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GRADUATE SCHOOL OF
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(MSC THESIS)

2,6-BIS(BENZIMIDAZOL-2-YL)PYRIDINE DERIVATES AND THEIR PROPERTIES

Salih GÜNNAZ
Department of Chemistry
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Supervisor: **Prof. Dr. Bekir ÇETİNKAYA**

Bornova-İZMİR

Salih GÜNNAZ tarafından **YÜKSEK LİSANS TEZİ** olarak sunulan "**2,6-Bis(benzimidazol-2-il)piridin türevleri ve özelllikleri**" başlıklı bu çalışma E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 10.08.2007 tarihinde yapılan tez savuma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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ÖZET

2,6-BİS(BENZİMİDAZOL-2-İL)PİRİDİN TÜREVLERİ VE ÖZELLİKLERİ

Salih GÜNNAZ

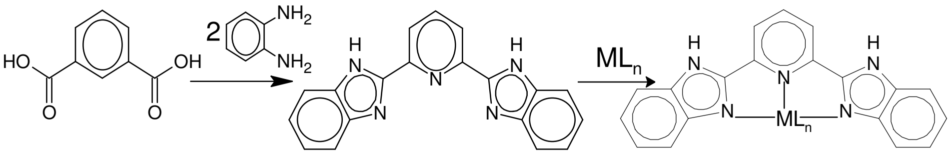
Yüksek Lisans Tezi, Kimya Anabilim Dalı

Danışman: **Prof. Dr. Bekir ÇETİNKAYA**

10.08.2007, 103sayfa

Tez üç bölümden oluşmaktadır. Birinci bölümde üç dişli triamin ligantlar üzerindeki çalışmalar özetlenmiştir. İkinci bölümde deneysel çalışmalara yer verilmiştir. Üçüncü bölümde 2,6-Bis(benzimidazol-2-il)piridin ligandı içeren Ru(II) ve Pd(II) komplekslerinin sentezi, karakterizasyonu ve katalitik incelemeler sunulmuştur.

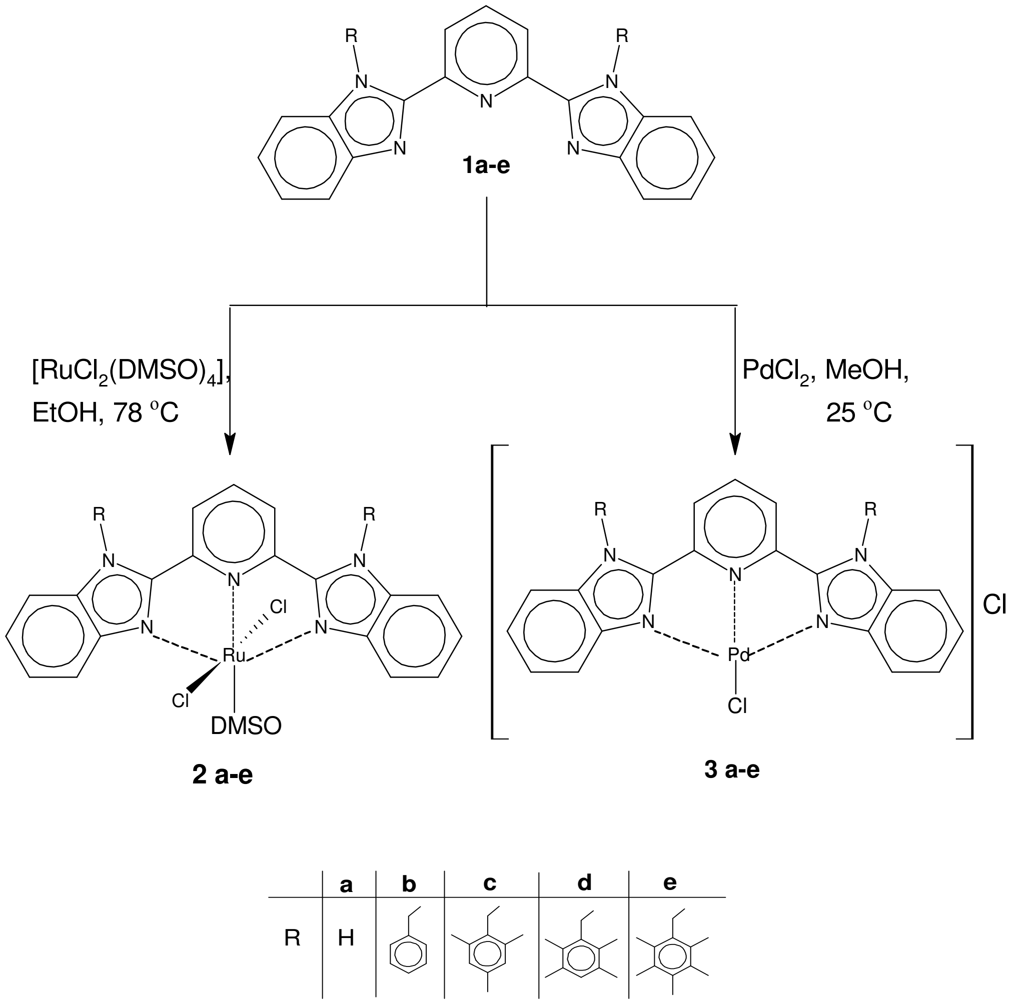
Üç dişli triamin ligantlar kompleks kararlılığını arttırmaları ve metal merkezindeki reaktiviteyi kontrol eden sterik ve elektronik parametrelerin kullanımına izin vermeleri sebebiyle geçiş metal kimyasında önemli bir rol oynamaktadır. En ilgi çekici üç dişli triamin ligantlardan biri merkezde piridin halkası içeren nötral bzimpy (**I**) ligandıdır. Geçiş metaline koordinasyon durumunda, 5-üyeli kelat yapı (**II**) böyle komplekslerde ilginç stokiyometrik ve katalitik aktiviteye sebep olabilir.



I **II**

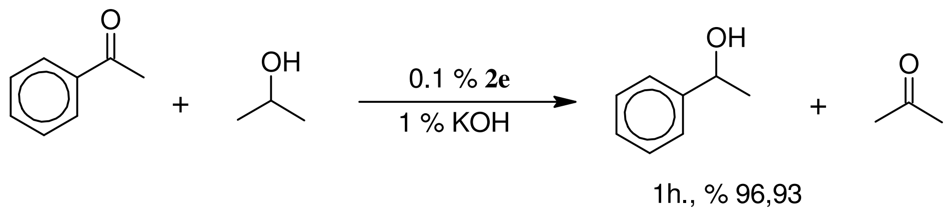
Üç-dişli 2,6-bis(benzimidazol-2-il)piridin, terpiridin veya piridindiminlere göre daha kolay hazırlandığı için, kompleksleri koordinasyon kimyasında son yıllarda sık çalışılmaya başlamıştır. Üç-dişli ligantlar N üzerinden metale (M) bağlanarak 5-üyeli iki halka oluşturduğundan kompleksleri termodinamik yönden tek-dişlilere göre daha kararlıdır. Ancak, benzimidazol azotu veya benzen halkasında hacimce kalabalık grup taşıyan türevler literatürde henüz rapor edilmemiştir.

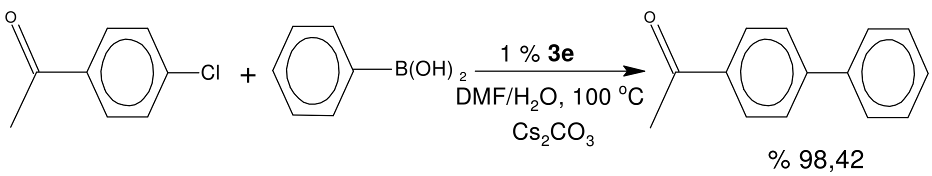
Sterik engel oluşturan komplekslerin daha iyi katalitik davranış göstermesi beklendiğinden, bu çalışmada 2,6-bis(benzimidazol-2-il) piridin iskeleti içeren Ru(II)-bzimpy ve Pd(II)-bzimpy kompleksleri sentezlenmiştir (Şema).



Şema

Ru(II)-bzimpy kompleksleri (**2a-e**) KOH ve 2-propanol varlığında asetofenonun transfer hidrojenasyonunda, Pd(II)-bzimpy kompleksleri (**3a-e**) ise Suzuki reaksiyonunda katalizör olarak test edildi. Asetofenonun transfer hidrojenasyonunda **2e** ile, Suzuki reaksiyonunda **3e** ile en iyi sonuçlar elde edilmiştir.





Anahtar kelimeler: Üçdişli triamin ligantlar, hidrojenasyon katalizörleri, asetofenonun transfer hidrojenasyonu, palladyum, C-C bağ oluşumu.

ABSTRACT

2,6-BIS(BENZIMIDAZOLE-2-YL)PYRIDINE DERIVATES AND THEIR PROPERTIES

Salih GÜNNAZ

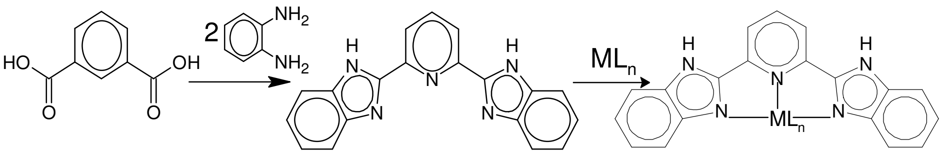
Master Thesis in Chemistry

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

10.08.2007, 103 pages

This thesis consists of three parts. The first part is a concise review of tridentate triamine ligands. In part 2, the experimental details are explained. In part 3, the synthesis, characterization and catalytic studies of Ru(II) and Pd(II) complexes containing 2,6-bis(benzimidazol-2-yl)pyridine ligand were presented.

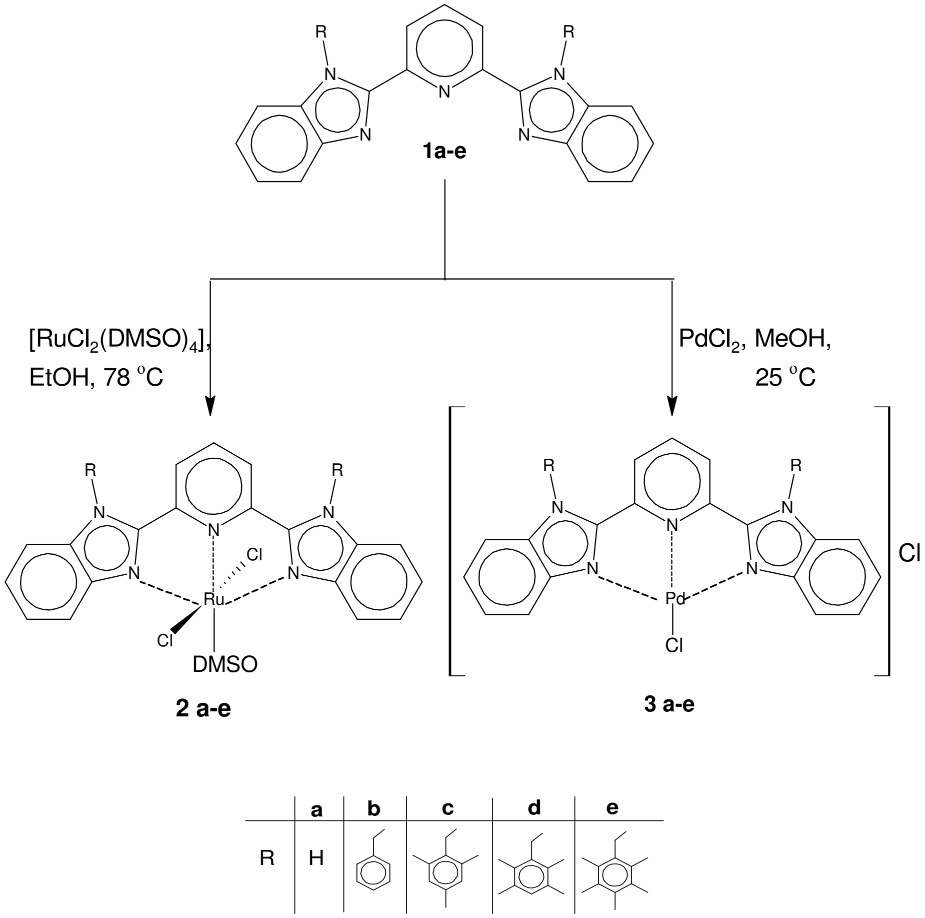
Tridentate triamine ligands play an important role in transition metal chemistry, enhancing the stability of complexes and allowing in the manipulation of steric and electronic parameters which control reactivity at the metal center. An attractive tridentate triamine ligand is a neutral bzimpy (**I**). Upon coordination to transition metal (**II**), the five membered chelate framework may confer interesting stoichiometric and catalytic reactivities on such complexes.



I **II**

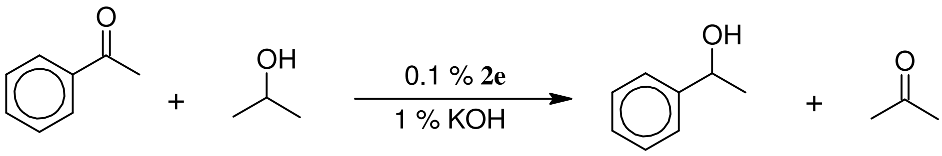
Among three-dentate ligands 2,6-bis(benzimidazol-2-yl)pyridine is more easily prepared than terpyridine or pyridindimines. Therefore, recently the complexes of such ligands have been studied more frequently. Three-dentate ligands bounds to metals (M) over N atoms to form two 5-membered rings which are thermodynamically more stable then mono-dendate ligands. However, sterically hindered groups on the benzimidazole nitrogen or benzene ring has not been reported in the literature.

In this thesis synthesis of 2,6-bis(benzimidazol-2-yl)pyridine skeletone containing Ru(II)-bzimpy and Pd(II)-bzimpy complexes are investigated since such bulky complexes are expected to show good catalytic activities (Scheme).

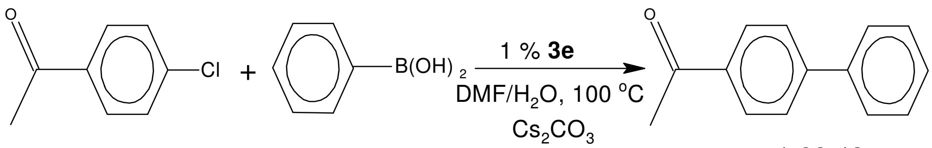

1a-e
[RuCl2(DMSO)4],
EtOH, 78 °C
PdCl2, MeOH,
25 °C
2 a-e
3 a-e
Cl
DMSO
R
a
b
c
d
e
H

Scheme

The Ru(II)-bzimpy complexes have been employed as catalyst for the transfer hydrogenation of acetophenone in the presence of KOH using 2-propanol as a hydrogen source and Pd(II)-bzimpy complexes are used as a catalyst for the Suzuki reaction. The best result in the transfer hydrogenation of acetophenone with **2e,** Suzuki reaction with **3e** were obtained.



1h., % 96,93



% 98,42

Keywords: Tridentate triamine ligands, hydrogenation catalyst, transfer hydrogenation of acetophenone, palladium, C-C bond formation.

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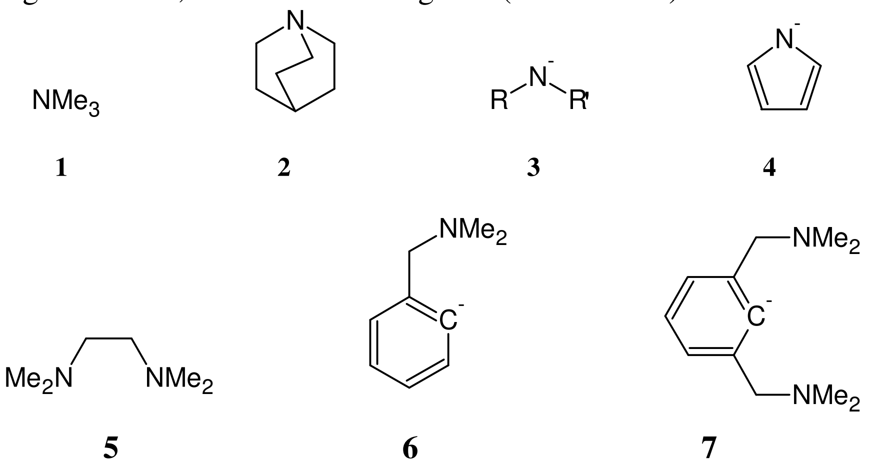
ABBREVIATIONS

Abbreviations		**Explanations**
^{13}C-NMR	:	Carbon Nuclear Magnetic Reconance Spectroscopy
^{1}H-NMR	:	Proton Nuclear Magnetic Reconance Spectroscopy
d	:	Dublet
DCM	:	Dichloromethane
dd	:	Dublets of dublet
dec.	:	Decomposition
dt	:	Dublets of triplet
GC	:	Gas Chromatography
IR	:	Infrared Spectroscopy
J	:	Coupling constant
L	:	Ancillary ligand (generally)
M	:	Transition metal (generally)
m-	:	Meta
m.p	:	Melting Point
Me	:	Methyl
Napht	:	Naphtyl
o-	:	Ortho
p-	:	Para
Ph	:	Phenyl
phen	:	1,10-phenanthroline
Py	:	Pyridine
s	:	Singlet
t	:	Triplet
X	:	Halogen (generally)

1. INTRODUCTION

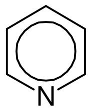
1.1 Nitrogen donors in coordination chemistry

An appropriate classification of nitrogen donors can be based on the hybridization of this atom; sp^3, sp^2 and sp. The types of compounds containing sp^3-hybridized nitrogen atoms are summarized in Scheme 1.1. Complexes with nitrogen donors containing N-H bonds are generally not suitable for most organometallic reactions as the H atom (or atoms) on coordinated nitrogen are sufficiently acidic to react with a nucleophile. Furthermore, coordinated nitrogen atoms containing nonbonding pairs of electrons are susceptible to electrophilic attack by suitable reagents. However, coordinated "nitrogen anions" also listed in Scheme 1.1. show an extensive and useful coordination chemistry, particularly when associated with sp^2-hybridized carbon atoms. The coordination chemistry of compounds containing one or several nitrogen atoms of sp^3 hybridization is dominated by substituted monoamines, diamines or triamines [Hambley *et al.,* 1994; de Bruin *et al.,* 1997; Itoh *et al.,* 1998] acting the mono-, bi- or tridentate ligands (Scheme 1.1.).



Scheme 1.1. Some nitrogen-donors with tertiary sp^3-hybridized N atoms.

In the same way, ligands containing sp^2-hybridized nitrogen atoms, particularly when the N-atom is a part of an aromatic system (see, for example Scheme 1.2.), have very extensive coordination chemistry. Also for donors of this type, a much more extensive and useful coordination chemistry is possible when they are bi- or tridentate ligands [Kirchner *et al.,* 1987; Constable and Steel, 1989, Steel, 1990].



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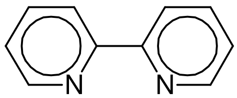

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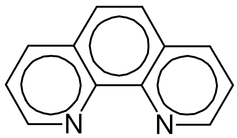

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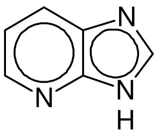

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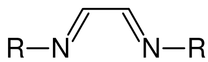

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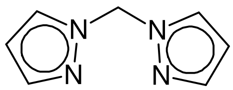

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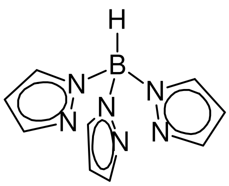

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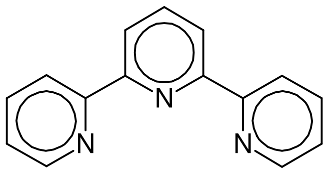

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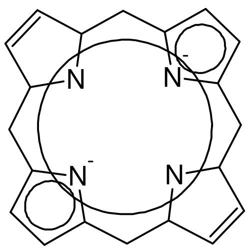

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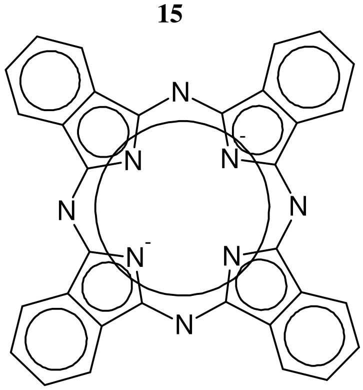

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Scheme 1.2. Some nitrogen-donors with *sp*^{2}-hybridized N atoms.

The presence of C-N and C-C double bonds in these molecules renders them susceptible to further reactions, such as nucleophilic attack or, under appropriate conditions, hydrogenation. This is particularly true for Schiff bases.

Nitriles are the only class of organic nitrogen donors with *sp* hybridization [Catsikis and Good, 1969; Roh and Bruno, 1986; Renn *et al*., 1995; van Ablada *et al*., 1995; Kukushkin *et al*., 2000]. Their main function is to be replaced by appropriate reagents as labile ligands. Furthermore, once coordinated, nitriles are quite susceptible towards nucleophilic attack.

1.1.1 The tridentate triamine ligands

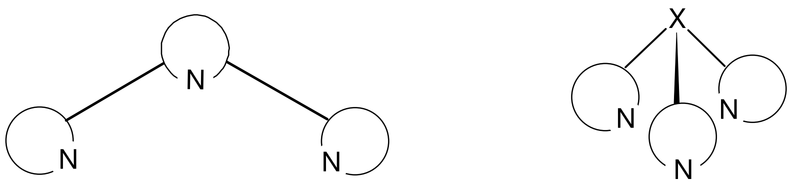
The heterocyclic nitrogenous compounds represent important ligands in the coordination chemistry of the transition metals. In particular, the ligands belonging to the family of the azines such as 2,2'-bipyridine (bipy) (**9**), 1,10-phenanthroline (phen) (**10**) and 2,2',2"-terpyridine (terpy) (**15**) and their derivatives caused an immense interest in analytic and organometallic chemistry for fifty years [Kene *et al.,* 1985; Kirchner *et al.,* 1987; Juris *et al.,* 1988; Ross *et al.,* 1989; Steel, 1990].

The nature of the nitrogenous-heterocyclic fragments coordinated to the transition metals has a significant influence on the qualities of chemical, catalytic and same physical properties of the resulting complexes. This influence is not only linked to the *s*-donor character of the present nitrogen atom in the different substituting nitrogenous, but also depends on the *p*-acceptor/donor character of the ligand. The great majority of the azine compounds are of excellent *p*-acceptors for the d orbital of the transition metals, whereas the azole compounds are rather *p*-donors. These two characters *p*-acceptor/donor lead to transfers of charge between metal and the ligand and influence the qualities of electrochemical properties of the complexes that contain such ligands.

18	**19**	**20**	**21**
pyrrole	oxazole	pyrazole	imidazole

Toward the end of 1980s, the survey of the coordination chemistry of resulting ligands to the combination of azine/azole fragments was very important, and many NN'-bidentate ligands containing the pentacyclic nitrogenous (**18-21**) were synthesized and used for the coordination chemistry [Constable and Steel, 1989]. However, the synthesis of tridentate triamine compounds constituted of one or several substituting pentacyclics nitrogenous was less developed and was now even restricted to some type.

These tridentate triamine ligands could be classified in two separate groups, of which one includes compounds of C_2 symmetry, while the other contains some tripod triamines of C_3 symmetry (Figure 1.1.).



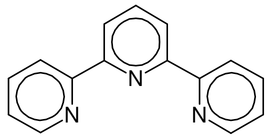
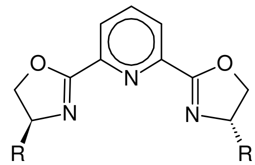
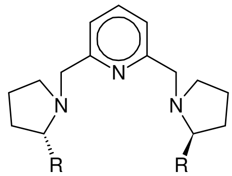
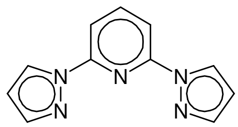
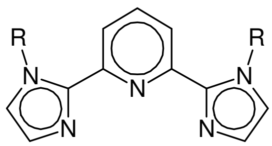
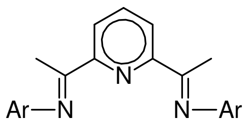
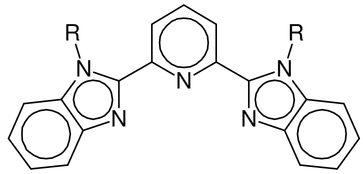
(**a**) (**b**)

Figure 1.1. Tridentate triamine ligands type (**a**) C_2 symmetry (**b**) C_3 symmetry

1.1.2. Tridentate triamine ligands in C_2 symmetry

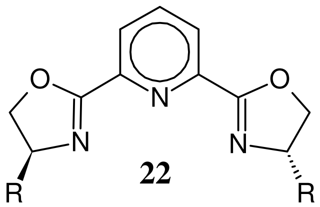
The compounds of this type are summarized on Table1.1.

Table 1.1 Tridentate triamine ligands in C_2 symmetry

C_2 **Symmetry**	
terpyridine	
bis(hydrooxazolyl)pyridine	
bis(pyrrolidinyl)pyridine	
bis(pyrazol-1-yl) pyridine	
bis(imidazol-2-yl)pyridine	
pyridine-2,6-diimine	
bis(benzimidazol-2-yl)pyridine	

1.1.2.1 The bis(hydrooxazolyl)pyridines

The synthesis of bis(hydrooxazolyl)pyridines (pybox) (**22**) and the catalytic properties of their complexes were achieved by H. Nishiyama *et al*. in 1989.



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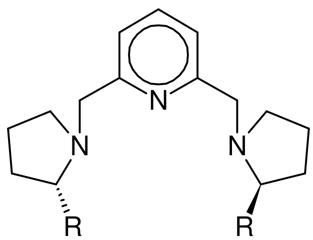
The catalytic activity and the enantioselective efficiency of the complexes containing a pybox have been demonstrated extensively for the hydrosilylation of ketones [Nishiyama *et al.,* 1989 and 1991], the cyclopropanation of alkenes [Small *et al.,* 1998], the epoxydation of alkenes [Nishiyama *et al.,* 1997] as well as Diels-Alder reactions [Evans *et al.,* 1995] or Michael reactions [MacMillan *et al*., 1997; Evans *et al*., 1997 and 1999; Burgey *et al*., 1999].

1.1.2.2 The bis(pyrrolidinyl)pyridines

In the beginning of the 1990s, some bis(pyrolidinyl)pyridines (**23a-c**) have been synthesized and studied by K. Bernauer *et al*., [Bernauer and Gretilla, 1989]. The copper complexes of these compounds served as asymmetric catalysts for the enantioselective synthesis of amino acids such as phenylalanine, serine or threonine [Bernauer *et al*., 1993].

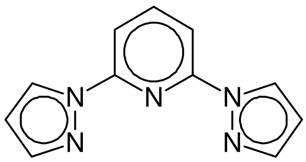


	R
a :	CH_2OH
b :	CH_2OCH_3
c :	CH_2OBz

23a-c

1.1.2.3 The bis(pyrazolyl)pyridines

The coordination chemistry of the bis(pyrazolyl)pyridines is again enough uncharted although these ligands are analogs of the terpy (**15**). The bis(pyrazolyl)pyridines exist under two types: The bis(pyrazol-1-yl)pyridines (**24**) and the bis(pyrazol-3-yl)pyridines (**25**) that differ by the position of the atom of the pyrazole joining the pyrazole and pyridine units.



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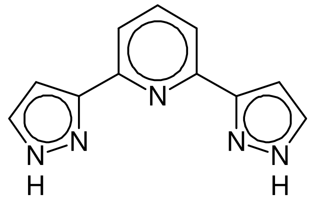
bis(pyrazol-1-yl)pyridine



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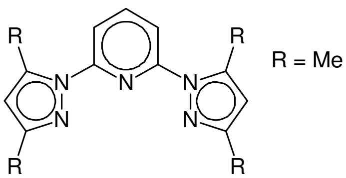
bis(pyrazol-3-yl)pyridine

The compounds of bis(pyrazol-1-yl)pyridine (**25**) are relatively easy to synthesize [Jameson *et al.,* 1990] and represent a good alternative for the coordination chemistry of terpy for which the synthesis of derivatives is relatively arduous. Jameson *et al.* synthesized this type compounds for the first time and got the first complexes in 1989.



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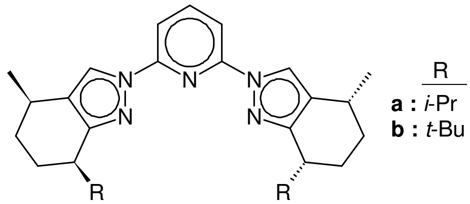

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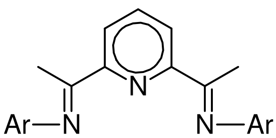
The catalytic potential of rhodium and copper complexes containing **24** for the asymmetric cyclopropanation of the styrene was showed by Christenson *et al.* in 1995. The transfer hydrogenation of ketones was efficiently carried out with a ruthenium complex bearing

2,6-bis(3,5-dimethylpyrazol-1-yl) pyridine (**24**), i.e. [$RuCl_2(PPh)_3$(**24**)], in 2-propanol at 82 °C by Deng H. *et al.* in 2005. The qualities of very interesting electrochemical properties as well as the catalytic applications of these complexes are the innovatory points of the development of the coordination chemistry of these compounds.

1.1.2.4 The pyridine-2,6-diimines

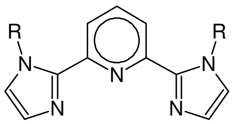


pydim

Although many pydim-based transition metal complexes have been reported (pydim is pyridine-2,6-diimine; Small & Brookhart, 1998, 1999; Britovsek *et al.*, 1999; Gibson & Spitzmesser, 2003; Nakayama et al., 2005; Humphries *et al.,* 2005), examples of the related Ru complexes are scarce (Çetinkaya et al., 1999; Bianchini & Lee, 2000; Dias *et al.*, 2000; Seçkin *et al.*, 2004; Dayan & Çetinkaya; 2005). The structural feature of five-coordination results in the formation of coordinatively unsaturated Ru^{II} complexes containing the pydim ligand and makes these complexes interesting from the viewpoint of potential application in homogeneously Ru^{II}-catalyzed reactions. The presence of a labile ligand makes these complexes potentially interesting as precursors for the synthesis of a variety of Ru^{II} complexes of the type [$RuCl_2$(pydim)L], where L is a neutral ligand. For example, [$RuCl_2$(pydim)(CH_3CN)] compounds (Ar = 2,6- $Me_2C_6H_3$) exhibit efficient activity for the epoxidation of cyclohexane (Çetinkaya *et al.*, 1999).

1.1.2.5 The bis(imidazolyl)pyridines

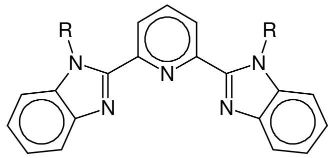
For thirty years, the compounds containing one or several imidazole units play an important role in the coordination chemistry of the specific transition metals in the biological systems (Cu, Fe and Zn,) [McKee *et al.,* 1981; Strothkamp *et al.,* 1982; Nishida *et al.,* 1985; Guss *et al.,* 1986].



R
a : H
b : Me

26a-b

bis(imidazole-3-yl)pyridine



R
a : H
b : Me

27a-b

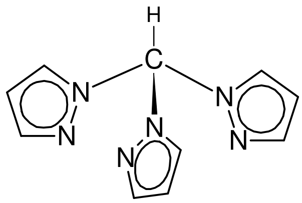
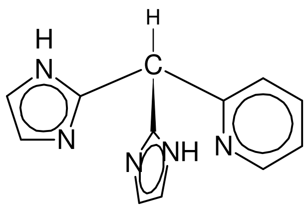
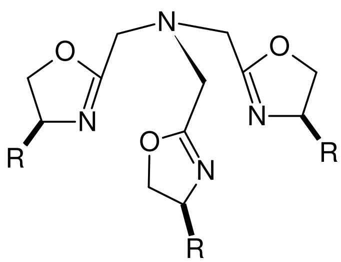
bis(benzimidazol-2-yl)pyridine

In particular, the copper complexes containing some bis(benzimidazolyl)pyridines (**27a**) are recognized as being of good models for the survey of the reactivity of the oxygen in the living organisms (transportation of the oxygen, decrease of the oxygen) [Sorrell *et al.*,1985; van Rijn *et al.*,1987]. This mimetism of biological systems was the origin of the development of the coordination chemistry of this type of compounds with transition metals such as manganese [Shuangxi *et al.*, 1992], iron [Linert *et al.*, 1994; Boca *et al.*, 1997; Carina *et al.*, 1998], cobalt [Shklover *et al.*, 1994] and the ruthenium [Haga *et al.*, 1996; Arakawa *et al.*, 1996].

1.1.3 Tridentate triamine ligands in C_3 symmetry

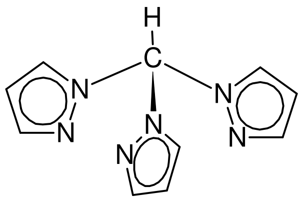
The compounds of this type are summarized on Table1.2.

Table 1.2 Tridentate triamine ligands in *C_3* symmetry

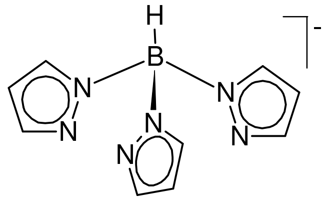
***C_3* Symmetry**	
tri-pyrazoles	
tri-imidazoles	
tri-hydrooxazolines	

1.1.3.1 The tris-pyrazoles

The coordination chemistry of the tris-pyrazoles especially developed for the tris(pyrazol-1-yl)methanes (**28**) [Esteruelas *et al.,* 1989; Fajardo *et al.,* 1993; Field *et al.,* 2001] and the tris(pyrazol-1-yl)hydroborates (**29**) [Trofimenko *et al.,* 1993; Reger, 1996; Pellei *et al.,* 2000]. The catalytic activity of the copper complex [Cu(C_2H_4)(**30**)] [Perez, *et al.,* 1993] for the cyclopropanation of styrene encouraged the synthesis of complexes containing tris-pyrazoles [Gemel *et al.,* 1997; Teuma *et al.,* 2001; Santos *et al.,* 2001].



28



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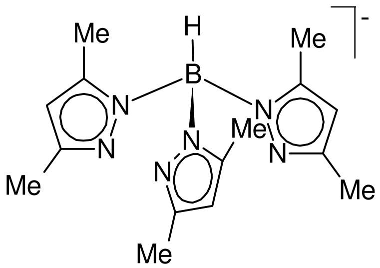
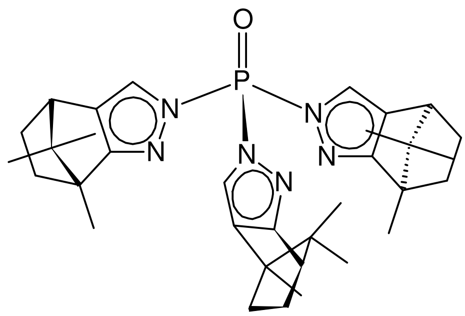


30

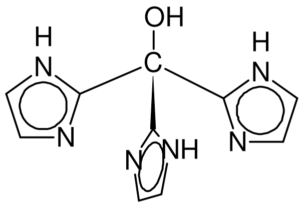


31

The synthesis of chiral derivatives as tris-{(4*R*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-2-indazolyl}phosphineoxyde (**31**) [Watson *et al.,* 1991], and the catalytic activity for the asymmetric cyclopropanation of alkenes of the corresponding copper complex fostered the development of the synthesis of these complexes [Tokar *et al.,* 1992, LeCloux and Tolman, 1993; LeCloux *et al.,* 1994].

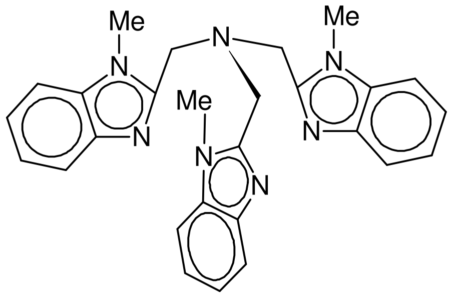
1.1.3.2 The tris-imidazoles

The tris(imidazolyl)pyridines have essentially been used for the synthesis of copper complexes for the survey of the role of metalo-enzymes in the living organism [Hendriks *et al.*, 1982; Tolman *et al.*, 1989].



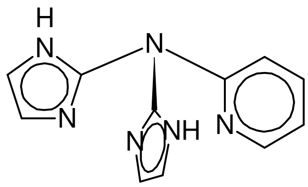
32

tris(imidazol-2-yl)methanol



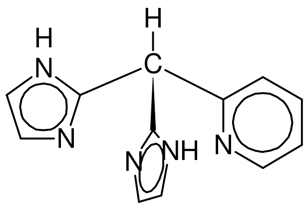
33

tris(methyl-benzimidazol-2yl-methyl)amine



34

bis(imidazol-2yl)pyridyl-amine



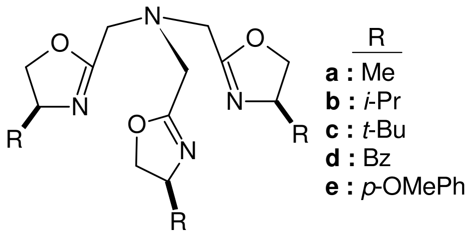
35

bis(imidazol-2-yl)pyridyl-methane

The coordination chemistry of these tri-imidazole tripods is relatively poor [Elgafi *et al.,* 1997] contrary to their analogs bis-imidazoles: bis(imidazolyl)pyridyl-amines (**34**) and bis(imidazolyl) pyridyl-methanes (**35**) [Brown *et al.,* 1990; Byers *et al.,* 1990; Wei *et al., 1994*].

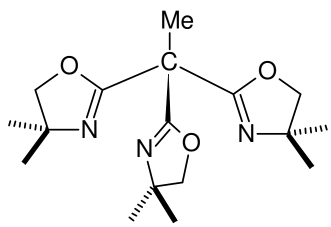
1.1.3.3 The tris-hydrooxazolines

The big catalytic potential of the pybox complexes encouraged the synthesis of the tris-hydrooxazolines. Thus, the first compound, the tris(methylhydrooxazolylmethyl)amine (**36a**) was synthesized by Sorrell *et al.* who got a dimer complex of the Cu (I) with this ligand in 1993.



36a-d

tris(R-hydrooxazolylmethyl)amine



37

tris(Me_2-hydrooxazolyl)ethane

Thereafter, K. Kawasakis *et al.* synthesized a wide variety of tris(hydrooxazolyl)amines and showed the catalytic power of their copper complexes for the asymmetric allylic oxidation [Kawasaki *et al.,* 1995 and 1997]. The tris(Me_2-hydrooxazolyl)ethane (**37**) was synthesized by Bellemin-Laponnaz and Gade in 2002. The copper complex obtained from this ligand was a tetrameric complex; [Cu_4(**37**)$_4$][BF_4] [Bellemin-Laponnaz and Gade, 2002].

1.2 Coupling Reactions

A coupling reaction or oxidative coupling in organic chemistry is a catch-all for a range of reactions in Organometallic chemistry where two hydrocarbon radicals are coupled with the aid of a metal containing catalyst.

Coupling reactions should be divided into two main classes, there are the cross couplings in which two different molecules react to form one new molecule. For example the nickel chloride catalyzed reaction of an aryl magnesium halide with an aryl halide to form a biaryl.

A common metal in this type of chemistry is palladium often added in the form of tetrakis(triphenylphosphine) palladium(0). This is an air sensitive compound which is very good for coupling unsaturated halogen compounds with organometallics such as tributyltin hydride.

While many coupling reactions involve reagents that are extremely susceptible to presence of water or oxygen, it is unreasonable to assume that all coupling reactions need to be performed with strict exclusion of water. It is possible to perform palladium based coupling reactions in aqueous solutions using the water soluble sulfonated phosphines made by the reaction of triphenyl phosphine with sulfuric acid. In general the oxygen in the air is more able to disrupt coupling reactions, this is because many of these reactions occur via unsaturated metal complexes which do not have 18 valence electrons. For example in nickel and palladium cross couplings a zerovalent complex with two vacant sites (or labile ligands) reacts with the carbon halogen bond to form a metal halogen and a metal carbon bond. Such a zerovalent complex with labile ligands or empty coordination sites is normally very reactive towards oxygen.

Table 2.3 Types of Coupling Reactions

Reaction	Year	Reactant A		Reactant B		Homo/ Cross	Catalyst
Wurtz reaction	1855			R-X	sp^3	Homo	Na
Glaser coupling	1869			R-X	sp	Homo	Cu
Ullmann reaction	1901			R-X	sp^2	Homo	Cu
Gomberg-Bachmann reaction	1924			$R\text{-}N_2X$	sp^2	Homo	
Cadiot-Chodkiewicz coupling	1957	Alkyne	sp	R-X	sp	Cross	Cu
Castro-Stephens coupling	1963	R-Cu	sp	R-X	sp^2	Cross	
Kumada coupling	1972	R-MgBr	sp^2, sp^3	R-X	sp^2	Cross	Pd or Ni
Heck reaction	1972	Alkene	sp^2	R-X	sp^2	Cross	Pd
Sonogashira coupling	1973	Alkyne	sp	R-X	sp^3 sp^2	Cross	Pd and Cu
Negishi coupling	1977	R-Zn-X	sp^2	R-X	sp^3 sp^2	Cross	Pd or Ni
Stille Cross coupling	1977	$R\text{-}SnR_3$	sp^2	R-X	sp^3 sp^2	Cross	Pd
Suzuki reaction	1979	$R\text{-}B(OR)_2$	sp^2	R-X	sp^3 sp^2	Cross	Pd
Hiyama coupling	1988	$R\text{-}SiR_3$	sp^2	R-X	sp^3 sp^2	Cross	Pd
Buchwald-Hartwig reaction	1994	$R_2N\text{-}SnR_3$	sp	R-X	sp^2	Cross	Pd

1.2.1 Wurtz reaction

The Wurtz reaction is a coupling reaction in organic chemistry, organometallic chemistry and recently inorganic main group polymers where by two alkyl halides are reacted with sodium to form a new carbon-carbon bond:

$2R\text{-}X + Na \rightarrow R\text{-}R + 2Na^{+}X^{-}$

This reaction involves the radical species R•.

Mechanism: One electron from sodium is transferred to the halogen to produce a sodium halide and an alkyl radical.

$R\text{-}X + Na \rightarrow R\bullet + Na^{+}X^{-}$

The alkyl radical then accepts an electron from another sodium atom to form an alkyl anion and the sodium becomes cationic.

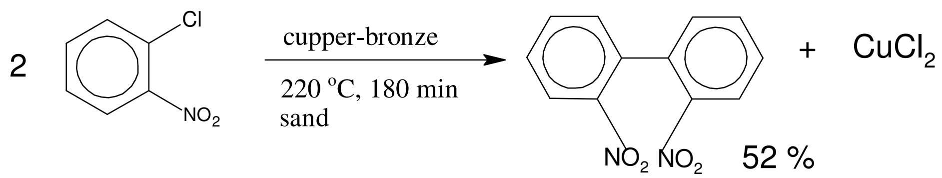
$R\bullet + Na \rightarrow R^{-}Na^{+}$

The alkyl anion then displaces the halide in an S_N2 reaction, forming a new carbon-carbon covalent bond.

$R{-}Na^{+} + R\text{-}X \rightarrow R\text{-}R + Na^{+}X^{-}$

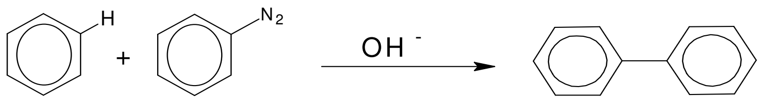
1.2.2 Ullmann reaction

The Ullmann reaction is a coupling reaction between aryl halides with copper. The reaction is named after Fritz Ullmann. A typical example is the coupling of *o*-chloronitrobenzene to 2,2'-dinitrobiphenyl with a copper - bronze alloy.



1.2.3 Gomberg-Bachmann reaction

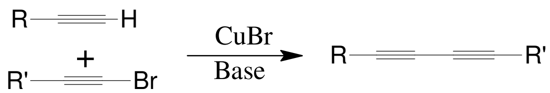
The Gomberg-Bachmann reaction is an aryl - aryl coupling reaction via a diazonium salt.



The arene compound (here benzene) is coupled with base with the diazonium salt to the biaryl . Many aromats have been tested but yields are generally low (less than 40%) given the many side-reactions of diazonium salts.

1.2.4. Cadiot-Chodkiewicz coupling

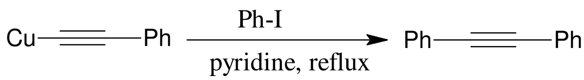
The Cadiot-Chodkiewicz coupling in organic chemistry is a coupling reaction between a terminal alkyne and a haloalkyne catalyzed by a copper(I) salt such as copper(I) bromide and an amine base . The reaction product is a di-acetylene or di-alkyne.



The reaction mechanism involves deprotonation by base of the acetylenic proton followed by formation of a copper(I) acetylide. A cycle of oxidative addition and reductive elimination on the copper center then creates a new carbon carbon bond.

1.2.5 Castro-Stephens coupling

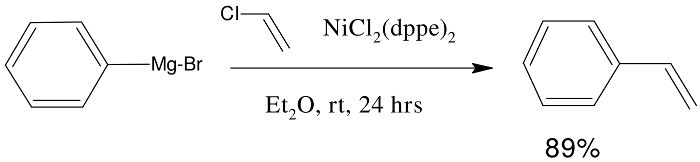
The Castro-Stephens Coupling is a cross coupling reaction between a Copper(I) acetylide and an aryl halide forming a disubstituted alkyne and a copper(I) halide. A typical reaction:



1.2.6 Kumada coupling

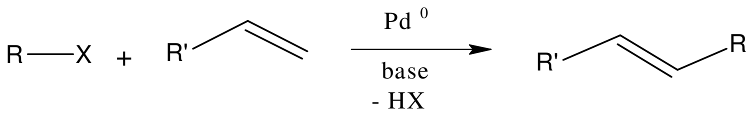
A Kumada coupling is a cross coupling reaction in organic chemistry between a alkyl or aryl Grignard reagent and an aryl or vinyl halocarbon catalysed by nickel or palladium. This reaction is relevant to organic synthesis because it gives access to styrene compounds.

The first report by the Kumada group described the reaction of a Grigard reagent for instance phenylmagnesium bromide with an aryl or vinyl chloride such as vinyl chloride to the coupled product (styrene) catalyzed by a nickel chloride with two dppe ligands ($NiCl_2dppe_2$):



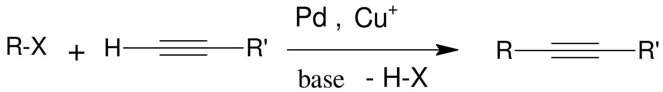
1.2.7 Heck reaction

The Heck reaction is the chemical reaction of an unsaturated halide (or triflate) with an alkene and a strong base and palladium catalyst to form a substituted alkene.



1.2.8 Sonogashira coupling

Sonogashira coupling is a coupling reaction of terminal alkynes with aryl or vinyl halides.



X= I, Br, Cl

R= Ar, Alkenyl

1.2.9 Negishi coupling

The Negishi coupling is a cross coupling reaction in organic chemistry involving an organozinc compound, an organic halide and a nickel or palladium catalyst creating a new carbon-carbon covalent bond.

$$R{-}X + R'{-}Zn{-}X' \longrightarrow R{-}R'$$

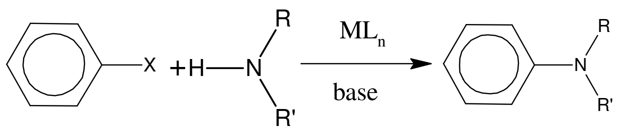
1.2.10 Stille reaction

The Stille reaction is a chemical reaction coupling an organotin compound with a sp^3 hybridized organic halide catalyzed by palladium. The reaction is widely used in organic synthesis.

$$R{-}Sn(R)_3 + R'{-}X \longrightarrow R{-}R' + X{-}Sn(R)_3$$

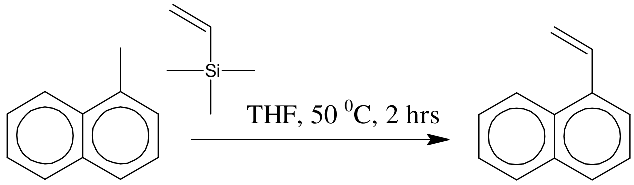
1.2.11 Buchwald-Hartwig reaction

The Buchwald-Hartwig reaction in its original scope is an organic reaction describing a coupling reaction between an aryl halide and an amine in presence of base and a palladium catalyst forming a new carbon-nitrogen bond.



1.2.12 Hiyama coupling

Hiyama coupling is a cross coupling reaction of organosilanes with organic halides or triflates.



1.2.13 Suzuki reaction

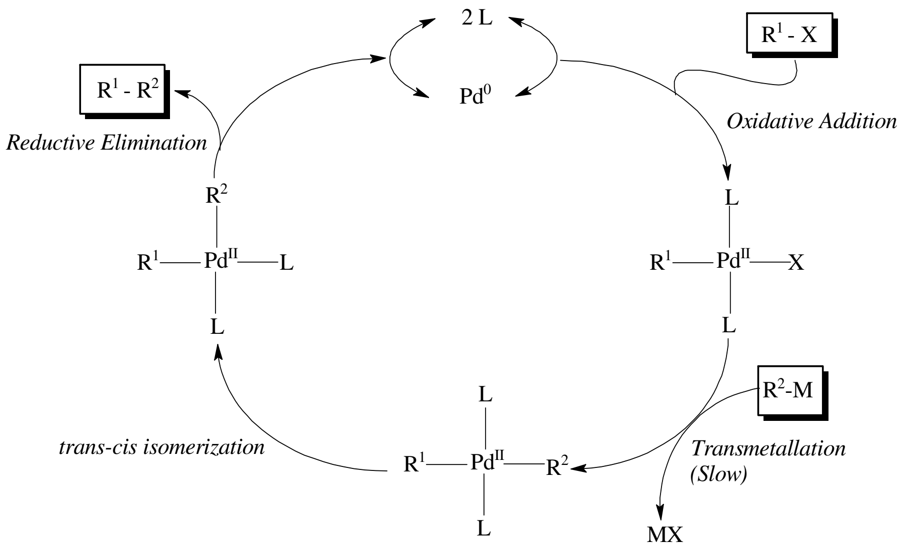
The Suzuki reaction is the organic reaction of an aryl- or vinyl-boronic acid with an aryl- or vinyl-halide catalyzed by a palladium(0) complex. It is widely used to synthesize poly-olefins, styrenes, and substituted biphenyls. Several reviews have been published.

$$R_1\text{—}BY_2 + R_2\text{—}X \xrightarrow[\text{Base}]{\text{catalyst}} R_1\text{—}R_2$$

The reaction also works with pseudohalides, such as triflates instead of halides, and also with boron-esters instead of boronic acids.

Relative reactivity: R_2-I > R_2-Br >> R_2-Cl

The mechanism of the Suzuki coupling reactions consists of four main steps (Scheme 1.3) (Moreno-Manas *et al.*, 1996): Oxidative addition of aryl halides to palladium catalyst; 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 1.3 General mechanism of Suzuki coupling reactions

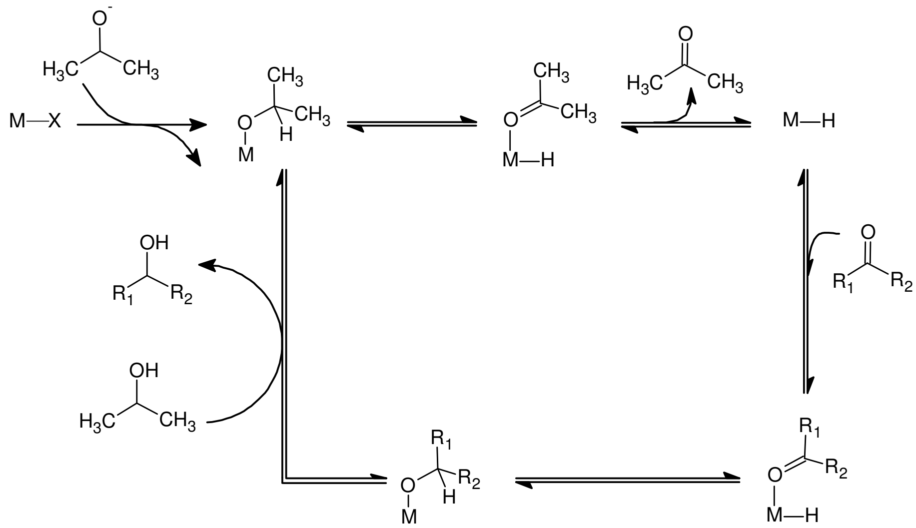
1.3 Hydrogenation

Hydrogenation and transfer hydrogenation of unsaturated compounds are among the most important synthetic reactions in view not only of academic interest but also of industrial significance due to operational simplicity, environment-friendliness, and economics [Rylander, 1979; Hudlicky, 1984 and 1996]. A hydrogen donor such as molecular hydrogen, alcohol, formic acid is catalytically activated by appropriate metals or metal complexes so that two hydrogen atoms are delivered to unsaturated bonds to give the corresponding reduction products. The discovery of RuO_2 [Behr *et al*., 1946; Barkdoll *et al*., 1953] and $RuCl_2(PPh_3)_3$ [Evans *et al*., *1965*] as selective hydrogenation catalysts provided an impetus to the development of Ru-based catalysts. Now, a number of Ru compounds are known to reduce, both in homogeneous and heterogeneous phases, a variety of substrates including unfunctionalized or functionalized olefins, ketones and aldehydes, other carbonyl compounds, imines, nitriles, and nitro compounds [Naota *et al*., 1998; Bennett and Matheson, 1982]. This section reviews Ru-tridentate triamine ligands catalyzed transfer hydrogenation by classifying the substrates into ketones.

1.3.1 Transfer hydrogenation of ketones

Transfer hydrogenation of ketones is catalyzed by a variety of Ru complexes, including Ru-tridentate triamine ligands. 2-Propanol [Morrison and Mosher, 1971; Zassinovich *et al*., 1992; Graauw *et al.,* 1994; Gladiali and Mestroni, 1998; Chaloner *et al., 1994*] and formic acid [Murahashi, 2004] are most preferably used as hydrogen donors, but methanol, tetrahydrofuran, and tetrahydronaphthalene are also utilized [Imai *et al.,* 1976]. The addition of a strong base in the reaction using an alcoholic hydrogen donor increases the reactivity, because the time required to attain equilibrium between the ketonic substrate and the alcoholic product is shortened. The equilibrium position is highly dependent on the concentration of the substrate and the reduction potential difference between the two alcohols. The use of formic acid or its salt makes the reaction irreversible by the liberation of CO_2, thus increasing the efficiency. Transfer hydrogenation is a simple operation that does not require special apparatus, and may also prefer carbonyl-selective reduction.

As illustrated in Scheme 1.4, aromatic ketones are reduced in high yields in an alkaline base containing 2-propanol by use of divalent Ru complexes possessing nitrogenous ligands [Zassinovich *et al.,* 1992].

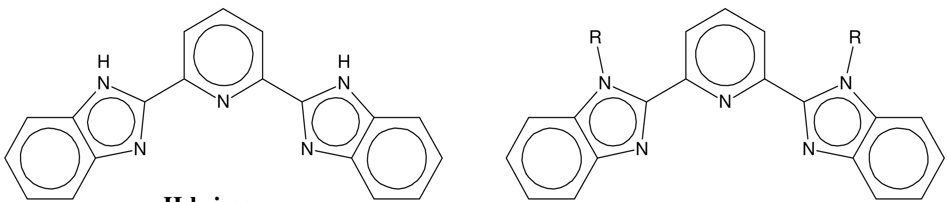


Scheme 1.4 Hydride mechanism in transfer hydrogenation

1.4. Aim of the study

Most common tridentate triamine ligands (NΛNΛN) with C_2 symmetry are compiled in Table 1.1. The coordination chemistry of these ligands are analogs of the terpy (15), derivates of which are rather difficult to synthesize. On the other hand, the compounds of 2,6-bis(benzimidazol-2-yl)pyridines (bzimpy) are relatively easy to synthesize and represents a good alternative for the coordination chemistry of terpy.

Prototype 2,6-bis(benzimidazol-2-yl)pyridine (H_2bzimpy) has been explored as a potential complexing agent. Furthermore, chromium (III) and zirconium (IV) complexes were found to be efficient polymerization catalyst for various alkenes in the presence of methylaluminoxane MAO. However, the complexes with N-alkyl substituents have not been investigated.



H_2bzimpy

Because of the above reasons, the synthesis and catalytic potential of second row transition metal (mainly ruthenium (II) and palladium (II)) complexes containing H_2bzimpy and bzimpy have been exploited in this study.

2. EXPERIMENTAL

Reactions involving air-sensitive components were performed by using Schlenk-type flask 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, methanol, toluene, diethylether, pentane), P_2O_5 (dichloromethane).

Reagents: Toluene, dichloromethane, and ethanol (Merck), pentane, diethylether, 2-propanol and methanol (J.T. Baker), $RuCl_3.3H_2O$ (Johnson and Mathey), bzimpy was synthesized according to the literature (Addison et al., 1981) 2,4,6-trimethylbenzyl chloride Alfa Aesar, 2,3,5,6-tetramethylbenzyl bromide, 2,3,4,5,6-pentamethylbenzyl bromide were prepared according to literature (van der Made, 1993). Polyphosphoric acid (PPA) is most conveniently used by generating it. Approximately 25 mL is prepared by mixing 18g P_2O_5 and 10g %85 H_3PO_4. The reagents are stirred at 100^{o}C under a dry atmosphere until a homogenous, clear viscous liquid has formed. Tpically this takes around 24h.

Instruments: ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian 400 MHz spectrometer. Melting points were determined by Electro Thermal melting point detection apparatus. The measurements for catalytic experiments were performed with Agillent 6890N GC system (Thermo-Finnigan on a HP-5 capillary column and with a FID detector) in Ege University, Faculty of Science- Department of Chemistry.

2.1. Synthesis of Ligands

2.1.1. Synthesis of 2,6-Bis(2-benzimimidazolyl)pyridine, 1a.

Compound **1a** was prepared by modification of the method of the published procedure [Addison et al., 1981].

Pyridine-2,6-dicarboxylic acid (3,35 g; 20 mmoles) was stirred with o-phenylendiamine (4,7 g; 44 mmoles) in PPA (50 mL) at ca. 230° for 4 hours. The colored melt was poured into 500 mL of vigorously stirred cold water. The bulky blue-green precipitate was collected by filtration and then treated with hot %10 aqueous Na2CO3 solution was filtered off, dissolved in hot MeOH (~500 mL). Upon colling, needle light-brown and pinkish crystalls were filtered off and recyrstallized from hot MeOH using decolorizing carbon to obtain white needle crystalls. Yield: 9,9 g; 80%, m.p.: 338-340 °C.

The ligands **1b-1e** were prepared in high yields via-N-alkylation of **1a** in acetone at 60 °C.

2.1.2. Synthesis of 2,2'-pyridine-2,6-diylbis(1-benzyl-1H-benzimidazole), 1b.

2,6-Bis(2-benzimimidazolyl)pyridine (0,5 g; 1,6 mmoles) and KOH (0,1885 g; 3,375 mmoles) were dissolved in acetone. The mixture was stirred and heated under reflux for 1 hour. Then, benzyl chloride (0,4 mL; 3,2 mmoles) was added and kept on refluxing for 6 hours. The volatiles were removed under vacuum and then the residue was dissolved with DCM (10 mL) and filtered with cannula. Diethyl ether (20 mL) was added to the solution. Yellow crystals obtained were filtered and dried under vacuum. Yield: 0,65 g; 83%, m.p.:240-242 °C.

2.1.3. Synthesis of 2,2'-pyridine-2,6-diylbis[1-(mesitylmethyl)-1H-benzimidazole], 1c.

2,6-Bis(2-benzimimidazolyl)pyridine (0,5 g; 1,6 mmoles) and KOH (0,1885 g; 3,375 mmoles) were added in toluene and stirred at room temperature for 1 hour. Then 2,4,6-trimethylbenzyl chloride (0,542 g; 3,2 moles) added into mixture and refluxed for 1 day. After cooling the toulen phase filtered with cannula and toluene was removed by distillation and the remaining yellow viscous liquid was treated with diethylether for 4 hours. Obtained orange precipitate were filtered and dried under vacuum. Yield: 0,63 g; 68%, m.p.:248-250 °C.

2.1.4. Synthesis of 2,2'-pyridine-2,6-diylbis[1-(tetramethylbenzyl)-1H-benzimidazole], 1d.

2,6-Bis(2-benzimimidazolyl)pyridine (171 mg; 0,55 mmoles) and KOH (65 mg; 1,16 mmoles) were dissolved in acetone. The mixture was stirred and heated under reflux for 1 hour. Then, tetramethylbenzyl bromide (250 mg; 1,1 mmoles) added and kept on refluxing for 8 hours. The volatiles were removed under vacuum and then the residue was dissolved with DCM (5 mL) and filtered with cannula. Hexane (10 mL) was added to the solution and the solution was left in deep-freeze for 1 day. Obtained white crystals were filtered and dried under vacuum. Yield: 0,23 g; 71%, m.p.:262-264 °C.

2.1.5. Synthesis of 2,2'-pyridine-2,6-diylbis[1-(pentamethylbenzyl)-1H-benzimidazole], 1e.

2,6-Bis(benzimimidazol-2-yl)pyridine (0,2 g; 0,64 mmoles) and KOH (76 mg; 1,35 mmoles) were dissolved in acetone. The mixture was stirred and heated under reflux for 1 hour. Then, pentamethylbenzyl bromide (310 mg; 1.285 mmoles) was added and kept on refluxing for 8 hours. The volatiles were removed under vacuum and then the residue was dissolved with DCM (5 mL) and filtered with cannula. Diethyl ether (10 mL) was added to the solution. Obtained white crystals were filtered and dried under vacuum. Yield: 0,33 g; 82%, m.p.:270-272 °C.

2.2. Synthesis of Ru(II)-bzimpy complexes

The six-coordinated [(bzimpy)$RuCl_2$(DMSO)] complexes, **2a-e**, were prepared reaction of 2,6-bis(benzimidazol-2-yl) pyridine derivates with $RuCl_2(DMSO)_4$.

2.2.1. Synthesis of {(dichloro)(dimethyl sulfoxide)(2,2'-pyridine-2,6-diylbis-1H-benzimidazole)ruthenium(II)}, [Ru(1a)(DMSO)Cl_2)], (2a).

1a (51,4 mg, 0,165 mmoles) and $Ru(DMSO)_4Cl_2$ (80 mg, 0,165 mmoles) were placed in the same Schlenk tube and ethanol (5 mL) was added. Then the mixture was stirred and heated under reflux for 1 day. The volatiles were removed under vacuum and then the residue was treated with $CHCl_3$ (5 mL) by heating and then diethyl ether (10 mL) was added to filtered off precipitated the brown solid. The desired product was dried under vacuum. Yield: 0,057 g; 62%, m.p.:318-320 °C.

2.2.2. Synthesis of {(dichloro)(dimethyl sulfoxide)(2,2'-pyridine-2,6-diylbis(1-benzyl-1H-benzimidazole) ruthenium(II)}, [Ru(1b)(DMSO)Cl_2)], (2b).

1b (61,4 mg, 0,125 mmoles) and $Ru(DMSO)_4Cl_2$ (60.6 mg, 0,125 mmoles) were placed in the same Schlenk tube and ethanol (5 mL) was added Then the mixture was stirred and heated under reflux for 1 day. The volatiles were removed under vacuum and then the residue was dissolved with DCM and precipitated by addition of diethylether. The solid was washed with diethylether. The desired product was dried under vacuum. Yield: 0,065 g; 71%, m.p.:210-212 °C.

2.2.3. Synthesis of {(dichloro)(dimethyl sulfoxide)(2,2'-pyridine-2,6-diylbis[1-(mesitylmethyl)-1H-benzimidazole])ruthenium(II)}, [Ru(1c)(DMSO)Cl_2)], (2c).

This compound was prepared in the same manner as **2b** using **1c** (72 mg, 0,125 mmoles) and $Ru(DMSO)_4Cl_2$ (60.6 mg, 0,125 mmoles). The dark brown solid was obtained. Yield: 0,072g; 70%, m.p.:226-228°C.

2.2.4. Synthesis of {(dichloro)(dimethyl sulfoxide)(2,2'-pyridine-2,6-diylbis[1-(tetramethylbenzyl)-1H-benzimidazole])ruthenium(II)}, [Ru(1d)(DMSO)Cl_2)], 2d).

This compound was prepared in the same manner as **1b** using **1d** (63 mg, 0,103 mmoles) and $Ru(DMSO)_4Cl_2$ (50 mg, 0,103 mmoles). The dark brown solid was obtained. Yield: 0,068g; 77%, m.p.:244-246 °C.

2.2.5. Synthesis of {(dichloro)(dimethyl sulfoxide)(2,2'-pyridine-2,6-diylbis[1-(pentamethylbenzyl)-1H-benzimidazole])ruthenium(II)}, [Ru(1e)(DMSO)Cl2)], 2e).

This compound was prepared in the same manner as **1b** using **1e** (79 mg, 0,125 mmoles) and $Ru(DMSO)_4Cl_2$ (60.6 mg, 0,125 mmoles). The dark brown solid was obtained. Yield: 0,086g; 78%, m.p.:260-262 °C.

2.3 Synthesis of Pd(II)-bzimpy complexes

The four-coordinated [(bzimpy)PdCl]Cl complexes, **3a-e**, were prepared reaction of 2,6-bis(benzimidazol-2-yl) pyridine derivates with $PdCl_2$.

2.3.1. Synthesis of {(chloro) (2,2'-pyridine-2,6-diylbis-1H-benzimidazole)palladium(II)} chloride, [Pd(1a) Cl)]Cl, (3a).

1a (43 mg, 0,14 mmoles) and $PdCl_2$ (60.6 mg, 0,14 mmoles) were placed in the same schlenk tube and methanol was added Then the mixture was stirred at room temperature for 1 day. The volatiles were removed under vacuum and then the residue was washed with ethanole and diethyl ether. The desired product was dried under vacuum. Yield: 0,056g; 82%, m.p.:>350 °C.

2.3.2. Synthesis of {(chloro)(2,2'-pyridine-2,6-diylbis(1-benzyl-1H-benzimidazole) palladium(II)} chloride, [Pd(1b)Cl)] Cl, (3b).

This compound was prepared in the same manner as **3a** using **1b** (69 mg, 0,14 mmoles) and $PdCl_2$ (25 mg, 0,14 mmoles). The yellow solid was obtained. Yield: 0,073g; 78%, m.p.:>350 °C.

2.3.3. Synthesis of {(chloro)(2,2'-pyridine-2,6-diylbis(1-mesitylmethyl -1H-benzimidazole) palladium(II)} chloride, [Pd(1b)Cl)] Cl, (3c).

This compound was prepared in the same manner as **3a** using **1c** (80 mg, 0,14 mmoles) and $PdCl_2$ (25 mg, 0,14 mmoles). The yellow solid was obtained. Yield: 0,093g; 88%, m.p.:>350 °C.

2.3.4. Synthesis of {(chloro)(2,2'-pyridine-2,6-diylbis(1-tetramethylbenzyl -1H-benzimidazole) palladium(II)} chloride, [Pd(1b)Cl)] Cl, (3d).

This compound was prepared in the same manner as **3a** using **1d** (84 mg, 0,14 mmoles) and $PdCl_2$ (25 mg, 0,14 mmoles). The yellow solid was obtained. Yield: 0,091g; 83%, m.p.:>350 °C.

2.3.5. Synthesis of {(chloro)(2,2'-pyridine-2,6-diylbis(1-pentamethylbenzyl -1H-benzimidazole) palladium(II)} chloride, [Pd(1b)Cl)] Cl, (3e).

This compound was prepared in the same manner as **3a** using **1e** (88 mg, 0,14 mmoles) and $PdCl_2$ (25 mg, 0,14 mmoles). The yellow solid was obtained. Yield: 0,096g; 85%, m.p.:>350 °C

2.4 Catalytic experiments

2.4.1. General method for transfer hydrogenation of acetophenone using Ru(II) complexes

A mixture of acetophenone (10 mmol), the catalyst (0.01 mmol Ru(II)) and propan-2-ol (19 mL) were stirred at 82 ºC for 10 minutes. 1 mL of 0.1 M KOH (0.1 mmol) solution in 2-propanol was then introduced. The mixture was stirred at the refluxing temperature and the reaction was monitored by GC.

2.4.2. General method for the Suzuki coupling reactions

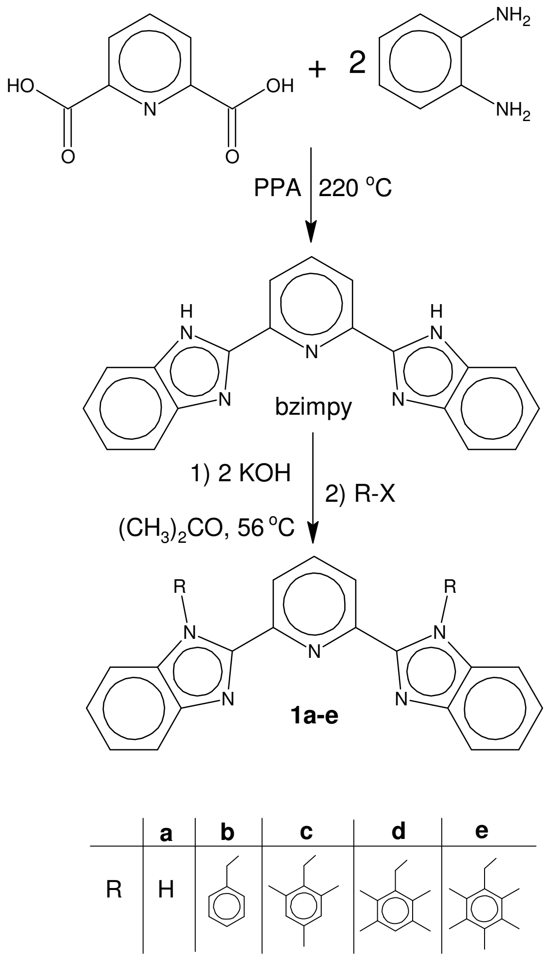
In a typical run, a two-necked 25 mL flask fitted with a reflux condenser and septum was charged with aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), Cs_2CO_3 (2 mmol), diethyleneglicol di-*n*-butyl ether (internal standard) and the catalyst (1 mmol% Pd(II)) in 3 mL of DMF and 3 mL H_2O was added. The flask was placed in a preheated oil bath under an argon atmosphere. The reaction was monitored by GC.

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization of bzimpy ligands

The bzimpy ligands were synthesized according to the steps illustrated in Scheme 3.1. At the first step, 2,6-bis(benzimidazol-2-yl) pyridine were prepared by reaction of pyridine-2,6-dicarboxylic acid with *o*-phenylendiamine in PPA. Bzimpy ligands (**1b-e**) were obtained via alkylation of the latter product with benzyl chloride, 2,4,6-trimethylbenzyl chloride, 2,3,5,6-tetramethylbenzyl bromide and 2,3,4,5,6-pentamethylbenzyl bromide in the presence of KOH in acetone at reflux.

Compounds **1a-e** have been characterized by ^{1}H and ^{13}C NMR spectroscopy. In ^{1}H NMR spectra the Py-H_p and -H_m protons were observed as dublets and triplets in 2:1 ratio at around δ 8.11 - 8.56 ppm. The protons of the phenyl rings of each ligand appear as eight-proton multiplets around 6.6 - 7.8 ppm.


HO
OH
N
O
O
+ 2
NH2
NH2
PPA
220 °C
H
N
N
N
H
N
N
bzimpy
1) 2 KOH
$(CH_3)_2CO$, 56 °C
2) R-X
R
N
N
N
R
N
N
1a-e
a
b
c
d
e
R
H

Scheme 3.1

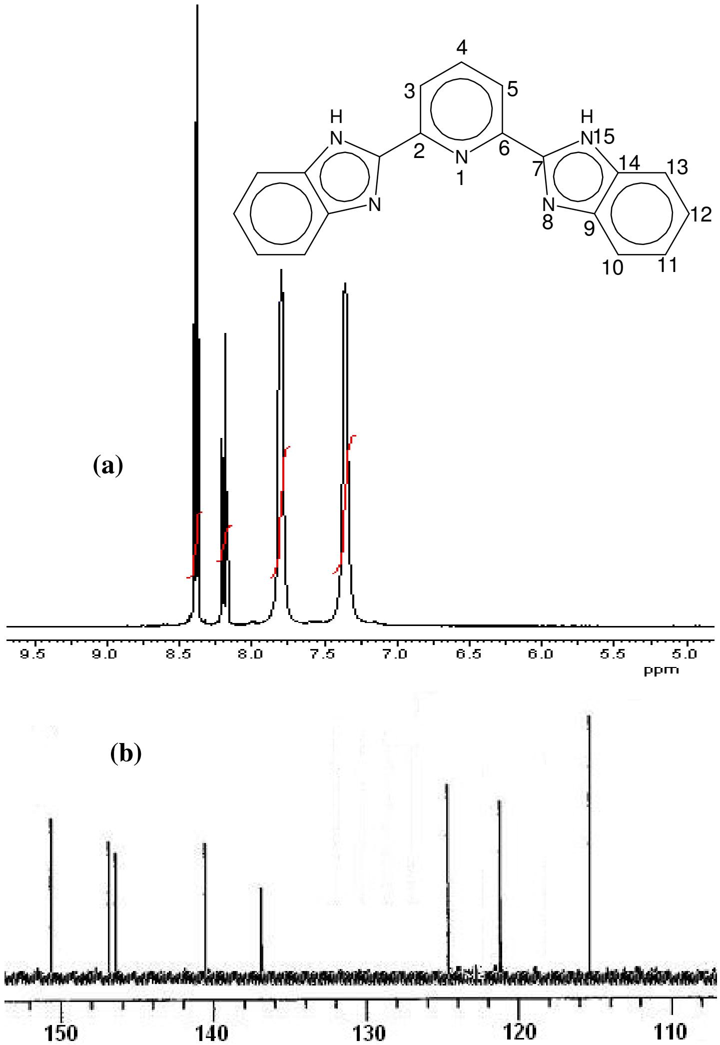


Figure 3.1 (a) ^{1}H-NMR, (b) ^{13}C-NMR spectra of **1a** (See **Table 3.1**)

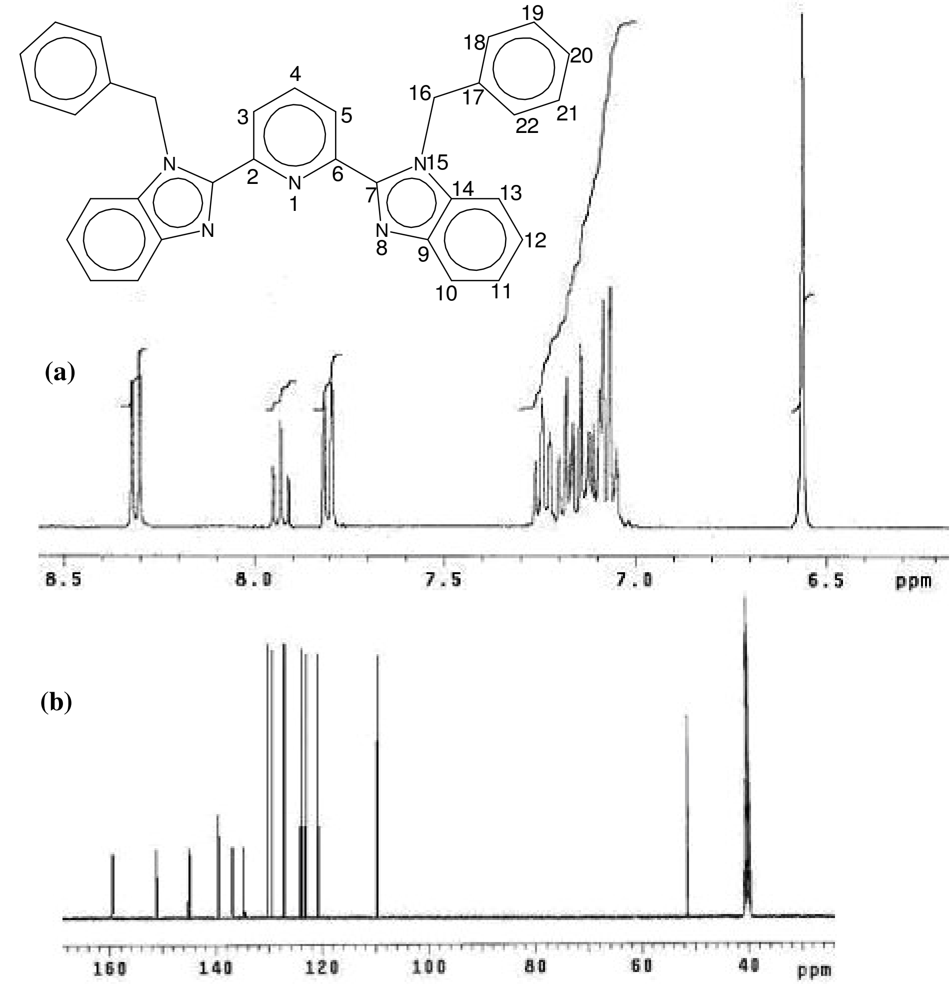


Figure 3.2 (a) ^{1}H-NMR, (b) ^{13}C-NMR spectra of **1b** (See **Table 3.2**)

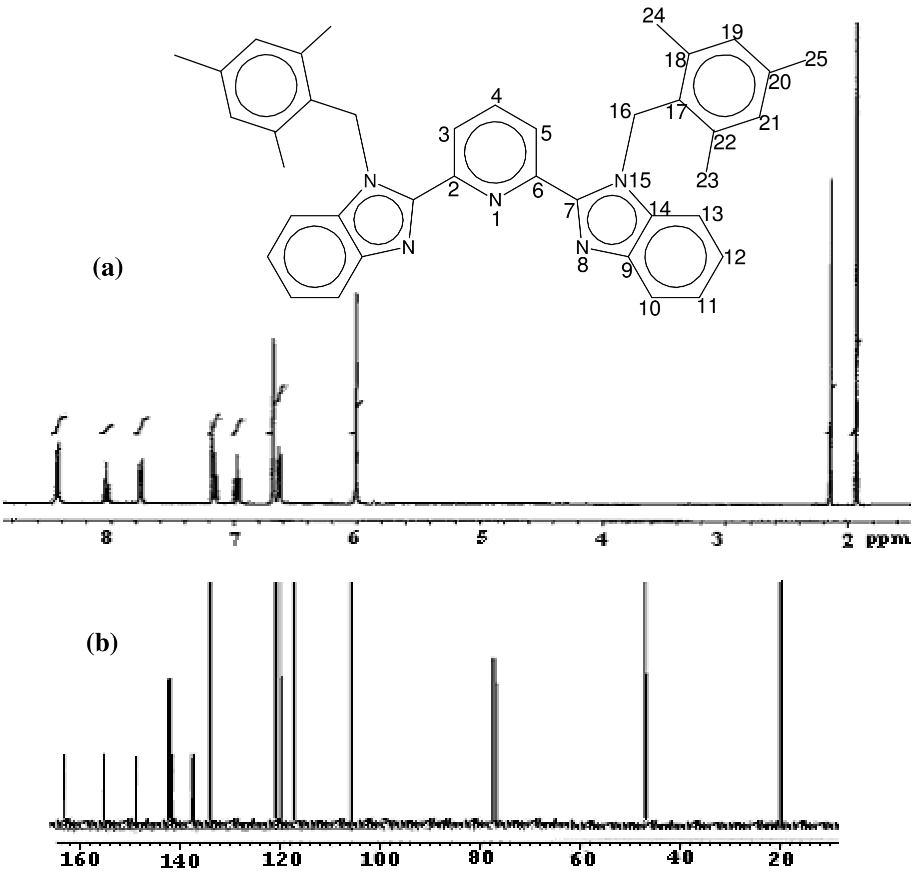


Figure 3.3 (a) ^{1}H-NMR, (b) ^{13}C-NMR spectra of **1c** (See **Table 3.3**)

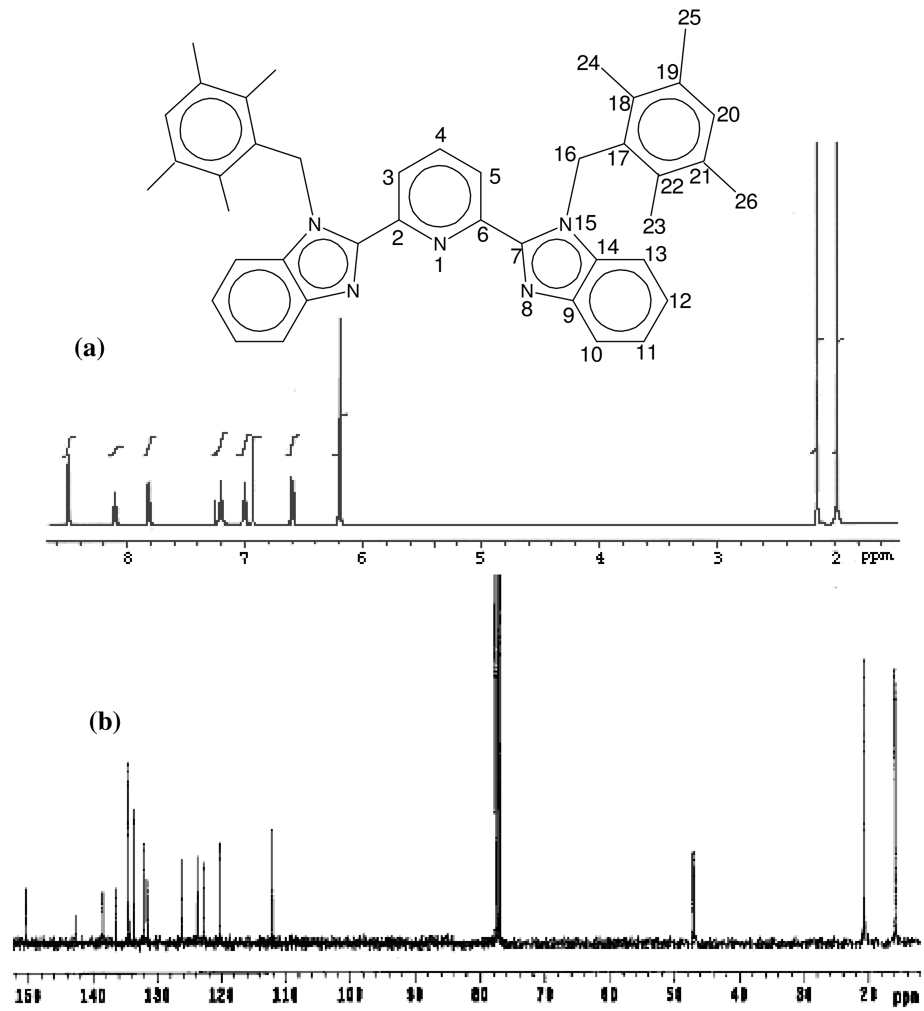


Figure 3.4 (a) ^{1}H-NMR, (b) ^{13}C-NMR spectra of **1d** (See **Table 3.4**)

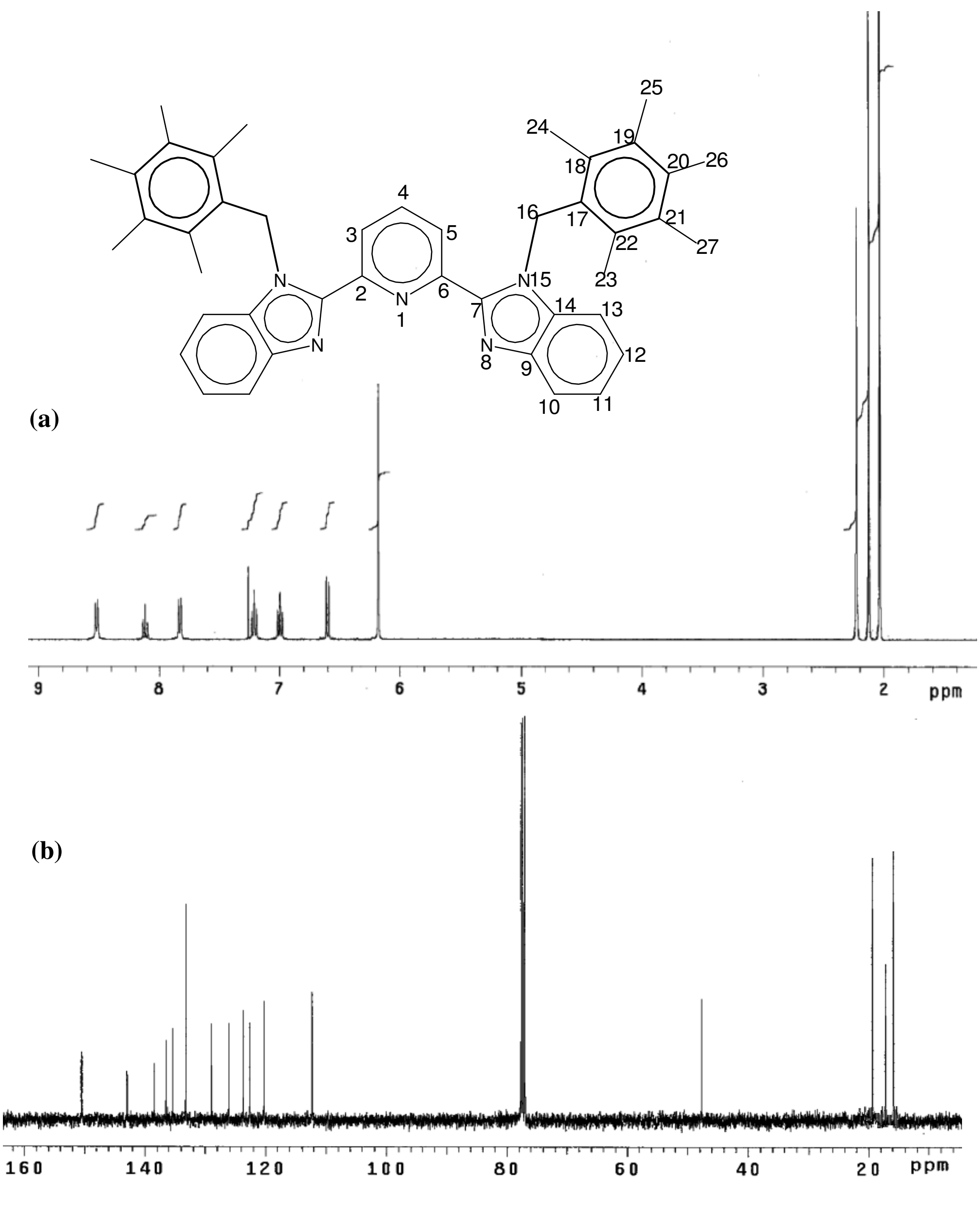


Figure 3.5 (a) ^{1}H-NMR, (b) ^{13}C-NMR spectra of **1e** (See **Table 3.5**)

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

Location of atom(s)	*^{1}H-NMR (δ ppm)*	*J (Hz)*	*^{13}C-NMR (δ ppm)*
11, 12	7.41 (4H, m)	—	115.83
10, 13	7.76 (4H, m)	—	121,61
4	8.21 (1H, t)	J_1=7.8, J2=7.7	140,38
3, 5	8.41 (2H, d)	8.0	124.30
others	—	—	136.41, 146.12, 147.13, 150.53

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

Location of atom(s)	*^{1}H-NMR (δ ppm)*	*J (Hz)*	*^{13}C-NMR (δ ppm)*
16	6.57 (4H, s)	—	51.81
11, 12, 13, 18, 19, 20, 21, 22	7.04 – 7.26 (16H, m)	—	122.61, 124.0, 110.01, 129.66, 130.18, 128.27
10	7.81 (2H, d)	7.9	121.02
4	7.93 (1H, t)	J_1=7.9, J_2=7.9	139.85
3, 5	8.41 (2H, d)	8.0	127.03
others	—	—	135.51, 137.89, 144.67, 151.01, 159.33

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

Location of atom(s)	*^{1}H-NMR (δ ppm)*	*J (Hz)*	*^{13}C-NMR (δ ppm)*
23, 24	1.93 (12H, s)	—	19.83
25	2.19 (6H, s)	—	19.88
16	6.03 (4H, s)	—	46.83
13	6.67 (2H, d)	7.6	105.88
19, 21	6.71 (4H, s)	—	134.0
12	6.98 (2H, t)	J_1=7.7, J_2=7.7	120.58
11	7.19 (2H, t)	J_1=7.5, J_2=7.5	120.0
10	7.76	7.9	115.03
4	8.07	J_1=7.8, J_2=7.7	142.02
3,5	8.42	7.6	121.08
others	—	—	135.07, 135.23, 142.26, 149.0, 155.41, 163.18

Table 3.4 ^{1}H- and ^{13}C-NMR spectra of **1d**

Location of atom(s)	*^{1}H-NMR (δ ppm)*	*J (Hz)*	*^{13}C-NMR (δ ppm)*
23, 24	1.98 (12H, s)	—	16.0
25, 26	2.18 (12H, s)	—	21.18
16	6.19 (4H, s)	—	47.11
13	6.63 (2H, d)	7.6	111.97
20	6.91 (2H, s)	—	134.21
12	7.0 (2H, t)	J_1=7.7, J_2=7.7	126.0
11	7.21 (2H, t)	J_1=7.5, J_2=7.5	122.91
10	7.81 (2H, d)	7.9	120.03
4	8.14 (1H, t)	J_1=7.8, J_2=7.7	138.22
3,5	8.52 (2H, d)	7.6	124.08
0thers	—	—	131.27, 134.68, 138.07, 142.11, 150.08

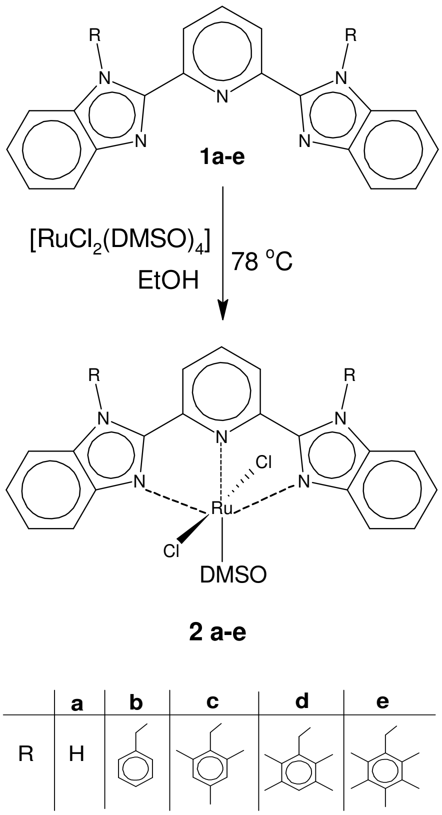
Table 3.5 ^{1}H- and ^{13}C-NMR spectra of **1e**

Location of atom(s)	*^{1}H-NMR (δ ppm)*	*J (Hz)*	*^{13}C-NMR (δ ppm)*
23, 24	2.02 (12H, s)	—	19.92
25, 27	2.13 (12H, s)	—	15.94
26	2.21 (6H, s)	—	17.73
16	6.19 (4H, s)	—	47.82
13	6.59 (2H, d)	7.6	112.0
12	7.0 (2H, t)	J_1=7.5, J_2=7.5	123.89
11	7.22 (2H, t)	J_1=7.7, J_2=7.7	122.51
10	7.81 (2H, d)	7.8	120.0
4	8.11 (1H, t)	J_1=7.8, J_2=7.7	136.03
3, 5	8.72 (2H, d)	7.9	126.07
0thers	—	—	128.21, 133.41, 134.87, 138.71, 142.38, 150.67

3.2 Synthesis of Ru(II)-bzimpy complexes

Ru(II)-bzimpy complexes were synthesized by reaction of $RuCl_2(DMSO)_4$ with bzimpy ligands (**1a-e**) in ethanol (Scheme 3.2).

Compounds **2a-e** gave ^{1}H- and ^{13}C-NMR spectra corresponding to the proposed formulation. The ^{1}H-NMR spectra of these complexes showed some differences from their respective ligands, especially pyridine backbone. Py–H_m and –H_p protons for **2a-e** complexes were observed as dublets and triplets in 2:1 ratio with general shift towards lower fields as compared to their respective ligands. On the other hand ^{13}C-NMR signals shifted to higher fields (Table 3.6).



Scheme 3.2

Table 3.6 Selected NMR data for **2a-e** complexes as compared to the respective ligands

Compounds	Py-H_m		Py-H_p	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
1a	8.41	124.30	8.21	140.38
2a	8.65	119.82	8.49	143.91
1b	8.41	127.03	7.93	139.85
2b	8.53	118.05	8.16	146.43
1c	8.42	121.08	8.07	142.02
2c	8.72	116.02	8.26	151.33
1d	8.52	124.08	8.14	136.21
2d	8.92	116.23	8.21	145.38
1e	8.72	126.07	8.11	126.07
2e	9.13	114.28	8.21	143.38

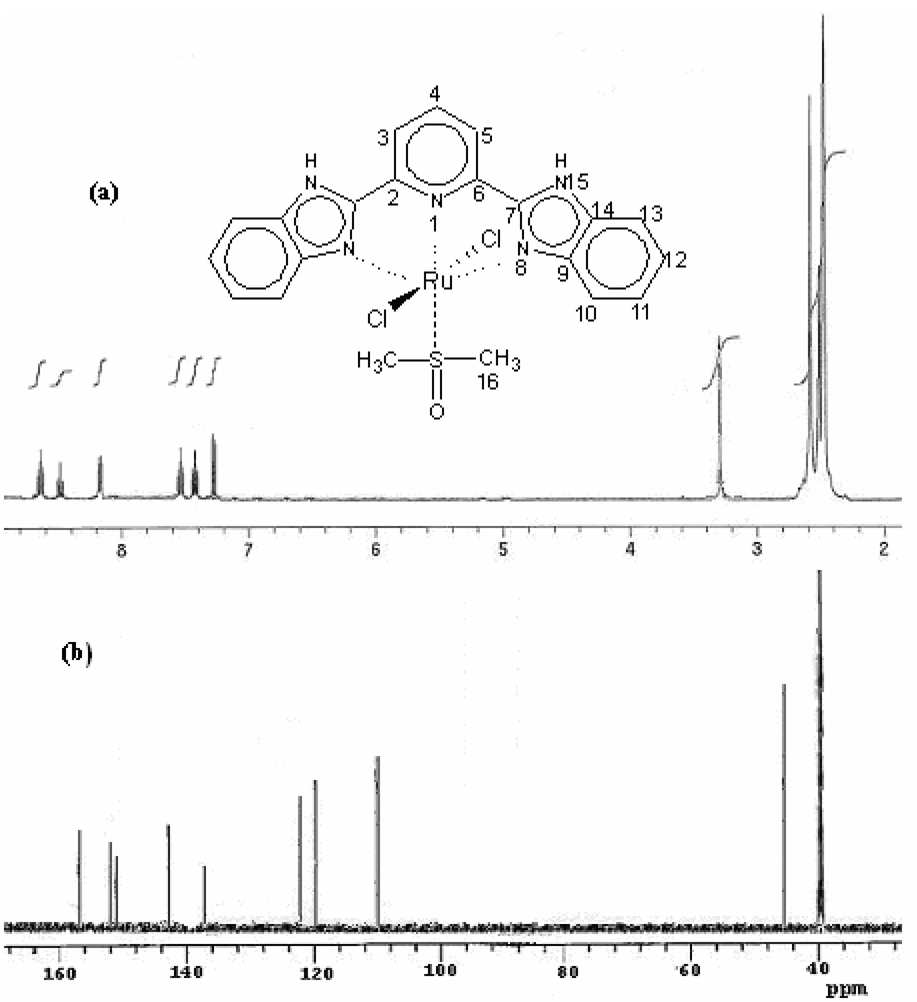


Figure 3.6 (a) ^{1}H-NMR, (b) ^{13}C-NMR spectra of **2a** (See **Table 3.7**)

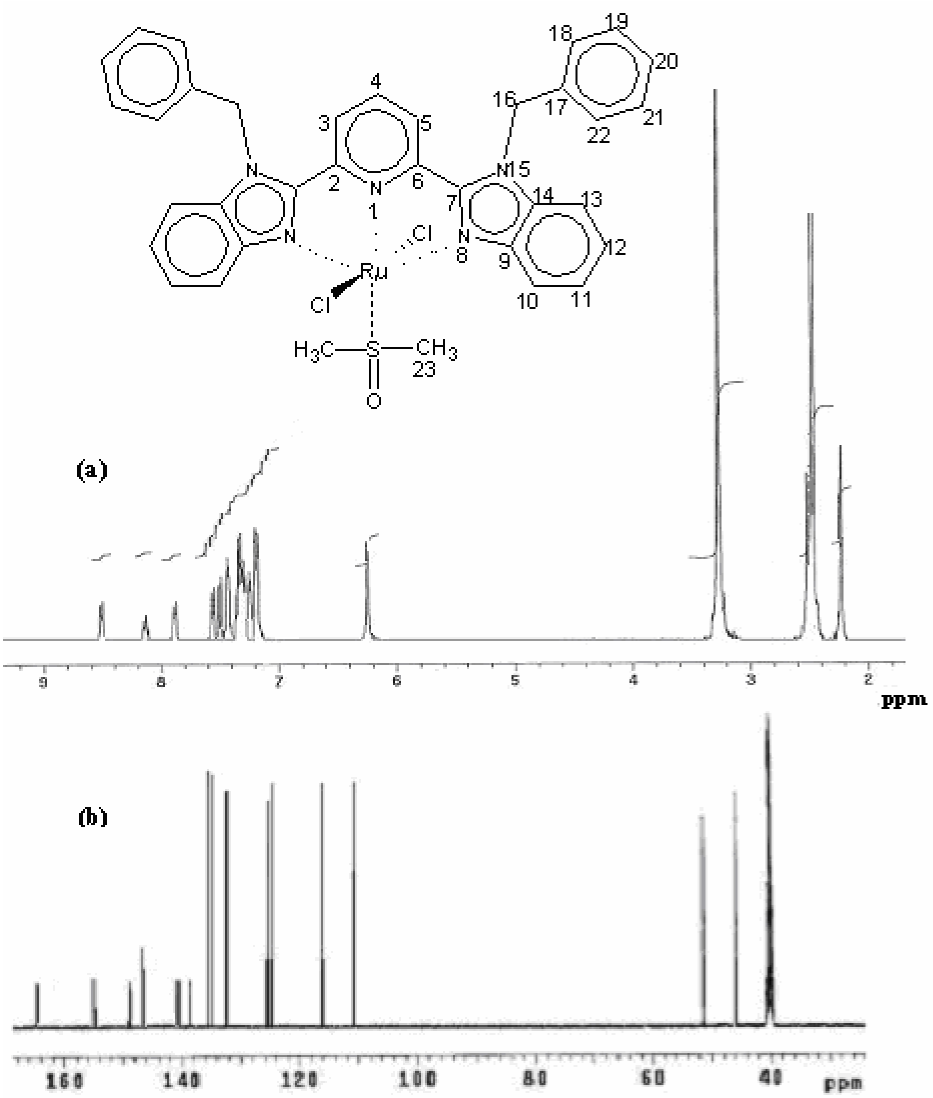


Figure 3.7 (a) ^{1}H-NMR, (b) ^{13}C-NMR spectra of **2b** (See **Table 3.8**)

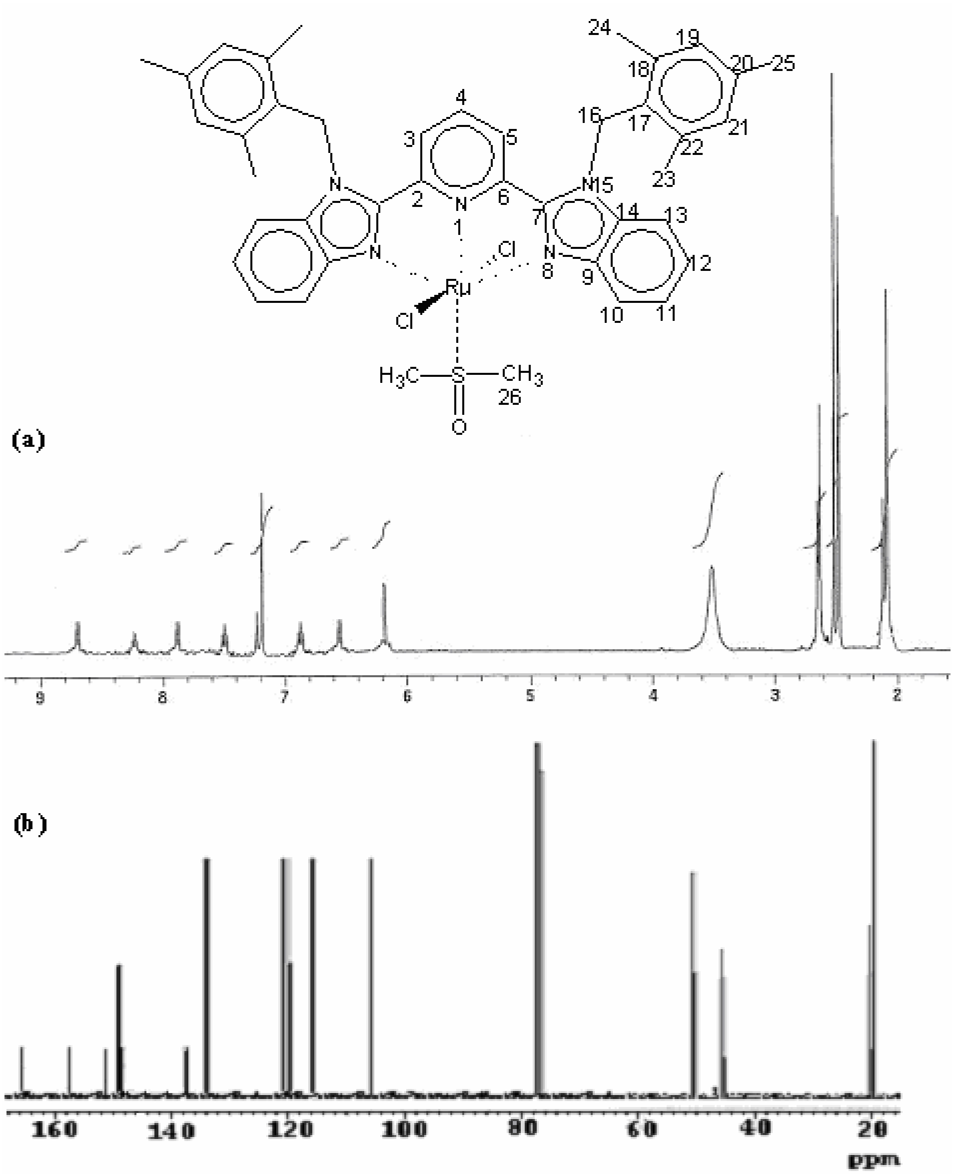


Figure 3.8 (a) ^{1}H-NMR, (b) ^{13}C-NMR spectra of **2c** (See **Table 3.9**)

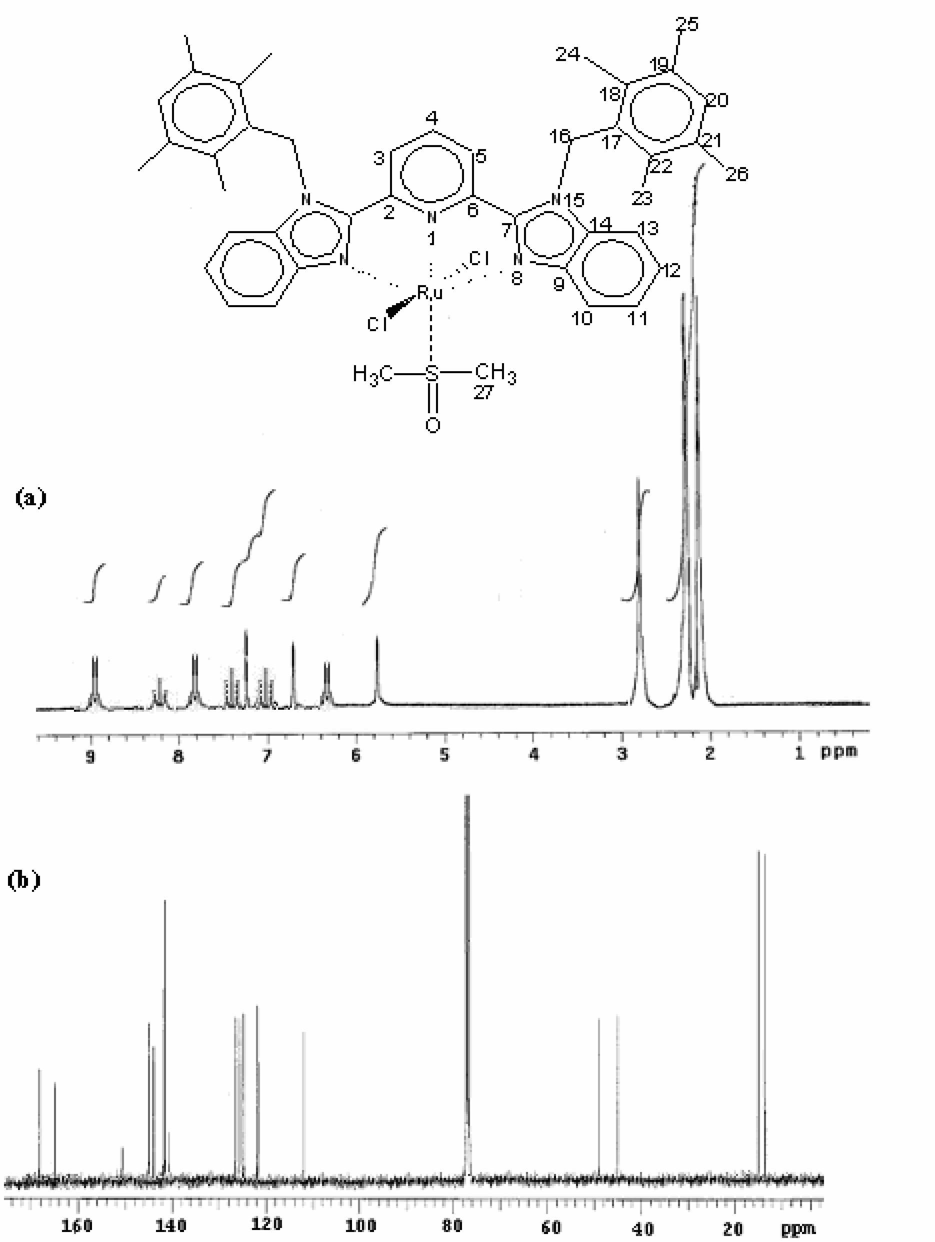


Figure 3.9 (a) ^{1}H-NMR, (b) ^{13}C-NMR spectra of **2d** (See **Table 3.10**)

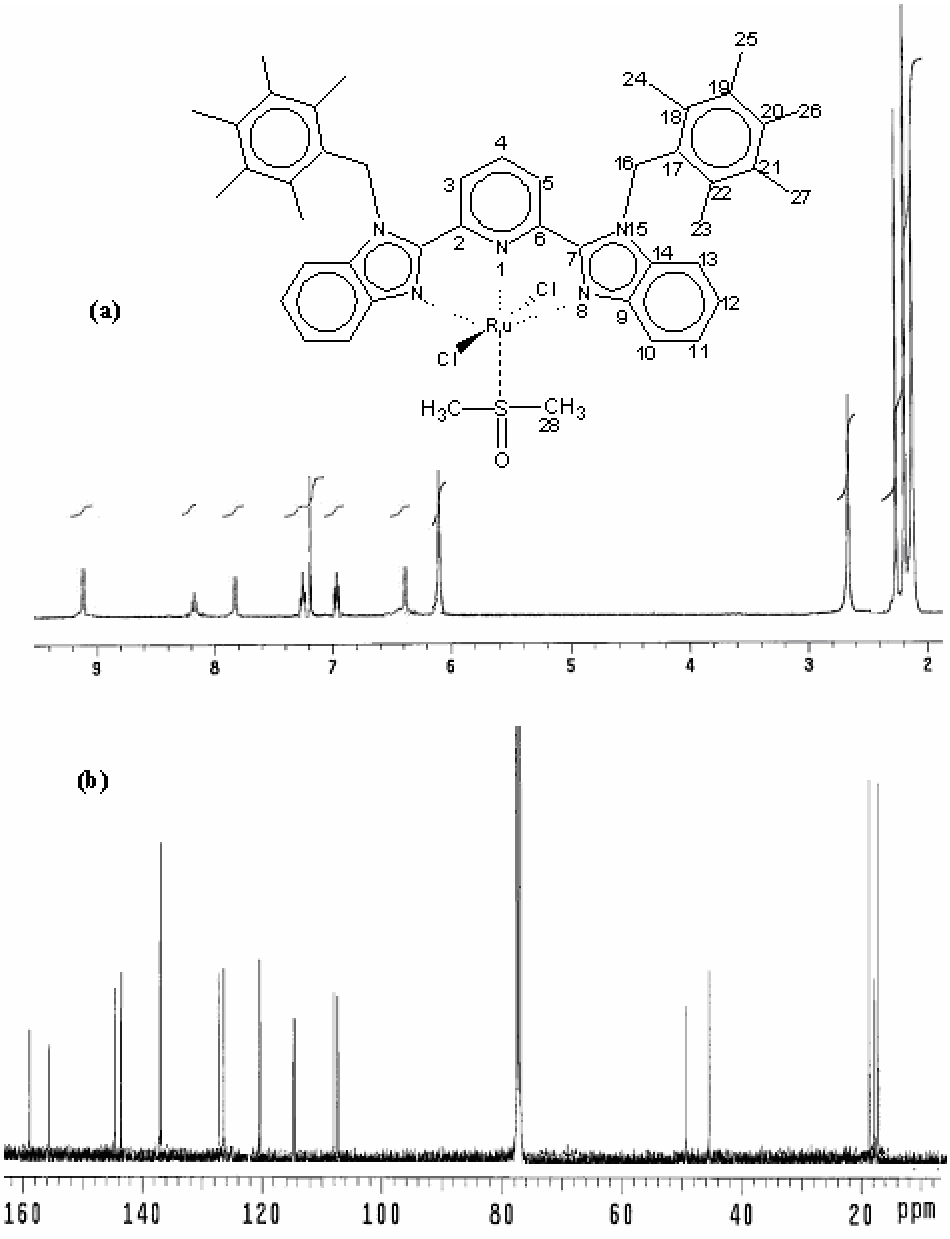


Figure 3.10 (a) ^{1}H-NMR, (b) ^{13}C-NMR spectra of **2e** (See **Table 3.11**)

Table 3.7 ^{1}H- and ^{13}C-NMR spectra of **2a**

Location of atom(s)	*^{1}H-NMR (δ ppm)*	*J (Hz)*	*^{13}C-NMR (δ ppm)*
16	2.61 (6H, s)	—	45.63
13	7.29 (2H, d)	7.6	110.03
12	7.43 (2H, t)	J_1=7.4, J_2=7.4	123.11
11	7.54 (2H, t)	J_1=7.6, J_2=7.6	123.11
10	8.19 (2H, d)	7.8	110.03
4	8.49 (1H, t)	J_1=7.8, J_2=7.8	143.91
3, 5	8.65 (2H, d)	8.0	119.82
others	—	—	137.12, 151.42, 152.13, 156.21

Table 3.8 ^{1}H- and ^{13}C-NMR spectra of **2b**

Location of atom(s)	*^{1}H-NMR (δ ppm)*	*J (Hz)*	*^{13}C-NMR (δ ppm)*
23	2.24 (6H, s)	—	45.58
16	6.23 (4H, s)	—	50.88
11, 12, 13, 18, 19, 20, 21, 22	7.17 – 7. 61 (16H, m)	—	111.28, 116.03, 132.0, 134.13, 135.71,
10	7.82 (2H, d)	7.9	111.28
4	8.16 (1H, t)	J_1=7.8, J_2=7.8	146.43
3, 5	8.53 (2H, d)	8.0	118.05
others	—	—	135.51, 137.89, 144.67, 151.01, 159.33

Table 3.9 ^{1}H- and ^{13}C-NMR spectra of **2c**

Location of atom(s)	*^{1}H-NMR (δ ppm)*	*J (Hz)*	*^{13}C-NMR (δ ppm)*
25	2.11 (6H, s)	—	19.53
23, 24	2.45 (12H, s)	—	20.01
26	2.53 (6H, s)	—	45.28
16	6.18 (4H, s)	—	50.17
13	6.58 (2H, d)	7.6	105.83
12	6.84 (2H, t)	J_1=7.8, J_2=7.8	120.32
19, 21	7.21 (4H, s)	—	134.01
11	7.51 (2H, t)	J_1=7.7, J_2=7.7	120.32
10	7.82 (2H, d)	7.9	105.83
4	8.26 (1H, t)	J_1=7.8, J_2=7.7	134.86
3,5	8.72 (2H, d)	7.6	119.18
others	—	—	116.03, 148.51, 151.63, 157.14, 165.91

Table 3.10 ^{1}H- and ^{13}C-NMR spectra of **2d**

Location of atom(s)	*^{1}H-NMR (δ ppm)*	*J (Hz)*	*^{13}C-NMR (δ ppm)*
23, 24	2.11 (12H, s)	—	14.02
25, 26	2.24 (12H, s)	—	15.38
27	2.79 (6H, s)	—	45.39
16	5.74 (4H, s)	—	49.31
13	6.33 (2H, d)	7.5	112.06
20	6.64 (2H, s)	—	142.18
12	7.03 (2H, t)	J_1=7.6, J_2=7.6	124.08
11	7.39 (2H, t)	J_1=7.5, J_2=7.5	124.08
10	7.81 (2H, d)	7.6	112.06
4	8.21 (1H, t)	J_1=7.8, J_2=7.8	145.38
3,5	8.92 (2H, d)	8.0	122.04
0thers	—	—	126.14, 145.37, 150.17, 165.21, 168.09

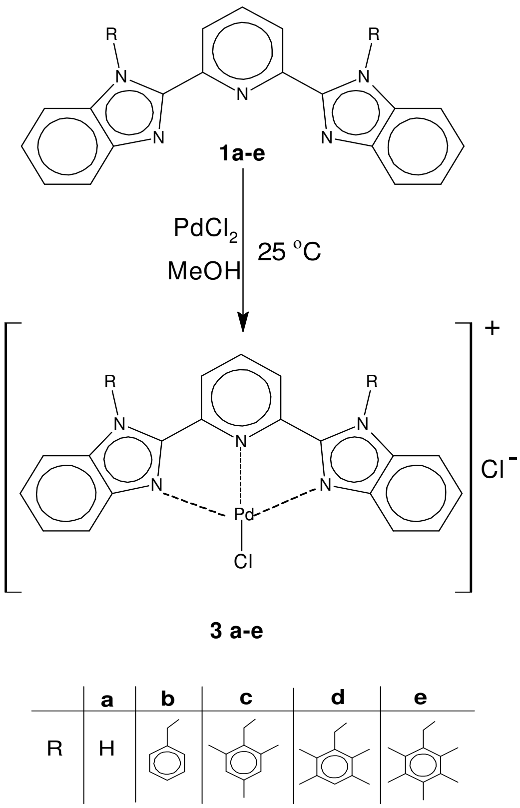
Table 3.11 ^{1}H- and ^{13}C-NMR spectra of **2e**

Location of atom(s)	*^{1}H-NMR (δ ppm)*	*J (Hz)*	*^{13}C-NMR (δ ppm)*
23, 24	2.08 (12H, s)	—	19.03
25, 27	2.19 (12H, s)	—	17.76
26	2.23 (6H, s)	—	18.02
28	2.65 (6H, s)	—	45.23
16	6.08 (4H, s)	—	48.63
13	6.38 (2H, d)	7.6	108.03
12	6.85 (2H, t)	J_1=7.6, J_2=7.6	120.07
11	7.21 (2H, t)	J_1=7.7, J_2=7.7	120.07
10	7.82 (2H, d)	7.8	108.03
4	8.18 (1H, t)	J_1=7.8, J_2=7.7	143.38
3, 5	9.13 (2H, d)	7.9	114.28
0thers	—	—	126.12, 137.03, 144.47, 155.94, 159.07

3.3 Synthesis of Pd(II)-bzimpy complexes

Pd(II)-bzimpy complexes were synthesized with $PdCl_2$ and bzimpy ligands (**1a-e**) in methanol (Scheme 3.3). All complexes synthesized at room temperature.

Compounds 3a-e gave ^{1}H- and ^{13}C-NMR spectra corresponding to the proposed formulation. The ^{1}H-NMR spectra of these complexes showed some differences from their respective ligands, especially pyridine backbone. Py–H_o and –H_m protons for **3a-e** complexes were observed as dublets and triplets in 2:1 ratio with general shift towards higher fields as compared to their respective ligands (Table 3.12).



Scheme 3.3

Table 3.12 Selected NMR data for **3a-e** complexes as compared to the respective ligands

Compounds	Py-H_m		Py-H_p	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
1a	8.41	124.30	8.21	140.38
3a	8.84	120.36	8.18	141.52
1b	8.41	127.30	7.93	139.85
3b	8.94	123.89	8.71	140.46
1c	8.42	121.08	8.07	142.02
3c	8.73	116.02	8.54	151.33
1d	8.52	124.08	8.14	136.21
3d	9.26	121.11	8.82	148.81
1e	8.72	126.07	8.11	138.22
3e	8.89	121.82	8.25	149.32

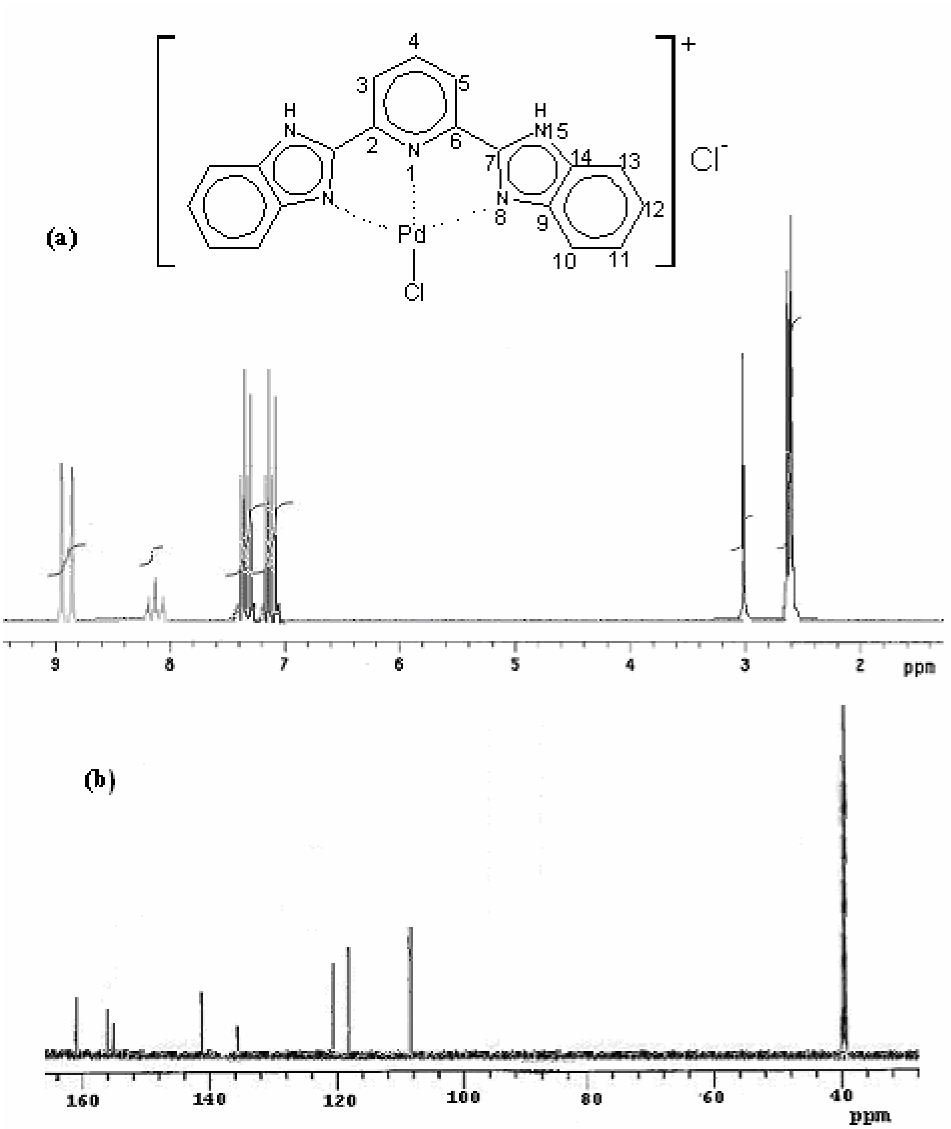


Figure 3.11 (a) ^{1}H-NMR, (b) ^{13}C-NMR spectra of **3a** (See **Table 3.13**)

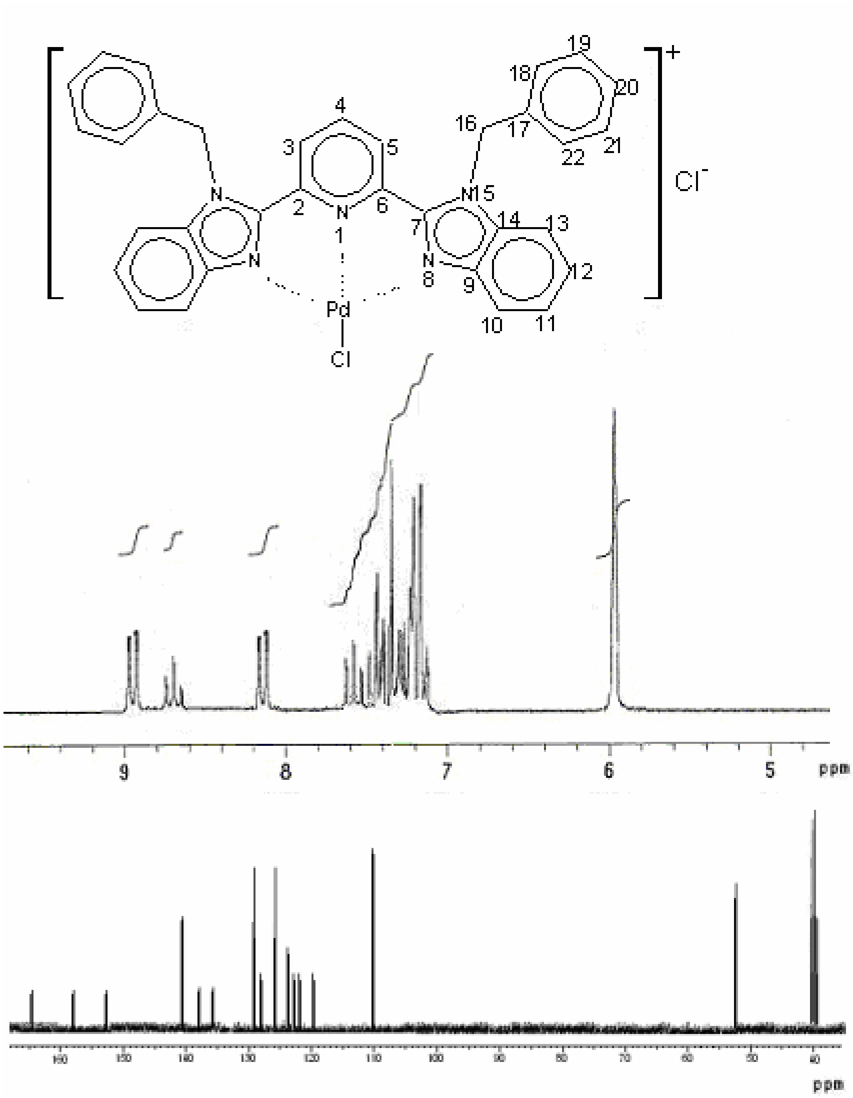


Figure 3.12 (a) ^{1}H-NMR, (b) ^{13}C-NMR spectra of **3b** (See **Table 3.14**)

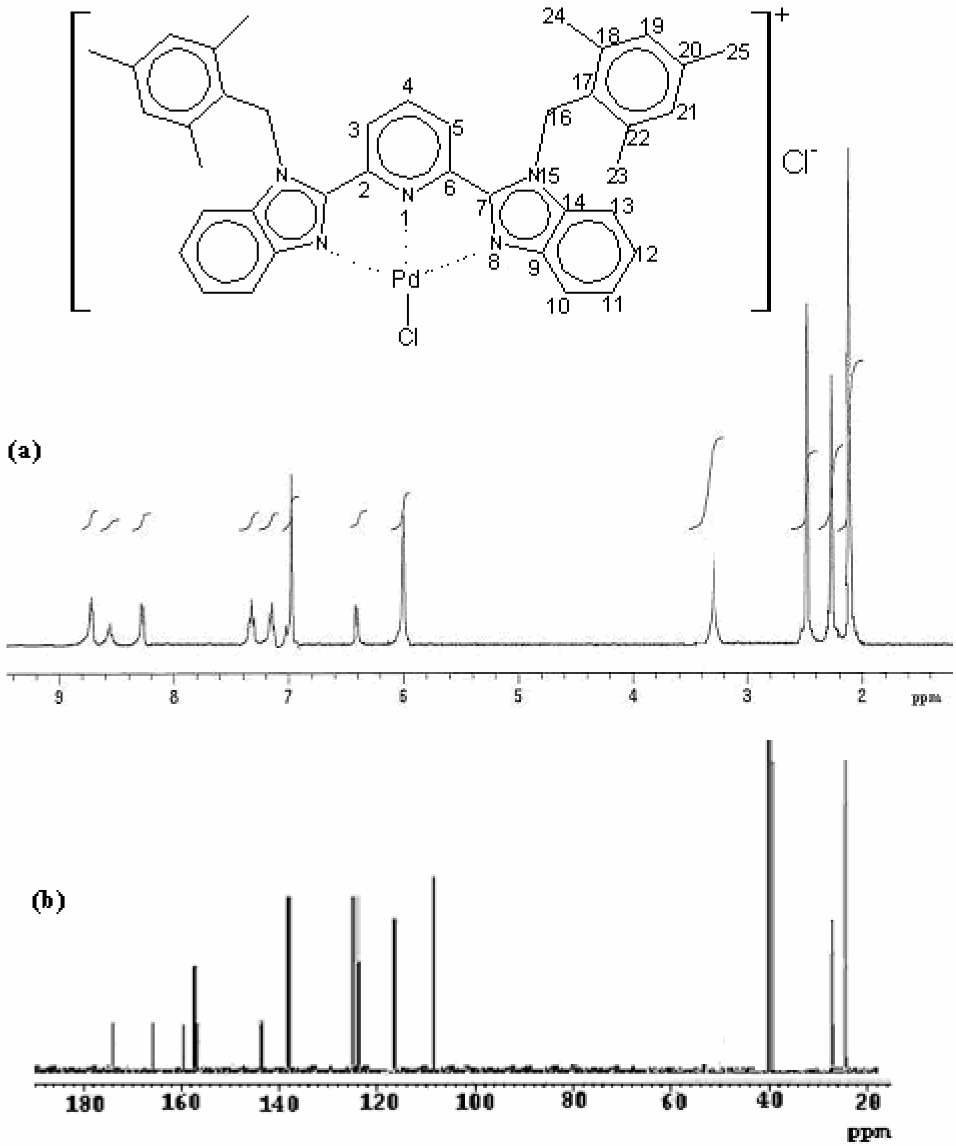


Figure 3.13 (a) ^{1}H-NMR, (b) ^{13}C-NMR spectra of **3c** (See **Table 3.15**)

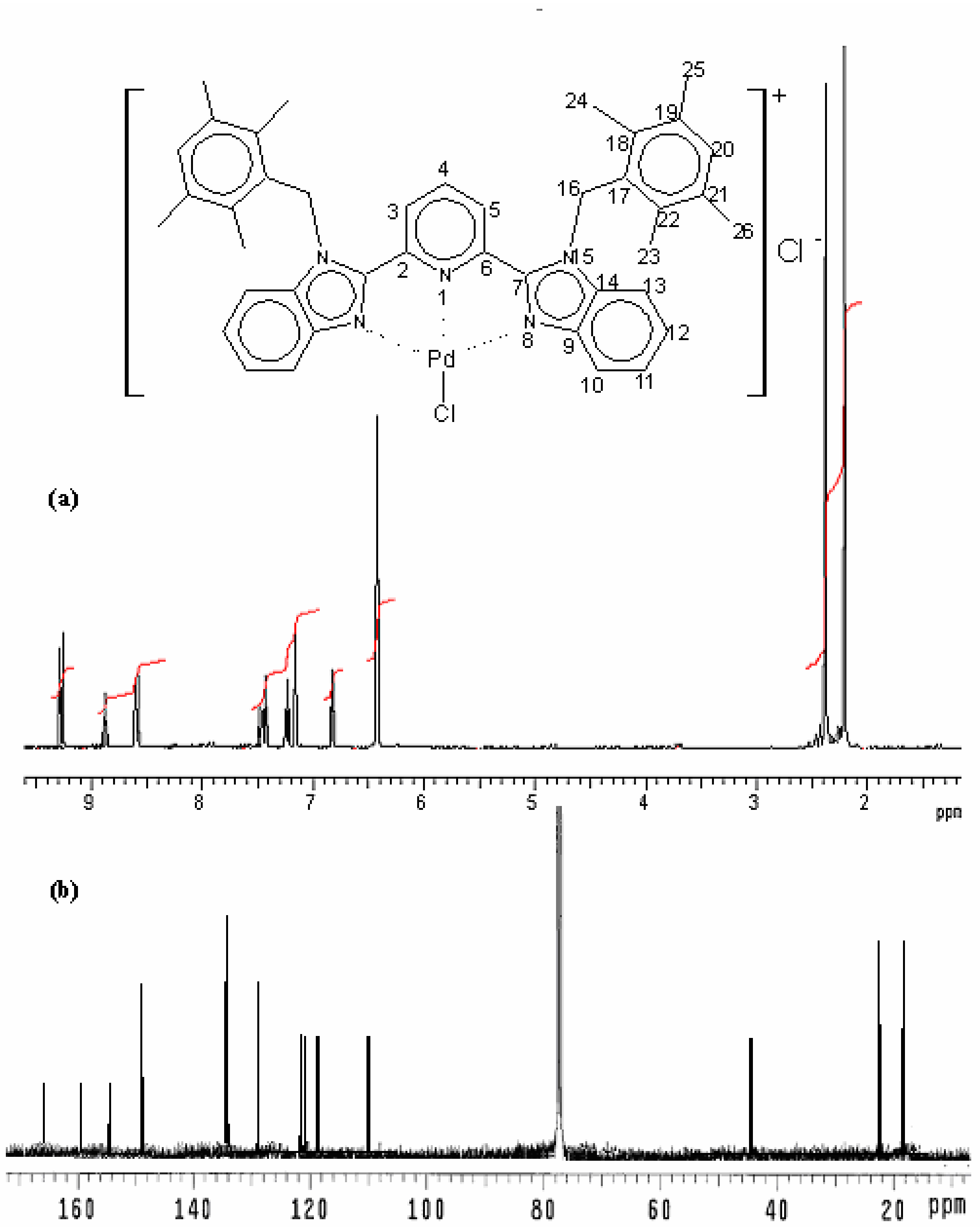


Figure 3.14 (a) ^{1}H-NMR, (b) ^{13}C-NMR spectra of **3d** (See **Table 3.16**)

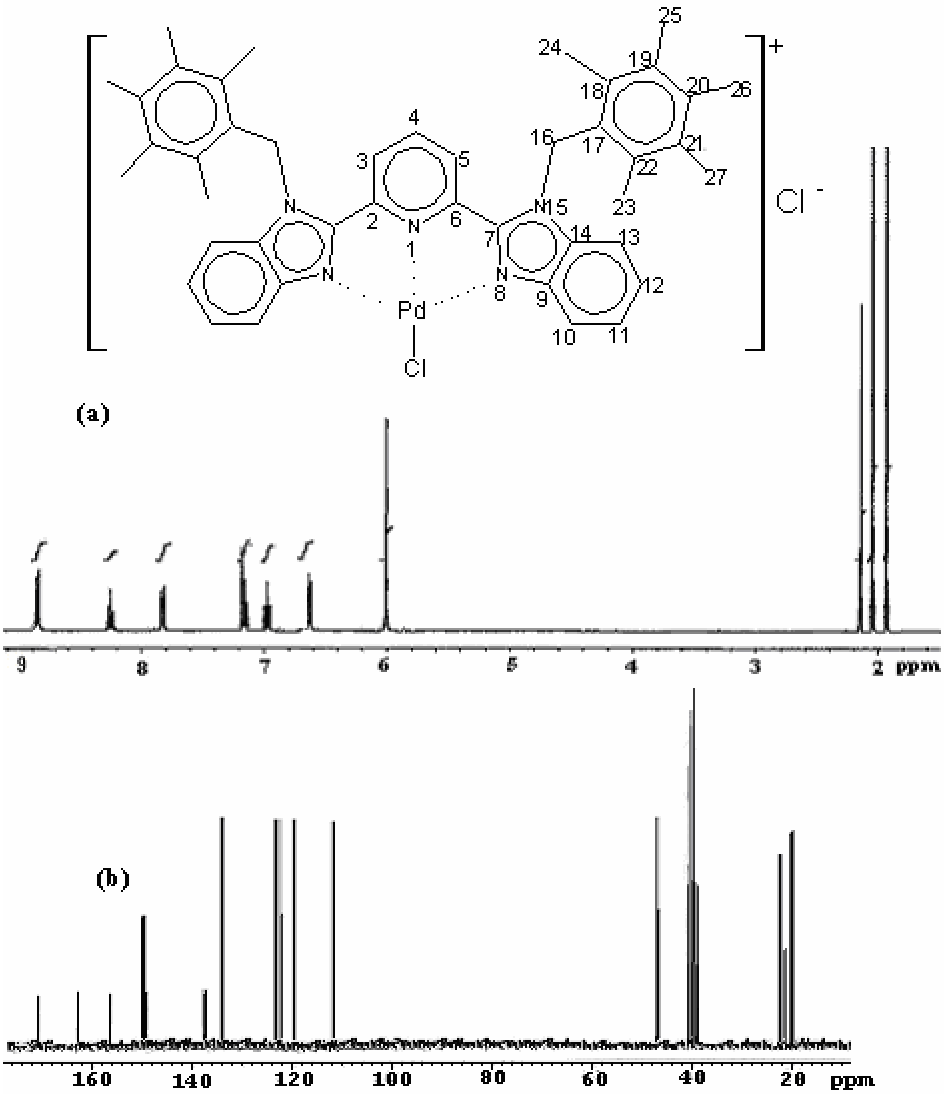


Figure 3.15 (a) ^{1}H-NMR, (b) ^{13}C-NMR spectra of **3e** (See **Table 3.17**)

Table 3.13 ^{1}H- and ^{13}C-NMR spectra of **3a**

Location of atom(s)	*^{1}H-NMR (δ ppm)*	*J (Hz)*	*^{13}C-NMR (δ ppm)*
11, 12	7.01 - 7.41 (4H, m)	—	118.27
10, 13	7.43 – 7.78 (4H, m)	—	108.04
4	8.17 (1H, t)	J_1=7.8, J_2=7.7	141.52
3, 5	8.84 (2H, d)	8.0	121.36
others	—	—	135.62, 153.28, 158.12, 161.17

Table 3.14 ^{1}H- and ^{13}C-NMR spectra of **3b**

Location of atom(s)	*^{1}H-NMR (δ ppm)*	*J (Hz)*	*^{13}C-NMR (δ ppm)*
16	5.97 (4H, s)	—	52.50
11, 12, 13, 18, 19, 20, 21, 22	7.11 – 7.63 (16H, m)	—	110.43, 122.09, 122.87, 126.04, 128.27, 129.23
10	8.16 (2H, d)	7.5	119.84
4	8.71 (1H, t)	J_1=7.8, J_2=7.8	140.46
3, 5	8.94 (2H, d)	7.6	123.89
others	—	—	135.77, 137.79, 152.91, 158.21, 164.78

Table 3.15 ^{1}H- and ^{13}C-NMR spectra of **3c**

Location of atom(s)	*^{1}H-NMR (δ ppm)*	*J (Hz)*	*^{13}C-NMR (δ ppm)*
23, 24	2.09 (12H, s)	—	24.03
25	2.32 (6H, s)	—	25.68
16	6.01 (4H, s)	—	48.17
13	6.41 (2H, d)	7.6	108.17
19, 21	6.98 (4H, s)	—	138.26
12	7.18 (2H, t)	J_1=7.6, J_2=7.6	123.64
11	7.36 (2H, t)	J_1=7.5, J_2=7.5	123.64
10	8.29 (2H, d)	7.8	108.17
4	8.53 (1H, t)	J_1=7.8, J_2=7.7	144.17
3,5	8.72 (2H, d)	7.6	124.78
others	—	—	116.29, 128.63, 152.03, 159.88, 166.02

Table 3.16 ^{1}H- and ^{13}C-NMR spectra of **3d**

Location of atom(s)	*^{1}H-NMR (δ ppm)*	*J (Hz)*	*^{13}C-NMR (δ ppm)*
23, 24	2.11 (12H, s)	—	18.23
25, 26	2.38 (12H, s)	—	22.18
16	6.41 (4H, s)	—	44.47
13	6.82 (2H, d)	7.6	110.08
20	7.12 (2H, s)	—	136.42
12	7.21 (2H, t)	J_1=7.7, J_2=7.7	121.17
11	7.43 (2H, t)	J_1=7.5, J_2=7.5	121.17
10	8.38 (2H, d)	7.9	110.08
4	8.82 (1H, t)	J_1=7.8, J_2=7.7	148.83
3,5	9.26 (2H, d)	7.6	121.11
0thers	—	—	118.38, 128.97, 154.21, 159.33, 166.12

Table 3.17 ^{1}H- and ^{13}C-NMR spectra of **3e**

Location of atom(s)	*^{1}H-NMR (δ ppm)*	*J (Hz)*	*^{13}C-NMR (δ ppm)*
23, 24	1.93 (12H, s)	—	19.36
25, 27	2.07 (12H, s)	—	21.87
26	2.18 (6H, s)	—	21.18
16	6.01 (4H, s)	—	47.45
13	6.61 (2H, d)	7.6	111.36
12	6.96 (2H, t)	J_1=7.6, J_2=7.6	118.62
11	7.17 (2H, t)	J_1=7.7, J_2=7.7	118.62
10	7.82 (2H, d)	7.8	111.36
4	8.25 (1H, t)	J_1=7.8, J_2=7.8	149.32
3, 5	8.89 (2H, d)	8.0	121.82
0thers	—	—	133.92, 137.38, 149.32, 162.69, 170.07

3.4 Catalytic experiments

3.4.1. Transfer hydrogenation of acetophenone catalyzed by Ru(II)-bzimpy complexes

Transfer hydrogenation has been studied extensively in the last decade and catalysts that combine known metal complexes with new ligands are reported continuously. However, except for the discovery and exploration of effective Ru(arene)-complexes no other major breakthrough has been published in the recent years. We are not aware of any previous reports of transfer hydrogenation of acetophenone with Ru(II)-bzimpy complexes as catalyst. In this work, we described the synthesis of Ru(II)-bzimpy complexes (**2a-e**).

Catalytic studies with the complexes of type **2a-e** were performed for the transfer hydrogenation of acetophenone in the presence of KOH by 2-propanol. Reactions were performed under identical conditions to allow comparison of results.

To investigate the time dependency of auxiliary ligands on catalytic activity the properties of benzyl, mesityl, tetramethyl benzyl, and pentamethyl benzyl coordinated complexes **2a-e** were also studied, Figure 3.16.

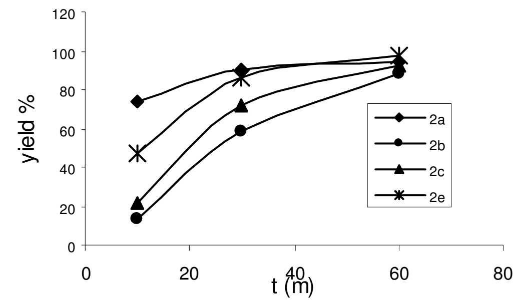
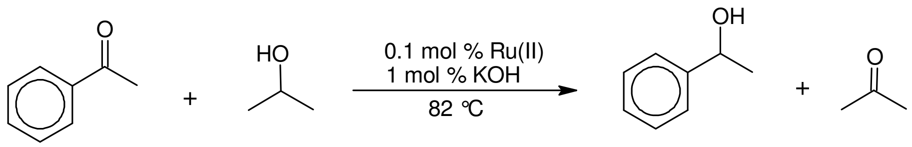


Figure 3.16. Time dependency of transfer hydrogenation of acetophenone catalyzed by the Ru(II)-bzimpy complexes of type **2a-e**

Reactions were carried out at 82 ºC using 10 mmol acetophenone with 0.1mol % Ru(II) in 20 mL of 2-propanol for 1 h

As can be seen from Figure 3.16, the Ru(II)-bzimpy complexes (**2a-e**) are found to be active catalysts in transfer hydrogenation of acetophenone. The results were summarized in Table 3.18.

Table 3.18. Catalytic activity for transfer hydrogenation of acetophenone catalyzed by Ru(II) complexes



Entries	Catalyst	Yield [%]	Time (minute)
1	**2a**	73,916	10
2	**2b**	13,284	
3	**2c**	21,632	
4	**2d**	32.767	
5	**2e**	46,801	
6	**2a**	90,541	30
7	**2b**	58,142	
8	**2c**	72,028	
9	**2d**	79,981	
10	**2e**	85,567	
11	**2a**	94,370	60
12	**2b**	88,516	
13	**2c**	91,964	
14	**2d**	93,769	
15	**2e**	96,934	

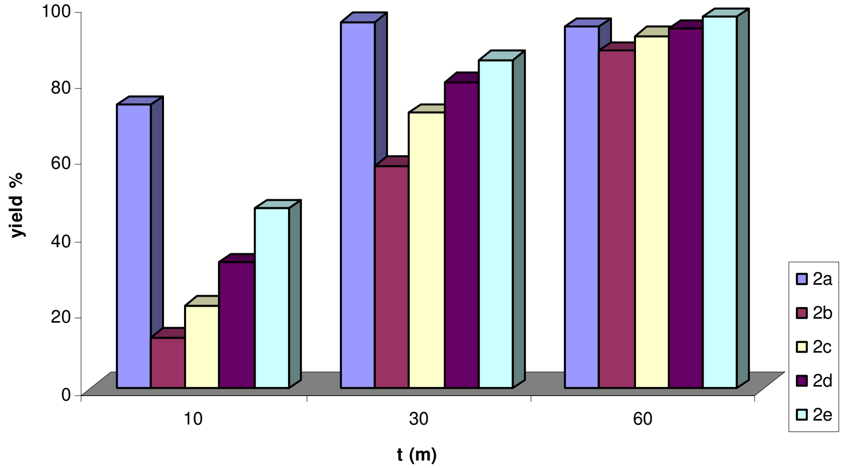


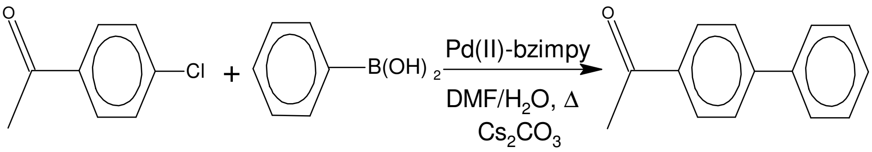
Figure 3.17. Catalytic activity for transfer hydrogenation of acetophenone catalyzed by the Ru(II)-bzimpy complexes of type **2a-e**

3.4.2 Suzuki coupling reactions catalyzed by Pd(II)-bzimpy complexes

Biaryls are an important class of organic compounds. Natural products, polymers, advanced medicinal materials area interest in these biaryl derivatives. When the coupling reactions of organoboron compounds with aryl, alkenyl and alkynyl halides are performed these reactions are called the Suzuki reactions or Suzuki-Miyaura coupling. The reactions are usually carried out homogeneously in the presence of a base under inert atmosphere. The reactivity of the aryl halide component decreases drastically in the order X = I > Br > CI and electron drawing substituents R are required for the chlorides to react.

The palladium-catalyzed cross-coupling of arylboronic acids with-aryl halides has been shown to proceed under a variety of conditions: a wide range of bases and solvents, as well as catalysis, have been employed with varying degrees of success according to the substrates (Suzuki, 1999; Stanforth, 1998). To find optimum conditions a series of experiments has been performed with aryl halide and phenylboronic acid as model compounds and as a base, Cs_2CO_3 was the best choice and as a solvent DMF/H_2O mixture was found to be better than other solvents. This optimized coupling reaction conditions used for catalytic experiments. The scope of the reaction and efficiencies of the salts were evaluated by investigating the coupling of $C_6H_5B(OH)_2$ with various p-substituted aryl chlorides. The results were summarized in Table 3.19.

Table 3.19. The Suzuki Coupling reaction of aryl halides with phenylboronic acid



Entries	Catalyst	Time (min)	Yield [a,b] %
1	**3c**	30	29[a]
2	**3d**	30	38[a]
3	**3e**	30	52[a]
4	**3c**	60	41[a]
5	**3d**	60	47[a]
6	**3e**	60	59[a]
7	**3c**	120	53[a]
8	**3d**	120	62[a]
9	**3e**	120	68[a]
10	**3b**	30	48[b]
11	**3c**	30	77[b]
12	**3d**	30	89[b]
13	**3e**	30	98[b]

[a] Reaction temperature 50 °C.
[b] Reaction temperature 100 °C.

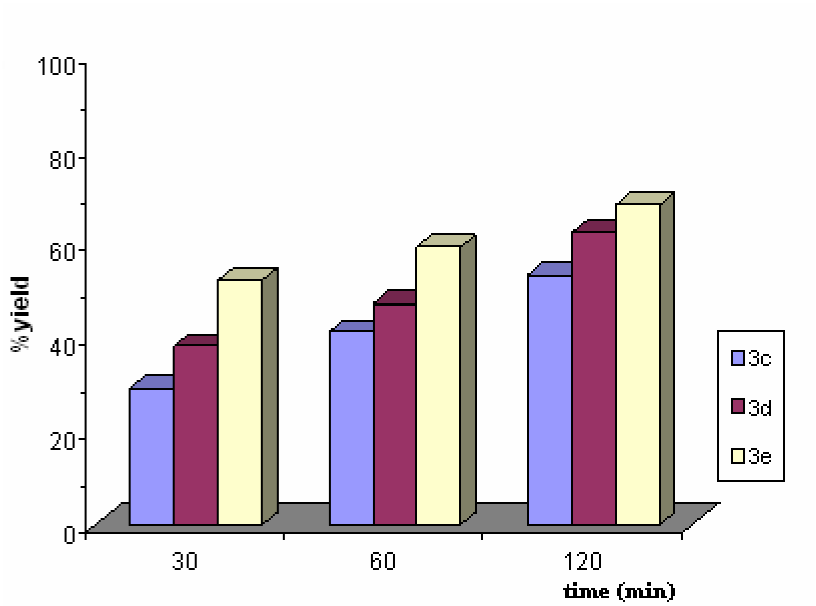


Figure 3.18. The results of Suzuki coupling reactions at 50°C catalyzed by the Pd(II)-bzimpy complexes of type **3c-e.**

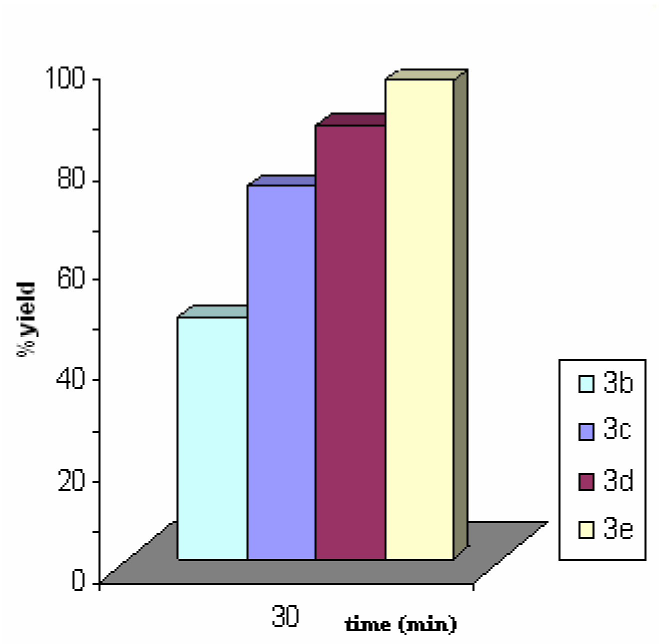
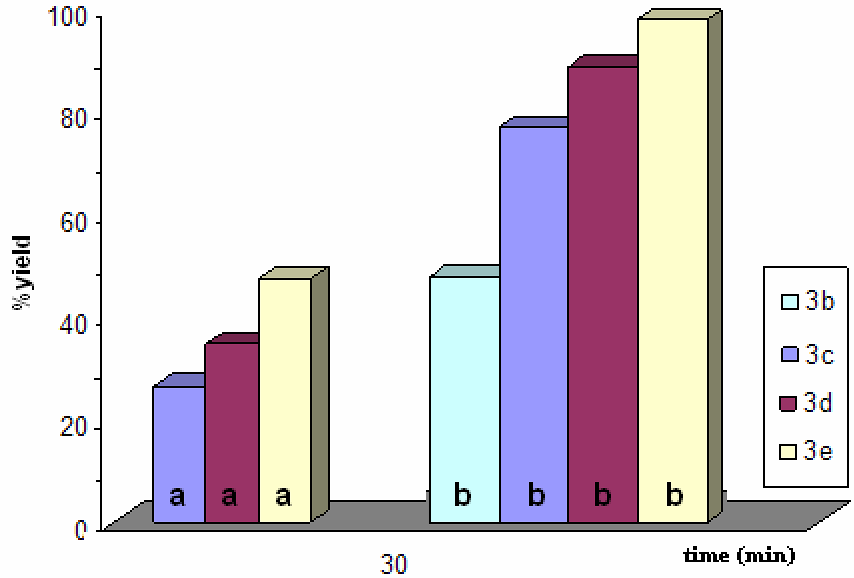


Figure 3.19. The results of Suzuki coupling reactions at 100°C catalyzed by the Pd(II)-bzimpy complexes of type **3b-e.**



[a] Reaction temperature 50 °C.
[b] Reaction temperature 100 °C

3.5 Conclusions

Control over the electronic and/or steric properties of ligand is of critical importance for optimization of the catalytic activity of transition metal complexes. Subtle variations of electron density and streic bulk at the active site may have drastic effects on the catalytic efficinces. Therefore, we wished to modify in a systematic manner one of a common tridentate ligand bzimpy to allow the systematic tuning of the electron density of Ru(II) and Pd(II) bonded bzimpy ligands. Such ligand complexes were prepared in a straightforward manner.

We have used two different catalytic reactions to probe the substituent influence of R groups on N_1 atom of benzimidazole ring. The described Ru(II) complexes bearing tridentate bzimpy ligands reveal differences in their behaviour as precatalysts for transfer hydrogenation of acetophenone. Time dependency is also drastic. For example for the 10 and 30 min periods **2a** is best. In other words, complexes with N-alkyl substitution show lower activities than the complexes with N-H. But for 60 min period catalytic activity increases in the following order **2b** < **2c** < **2d** < **2a** < **2e**. This observation is consistent with the proposed mechanism.

The ionic palladium(bzimpy) complexes were used as catalyst for the Suzuki coupling reactions of *p*-chloroacetophenone with $PhB(OH)_3$. Catalitic activity is efficient at 100 ^oC and proportional with the electron donating ability of the phenyl ring. The following order was obtained: **3b < 3c < 3d < 3e.**

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CURRICULUM VITAE

Name Surname	**:**	Salih GÜNNAZ
Profession	**:**	Chemist
Date / Place of Birth	**:**	1981/ Ankara
Nationality	**:**	Turkish
Sex	**:**	Male
Marital Status	**:**	Single
Address	**:**	Ege University, Faculty of Science, Department of Chemistry, Division of Inorganic Chemistry, Bornova-Izmir / Turkey
E-mail	**:**	salihgunnaz@msn.com

EDUCATIONAL BACKGROUND

B.S in Chemistry, 2005, Ege University, Izmir-Turkey
M.S in Chemistry, 2007, Ege University, Izmir-Turkey