CHAPTER 1

GENERAL INTRODUCTION

1.1. Introduction

1.1.1. Metal nanoparticles as catalyst and its importance

The term catalyst was first coined by Baron J. J. Berzilius in 1835, is a substance with unique properties that facilitates a chemical reaction without being itself consumed [1]. In order to do it the catalyst generally alters the reaction pathway by lowering the activation energy and thereby speeds up the reaction to achieve the equilibrium position rapidly [2]. In recent times, nanosciences and nanotechnology attained considerable interest due to their widespread applications in the field of catalysis, medicine, bio-sciences, electronics and optoelectronics, drug delivery, sensors, gas sensing, heavy metal removals from water etc. [3, 4].

1.1.2. Basic concept of nanoscience and nanotechnology

The term 'nano' is originally derived from a Greek word 'dwarf', 'nanos' which means extremely small and its placement on a metric scale (1 nm=10^{-9} m), clearly reveals its size. This can be more clarified by comparison, generally the spacing between carbon atoms in a molecule (carbon-carbon bond) are normally in the range of 0.12-0.15 nm, and DNA double helical DNA helix has a diameter of 2 nm in length. 'Nanoscience' is the study of phenomena manifested by materials at atomic and molecular level of dimensions ranging from a few nm to less than 100 nm. Normally, in nm length, materials exhibits unusual behavior intermediate between those of the smallest forms of elements from which they can be composed of (such as metal atom) and those of the bulk materials [5]. Professor Alivisatos told about nano that "At this size scale, everything, regardless of what it is, has new properties and that is, where a lot of scientific interest is." Because of this "nano" is so interesting [6].

"Nanotechnology" refers to research and technological development which is associated with materials of size ranging from 0.1 to 100 nm in any dimension (i.e. nanoscale). The U.S. National Nanotechnology Initiative (NNI) gives the following definition for nanoscience and nanotechnology: "Research and technology development at the atomic, molecular and macromolecular levels in the length scale of approximately the 1-100 nm range, to provide a fundamental understanding of phenomena and materials at the nanoscale and to create and use structures, devices and systems that have novel properties and functions because of their small and/or intermediate size".

1.1.3. History of nanotechnology

Although modern nanoscience and nanotechnology are considered as the invention of modern science, but its entire concept is not new. Recently, study reveals that the secret of Glass Lycurgus Cup are nanoparticles (NPs) which appear red in transmitted light and green in reflected light [7]. Another example is the Damascus steel which is used to make blades about 500 AD in Damascus. Later, it was found that the main reason behind the unique properties of these blades is due to the presence of multi-walled carbon nanotubes in the material. One of the most interesting examples of nanotechnology is the history of medieval stained glass artisans. Long years ago people know that alternate-sized gold (Au) and silver (Ag) particles created colors in the stained glass windows of medieval churches. The beautiful color of the windows is due to the presence of metal NPs in the glass [8]. In 18th century, Ag NPs sensitive to light were developed which are used in photography plates. The widespread concept of modern nanoscience and nanotechnology were first described in 1959 by famous Physicist Richard P Feynman in his speech, "There's plenty of room at the bottom, where he outlined the possibility of synthesis via direct manipulation of atoms". Over a decade later in 1974, Professor Norio Taniguchi first used the term "nanotechnology". However, until 1980, when Scanning Tunneling Microscope (STM) and other advanced analytical measurements were invented, not much progress was made in the field of nanoscience and nanotechnology. Actually, after the development of highly advanced analytical instruments like STM, Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM), which enables the researcher to characterized and manipulate small objects to few nm, and scientists began to explore the nanoworld.

1.2. Classifications of nanomaterials

The classification of nanomaterials is generally done based on the number of dimensions of a material, which are outside the nanoscale range (<100 nm). Accordingly, they are classified as zero, one, two and three dimensional.

1.2.1. Zero dimensional nanomaterials (0-D)

If all of its three dimensions are within the nanoscale range than it is called zero-dimensional nanomaterials, 0-D (i.e. no dimensions are larger than 100 nm) range. Generally, NPs are the examples of zero dimensional NPs.

1.2.2. One dimensional nanomaterials (1-D)

In one dimensional nanomaterials (1-D), one of its dimension is outside the nanoscale range and rest two are in the nanorange. Examples are nanotubes, nanorods and nanowires.

1.2.3. Two dimensional nanomaterials (2-D)

In two dimensional nanomaterials (2-D), only one dimension is within the nanoscale range, the rest two are outside the nanoscale range. Some of the examples of this class are graphene, nanofilms, nanolayers and nanocoatings.

1.2.4. Three dimensional nanomaterials (3-D)

Three dimensional nanomaterials (3-D) are the materials that are not limited to the nanoscale range in any dimensions, e.g. bulky powder, dispersions of NPs, bundles of nanowires, and nanotubes as well as multi-nanolayers.

1.3. Synthesis of NPs

There are two different ways for the synthesis of colloidal metal NPs:

Either by subdivision of bulk metals which employ physical methods (top-down approach), or by the growth of particles from metal atoms which utilize solution-phase colloidal chemistry (bottom-up approach) [9]. The key advantage of the former method is the generation of large quantities of nanocrystals along with the major issue of not being able to effectively control the size of nanocrystals produced. Colloidal chemical

synthetic methods, on the contrary to the previous method, provides control over size of nanocrystals produced to ensure production of uniformly sized NPs, which comes with a tradeoff of yielding smaller quantities. In this method, varied reaction conditions can be used to synthesize different shaped nanocrystals such as nanorods and nanowires. Large varieties of stabilizers are generally used to control the growth of nanoclusters and to prevent them from agglomerization, e.g. donor ligands, polymers and surfactants.

Four major ways of chemical synthesis of transition metal NPs are as follows:

1) Chemical reduction of metal salt precursor.
2) Thermal, photochemical and sonochemical reduction method.
3) Electrochemical reduction and
4) Biogenic approach.

1.3.1. Chemical reduction of metal salt precursor

This is the most commonly used method for the synthesis of metal NPs. This method uses hydrazine, molecular hydrogen, carbon monoxide, sodium borohydride ($NaBH_4$) as well as sodium citrate and alcohol solvents as reducing agents which are mixed with salt precursor in the presence of stabilizing agents such as ligands, surfactant or polymers. The latter prevent the undesired agglomeration and thereby helped in the formation of well dispersed metal NPs. The schematic approach of this is as follows.

$$x M^{n+} + nxe^- + \text{stabilizer} \rightarrow M^0 n \text{ (cluster)}$$

Factors such as metal precursor, reducing agent, solvent, temperature, concentration and reaction time greatly influence the size and shape of metal NPs formed. For example: Au NPs of size 1-5 nm can be prepared using polyvinylalcohol (PVA) as stabilizer and $NaBH_4$ as reducing agent [10]. The NPs show high catalytic activity for CO oxidation after deposition on metal oxide.

1.3.2. Thermal, photochemical or sonochemical reduction method

Thermolysis, a thermal decomposition reaction of transition metal salt, is a method of reduction involving decomposition of precursor material to zero valent form. A traditional thermolysis reaction, in the absence of stabilizers, yields colloidal Pd, Pt and

bimetallic Pd/Cu NPs with broad size distributions. However, when the reduction was done in the presence of stabilizing agents such as poly(N-vinyl-2-pyrrolidine) [11], the results were found to be greatly improved. Organic-phase synthetic methods have been used for their ability to synthesize NPs of high crystallinity, monodispersity and dispersibility in organic solvent.

Colloidal metal NPs can be synthesized by photochemical decomposition reaction in two ways: either by reduction of the transition metal salt by radiolytically produced reducing agent or by degradation of the organometallic complex by irradiation. The irradiation method generally employed includes X-ray or gamma ray irradiation and also UV-visible radiation.

Sonochemical decomposition reaction is a new method of synthesizing colloidal metal NPs [12]. The method involves generation of active species, reduction of the transition metal and growth of the colloid in a sonicated liquid medium.

1.3.3. Electrochemical Reduction methods

This method for the development of mono and bimetallic colloidal NPs was first developed in 1994 by Reetz and his group [13]. The process can be summarized in the following steps:

(i)   Oxidative dissolution of the sacrificial bulk anode.

(ii)   Migration of M^{n+} ion to the cathode.

(iii)   Formation of zero valent metal atoms at the cathode by reduction.

(iv)   Metal particle formation by nucleation and growth.

(v)   Growth process restriction and stabilization of the NPs by stabilizing agent, e.g. tetraalkylammonium ion.

(vi)   Precipitation of the nanostructure metal colloids.

Pd [14, 15], Ni [15], Ag [16] and Au NPs [17] have been successfully synthesized using this method. This method provides control over size of NPs by varying current intensity.

1.3.4. Biogenic approach

Though the uses of various physical and chemical methods for the synthesis of NPs are more popular and extensively used, but the use of toxic chemicals for the synthesis and their stability is the matter of concern. The demerit of these types of chemical methods is that the synthesized NPs usually possess some reactive functional groups that can be toxic to biological system. Also, the production of toxic byproducts during the synthesis process restricts their application in clinical processes. Therefore, nowadays the development of nontoxic, eco-friendly and rapid methods for the synthesis of NPs deserves special attention in nanotechnology. Biological methods for the synthesis of NPs (Fig. 1) are generally regarded as sustainable, cost effective, safe, and environment friendly processes. These types of biological synthetic methods however possess some demerits like culturing of microbes, which is generally a time consuming process, and also the rate of synthesis is comparatively slow. However, optimizing conditions like pH, incubation temperature and time, concentration of metal ions, and the amount of biological materials can reduce the issue that are associated with biological synthesis and can be used for large scale and commercial application.

The biosynthesis of NPs is normally based on bottom-up principle where reduction/oxidation is the main reaction involved [18]. In this process, the naturally occurring materials such as vitamins, sugars, plant extracts, microorganisms including fungi [19] and bacteria [20], vitamins, sugars, biodegradable polymers are generally employed as the reducing and capping agents [21].
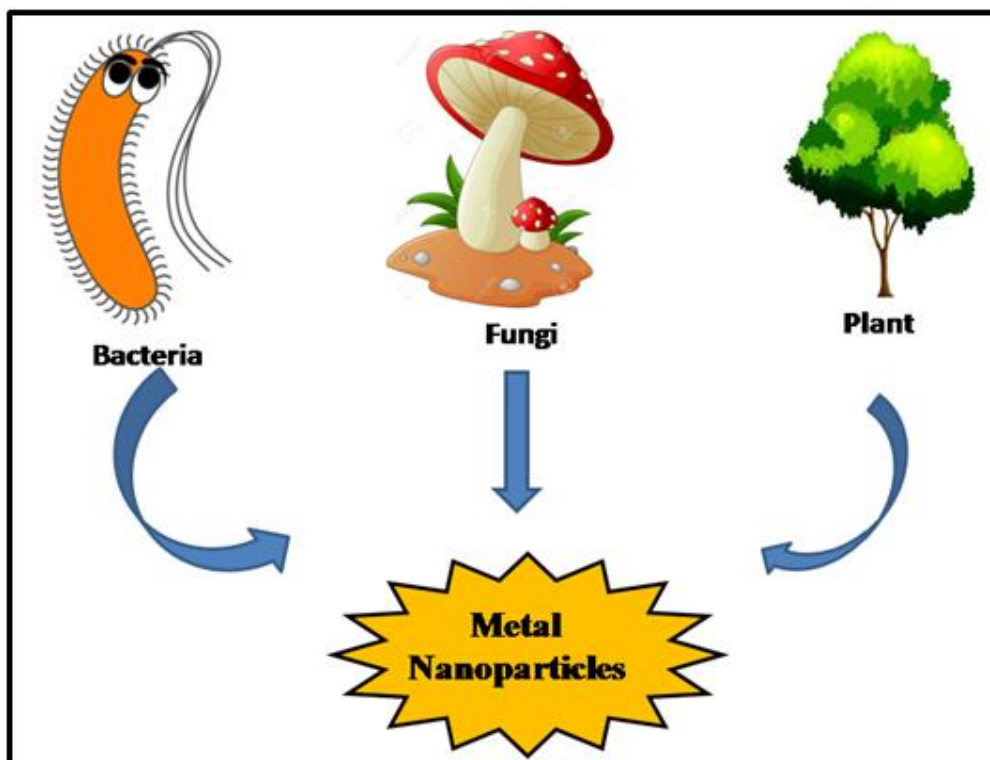
Fig. 1: Schematic representation of biosynthesis of metal NPs.

1.3.4.1. Synthesis of metal NPs by plants

In recent times, plant extracts can be used as source for the synthesis of metal NPs. This method has significance advantage over microbial synthesis of NPs, which requires an additional purification procedure for elimination of microbial contamination [22]. Moreover this method is less expensive, easily available, safe to handle and they possess a large varieties of metabolites that can assist the reduction process [23].

Leaf extract, root extract, bark, fruit bodies, callus extracts, peel extracts, seed etc. can be used to synthesize metal NPs. Different NPs like Pd [32,33], Au [24], Ag [25], Ni, Cu [26], Co, Zn [27], Fe [28], Se [29] NPs etc. have been efficiently synthesized by using plant extracts of different parts of plants.

The exact mechanism of reduction by plants extracts is not well explored yet. However it is believed that the phytochemicals that are present in the plant extracts are mainly responsible for reduction and stabilization of the NPs. The infra-red (IR) spectroscopic study reveals that the main phytochemicals like flavonoids, terpenoids, ketones,

aldehydes, amides, carboxylic acids and citric acids present in the plant extract are responsible for bio-reduction of the metal ions. This is the approach that this thesis will rely on.

1.3.4.2.   Synthesis of palladium nanoparticles (Pd NPs) by plants extracts

Though literature reveals ample numbers of reports on the biogenic synthesis of Au and Ag NPs, but few reports are available on biological synthesis of Pd NPs. The development of eco-friendly route for the synthesis of Pd NPs is of growing interest nowadays, as the synthesized Pd NPs has a wide varieties of applications as catalyst in various chemical transformation reactions such as in carbon-carbon bond formation reactions like Suzuki-coupling reactions, Mizorki-Heck reactions, still reactions and Sonogashira reactions and also in hydrogenation reactions, in fuel cell electrochemical reactions etc. Reports on plant mediated synthesis of various NPs showed that during the synthesis process the metal salt solution is first mixed with plant extract at room temperature or at elevated temperature and then the whole mixture was agitated to reduce the metal leading to nucleation and growth of metal NPs. In these types of synthetic methods the plant extracts plays the role of reducing agent as well as stabilizing agent. The various factors that can affect the size and morphology of the synthesized NPs are concentration of plant extract, metals salts, pH, temperature, reaction time etc. [30, 31]. Literature reveals that plants of various types and their parts such as leaves, fruits and roots has been utilized for the synthesis of Pd NPs. A few examples for the synthesis of Pd NPs using plant extracts are illustrated here.

Amongst the various parts of plant, leaf is considered to be the best raw material for the synthesis of NPs. An example is the spherical shaped Pd NPs of size 2.5 to 4.5 nm that has been synthesized from the leaf extracts of *Anacardium occidentale* plant [32]. Another report showed that the leaf extract of Soybean (*Glycine max*) could be used for the synthesis of Pd NPs of size 15 nm [33]. The different phytochemicals such as proteins, enzymes and some amino-acids present in the soyabean leaf are main sources responsible for its reduction potential.

It was also reported that fruit extracts of some plants could also be used for the synthesis of Pd NPs. Recent report showed that Pd NPs supported on reduced graphene oxide

nanocomposites can be synthesized using the fruit extract of *Berberis vulgaris* [34]. The presence of flavonoids, vitamins (Vit C), phenolic acids are mainly responsible for the bio-reduction process. Apart from leaf and fruit extracts, other parts of the plants are also being used for the synthesis of Pd NPs. Reports are also available in the literature that the root extract could be used for the synthesis of Pd NPs. For example, the root extract of *Asparagus racemosus* Linn has been used for the synthesis of highly stable Pd NPs of spherical morphology with particle size ranging from 1 nm to 6 nm [35]. Phytochemicals present in the root extract like phototropins and flavones are assumed to be responsible for the reduction. Similarly, Kumar and his coworkers reported the synthesis of spherical Pd NPs using bark extract of *Cinnamon zeylanicum* [36].

1.4. Synthesis of copper oxide NPs (CuO NPs)

Metals can form a large numbers of oxides, which plays vital role in many areas of chemistry, physical and material sciences [37]. Due to the vast applications of Cu based NPs particularly in catalytic organic transformations, electrocatalysis and photocatalysis [38] they are considered superior amongst other metal NPs. This is because of the fact that Cu can access a number of oxidation states (Cu^0, Cu^I, Cu^{II}, Cu^{III}), which enables them to take both one and two electron pathways. CuO NPs is a brownish-black powdered solid and find growing interest due to their catalytic, optical, electrical and mechanical properties [39]. Nano CuO exhibit much improved properties such as catalytic activity and selectivity compared to ordinary copper oxide. A few synthetic approaches for CuO NPs synthesis are discussed below:

Tamaekong and his co-workers. first reported a method for the synthesis of CuO NPs using thermal route [40]. The precursors materials that they had used in this method were Copper (II) acetate [$Cu(CH_3COO)_2 \cdot xH_2O$] and Sodium hydroxide (NaOH) and ethanediol ($C_2H_6O_2$) was used as solvent. During the synthetic process, they dissolved 25 mM of $Cu(CH_3COO)_2 \cdot xH_2O$ and 100 mM of NaOH in ethanediol at 80 ºC and then allowed to stir for 2 h. The pH was maintained around 9 throughout the process. Finally, the product was washed with deionized water and dried to get the desired NPs.

Another group reported a method for the synthesis of CuO NPs in liquid ammonia in presence of sodium metal [41]. First, by reducing copper nitrate with alkali metal in

liquid ammonia they obtained the Cu NPs and thereafter CuO NPs were formed in the ambient conditions.

Zhang and his co-workers reported a method for the synthesis of hollow CuO microspheres with diameters 1-1.5 μm *via* a rational complexing-reagent assisted approach at low temperature, where they used $Cu(CH_3COO)_2 \cdot H_2O$ as copper source and $(CH_2)_6N_4$ (HMTA) served not only as complexing reagent but also as indirect template [42]. An aqueous solution containing 1.25 mmol $Cu(CH_3COO)_2 \cdot H_2O$ and 2.5 mmol $(CH_2)_6N_4$ was stirred continuously for 2 h. The reaction was stopped and allowed the solution to stand at room temperature for 1 day. The precipitate was filtered and washed and dried in an oven at 50 ºC to obtain $[Cu(C_6H_{12}N_4)_2](OOCCH_3)_2$ nanosheets. Appropriate amount of the nanosheet was then loaded in an autoclave and heated upto 180 ºC for 18 h and cooled to room temperature in open air. The precipitate was filtered off, washed and dried in an oven to get the CuO nanocatalyst.

1.5.   General characterization techniques

Generally, the principle of nanotechnology lies on the fact that the properties changes dramatically as the size of the material reduces from the bulk size to nm size. As the study of these materials at this nanodimension scale is not an easy task and requires highly advanced sophisticated instruments and thus nanotechnology motivated the scientists to invent some highly sophisticated nanoscopic characterization techniques to allow better control over morphology, dimension and size of the materials in this nanoscale range. The X-ray diffraction (XRD) technique based on Bragg's law is a powerful method for the study of nanomaterials. This method is useful for determining crystallinity, crystal structure and lattice constants of NPs. Using Scherre's formula, the method is also helpful for determining the approximate particle size of the NPs formed.

SEM [43] and TEM [44] are electron microscopic techniques commonly used to take surface image and transmitted image of NPs. Even though both techniques are invented within the same decade but, there is a distinct difference in their uses. While SEM uses the scattered or secondary electrons to generate a three dimensional images of the sample, the transmission electron microscope directly project electron through an ultrathin specimen slice to produce a two dimensional image. SEM is generally used to

visualize the surface morphology of the samples while TEM allows one to study the inner surface. Energy dispersive X-ray technique referred to as EDS or EDAX is an X-ray technique associated with SEM or TEM, and used to determine the elemental composition of the sample. High resolution transmission electron microscopy (HRTEM) associated with TEM is an additional imaging mode associated with TEM that allows the researcher to imagine directly at an atomic resolution scale.

Apart from these well-established techniques of electron microscopy, scanning probe microscopy (SPM) is relatively a new branch of microscopy where a physical probe (3-50 nm radius of curvature) was used, which scans the specimen to forms images of surfaces atoms. STM and AFM are the two most common techniques of scanning probe techniques. Because of these two techniques nanofabrication and processing have achieved great advances during the last decade. AFM generally measures the interaction force by moving a nm sized tip across the surface and thereby precisely captures the image, while the STM record images using quantum mechanical tunneling principle. The resolution of AFM is however better than STM. STM is normally applicable to conductors, while AFM is applicable both to conductors and insulators. In spite of these advanced techniques there are also some common spectroscopic techniques like Fourier Transform-Infrared (FT-IR) and Ultraviolet (UV)-visible spectroscopy that are generally used to determine the nature of bonds/conjugation etc. whenever these parameters are necessary.

1.6. Historical background and aspects of C-C and C-Heteroatom bond forming reactions

In the domain of synthetic organic chemistry, carbon-carbon, carbon-heteroatom bond formation reactions possess profound importance. They are regarded as the heart of chemical science and the key to set up the carbon backbone of organic molecules and life itself. Such types of coupling reactions have vast applications in the production of polymers, agrochemicals and pharmaceutical intermediates [45].

During the past 20-30 years, a vast development has been observed in organic synthesis particularly in the domain of C-C and C-heteroatom bond forming reactions [46]. The main motive for all these was to discover new kinds or to improve the efficiency of

already existed drugs to treat all kind of diseases and also for improvement of our daily life. Although a numbers of methodologies are available in the literature for the synthesis of C–C and C–Heteroatom containing compounds but, generally they are associated with shortcoming like difficulties in products isolation, low yields, less electivity and limited substrate scopes. As a consequence, the development of new methods which are relatively cost effective, efficient and selective for the generation of C–C and C–Heteroatom containing compounds still remains a challenging task among modern synthetic organic chemists.

In synthetic organic chemistry, cross-coupling reactions are an important class of reactions for the construction of various types of carbon-carbon and carbon-heteroatom bonds. Different types of transition metals like Cu, Pd, Ni, Co, Ru, Rh etc. are commonly used as catalysts for these reactions and are often termed as transition metal catalyzed cross-coupling reactions. But, the high cost, stability and toxicity of these types of transition metals along with the addition of ligands often restrict their use. Thus, nowadays the developments of less expensive and eco-friendly catalyst for C-C and C-heteroatom formation reaction are much more popular among researchers. Again, this is an era of nanocatalysis and different nanocatalysts have been used widely in various C–C and C–Heteroatom bond formation reactions owing to their high surface area. Also, the heterogeneous nature of the catalyst is one of the most important advantages to the field of catalysis as it overcomes the limitation of homogeneous catalyst of non-recoverability from the reaction medium. Some of the efforts taken by us on the development of Pd and Cu based nanocatalyst and their applications in C-C and C-heteroatom bond forming reactions are described in this thesis.
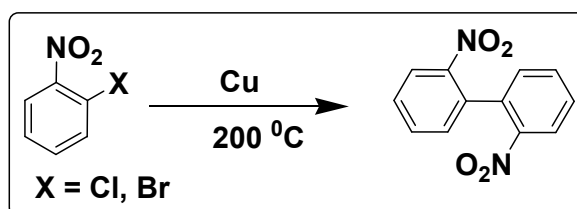
1.7.   A review on C-C bond formation reactions

The carbon-carbon bond formation reactions are the most fundamental reactions for the construction of a molecular framework in synthetic organic chemistry and hence they represent the cutting edge of research in organic chemistry [47-51]. Traditionally, Friedal-Craft reaction, Wurtz type reactions, nucleophilic addition and substitution reaction, can be recognized as the basic methods for construction of C–C bond. Introduction of transition metal catalyst increases the efficiency of these reactions. In 1869, Curl Glaser first report the transition metal catalyzed C–C bond forming reaction.

He showed that in presence of Cu catalyst, phenyl acetylene undergoes smooth oxidative dimerization to form diphenyldiacetylene (scheme 1) [52].
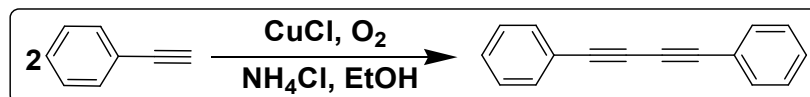

Scheme 1: Cu catalyzed Glaser coupling reaction.

After few years, Ullmann reported another method for Cu catalyzed homocoupling reaction [53]. The reaction Scheme is shown below (scheme 2).


Scheme 2: Ullmann homocoupling reaction.

The chemistry of palladium catalysis is considered as one of the historic developments in the field of C–C bond formation reactions. Richard Heck was considered as the pioneer person in this field. In his report, he described a cross-coupling reaction between organomercuric compounds and alkene in the presence of catalytic amount of Li_2PdCl_4 [54]. Later on, the work was modified by replacing toxic organomercuric compounds with aryl halide by Mizoroki and Heck and the reaction is known as Heck reaction (or also called the Mizoroki-Heck reaction) (Scheme 3).
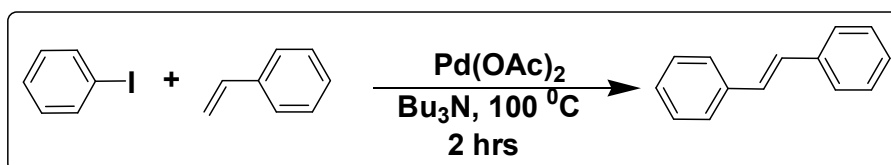

Scheme 3: Mizoroki-Heck reaction between Iodobenzene and Styrene.

In the year 1975, Kenkichi Sonogashira, Yasou Tohda and Nobue Hagihara reported a palladium catalysed cross-coupling reaction of terminal alkyne *sp* hybridized carbon with a *sp²* hybridized carbon of an aryl or vinyl halide (or triflate) producing a substituted alkyne product [55] popularly known as Sonogashira reaction. The reaction is generally accelerated by the addition of Cu-salt as co-catalyst and an amine base in the presence of suitable phosphine based ligands. The reaction name arises from its discoverer Sonogashira, Tohda and Hagihara and is now become one of the most important methods to prepare arylalkynes and conjugated enynes, which are the precursors found in natural products, pharmaceuticals and molecular organic materials.
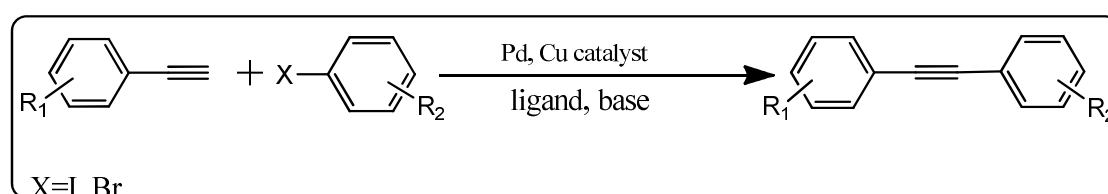
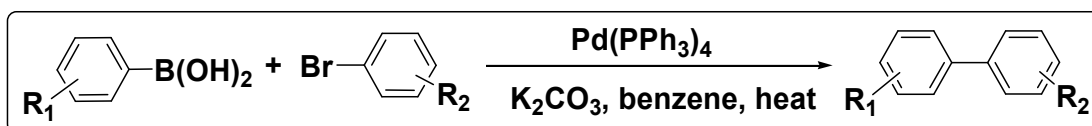Scheme 4: Sonogashira cross-coupling reaction.

Negishi [56], during the same period, reported another method for synthesizing biaryl compounds by using a cross-coupling reaction between organozinc compounds and organic halides (Scheme 5).
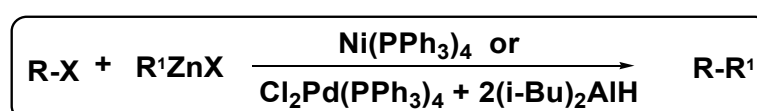
Scheme 5: Negishi coupling reaction.

In 1979, Suzuki and Miyaura reported a synthetic protocol, in which they used a coupling reaction between organic electrophiles including halides or triflates with different types of organoboron reagents (arylboronic acids, arylboronic esters, tetraphenylborate, organotrifluoroborates) have probably become one of the most extensively used methods for the formation carbon-carbon bond formation reaction in presence of palladium catalyst [57]. The key advantages it bears over other cross-

coupling reactions is the mild nature of organoborons, which are generally non-toxic and stable to air, heat and moisture with great functional group tolerance. It's because of such an impactful discovery, Akira Suzuki together with Richard F. Heck and Eiichi Negishi were awarded the Nobel Prize in Chemistry "for palladium-catalyzed cross-couplings in organic synthesis" in 2010.

Scheme 6: Suzuki-Miyaura cross-coupling reaction.

Apart from these well-known reactions for the formation of C-C bond, a numbers of other reactions are also there in the mentioned area. Stille reaction [58], Kumada reaction [59], Tsuji-Trost reaction [60] etc. are the name of some common reactions in this field. As in all of the mentioned reactions, oxidative addition is the major step in the reaction, and so they are commonly termed as oxidative addition C-C bond formation reaction. Though these types of reactions provide some general procedures for C-C bond formation reaction, but they are associated with some major drawbacks like using harsh conditions like high temperature, expensive ligands, inert atmosphere etc. which are against the green chemistry principle. Therefore, avoiding the use of such types of harsh conditions and therefore tuning the reaction is very much necessary and nowadays become the burning topic among research groups. In this thesis we mainly focused on Suzuki-Miyaura and Sonogashira reaction.

1.7.1. Suzuki-Miyaura cross-coupling reaction

Since from its discovery in 1979 [57], the palladium-catalyzed Suzuki-Miyaura cross-coupling reaction between organic electrophiles including halides or triflates with different types of organoboron reagents (arylboronic acids, arylboronic esters, tetraphenylborate, organotrifluoroborates) have probably become one of the most widely used synthetic methods for the construction of C-C bond (Scheme 6). As already mentioned its main advantages over other cross-coupling reactions are the fact that

organoborons are mild in nature, non-toxic and stable to air, heat and moisture with great functional group tolerance. The, biaryl derivatives which are the product of the reaction are the structural components of numerous drugs, natural products, optical devices, herbicides, pharmaceuticals, conducting polymers and advanced functional materials [61]. The general mechanism of Suzuki-Miyaura reaction proceeds through oxidative addition, transmetalation and reductive elimination stages (Fig. 2).

Mechanistically, in the first step, oxidative addition of the organohalides to the Pd(0) species occur to form a organopalladium complex along with the oxidation of Pd(0) to Pd(II). This step is the rate determining step of the catalytic cycle. The addition of sigma-donating ligands generally accelerates the oxidative addition step and hence enhances the reaction. During this oxidative addition step, *cis*-palladium complex forms which rapidly isomerizes to trans-complex.

Transmetallation is the second step in Suzuki coupling reaction. A molecule of the base (hydroxide or alkoxide) exchanges the halide on the palladium complex while another molecule binds to the organoborane to form a borate reagent, thereby making its organo (R) group more nucleophilic. During the transmetallation step, the nucleophilic organic group bound to the electropositive boron group shifts to the palladium metal complex. Thus, this transmetallation step is dependent on the strength of the base.

The final step, known as reductive elimination step, where the palladium complex eliminates the product and regenerating the Pd(0) species. Generally, the reductive elimination steps proceeds through retention of configuration.

Different types of ligands based on phosphorous and nitrogen are generally used in Suzuki-Miyaura cross-coupling reactions, as these ligands are believed to increase the electron density over palladium, which in turn accelerates the oxidative addition step. It was found that till 1998, triarylphosphine ligands were the most commonly used ligand for Suzuki-Miyaura cross-coupling reactions. But, later on the effect of different phosphorus based ligand on the activity of Pd complexes was studied by different research groups. The enhanced catalytic activity of Pd complex using bulky tri-*o*-tolylphosphine ligand was reported by Heck and his co-workers [62]. Similarly, Osburn reported the higher catalytic activity of phosphanes which had well defined steric volume and also basic in nature [63]. From these kinds of studies, it was revealed that the

bulkiness of phosphine ligands had a strong influence on oxidative addition reaction as well as the Suzuki-Miyaura cross-coupling reactions.
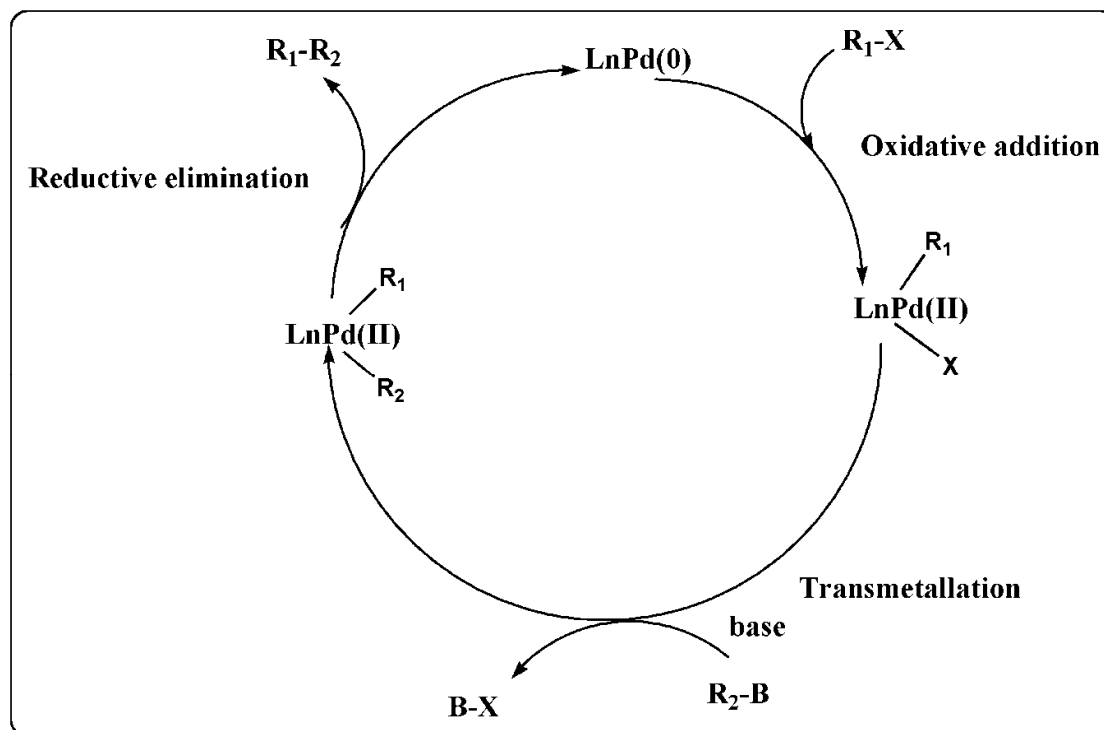

Fig. 2: Mechanism of Suzuki-Miyaura cross-coupling reaction.

Likewise phosphine ligands, *N*-based ligands are also used in Suzuki-Miyaura cross-coupling reaction. The first application of Pd-*N*-heterocyclic carbene (Pd-NHC) was reported by Hillier and his coworkers in the year 2002 [64]. After this initial assessment, a number of examples are reported for Suzuki-Miyaura cross-coupling reactions using Pd-NHC.

Apart from NHC a large numbers of other NHCs are also there which are successfully applied for efficient Suzuki-Miyaura cross-coupling reactions. In the year 2004, Boykin *et. al.* reported a new catalyst, DAPCy for cross-coupling reaction [65]. Li and his coworkers reported a highly efficient catalytic system, Pd(OAc)$_2$/DABCO towards an efficient Suzuki-Miyaura cross-coupling reactions [66]. Some examples of nitrogen and phosphorous based ligands are listed in Scheme 7.
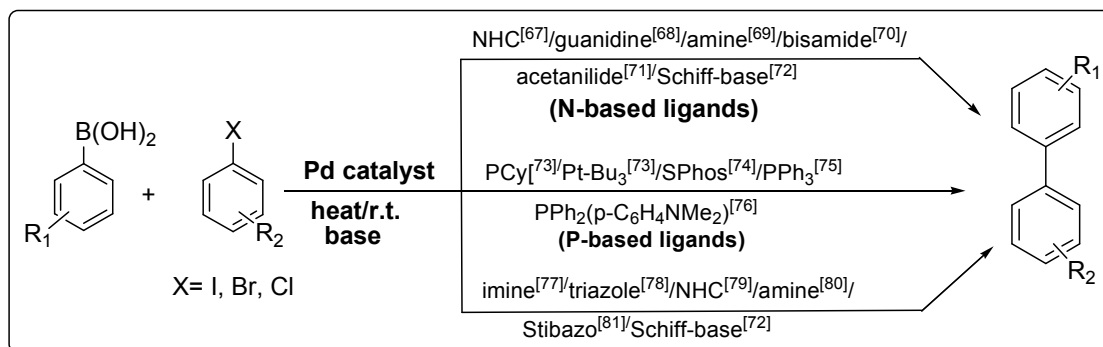
Scheme 7: Ligand based conventional Suzuki-Miyaura reaction.

Though these kinds of complexes containing such kind of ligands show excellent catalytic reactivity towards Suzuki-Miyaura cross-coupling reactions, but, they come with setbacks of being unstable, less available, and expensive. Moreover, these are air and moisture sensitive, which requires an inert environment essential. Apart from this, the palladium that are ligated with substituted phosphine are usually toxic and often create problem in isolation and purification process of desired products by generating unwanted side-products [82]. Hence, catalytic systems that are free from these pronounced issues are in need to be developed.

Nowadays, Pd NPs are considered an equivalent substitute for Pd-complexes for Suzuki-Miyaura cross-coupling reaction, which is because of their high surface to volume ratio, their highly active surface atoms, and usability in milder reaction conditions compared to the bulky counterparts. Pd NPs allow "ligand free" synthesis over traditional Pd^{II}/Pd^0 complexes catalyzed coupling reaction in the presence of phosphine or other ligands. This in turn, reduces the costs, simplifies workup procedures and facilitates the separation of the final product. Despite of these advantages, there are tradeoffs to be considered. For example, they require high temperature [83], ultra-sonication [84], strong reducing agent [85] etc., thereby making the process tedious and time consuming. Consequently, there has been urgency in the development of protocols for the synthesis of Pd NPs which are eco-friendly, constitute a single step with minimum usage of chemicals or by using environmentally acceptable solvent. Biological resources such as plant extracts, micro-organisms etc. could be used for the synthesis of NPs as they have the reduction potential required for NPs synthesis. Synthesis of NPs using biological resources has been discussed earlier. Development of cleaner and efficient chemistry had never been so important as it is now due to increased strain in nature itself. This is why

Green Chemistry has become necessary approach of "Sustainable Chemistry" to enforce reduction of a strain in natural resources to ensure a sustainable future. This phenomenon has greatly influenced the growing interest in Suzuki-Miyaura reaction and the implication of plant materials for the synthesis of NPs.

Supporting Pd NPs on different nanostructured materials generally magnifies their recyclability properties which thereby simplifies the separation of the products from the reaction mixture. Different types of supports like alumina [87], graphene oxide [89], graphene [88], graphite oxide [90], reduced graphene oxide [91], mesoporous silica [86], or other carbon-based materials [92] are being developed by research groups across the globe for the cause of for the development of novel catalytic systems. However, there are substantial amount of work to be done in order to increase the versatility of the reagents for C-C coupling reactions.

1.7.2. **Sonogashira cross-coupling reaction**

The palladium catalysed Sonogashira cross-coupling reaction of sp hybridized carbon of terminal alkyne with a sp^2 hybridized carbon of an aryl or vinyl halide (or triflate) is one of the most reliable methods for the construction of C-C bond (Scheme 4). The reaction is generally hastened by the inclusion of Cu-salt as co-catalyst and an amine base in presence of suitable phosphine based ligands. The reaction has become one of the vital methods to prepare arylalkynes and conjugated enynes, which are the precursors found in natural products, pharmaceuticals and molecular organic materials.

Though the exact reaction mechanism is not clearly demonstrated, here a possible mechanistic route has been suggested to explain the mechanism of copper assisted Sonogashira cross-coupling reaction. The reaction proceeds through two independent cycles, viz., Pd-cycle and Cu-Cycle (Fig. 3). The first step involves the oxidative addition where the active Pd^0 species is transformed Pd^{II} complex by interacting with aryl or vinyl halide substrate. The next step is the transmetallation step, where the Pd^{II} complex reacts with the copper acetylide, which is generated from the copper cycle, yielding complex B and regenerating the copper catalyst. In the final step, the complex B, undergoes reductive elimination to yield the final product and regenerating the original Pd^0 species.
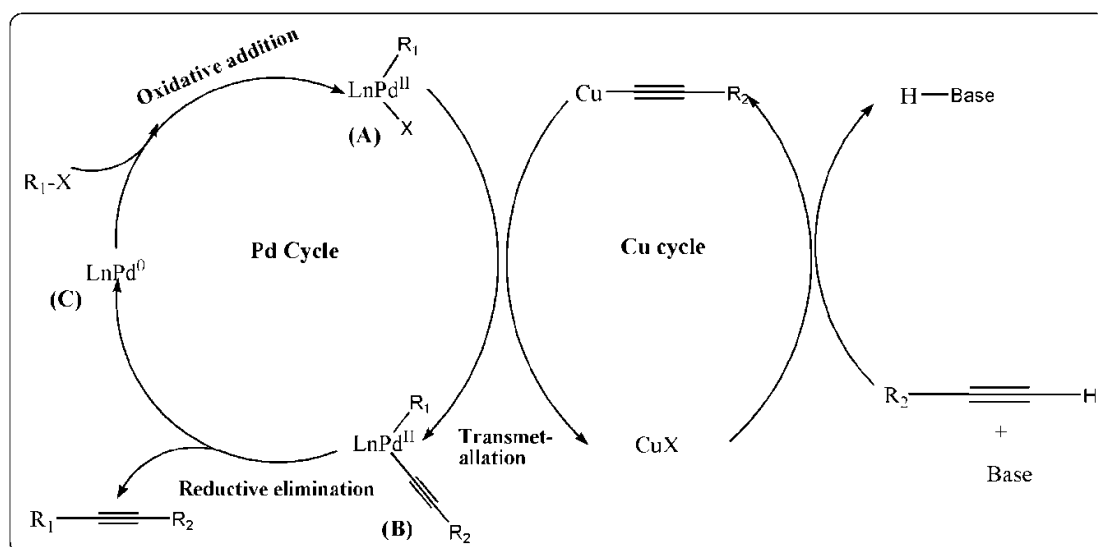
Fig. 3: Mechanism of Sonogashira cross-coupling reaction.

Addition of copper, even though increases the reactivity of the system, has some drawbacks. The copper acetylides that are formed under the reaction condition often create homocoupling products of the terminal alkyne (so called Glacer coupling) along with the main products and thereby decrease the product efficiency. As a matter, continuous efforts have been dedicated by different researcher groups to develop a copper free procedure. These types of methodologies are usually called copper-free Sonogashira cross-coupling methods. Till now, the exact mechanism by which the copper-free reaction occurs was not accurately determined. Soheili and Heck suggested two mechanisms for palladium-catalyzed copper free cross-coupling reaction. The first one is deprotonation and the second one is called carbopalladation mechanism. In deprotonation mechanism (Fig. 4), deprotonation of the alkyne proton and coordination of the ligands occurs, which leads to a square planner intermediate Pd-complex, from which the coupled product is obtained by reductive elimination.

On the other hand, in carbopalladation mechanism (Fig. 5), Pd-R complex coordinates to the alkyne and is added over the triple bond. This is followed by ligand co-ordination and subsequent reductive elimination to get the coupled product. Though these two mechanisms may be regarded as the usual mechanistic pathway for Cu-free Sonogashira reactions, still the actual mechanism is not clear till date.
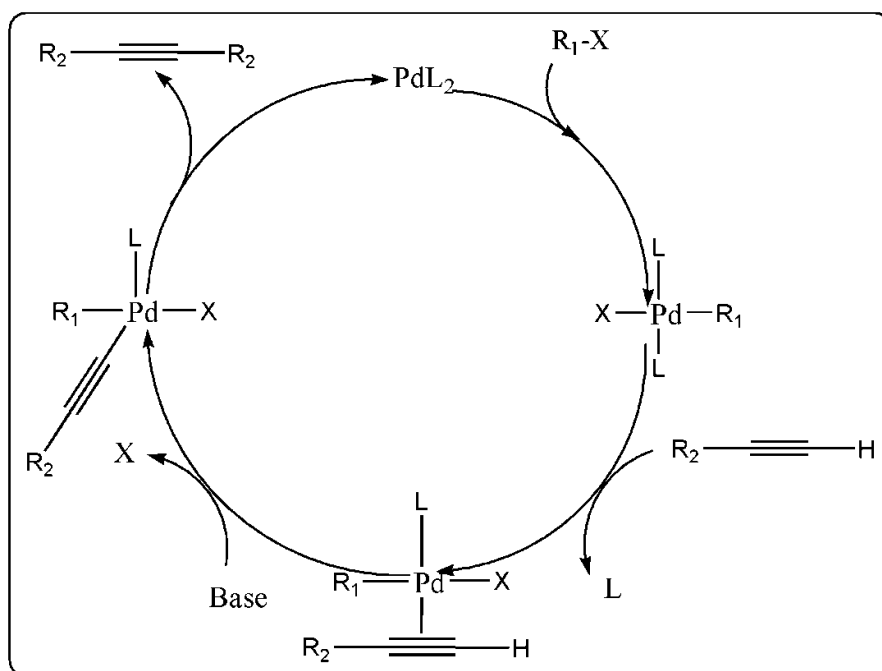
Fig. 4: Deprotonation mechanism for Cu-free Sonogashira cross-coupling reaction.

It has been found that ligands play a critical role in the palladium catalyzed Sonogashira reaction because it stabilizes the active Pd species during the course of reaction. Also, the electron-rich bulky phosphine ligands enhance the oxidative addition step, thus the steric effect makes easy to form low co-ordinated Pd-complex with high activity. Examples of ligands based on phosphine and nitrogen that found notable success in Sonogashira reactions are bulky phosphanes [93], water soluble phosphanes like TPPTS and TXPTS [94], *N*-heterocyclic carbenes [95], oxime palladacycles [96], amines [97] and salene [98] etc. However, these suffer from major drawbacks of unavailability, instability and cost of palladium complex and the related legends, which are few of the many challenges to be tackled.
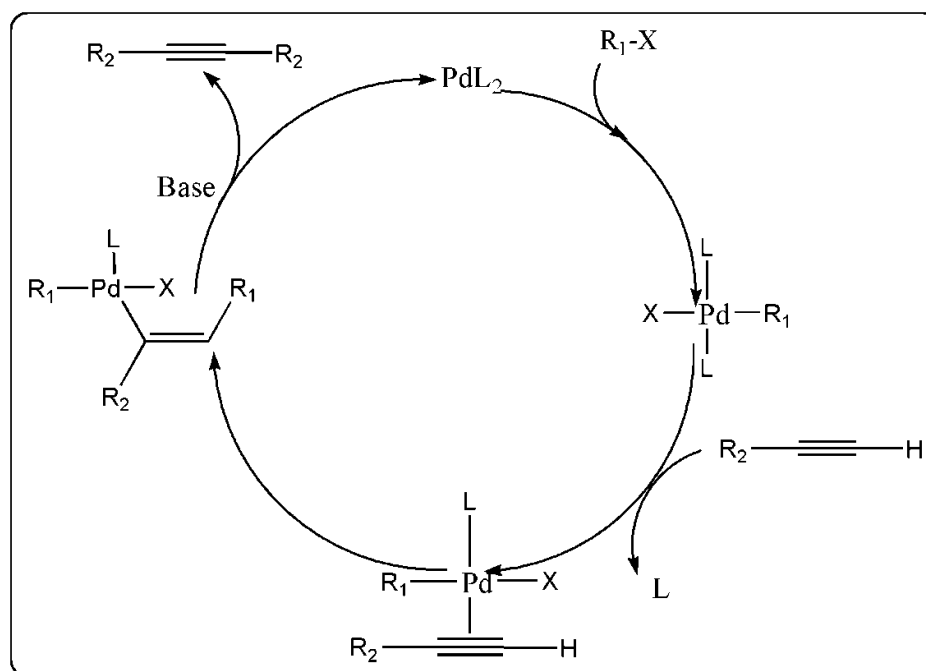
Fig. 5: Carbopalladation mechanism for Cu-free Sonogashira cross-coupling reaction.

Recent studies have been using Pd NPs in copper free Sonogashira reaction [99]. Its heterogeneous nature of is one of the biggest advantages in the field of catalysis, as the limitation of non-recoverability from the reaction medium associated with homogeneous catalyst has been overcome. Again, significant efforts have been dedicated by different research groups to stabilize and immobilize Pd NPs in different types of heterogeneous supports. Different inorganic supports such as carbon nanotubes, alumina [100], silica, zeolite [101], clays [102] and zinc ferrite [103] are generally used to stabilize Pd NPs. The chemical stability in various aggressive media, profusion, light weight, inertness to supported metals are some characteristics that supports are required to have.

Apart from C-C bond formation reactions, different types of C-heteroatom bond formation reactions like C-N, C-S and C-O bond formation reactions are there. However, in this thesis we have focused on C-N bond formation reaction only. Synthetic organic chemistry and its growth are predicated substantially upon transition metal C-N bond forming reactions. Nitrogen containing compounds can be produced using transition-metal-catalyzed protocols that find vast applications in the field of organic synthesis, especially in ubiquitous *N*-containing organic compounds in pharmaceuticals, material science and natural product chemistry [104]. For example, diarylamines, *N*-

arylimidazoles are types of compounds privileged with structural scaffolds which have vast applications in the above mentioned areas [104, 105].

Ullmann and Golberg in 1903 (Scheme 8) first reported a copper mediated C-N cross-coupling reaction between aniline and aryl halide [106]. They used Copper salts in this method to activate the aryl (pseudo) halides substrate. However, the involvement of harsh conditions such as high temperature and/or strong base in this method limits the synthetic utility of this reaction procedure.
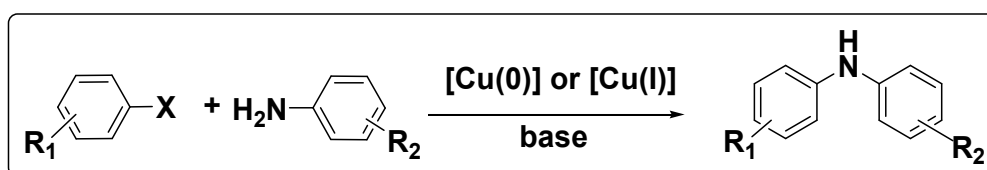

Scheme 8: Ullmann and Goldberg coupling reactions.

In 1990, Buchwald and Hartwig, independently reported a new method for the construction of C-N bond where they used the Pd as catalyst using suitable diamine or phosphine ligands [107]. During the past decades, the reaction achieved significant recognition from the research community and is now considered as one of the most important protocols for the construction of C-N bond (Scheme 9).
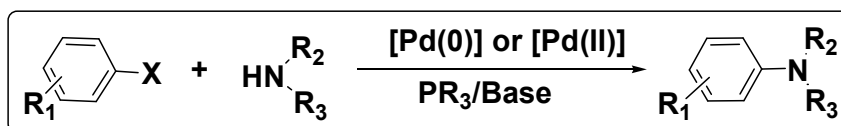
Scheme 9: Buchwald and Hartwig coupling reactions.

In the year 1998, Chan and Lam [108] proposed a relatively mild protocol for the construction of C-N, C-O and C-S bonds, which have several advantages in terms of stability, toxicity and structural diversity issues (Scheme 10). Arylboronic acid, which is a coupling partners of the reaction offer advantages and wide range of applications in organic synthesis owing to its structural diversity, moisture resistance and low toxicity. The exact mechanism for Chan-Lam reaction still remains a matter of conflict, however

a mechanism had been proposed by Chan-Lam for the reaction which involves oxidation, ligand exchange, transmetallation and reductive elimination as the major steps (Fig. 6).
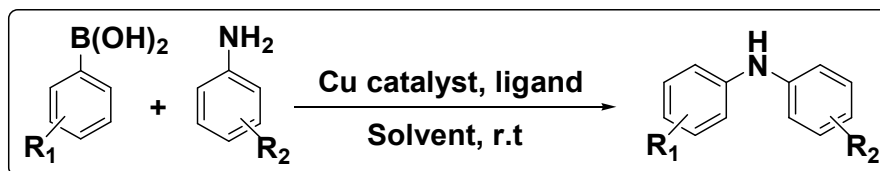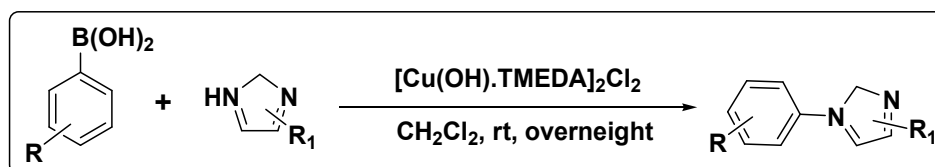

Scheme 10: Cu catalyzed Chan-Lam cross-coupling reaction.

However, the reaction bears disadvantages of prolonged reaction time [109], use of excessive amount of copper catalyst, additives and expensive ligand promoted reaction condition [110], usage of toxic and flammable halogenated organic solvents [111] etc. Collmann and Zhong reported an *in-situ* generated Cu-catalyst [Cu(OH)˙TMEDA]$_2$Cl$_2$ for *N*-arylation of imidazole (Scheme 11) in which the problem regarding the use of excessive or stoichiometric amount of copper salt can be targeted [112].

However, in order to obtain higher yield of the product, it was necessary to keep the pH of the reaction medium at neutral. After several investigations, it was confirmed that TMEDA [113] was the most efficient ligand, even though the related ligands give acceptable result.

Later on Lam [114] reported a method where they used 10 mol% of Cu(OAc)$_2$ as the catalyst in presence of different types of oxidants like molecular oxygen, pyridine-*N*-oxide, TEMPO [115] etc. for *N*-arylation reaction.

Another report of *N*-arylation of aliphatic and aromatic amines was reported by Yokomatsu and his coworkers in water media, where they used Cu$_2$β-cyclodextrin as catalyst at room temperature [117].

Scheme 11: Collmann and Zhong method.
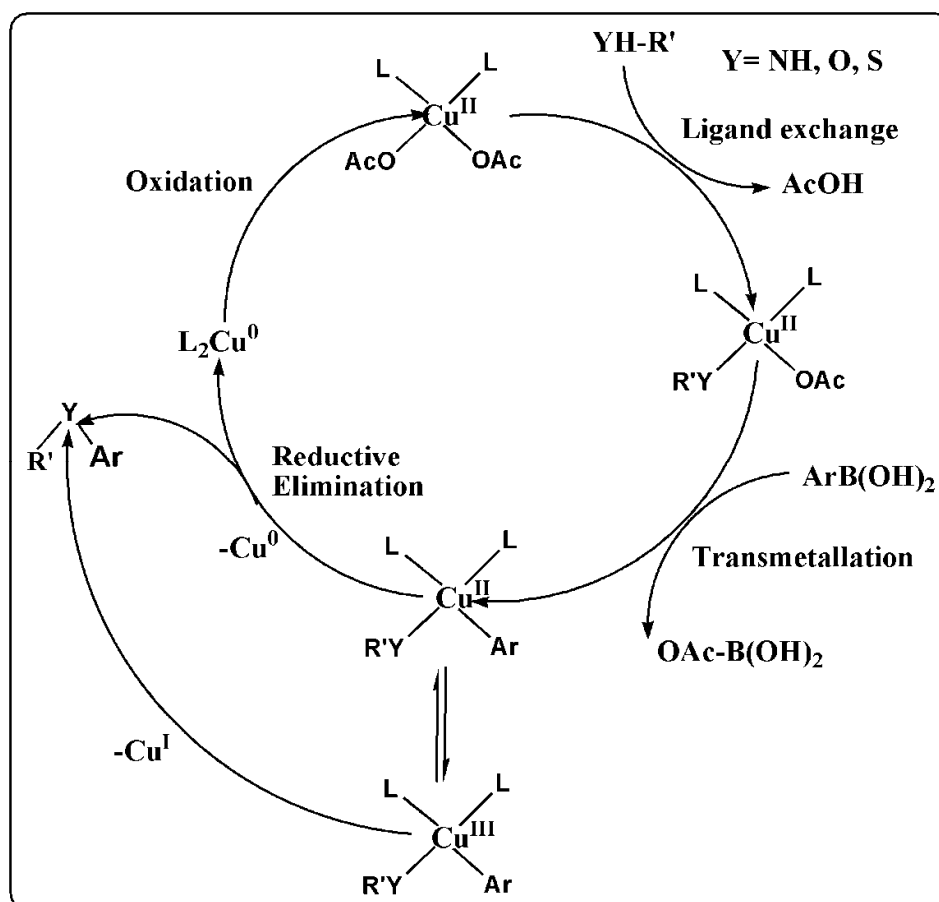
Fig. 6: Mechanism of Chan-Lam cross-coupling reaction.

Kantam and her coworkers developed a very effective catalyst copper fluoro apatite (CuFAP) for *N*-arylation reaction at room temperature [118]. The catalyst was found to be reusable with no loss of its activity even after fourth run.

Again in the year 2016, Islam and his co-workers reported a method for *N*-arylation of anilines and imidazoles using polymer supported Cu catalyst in MeOH [119]. They did not use any base during the reaction.

Microwave assisted synthetic protocols for *N*-arylation was also reported by Singh and his coworkers using $Cu(OAc)_2$, Et_3N and pyridine[120].

Recently, a simple and quick method using DMAP/Cu promoted Chan-Lam reaction has been reported by Phukon and his co-workers [121].

Despite the various methods available for Chan-Lam coupling reaction, it is still a need among researches to establish a more efficient and simple method eliminating all the drawbacks.

1.8.   Aims and objectives of the thesis

Keeping all these in mind our foremost objective was to synthesize Pd and Cu based NPs by using comparatively cheaper and less time consuming greener approach and their successive application in some C-C bond formation reactions like Suzuki-Miyaura cross-coupling reaction and Sonogashira cross-coupling reactions and also in some C-N bond formation reaction like Chan-Lam reaction.

Keeping these in mind we propound to endeavour our complete study with the following objectives:

1. To develop some greener and relatively non-toxic protocols for the synthesis of Pd and CuO NPs.
2. To develop environmentally sustainable protocols for C-C and C-N bond forming reactions using the nanocatalyst thus prepared. The synthesized catalyst should be relatively non-toxic, easily recyclable, easy to handle and sufficiently stable in ambient conditions.
3. To characterize the synthesized NPs by using FTIR, PXRD, SEM, high resolution TEM, BET and other techniques.
4. Any other issues that may arise during the course of the study.

References

[1] Chapter 5: Heterogeneous catalysis. In Moulijn, J. A., van Leeuwen P. W. N. M. and van Santen, R. A., editors, *Studies in Surface Science and Catalysis*, volume 79, pages 159-197, 1993.

[2] Atkins, P. *Physical Chemistry*, Oxford University Press, 9th Edition, 2006.

[3] Rao, C. R., Kulkarni, G. U., Thomas, P. J., and Edwards, P. P. Metal nanoparticles and their assemblies. *Chemical Society Reviews*, 29(1):27-35, 2000.

[4] (a) Goesmann, H. and Feldmann, C. Nanoparticulate functional materials. *Angewandte Chemie International Edition*, 49(8):1362-1395, 2010. (b) Campelo, J. M., Luna, D., Luque, R., Marinas, J. M., and Romero, A. A. Sustainable preparation of supported metal nanoparticles and their applications in catalysis. *ChemSusChem: Chemistry & Sustainability Energy & Materials*, 2(1):18-45, 2009. (c) Templeton, A. C., Wuelfing, W. P., and Murray, R. W. Monolayer-protected cluster molecules. *Accounts of Chemical Research*, 33(1):27-36, 2000.

[5] Roduner, E. Size matters: why nanomaterials are different. *Chemical Society Reviews*, 35(7):583-592, 2006.

[6] (a) Antonelli, D. M. and Ying, J. Y. Synthesis and characterization of hexagonally packed mesoporous tantalum oxide molecular sieves. *Chemistry of Materials*, 8(4):874-881, 1996. (b) Corma, A., Atienzar, P., Garcia, H., and Chane-Ching, J. Y. Hierarchically mesostructured doped CeO_2 with potential for solar-cell use. *Nature Materials*, 3(6):394, 2004. (c) Wang, H., Uehara, M., Nakamura, H., Miyazaki, M., and Maeda, H. Synthesis of Well-Dispersed Y_2O_3: Eu Nanocrystals and Self-Assembled Nanodisks using a simple non-hydrolytic route. *Advanced Materials*, 17(20):2506-2509, 2005.

[7] Daniel, M. C. and Astruc, D. Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chemical Reviews*, 104(1):293-346, 2004.

[8] Delgado, J., Vilarigues, M., Ruivo, A., Corregidor, V., da Silva, R.C. and Alves, L.C. Characterisation of medieval yellow silver stained glass from Convento de Cristo in

Tomar, Portugal. Nucl. Instrum. Methods B. *Nanotechnology: from the ancient time to nowadays*, 269:2383–2388, 2011.

[9] Jia, C. J. and Schüth, F. Colloidal metal nanoparticles as a component of designed catalyst. *Physical Chemistry Chemical Physics*, 13(7):2457-2487, 2011.

[10] Comotti, M., Li, W. C., Spliethoff, B., and Schüth, F. Support effect in high activity gold catalysts for CO oxidation. *Journal of the American Chemical Society*, 128(3):917-924, 2006.

[11] Esumi, K., Tano, T., Torigoe, K., and Meguro, K. Preparation and characterization of bimetallic palladium-copper colloids by thermal decomposition of their acetate compounds in organic solvents. *Chemistry of Materials*, 2(5):564-567, 1990.

[12] Fujimoto, T., Terauchi, S. Y., Umehara, H., Kojima, I., and Henderson, W. Sonochemical preparation of single-dispersion metal nanoparticles from metal salts. *Chemistry of Materials*, 13(3):1057-1060, 2001.

[13] Reetz, M. T. and Helbig, W. Size-selective synthesis of nanostructured transition metal clusters. *Journal of the American Chemical Society*, 116(16):7401-7402, 1994.

[14] Pan, W., Zhang, X., Ma, H., and Zhang, J. Electrochemical synthesis, voltammetric behavior, and electrocatalytic activity of Pd nanoparticles. *The Journal of Physical Chemistry C*, 112(7):2456-2461, 2008.

[15] Reetz, M. T., Winter, M., Breinbauer, R., Thurn-Albrecht, T., and Vogel, W. Size-Selective Electrochemical Preparation of Surfactant-Stabilized Pd-, Ni- and Pt/Pd Colloids. *Chemistry–A European Journal*, 7(5):1084-1094, 2001.

[16] Yin, B., Ma, H., Wang, S., and Chen, S. Electrochemical synthesis of silver nanoparticles under protection of poly(*N*-vinylpyrrolidone). *The Journal of Physical Chemistry B*, 107(34):8898-8904, 2003.

[17] Zhu, J., Shen, Y., Xie, A., Qiu, L., Zhang, Q., and Zhang, S. Photoinduced synthesis of anisotropic gold nanoparticles in room-temperature ionic liquid. *The Journal of Physical Chemistry C*, 111(21):7629-7633, 2007.

[18] Durán, N., Marcato, P. D., Durán, M., Yadav, A., Gade, A., and Rai, M. Mechanistic aspects in the biogenic synthesis of extracellular metal nanoparticles by

peptides, bacteria, fungi, and plants. *Applied Microbiology and Biotechnology*, 90(5):1609-1624, 2011.

[19] (a) Ahmad, A., Mukherjee, P., Senapati, S., Mandal, D., Khan, M. I., Kumar, R., and Sastry, M. Extracellular biosynthesis of silver nanoparticles using the fungus Fusarium oxysporum. *Colloids and surfaces B: Biointerfaces*, 28(4):313-318, 2003. (b) Mukherjee, P., Ahmad, A., Mandal, D., Senapati, S., Sainkar, S. R., Khan, M. I., and Sastry, M. Fungus-mediated synthesis of silver nanoparticles and their immobilization in the mycelial matrix: a novel biological approach to nanoparticle synthesis. *Nano Letters*, 1(10):515-519, 2001.

[20] Jena, S., Das, B., Bosu, R., Suar, M., and Mandal, D. Bacteria generated antibacterial gold nanoparticles and potential mechanistic insight. *Journal of Cluster Science*, 26(5):1707-1721, 2015.

[21] Kharissova, O. V., Dias, H. V. R., Kharisov, B. I., Pérez, B. O. and Pérez, V. M. J. The greener synthesis of nanoparticles. *Trends in Biotechnology*, 31:240-248, 2013.

[22] Priyadarshini, S., Gopinath, V., Priyadharsshini, N. M., MubarakAli, D., and Velusamy, P. Synthesis of anisotropic silver nanoparticles using novel strain, Bacillus flexus and its biomedical application. *Colloids and Surfaces B: Biointerfaces*, 102:232-237, 2013.

[23] Nath, D. and Banerjee, P. Green nanotechnology–a new hope for medical biology. *Environmental Toxicology and Pharmacology*, 36(3):997-1014, 2013.

[24] Elia, P., Zach, R., Hazan, S., Kolusheva, S., Porat, Z. E., and Zeiri, Y. Green synthesis of gold nanoparticles using plant extracts as reducing agents. *International Journal of Nanomedicine*, 9:4007, 2014.

[25] Gogoi, N., Babu, P. J., Mahanta, C., and Bora, U. Green synthesis and characterization of silver nanoparticles using alcoholic flower extract of Nyctanthesarbortristis and *in vitro* investigation of their antibacterial and cytotoxic activities. *Materials Science and Engineering: C*, 46:463-469, 2015.

[26] Sivaraj, R., Rahman, P. K., Rajiv, P., Narendhran, S., and Venckatesh, R. Biosynthesis and characterization of Acalypha indica mediated copper oxide

nanoparticles and evaluation of its antimicrobial and anticancer activity. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 129:255-258, 2014.

[27] Yuvakkumar, R., Suresh, J., Nathanael, A. J., Sundrarajan, M., and Hong, S. I. Novel green synthetic strategy to prepare ZnO nanocrystals using rambutan (Nephelium lappaceum L.) peel extract and its antibacterial applications. *Materials Science and Engineering: C*, 41:17-27, 2014.

[28] Herlekar, M., Barve, S., and Kumar, R. Plant-mediated green synthesis of iron nanoparticles. *Journal of Nanoparticles*, 2014, DOI: http://dx.doi.org/10.1155/2014/140614

[29] Sharma, G., Sharma, A. R., Bhavesh, R., Park, J., Ganbold, B., Nam, J. S., and Lee, S. S. Biomolecule-mediated synthesis of selenium nanoparticles using dried Vitis vinifera (raisin) extract. *Molecules*, 19(3):2761-2770, 2014.

[30] Khan, M., Khan, M., Adil, S. F., Tahir, M. N., Tremel, W., Alkhathlan, H. Z., Al-Warthan, A and Siddiqui, M. R. H. Green synthesis of silver nanoparticles mediated by Pulicaria glutinosa extract. *International Journal of Nanomedicine,* 8:1507, 2013.

[31] Khan, M., Kuniyil, M., Adil, S. F., Al-Warthan, A., Alkhathlan, H. Z., and Siddiqui, M. R. H. Biogenic synthesis of palladium nanoparticles using Pulicaria glutinosa extract and their catalytic activity towards the Suzuki coupling reaction. *Dalton Transactions*, 43(24):9026-9031, 2014.

[32] Sheny, D. S., Philip, D., and Mathew, J. Rapid green synthesis of palladium nanoparticles using the dried leaf of Anacardium occidentale. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 91:35-38, 2012.

[33] Petla, R. K., Vivekanandhan, S., Misra, M., Mohanty, A. K., and Satyanarayana, N. Soybean (Glycine max) leaf extract based green synthesis of palladium nanoparticles. *Journal of Biomaterials and Nanobiotechnology*, 3(1):14-19, 2012.

[34] Nasrollahzadeh, M., Sajadi, S. M., Rostami-Vartooni, A., Alizadeh, M., and Bagherzadeh, M. Green synthesis of the Pd nanoparticles supported on reduced graphene oxide using barberry fruit extract and its application as a recyclable and heterogeneous catalyst for the reduction of nitroarenes. *Journal of Colloid and Interface Science*, 466:360-368, 2016.

[35] Raut, R. W., Haroon, A. S. M., Malghe, Y. S., Nikam, B. T., and Kashid, S. B. Rapid biosynthesis of platinum and palladium metal nanoparticles using root extract of Asparagus racemosus Linn. *Advanced Material Letters,* 4(8):650-654, 2013.

[36] Sathishkumar, M., Sneha, K., Kwak, I. S., Mao, J., Tripathy, S. J., and Yun, Y. S. Phyto-crystallization of palladium through reduction process using Cinnamom zeylanicum bark extract. *Journal of Hazardous Materials*, 171(1-3):400-404, 2009.

[37] (a) Kung, H. H. *Transition metal oxides: surface chemistry and catalysis*. Elsevier, 1st edition, 1989. (b) Fernandez-Garcia, M., Martinez-Arias, A., Hanson, J. C., and Rodriguez, J. A. Nanostructured oxides in chemistry: characterization and properties. *Chemical Reviews*, 104(9):4063-4104, 2004.

[38] (a) Ranu, B. C., Dey, R., Chatterjee, T., and Ahammed, S. Copper nanoparticle-catalyzed carbon-carbon and carbon-Heteroatom bond formation with a greener perspective. *ChemSusChem*, 5(1):22-44, 2012. (b) Allen, S. E., Walvoord, R. R., Padilla-Salinas, R., and Kozlowski, M. C. Aerobic copper-catalyzed organic reactions. *Chemical Reviews*, 113(8):6234-6458, 2013. (c) Pan, K., Ming, H., Yu, H., Liu, Y., Kang, Z., Zhang, H., and Lee, S. T. Different copper oxide nanostructures: Synthesis, characterization, and application for C-N cross-coupling catalysis. *Crystal Research and Technology*, 46(11):1167-1174, 2011. (d) Pawar, R. C., Choi, D. H., Lee, J. S., and Lee, C. S. Formation of polar surfaces in microstructured ZnO by doping with Cu and applications in photocatalysis using visible light. *Materials Chemistry and Physics*, 151:167-180, 2015. (e) Poreddy, R., Engelbrekt, C., and Riisager, A. Copper oxide as efficient catalyst for oxidative dehydrogenation of alcohols with air. *Catalysis Science & Technology*, 5(4):2467-2477, 2015.

[39] (a) Xi, Y., Hu, C., Gao, P., Yang, R., He, X., Wang, X., and Wan, B. Morphology and phase selective synthesis of Cu_xO (x=1, 2) nanostructures and their catalytic degradation activity. *Materials Science and Engineering: B*, 166(1):113-117, 2010. (b) He, Y. A novel solid-stabilized emulsion approach to CuO nanostructured microspheres. *Materials Research Bulletin*, 42(1):190-195, 2007.

[40] Tamaekong, N., Liewhiran, C., and Phanichphant, S. Synthesis of thermally spherical CuO nanoparticles. *Journal of Nanomaterials*, 2014. DOI: http://dx.doi.org/10.1155/2014/507978.

[41] Sun, L., Zhang, Z., Wang, Z., Wu, Z., and Dang, H. Synthesis and characterization of CuO nanoparticles from liquid ammonia. *Materials Research Bulletin*, 40(6):1024-1027, 2005.

[42] Zhang, Y., Wang, S., Qian, Y., and Zhang, Z. Complexing-reagent assisted synthesis of hollow CuO microspheres. *Solid State Sciences*, 8(5):462-466, 2006.

[43] Seligman, A. M., Wasserkrug, H. L., and Hanker, J. S. A new staining method (OTO) for enhancing contrast of lipid-containing membranes and droplets in osmium tetroxide-fixed tissue with osmiophilic thiocarbohydrazide (TCH). *The Journal of cell biology*, 30(2):424, 1966.

[44] (a) Russell, S. D., and Daghlian, C. P. Scanning electron microscopic observations on deembedded biological tissue sections: comparison of different fixatives and embedding materials. *Journal of Electron Microscopy Technique*, 2(5):489-495, 1985. (b) Kawase, N., Kato, M., Nishioka, H., and Jinnai, H. Transmission electron microtomography without the "missing wedge" for quantitative structural analysis. *Ultramicroscopy*, 107(1):8-15, 2007.

[45] (a) Torborg, C. and Beller, M. Recent applications of palladium-catalyzed coupling reactions in the pharmaceutical, agrochemical, and fine chemical industries. *Advanced Synthesis & Catalysis*, 351(18):3027-3043, 2009. (b) Magano, J., and Dunetz, J. R. Large-scale applications of transition metal-catalyzed couplings for the synthesis of pharmaceuticals. *Chemical Reviews*, 111(3):2177-2250, 2011.

[46] Beccalli, E. M.,Broggini, G., Martinelli, M., and Sottocornola, S. C−C, C−O, C−N bond formation on sp2 carbon by Pd(II)-catalyzed reactions involving oxidant agents. *Chemical Reviews*, 107(11):5318-5365, 2007.

[47] March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*. John Wiley & Sons, 6th edition, 1992.

[48] Foote, C. S. Catalytic asymmetric synthesis special issue. *Accounts in Chemical Research,* 33:323, 2000.

[49] Trost, B. M. and Fleming, I, *Comprehensive Organic Synthesis*; Pergamon, New York, 1st edition, 1991.

[50] Scolastico, C. and Nicotra, C.; *Current Trends in Organic Synthesis*, Springer, Berlin 1999.

[51] Jacobsen, E. N.; Pfaltz, A. and Yamamoto, H. *Comprehensive Asymmetric Catalysis*, Springer, Berlin, 1999.

[52] Siemsen, P., Livingston, R. C., and Diederich, F. Acetylenic coupling: a powerful tool in molecular construction. *Angewandte Chemie International Edition*, 39(15):2632-2657, 2000.

[53] Casitas, A., King, A. E., Parella, T., Costas, M., Stahl, S. S., and Ribas, X. Direct observation of Cu^I/Cu^{III} redox steps relevant to Ullmann-type coupling reactions. *Chemical Science*, 1(3):326-330, 2010.

[54] Heck, R. F. The palladium-catalyzed arylation of enol esters, ethers, and halides. A new synthesis of 2-aryl aldehydes and ketones. *Journal of the American Chemical Society*, 90(20):5535-5538, 1968.

[55] Sonogashira, K., Tohda, Y., and Hagihara, N. A convenient synthesis of acetylenes: catalytic substitutions of acetylenic hydrogen with bromoalkenes, iodoarenes and bromopyridines. *Tetrahedron Letters*, 16(50):4467-4470, 1975.

[56] Negishi, E., King, A. O., and Okukado, N. Selective carbon-carbon bond formation via transition metal catalysis. 3. A highly selective synthesis of unsymmetrical biaryls and diarylmethanes by the nickel-or palladium-catalyzed reaction of aryl-and benzylzinc derivatives with aryl halides. *The Journal of Organic Chemistry*, 42(10):1821-1823, 1977.

[57] Miyaura, N., Yamada, K., and Suzuki, A. A new stereospecific cross-coupling by the palladium-catalyzed reaction of 1-alkenylboranes with 1-alkenyl or 1-alkynyl halides. *Tetrahedron Letters*, 20(36):3437-3440, 1979.

[58] Stille, J. K. The palladium-catalyzed cross-coupling reactions of organotin reagents with organic electrophiles [new synthetic methods (58)]. *Angewandte Chemie International Edition, English*, 25(6):508-524, 1986.

[59] Corriu, R. J. P. and Masse, J. P. Activation of Grignard reagents by transition-metal complexes. A new and simple synthesis of *trans*-stilbenes and polyphenyls. *Journal of Chemical Society, Chemical Communications*, 3:144a-144a, 1972.

[60] (a) Tsuji, J., Takahashi, H., and Morikawa, M. Organic syntheses by means of noble metal compounds XVII. Reaction of π-allyl palladium chloride with nucleophiles. *Tetrahedron Letters*, 6(49):4387-4388, 1965. (b) Trost, B. M., and Fullerton, T. J. New synthetic reactions. Allylic alkylation. *Journal of the American Chemical Society*, 95(1):292-294, 1973.

[61] (a) Suzuki, A. Cross-Coupling Reactions Of Organoboranes: An easy way to construct C-C bonds (nobel lecture). *Angewandte Chemie International Edition*, 50(30):6722-6737, 2011. (b) Kotha, S., Lahiri, K. and Kashinath, D. Recent applications of the Suzuki–Miyaura cross-coupling reaction in organic synthesis. *Tetrahedron*, 58(48):9633-9695, 2002.

[62] Heck, R. F. Palladium-catalyzed vinylation of organic halides. *Organic Reactions*, 27:345-390, 2004.

[63] Huser, M., Youinou, M. T., and Osborn, J. A. Chlorocarbon activation: Catalytic carbonylation of dichloromethane and chlorobenzene. *Angewandte Chemie International Edition,* 28(10):1386-1388, 1989.

[64] Hillier, A. C., Grasa, G. A., Viciu, M. S., Lee, H. M., Yang, C., and Nolan, S. P. Catalytic cross-coupling reactions mediated by palladium/nucleophilic carbene systems. *Journal of Organometallic Chemistry*, 653(1-2):69-82, 2002.

[65] Tao, B. and Boykin, D. W. Simple amine/Pd(OAc)$_2$-catalyzed Suzuki coupling reactions of aryl bromides under mild aerobic conditions. *The Journal of Organic Chemistry*, 69(13):4330-4335, 2004.

[66] Li, J. H. and Liu, W. J. Dabco as an inexpensive and highly efficient ligand for Palladium-catalyzed Suzuki-Miyaura cross-coupling reaction. *Organic Letters*, 6(16):2809-2811, 2004.

[67] (a) Herrmann, W. A., Reisinger, C. P., and Spiegler, M. Chelating *N*-heterocyclic carbene ligands in palladium-catalyzed heck-type reactions. *Journal of Organometallic Chemistry*, 557(1):93-96, 1998. (b) Navarro, O., Kaur, H., Mahjoor, P., and Nolan, S. P.

Cross-coupling and dehalogenation reactions catalyzed by (*N*-heterocyclic carbene)Pd(allyl)Cl complexes. *The Journal of Organic Chemistry*, 69(9):3173-3180, 2004.

[68] (a) Li, S., Lin, Y., Cao, J., and Zhang, S. Guanidine/Pd (OAc)$_2$-catalyzed room temperature Suzuki cross-coupling reaction in aqueous media under aerobic conditions. *The Journal of Organic Chemistry*, 72(11):4067-4072, 2007. (b) Ye, C., Chen, Z., Wang, H., and Wu, J. Generation of diverse 1-(isoquinolin-1-yl)guanidines via a sequential multi-component/cross-coupling reaction. *Tetrahedron*, 68(26):5197-5202, 2012.

[69] Tao, B. and Boykin, D. W. Simple amine/Pd(OAc)$_2$-catalyzed Suzuki coupling reactions of aryl bromides under mild aerobic conditions. *The Journal of Organic Chemistry*, 69(13):4330-4335, 2004.

[70] da Costa, D. P.and Nobre, S. M. Bisamides as ligands in Suzuki coupling reactions catalyzed by palladium. *Tetrahedron Letters*, 54(34):4582-4584, 2013.

[71] Dewan, A., Buragohain, Z., Mondal, M., Sarmah, G., Borah, G., and Bora, U. Acetanilide palladacycle: an efficient catalyst for room-temperature Suzuki–Miyaura cross-coupling reaction. *Applied Organometallic Chemistry*, 28(4):230-233, 2014.

[72] (a) Banik, B., Tairai, A., Shahnaz, N., and Das, P. Palladium (II) complex with a potential N4-type Schiff-base ligand as highly efficient catalyst for Suzuki–Miyaura reactions in aqueous media. *Tetrahedron Letters*, 53(42):5627-5630, 2012. (b) Dewan, A., Bora, U., and Borah, G. A simple and efficient tetradentate Schiff base derived palladium complex for Suzuki–Miyaura reaction in water. *Tetrahedron Letters*, 55(10):1689-1692, 2014.

[73] Bellina, F., Carpita, A., and Rossi, R. Palladium catalysts for the Suzuki cross-coupling reaction: an overview of recent advances. *Synthesis*, 2004(15):2419-2440, 2004.

[74] Barder, T. E., Walker, S. D., Martinelli, J. R., and Buchwald, S. L. Catalysts for Suzuki− Miyaura coupling processes: scope and studies of the effect of ligand structure. *Journal of the American Chemical Society*, 127(13):4685-4696, 2005.

[75] (a) Suzuki, A. Cross-coupling reactions of Organoboranes: An easy way to construct C-C bonds (Nobel Lecture). *Angewandte Chemie International Edition*,

50(30):6722-6737, 2011. (b) Kotha, S., Lahiri, K., and Dhurke, K. Recent applications of the Suzuki–Miyaura cross-coupling reaction in organic synthesis, *Tetrahedron*, 58:9633-9695, 2002.

[76] Sarmah, C., Borah, M., and Das, P. Iron (0), Rhodium(I) and Palladium(II) complexes with *p*-(*N,N*-dimethylaminophenyl)diphenylphosphine and the application of the palladium complex as a catalyst for the Suzuki–Miyaura cross-coupling reaction. *Applied Organometallic Chemistry*, 25(7):552-558, 2011.

[77] Zhou, J., Guo, X., Tu, C., Li, X., and Sun, H. Aqueous Suzuki coupling reaction catalyzed by water-soluble diimine/Pd(II) systems. *Journal of Organometallic Chemistry*, 694(5):697-702, 2009.

[78] Amadio, E., Scrivanti, A., Beghetto, V., Bertoldini, M., Alam, M. M., and Matteoli, U. A water-soluble pyridyl-triazole ligand for aqueous phase palladium catalyzed Suzuki–Miyaura coupling. *RSC Advances*, 3(44):21636-21640, 2013.

[79] (a) Schaper, L. A., Hock, S. J., Herrmann, W. A., and Kuehn, F. E. Synthesis and Application of Water-Soluble NHC Transition-Metal Complexes. *Angewandte Chemie International Edition*, 52(1):270-289, 2013. (b) Fleckenstein, C., Roy, S., Leuthäußer, S., and Plenio, H. Sulfonated *N*-heterocyclic carbenes for Suzuki coupling in water. *Chemical Communications*, 27:2870-2872, 2007.

[80] Das, P., Sarmah, C., Tairai, A., and Bora, U. Highly efficient amine-based catalytic system for room temperature Suzuki–Miyaura reactions of aryl halides with arylboronic acids. *Applied Organometallic Chemistry*, 25(4):283-288, 2011.

[81] Peng, Y. Y., Liu, J., Lei, X., and Yin, Z. Room-temperature highly efficient Suzuki–Miyaura reactions in water in the presence of Stilbazo. *Green Chemistry*, 12(6):1072-1075, 2010.

[82] (a) LeBlond, C. R., Andrews, A. T., Sun, Y., and Sowa, J. R. Activation of aryl chlorides for Suzuki cross-coupling by ligandless, heterogeneous palladium. *Organic Letters*, 3(10):1555-1557, 2001. (b) Leadbeater, N. E. and Marco, M. Transition-Metal-Free Suzuki-Type Coupling Reactions. *Angewandte Chemie International Edition*, 115(12):1445-1447, 2003. (c) Hu, H., Ge, C., Zhang, A. and Ding,

L. Synthesis of novel 3,5-Dichloro-2-arylpyridines by Palladium acetate-catalyzed ligand-free Suzuki reactions in aqueous media. *Molecules*, 14(9):3153-3160, 2009.

[83] Kim, S. W., Park, J., Jang, Y., Chung, Y., Hwang, S., Hyeon, T., and Kim, Y. W. Synthesis of monodisperse palladium nanoparticles. *Nano Letters*, 3(9):1289-1291, 2003.

[84] Zhang, Z., Zha, Z., Gan, C., Pan, C., Zhou, Y., Wang, Z. and Zhou, M. M. Catalysis and regioselectivity of the aqueous Heck reaction by Pd(0) nanoparticles under ultrasonic irradiation. *The Journal of Organic Chemistry*, 71(11):4339-4342, 2006.

[85] Cano, M., Benito, A. M., Urriolabeitia, E. P., Arenal, R. and Maser, W. K. Reduced graphene oxide: firm support for catalytically active palladium nanoparticles and game changer in selective hydrogenation reactions. *Nanoscale*, 5(21):10189-10193, 2013.

[86] Sayah, R., Glegoła, K., Framery, E. and Dufaud, V. Suzuki–Miyaura reactions of Aryl chloride derivatives with Arylboronic acids using mesoporous silica-supported Aryl dicyclohexylphosphine. *Advanced Synthesis & Catalysis*, 349(3):373-381, 2007.

[87] Biffis, A., Zecca, M. and Basato, M. Metallic Palladium in the Heck Reaction: Active Catalyst or Convenient Precursor? *European Journal of Inorganic Chemistry,* 5:1131-1133, 2001.

[88] Ghasemi, S., Hosseini, S. R., Nabipour, S., and Asen, P. Palladium nanoparticles supported on graphene as an efficient electrocatalyst for hydrogen evolution reaction. *International Journal of Hydrogen Energy*, 40(46):16184-16191, 2015.

[89] Yang, J., Tian, C., Wang, L., and Fu, H. An effective strategy for small-sized and highly-dispersed palladium nanoparticles supported on graphene with excellent performance for formic acid oxidation. *Journal of Materials Chemistry*, 21(10):3384-3390, 2011.

[90] Xu, T. Q., Zhang, Q. L., Zheng, J. N., Lv, Z. Y., Wei, J., Wang, A. J., and Feng, J. J. Simultaneous determination of dopamine and uric acid in the presence of ascorbic acid using Pt nanoparticles supported on reduced graphene oxide. *Electrochimica Acta*, 115:109-115, 2014.

[91] Santra, S., Hota, P. K., Bhattacharyya, R., Bera, P., Ghosh, P., and Mandal, S. K. Palladium nanoparticles on graphite oxide: A recyclable catalyst for the synthesis of biaryl cores. *ACS Catalysis*, 3(12):2776-2789, 2013.

[92] Chen, X. M., Lin, Z. J., Chen, D. J., Jia, T. T., Cai, Z. M., Wang, X. R., Chen, G. and Oyama, M. Nonenzymatic amperometric sensing of glucose by using palladium

nanoparticles supported on functional carbon nanotubes. *Biosensors and Bioelectronics*, 25(7):1803-1808, 2010.

[93] Kosugi, M., Kameyama, M., and Migita, T. Palladium-catalyzed aromatic amination of aryl bromides with *N,N*-di-ethylamino-tributyltin. *Chemistry Letters*, 12(6):927-928, 1983.

[94] Vrábel, M., Pohl, R.,Klepetářová, B., Votruba, I., and Hocek, M. Synthesis of 2′-deoxyadenosine nucleosides bearing bipyridine-type ligands and their Ru-complexes in position 8 through cross-coupling reactions. *Organic & Biomolecular Chemistry*, 5(17):2849-2857, 2007.

[95] Roy, S. and Plenio, H. Sulfonated *N*-heterocyclic carbenes for Pd-catalyzed Sonogashira and Suzuki–Miyaura coupling in aqueous solvents. *Advanced Synthesis & Catalysis*, 352(6):1014-1022, 2010.

[96] Dupont, J., Consorti, C. S., and Spencer, J. The potential of palladacycles: more than just precatalysts. *Chemical Reviews*, 105(6):2527-2572, 2005.

[97] Doucet, H. and Hierso, J. C. Palladium-based catalytic systems for the synthesis of conjugated enynes by Sonogashira reactions and related alkynylations. *Angewandte Chemie International Edition*, 46(6):834-871, 2007.

[98] Gogoi, A., Dewan, A., Borah, G., and Bora, U. A palladium salen complex: an efficient catalyst for the Sonogashira reaction at room temperature. *New Journal of Chemistry*, 39(5):3341-3344, 2015.

[99] (a) Gholap, A. R., Venkatesan, K., Pasricha, R., Daniel, T., Lahoti, R. J., and Srinivasan, K. V. Copper-and ligand-free Sonogashira reaction catalyzed by Pd(0) nanoparticles at ambient conditions under ultrasound irradiation. *The Journal of Organic Chemistry*, 70(12):4869-4872, 2005. (b) Son, S. U., Jang, Y., Park, J., Na, H. B., Park, H. M., Yun, H. J., and Hyeon, T. Designed synthesis of atom-economical Pd/Ni bimetallic nanoparticle-based catalysts for Sonogashira coupling reactions. *Journal of the American Chemical Society*, 126(16):5026-5027, 2004.

[100] Biffis, A., Zecca, M., and Basato, M. Metallic palladium in the Heck reaction: active catalyst or convenient precursor? *European Journal of Inorganic Chemistry*, 2001(5):1131-1133, 2001.

[101] Li, F., Zhang, Q., and Wang, Y. Size dependence in solvent-free aerobic oxidation of alcohols catalyzed by zeolite-supported palladium nanoparticles. *Applied Catalysis A: General*, 334(1-2):217-226, 2008.

[102] Varadwaj, G. B. B., Rana, S., and Parida, K. Pd(0) nanoparticles supported organofunctionalized clay driving C–C coupling reactions under benign conditions through a Pd(0)/Pd(II) redox interplay. *The Journal of Physical Chemistry C*, 118(3):1640-1651, 2014.

[103] Singh, A. S., Patil, U. B., and Nagarkar, J. M. Palladium supported on zinc ferrite: A highly active, magnetically separable catalyst for ligand free Suzuki and Heck coupling. *Catalysis Communications*, 35:11-16, 2013.

[104] Waring, D. R. and Hallas, G. *The chemistry and application of dyes*. Springer Science & Business Media, New York and London, 2004.

[105] Craig, P. N. and Drayton, C. J. *Comprehensive Medicinal Chemistry*, Pergamon, Oxford, 1991.

[106] Kunz, K., Scholz, U., and Ganzer, D. Renaissance of Ullmann and Goldberg reactions-progress in copper catalyzed CN-, CO- and CS-coupling. *Synlett.*, 2003(15):2428-2439, 2003.

[107] Guram, A. S., Rennels, R. A., and Buchwald, S. L. A simple catalytic method for the conversion of aryl bromides to arylamines. *Angewandte Chemie International Edition, English*, 34(12):1348-1350, 1995.

[108] Chan, D. M., Monaco, K. L., Wang, R. P., and Winters, M. P. New *N-* and *O-*arylations with phenylboronic acids and cupric acetate. *Tetrahedron Letters*, 39(19):2933-2936, 1998.

[109] Gonzalez, I., Mosquera, J., Guerrero, C., Rodriguez, R., and Cruces, J. Selective monomethylation of anilines by Cu(OAc)$_2$-promoted cross-coupling with MeB(OH)$_2$. *Organic Letters*, 11(8):1677-1680, 2009.

[110] Xu, H. J., Zhao, Y. Q., Feng, T., and Feng, Y. S. Chan–Lam-type S-Arylation of thiols with boronic acids at room temperature. *The Journal of Organic Chemistry*, 77(6):2878-2884, 2012.

[111] (a) Moon, P. J., Halperin, H. M., and Lundgren, R. J. Oxidative coupling of Aryl Boron eagents with sp^3-carbon nucleophiles: The Enolate Chan–Evans–Lam reaction. *Angewandte Chemie International Edition*, 55(5):1894-1898, 2016. (b) Chan, D. M., Monaco, K. L., Wang, R. P., and Winters, M. P. New *N-* and *O*-arylations with phenylboronic acids and cupric acetate. *Tetrahedron Letters*, 39(19):2933-2936, 1998.

[112] Collman, J. P., Zhong, M., Zeng, L., and Costanzo, S. The [Cu(OH):TMEDA]$_2$Cl$_2$-catalyzed coupling of Arylboronic acids with Imidazoles in water. *The Journal of Organic Chemistry*, 66(4):1528-1531, 2001.

[113] Collman, J. P., Zhong, M., Zhang, C., and Costanzo, S. Catalytic activities of Cu(II) complexes with nitrogen-chelating bidentate ligands in the coupling of imidazoles with arylboronic acids. *The Journal of Organic Chemistry*, 66(23):7892-7897, 2001.

[114] Lam, P. Y., Vincent, G., Clark, C. G., Deudon, S., and Jadhav, P. K. Copper-catalyzed general C-N and C-O bond cross-coupling with arylboronic acid. *Tetrahedron Letters*, 42(20):3415-3418, 2001.

[115] Antilla, J. C. and Buchwald, S. L. Copper-catalyzed coupling of arylboronic acids and amines. *Organic Letters*, 3(13):2077-2079, 2001.

[116] Quach, T. D. and Batey, R. A. Ligand-and base-free copper (II)-catalyzed C− N bond formation: cross-coupling reactions of organoboron compounds with aliphatic amines and anilines. *Organic Letters*, 5(23):4397-4400, 2003.

[117] Kaboudin, B., Abedi, Y., and Yokomatsu, T. Cu^{II}–β-Cyclodextrin complex as a nanocatalyst for the homo- and cross-coupling of Arylboronic acids under ligand- and base-free conditions in air: Chemoselective cross-coupling of Arylboronic acids in water. *European Journal of Organic Chemistry*, 33:6656-6662, 2011.

[118] Kantam, M. L., Venkanna, G. T., Sridhar, C., Sreedhar, B., and Choudary, B. M. An efficient base-free *N*-arylation of imidazoles and amines with arylboronic acids using copper-exchanged fluorapatite. *The Journal of Organic Chemistry*, 71(25):9522-9524, 2006.

[119] Islam, S. M., Mondal, S., Mondal, P., Roy, A. S., Tuhina, K., Salam, N., and Mobarak, M. A reusable polymer supported copper catalyst for the C–N and C–O bond cross-coupling reaction of aryl halides as well as arylboronic acids. *Journal of Organometallic Chemistry*, 696(26):4264-4274, 2012.

[120] Singh, B. K., Stevens, C. V., Acke, D. R., Parmar, V. S., and Van der Eycken, E. V. Copper-mediated *N*- and *O*-arylations with arylboronic acids in a continuous flow microreactor: a new avenue for efficient scalability. *Tetrahedron Letters*, 50(1):15-18, 2009.

[121] Roy, S., Sarma, M. J., Kashyap, B., and Phukan, P. A quick Chan–Lam C–N and C–S cross coupling at room temperature in the presence of square pyramidal [Cu(DMAP)$_4$I]I as a catalyst. *Chemical Communications*, *52*(6):1170-1173, 2016.