

**SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF
PALLADIUM(II) AROYLHYDRAZONE COMPLEXES IN MIZOROKI-
HECK REACTION**

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REACTION

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Special dedication to my parents, family and friends for their support and love.

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ABSTRACT

The palladium catalyzed Mizoroki-Heck reaction represents one of the most important methods for the formation of carbon-carbon bond in organic synthesis. The application of palladium(II) Schiff base complexes as homogenous catalyst have gained interest due to their high stability and flexibility. This dissertation reports on the synthesis, characterization and catalytic activity performance of new palladium(II) aroylhydrazone complexes in the homogenous Mizoroki-Heck cross-coupling reaction under optimum condition. Two new aroylhydrazone ligands have been synthesized by condensation reaction between salicyloylhydrazide with 2-acetylpyridine and 2-benzoylpyridine in a 1:1 molar ratio. The corresponding palladium(II) complexes were synthesized by treating the ligands with one mole equivalent of bis(benzonitrile)palladium(II) chloride at room temperature. All the obtained products were fully characterized by FTIR, $^1\text{H-NMR}$ and UV-Vis spectroscopic techniques. The spectroscopic data revealed that the aroylhydrazone ligands acted as monobasic tridentate donor, coordinating through the enolic oxygen, imine nitrogen and pyridyl nitrogen atoms to the palladium $^{2+}$ ion. The performance of the palladium(II) complexes as homogeneous catalysts were evaluated in the Mizoroki-Heck reaction of arylbromide with methyl acrylate in the presence of triethylamine as base and *N,N*-dimethylacetamide as solvent at 120 °C. Both catalysts gave the conversion of 4-bromoacetophenone up to 100% after 24 hours with almost 100% selectivity of the expected *trans*-methyl 3-(4-acetylphenyl)acrylate.

ABSTRAK

Tindak balas Mizoroki-Heck bermangkinkan kompleks paladium(II) merupakan salah satu kaedah yang paling penting untuk pembentukan ikatan karbon-karbon dalam organik sintesis. Aplikasi kompleks paladium(II) bes Schiff sebagai pemangkin homogen telah menarik minat kerana kestabilan yang tinggi dan fleksibel. Disertasi ini melaporkan mengenai sintesis, pencirian dan pencapaian aktiviti pemangkinan bagi kompleks paladium(II) aroilhidrazon yang baru dalam tindak balas homogen ikatan karbon-karbon Mizoroki-Heck pada keadaan optimum. Dua ligan baru aroilhidrazon telah disintesis melalui tindak balas kondensasi antara saliseloihidrazida dengan 2-asetilpiridina dan 2-benzoilpiridina dalam nisbah molar 1:1. Kompleks paladium(II) yang sepadan telah disintesis melalui tindak balas antara ligan aroilhidrazon dan bis(benzonitril)paladium(II) klorida dalam nisbah satu mol yang setara pada suhu bilik. Kesemua produk yang diperolehi, dicirikan sepenuhnya menggunakan teknik spektroskopi FTIR, ^1H -NMR dan UV-Vis. Data spektroskopi mendedahkan bahawa ligan aroilhidrazon bertindak sebagai penderma tridentat monobes yang terkoordinat melalui atom oksigen enol, nitrogen imina dan nitrogen pyridil pada ion paladium²⁺. Prestasi kompleks paladium(II) sebagai pemangkin homogen telah dinilai dalam tindak balas Mizoroki-Heck antara arilbromida dengan metil akrilat dengan bantuan trietilamina sebagai bes dan *N,N*-dimetilasetamida sebagai pelarut pada 120 °C. Kedua-dua pemangkin memberikan penukaran 4-bromoasetofenon sebanyak 100% selepas 24 jam dengan hampir 100% pemilihan terhadap *trans*-metil 3-(4-asetilfenil)akrilat yang dijangkakan.

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Transition-metal catalyzed reactions are recognized as important protocols in organic synthesis among which the palladium-catalyzed Heck reaction has occupied a special place. The Mizoroki-Heck reaction has remained an effective methodology in carbon-carbon bond formation over the past four decades, as highlighted by the numerous review articles and book (Shimada and Rao, 2012; Beletskaya and Cheprakov, 2000; Heck, 1979). Indeed, such coupling reactions have been widely used to prepare arylated alkene in fine chemicals, drug intermediates, natural products, bioactive compounds, UV absorbers, antioxidants by the chemical industry (Liu *et al.*, 2008; De Vries, 2001; Kagechika and Shibasaki, 1991). This wide application is made possible because the Mizoroki-Heck reaction is commonly used under mild conditions and can almost tolerate any sensitive functionality (Thathagar, 2006).

The effect of ligand on the structure and reactivity of transition metal complexes is an important topic of research in coordination and organometallic chemistry as well as in catalysis (Zanello *et al.*, 1987). The Mizoroki-Heck reactions are commonly carried out in the presence of phosphine ligands which have made use

of sterically demanded electron-rich tertiary phosphines as catalyst modifiers (Stambuli *et al.*, 2001; Ehrentraut, *et al.*, 2000; Littke and Fu, 1999). Considering the negative environmental effect, air-sensitivity, and cost of phosphine ligands, the development of phosphine-free catalysts for Heck reaction would be an important subject regarding academic and industrial application.

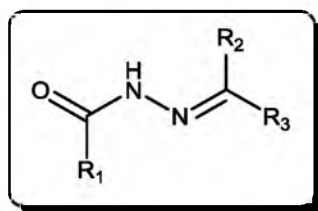


Figure 1.1 General structure of aroylhydrazones

Hydrazones which belong to a class of azomethines having the group -C=N-N- are interesting ligands in coordination chemistry. Introduction of a C=O group in the hydrazone part increases the electron delocalization and denticity of the hydrazone and the resulting compound is known as an aroylhydrazone. Aroylhydrazones with the general formula, $R_1C(=O)NHN=CR_2R_3$, where, $R_1, R_2, R_3 = H, \text{ alkyl or aryl}$, are derived from the condensation reaction between aliphatic or aromatic acid hydrazide with aliphatic or aromatic carbonyl compounds (Becker *et al.*, 2003 and Lovejoy and Richardson, 2002). They are an important class of Schiff base compounds with interesting ligation properties due to the presence of several coordination sites.

Furthermore, aroylhydrazones have well established to form stable chelate complex with transition metal cations by utilizing both their oxygen and imine nitrogen as donor atom, thereby producing a variety of molecular architecture and geometry. In addition, properties of aroylhydrazones can be tuned by modification of either the aromatic aldehyde or the hydrazide component (Pasayat *et al.*, 2014). They allow additional donor sites to be introduced (via R_1, R_2, R_3) in order to increase the denticity of the resulting ligands. In an aroylhydrazone, the basic sites

are carbonyl oxygen and the azomethine nitrogen.

Indeed, aroylhydrazones can act as potential multifunctional ligands with interesting coordination modes. The coordination mode adopted by an aroylhydrazone depends on different factors like tautomerism, reaction conditions, stability of the complex formed, number and nature of the substituent on hydrazone skeleton, with interesting ligation for variety of metal ion especially palladium (Monfared *et al.*, 2014).

It is interesting to note that aroylhydrazones can potentially form amido/iminol tautomers and *syn/anti* forms as indicated in Figure 1.2 and 1.3. This property offers the formation of a variety of complexes, where the aroylhydrazones can coordinate to the metal either in neutral amido form or in deprotonated iminolate form. The π -conjugation over the hydrazone moiety is increased by the enolization of the ligand which improves the electron delocalization (Manuel, 2012).

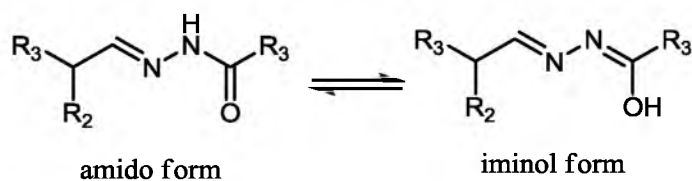


Figure 1.2 Tautomerism in aroylhydrazone

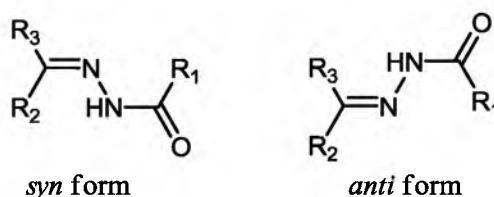


Figure 1.3 Geometrical isomers of aroylhydrazone

1.2 Problem Statement

The ligand assisted palladium-catalyzed cross-coupling reactions have become one of the most powerful synthetic methods of carbon-carbon bond formation in organic and organometallic chemistry. The ligand choice is known to be crucial for the success of a catalytic reaction. Until now, phosphine-based ligands have remained to be the most popular selection in the palladium-catalyzed cross-coupling reactions. However, these ligands usually need to be handled under inert atmosphere or dry conditions. In addition, they sometimes suffer from significant P-C bond degradation at elevated temperatures which leads to palladium aggregation and eventually affects the overall catalytic performance (Patil *et al.*, 2009). Furthermore, most of phosphine-based ligands are not readily available and some are cumbersome to synthesize; and of those that are commercially available many are expensive (Tao and Boykin, 2004).

Therefore, there has been considerable interest in the development of new nonphosphine-based palladium catalysts for higher activity, stability and substrate tolerance that allow reactions to be carried out under milder reaction conditions. Hence, among variety of synthesized ligands, hydrazones have been found to be very interesting because they can form stable complexes with almost all metal ions. Moreover, they are easily synthesized and economical since the starting material are cheap and easily accessible have made them a preferable choice (Andrade and Barros, 2010).

In this research, palladium(II) complexes containing aroylhydrazone ligands are investigated as catalyst in the Heck reaction between methyl acrylate and arylbromides. The selection of these ligands is due to their special advantages such as facile approach, tuneable steric and electronic environments on the metal centers. Meanwhile, the use of palladium as the metal center for the complex is due to its high selectivity, stability, and activity. In addition, palladium compounds are convenient reagent since they are usually stable and easy to handle which are not

very sensitive to heat, oxygen and moisture.

1.3 Objectives of the Study

The objectives of this study are:

1. To synthesize new aroylhydrazone ligands and their corresponding palladium(II) complexes.
2. To characterize the spectroscopic properties of the synthesized aroylhydrazone ligands and palladium(II) aroylhydrazone complexes using Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance spectroscopy (NMR), and Ultraviolet–visible (UV-Vis) spectroscopy.
3. To investigate the catalytic performance of the synthesized palladium(II) aroylhydrazone complexes in Heck coupling reaction between methyl acrylate and arylbromides.

1.4 Scope of the Research

This study involves the synthesis, characterization and catalytic activity evaluation of palladium(II) aroylhydrazone complexes with different pyridyl moiety. All the synthesized ligands and the corresponding palladium(II) complexes were structurally characterized by FTIR, $^1\text{H-NMR}$, and UV-Vis spectroscopic techniques.

The performance of the synthesized palladium(II) aroylhydrazone complexes as catalyst was evaluated in Mizoroki-Heck reaction between methyl acrylate and arylbromide using triethylamine (Et_3N) as base and dimethylacetamide (DMA) as a solvent. The percentage conversion of the products was monitored by gas chromatography (GC) and $^1\text{H-NMR}$ spectroscopy. The confirmation of the products

obtained was characterized by using FTIR and NMR spectroscopies.

1.5 Significance of the Research

This research demonstrates the catalytic efficiency of palladium(II) complexes bearing aroylhydrazone ligands which act as good catalyst for Mizoroki-Heck cross-coupling reaction. In particular, this study is a part of endeavors to develop new potential phosphine-free catalyst in order to achieve better reactivity and stability of Mizoroki-Heck reaction of carbon-carbon bond formation in organic and organometallic chemistry.

1.6 Thesis Outline

This thesis consists of five main chapters. A brief overview of the research background and objectives of this thesis are described in Chapter 1 followed by the discussion of literature reviews in Chapter 2. Chapter 3 provides the experimental methods that have been used in this study while the data and concise discussion of the findings obtained are presented in Chapter 4. Finally, Chapter 5 provides the conclusion of all the chapters and suggestions for future work.

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