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Palladium Catalyzed Heck–Mizoroki and Suzuki–Miyaura Coupling Reactions (Review)[1]

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Abstract—This article is about the progress of palladium compounds as a catalyst for Heck–Mizoroki and Suzuki–Miyaura coupling reactions. Industrial catalysts with broad applicability need continuous catalyst development process through modification of ligand design, geometry and functionality. Recently catalysts have been synthesized through attachment of the activated palladium complexes on the surface of polymer support, particularly, insoluble in reaction medium. An appropriate mixture of palladium salt and ligand is also used as an important modification in some cases to get better results. We surveyed the important palladium compounds synthesized up to early 2014 for Heck–Mizoroki and Suzuki–Miyaura coupling reactions and summarize their progress in terms of ligand modification and other associated parameters.

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INTRODUCTION

Palladium(II) is considered as soft metal (class B) which is depicted in its rich chemistry that is not limited to soft bases like phosphorous and sulfur but also for hard ligands e.g. nitrogen and oxygen [1]. The study of palladium(II) metal complexes was greatly enhanced when it was discovered that they have good catalytic activity. Transition metal complexes of Pd(I) found rarely and mostly used as precatalysts in organic synthesis [2–4]. The organometallic chemistry of Pd(III) found in its initial stages when compared with Pd(0), Pd(II) and Pd(IV). Limited complexes of Pd(III) are also well known [5]. Palladium can exist in a number of different oxidation states but useful organic methods are dominated by the use of Pd(0) and Pd(II) [6–34], although the utility of Pd(IV) [35–38] has been steadily emerging in its own right. The types of transformations carried out by palladium in 0, +2 and +3 oxidation states are given in Table 1. The remaining oxidation states have not, as of yet, found practical applications hence their observation remains rare [39–44].

Cross-coupling is an extremely powerful tool available to synthetic chemists in their quest to create or reproduce intricate organic scaffolds. This reaction has enabled chemists to join two organic fragments using relatively mild conditions allowing for the manipulation and creation of delicate, complex molecules. Cross-coupling plays an important role in the synthesis of many drugs, natural products, optical devices and industrially important starting materials [45–58]. Its importance was also recognized by the Nobel committee in 2010 by awarding Richard F. Heck, Ei-ichi Negishi and Akira Suzuki the Nobel prize in Chemistry for what it termed “artwork in a test-tube.” The cross-coupling reactions of vinyl, aryl, benzyl, allyl halides, triflates and acetates with alkenes recognized as Heck reactions and that of organo-boron compounds with pseudohalides or organic halides is termed as Suzuki–Miyaura reaction. Development of

Table 1. Types of transformation catalyzed by palladium in various oxidation states

Pd(0)	Pd(II)	Pd(III)
Cross couplings	Wacker process	Oxidative C–H coupling reactions
Allylic alkylation	Cycloisomerization	Oxidative carbon–heteroatom Bond-forming reactions
Hydrogenation	Alcohol oxidation	Kumada and Negishi coupling reactions
Hydrogenolysis	Allylic oxidation	O_2 Insertion reactions
Carbonylation	Allylic rearrangements	C–H Acetoxylation

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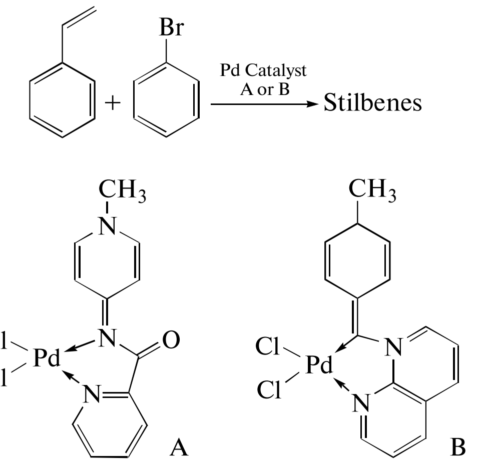
Table 2. Summary of the results from Heck reactions using palladium–pyridinium amidate (A) and palladium–pyridinium amide (B) catalyst



Entry	Catalyst	Time, h	Stilbenes formed, %
1	A	06	61
2	A	24	94
3	B	06	49.5
4	B	24	84.5

these technologies lies inherently in the development of the specific methods used. In a world where natural resources are becoming more strained, the execution and development of clean and efficient chemistry has become a common goal for many chemists.

Mizoroki–Heck coupling. In the early 1970s Mizoroki and Heck first revealed the use of certain palladium catalysts in the mediation of carbon–carbon coupling reactions. The first of these catalysts were based on zerovalent palladium complexes with labile tertiary phosphanes. Subsequently it was found that complexes of divalent palladium could be just as effective and far more convenient due to their oxidative stability [53]. Typical catalysts for the Heck–Mizorki reaction with the active species $Pd^0(PPh_3)_2$ and $[Pd^0(PPh_3)_2(OAc)]^-$ are given below:

$$Pd^0(PPh_3)_4 \rightleftharpoons \underset{PPh_3}{\overset{}{Pd^0(PPh_3)_4 +}} \xrightarrow{-PPh_3} Pd^0(PPh_3)_2$$

$$\begin{matrix} Pd^{II}(OAc)_2 \\ + \\ 2PPh_3 \end{matrix} \rightleftharpoons [Pd^0(PPh_3)_2(OAc)]^-$$

There is scope within the C–C coupling mechanism for reduction of palladium(II) to palladium(0) by a number of species including the solvent, added amine, the accompanying ligand and the alkene. Therefore, generation of the active species in the reaction mixture often allows the use of oxidized catalyst at the outset. Similarly, Pd(II) and Pd(IV) species have been identified and proposed as the active species in a number of Heck reactions. However, in the case of doubly ligated NHCs, Pd(0) and Pd(II) are generally accepted as the operative metal oxidation states [59].

To enhance the productivity and catalytic activity in Heck reaction, initial efforts were made by spencer in early 1980s [60]. He set up the experimental basis for arylation of olefins with activated aryl bromides and concluded that a high TON process can be carried out only in polar aprotic solvents, such as DMF, HMPA, DMA, NMP, in the presence of sodium acetate as a base, and phosphine ligands if using low loads of palladium catalyst (0.1 mol % of $Pd(OAc)_2$ and 0.4 mol % of $P(o\text{-}Tol)_3$). Gradual progress in Heck reaction showed that activated aryl chlorides, nonactivated chlorobenzene itself, even deactivated *p*-methoxychlorobenzene and *o*-chlorotoluene can be utilized for this type of reaction by using 1.5 mol % of $Pd_2(Dba)_3$ (Dba = dibenzylideneacetone) and 4 mol % $P(t\text{-}Bu)_3$ as a catalyst [61]. However, palladium acetate with ligands **1** and **2** lost its activity at lower temperatures. This proved that these bidentate phosphine containing catalystic systems are less effective than monodenate phosphine system [62]. Dimeric palladium complex such as **3** was a big step forward in palladium catalysed coupling reactions. This Herrmann's catalyst can be used conveniently in applied homogeneous catalysis [63–65].

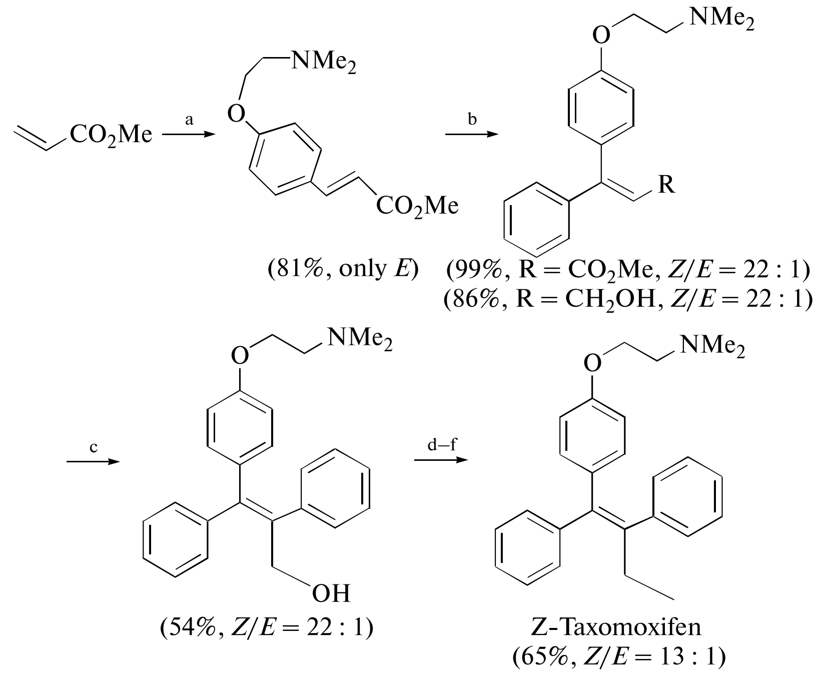
The ligand design, geometry and its electron donor strength plays a vital role in predicting the stability of metal complex. For Heck coupling reaction, the metal complex as a catalyst is more stable if its metal is strongly bonded with the ligand. Greater stability can lead to the better chances of catalyst survival under more severe reaction conditions. Due to the special design and better electron donor property, P–C–P pincer ligands [66, 32, 67] already proved successful for palladium catalyzed coupling reactions. Phosphorous donor ligands are very rapidly replacing by N-hetrocyclic carbenes (NHCs). The main reason is stronger interaction of NHCs donor function with palladium than its analogous phosphine complex. The literature quite clearly indicates that the combination of palladium and NHCs is perfect for Heck coupling reaction [68–75]. The concept of donor-functionalized carbene ligands has been expanded to pincer-type complexes [76] resulting in replacing P–C–P ligands by NHCs pincer [77, 78]. Crabtree [77] (**4**) in 2001 and Hahn [78] (**5**) in 2005 prepared famous palladium NHCs pincer complexes for Heck reactions. Mixed ligands (with two functionality) like imidazolin-2-ylidenes bridged by a neutral pyridine [77, 79–81] or a carbanionic function [82, 83] with two metallacycles also resulted in very active and stable palladium coupling catalysts.

CHART 1

In our past study [84] palladium complexes of pyridinium amidate (PYA, A) and amide (PYE, B) both showed catalytic activity for both Heck coupling reactions (Table 2). However, PYA is more active than PYE catalyst. The modified Crabtree procedure [84] was initially used to find out the catalytic ability of PYA complex of palladium and the results were compared with those obtained for PYE palladium complex. The results are also summarized in Table 2 and entries 1–4 were carried out in dimethylacetamide solvent. The base employed was sodium acetate (1.1 mole equivalent), one mol % of catalyst was used and the temperature was 140°C. The blank was run without catalyst but with base present, and showed zero catalytic activity. The results are each reported as the average of two runs. The results showed that both catalysts acted as pre-catalysts in the Heck–Miroroki coupling reaction.

In 2011, C. Zhu et al. worked on oxidative Heck reaction. The regioselectivities was attained by the hydroxyl group of a homoallylic alcohol that coordinates with palladium (the yield was 61–80%) [85]. A variety of tetrahydrofurans with functionalized scaffolds was achievable by using small amount of TFA that carry out oxyarylation of penultimate Heck intermediate (Table 3). In the same year, highly selective (*E*)-styrenyl products were obtained by Matthew S. Sigman in the absence of substrate bias with the Pd(0)-catalyzed Heck reaction [86]. The main advantage of this method is the use of low temperature, no use of any base or additional oxidant, and compatibility with greater number of functional groups (Table 4).

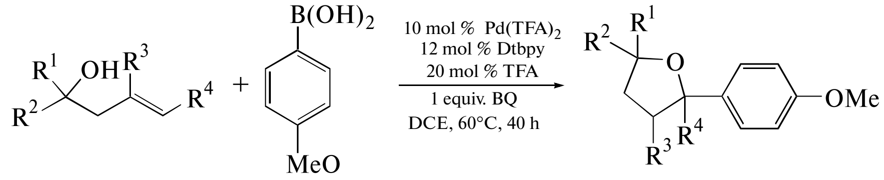
In 2012, Armido Studer and his coworkers suggested that the nature of oxidant play more important role than the protecting groups in oxidative Heck arylation for the stereoselective synthesis of tetrasubstituted olefins [87]. They were able to synthesize Z-Tamoxifen by using variety of palladium catalysts and nitroxide as oxidant in 65% yield under mild conditions. Synthesis of Z-Tamoxifen is given below:



a) 4-(2-dimethylaminoethoxy)phenylboronic acid (2 equiv.), TEMPO (2 equiv.), KF (2 equiv.), $[Pd(Acac)_2]$ (5 mol %), $EtCO_2H$, RT, 24 h
b) $PhB(OH)_2$ (4 equiv.), HO-TEMPO (2 equiv.), KF (4 equiv.), $Pd(OAc)_2$ (5 mol %), $EtCO_2H$, RT, 24 h
c) $PhB(OH)_2$ (4 equiv.), 8 (4 equiv.), KF (4 equiv.), $Pd(OAc)_2$ (10 mol %), $EtCO_2H$, 40°C, 24 h
d) Tetrapropylammonium perruthenate (5 mol %), NMO (2 equiv.), RT, 0.5 h (80%, $E/Z = 18 : 1$)
e) NaH, Ph_3PCH_3Br, THF, reflux, 4 h (85%, $Z/E = 13 : 1$)
f) H_2, Pd/C, EtOAc, RT, 2 h (95%, $Z/E = 13 : 1$)

In the same year, J. Zhou and his team solved a problem in intermolecular Heck reactions that is to control the specific site where aryl groups insert into olefins [88]. They used 2–5 mol % $[Pd(Dba)_2]$ along with 4–10 mol % ferrocene-based bisphosphine ligands in order to achieve above mensioned target. Intermolecular Heck reactions of aliphatic olefins are the following:

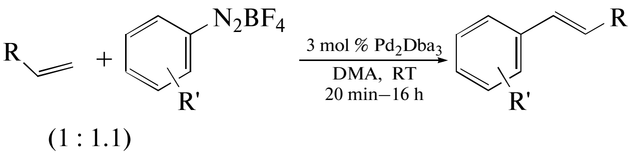
Table 3. Oxyarylation of homoallylic alcohols using $Pd(TFA)_2$ catalyst



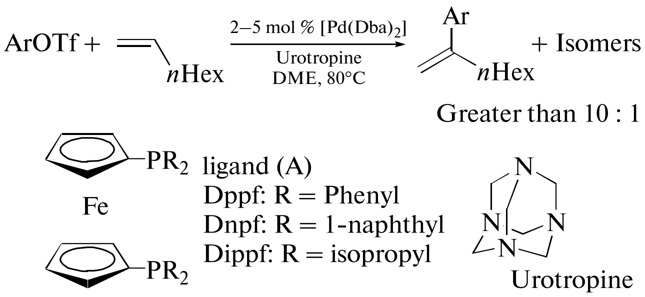
Entry	R^1	R^2	R^3	R^4	Yield, %*
1	Bn	Bn	H	H	75
2	H	H	H	H	65
3	H	Ph	H	H	74
4	$PhCH_2$	H	OH	H	80
5	Et	Et	H	H	72
6	H	H	H	Et	70
7	H	H	CH_3	H	61

* Yield of the isolated product. DCE = dichloroethane, Dtbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridyl.

Table 4. Heck reaction for highly selective (*E*)-styrenyl products using Pd_2Dba_3 catalyst



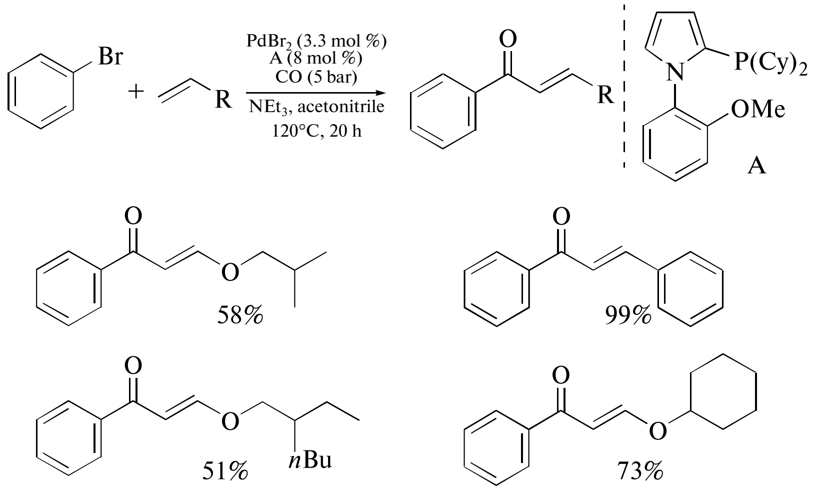
Entry	Product	Time	Yield, %
1	$CH_3CO(CH_2)_2CH{=}CH{-}Ph$	20 min	89
2	$CH_3(CH_2)_4CH(OAc)CH{=}CH{-}Ph$	16 h	87
3	$CN(CH_2)_3CH{=}CH{-}Ph$	3 h	96
4	$CH_3(CH_2)_4CH(OH)CH{=}CH{-}Ph$	16 h	55
5	$CH_3OCO(CH_2)_2CH{=}CH{-}Ph(p{-}NO_2)$	20 min	97



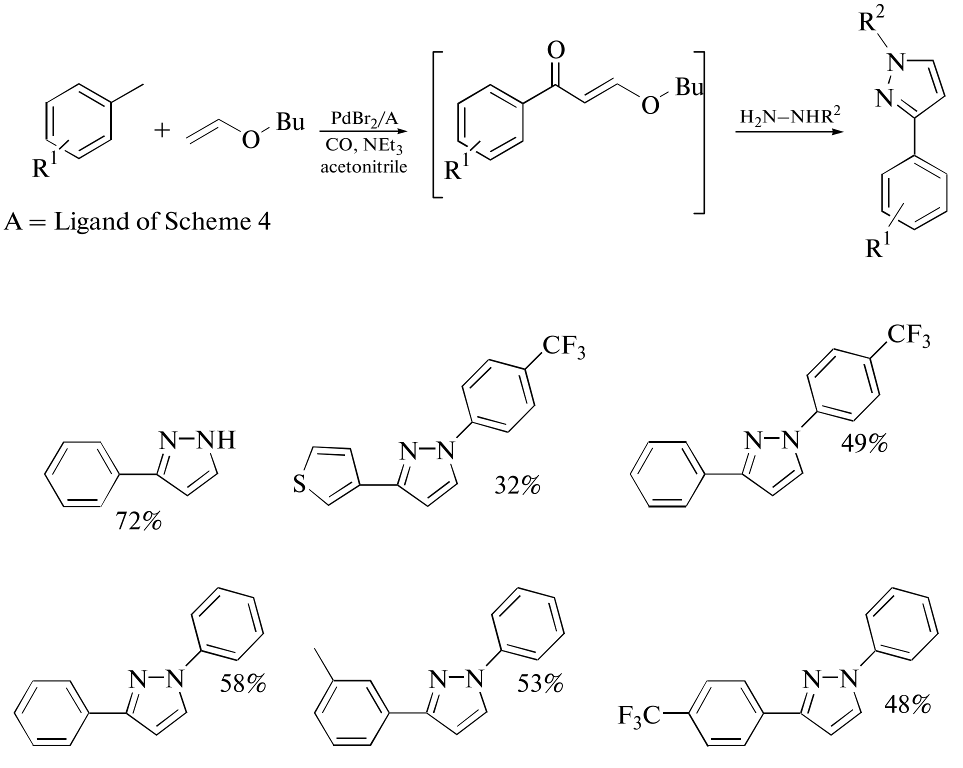
Tf = trifluoromethanesulfonyl,
Dppp = 1,3-bis(diphenylphosphino)propane,
Dba = dibenzylideneacetone, DMA = dimethylacetamide

Studies revealed that the steric effects of Dnpf ligand hindered the formation of minor product. Carbonylative Heck reaction of aryl bromides with vinyl ethers to 3-alkoxy alkenones and pyrazoles was carried out in 2012 by Matthias Beller and his coworkers [89]. They used the combination of palladium bromide and ligand (A) as catalyst system to generate the useful synthetic products.

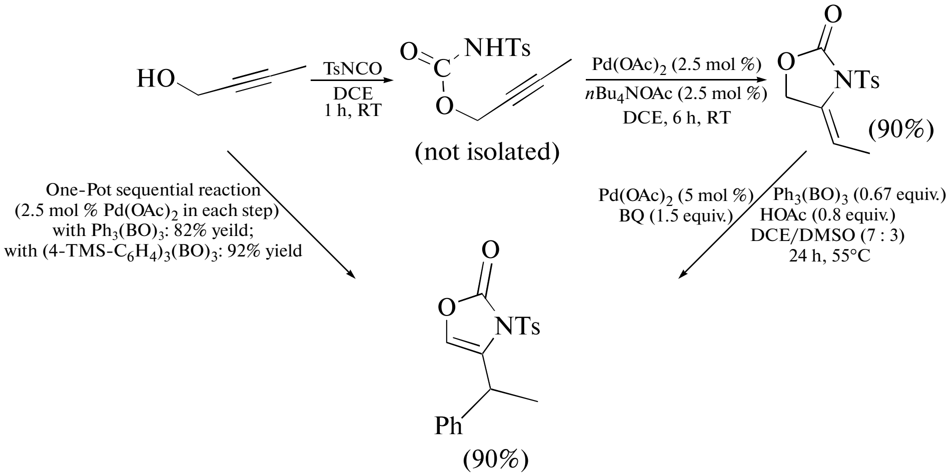
Palladium-catalyzed coupling of aryl bromides with *n*-butyl vinyl ether (isolated yields are given) are the following:



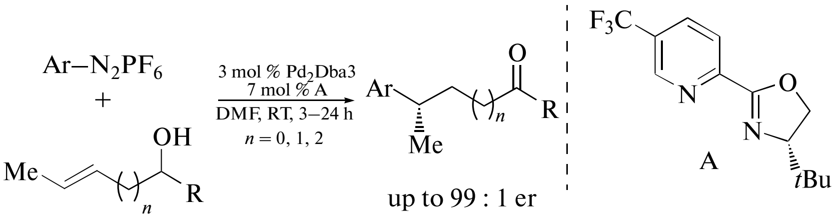
One-pot synthesis of pyrazoles looks like:



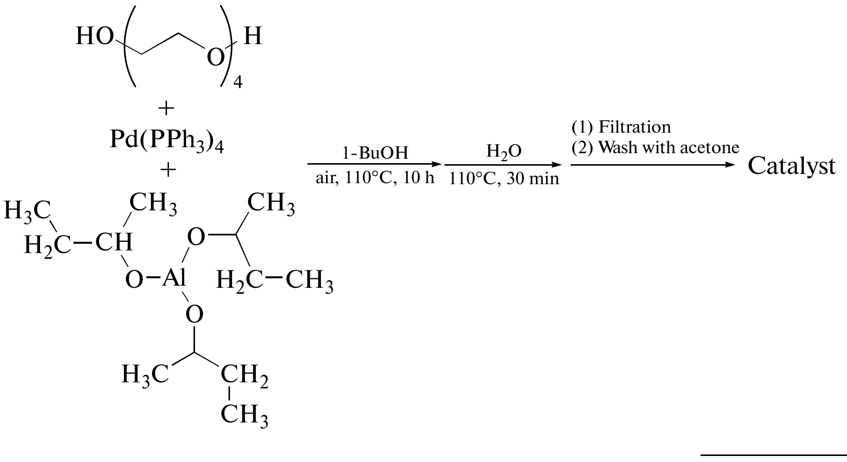
E. Backvall and his co-workers in 2013 carried out scalable synthesis of oxazolones (the yeild was 90%) for the synthesis of biologically active compounds from propargylic alcohols through multistep palladium(II) catalysis [90]. Scaleup and one-pot sequential oxidative Heck reaction starting from the propargylic alcohol are given below:



They also improved the yield to 92% by one pot sequential reaction adding 2.5 mol % Pd(OAc)$_2$ in each step with (4-TMS–C_6H_4)$_3$(BO)$_3$ and however with Ph$_3$(BO)$_3$ yield decreased to 82%. In the same year, S. Sigman reported a general, highly selective asymmetric redox-relay oxidative Heck reaction using achiral or racemic acyclic alkenols and boronic acid derivatives [91]. Enantioselective redox-relay oxidative Heck reaction looks like:



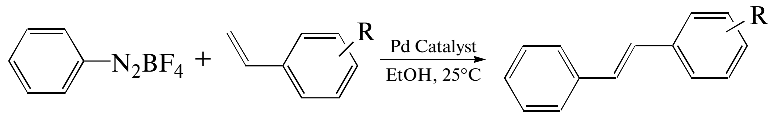
The main advantage of this method is that the variety of useful functionality in excellent enantioselectivity under mild conditions. W. Wei et al. used aluminium hydroxide-supported palladium nanoparticles as catalyst for the arenediazonium tetrafluoroborate salts cross-couplings [92]. Synthesis of palladium nanoparticles (catalyst used in Table 5) is:



The main significance of this method includes good yield of product in open air even at room temperature without addition of any base or ligand (Table 5).

In this year, J. Zhou gives an easy method for longstanding problem of intermolecular Heck reaction of common alkyl halides [93]. They worked out

Table 5. Cross-coupling reactions of benzenediazonium tetrafluoroborate and substituted styrenes with Pd catalyst*

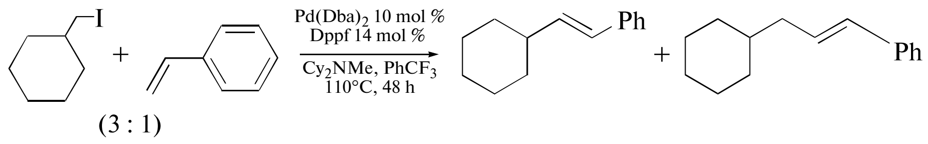


Entry	R	Yield, %**
1	*m*-Methyl	60
2	*p*-Methyl	65
3	*o*-Chloro	71
4	*p*-Chloro	85
5	*p*-Bromo	71

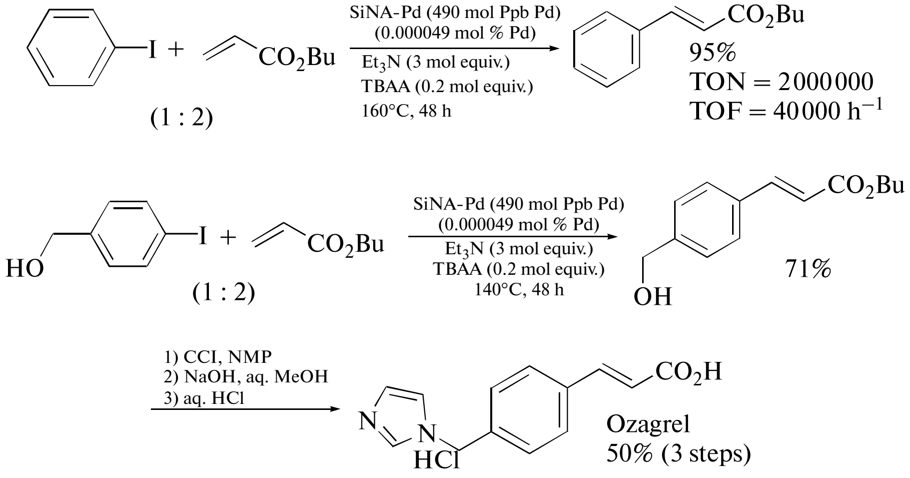
* Reaction conditions: olefin (1.0 equiv.), benzenediazonium tetrafluoroborate (1.5 equiv.), Pd catalyst (2.0 mol % Pd), EtOH, 25°C, 48 h.

** Isolated yield, 2.0 equiv. of benzenediazonium tetrafluoroborate.

$Pd(Dba)_2$–Dppf (catalytic system) (Dppf = 1,1'-bis(diphenylphosphino)ferrocene), $PhCF_3$ (solvent) and Cy_2NMe (base) are optimum for this reaction. Zhou's reaction for intermolecular Heck reaction is:

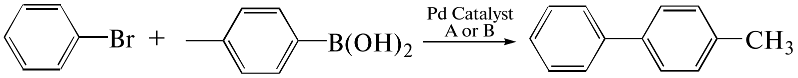


A. Yamada in the current year, also reported the synthesis and use of a silicon nanowire array-stabilized palladium nanoparticle catalyst, SiNA-Pd, in the palladium-catalyzed Mizoroki–Heck reaction [94]. The turnover number (TON) and turnover frequency (TOF) are two million (the highest TON for the Mizoroki–Heck reaction with heterogeneous catalysts) and 40000 h^{-1}, respectively. They also reported the synthesis of Ozagrel, an important anti-asthmatic agent, in 50% yield in three steps mentioned in the following Scheme:



Suzuki–Miyaura coupling. In 1979, Akira Suzuki published for the first time that organo-boronic acids couples with halides in the presence of four coordinated tetrakis(triphenylphosphine)palladium(0) as catalyst [26, 95–97, 98]. Gradual progress in this field [99–105] covers a broad spectrum of commonly encountered substrates like coupling of aryl/vinyl halide (including chlorides) and aryl/vinyl triflates with aryl-

Table 6. Summary of the results from Suzuki–Miyaura reaction using palladium catalysts (palladium–pyridinium amidate (A) or palladium–pyridinium amide (B) of Table 3)*



Entry	Catalyst	Time, h	Product, %
1	A	04	49
2	A	06	76
3	B	04	38
4	B	06	56

* Reaction conditions: bromobenzene (1.0 equiv.), tolylboronic acid (1.5 equiv.), Pd catalyst (A or B) (0.01 equiv.), DMF, 100°C, 48 h, Cs_2CO_3 base.

boroic acid. The earlier reaction can be carried out by $Pd_2(Dba)_3/P(t\text{-}Bu)_3$ and later by using $Pd(OAc)_2/PCy_3$ as catalysts at room temperature.

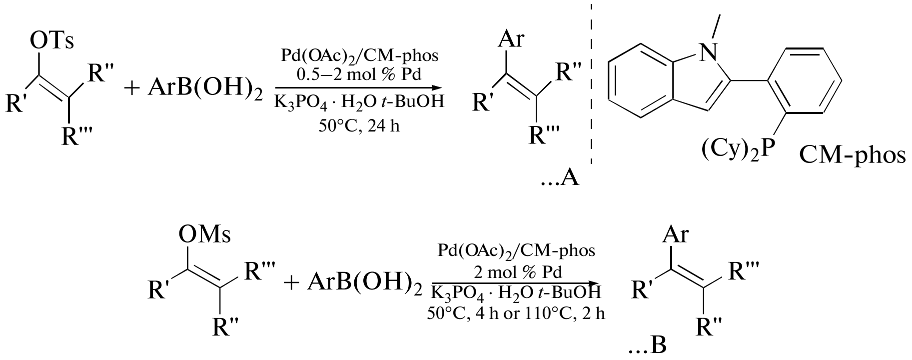
Recently this work is extended to green solvents as a medium for Suzuki coupling reaction. Water-soluble cyclopalladated complexes (**6**, Chart 2) [106] (with five- or six-membered rings as air-stable solids from Schiff base ligands bearing N-phenyl sulfonate groups) showed high catalytic efficiency for the reactions of aryl bromides with phenylboronic acid in aqueous solvents under mild conditions. Yin [107] successfully employed room temperature conditions for highly efficient Suzuki–Miyaura reactions in water. He used palladium acetate (5 mol %) in the presence of Stilbazo (**7**, Chart 2). In 2008, However Fujihara [108] carried out asymmetric Suzuki–Miyaura coupling reactions catalyzed by chiral palladium nanoparticles stabilized by optically active mono- and bisphosphines at room temperature. Palladium nanoparticles stabilized by (*S*)-BINAP (**8**, Chart 2) gave best results.

Welton [109, 110] used nitrogen donor imidazole palladium complexes as catalysts for Suzuki coupling reactions. This system provided a stable, recyclable method for using iodo- and bromoarenes in this reaction. He used 110°C reaction temperatures and 20 min reaction time. He got a maximum of 87% yield upon using a 4-methylthiazole palladium complex. In 2003, Glorius synthesized an N-heterocyclic carbene palladium complex (**9**, Chart 2) with flexible steric bulk that allowed Suzuki cross coupling of sterically hindered aryl chlorides at room temperature [111]. In 2006, Yu synthesized palladium complexes of unsymmtrical pyridyl-supported pyrazolyl N-heterocyclic carbene ligands (**10**, Chart 2) [112]. Steric strain of the ligand was released by the introduction of methylene linkers to the ligand molecule. All the palladium complexes exhibited good to excellent catalytic activity in Suzuki–Miyaura reactions of phenyl or *p*-tolylboronic acid with aryl halides including iodobenzene, aryl bromides, and activated aryl chlorides under mild conditions. In the same year, Nolan synthesized a series of (NHC)Pd(R-allyl)Cl complexes (11–14, Chart 2) which showed higher catalytic activity in the Suzuki–Miyaura coupling reaction of unactivated aryl chlorides at room temperature in minutes using very low catalyst loading [113].

CHART 2

Our past study [84] revealed that both PYA-Pd (A) and PYE-Pd (B) complexes showed catalytic activity for suzuki coupling reactions (Table 6). However, A is more active than B catalyst. The substrates bromobenzene and tolylboronic acid were selected in order to facilitate detection of starting materials and the 4-methylbiphenyl product via ^1H NMR spectroscopy. A typical Suzuki–Miyaura coupling procedure was used for a study of the C–C coupling reaction between bromobenzene and tolylboronic acid [112]. The Suzuki–Miyaura reaction and actual conditions employed are shown below in Table 6. Tabulated summary of the findings are also presented in Table 6. The results showed that complexes of both PYA and PYE acted as catalysts in the Suzuki–Miyaura coupling reaction. Significantly, no visual signs of palladium black formation were noted during reactions with the palladium amidate complexes (A, entries 1, 2, Table 6). However, it was observed that in the reactions involving B (entries 3, 4, Table 6) significant amounts of palladium black was formed under these conditions.

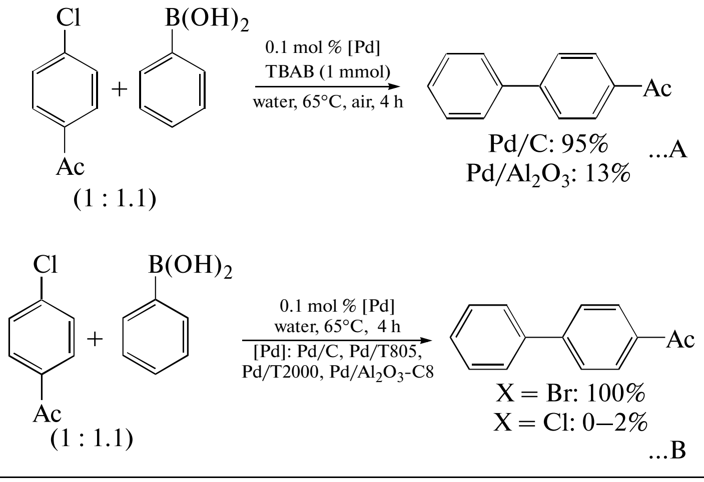
In 2011, Y. Kwong and his coworkers used $Pd(OAc)_2$/CM-phos for making alkenyl carbon–carbon bond [114]. Palladium-catalyzed Suzuki–Miyaura coupling of alkenyl tosylates and mesylates are in the following Scheme:



This group achieved the first examples of synthesis of alkenyl mesylate coupling with organoboron coupling partners. The special thing is that the reactions were carried out under very mild reaction conditions with functional group tolerances and the unique alkenyl tosylate/mesylate pattern with respect to vinyl halides that is not readily available (equation A and B, see the scheme above, yields = 80–98%, where R = alkyl, cycloalkyl, phenyl, biphenyl and various substitutions on phenyl rings). In the same year, K. Kohler and his team found out that the catalytic activity of palladium in water is highly dependent on the surface properties of the support materials (Table 7) [115]. They used different supporting materials for palladium catalysts having varied surface properties (hydrophilic, hydrophobic, amphiphilic). They concluded that for hydrophilic surface, excess base is vital. Hydrophobic supports are valuable to work under trivial conditions. Bromide ions helps in the dissolution of palladium species on the other hand tetrabutylammonium ions provide activating counterions for the boronate and palladate species. Tetrabutylammonium bromide (TBAB) activates the aryl chlorides by several synergistic mechanisms.

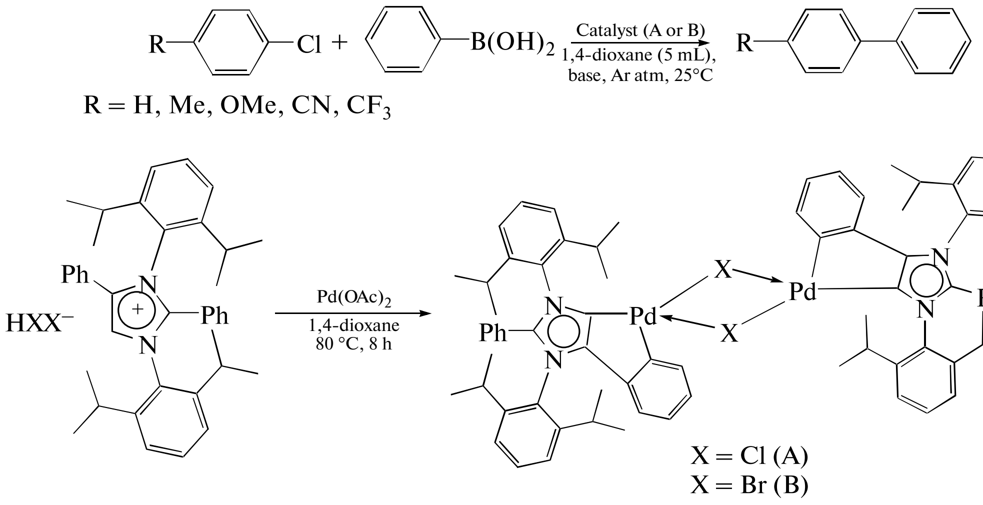
In 2012, K. Mandal and his research group used palladium complexes bearing abnormal N-heterocyclic carbene (Table 8) as catalysts in Suzuki–Miyaura cross coupling of aryl chlorides at 25°C [116]. They found that the catalyst remained active for ten successive catalytic runs and can activate 4-chlorotoluene at

Table 7. Suzuki coupling reaction of 4'-chloro- and 4'-bromoacetophenone catalyzed by palladium catalysts with varied metal oxide support for palladium



Support	Surface characteristics	Mean particle size
T805	45 $m^2 g^{-1}$: hydrophobic, octyl silane coating on the surface	15–20 nm
T2000	100 $m^2 g^{-1}$: amphiphilic, titania (80%) surface is coated with Al_2O_3 (~8%) and simethicone (a mixture of silica gel (~3%) and polydimethylsiloxane), primary particles aggregate to give roughly 100 nm sized needles	10–15 nm
Al_2O_3-C8	100 $m^2 g^{-1}$: hydrophobic, modified using *n*-octyl-dimethylchlorosilane before using it for catalyst preparation	13 nm
Al_2O_3	100 $m^2 g^{-1}$: hydrophilic, hydroxy groups on the surface	13 nm

Table 8. Suzuki–Miyaura cross coupling reactions of aryl chlorides at room temperature with abnormal *N*-heterocyclic carbine*

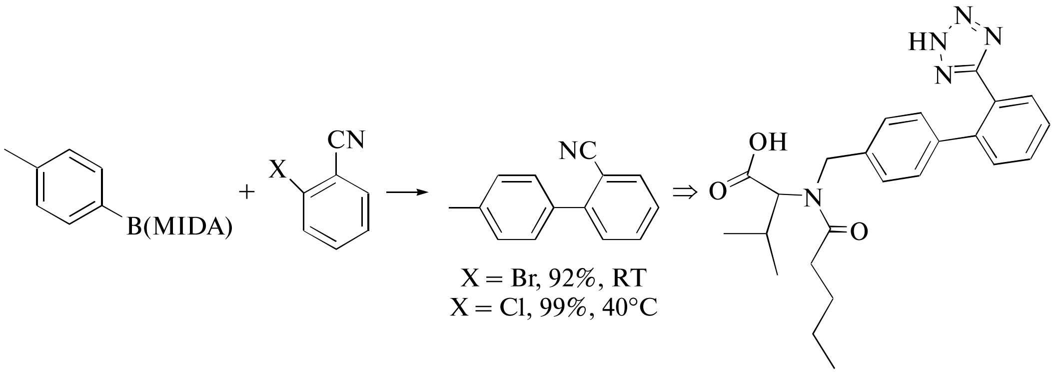


Entry	R	Catalyst	Time, h	Yield, %**
1	Me	A	4	98
2	Me	B	4	97
3	OMe	A	8	98
4	OMe	B	7	98
5	H	A	3	97
6	H	B	3	98
7	CN	A	2	98
8	CN	B	2	98
9	CF_2	A	2	98
10	CF_2	B	2	98

* Reaction conditions: 0.73 mol % catalyst (23 or 24), aryl chloride (1 mmol), phenylboronic acid (1.5 mmol) and base (2 mmol, NaOMe for entries 1–6 and Cs_2CO_3 for entries 7–10), 5 mL dry 1,4-dioxane. **Isolated yield after chromatography.

room temperature with 0.01 mol % catalyst loading resulting in a TON of 9500 within 6 h. The catalyst exhibits its activity at very low catalyst loading up to 0.005 mol % at room temperature. DFT calculation revealed that strong Pd—carbene bond prevented any palladium leaching in solution and thus it's remained active for ten successive catalytic runs without any loss of its activity. In the same year, VOL. Polshettiwar loaded fibrous high-surface-area nano-silica (KCC-1) with aminopropyl groups and Pd nanoparticles (1–5 nm) [117]. KCC-1-NH_2/Pd nano-catalyst found to be highly active for the reactions involving range of aryl chlorides, bromides and iodides with aryl boronic acids. The main advantages of this system are excellent yields of coupled product (80–98%), sustainable ligand-free conditions; recoverable and reusable catalyst (Table 9).

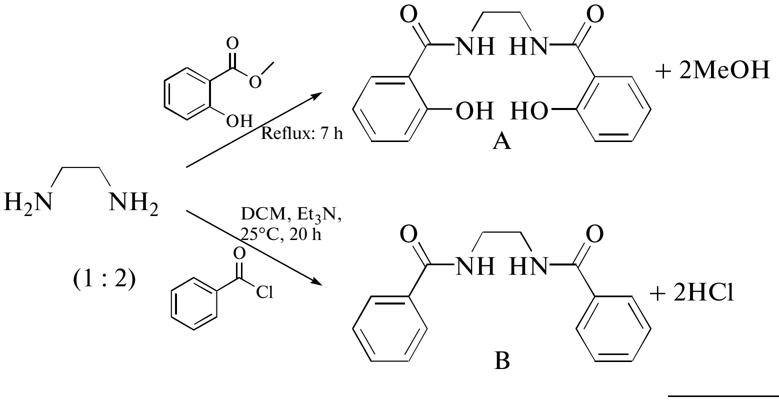
In 2013, H. Lipshutz et al. carried out coupling at conditions where *E* factor (a measure of greenness) approaches zero [118]. They revolutionize the concept by carrying out the reaction at room temperature in water using MIDA boronates (MIDA = *N*-methyliminodiacetic). They synthesized a drug name Diovan in good yield for high blood pressure using same technology. Synthesis of the biaryl core within valsartan can be represented as follows:



Valsartan (Diovan)

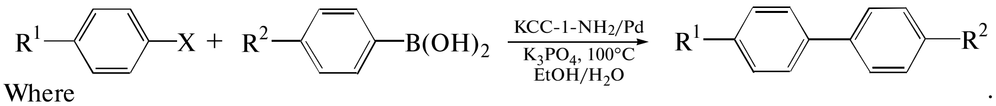
Conditions: $PdCl_2$(Dtbpf) (2 mol %). Et_3N (3 equiv.): 2 wt % TPGS-750-M/H_2O (0.5 M)

The common intermediate (biaryl) can be synthesized from 2-bromobenzonitrile and 4-tolyl MIDA boronate cross coupling at room temperature in very high yield. However, high yield with 2-chlorobenzonitrile can be obtained at 40°C. In the same year this group also tested 2-pyridyl MIDA boronate with both chloro and bromo aryl halides and found excellent results (Table 10). In the last year, M. Nobre used palladium chloride and bisamides as ligands for Suzuki cross-coupling reactions, in mild (25°C for 2 h) aerobic conditions [119]. Synthesis of symmetrical bisamides is given below:



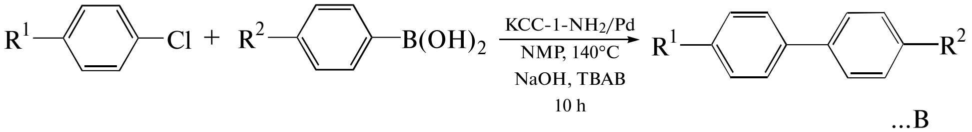
This study was efficient for arylboronic acids and/or aryl bromides with activating or deactivating substituents in the ring with high yields (81–95%). In the previous year, L. Buchwald had developed an easy method for palladium-catalyzed Suzuki–Miyaura coupling of 3-substituted allylboronates with aryl bromide that yeild allylated arenas [120]. They proposed a method (summarized in Table 11) that features excellent regioselectivity, enhanced operational simplicity, and a broad scope of aryl halides.

Table 9. Suzuki coupling reactions using the KCC-1-NH_2/Pd nano-catalyst*



...A

Where
R^1 = H, NO_2, CN, MeCO, Cl, OH
R^2 = H, OMe, etc.
X = I, Br

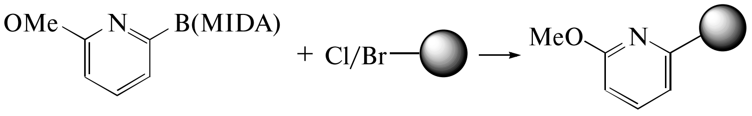


...B

Entry	R^1	R^2	Yield, %
1	MeCO	H	94
2	MeCO	MeO	95
3	CN	MeO	93
4	NO_2	MeO	91

* Reaction conditions: aryl chloride (1 equiv.), arylboronic acid (1.5 equiv.), and NaOH (3 equiv.) were heated in 5 mL *N*-methyl-2-pyrrolidone (NMP) at 140°C for 10 h in the presence of tetra-*n*-butylammonium bromide (0.1 equiv.) and KCC-1-NH_2/Pd (2.5 mol % of Pd).

Table 10. Preliminary examples using a 2-pyridyl MIDA boronate in Suzuki–Miyaura couplings in water*



(1 : 1)

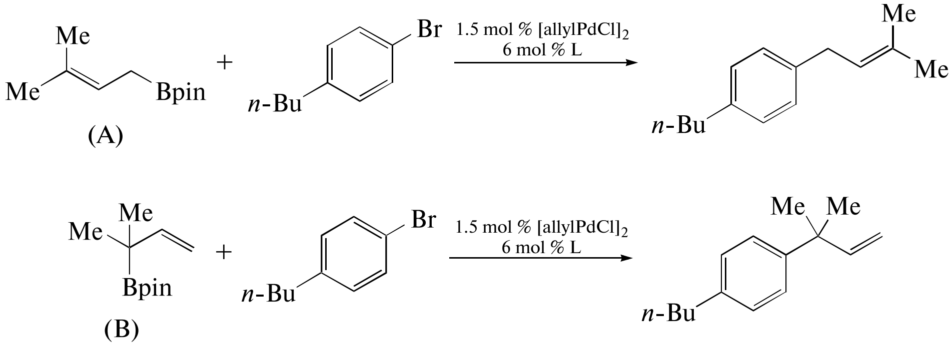
Product	Yield, %**	Product	Yield, %***
MeO–Py–Ph–OMe	87	MeO–Py–Ph–CN	84

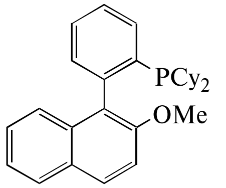
* Reaction conditions: $PdCl_2$(Dtbpf) (2 mol %), Et_3N (3 equiv.), 2 wt % TPGS-750-M/H_2O (0.5 M), 40°C, 16–24 h.

** The coupling partner was the corresponding aryl bromide.

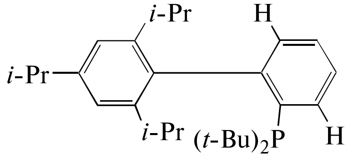
*** The coupling partner was the corresponding aryl chloride.

Table 11. A complementary set of palladium-catalyzed regiodivergent protocols for the Suzuki–Miyaura coupling of 3-substituted allylboronates





C



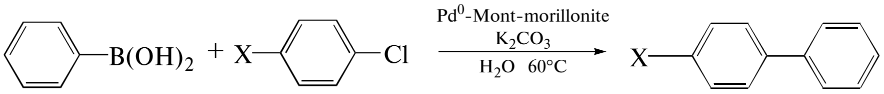
D

Entry	L	Boronate	α/γ	Yield of α, %	Yield of γ, %
1*	C	A	<1 : 99	<1	99
2*	C	B	25 : 75	20	52
3**	D	A	98 : 2	84	<1
4**	D	B	>99 : 1	92	<1

* Reaction was carried out in THF/aq K_3PO_4 at 40°C for 12 h.

** Reaction was carried out in MeCN/aq K_3PO_4 at 70°C for 12 h.

Table 12. K. Dutta's Suzuki–Miyaura cross coupling with Pd(0)-nanoparticles into the nanopores of modified montmorillonite clay as catalyst*



Entry	X	Time, h	Yield, % age	TON**	TOF***
1	H	8	82	310.6	38.8
2	H_3CO	8	85	321.9	40.2
3	NO_2	8	80	303	37.8

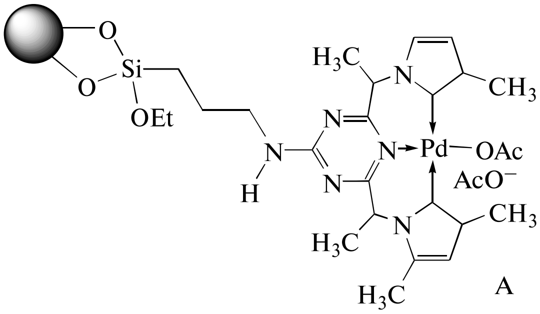
* Reaction conditions: aryl chloride (1 mmol), arylboronic acid (1.2 mmol), K_2CO_3 (3 mmol), 25 mg Pd(0)-Mont-morillonite (0.07 mol % of Pd), solvent: H_2O, $T = 60°C$.

Yields are given for isolated products; selectivity: 100%.

** Moles of product formed/moles of catalyst.

*** Moles of product formed/moles of catalyst used per hour.

Table 13. Suzuki–Miyaura cross coupling of aryl halides and $ArB(OH)_2$ in presence of catalyst nano Pd-NHC complex (A)



A

Entry	$R^1C_6H_4X$	$R^2C_6H_4B(OH)_2$	X	Conventional heating*		Microwave irradiation**	
				time, h	Y, %***	time, min	Y, %***
1	H	H	I	4	91	2	95
2	H	4-CH_3O	I	5	87	3	93
3	H	H	Br	6	82	4	88
4	H	4-CH_3O	Br	7	83	6	87
5	4-CH_3O	H	Br	6	85	7	91
6	4-CH_3O	4-CH_3O	Br	8	86	5	92
7	4-CH_3CO	H	I	5	85	2	90
8	4-CH_3CO	H	Br	10	84	7	89
9	4-CH_3CO	4-CH_3O	Br	11	89	6	90

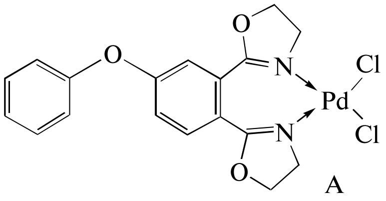
* Reactions were carried out under aerobic conditions in 2 mL of mixture of DMF and H_2O (1 : 2), 1.0 mmol arylhalide, 1.1 mmol arylboronic acid and 1.5 mmol K_2CO_3 in the presence of Pd catalyst (0.074 g, 0.002 mol % Pd). ** Applied power: 200 W, 70°C. *** Isolated yields.

Table 14. Mizoroki–Heck cross coupling of aryl halides and styrene in the presence of catalyst nano Pd-NHC complex (A)

Entry	$R^1C_6H_4X$	$R^2C_6H_4CH–CH_2$	X	Conventional heating*		Microwave irradiation**	
				time, h	Y, %	time, h	Y, %
1	H	H	I	2	90	4	96
2	H	4-CH_3	I	8	87	7	92
3	H	H	Br	7	82	4	91
4	H	4-CH_3	Br	9	81	5	87
5	4-CH_3O	4-CH_3	I	6	82	5	90
6	4-CH_3	H	Br	8	80	6	88
7	4-CH_3	4-CH_3	Br	9	81	8	87
8	4-CH_3	H	I	8	78	7	83
9	4-CH_3	4-CH_3	I	10	77	9	81
10	4-CH_3O	H	Br	7	82	5	88
11	4-CH_3O	4-CH_3	Br	8	84	6	90

* Reactions were carried out under aerobic conditions 1.0 mmol aryl halide, 1.5 mmol styrene in 2 mL of DMF and 1.5 mmol K_2CO_3 in the presence of nano Pd-NHC complex (A) (0.074 g, containing of 0.002 mol % Pd). ** Applied power: 200 W, 70°C.

Table 15. Mizoroki–Heck coupling reactions of aryl iodides with olefins catalyzed by palladium-bis(oxazoline) (Pd-BOX) complex (A)*



A

Entry	Aryl halides	Olefins	Product	Yield, %
1	O_2N–Ph–I	CH_2=CH–CO–OMe	O_2N–Ph–CH=CH–CO–OMe	97
2	H_3COC–Ph–I	CH_2=CH–CO–OMe	H_3COC–Ph–CH=CH–CO–OMe	96
3	H_2N–Ph–I	CH_2=CH–CO–OMe	H_2N–Ph–CH=CH–CO–OMe	94
4	OMe–Ph–I	CH_2=CH–CO–OMe	OMe–Ph–CH=CH–CO–OMe	94
5	Ph–I	CH_2=CH–Ph	Ph–CH=CH–Ph	92

* Reaction conditions: Pd-BOX A or B (0.0100 mmol), aryl halide (0.500 mmol), olefin (0.750 mmol), K_2CO_3 (2.00 mmol), DMF (5.0 mL), 70°C, 12 h.

Table 16. Effect of various aryl halides and arylboronic acids in Suzuki–Miyaura coupling reaction using palladium-bis(oxazoline) (Pd-BOX) complex (A)*

Entry	Aryl halides	Aryl boronic acids	Product	Yield, %
1	O_2N–Ph–I	Ph–$B(OH)_2$	O_2N–Ph–Ph	89
2	H_3COC–Ph–I	Ph–$B(OH)_2$	H_3COC–Ph–Ph	86
3	H_2N–Ph–I	Ph–$B(OH)_2$	H_2N–Ph–Ph	81
4	Ph–I	(m-Cl)$_2$Ph–$B(OH)_2$	(m-Cl)$_2$Ph–Ph	87
5	Ph–I	(p-CF_3)Ph–$B(OH)_2$	(p-CF_3)Ph–Ph	95
6	Ph–I	(p-CF_3)Ph–$B(OH)_2$	(p-CH_3)Ph–Ph	94

* Reaction conditions: Pd-BOX (0.0100 mmol), aryl halide (0.500 mmol), arylboronic acid (0.600 mmol), K_2CO_3 (2.00 mmol), DMF (5.0 mL), 70°C, 6 h.

In 2014, K. Dutta synthesized Pd(0)-nanoparticles into the nanopores of modified montmorillonite clay and found out that they are very efficient as catalysts in various organoboronic acids and aryl chloride cross coupling reactions [121]. The advantageous of this method includes 80–90% isolated yield, no ligand, 100% selectivity, water as a solvent and recyclable nanocatalysts (Table 12). There are many catalytic systems that can catalyze both Heck and Suzuki cross coupling reactions for example in the current year a novel, stable and powerful nano Pd-NHC complex (A, Table 13) utilizing N-methylimidazole bounded to 1,3,5-triazine tethered SPIONs (superparamagnetic iron oxide nanoparticles) as a bidentate NHC ligand is reported [122]. These cross coupled products were produced in excellent yields under conventional heating or microwave irradiation at extremely low palladium loading (~0.002 mol %) with perfect high turnover frequencies (TOFs) (103–106 h^{-1}). Moreover, the catalyst could be quickly and completely recovered by external magnetic field and be reused for seven reaction cycles without any change in catalytic activity (Tables 13 and 14). In the same year, B. Ali synthesized new palladium–bis(oxazoline) (Pd–BOX) complexes and evaluated their catalytic activities in Mizoroki–Heck (Table 15) and Suzuki–Miyaura (Table 16) coupling reactions [123]. The complexes showed high catalytic activities with various aryl halides, aryl boronic acids, alkenes and alkynes. The reactions were optimized for the most suitable temperature, solvent, and base system.

The immobilization of homogeneous catalysts onto polymeric inorganic or organic [124–130] support, provides the benefits of easy catalyst recovery, product separation, inhibiting the loss of metal and reusing property. Mostly the coupling reactions were accomplished using palladium catalysts containing ligands i.e., amines, dibenzylidine acetone, phosphine, carbene, etc. [49]. Substitution of phosphine ligand in palladium-catalyzed coupling reaction was achieved with nitrogen-chelating ligands that were inexpensive and stable. Polynitrogenated compounds permit functional-ligands which could make coordination with palladium [54]. Within these compounds, because of beginning material availability and flexibility to facilitate chemical amendment imidazolium types are of great interest. Until now, functional polymer comprising imidazolium groups and imidazolium ligands immobilized onto silica supports [131, 132] have been added in Pd-catalyzed coupling reactions. Imidazolium type ligands adsorbed onto silica support permit greater catalytic activity.

Moreover, literature review provides sufficient information about carbon–carbon coupling reactions catalysed through amended mesoporous (molecular sieves based) catalysts, i.e. palladium catalysts settled on S-B-A-15 type molecular sieves improved with amines donor group [133], mesoporous organo-silica consisting of a carbonpalladacycle complex [134], mesoporous molecular sieve substituted with various nitrogenous groups [135], palladium catalyst settled on silica supports [136], and Pd-nanoparticles adsorbed in sponge like porous silica [137] etc. By taking consideration about demands and applications of heterogeneous silica-based palladium catalysts, the other requirement was to establish and design active, stable, reusable and reproducible catalysts. In extension of past research on heterogeneous polymer support palladium catalysts [138] and polymers grafted silica palladium catalysts, [139, 140] the production and applications of poly (*N*-vinyl imidazole) grafted-silica palladium complex was reported. This heterogeneous palladium catalyst was efficient for both Heck and Suzuki reactions using different substrates in addition to chloro-arenes as well as reproducible and beneficial to environment. The catalyst was successfully used with a variety of aryl halides in both coupling reactions. Distinct aryl halides showed good reactivity including readily obtained chloroarenes to create the relevant products in good to excellent amount produced. XRD and TEM study of catalyst exposed small particles size in nanoscale and high metal dispersal. Coupling reactions were explained for high competence of catalyst, good dispersion into the reaction system, easy purification of product, better yield, short reactions time and air protected reactions [141].

In addition to above, literature review explores the synthesis and applications of palladium(II) supported hydro-talcites (Pd-HT) [142, 143]. Pd-HT also showed well functionality and reusability for Heck reaction between olefins and aryl halide to make carbon–carbon coupling products with optimum yield [144]. In functionalized and activated aromatics, C–H bonds will be attacked by Pd-salts, such as acetoaniline to make palladium carbon bond that afterward experiences insertion of alkene [145]. Palladium catalysis of carbon–carbon bond formation is precisely studied from the angles of nanoparticle whether these are heterogeneous or homogeneous precatalysts and are deliberately produced or preformed from a palladium derivatives, i.e. $Pd(OAc)_2$. The Heck coupling of halogenoarenes with olefins is the most studied reaction that mostly proceeds at high temperature (120–160°C). Species generated from preformed Pd-nanoparticles can also catalyze Suzuki coupling reaction. Leaching of active palladium atoms from the Pd-nanoparticles for catalysis of these reactions, may also supply a practicable molecular mechanistic plan of action. Thus, Pd-nanoparticles acts as precursor of catalytically active palladium specie, i.e. the Pd-nanoparticles are precatalysts of carbon–carbon coupling reactions [58].

Thus, this review reveals that research interest in palladium catalysis has increased within short time. Electron donating ligands such as carbenes, phosphines and nitrogen donor ligands can increase the activity, selectivity and stability of its catalysts. Palladium nanoparticles and palladacycle can also act as precatalysts for Heck and Suzuki coupling reactions. Both homogenous and heterogeneous catalytic systems approach were used for coupling reactions. The technological hurdles in using homogeneous catalysts have undoubtedly been minimized by putting the catalyst on a polymer support.

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