



Review

Functionalized nitrogen ligands for palladium catalyzed cross-coupling reactions (part I)



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ABSTRACT

The Pd catalyzed cross coupling reactions of compounds containing C-X bonds (C-I, C-Br, C-Cl, C-N, C-O and C-H) with a variety of nucleophiles is one of the most efficient and reliable approaches for the construction of new C-C and C-heteroatom bonds. In recent years, great achievements have been made in this field, and many powerful catalytic systems based on ligand design have been developed. This comprehensive review covers recent effort made in the constructions of C-C and C-heteroatom bonds through Pd complexes based on the N ligands. We divided this topic into two parts. In present part we have focused on the applications of the ligands containing only N as a donor atom. In the next part we will cover all ligands and complexes containing N in combination with C, P, O and S as a donor atom.

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1. Introduction

Since the early 20th century the transition metal catalyzed reactions have been indispensable to all facets of modern chemical synthesis [1]. It is difficult to imagine the reactivity and selectivity of all known homogeneous metal catalysts. But from the last few decades, advances in ligand design bridged this divide, such that today many of the C-C and C-heteroatom bond forming reactions have been well understood. Over the past 50 years a great number of contributions have emerged from a wide range research groups with vast improvements on the Pd catalyzed cross coupling reactions [2].

Special advances have been made in the way of reaction scope including;

- (1) The use of different substrates like aryl halides, triflates, tosylates, mesylates, diazonium salts and many more.
- (2) Direct activation of C-H bonds selectively by proper selection of functional groups containing N as a donor atom (directing group).
- (3) The ability to conduct the coupling reactions at very low metal catalyst loadings.
- (4) Reactions at comparatively low temperatures.
- (5) Use of environmentally benign solvents like water or mixture of solvents containing water.
- (6) Easily recoverable and recyclable catalysts.
- (7) The procedures that utilize "ligand-free" conditions and

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- (8) Most importantly, an improvement in reaction conditions that have relied on the increased reactivity and stability of the metal catalysts by use of increasing efficacious supporting ligands.

For many Pd catalyzed functionalizations, the ligand design has driven many areas of homogeneous as well as heterogeneous catalysis. Thus, in this field ligand design that matches to a particular substrate with specific transformations has been of great importance. Additionally, it is also important how ligand behaviors such as tunability and modularity can be advantageous in the discovery of new reaction pathways.

1.1. The role of ligand

Activation of chemical bonds like C-X bond (C-I, C-Br, C-Cl, C-N, C-O, C-H etc.) by transition metals, especially Pd catalysts is one of the most significant and important areas of synthetic chemistry. This activation mainly depends on the nature of Pd complexes used in the catalytic processes.

The activity and stability of Pd complexes is highly dependent on the nature of Pd complexation by ligands *i.e.* the proper geometry at the metal center. Other than good catalytic activity, complexation also offers the inherent stability to metal. Hence, the design of proper ligands as well as the complex is very important for successful catalytic applications of metals. Recently, the role of ligand design in transition-metal catalysis for Pd(II)-catalyzed C-H functionalization was reported by Engle and Yu [3].

The ligand is an important variable in the catalytic cycle. It plays a very important role in transition-metal catalysis in the following ways:

- (1) Ligand coordination changes the structure and reactivity of a metal catalyst.
- (2) The ligand inherently changes the energy of activation of elementary steps involved in catalytic processes;

consequently, this change affects the kinetics which also broaden the substrate scope in the reaction.

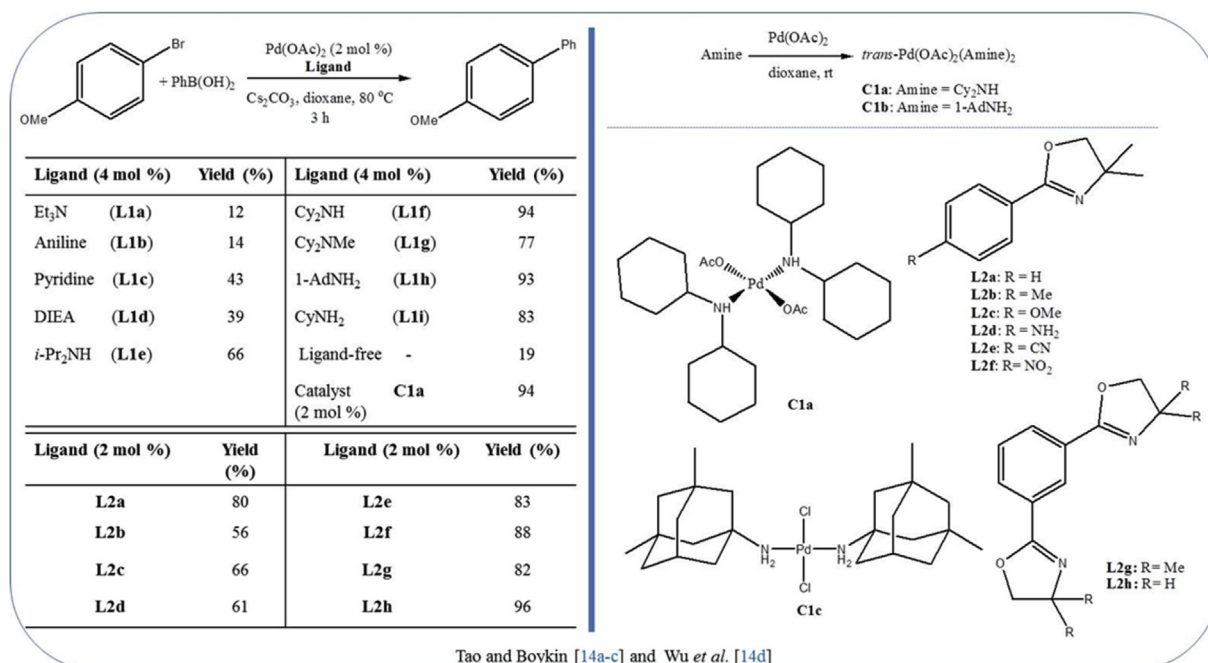
- (3) In addition, ligands can influence the selectivity of metal catalysts, including chemo, regio as well as stereoselectivity.
- (4) The ligand increases the solubility of metal catalysts in solvents, and hence prolongs the life time of catalysts by suppressing its degradation.
- (5) In many cases the precipitation of Pd as nanoparticles (PdNPs) and consequently its agglomeration into catalytically inactive Pd black are one of the main catalyst deactivation pathways. In this regard, many ligands strongly bind with Pd(0) and protect it from contacting one another and hence avoid its agglomeration.

As a consequence of the above points, the ligand can affect the operational properties of the reaction. In principle, ligands are “chemist’s hands” which improve the bond-making and bond-breaking processes that occurs at metal centers. In summary, over the last several decades, ligand design has been the prime driving force that improves known catalytic reactions and also the discovery of new ones.

The most common ligands reported for transition metal catalysis are based on P, N, S and or combination of P, N, S and O atoms. Much of the early research has been focused on phosphines as these are highly effective ligands. But due to some inherent disadvantages of phosphines, substitution of P by other donor atoms like N containing ligands are an emerging in the field of catalysis.

1.2. Objectives and organization

Since the first report, the construction of N based ligands for Pd catalyzed coupling has been attracting much interest and many excellent results have been achieved in recent years. Herein, this review presents a full survey of a catalytic system that enables the use of N ligands in many cross-coupling reactions of aryl, heteroaryl, electron-rich, electron-poor and sterically hindered aryl halides with different nucleophiles. In this report we discuss



Scheme 1. Suzuki coupling reaction using *trans*-[Pd(OAc)₂(Amine)₂] complexes.

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