

## **ABSTRACT**

M. Sc. Thesis

# **PALLADACYCLIC COMPLEXES AND THEIR CATALYTIC PROPERTIES**

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Palladium-catalyzed coupling reactions provide an efficient and powerful method for the formation of carbon-carbon and carbon-heteroatom bonds. They have recently become the most simple and efficient catalyst in applying to Suzuki-Miyaura and Heck-Mizoroki reactions. The advantages of such palladacyclic catalysts include their easy of synthesis, facile modification, and high activity, convenience of handling and comparative stability. Palladacycles are one of the most popular classes of organopalladium derivatives, which are widely applied in organic synthesis, organometallic catalysis, and new molecular materials.

Rapid developments in the area of metal-mediated cross-coupling reactions have highlighted both the positive and negative properties of phosphines as supporting ligands. The difficulties associated with removal of the ligands and their degradation byproducts, phosphines oxides, have encouraged researchers to explore alternative catalytic systems. To this end *N*-heterocyclic carbenes (NHCs) and metallacycle scaffolds have been used as ancillary ligands.

The NHCs have the general advantage of being better  $\sigma$ -donors than phosphines. In addition, significant steric demand brought by the presence of bulky substituents on the NHC facilitates elimination of the product. The strong interaction between metal and carbenic carbon of the imidazole moiety inhibits the dissociation, thereby minimizing the need for excess ligand.

Recently, the combination of a palladacycle framework and *N*-heterocyclic carbene (NHC) has been reported. There are a few studies in the literature about the synthesis of these complexes. These catalysts combine the stability induced by the presence of a palladacycle framework with the high activity associated with the NHCs. The advantages of such palladacyclic catalysts include their ease of synthesis, facile modification and convenience of handling. The second class of alternative catalysts focuses on palladacycles.

In this study has been characterized and prepared a series NHC-substituted palladacyclic complexes and also examined their catalytic activity in the Suzuki-Miyaura coupling reaction. Three major routes were applied for the synthesis of palladacyclic complexes. In the first step, the NHC precursor was prepared (**2a-c**). In the second step, acetate- and chloro-bridged palladacyclic complex was synthesized and the last step, as a result of the reaction between dimeric palladacyclic complex and NHC ligand was synthesized NHC-substituted palladacyclic complexes (**6a-c**, **7a-c**). These new compounds were characterized by elemental analysis,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy. The single crystal structure of **6c** was determined by single-crystal X-ray analysis.

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**Key Words:**

Palladacyclic, *N*-heterocyclic carbene, imidazolium salt, carbene precursor, C-C bond formation, palladium, X-ray diffraction, Suzuki coupling reaction.