

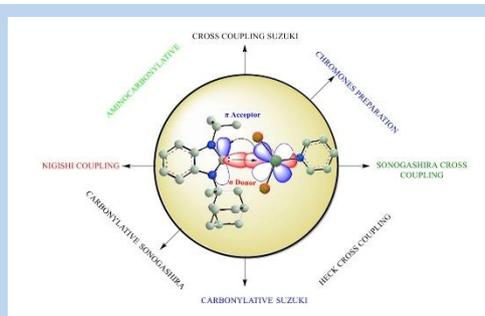
Recent Trends in the Catalysis of Cross Coupling and Carbonylation Reactions Using Pd (II)-N-Heterocyclic Carbene-Stabilized Complexes

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Abstract: Carbonylation processes and couplings catalyzed by transition metals have advanced significantly in the production of practical materials and in commercial applications. Choosing the right ligand is very important in these reactions. Even though this field has developed a lot in recent years, most commonly used ligands are phosphine-based compounds that have many problems such as difficult synthesis, harmful effects, high cost, and the poor stability under air or moisture conditions. On the other hand, there are many numerous benefits with N-heterocyclic carbene (NHC) ligands synthesis. These include lower cost, strong sigma donor, and easy to synthesize. Also, NHCs can be created from many N-heterocyclic rings, their stability toward air and moisture and lack of toxicity make them a useful ligand precursor. An overview of using NHC as donor ligands with palladium to aid the catalyzing of different coupling and carbonylation reactions that can be used in production of bioactive compounds and other medications.



Keywords: Cross Coupling Reactions, Carbonylation Reactions, NHCs Donor Ligands, N- Heterocyclic Carbene.

Introduction

Transition metal-catalyzed cross coupling and carbonylation reactions have become very popular in the last decade due to its importance for making useful materials in organic chemistry and for industrial processes [1]. This field is still challenging and interesting because there is a lot of work to improve the conditions used in these reactions for synthesis of organic compounds and in industrial applications. Today, cross-coupling and carbonylation reactions are widely used in different stages of chemical production and industries such as, fine chemicals, agrochemicals, pharmaceuticals, petrochemicals, polymers, and dyes [1-2]. For this reason, researchers are trying to develop better catalysts that are more active, reliable, cheaper, and environmentally friendly [1-3]. One of the most commonly used ligands are phosphine-based compounds, but they have some drawbacks like being expensive and not stable in air or moisture [2-3]. In particular, and contrary to phosphine ligands, the N-heterocyclic carbene (NHC) ligands are advantages of low cost, strong sigma donation, and simple synthesis. Although, vast numbers of N-heterocyclic rings can be used to produce NHCs, they are more useful as ligand precursors due to their stability against air and moisture and their non-toxic nature properties. [3]. Scientists are now interested in studying N-heterocyclic carbene (NHC) ligands. These ligands have strong σ donation and good π back donations, making them flexible for designing ligands which are suitable for different reactions [4]. Also, they

are cheaper and easier to make. Even though many N-heterocyclic rings have been reported in the literature for making NHCs [5], they are more useful as ligand precursors since they are stable in air and moisture and are not toxic [5-6]. This work will discuss the use of NHC ligands in both cross-coupling and carbonylation reactions.

Coupling Reactions

Carbon-carbon bond formation is a versatile process in organic chemistry that helps in synthesizing different kinds of molecules, that can be used in a lot of industries, like petrochemicals, medicine, plastics, and dyes. Some of these molecules include different functional groups as biaryls, aromatic esters, amides, ketones, and amino acids [1-7]. For example, Biaryls are special kind of molecules that are used as building blocks for new materials, such as strong rigid-rod polymers, molecular wires, control light materials, and liquid crystals [7-8].

There are many types of cross-coupling reactions that have been studied, but some of the most effective and well-known ones are the Suzuki-Miyaura [9], Heck-Mizoroki [10], and Sonogashira [11] reactions.

Most of these reactions prefer to use palladium as efficient catalysts although the cost of palladium catalysts,

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one of the reasons is the catalytic cycle of these reactions, the catalytic cycle usually involves three main steps: Oxidative addition, Transmetalation (or Insertion in Heck) and Reductive elimination [6]. In these steps the palladium can easily change the oxidation state between Pd(0) ↔ Pd(II) better than different metal complexes as shown in catalytic cycle of Mizoroki–Heck cross coupling reaction Figure. 1 [6].

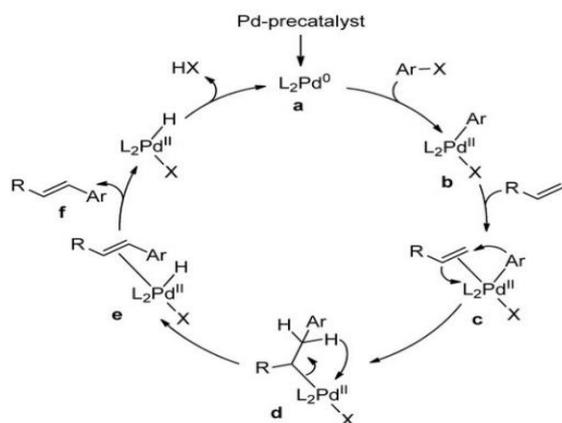
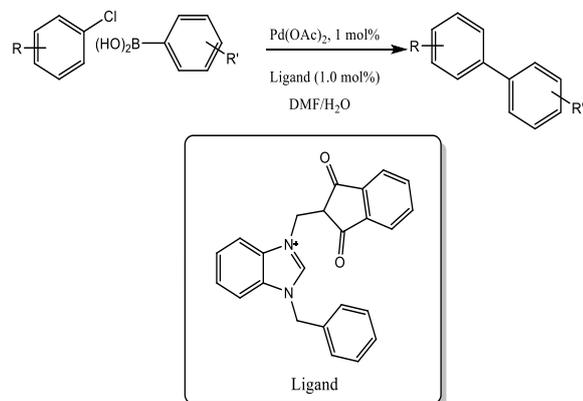


Figure (1): Overall catalytic cycle for the Heck olefination reaction [6].

These reactions are used to form simple molecules as well as the complex molecules. In order to construct new, intricate molecular structures, they are also highly helpful in the creation of specially designed ligands that can bond to metal ions. Also, these structures can act as catalysts in various chemical reactions, making them very useful in organic chemistry [12].

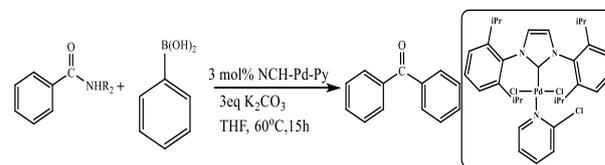
Suzuki-Miyaura cross-coupling reactions

Since the discovery of Suzuki-Miyaura coupling reaction, many different types of palladium complexes both heterogeneous and homogeneous, have been used for this reaction with various kinds of substrates that have different functional groups. In the literature, several methods for synthesis Pd-NHC complexes have been described by using NHC salts and Pd(OAc)₂ in order to create efficient catalysts for the Suzuki-Miyaura reaction. For example, bulky phenanthryl NHC ligands were made, and then palladium complexes were formed right there to help catalyze the Suzuki-Miyaura coupling of different aryl and vinyl chlorides with organoboron compounds at room temperature. This method produced tri- and tetra-ortho-substituted products in high yields under mild conditions [13]. Another example is the work by Kayser and Co-worker who made active palladium-NHC catalysts from benzimidazolium salts and Pd(OAc)₂ using in situ generation (Scheme 1). They investigated the prepared catalysts in the Suzuki-Miyaura coupling of various aryl and vinyl chlorides with boronic acid in DMF/H₂O as solvent [14].



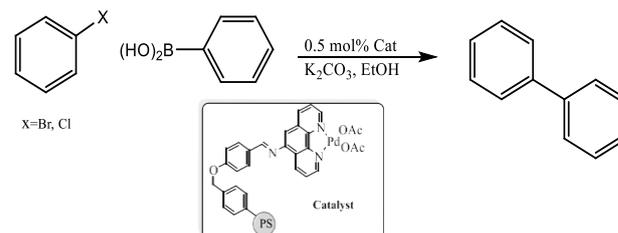
Scheme (1): In situ generation of active palladium-NHC catalysts based on Pd(OAc)₂ and benzimidazolium salts [14].

Numerous studies at the new Pd(II)-NHC and Pd(II)-NHC-pyridine complexes as catalysts have been checked for the Suzuki coupling process between aryl boronic acids and various aryl halides and activated aryl chlorides [15–18]. One notable study about the Suzuki-Miyaura coupling of amides with different aryl boronic acids using a palladium-NHC-pyridine complex that works well even in air and moisture [19]. In this method, 3% of the catalyst, 15 hours stirring at 60°C were used and gave much better results compared to other known Pd/phosphine catalysts when it comes for activating the N-C bond in amides.



Scheme (2): A stable catalyst for the Suzuki-Miyaura coupling of amides with various aryl boronic acids is the palladium-NHC-pyridine complex [19].

Besides that, many different types of palladium-based catalysts were used to help carry out various Suzuki-Miyaura reactions. For instance, palladium nanoparticles attached to PVC were used as good catalysts for these reactions at room temperature in water [20]. In 2005, Gao and their team showed that using iron oxide nanoparticles as a support for Pd-NHC complexes worked well for these reactions [21]. Another example involved a recyclable catalyst made from a simple Merrifield Resin that held a phenanthroline-palladium (II) complex. This catalyst was effective in catalyzing the reactions with only 0.5 mol% at normal temperature as in Scheme 3 [21].



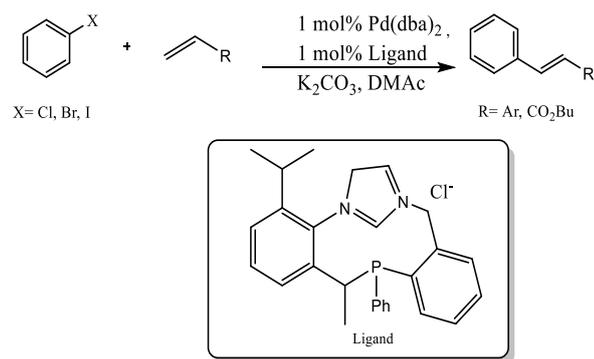
Scheme (3): As effective catalysts for Suzuki-Miyaura reactions, recyclable catalysts made of a basic Merrifield Resin supported phenanthroline-palladium (II) complex were used [21].

Mizoroki-Heck coupling reactions

In last years, imidazolium and benzimidazolium-based NHC compounds have become popular as starting materials for creating stable carbene ligands and carbene metal complexes. These NHCs are especially useful when paired with palladium to form organometallic catalysts used in homogeneous catalysis, and a lot of research has been done in this field [23-25]. The effectiveness of NHCs as ligands in these reactions comes from their ability to be modified in ways that adjust their size and electronic behavior by changing the structure of the heterocyclic part [26]. The strength of carbon-palladium bonds in Pd-NHC complexes made these compounds more stable, which avoiding the formation of inactive palladium black during the catalytic process [23]. Even though there have been many improvements in making and using Pd-NHC catalysts for different chemical reactions, this issue is still quite difficult to solve [27-30].

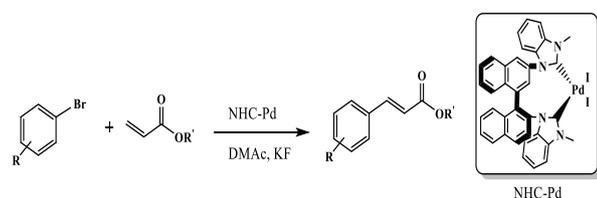
Recently, a new method was developed to make Pd-NHC-phosphine complexes right where they are needed for Heck reactions. This method uses a special type of catalyst made from a triaryl phosphine-linked imidazolium salt and a palladium (0) compound called Pd(dba)₂. This catalyst works very well for coupling a wide range of aryl bromides and iodides with acrylates, as shown in scheme 4. It also works well when coupling para-bromotoluene with different styrene compounds.

The reason this catalyst is so effective is because of the large groups attached to the N-phenyl ring of the phosphine-linked NHC ligands, as reported in reference [31].



Scheme (4): The generation of Pd-NHC-Phosphine complexes in situ for the Heck reactions [31].

Surprisingly, some examples in the literature mentioned the use of bis-carbene complexes made from chelating diazolum salts. One of these examples showed high efficiency for the synthesized Pd(II)-NHC complexes, which have a regular cis-chelating, bidentate structure in the Heck-type reaction (Scheme 5) [32].

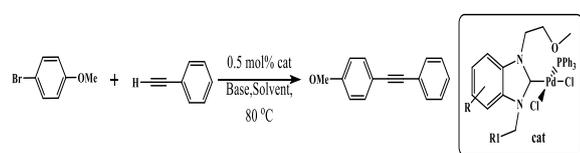


Scheme (5): Synthesized Pd(II)-NHC complexes, which has a 'normal' *cis*-chelating, bidentate structure in the Heck-type reaction [32].

In another study, the relationship between catalytic activity and softness in Mizoroki-Heck reactions—in which aryl bromides react with styrene or acrylate compounds to form diarylethene and cinnamic acid derivatives—was examined using DFT calculations on 1,3-propanediyl bridged bis(N-heterocyclic carbene) palladium (II) complexes. According to the study, catalytic activity rises with softness, but the +I effect of N-substituents on the ligands had no effect [33].

Sonogashira coupling reactions

are in general, the Sonogashira coupling reactions, which are the main way to make internal alkynes, are carried out using palladium complexes along with copper salts and an excess amine as a base [34]. However, when copper(I) co-catalysts are present, they can form some copper(I) acetylides on their own, which causes alkynes to undergo oxidative homo-coupling [34-35]. Many researchers have worked hard to prevent these homocoupling reactions. One approach has been to create new types of active palladium complexes that work better as catalysts in the Sonogashira reaction. Pd (II)-NHC complexes have been seen as a useful solution to avoid the issues caused by copper salts (Scheme 6) [36-37]. Internal alkynes are important parts of active molecules and materials and play a significant role as essential parts in synthesis chemicals used in many medicines [38].



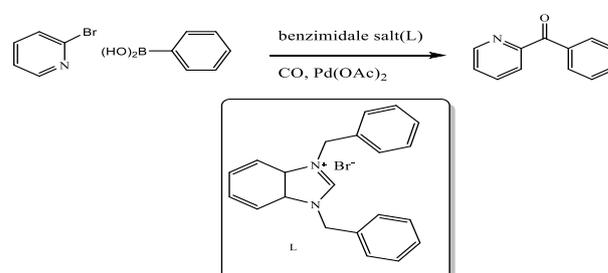
Scheme (6): Synthesized Phosphate-Pd (II)-NHC complexes, which has bidentate structure in the Sonogashira reaction [38].

Carbonylation reactions

The process of adding a carbonyl group to alkynes using nucleophiles that can donate protons was first discovered in the 1930s [39-40]. This method can make a lot of useful chemicals for different purposes. The kind of nucleophile used affects what products can be made. These consist of different α,β -unsaturated carboxylic acids, esters, and amides that are chains, branched, and cyclic [41-42]. In the future, carbonyl reactions like Suzuki and Sonogashira carbonylation reactions were also added to the list of carbonyls coupling reactions. Carbonylation reactions make many useful things, like diaryl ketones, alkyones, chromones, aryl esters, and aryl amides. These species (moieties or intermediates) are the first steps to make other compounds that are important for medicine. Most reactions that join carbon and oxygen together use carbon monoxide as the starting material. Possible Palladium is the most common catalyst for carbon-carbon bonds formation from carbon monoxide and other carbon-containing molecules. Many other metals can do this, but palladium is the best.

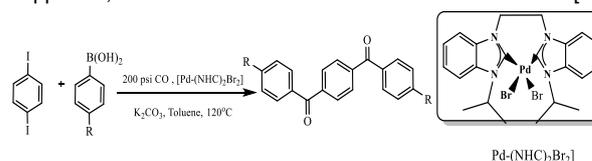
Carbonylative Suzuki-Miyaura coupling reactions

Because of their favorable thermal, optical, and electrochemical characteristics, biaryl ketones are highly valuable organic molecules. And these advantages make them useful in biological and medical areas, such as medicine dosing, tracking DNA activity, internal radiation measurements, and sun protection. Pd-NHCs complexes can be used to create these types of compounds. For example, Hamdi and his team recently showed that Pd-NHCs complexes can be made in real time from Pd (OAc)₂ and a benzimidazole NHC salt [43-46]. This method was used to speed up effectively a reaction called carbonylative Suzuki coupling, where aryl boronic acids react with 2-bromopyridine under safe, inert conditions [47-48]. This process helped the synthesis of unsymmetrical aryl pyridine ketones, as shown in Scheme 7.



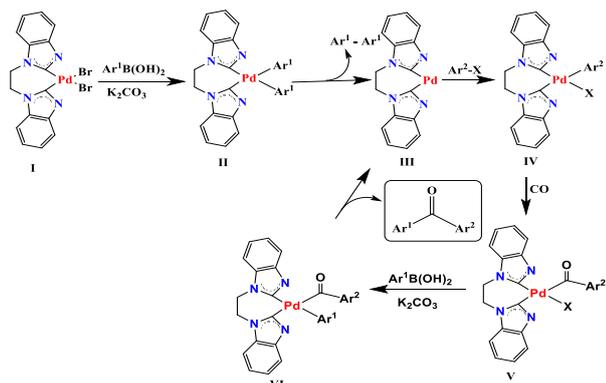
Scheme (7): Pd-NHC complexes are produced in situ using benzimidazole NHCs salt as a ligand precursor and Pd(OAc)₂ [47].

The useful chemicals from butterflies that used in drug delivery were made using a special chemical process called carbonylative Suzuki-Miyaura coupling. This process involved combination of aryl boronic acids with aryl halides using a specific type of catalyst called bridged bis(N-heterocyclic carbene)palladium(II) complexes. These catalysts were tested and showed high effectiveness even with small amounts. The reactions with aryl bromides favored making the carbonylated product when a higher pressure of carbon monoxide is supported, as shown in Scheme 8 [49].



Scheme (8): Carbonylative Suzuki-Miyaura coupling reaction of aryl diiodides with aryl boronic acids and aryl iodides with aryl diboronic acids by the palladium complex [49].

The proposed mechanism for this reaction was illustrated from kinetic study as shown in Scheme 9. The palladium (0) active species III is formed through two steps starting from the chelate dibromido pre-catalyst Pd(II) II by transmetalation of palladium complex I with aryl boronic acid in the presence of strong base such as K_2CO_3 , then diaryl were removed by reductive elimination step. Next step is oxidative addition of aryl halide to the Pd(0) species produce the palladium (II) intermediate IV. Formation of the acyl Pd intermediate V was reached by insertion of CO gas into the Ar-Pd bond. Followed by transmetalation of V with aryl boronic acid in the presence of K_2CO_3 forms the Pd intermediate VI. The last step is a reductive elimination of the diaryl ketone with the regeneration of the Pd(0) active catalyst III [49].



Scheme (9): A proposed mechanism for the carbonylative Suzuki-Miyaura coupling reaction catalyzed by the chelate bis(*N*-heterocyclic carbene) palladium(II) complex [49-50].

Carbonylative Sonogashira Reactions

Ynones are compounds that contain both an acetylene group and a carbonyl group. These compounds are important because they have specific structures that are found in many natural products and chemicals used in agriculture. Some Ynones show useful biological effects, like fighting cancer or preventing fungal growth. These active compounds can be found in different organisms or made in factories (Figure 2).

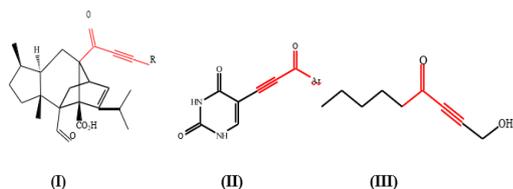
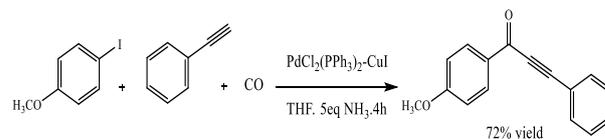


Figure (2): (I) Anti-cancer cytotoxic uracil analogue, (II) Antifungal isolated from fermentation of schnoodle benzoin, (III) Antifungal sordaricin analogue.

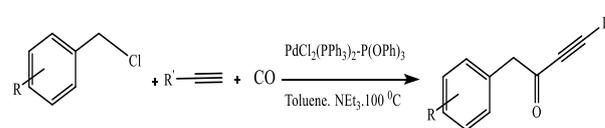
Ynones are also seen as important in making medicines like bryostatin 1, which has been used in different medical treatments. These include helping with HIV-1 latency and the virus reservoir in patients who are on antiretroviral therapy, treating severe Alzheimer's disease, and cancer treatment plans [53-55]. Making ynones usually involves many steps, which can create unwanted byproducts and result in lower amounts of the final product [55]. A better way to make ynones is the carbonylative Sonogashira coupling reaction, where aryl halides are joined with terminal alkynes using palladium-based catalysts. This method allows ynones to be made in a single step under mild conditions [55]. Researchers have tested this reaction using different types of palladium catalysts [56-58]. For example, using 5 mol% of $PdCl_2(PPh_3)_2$ along with 2 mol% of CuI as a supported catalyst, they were able to carry out the carbonylative Sonogashira coupling between para-methoxy-1-iodobenzene

and phenylacetylene. This was achieved in the presence of 2 equivalents of 0.5 M aqueous ammonia, 1 atm of carbon monoxide, to produce the corresponding α,β -alkynones (Scheme 10) [56].



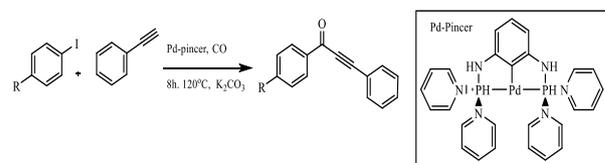
Scheme (10): Copper-palladium acts as a cocatalyst in the carbonylative Sonogashira coupling reaction between aryl iodides and terminal alkynes [56].

M. Beller and his group created a new catalyst system that uses an efficient method without copper for the Sonogashira carbonylative coupling reaction. This process combines benzyl chlorides with terminal acetylenes in presence of triethylamine as a base at 100 °C temperature. The reaction involves a mixed catalyst made of $Pd(PPh_3)Cl_2$ and $P(OPh)_3$, along with carbon monoxide, to form the desired alkynone products (Scheme 11) [58].



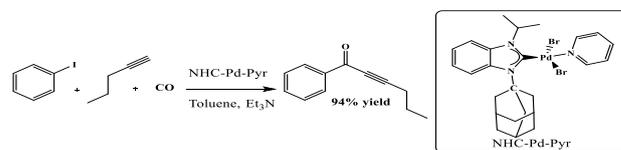
Scheme (11): Sonogashira carbonylative coupling of benzyl chlorides with terminal acetylenes in presence of triethylamine as a base and mixed $Pd(PPh_3)Cl_2/P(OPh)_3$ as catalyst [58].

Despite some issues, scientists have kept working on producing different palladium complexes to fix problems and come up with better solutions. These problems include a lot of catalyst needs, the low effectivity of the catalyst, long time reactions, high temperatures, and high levels of CO pressure [59-61]. Recently, as part of this ongoing work, a new type of palladium complex called an amino phosphine palladium pincer complex was made and then used as a good catalyst for the Sonogashira and Suzuki-Miyaura reactions in propylene carbonate (Scheme 12) [62].



Scheme (12): Sonogashira carbonylative coupling of aryl iodide with terminal acetylenes by amino phosphine palladium pincer as catalyst [62].

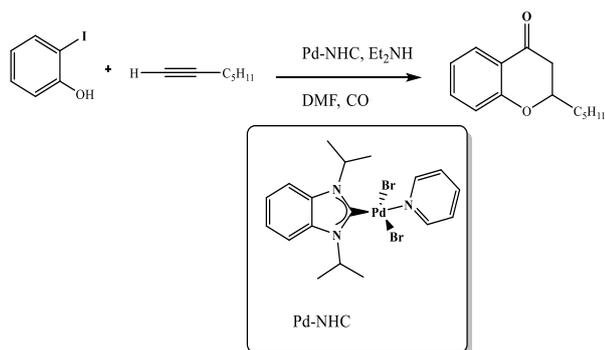
In earlier studies, a series of heterolytic (NHC)-pyridine palladium (II) complexes based on novel pre-ligands based on *N*-substituted *N*-heterocyclic carbene (NHC) shown exceptionally high catalytic selectivity and activity in carbonylative Sonogashira coupling processes. The DFT quantum mechanical analysis of the frontier orbitals for these complexes shows that the species are softened by bulky alkyl groups donating. This refers likely to the steric and electronic characteristics of the bulky alkyl groups. This is equivalent to the complexes' highest catalytic efficiency when dealing with soft substrates (Scheme 13) [63].



Scheme (13): Pyridine-NHC-Pd Catalyzes Aryl Iodide-Aryl Alkyne Carbonylative Sonogashira Coupling Reactions [63].

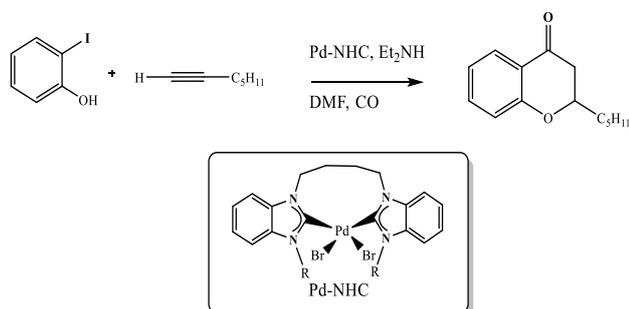
Cyclocarbonylative Sonogashira coupling reactions

Chromones, especially flavones, Chromones, especially flavones, are important compounds and very useful, especially in medicine and drug-making, that encourage many scientists and researchers to study [64-67]. These compounds can be prepared using the Cyclocarbonylative Sonogashira coupling a reaction. The studies about using Pd-NHC complexes in this type of reaction are not many. One example is that, when these complexes support the preparation of chromones and flavones, by reacting to ortho-functionalized aryl iodides with terminal aryl alkynes as shown in Scheme14. However, these palladium complexes work well with aryl alkynes but not so well with terminal alkyl alkynes. To improve their performance, they often need to be used with other compounds like pyridine or NHC as helper ligands [68].



Scheme (14): Pd-NHC complexes for the catalytic cyclocarbonylative of ortho-functionalized aryl iodides with terminal aryl alkynes, which results in the synthesis of chromones and flavones [68].

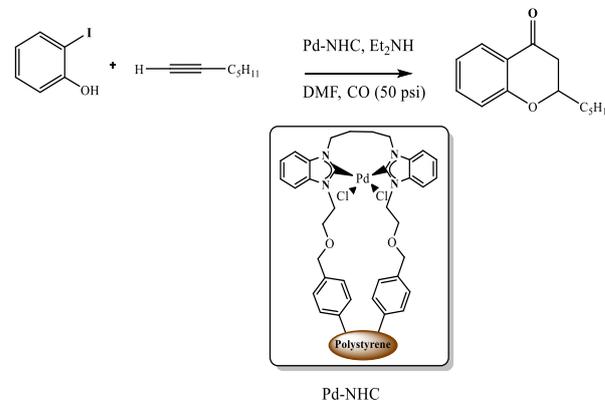
Bioactive chromones and flavones were produced via catalytic and one-pot regioselective methods employing phosphine-free Cyclocarbonylative Sonogashira coupling reactions between 2-iodophenols and aryl alkynes or other alkynes. These reactions were aided by new dibromides (NHC) palladium (II) complexes. Bridged N,N'-substituted benzimidazolium salts were formed into palladium complexes. In Cyclocarbonylative Sonogashira coupling methods, the generated compounds showed strong catalytic activity and outstanding stability even with little amounts of catalyst. To control the regioselectivity of these reactions, dimethylamine was used as the base and DMF as the solvent. (Scheme 15) [69].



Scheme (15): Using bridging bis(N-heterocyclic carbene) palladium (II) complexes as catalysts, 2-iodophenol and phenylacetylene undergo cyclocarbonylative Sonogashira coupling reactions [69].

On the other hand, it is well known that it is important to immobilize catalysts on different supports such as nanoparticles, clays or some polymers to manufacture recoverable and reusable catalysts. [70-74]. In the same context, other studies showed that chelating bis(N-heterocyclic carbene) ligand precursors and their palladium (II) complexes were successfully supported on different supports one of these examples is immobilization of Pd-NHC complexes on Co-MOF 74 microrods

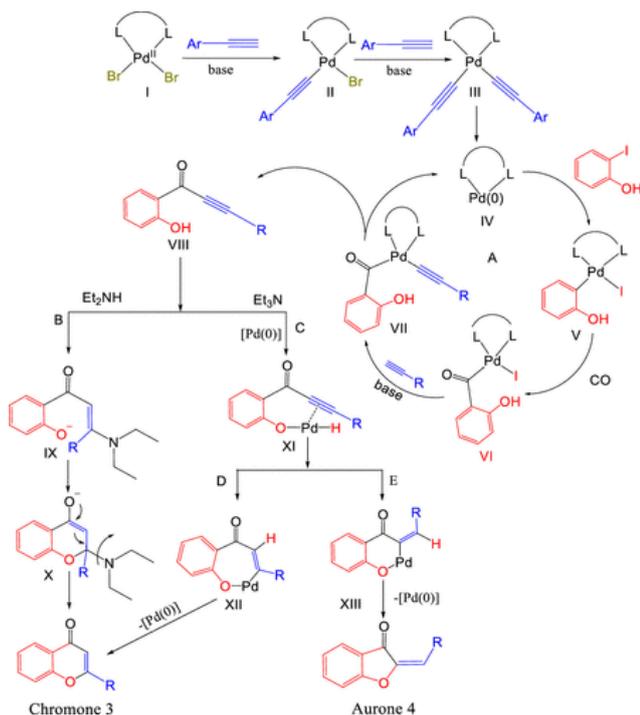
to catalyze cross coupling reactions [75]. Other bridging heterogenous Pd-NHCs complexes were attached to Merrifield's resin through covalent bonding. These attached complexes are very stable because of the strong chelate effect from the ligand. These systems work very well as catalysts in preparing different flavones and alkynes. They support a variety of aryl iodides and a broad set of aryl and alkyl alkynes in both carbonylative and cyclocarbonylative Sonogashira coupling processes. Additionally, they are quite reusable (Scheme16) [76].



Scheme (16): Robust Pd-NHC2@M, as a supported catalyst, and carbonylative Sonogashira coupling of distinct aryl iodides with different aryl alkynes [76].

Kinetic study of carbonylative sonogashira reactions and cyclo carbonylative Sonogashira reactions was used to collect data which correlated with DFT study of different Pd-NHC complexes. All of these data were used to propose the mechanism of cyclo carbonylative Sonogashira reactions [63, 69, 76]. Chromones and aurones were produced via carbonylative Sonogashira coupling reactions followed by the cyclization reactions. Initially, in the presence of the strong base, deprotonation of alkynes and the palladium (II) pre-catalyst (II) undergoes via substitution of the bromides by the acetylides to form the palladium (II) intermediate (III), followed reductive elimination of the dialkynes to generate the Pd (0) (IV) as the active catalytic species (Scheme 17, pathway A). The new palladium (II) intermediate (Ar-Pd-I) (V) is then formed via the oxidative addition of 2-iodophenol to the Pd (0). The acyl other palladium intermediate (VI) is generated by the insertion of carbon monoxide (CO) into the Ar-Pd bond. The next step is substitution of the iodide acetylide to produce the palladium intermediate VII. Then reductive elimination in the presence of the strong base yields the carbonylative Sonogashira product VIII with the subsequent regeneration of the Pd (0) catalyst.[69] The production of aurones or chromones depends on the type of base used in the reaction. In the presence of diethylamine, the favored Michael addition to the intermediate VIII forms the Michael Adduct IX (Scheme 17, pathway B), which is usually stabilized in DMF as an ideal solvent in these reactions. [63,69]. This Michael adduct (IX) was observed and identified in the reaction mixture by gas chromatography-mass spectrometry (GC-MS) [$m/z = 296.5$; $C_{19}H_{22}NO_2$ (MH^+)]. The diethylamine is then eliminated to produce the cyclic enolate X, which is formed the corresponding chromone. When triethylamine was used as a base, no reaction was observed without catalysts. Furthermore, the palladium catalyzed reaction in the presence of triethylamine led to the production of a mixture of aurones and chromones [69]. In this case, it is suggested that the oxidative addition of O-H to the Pd(0) species generates the palladium intermediate XI (Scheme 17, pathway C). The subsequent insertion of the alkyne into Pd-H proceeds following two pathways to generate either the seven-membered metallacycle XII (pathway D) or the six-

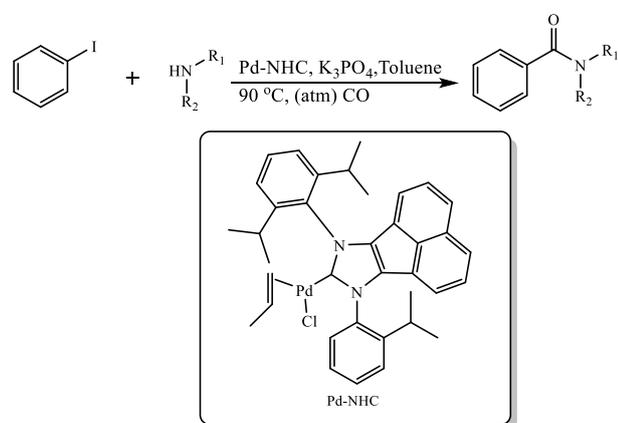
membered metallacycle XIII (pathway E) as intermediates. These undergo further reductive elimination to produce chromones and aurones, respectively.



Scheme (17): Plausible Mechanism for the Cyclocarbonylative Sonogashira Coupling Reaction Catalyzed by Bridged-Bis(NHC)PdBr₂ Complexes; Production of Chromone [Pathway B or (C,D)], and Aurone (Pathway C-E) [69].

Alkoxy and amino carbonylative coupling reactions

Recently, Recently, palladium-catalyzed reactions that use aryl halides along with amines or alcohols as starting materials in the presence of carbon monoxide, have been widely used in big industries to make useful fine and bulk chemicals. This method is very flexible and allows the creation of many types of carboxylic acids and their related derivatives in a single step, and from common starting materials. The carboxylic acids and related compounds include straight, branched, and ring-shaped ones, [77-79]. Few studies discuss the use of Pd-NHC complexes for alkoxy carbonylation or amino carbonylation reactions. For instance, the production of bioactive amides through the aminocarbonylation of different (hetero)aryl iodides with secondary amines using strong allylic palladium-NHC complexes as catalysts under normal CO pressure is shown in Scheme 18 [80].



Scheme (18): Allylic palladium-NHC complexes as a catalyst amino carbonylative coupling reactions [80].

Conclusion

After many years of quiet progress, scientists have recently worked on a new method to use Palladium (II) complexes with N-Heterocyclic carbene ligands as catalysts in coupling and carbonylation reactions. However, traditional protocols of using transition-metal complexes with phosphine ligands have some big problems. These difficulty of compounds synthesis, the harmful effects, the expensive costs, and poor stability in air and moisture are of the major problems faced by scientists. Recently, a new and promising method was developed, One of these methods is bridging between to different pre-ligands that can create new bis-bridged Pd(II)-NHCs complexes which produce rigid and stable catalysts for cross coupling and carbonylative coupling reactions that can work at high temperature, additional to that, some workers innovated hybrid catalysts between NHCs pre-ligands and pyridine to produce new catalysts that have strong sigma donation and can receive electron by pi back donation which can produce efficient catalysts for many carbonylation reactions, in these types of Pd(II)-complexes the effect of steric effect was studied based on spectroscopic techniques correlate with DFT data which proved that bulky substituents can make the complexes soft and efficient for these carbonylative reaction with high selectivity and low loading. All of these types can be immobilized on different heterogenous support which produced new recoverable heterogenous Pd (II)-NHCs catalysts that were recycled around 12 times with high TON. These current trends in the synthesis of Pd (II)-NHCs complexes open new windows for making a useful compound that can be used in medicines, pharmaceuticals, and other industries via cross coupling reactions and carbonylative reactions under mild conditions, high yields, low cost, highly selectivity and ecofriendly.

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- **Author's contribution:** The authors confirm contribution to the paper as follows: Conceptualization (Mansour W. and Bsharat O.); methodology ((Mansour W. and Bsharat O.); software, (Mansour W. and Bsharat O.); validation (Mansour W. ., Qrareya H and Bsharat O.); formal analysis (Mansour W. and Bsharat O.); investigation (Mansour W. ., Qrareya H and Bsharat O.); resources (Mansour W. and Bsharat O.); data curation (Mansour W. and Bsharat O.); writing—original draft preparation (Bsharat O., and Mansour W.); writing—review and editing (Bsharat O., Qrareya H., and Mansour W.). All authors reviewed the results and approved the final version of the manuscript.
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