-1} for **4-7**. From the IR data we may infer that the COOH group(s) on the pyridine ring were not involved in metal-bonding, at least under neutral conditions. Whilst, the versatility of 2-pyridinecarboxylic acid or 2,6-pyridinedicarboxylic acids as multidentate ligands is well known (Qin *et al.*, 2002; Aghabozorg *et al.*, 2006).

Table 3.4 Comparison of selected spectroscopic data of complexes, **4-7.**

Complex	IR($\nu_{C=O}$, ν_{O-H}, cm^{-1})	NMR(^{13}C, C-Pd, ppm)	UV-visible(nm)
4a	1752, 3712	161.4	231, 274, 280, 351
4b	1735, 3650	161.2	233, 270, 284, 350
4c	1739, 3674	161.3	230, 272, 279, 354
5a	1752, 3712	163.1	240, 273, 361
5b	1703, 3433	162.6	243, 246, 271, 361
5c	1731, 3423	162.6	234, 241, 244, 274, 361
6a	1750, 3722	163.6	235, 245, 274, 362
6b	1759, 3712	163.1	233, 242, 271, 362
6c	1705, 3437	163.1	233, 240, 242, 273, 362
7a	1740,3498	160.5	240, 277, 2.80, 351
7b	1750, 3712	160.6	233, 272, 2.81, 352
7c	1742, 3502	160.9	239, 279, 2.83, 352

The UV-visible absorption spectral data obtained for complexes, **4-7**, in CH_2Cl_2 are summarized in Table 3.1 The mixed NHC/pyridinecarboxylic acid complexes, **4-7**, showed weak absorption bands at 350-362 nm corresponding to the metal-to-ligand charge transfer (MLCT) (Heath, 2002). The absorbance maxima spectra of complexes **4-7** exhibited at 240-283 nm, which are assigned to intraligand $\pi \rightarrow \pi^*$ transitions.

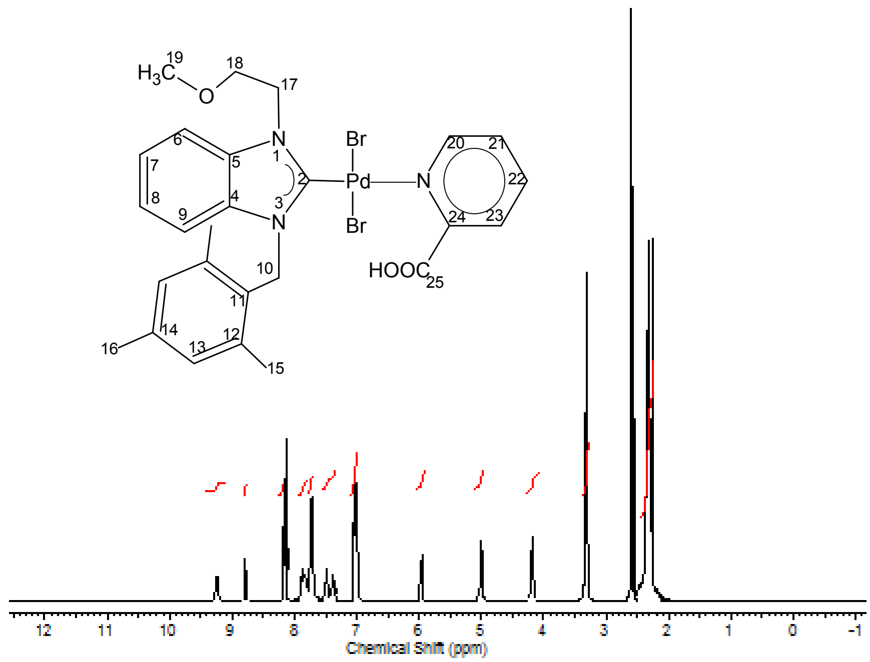


Figure 3.4 ^{1}H-NMR spectra of **4a**

Table 3.5 ^{1}H- and ^{13}C-NMR spectra of **4a**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	161.4
6, 9	6.98, 7.67 (2H, d)	6.8	111.2, 112.4
7, 8	7.31, 7.42 (2H, t)	6.4	123.8, 124.3
10	5.88 (2H, s)	-	49.4
13	6.99 (2H, s)	-	130.0
15	2.19 (6H, s)	-	21.0
16	2.25 (3H, s)	-	21.5
17	4.94 (2H, b)	-	48.5
18	4.16 (2H, b)	-	71.2
19	3.24 (3H, s)	-	59.0
20	9.17 (1H, b)	-	153.3
23	8.71 (1H, d)	4.4	149.2
25	-	-	166.1
21, 22	7.77-7.82 (1H, m) 8.0-8.17 (1H, m)	-	128.4, 129.5, 133.0, 134.5, 135.7, 138.6, 138.9, 140.2
4, 5, 11, 12, 14, 24	- -		

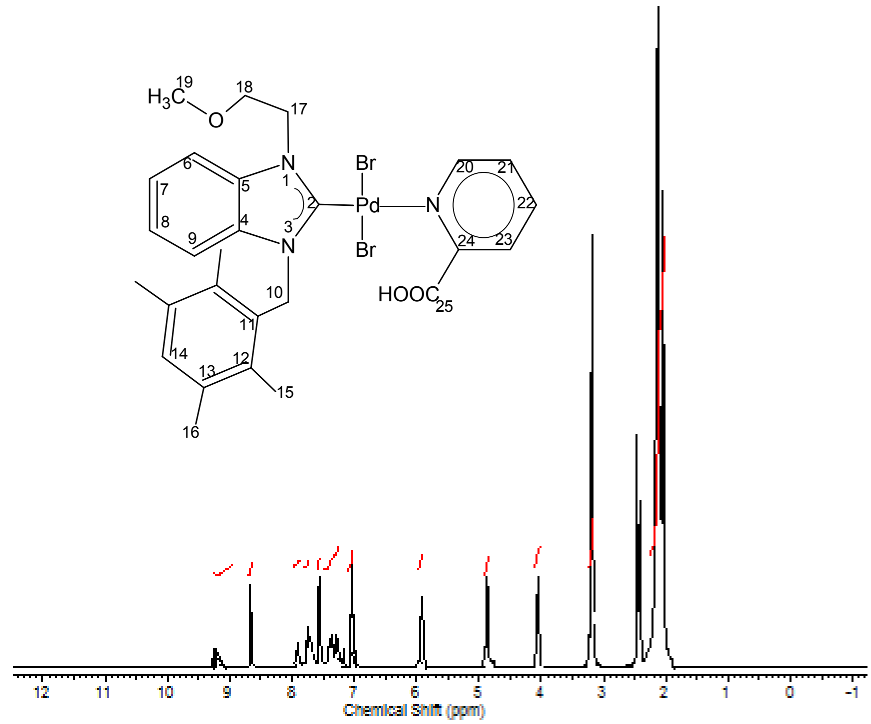


Figure 3.5 ^{1}H-NMR spectra of **4b**

Table 3.6 ^{1}H- and ^{13}C-NMR spectra of **4b**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	161.2
6, 9	7.10, 7.66 (2H, d)	8.8	111.0, 111.9
7, 8	7.17-7.47 (2H, m)	-	123.5, 124.3
10	5.97 (2H, s)	-	49.9
15, 16	2.19, 2.22 (12H, s)	-	20.0, 20.9
17	4.93 (2H, b)	-	48.6
18	4.12 (2H, b)	-	71.0
19	3.30 (3H, s)	-	58.9
20	9.18 (1H, b)	-	153.5
23	8.73 (1H, d)	4.8	149.0
25	-	-	166.0
14	7.11 (1H, s)	-	128.3, 128.5, 131.0, 133.5, 133.9, 135.1, 138.0, 139.9, 140.7
21, 22	7.80 (1H, t),7.98 (1H, t)	8.6, 7.6	
4, 5, 11, 12, 13, 24	- -	- -	

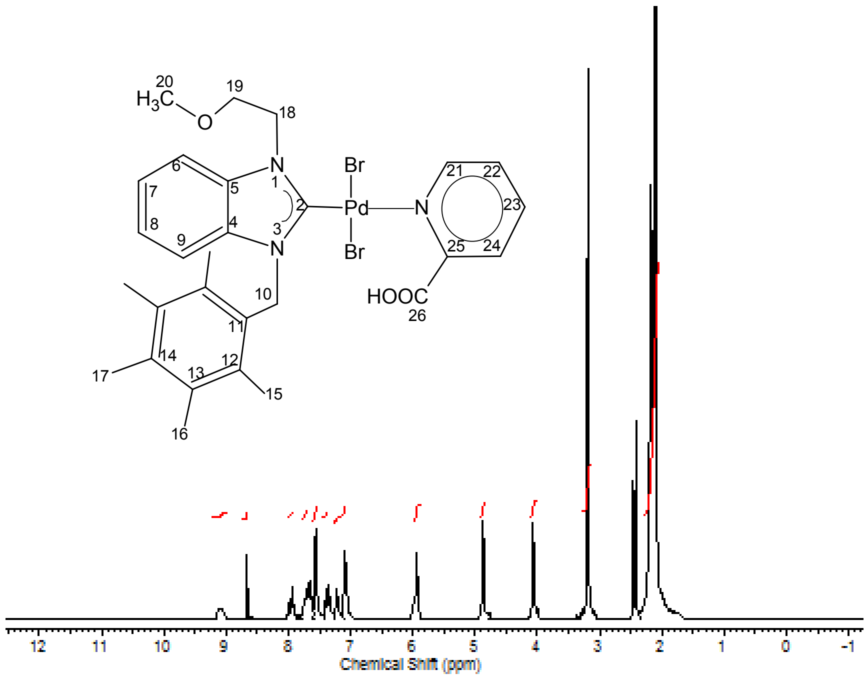


Figure 3.6 ^{1}H-NMR spectra of **4c**

Table 3.7 ^{1}H- and ^{13}C-NMR spectra of **4c**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	161.3
6, 9	7.15, 7.62 (2H, d)	6.8, 6.0	111.2, 112.0
7, 8	7.28, 7.45 (2H, t)	6.2, 7.0	123.3, 123.8
10	5.99 (2H, s)	-	49.8
15, 16, 17	2.15, 2.17, 2.19 (15H, s)	-	17.7, 19.9, 20.1
18	4.93 (2H, b)	-	48.5
19	4.13 (2H, b)	-	70.9
20	3.25 (3H, s)	-	59.0
21	9.14 (1H, b)	-	153.9
24	8.73 (1H, d)	4.4	147.9
25	-	-	166.0
22, 23	7.79 (1H, t), 8.00 (1H, t)	7.6, 7.4	125.5, 128.5, 128.7, 130.3, 131.0, 133.2, 134.9, 136.5, 139.9
4, 5, 11,	-	-	
12, 13, 14,	-	-	
25	-	-	

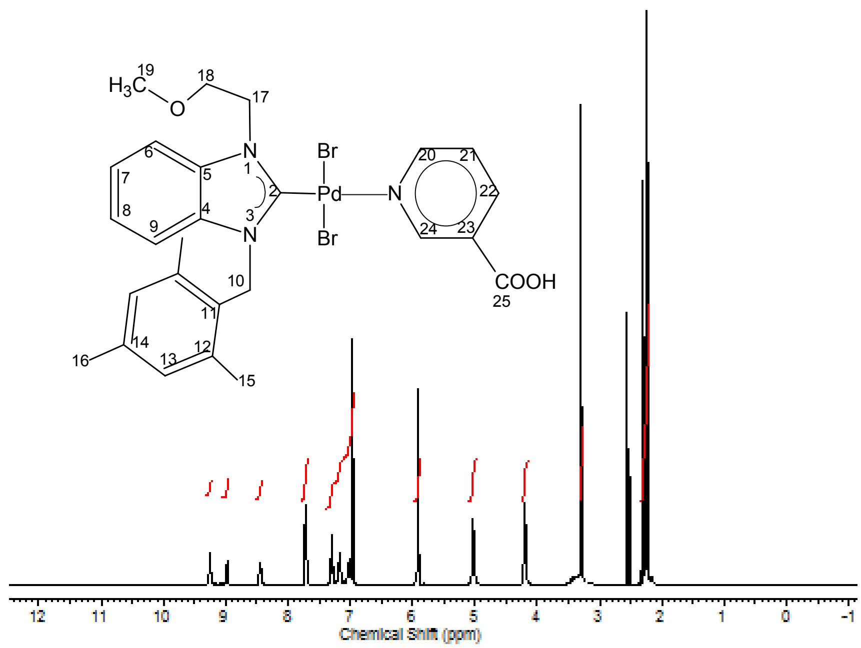


Figure 3.7 ^{1}H-NMR spectra of **5a**

Table 3.8 ^{1}H- and ^{13}C-NMR spectra of **5a**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	163.1
6, 9	6.99, 7.69 (2H, d)	8.8, 8.4	111.2, 112.5
7, 8	7.14, 7.27 (2H, t)	7.6, 7.8	123.6, 123.8
10	5.87 (2H, s)	-	49.1
13	6.92 (2H, s)	-	130.1
15	2.21 (6H, s)	-	21.3
16	2.26 (3H, s)	-	21.4
17	5.00 (2H, b)	-	48.7
18	4.16 (2H, t)	5.0	71.4
19	3.26 (3H, s)	-	59.1
20	8.95 (1H, b)	-	155.9
21	7.68 (1H, b)	-	125.6
22	8.41 (1H, d)	6.8	140.0
24	9.21 (1H, s)	-	153.3
25	-	-	165.5
4, 5, 11, 12, 14, 23	-	-	128.5, 128.8, 134.9, 135.5, 138.4, 138.8

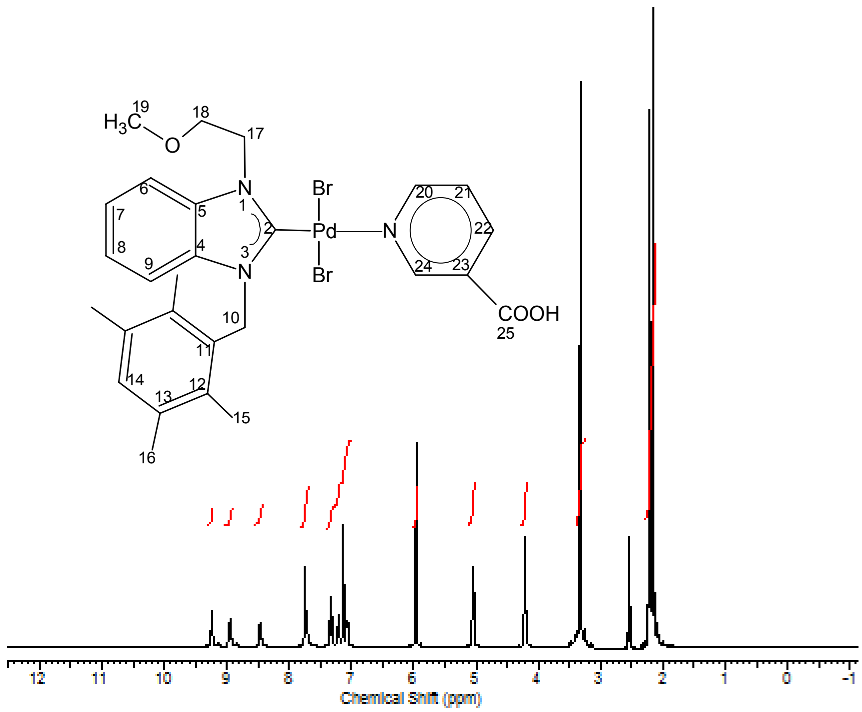


Figure 3.8 ^{1}H-NMR spectra of **5b**

Table 3.9 ^{1}H- and ^{13}C-NMR spectra of **5b**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	162.6
6, 9	7.03, 7.72 (2H, d)	7.6, 8.0	111.2, 112.4
7, 8	7.18, 7.30 (2H, t)	7.6	123.6, 123.8
10	5.93 (2H, s)	-	49.7
14	7.09 (1H, s)	-	131.6
15, 16	2.12, 2.17 (12H, s)	-	17.1, 20.5
17	5.02 (2H, t)	5.2	48.8
18	4.18 (2H, t)	5.6	71.3
19	3.28 (3H, s)	-	59.1
20	8.91 (1H, b)	-	155.8
21	7.72 (1H, b)	-	125.5
22	8.43 (1H, d)	6.4	140.0
24	9.19 (1H, s)	-	153.3
25	-	-	165.5
4, 5, 11, 13, 12, 23	-	-	128.4, 134.4, 132.7, 135.0, 135.1, 135.4

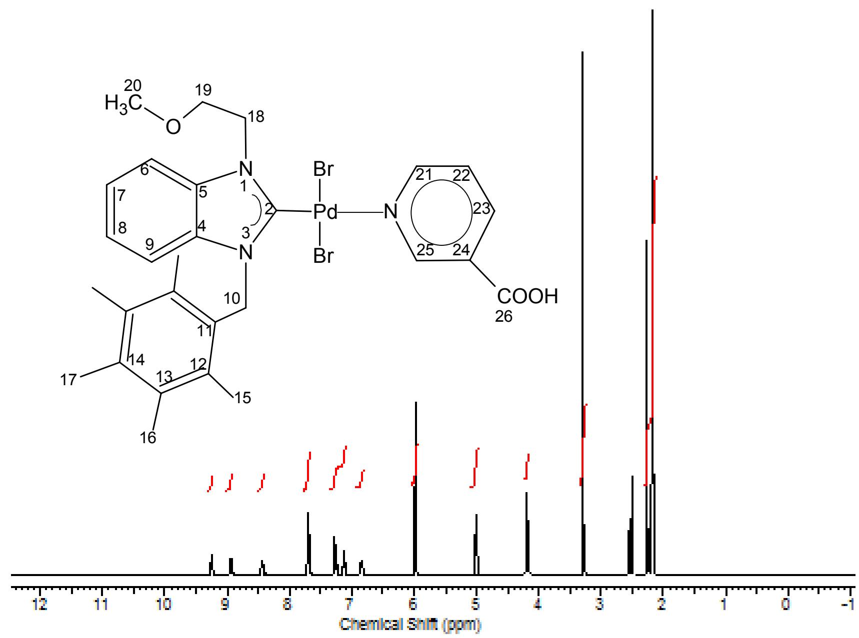


Figure 3.9 ^{1}H-NMR spectra of **5c**

Table 3.10 ^{1}H- and ^{13}C-NMR spectra of **5c**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	162.6
6, 9	6.83, 7.70 (2H, d)	6.4, 8.4	111.2, 112.4
7, 8	7.12, 7.27 (2H, t)	7.8	123.5, 123.8
10	5.97 (2H, s)	-	50.8
15, 16, 17	2.17, 2.27 (15H, s)	-	17.4, 17.7, 18.1
18	5.01 (2H, t)	5.4	48.7
19	4.18 (2H, t)	5.6	71.3
20	3.28 (3H, s)	-	59.1
21	8.94 (1H, b)	-	155.9
22	7.70 (1H, d)	8.4	125.5
23	8.44 (1H, d)	6.0	139.9
25	9.25 (1H, s)	-	153.3
26	-	-	165.6
4, 5, 11, 12, 13, 14, 24	-	-	128.5, 128.6, 133.3, 134.6, 134.9, 135.6, 135.9

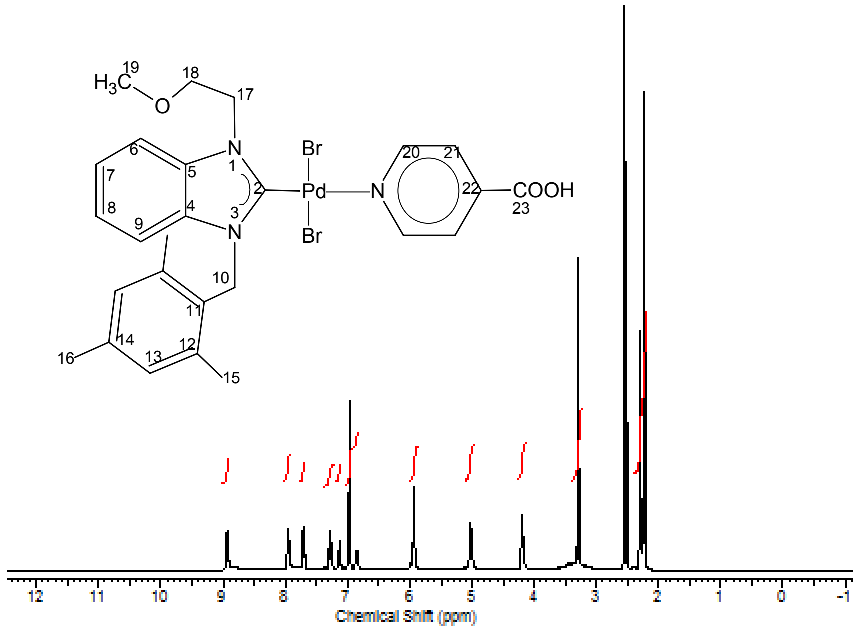


Figure 3.10 ^{1}H-NMR ^{13}C-NMR spectra of **6a**

Table 3.11 ^{1}H- and ^{13}C-NMR spectra of **6a**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	163.6
6, 9	6.85, 7.71 (2H, d)	8.0	111.2, 112.5
7, 8	7.14, 7.28 (2H, t)	7.8, 7.6	123.6, 123.8
10	5.93 (2H, s)	-	49.7
15	2.23 (6H, s)	-	21.3
16	2.30 (3H, s)	-	21.4
17	5.02 (2H, b)	-	48.7
18	4.19 (2H, b)	-	71.4
19	3.28 (3H, s)	-	59.1
23	-	-	165.9
13	6.96 (2H, s)	-	124.6, 128.6, 130.1, 134.7, 135.6, 138.5, 138.8, 140.9, 153.6
20, 21	7.95, 8.93 (2H, b)		
4, 5, 11, 12, 14, 22	-		

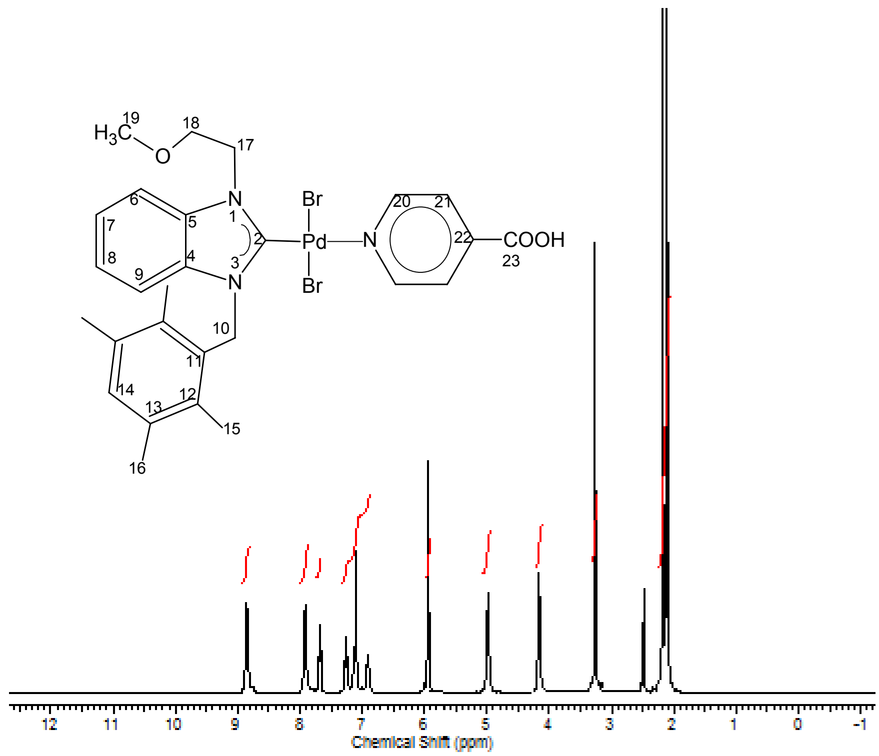


Figure 3.11 ^{1}H-NMR spectra of **6b**

Table 3.12 ^{1}H- and ^{13}C-NMR spectra of **6b**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	163.1
6, 9	6.90, 7.68 (2H, d)	7.6, 8.0	111.2, 112.4
7, 8	7.13, 7.26 (2H, t)	7.4	123.6, 123.8
10	5.93 (2H, s)	-	49.9
15, 16	2.10, 2.17 (12H, s)	-	17.1, 20.9
17	4.99 (2H, b)	-	48.7
18	4.16 (2H, b)	-	71.3
19	3.26 (3H, s)	-	59.1
23	-	-	165.9
14	7.09 (1H, s)		
20, 21	7.92, 8.85 (2H, b)	-	124.5, 131.5, 132.8, 134.5, 134.9, 135.1, 135.5, 140.9, 153.5
4, 5, 11, 12, 13, 22	-		

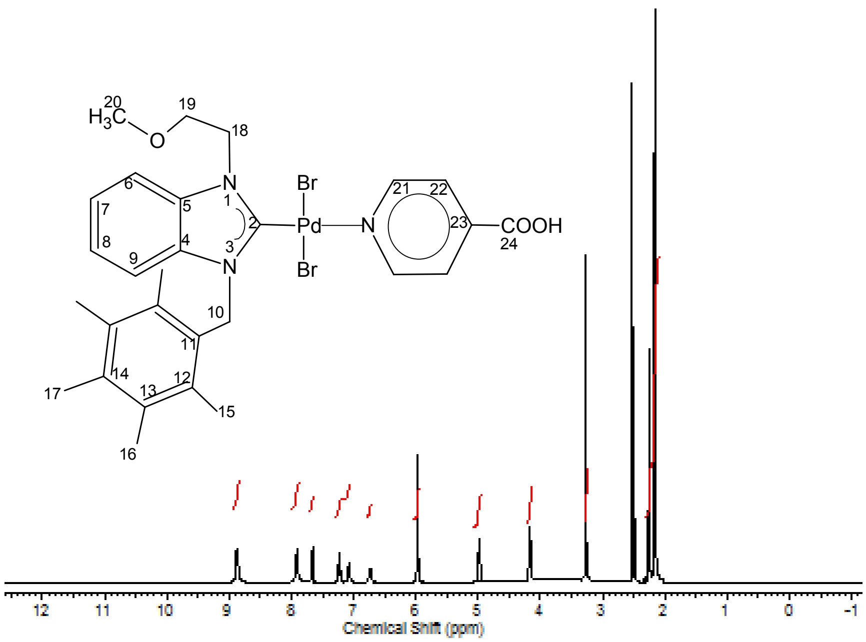


Figure 3.12 ^{1}H-NMR spectra of **6c**

Table 3.13 ^{1}H- and ^{13}C-NMR spectra of **6c**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	163.1
6, 9	6.73, 7.67 (2H, d)	8.0, 8.2	111.2, 112.4
7, 8	7.07, 7.24 (2H, t)	7.6	123.5, 123.8
10	5.97 (2H, s)	-	51.0
15, 16, 17	2.15, 2.26 (15H, s)	-	17.4, 17.7, 18.1
18	4.99 (2H, b)	-	48.7
19	4.16 (2H, t)	5.0	71.3
20	3.26 (3H, s)	-	59.1
24	-	-	165.9
21, 22	7.91, 8.87 (2H, b)		124.5, 128.6, 133.3,
4, 5, 11, 12,	-	-	134.6, 134.8, 135.6,
13,14, 23	-		136.0, 141.0, 153.5

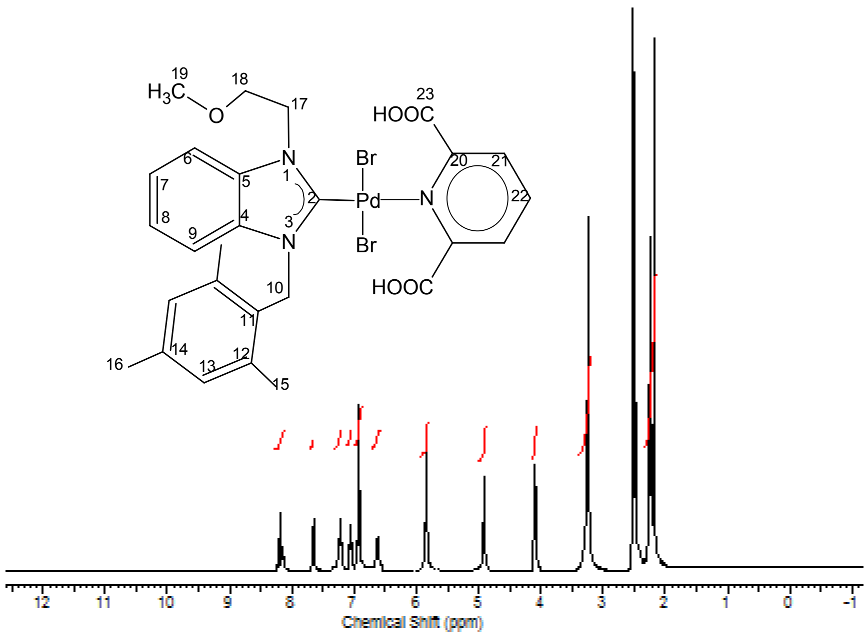


Figure 3.13 ^{1}H-NMR spectra of **7a**

Table 3.14 ^{1}H and ^{13}C-NMR spectra of **7a**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	160.5
6, 9	6.66, 7.69 (2H, d)	7.2, 8.2	111.0, 112.2
7, 8	7.09, 7.26 (2H, t)	7.6, 7.8	123.5, 123.6
10	5.87 (2H, s)	-	49.9
15	2.21 (6H, s)	-	20.8
16	2.28 (3H, s)	-	20.9
17	4.95 (2H, b)	-	48.7
18	4.12 (2H, b)	-	71.1
19	3.26 (3H, s)	-	58.7
23	-	-	165.8
13	6.96 (2H, s)	-	
21	8.24 (2H, d)	7.6	128.0, 128.1, 130.0,
22	8.18 (1H, t)	6.8	134.5, 135.6, 138.6,
4, 5, 11, 12, 14,	-	-	138.8, 140.0, 148.4
20	-	-	

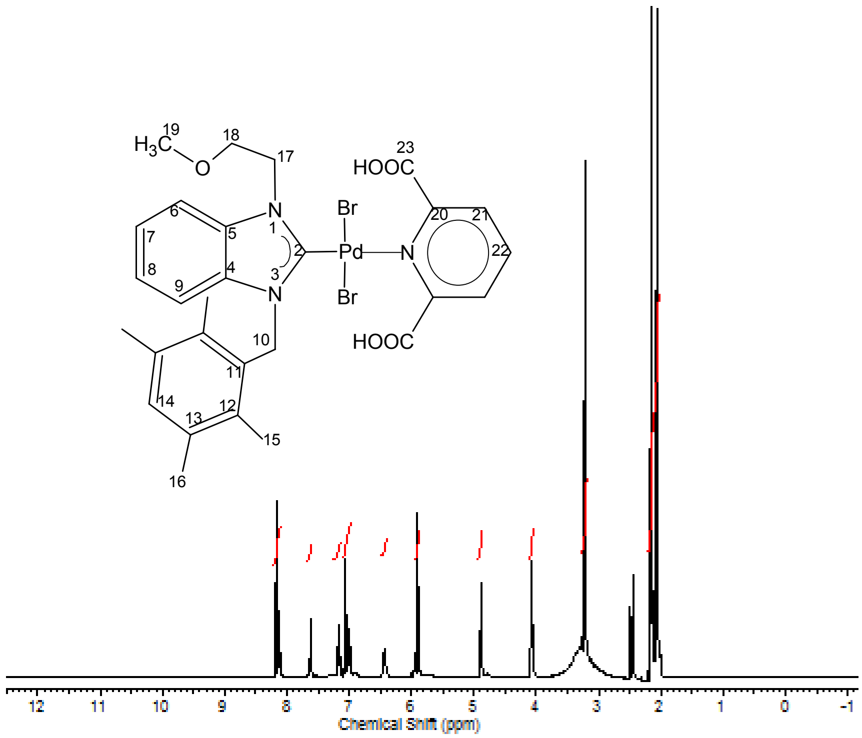


Figure 3.14 ^{1}H-NMR spectra of **7b**

Table 3.15 ^{1}H and ^{13}C-NMR spectra of **7b**

Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	160.6
6, 9	6.46, 7.65 (2H, d)	6.8, 8.4	111.2, 112.4
7, 8	7.02, 7.21 (2H, t)	7.8, 7.6	123.6, 123.9
10	5.93 (2H, s)	-	51.0
15, 16	2.09, 2.19 (12H, s)	-	16.9, 20.9
17	4.92 (2H, t)	5.4	48.6
18	4.10 (2H, t)	5.8	71.2
19	3.24 (3H, s)	-	59.1
23	-	-	166.1
14	7.08 (1H, s)	-	
21	8.21 (2H, d)	7.2	128.2, 130.8, 133.0,
22	8.13-8.17 (1H, m)	-	134.5, 134.6, 135.1,
4, 5, 11, 12, 13,	-	-	135.6, 139.9, 148.8
20	-	-	

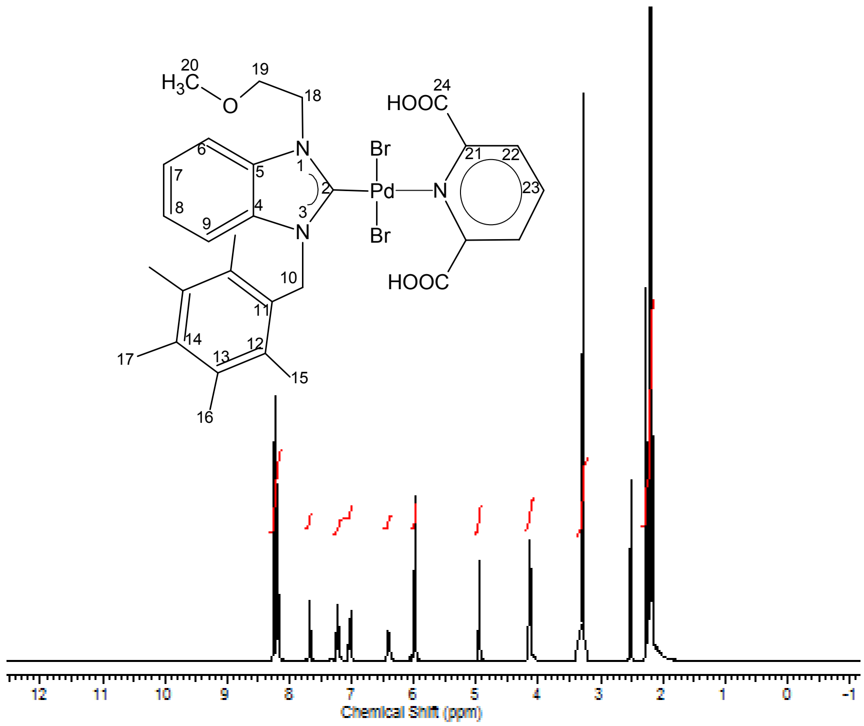


Figure 3.15 ^{1}H-NMR spectra of **7c**

Table 3.16 ^{1}H and ^{13}C-NMR spectra of **7c**

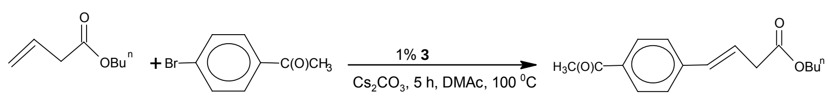
Numbers of atoms	*^{1}H NMR (δ ppm)*	*J (Hz)*	*^{13}C NMR (δ ppm)*
2	-	-	160.9
6, 9	6.37, 7.64 (2H, d)	7.6, 8.4	109.3, 110.6
7, 8	6.99, 7.19 (2H, t)	7.8	121.7, 122.0
10	5.95 (2H, s)	-	50.1
15, 16, 17	2.14, 2.17, 2.24 (15H, s)	-	15.5, 15.9, 16.1
18	4.92 (2H, t)	5.2	46.7
19	4.11 (2H, t)	5.6	69.3
20	3.24 (3H, s)	-	57.2
24	-	-	164.3
22	8.20-8.23 (2H, m)	-	126.1, 126.3, 131.5, 132.7, 132.8, 133.8, 134.4, 138.1, 147.0
23	8.13-8.17 (1H, m)	-	
4, 5, 11, 12, 13, 14, 21	- -	- -	

3.3. Catalytic Experiments

3.3.1. Heck coupling of 4-bromoacetophenone and n-butyl acrylate

Initially the catalytic tests were performed in the Heck reactions of the mono carbene-mono imeo palladium (II) bromide complexes (**3a-c**) (Table 3.17). As a base Cs_2CO_3 was the best choice and as a solvent N,N-dimethylacetamide was found to be better than other solvents. In general low yields has been observed. However, heterogenation process was carried out by immobilising one of the complexes (**3c**) with silica. In heterogenous system (**3c'**), catalytic tests were repeated for the Heck reaction. There were no significant changes in the activity.

Table 3.17 The Heck coupling reaction of 4-bromoacetophenone with n-butyl acrylate.

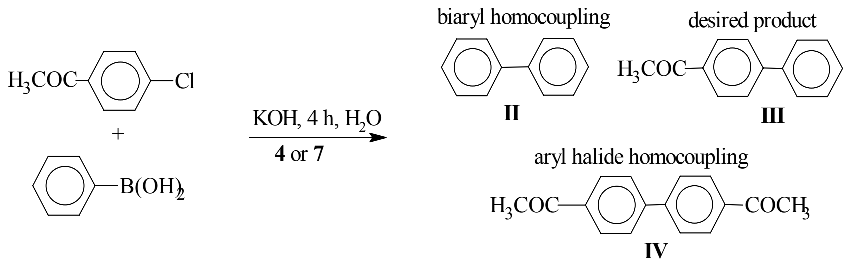


Entry	Complex	Yield
1	**3a**	15
2	**3b**	10
3	**3c**	21
4	**3c'**	17

3.3.2. Suzuki coupling of aryl halides and phenylboronic acid

We have found that the NHC ligands containing the ansymmetric substituents on the N atoms of the ring are more efficient than the symmetrical ones for C-C coupling reactions (Türkmen *et al.*, 2009). Therefore, we have chosen the NHC substituents shown in Scheme 1. First of all, we studied the influence of temperature on the distribution of the possible coupling products (**II**-**IV**) formed from *p*-chloroacetophenone-phenylboronic acid in the presence of (**4**) and (**7**) and observed that as the temperature increased the yield of desired product (**III**) also increased (Table 3.18).

Table 3.18. Effect of temperature on the distrubition of coupling by produces under Suzuki reaction conditions.

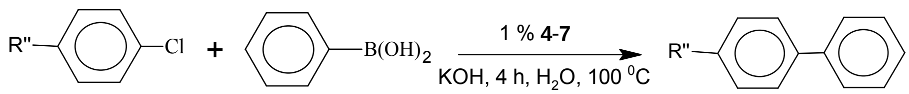


Complex	Temperature (^{0}C)	Conversion (%)	**II**(%)	**III**(%)	**IV**(%)
4a (**7a**)	25	80(83)	60(61)	14(11)	5(9)
4b (**7b**)	“	77(78)	57(59)	13(12)	4(5)
4c (**7c**)	“	82(81)	58 (63)	13(14)	8(3)
4a (**7a**)	50	87(88)	51(52)	27(30)	3(4)
4b (**7b**)	“	80(85)	55(58)	20(22)	5(3)
4c (**7c**)	“	83(88)	42(48)	32(34)	4(4)
4a (**7a**)	80	88(89)	20(21)	62(64)	4(2)
4b (**7b**)	“	90(91)	20(20)	67(66)	2(3)
4c (**7c**)	“	93(94)	13(12)	76(78)	3(3)
4a (**7a**)	100	100(100)	04(05)	94(93)	-
4b (**7b**)	“	100(100)	05(03)	91(92)	-
4c (**7c**)	“	100(100)	03(01)	94(96)	-

At room temperature biphenyl formation from the homocoupling of phenylboronic acid is a dominant reaction which gradually subsides as the temperature rises. Therefore, we set to 100 ^{0}C as the standard temperature.

In order to determine the influence of the ligands *e.i.* NHC and pyridinecarboxylic acids (L) on Suzuki reaction in neat water, coupling reaction of *p*-chloroacetophenone and phenylboronic acid was selected as a model reaction and KOH was used as the base. The yield of unsymmetrical biaryls (**III**) ranged from 81% to 96 % (Table 3.19, Entry 1).The activated and unactivated aryl chloride substrates also were treated under identical conditions (Table 3.19, Entries 2-4), to give good to excellent yields of the biaryls. The similar reactivity trends with our previous report (Türkmen *et. al.*, 2009) is in agreement with the stronger donating ability of alkyl substituents, making the donor atoms more electron-rich. Among the complexes tested, **4** and **7** gave the highest yield while the complexes **5** and **6**, with 3- and 4-pyridinecarboxylic acids gave moderate or good yields. This result implies that the COOH(K) functionality ortho to the N atom of the pyridine has some influence on the stability of active species.

Table 3.19 The Suzuki coupling reaction of aryl chlorides with phenylboronic acid.

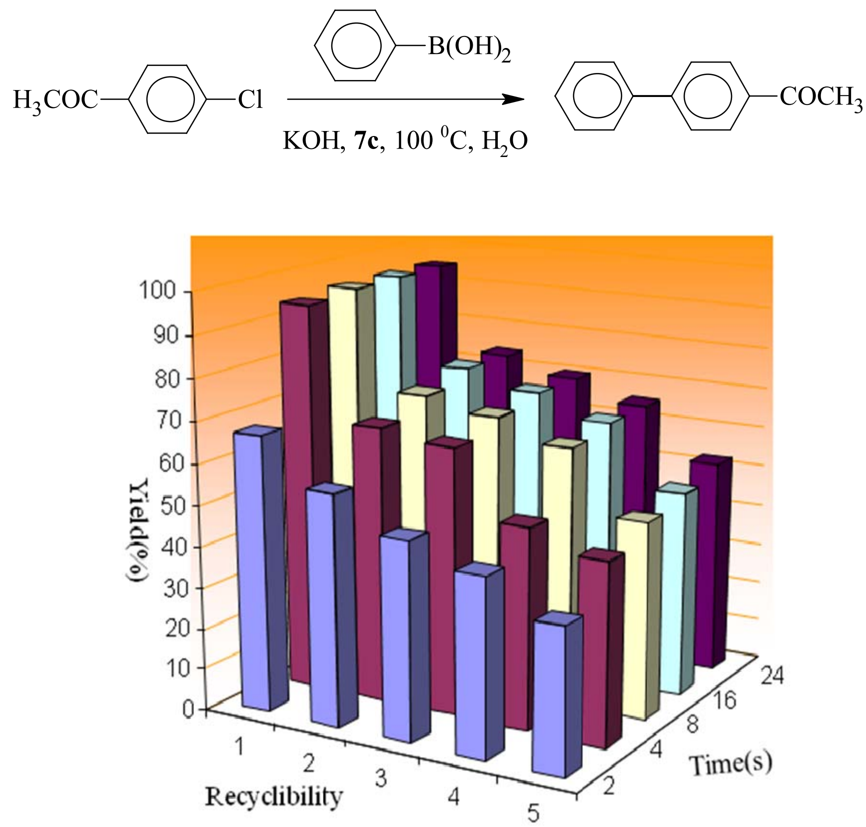


Entry	R"	Yield (%)											
		4a	**4b**	**4c**	**5a**	**5b**	**5c**	**6a**	**6b**	**6c**	**7a**	**7b**	**7c**
1	CH_3CO	92	90	93	89	81	94	87	85	88	93	91	96
3	CHO	89	87	92	82	81	84	83	83	87	91	88	92
2	CH_3	86	83	88	83	83	88	84	82	86	89	85	89
4	CH_3O	81	80	89	75	74	77	70	71	75	87	85	88

3.3.3. Catalyst Recycling

The potential recyclability of the catalysts derived from **7c** system was explored in the model cross-coupling reaction of 4-chloroacetophenone and phenylboronic acid (Figure 3.16). The reaction was carried out in water at 100 ^{0}C without any additive. After cooling to room temperature, the organic products were extracted by diethyl ether and the yields were determined by GC. The aqueous phase was then transferred to a new reaction flask for the next cycle. It was shown that the coupling reaction using 1 mol% catalyst could be reused by two cycles and the yield significantly dropped to *ca*. 52% for the forth cycle. On the other hand, the experiments with the substrate bromoacetophenone can be recycled three times with 90% yield.

Figure 3.16 Recycling of catalyst **7c**.



Precipitation of palladium black was observed during the heating of reaction mixtures which may be the main reason for the short cut in the recycling attempts. Therefore, efforts are underway to similar palladium complexes with increased steric bulk around the metal center, which should increase the thermal stability of the active species and activity of the precatalyst by facilitating the reductive elimination step of the catalytic cycle.

3.4. Conclusions

In this thesis, dimeric palladium-(NHC) complexes (**2**) were prepared and than cleaved with *N*-heterocycles such as {*N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole} and pyridine carboxylic acids. Catalytic tests were carried out for the Heck reactions of the resulting mono carbene-mono imeo palladium(II) bromide complexes (**3a-c**). Low yields has been observed. However, heterogenation process was carried out by immobilizing one of the complexes (**3c**) with silica. In heterogeneous system (**3c'**), catalytic tests were performed for the Heck coupling reactions. Very little changes were observed in activity. Therefore, immobilization in water was directed.

To render bromo bridged dimeric palladium-NHC complexes (**2a-c**) water soluble, they were cleaved with pyridinecarboxylic acids, since such catalysts have potential applications in industry. The resulting monomeric complexes (**4-7**) have been studied for their catalytic properties in the Suzuki coupling reaction of aryl chlorides and phenylboronic acid in neat water under ambient atmosphere. Low loading of catalyst (1 mol%) was necessary for the coupling without the need of any additive. The coupling 4-bromoacetophenone with $PhB(OH)_2$ gave very high yield and recyclibility. In the case of aryl chlorides, higher temperatures were required. Temperature of 100 ^{0}C decreased the formation of homo coupling by-products (II and IV) to negligible amount in neat water.

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