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Review

Functionalized nitrogen ligands (C—N) for palladium catalyzed cross-coupling reactions (part II)

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ABSTRACT

In recent years, considerable effort has been focused in Pd catalyzed cross-coupling reactions, especially the use of less reactive and economically viable substrates like aryl chlorides. Unfortunately, Pd complexes containing the ligands having only N as a donor atom has some limitations, as it couples, mostly aryl iodides and bromides with different nucleophiles, and shows less activity towards aryl chlorides. This restriction can overwhelm by the use of Pd complexes containing N in combination with the C as a donor atom such as palladacycles, pincers, PEPPSI and carbene ligands. The advantages of these ligands include high activity with enhanced selectivity, less toxicity, moisture, air as well as thermal stability. Most importantly, such complexes have broad applications in catalysis under ambient conditions. This part of compressive review highlights the results of the highly active C—N based Pd complexes and their applications in cross-coupling reactions. In the next part, we will cover all ligands and complexes containing N in combination with P, O and S as a donor atoms (Pd catalysts based on C—P, C—O and C—S ligands). Though, the number of C—N based Pd complexes containing Ferrocene and Buchwald ligands were reported for Pd catalyzed cross-coupling reaction, these complexes will be covered in the next part of the article.

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1. Introduction

The constant discovery of ligands for Pd catalysts in the area of cross coupling reactions has been focused by the advancement of novel ligands and complexes with improved activity and selectivity, which stimulate the use of less reactive aryl chlorides. Unfortunately, Pd complexes containing the ligand having only N as a donor atom has some limitations, as it couples, mostly aryl iodides and bromides with different nucleophiles, and shows less activity about aryl chlorides [1]. This restriction can overwhelm by the use of Pd complexes containing N in combination with C as a donor atom that includes palladacycles, pincers, PEPPSI and carbene complexes. The advantage of these complexes includes high activity with enhanced selectivity, and less toxicity. They are moisture, air and thermally stable. Most importantly, such complexes have broad applications in catalysis under ambient conditions.

In this perspective, this review focus on the Pd complexes with ligands containing C and N atoms, and their applications in catalysis, especially in cross-coupling reactions (Fig. 1).

2. Pd complexes having a ligands containing N and C atoms

The traditional Pd catalysts such as $Pd(PPh_3)_4$, $Pd_2(dba)_3$, $PdCl_2(PPh_3)_2$, $(\eta3\text{-allyl-PdCl})_2$, $PdCl_2(RCN)_2$ used for many cross-coupling reactions has its own drawbacks and limitations, like they are air and moisture sensitive, require higher Pd loading. Now a day 'Palladacycle, Pincer, N-Heterocyclic Carbene (NHC) and PEPPSI architectures' have become popular alternatives for traditional catalysts (Fig. 2). Hence, these complexes are thoroughly investigated class of organopalladium compounds in metal catalysis [2]. These catalysts have been emerging as a favorable option for traditional catalysts, as they are more stable towards the air and moisture as well as easy to handle.

3. Palladacycles

'Palladacycles are cyclic palladium complexes incorporating at least one C–Pd bond in their molecular architecture'. The Pd–C bond in most of the palladacycles is reactive towards a range of nucleophiles and electrophiles. Many of the palladacycles can be easily preparable, recoverable and recyclable. Since, the 1960s, numerous common palladacycles have been reported for many applications possessing anionic four-electron (bidentate) or six-electron (tridentate) donor ligands, with five-membered N containing rings [3]. Most importantly, it is possible to regulate the electronic and steric properties of palladacycles solely by following ways;

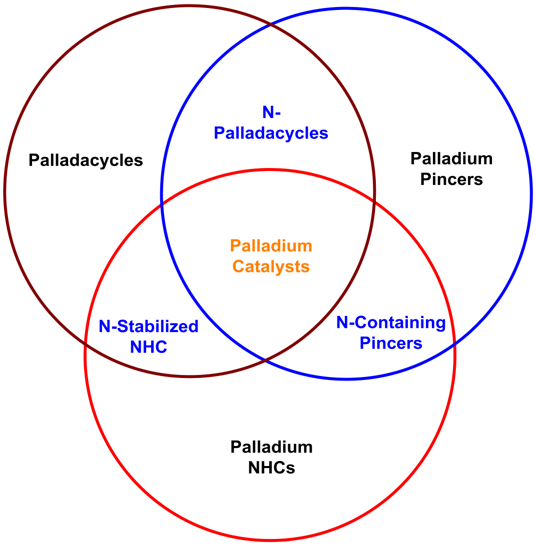


Fig. 1. The main area of this review.

(1) Changing the size of the metallacyclic rings (5–7).
(2) The nature of the metalled carbon atoms (aliphatic, aromatic, vinylic).
(3) The type of the donor group having N, P, S, O atoms as well as its substituents (alkyl, aryl) and
(4) The nature of ancillary ligands (halide, triflate, acetate, phosphine, nitrile or solvent).

The palladacycle works in two different ways; firstly the Pd–C bond remains intact in reaction sequence, *i.e.* cyclopalladated unit is used as an ancillary ligand, and secondly the palladated carbon atom can be functionalized by various groups. The application of palladacycles as reagents as well as catalysts for different reactions is recently reviewed by Beletskaya and Cheprakov [4a], Pfeffer [4b] and Dupont [4c]. The palladacycles are prepared by a number of methods such as C–H activation, oxidative addition, transmetallation, or nucleophilic addition onto an unsaturated bond which often organize a five or six membered chalets due to the establishment of a stable Pd–C bond and helped with the coordination of the two-electron donor group. The first use of palladacycle as a precatalyst is reported in the mid-1980s [5]. In 1995 Herrmann et al. [6] applied palladacycle for C–C coupling reaction, hence called 'Herrmann-Beller palladacycle'. Recently, there are many outstanding reports which addressed the importance of palladacycles for different cross coupling reactions. Consequently, most of studies showed that the mechanism of palladacycle involves Pd(0)/Pd(II) oxidation states [7]. Though the precise mechanism is yet changeable, there are many groups suggested the involvement of Pd(II)/Pd(IV) oxidation states [8]. The C–N palladacycle serves as a mere packaging for palladium that may call 'disposable wrapper' [4a].

Herein, we wish to report applications of C–N palladacycles as a precatalyst in various cross-coupling reactions. For simplification, we grouped these palladacycles into three groups.

3.1. Imine palladacycles

The imine palladacycles have been reported as highly stabile catalysts for many cross-coupling reactions. Additionally, these complexes can be easily modified to incorporate different functionalities, which will allow them to immobilize it on suitable supports so that the catalyst becomes easily recoverable and recyclable. These palladacycles are prepared by the complexation of Pd precursors with imine that are obtained from the corresponding aromatic aldehydes/ketones.

Milstein and coworkers [9a] reported thermally stable and recoverable dimeric cyclopalladated imine palladacycles (**C1a** and **C2a-b**) for the Heck arylation reaction (Scheme 1). The complexes were prepared by treatment of $Pd(OTf)_2$ or $Pd(OAc)_2$ with the corresponding imines in THF. All the catalysts ($0.35–0.70 \times 10^{-5}$ mmol) recorded excellent catalytic activity for the Heck coupling of different aryl halides (I and Br) and different olefins with TON 3000–1429000 in NMP using Na_2CO_3 or Et_3N as a base at 140 °C. The palladacycle **C1a** was also active towards the Suzuki coupling reaction of non-activated aryl bromides with TONs up to 10^5 using K_2CO_3 as a base in *o*-xylene at 130 °C [9b]. To get insight into the reaction mechanism, they carried out a competitive reaction with the five aryl bromides under pseudo-first order conditions.

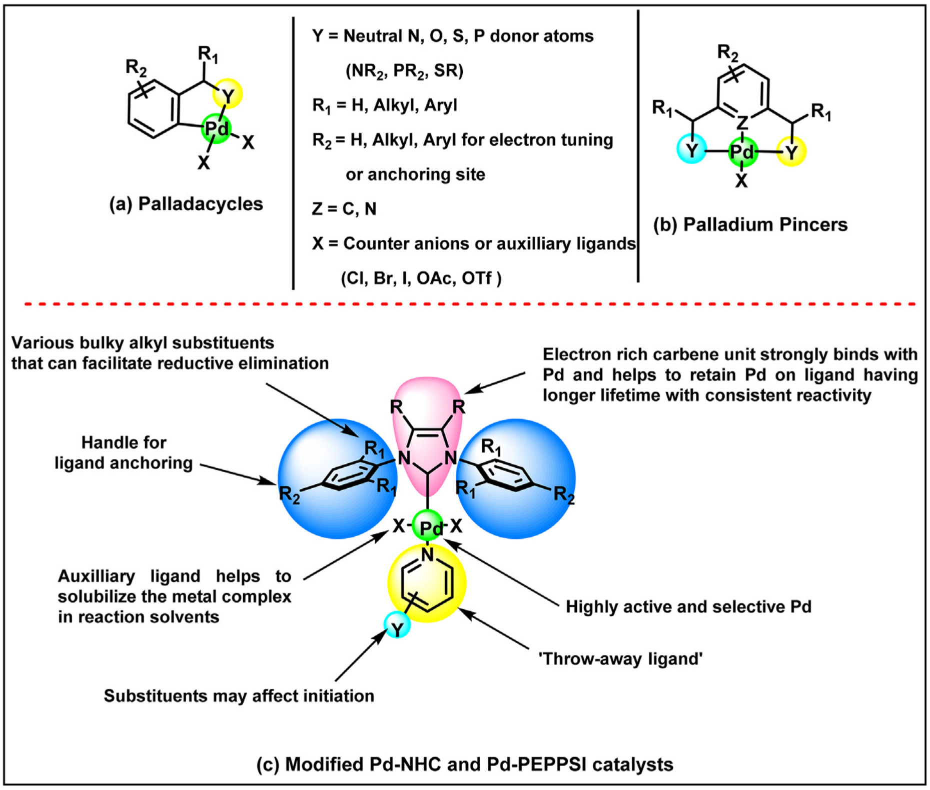


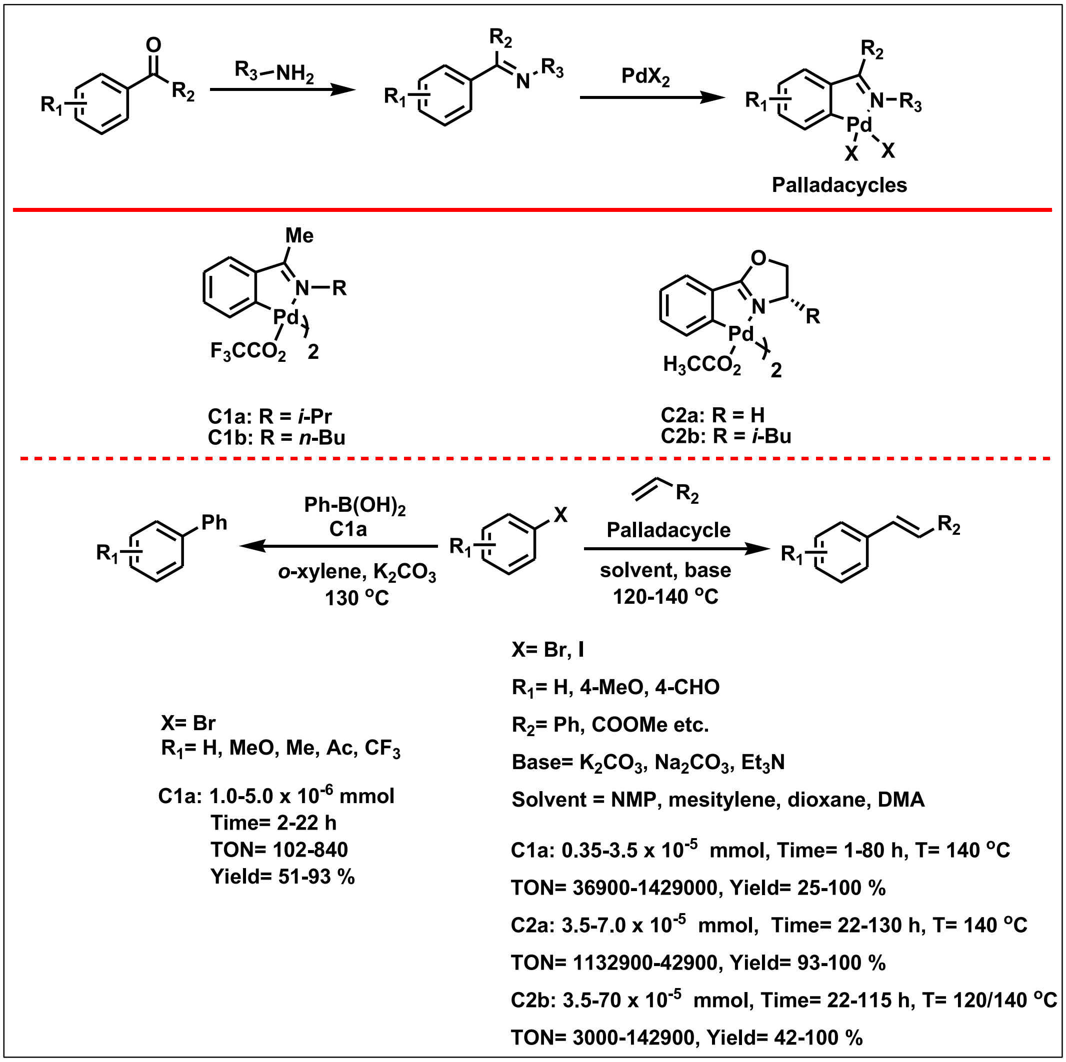
Fig. 2. Schematic representation of (a) Palladacycle, (b) Pincer, (c) Modified Pd–NHC and PEPPSI architectures.

A Milstein type homogeneous palladacycles **C1b** and **C3a-b** as well as palladacycle immobilized on polystyrene **C3c** (Scheme 2) was reported by Nowotny et al. [10]. The palladacycle **C3c** was prepared from amino methyl functionalized polystyrene beads with loading of 0.544 $\mathrm{mmol\,g^{-1}}$ as determined by XRF analysis. These cyclopalladated imines showed high TON ($>10^6$) for the Heck coupling of iodobenzene and styrene in the presence of n-$\mathrm{Pr_3N}$ in NMP at 100/140 °C. It was assumed that the n-$\mathrm{Pr_3NH^+I^-}$ formed in the catalytic cycle stabilize the PdNPs.

Song et al. [11] used cyclopalladated complexes of 2-(*m*-nitrophenyl)imidazolines (**C4a-c**) for the Suzuki coupling reaction of aryl bromides and phenylboronic acid in aqueous solution at room temperature under air (Scheme 3). The catalysts were prepared by cyclopalladation of the corresponding ligands using $\mathrm{Pd(OAc)_2}$ in refluxing acetic acid followed by the addition of LiCl to give the chloride-bridged palladacyclic dimers. This dimer on a bridge-splitting reaction with triphenylphosphine afford the monomeric palladacycles **C4a-c**. It was observed that the palladacycle **C4c** (0.5 mol %) was more active for the Suzuki coupling reaction of 3-methyl bromobenzene and phenylboronic acid in the presence of $\mathrm{K_2CO_3}$ and TBAB in $\mathrm{EtOH{:}H_2O}$ (1:1) mixture at room temperature under air.

The pioneer studies on *ortho* metallated N-donor ligands for the Suzuki coupling reaction was carried out by Bedford's group [12]. They reported a series of homogeneous (**C5a-c** and **C6a-g**) as well as heterogeneous (**C7a-b**) adducts of Pd complexes with *ortho*-metallated N-donor ligands for the Suzuki coupling reaction of aryl chlorides under aerobic conditions (Scheme 4). For comparison, they also synthesized complex **C5c** from the palladated imine complex **C5b**. They analyzed the function of the phosphine and the anionic ligands (X) in terms of both activity and lifetime of the palladacycle. Of all the catalysts, the palladacycle **C6a** (0.1–0.01 mol %) showed excellent catalytic activity for the Suzuki coupling reaction of a range of aryl chlorides using $\mathrm{Cs_2CO_3}$ as a base at 100 °C with 96–100% yield and 1000–99000 TON in dioxane. They immobilized monomeric as well as dimeric palladacycles derived from 2-bromobenzaldehyde and 3-aminopropyltriethoxysilane on mesoporous silica (**C7a** and **C7b**). The heterogeneous catalysts showed considerable lower activity and poor recyclability. The palladacycles **C5c** and **C6a-g** were highly active for amination reactions of aryl chlorides, using morpholine in the presence of NaO*t*-Bu as a base in toluene at 110 °C. They explained the high activity of these palladacycles as compared with classical precursors like $\mathrm{Pd(OAc)_2}$ and $\mathrm{[Pd_2(dba)_3]}$ on the concept of 'sacrificial role' of *ortho*-palladated amine and imine complexes in the activation of the catalysts (Scheme 4). The monophosphine Pd(0) species may be formed by the reaction of **C5c**/**C6a** with aryl boronic acids. The process involves (a) nucleophilic attack of the aryl boronic acid at the Pd center, (b) rearrangement, and then (c) reductive elimination to form *ortho* aryl N,N-dimethylbenzylamine, which undergo hydrolysis to form aldehyde in the case of **C5c**.

Liu et al. [13a,b] applied various palladacycles **C8a-f** (a six-membered chelating ring) and **C8g-h** (five-membered chelating ring) for the Suzuki coupling of aryl halides with arylboronic acids in aqueous medium under aerobic conditions (Scheme 5). The palladacycles **C8a-f** were prepared from the condensation of 2,4,6-trimethylbenzaldehyde and 2,6-diisopropylaniline followed by metallation with $\mathrm{PdCl_2(CH_3CN)_2}$ and ligand exchange reaction. While, the phosphine substituted palladacycle **C8g** was prepared from **C8h** and $\mathrm{PCy_3}$. The palladacycles **C8a** and **C8b** were found to be highly active in coupling 4-bromoacetophenone with phenylboronic acid using $\mathrm{Cs_2CO_3}$ as a base in dioxane at 100 °C. In

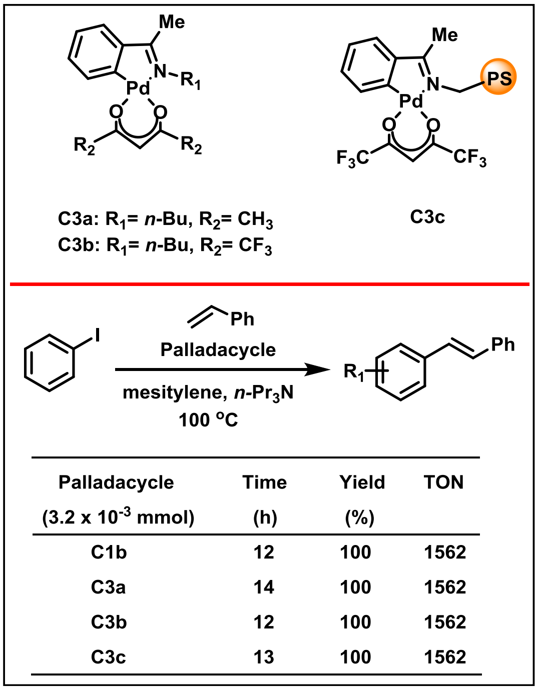


Scheme 1. Imine palladacycles used for the Heck and Suzuki coupling reactions.

addition, the **C8a** exhibited good activity in coupling 4-chloroacetophenone or 4-nitrochlorobenzene with phenyl boronic acid using Cs_2CO_3 as a base in water at reflux but require TBAB. The actual catalytic species are *in situ* generated PdNPs as analyzed by TEM analysis. They also showed that complex **C8b** readily reacts with ethanol in the presence of base and generate acetaldehyde (due to the substitution of chloride by ethoxide under basic conditions followed by β-elimination), the free imine ligand and PdNPs [13c].

To exploit the diverse function and role of imidate anionic ligands, Serrano et al. [14] synthesized and characterized the binuclear *ortho*-metallated Pd(II) complexes (**C9a-g** and **C10a-k**) possessing a N-phenylbenzaldimine backbone [15] with different bridging imidate ligands. The role and performance of imidate ligands were assessed in the Suzuki coupling reaction of aryl and benzyl bromides. The mononuclear complexes have a greater activity than their parent dinuclear complexes for the coupling benzyl bromide with arylboronic acids (Scheme 6). The catalysts **C10a** and **C10k** (1 mol %) were used as efficient precatalysts for the Suzuki coupling reactions of different electron deficient and electron rich arylboronic acids with benzyl bromide in THF using Na_2CO_3 as a base at 60 °C. The mechanism for catalysis was similar to proposed by Bedford et al. [12] and supported by GC-MS analysis.

As homogeneous Pd catalysts have a higher activity towards most of the coupling reactions, the difficulties in separation and recovery of the catalyst and contamination of the products with traces of the Pd metal are the main problems, which restrict its use in the synthesis of important pharmaceutical compounds. These problems can circumvent by supporting the Pd on a suitable support. One of these strategies involves the use of fluorous tagged Pd catalysts. The fluorous biphasic catalysis allow easy separation and recycling of catalysts due to its temperature dependent miscibility in organic as well as fluorous solvents. In this regard, Rocaboy and Gladysz [16] reported thermophilic fluorous palladacycles (**C11a-b**) for the Heck coupling reaction (Scheme 7). The dimeric cyclopalladated Schiff base catalysts tagged with three florous substituents R_{f8} ($R_{f8} = n\text{-}C_8F_{17}$, pony tails) were prepared from *p*-iodo benzaldehyde. Both the palladacycles were acting as extremely effective catalysts for the Heck coupling reaction in DMF with TON $>10^6$ at 80–140 °C. Though the catalyst recycling is possible (4 times) it gradually loses its activity due to the limited stability of the catalyst. This was anticipated on the basis that palladacycle works as only the reservoir of soluble colloidal PdNPs (10 nm). The catalyst **C11a** ($0.091–0.482 \times 10^{-3}$ mmol) was also applied to the Suzuki



Palladacycle (3.2×10^{-3} mmol)	Time (h)	Yield (%)	TON
C1b	12	100	1562
C3a	14	100	1562
C3b	12	100	1562
C3c	13	100	1562

Scheme 2. Homogeneous and heterogeneous imine palladacycles used in the Heck coupling reaction.

coupling reaction using K_3PO_4 as a base in toluene at 130 °C.

Wu et al. [17] synthesized and characterized cyclopalladated arylimine compounds (**C12a-c** and **C13a-c**) and applied for the Heck and Suzuki coupling reactions in water as homogeneous catalysts (Scheme 8). They also prepared organized monolayered catalysts **C14a–c** by Langmuir–Blodgett techniques and analyzed using π–A isotherms, UV–visible, XPS and AFM techniques. The activity of heterogeneous catalysts was relatively high with TON = 79–200 and TOF = 2640 h^{-1} due to a combination of its structure and change in conformation when deposited onto the substrate.

A neutral C,N palladacyclic complexes (**C15a-h**) (0.01 mol %) were also acts as highly efficient precatalysts for the Heck coupling reaction between bromobenzene and styrene under aerobic conditions using K_2CO_3 as a base in EGME:H_2O (EGME = ethylene glycol monomethyl ether) showing TOF of 10000 h^{-1} (Scheme 9) [18].

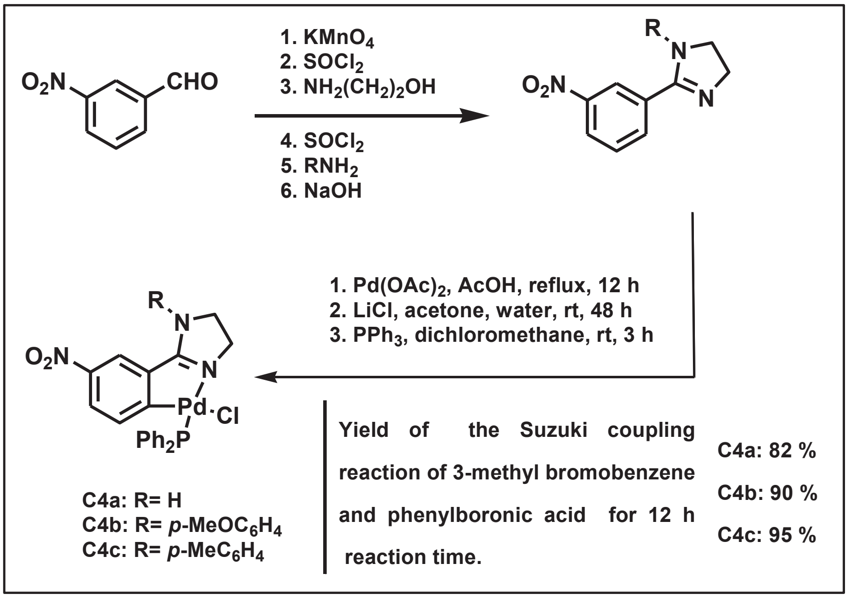
The diinuclear iminoisoindoline palladacycles (**C16a-d**) (Fig. 3) obtained from *para*-substituted iminoisoindoline and $Pd(OAc)_2$ in CH_2Cl_2 also examined in the Suzuki and Heck coupling reactions [19a]. The complexes can exist in *anti* or *cis* form and contains two Pd centers bridged with each other by acetato groups. Of all the complexes, palladacycles **C16b** and **C16c** showed good to excellent catalytic activities for the Suzuki (dioxane, Cs_2CO_3, 80 °C) and Heck (DMA, Cs_2CO_3, 140 °C) coupling reactions. They also synthesized palladacycles (**C17a-b**) obtained from γ-diimine ligands and applied for the Heck and Suzuki coupling reactions under similar reaction conditions [19b].

Thirupathi et al. [20] synthesized a series of cyclopalladated N,N′,N″-triarylguanidines (**C19a-e**) by the reaction of six membered cyclopalladated N,N′,N″-triarylguanidines (**C18a-g**) and pyrazole/3,5-dimethylpyrazole in CH_2Cl_2 (Scheme 10). Screening of all the palladacycles for the Suzuki coupling reaction of 4-bromotoluene and phenylboronic acid showed that **C19a**, **C19c**, and **C19g** were found to be highly efficient using K_2CO_3 as a base in DMF:H_2O (1:1) at 100 °C.

Bhaumik and coworkers carried out Suzuki coupling using *ortho*-metallated Pd (II) complex anchored on 2D-hexagonal mesoporous organosilica [21a], while cyclopalladium(II) complex supported on reduced graphene oxide acts as an excellent catalyst for the Suzuki reaction at room temperature [21b].

3.2. Oxime palladacycles

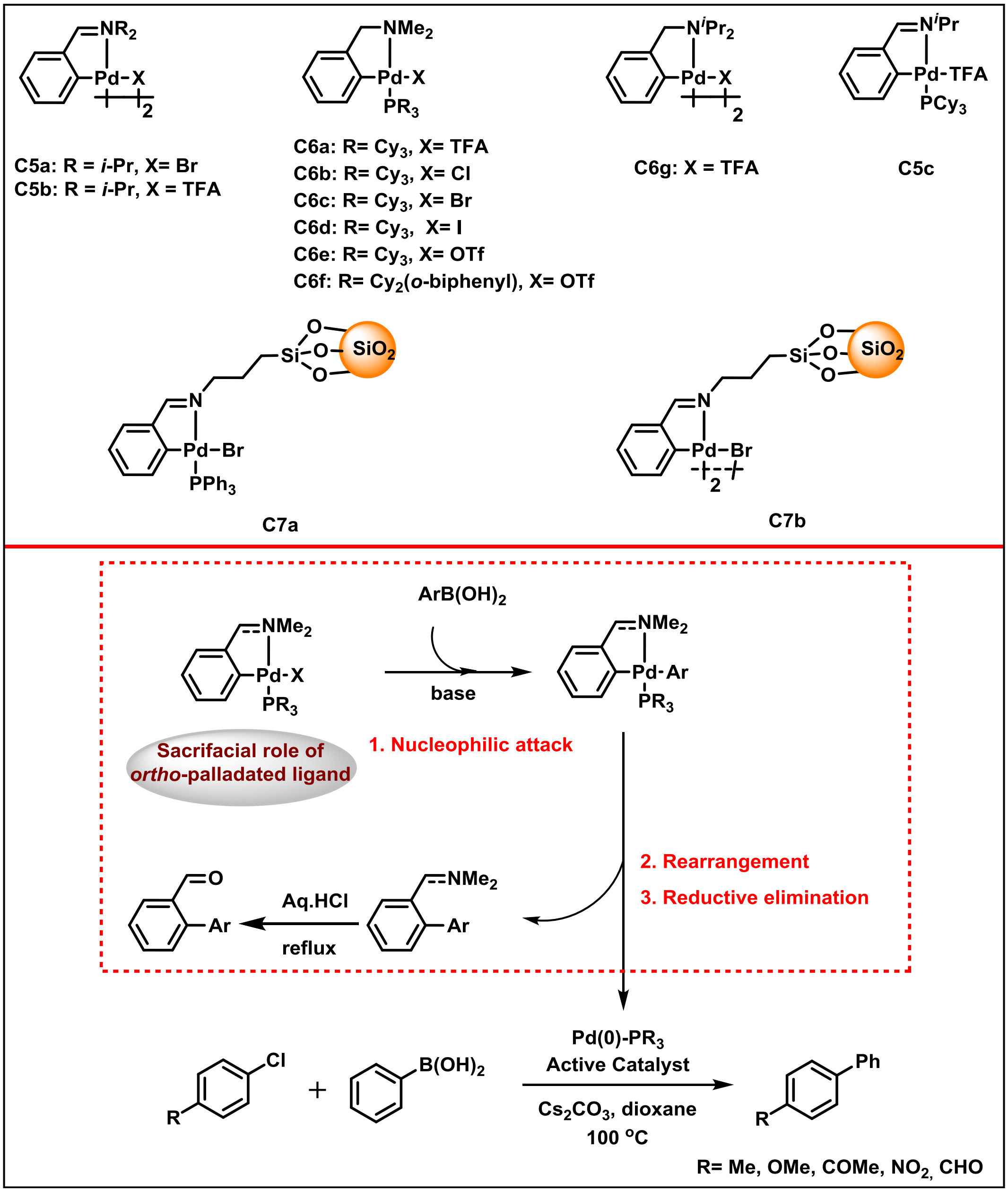
The oxime-derived palladacycles are especially important palladacycles obtained from a large variety of ketones and hydroxylamine. The attractive features of these palladacycles are that the ligand properties can either be tuned sterically or electronically by using various substituted ketones [22]. In addition, the aromatic ketoxime derived palladacycles are extraordinarily stable to heat, oxygen and moisture. Most of these palladacycles are obtained



Yield of the Suzuki coupling reaction of 3-methyl bromobenzene and phenylboronic acid for 12 h reaction time.

C4a: 82 %
C4b: 90 %
C4c: 95 %

Scheme 3. Cyclopalladated complexes of 2-(*m*-nitrophenyl)imidazoline used in the Suzuki coupling reaction.

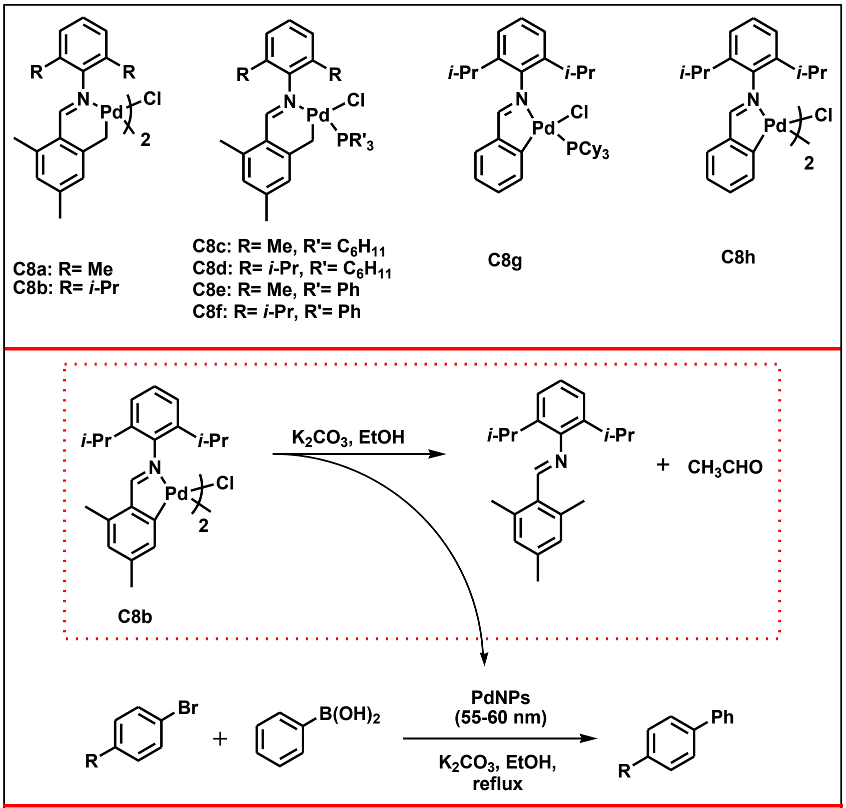


Scheme 4. Sacrificial role of *ortho* palladated N-donor ligands in the Suzuki coupling reaction.

from complexing the oximes by Li_2PdCl_4 in presence of NaOAc as a base in methanol.

Most of the oxime palladacycles (**C20a-i**) was reported by Najera and coworkers for a range of C–C cross coupling reactions (Scheme 11) [23a].

In their first report, they synthesized five oxime palladacycles (**C20a-d** and **C20h**) by carbopalladation of different ketoximes derived from acetophenone, benzophenone, 4,4′-dichlorobenzophenone, 4,4′-dimethoxybenzophenone, and fluorenone with Li_2PdCl_4 in good to excellent yields. These palladacycles were successfully used as precatalysts in various reactions such as Heck, Suzuki, Sonogashira, Stille, and Ullmann coupling reactions. The fluorenone derived palladacycle (**20h**) was comparably more active in terms of temperatures and reaction times for the Heck and Suzuki coupling reactions [23b]. The chloro bridged palladacycles (**C20a-d**, **C20i**) were also applied for the Heck coupling of phenyl iodide and methyl acrylate using TEA as a base, in DMF at 110 °C. The **C20b** further catalyzed the coupling of various aryl halides with methyl acrylate under different reaction conditions, and exhibited highest yield (>99%), TON (10000) and TOF (6667 h^{-1}) for the iodobenzene in Et_3N and DMF at 110 °C [23c]. As an extension the palladacycle **C20e** catalyzed mono and double Heck coupling reactions in water [23d]. By proper choice of the reaction conditions the dimeric 4-hydroxyacetophenone oxime derived palladacycle (**C20e**) gave cinnamaldehyde derivatives or 3-arylpropanoate esters by the chemoselective Heck arylation of acrolein diethyl acetal with iodo, bromo or chloroarenes using K_2CO_3 and TBAA as well as KCl in DMA at 120 °C followed by acid workup [23e]. The phenone



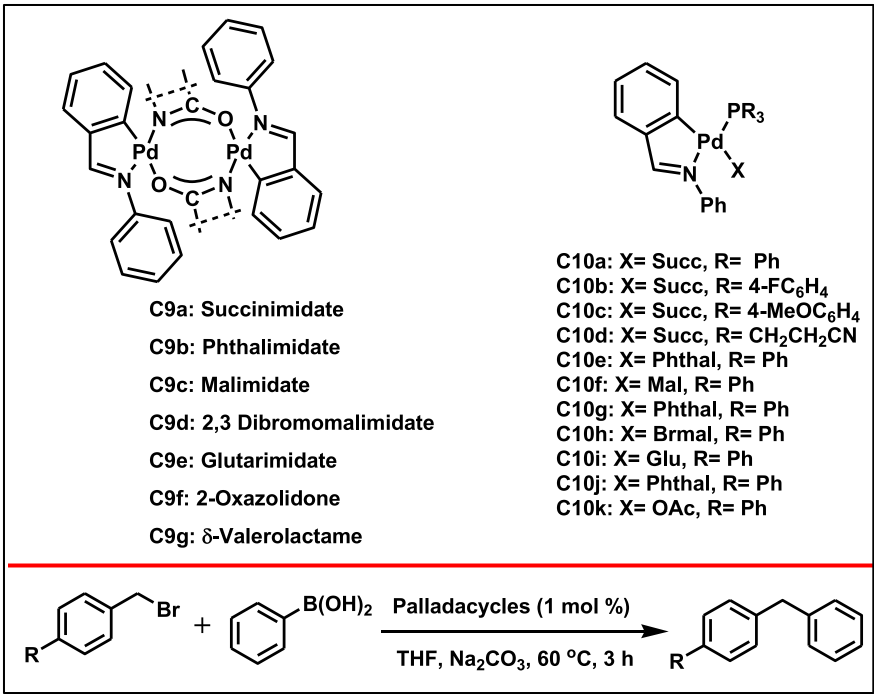
For R= OMe

Palladacycle (mmol)	Time (h)	Yield (%)	TOF
C8a (2 x 10^{-6}- 2 x 10^{-3})	3-20	62-100	20000-1000000
C8b (2 x 10^{-6}- 2 x 10^{-3})	3-20	28-100	20000-1000000
C8c (1 x 10^{-4})	3	100	20000
C8d (1 x 10^{-4})	3	92	20000
C8e (1 x 10^{-4})	3	85	20000
C8f (1 x 10^{-4})	3	95	20000
C8g (2 x 10^{-6}- 1 x 10^{-4})	3-16	26-86	20000-100000
C8h (1 x 10^{-4})	3	83	2000

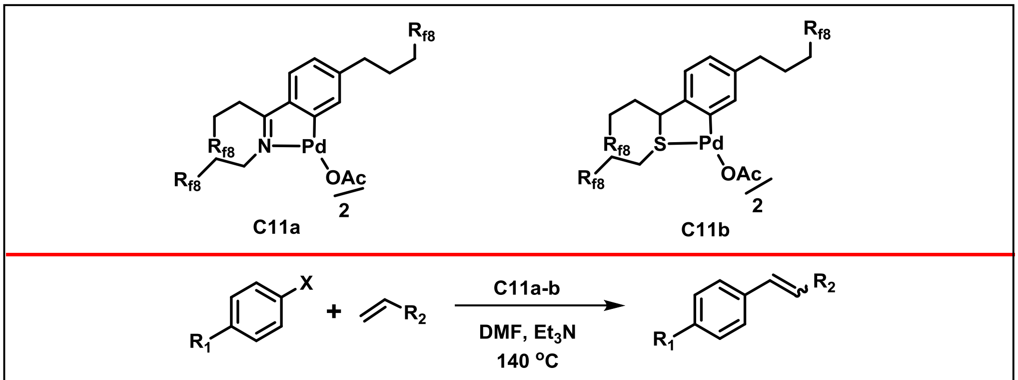
Scheme 5. Suzuki coupling reaction using palladacycles containing oxazoline group.

oxime palladacycles (**C20d-f**) were acting as good precatalysts for the Suzuki coupling reaction of aromatic and heteroaromatic bromides as well as chlorides with arylboronic acids in water at reflux [23f-g]. The reaction conditions were optimized for all catalysts under three different methods (Method A: K_2CO_3, water, reflux. Method B: K_2CO_3, TBAB (4 mmol), water, reflux. Method C: KOH, methanol:water (3:1), rt. Method D: KOH, TBAB (2 mmol), methanol:water (3:1), rt). Out of all palladacycles, **C20d** was acts as a very effective catalyst under all four methods and the presence of TBAB was crucial to enhance the rate of the coupling in case of chloro compounds. Palladacycle **C20e** showed high activity for the coupling of different aromatic and heteroaromatic bromides with phenyl boronic acid under both methods A and B with TON = 870–92000 and TOF = 58-70400 h^{-1}. Various aryl chlorides were also given good yields under both the method C and D. In addition, palladacycle **C20e** also showed good conversion for the Csp^2-Csp^3 coupling of trimethylboroxine (TMB) and butylboronic acid with aryl bromides, or chlorides in refluxing water and K_2CO_3 as a base and TBAB. Benzylic and allylic chlorides or acetates also reacted with arylboronic acids in acetone:water mixture at room temperature in the presence of **C20e**, KOH as a base and TBAB as an additive.

The palladacycle **C20b** also able to couple allyl and benzyl chlorides with phenylboronic acid in DMF:H_2O(95:5) mixture, in the presence of K_2CO_3 and TBAB at 130 °C with ~98% yield in 1–3 h. Different aryl iodides also undergo Ullmann coupling using **C20b** (0.5–2.0 mol %) in the presence of hydroquinone (50 mol %) as an additive at 100 °C in 5–7 h [23h]. They applied **C20b** for the Sonogashira coupling using TBOAc at 100 °C in NMP [23i] and for the synthesis of ynones by acylation of terminal alkynes with acid



Scheme 6. Dinuclear *ortho*-palladated complexes used in the Suzuki coupling reaction.

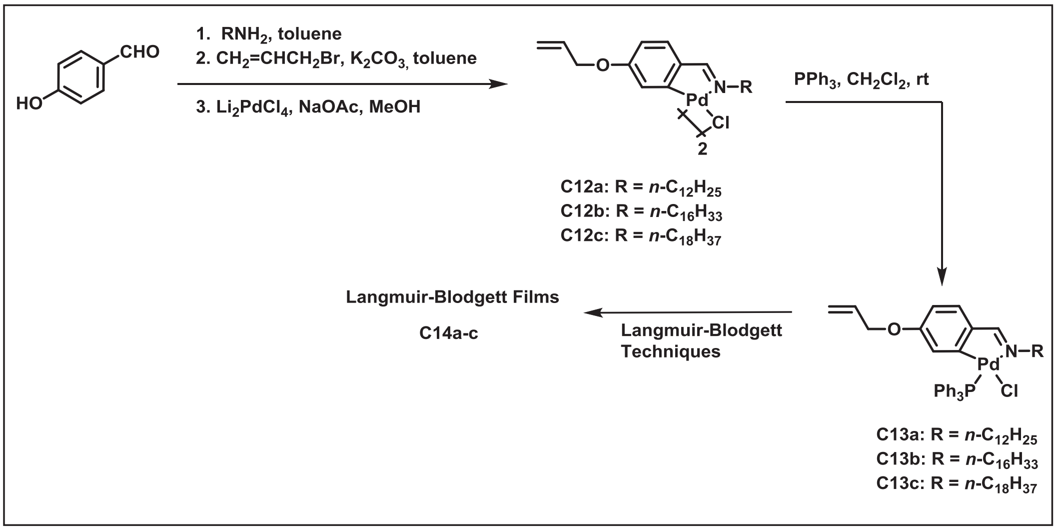


Palladacycle (mmol)	X	R_1	R_2	Time (h)	Conversion (%)	Yield (%)	TON
C11a (0.344×10^{-5})	I	C	COOMe	14	100	100	1460000
C11a (0.344×10^{-5})	I	H	Ph	24	94	88	1270000
C11a (0.917×10^{-4})	Br	COMe	COOMe	48	77	49	266000
C11b (0.415×10^{-5})	I	I	COOMe	18	100	100	1510000
C11b (0.415×10^{-5})	I	I	Ph	48	100	100	1510000
C11b (0.831×10^{-4})	Br	Br	COOMe	48	66	50	301000

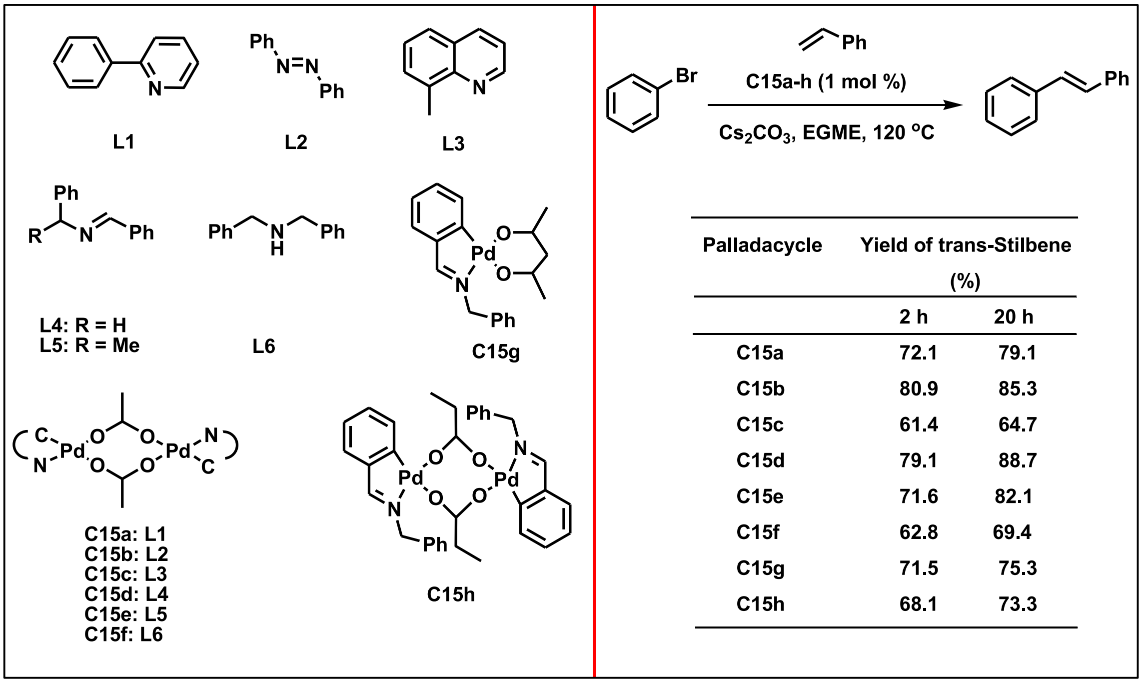
Scheme 7. Fluorous tagged palladacycles used in the Heck coupling reaction.

chlorides [23j].

Garcia and coworkers [24a] covalently anchored palladacycle **C20e** onto high surface mercaptopropyl modified silica (**C21a**) and applied to the Suzuki coupling reaction in water (Fig. 4). They showed that it is possible to perform the Suzuki coupling reaction in aqueous medium, and the catalyst could be recycled eight times without Pd leaching. The presence of TBAB has negative influence on the activity of catalysts, and one of the possible explanations is that the Pd atom could exchange Cl^- by Br^- and the higher donor ability of Br^- increases the softness of the active metal atom. The



Scheme 8. Langmuir–Blodgett films containing organized monolayered catalysts used for the Heck and Suzuki coupling reactions.



Palladacycle	Yield of trans-Stilbene (%)	
	2 h	20 h
C15a	72.1	79.1
C15b	80.9	85.3
C15c	61.4	64.7
C15d	79.1	88.7
C15e	71.6	82.1
C15f	62.8	69.4
C15g	71.5	75.3
C15h	68.1	73.3

Scheme 9. C,N-palladacycles used in the Heck coupling reaction.

catalyst gave the extensive homocoupling product in water:-dioxane mixture, while water play beneficial role in terms of the yield of desired coupling product and reaction time (>99% in <1 h) for coupling 4-bromoacetophenone and phenyl boronic acid using K_2CO_3 as a base at 100 °C. The catalyst also works best for coupling 4-chloroacetophenone giving >99% yield in 2 h, and could be recycled eight times. In 2004, they [24b] reported the similar catalyst anchored on MCM-41 (**C21b**), polystyrene-divinylbenzene (**C21c**) and ethylenglycol dimethylacrylate polymers (**C21d**) for the Suzuki coupling reaction in water, dioxane, and water:dioxane mixture for the wide range of bromo, chloro and even fluoroaromatics. They found that the catalytic activity depends on the nature of the support used and the Pd complexes supported on silica are being more active in water for coupling 4-chloroacetophenone with phenylboronic acid in the presence of K_2CO_3 at 100 °C. All the catalysts could be recycled many times. They compared the stability and activity of carbopalladacycle complex of 4-hydroxyacetophenone oxime in PEG and imidazolium ILs for the Suzuki and Sonogashira coupling reactions [24c]. It was found that the palladacycle decomposes easily in water as well as [BMIM]PF$_6$ to form PdNPs, while in [BMIM]Cl it forms $PdCl_4^-$. Though, the complex was stable in [BMIM]PF$_6$ as well as in PEG under heating, it showed higher activity in PEG, as the complex decomposes into the PEG to form PdNPs (2–5 nm size) which are

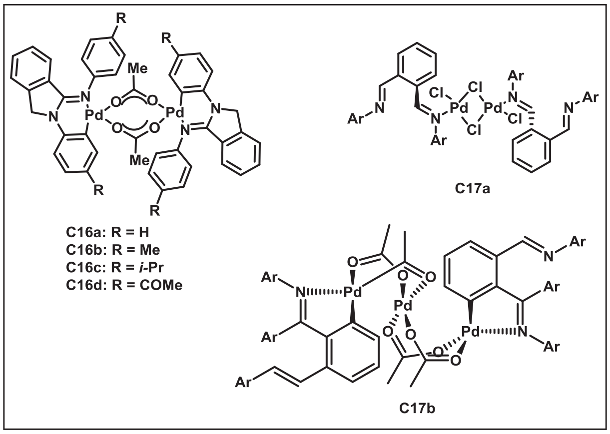


Fig. 3. Dinuclear iminoisoindoline palladacycles used in the Suzuki and Heck coupling reactions.

stabilized by PEG.

Recently, Najera et al. [24d] they supported oxime-derived palladacycle on clay OxPdCy@clay (**C21e**) that promoted the copper and phosphine free Sonogashira reaction of aryl halides (I, Br and Cl) with terminal alkynes in PEG-200 at 85 °C or 130 °C using 0.05–0.1 mol % of Pd. This catalyst showed a higher catalytic activity than dimeric oxime-palladacycles and could be recycled at least nine times with small decrease in activity.

A light fluorous, oxime-based palladacycle **C22** successfully coupled various substrates under Suzuki, Sonogashira and Stille coupling reactions in aqueous medium (Fig. 4) [25a]. The catalyst likewise applied for the Suzuki, Sonogashira, Stille, Heck and Kumada coupling reactions under MW irradiation [25b]. Palladacycle **C22** was prepared from the complexation of the corresponding fluorous oxime with Li_2PdCl_4 in the presence of NaOAc in acetone at reflux. The catalyst could be easily recycled five times for the Suzuki coupling reaction without significant loss in activity and Pd leaching.

3.3. *Amine palladacycles*

Beletskaya et al. [26] reported cyclopalladated complexes of general formula $[Pd_2(m\text{-}L)_2(NC)_2]$ and a six-membered palladacycles with C–O coordination (**C23a-o**) for the Heck arylation of olefins (styrene/ethyl acrylate) with different aryl halides (I and Br). The **C23a** and **C23f** exhibited highest activity in coupling iodobenzene with ethyl acrylate in DMAc or DMF in the presence of n-Bu_3N as a base at 85 °C, hence applied for coupling of various aryl bromides with styrene or ethyl acrylate. The catalyst **C23a** (0.1 mol %) achieved TON up to 4100000 and TOF up to 530000 for coupling iodobenzene with ethyl acrylate at 85 °C. The **C23o** also attained TON of 400–700 for coupling bromobenzene with ethyl acrylate in the presence of TBAB in DMAc at 140 °C. They showed the involvement of a conventional Pd(0)/Pd(II) catalytic cycle by kinetic curve and the effect of reductant in the reactions. The reduction of Pd(II) occurs with a simultaneous disassembly of palladacycle into to Pd(0) and amine ligand by the olefin in a non-catalytic Heck coupling reaction (Scheme 12) [27].

Indolese et al. [28a] investigated C–C (Heck, Suzuki and α-arylation of ketones) and C–N (Buchwald-Hartwig amination) coupling reactions of aryl chlorides using a combination of **C23c-d**, **C23g**, **C23**j, **23m** and **C24a-f** and secondary phosphanes (**L7** and **L8**) (Scheme 13). The catalytic system can either be prepared *in situ* by mixing **C23c-d**, **C23g**, **C23j**, **23m** and **C24a** with $HPCy_2$, $HPNor_2$ and phosphanes or corresponding isolated complexes (**C24c-f**) obtained from the chloride bridged palladacycle **C24b**. Out of all combinations, the **C24c**/$HPNor_2$ system was the most active catalytic system for all the coupling reactions. Similarly, Biscoe et al. [28b] reported Pd catalyzed stereospecific coupling reactions of nonactivated secondary alkylboron nucleophiles and aryl chlorides using **C24g**.

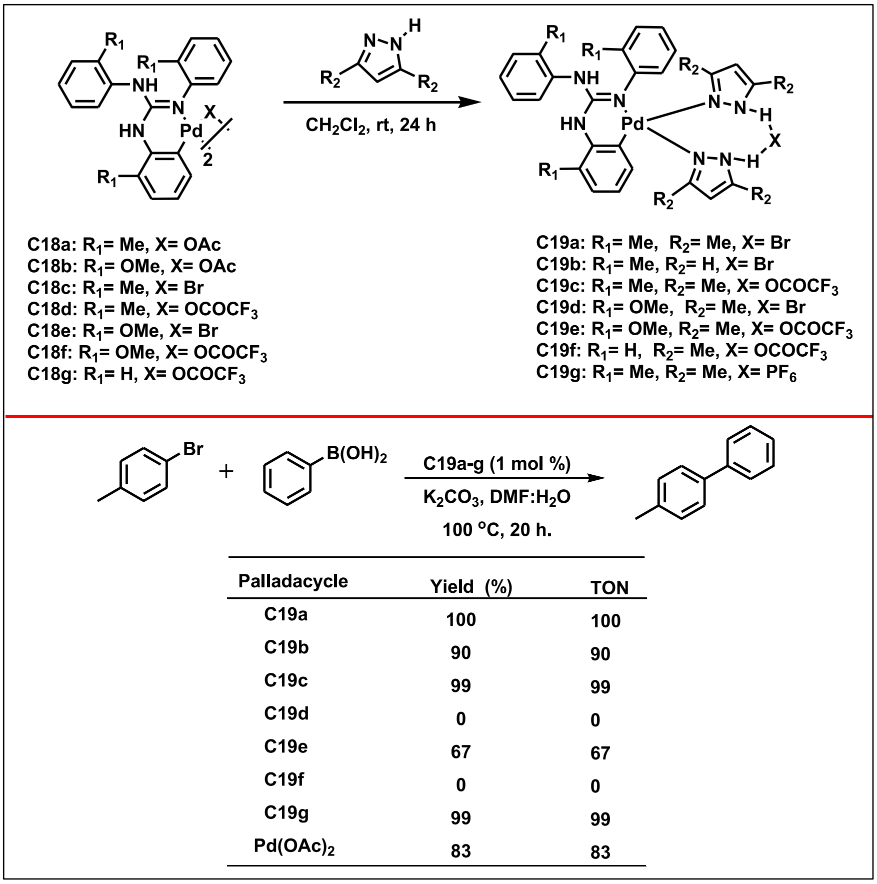
The chloropalladated propargyl amine based palladacycles (**C25a-c**) were found to be active catalysts for the Heck coupling reaction [29a]. While the palladacycles **C25b** and **C25c** [29b] was reported for the Sonogashira coupling reaction (Scheme 14). The palladacycle **C25a** prepared from the chloropalladation of 3-(dimethylamino)-1-phenyl-1-propyne by $PdCl_2$ was converted into the palladacycles **C25b** and **C25c** by the addition of $PH(t\text{-}Bu)_2$ or $P(4\text{-}CF_3C_6H_4)_3$ in the CH_2Cl_2. The catalyst **C25a** showed TON up to 85000 in the Heck coupling of deactivated arylbromides and TON up to 1000 for aryl iodides as well as activated aryl chlorides and arylbromides with *n*-butyl acrylate or styrene using NaOAc as a base at 30–150 °C in the presence of TBAB. The reaction involves the formation of catalytically active PdNPs as analyzed by Hg test and TEM analysis. They demonstrated that $[Bmim]PF_6$ is the choice of media for the *in situ* investigations of the changes in shape and size of colloidal Pd catalysts generated in the Heck coupling reaction using $(i\text{-}Pr)_2EtN$ as a base at 30–130 °C [29c]. The palladacycles **C25b** and **C25c** also enabled the Sonogashira coupling of aryl iodides as well as activated arylbromides with terminal alkynes. The TON of 10^5 has been achieved for aryl iodides at room temperature and up to 94% yield for deactivated arylbromides at 120 °C.

Though the use of water in organic synthesis has attracted much attention as a potential replacement for organic solvents mainly due to its low toxicity, and the environmental friendly nature, its main disadvantage is a low solubility of substrates in water. In this regard Huang and Shaughnessy [30] reported a family of novel water soluble hydrophilic homogeneous palladacycles (Fig. 5) for the Suzuki coupling of aryl bromides in water. The catalysts can be easily separable and highly recyclable. The desired dimeric chloride bridged palladacycles were prepared by treating the appropriate ligand precursor with $PdCl_2$ and NaOAc in methanol. The palladacycles derived from N,N-dimethyl-*p*-hydroxybenzylamine (**C26a**) and sodium 4-(N-benzylideneamino)benzenesulfonate (**C26k**) showed good activity (0.02 mol % Pd) for the Suzuki coupling of aryl bromides and activated aryl chlorides in combination with (2-di-tert-butylphosphinoethyl)-trimethylammonium chloride (*t*-Bu-Amphos). The catalytic system derived from **C26k**/*t*-Bu-Amphos showed 12 times recyclability in the coupling of 4-bromotoluene at 80 °C (yields > 86% with an average yield of 98% for the 12 cycles).

Karami et al. [31] reported thermally stable *ortho*-palladated complexes **C26c-h** and **C27a-g** for the Suzuki coupling reaction (Fig. 5). Out of all complexes, the palladacycle **C27c** exhibited good to excellent catalytic efficiency (yield 71–100%) in the reactions of several aryl bromides and chlorides with phenylboronic acid in the presence of Na_2CO_3 in MeOH at 60 °C.

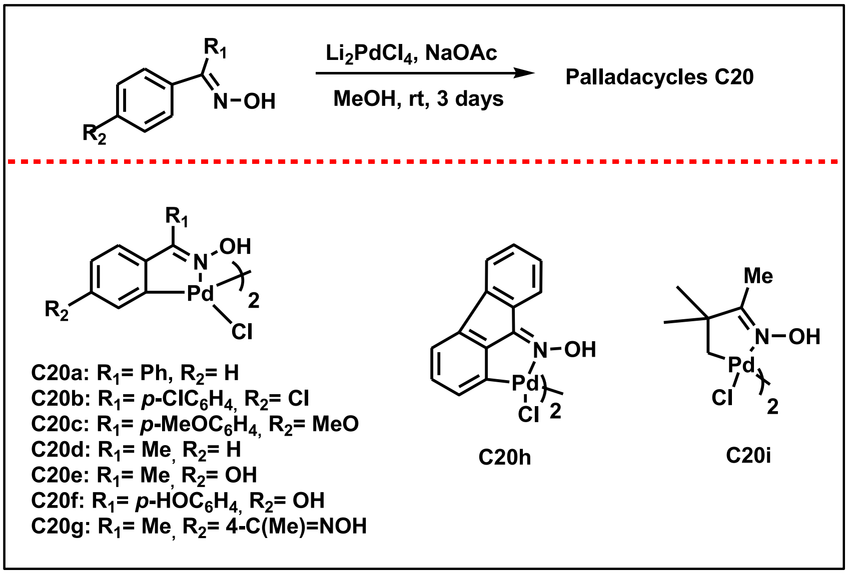
The palladacycle **C26i** also carried out Stille as well as Hiyama coupling reaction under MW irradiation [32a-b]. Similarly, *ortho*-palladated homoveratryl amine complexes (**C27h-i**) also showed efficient activity in the Suzuki, Stille, Hiyama as well as homocoupling reactions [32c-d]. Hollis and Overman [32e] used cyclopalladated benzylamine catalysts (**C27j-k**) for enantioselective rearrangement of allylic imidates to allylic amides.

Strassner et al. [33a] synthesized of cyclometalated 2-phenylimidazole Pd carbene complexes containing different N-1 groups and different substituents at the C-2 position of phenyl group. The dimeric palladacycles (**C28a-f**) were prepared by treatment of substituted imidazoles with $Pd(OAc)_2$ in glacial acetic



Palladacycle	Yield (%)	TON
C19a	100	100
C19b	90	90
C19c	99	99
C19d	0	0
C19e	67	67
C19f	0	0
C19g	99	99
$Pd(OAc)_2$	83	83

Scheme 10. Cyclopalladated N,N′,N″-triarylguanidines for the Suzuki coupling reaction.



Scheme 11. Synthesis of oxime palladacycles.

acid [33b], which on treatment with the various NHCs or its corresponding imidazolium salt gave the monomeric complexes **C28g-q**. They studied the steric and electronic influence of substituents present on these complexes on the Suzuki coupling reactions of aryl chlorides (Fig. 6). The activity of catalysts strongly depends on the steric substituent present on the N-1 center of the palladacycles. Though, the activity decreases with increasing steric demand, there was no influence on the catalytic activity of C-2 phenyl substituents as well as the counter ion of the precatalyst. Out of all the palladacycles, **C28g** (0.05 mol %) gave a good yield of the desired

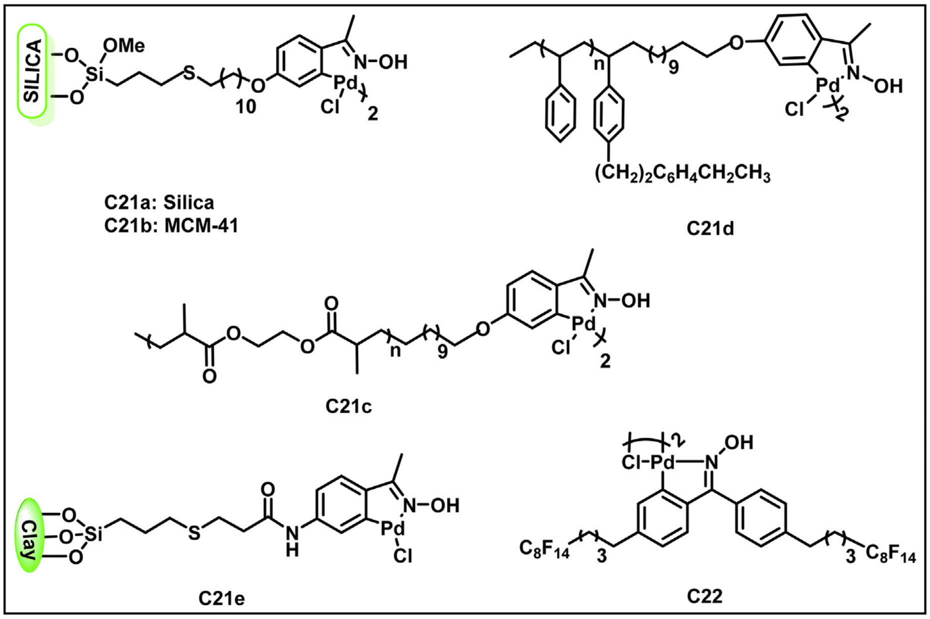


Fig. 4. Covalently anchored palladacycles used in the coupling reactions.

products for various aryl and benzyl chlorides.

Grig and coworkers [34] synthesized different pyrazole (**C29a-f**) and benzothiazole (**C30a-f**) palladacycles from the corresponding pyrazole/benzothiazole ligands and Pd(OAc)$_2$ in acetic acid at 100–120 °C. All the palladacycles showed excellent catalytic activity for the Heck coupling reaction of iodobenzene and *n*-butyl acrylate in DMF at 100 °C (Scheme 15). Thus the ligands containing F and CF$_3$ (−I and π donor) substituents (**C29b**, **C29c** and **C29e**) present at *para* and/or *ortho* to the C–Pd bond has a positive effect on the rate of the reaction. The HCOONa and HCOOK were found to be best bases (TON = 2×10^6 with 50% isolated yield) for catalysts **C29b** and **C29e**, while **C29a** showed a TON of 2×10^6 with 78% yield in the presence of K$_2$CO$_3$ as a base. The catalyst **C30a** also showed excellent activity for three-component cascade reaction.

Venkatasubbaiah et al. [35] used cyclometalated 1,3,5-triphenylpyrazole palladium dimer (**C29g**) in Heck, as well as Suzuki coupling reactions using low catalyst loadings (0.2 and 0.1 mol % respectively). Reddy and Krishna [36] applied Pd(dba)$_2$/N-substituted 2-(2-bromophenyl)benzimidazoles (3:1 mol %) system for the Heck coupling reactions in the presence of Et$_3$N in NMP at 50–116 °C. The electron rich ligands showed higher activities as compared to electron deficient ligands. The *in situ* formation of precatalyst (**C30g**) was studied by its synthesis and characterization by mass spectral studies.

The air and moisture stable cyclopalladated complexes (**C31a–j**) based on substituted 8-methyl quinoline synthesized from the corresponding aniline, 1,3-diketone [37] and Pd(OAc)$_2$ in glacial acetic acid [38] also exhibited the TON up to 25 million for the Heck vinylation of aryl iodides and bromides [39] (Scheme 16). It was shown that an electron donating group at C-5 and electron withdrawing group at C-2 increases the rate of reaction and TON by coupling iodobenzene and *n*-butyl acrylate/benzyl acrylate in DMF/DMA at 140 °C.

Serrano et al. [40] synthesized a new class of palladacyclopentadiene complexes (**C32–C34**) containing imidato ligands (succinimide, maleimide and phthalimide) for the Stille coupling reaction. Complexes **C32d**, **C32f** and **C33f** were found to be most efficient catalysts for the coupling of benzyl bromide with ethyl *Z*-vinylstannyl carboxylate in toluene at 60 °C under N$_2$ (Scheme 17).

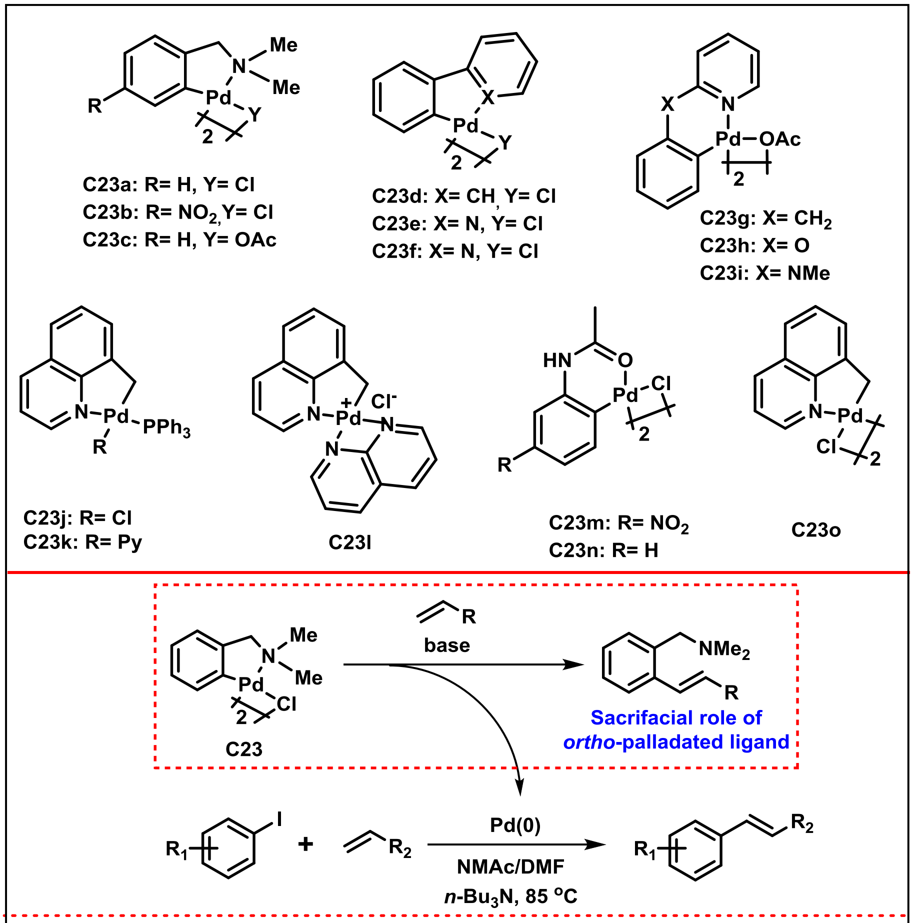
4. Pincer complexes

Pincer complexes are a subclass of palladacycles that contains two fused palladacycle species. As in the 1970s [41] the transition metal ECE type pincer complexes (PCP and NCN) attracted great interest as a new class of metal complexes for the study of a diverse range of catalytic applications [42]. The existence of the flanked Pd–C bond by two neutral electron donor atoms offer them higher stabilities towards air, heat, and moisture. Furthermore, it can be possible to tune their reactivity and stereoselectivity by modifying a careful selection of donor atoms (P, S, N and Se), substituents on the donor atoms and introducing the chiral functionalities on the pendant arms (Fig. 7). In addition, it may broadly classify as symmetrical and asymmetrical pincers. Recently, the chemistry of M-pincer complexes [43] especially, Pd-pincer complexes were reviewed by the group of Selander and Szabo [44]. In the present review, we consider only Pd-pincer complexes containing N as a donor atom in combination with other atoms like C from the viewpoint of catalysis in cross-coupling reactions.

The Y/Y′ species with spacer stabilize the pincer complexes and strongly affect the electronic properties of the Pd. The replacement of carbon (Z) with heteroatoms such as Si, P, and N sometimes leads to the improvement of the catalytic activity of complexes. In the NCN type of pincer complex Pd is electron rich due to the coordination of Pd with σ donor carbene and N atoms. Thus the high electron density on Pd appears to be an important factor for attaining high catalytic activity.

4.1. Symmetrical pincers (NCN)

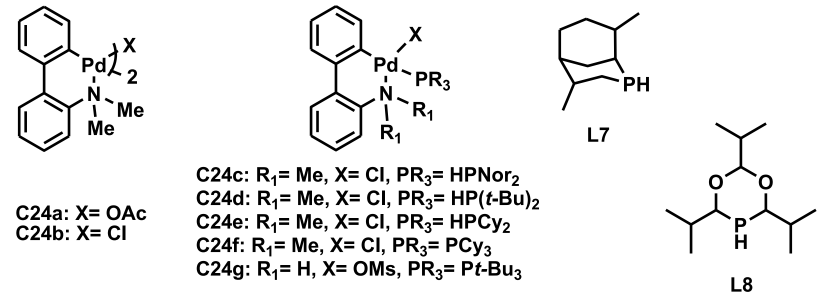
These types of complexes are most widely used pincer complexes containing aryl groups having symmetrical side arms. These can be easily synthesized in few steps from the commercially available compounds.



R_1= H and R_2= COOEt				
Palladacycle	Time (h)	Conversion (%)	TON	TOF (h^{-1})
C23a	12.8	83	830	65
C23b	4.5	100	1000	222
C23e	5.5	95	950	173
C23g	3	89	890	297
C23h	6	98	980	163
C23j	22	88	880	40
C23k	6.5	87	870	134
C23l	16	5	-	-
C23m	2.7	93	930	340
C23o	3	100	1000	333
C20d	17	97	970	57

Scheme 12. Cyclopalladated complexes $[Pd_2(m\text{-}L)_2(NC)_2]$ used in the Heck arylation reaction.

The large numbers of NCN–Pd pincer complexes have been introduced as catalysts for many coupling reactions, due to high stability, low cost and ease of preparation. One of the best properties of NCN–Pd catalyst is the rigidity of Pd–C bond by chelating arms, which may enhance the stability of complex and N coordination with Pd influence their actions. In this regards Chung et al. [45] prepared two NCN–Pd pincer complexes (**C35a** and **C35b**) from 1,8-diaminonaphthalene and isophthalic dicarboxaldehyde. Its structures were determined by single crystal XRD analysis. The **C35a** has C_2-symmetric geometry in which one of the two N form coordination with Pd. The catalytic activity of the complex **C35** and **C36** were studied for the Heck coupling reaction [46]. Thus **C35a** has shown no remarkable difference in activity for 4-tolyliodide. Though the remarkable difference in activity was observed for **C35a**



Palladacycle/L	Suzuki[a] (1.0)	Heck[b] (1.0)	Arylation[c] (0.5 %)	Amination[d] (0.5 %)
C24c/HPNor$_2$	95	100	100	100
C24d/HP(t-Bu)$_2$	45	100	60	94
C24e/HPCy$_2$	91	100	69	98
C24f/PCy$_3$	99	95	99	66

[a] Reaction condition: 4-chloroanisole, phenylboronic acid, K_3PO_4, dioxane, 100 °C, 20 h.

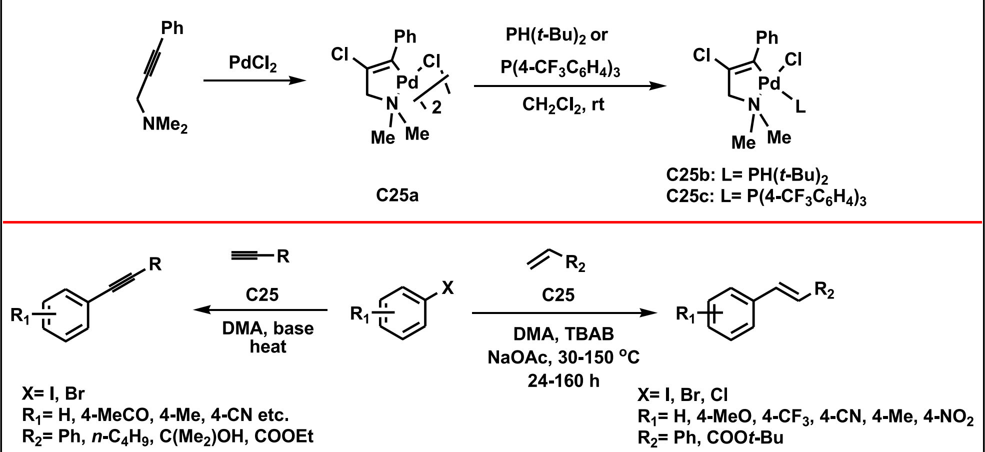
[b] Reaction condition: 4-chloroanisole, methyl acrylate, Na_2CO_3, DMAc, 140 °C, 20 h.

[c] Reaction condition: 4-chloroanisole, ethyl phenyl ketone, NaOt-Bu, toluene, 110 °C, 15 h.

[d] Reaction condition: 4-chloroanisole, N-methylaniline, NaOt-Bu, toluene, 110 °C, 15 h.

Scheme 13. C–C and C–N coupling reactions using a combination of palladacycles and secondary phosphanes.

and **C35b** for the coupling 4-nitrobromobenzene with methyl acrylate in DMF using TEA as a base at 110 °C (TON 6.7 × 10^4 and 100 for **C35a** and **C35b** respectively), but not so effective for coupling non-activated bromobenzenes and chlorobenzenes. The complex **C35a** was more active and stable as compared to **C36**. The higher activity and stability of **C35a** was ascribed on the basis of the



Palladacycle [ArX]/[Pd]	T (°C)	Time (h)	Conversion (%)	Yield (%)
C25a (1 x 10^2)	30	4	100	97
C25a (5 x 10^4)	120	24	98	95
C25b (1 x 10^2)	30	4	52	43
C25c (1 x 10^2)	30	4	100	97
C25c (5 x 10^4)	120	24	100	97

X	Yield (%)	TON
I	40-100	76-1000000
Br	50-100	50-100000
Cl	33-100	330-1000

Scheme 14. Chloropalladated propargyl amine based palladacycles for the Heck and Sonogashira coupling reactions.

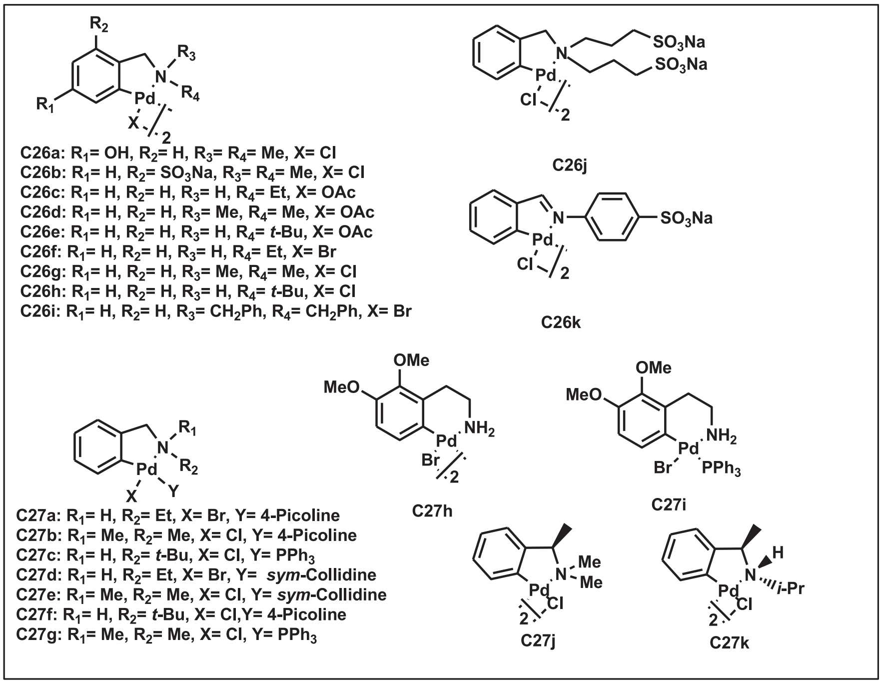


Fig. 5. Various palladacycles used in coupling reactions.

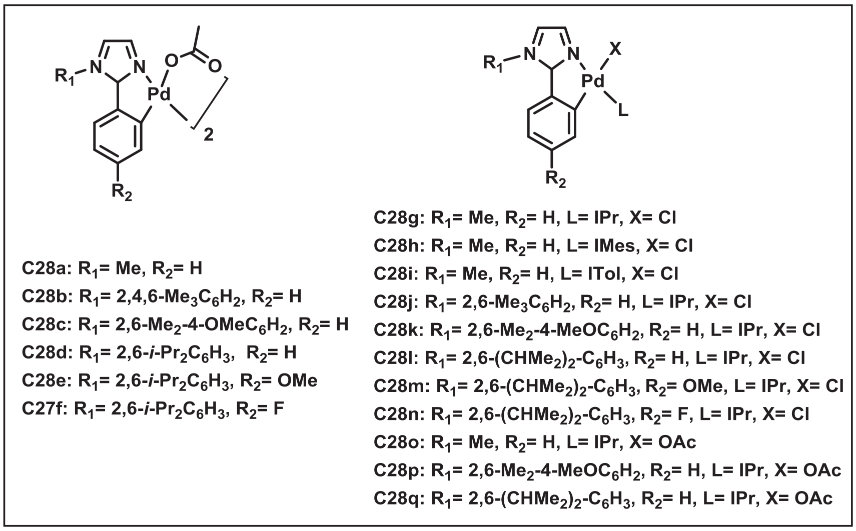
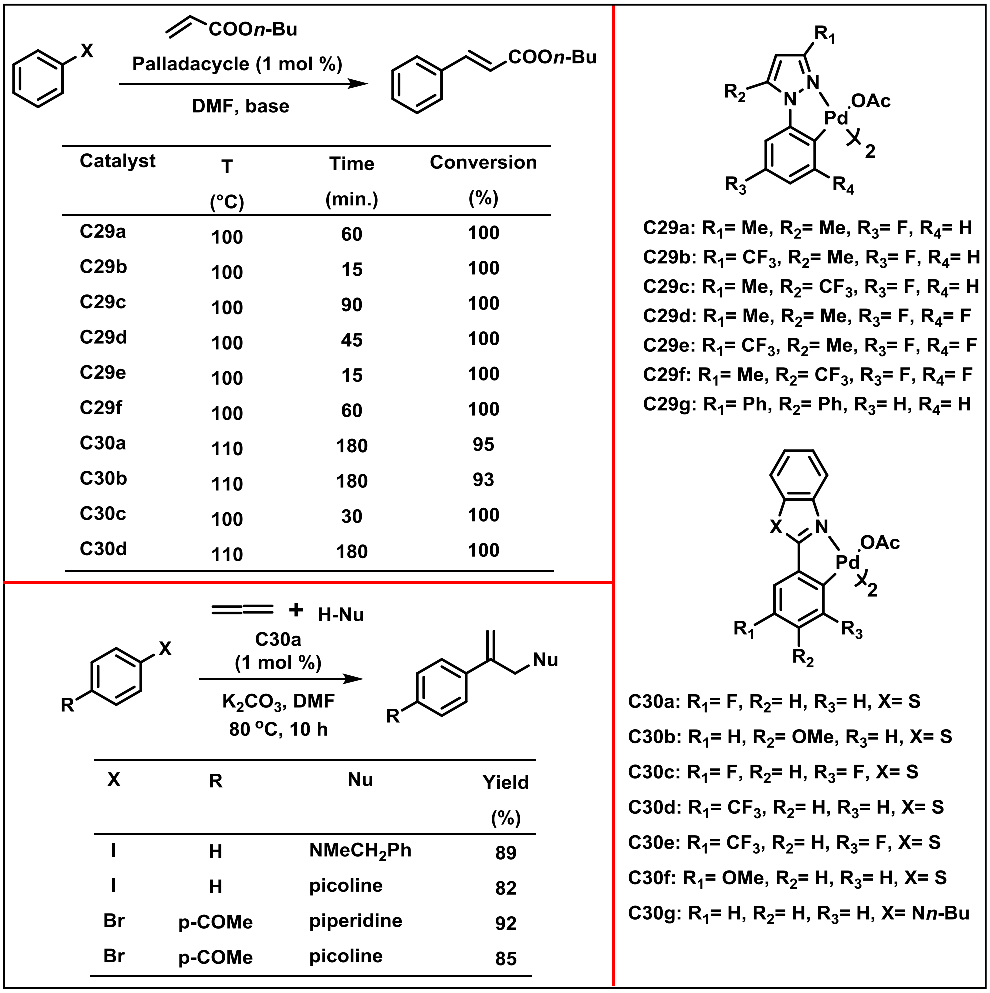


Fig. 6. Cyclometalated 2-phenylimidazole Pd complexes containing different N-1 groups and substituents at the C-2 phenyl group.

fluxional behavior of **C35a** as analyzed by dynamic NMR study (40–90 °C in DMF-d6). At elevated temperature the additional N coordination site present on ligand could participate in coordination with Pd as methyl group attached to the N arms shows two site exchange dynamic behavior. As a result, complex **C35a** interconvert with each other through octahedral transition state and hence more stable at high temperature (Scheme 18).

While, Szab and coworkers [47] carried out selective C–H borylation of alkenes by **C36** catalyzed oxidative functionalization under different reaction conditions (Method A: reaction in neat alkene, Method B: reaction in CH_2Cl_2 (0.1 mL) and Method C: the reaction terminated by a Suzuki coupling). The plausible catalytic cycle is depicted in following scheme (Scheme 19).

Soro and coworkers [48] studied the activity of mononuclear NCN–Pd pincers (**C37a-d** and **C38a-b**) in the Heck coupling reaction of iodobenzene and methyl acrylate under MW heating at the nominal temperature of 135 °C (Scheme 20). It was proposed that the pincer complex **C37c** was expected to have a certain degree of bond angle strain around the Pd center, which may affect the catalytic properties of the pincer complex. In this connection, Ahn et al. [49] synthesized less strained pincer complex by insertion of O, S, and CH_2 between the central benzene ring and side arm containing pyridine rings that would decrease the bond angle strain. They reported NCN–Pd pincer complexes (**C39a-b**) composed of six membered fused metallacycles synthesized directly from 1,3-bis(2-pyridyloxy)benzene. The decreased bond



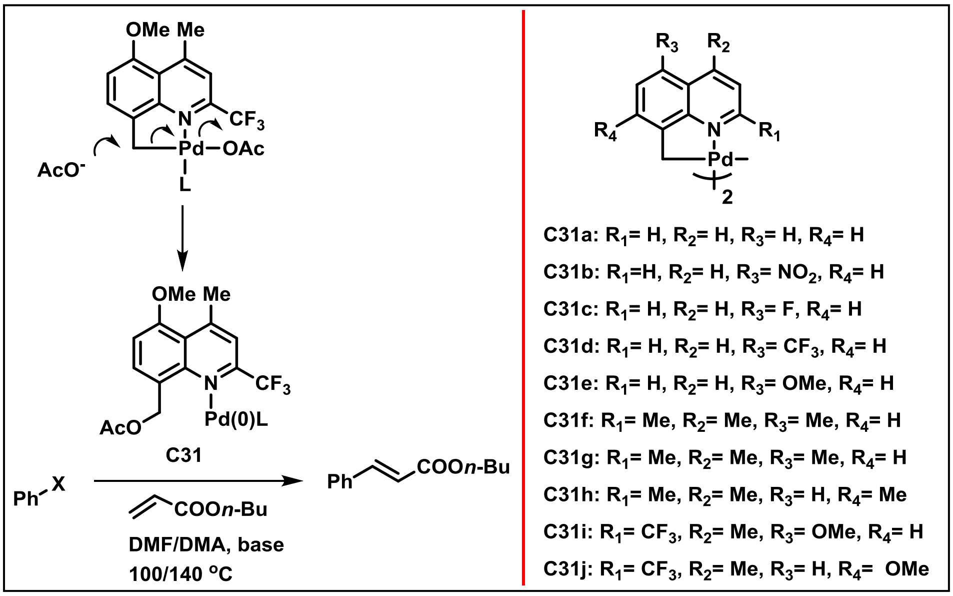
Catalyst	T (°C)	Time (min.)	Conversion (%)
C29a	100	60	100
C29b	100	15	100
C29c	100	90	100
C29d	100	45	100
C29e	100	15	100
C29f	100	60	100
C30a	110	180	95
C30b	110	180	93
C30c	100	30	100
C30d	110	180	100

C29a: R_1= Me, R_2= Me, R_3= F, R_4= H
C29b: R_1= CF_3, R_2= Me, R_3= F, R_4= H
C29c: R_1= Me, R_2= CF_3, R_3= F, R_4= H
C29d: R_1= Me, R_2= Me, R_3= F, R_4= F
C29e: R_1= CF_3, R_2= Me, R_3= F, R_4= F
C29f: R_1= Me, R_2= CF_3, R_3= F, R_4= F
C29g: R_1= Ph, R_2= Ph, R_3= H, R_4= H

X	R	Nu	Yield (%)
I	H	$NMeCH_2Ph$	89
I	H	picoline	82
Br	p-COMe	piperidine	92
Br	p-COMe	picoline	85

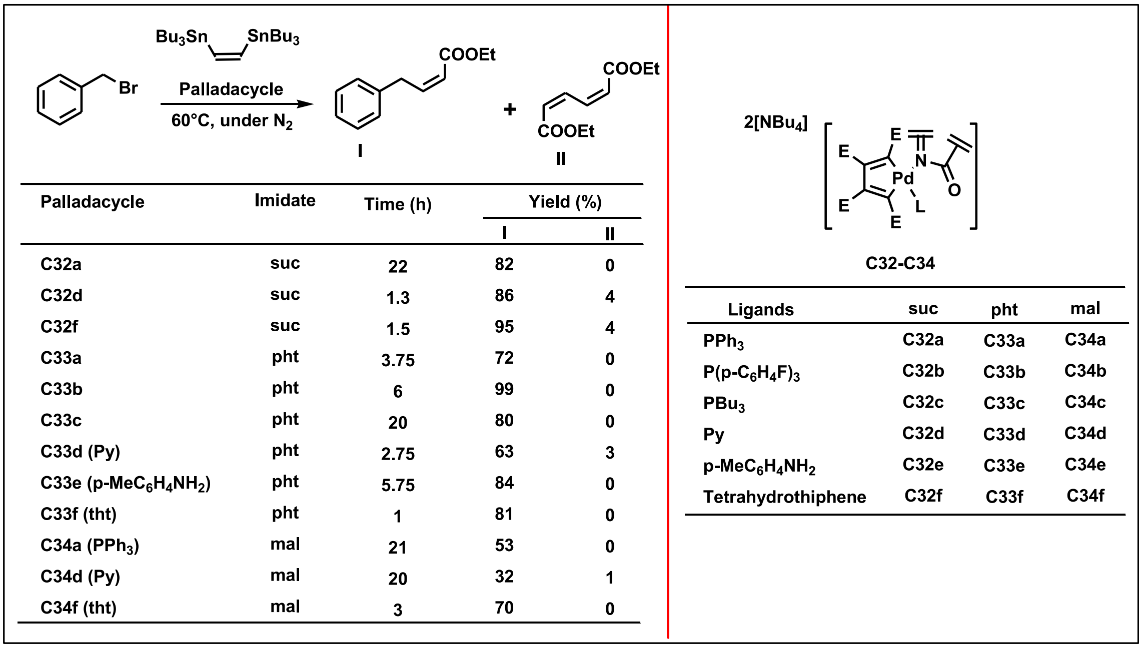
C30a: R_1= F, R_2= H, R_3= H, X= S
C30b: R_1= H, R_2= OMe, R_3= H, X= S
C30c: R_1= F, R_2= H, R_3= F, X= S
C30d: R_1= CF_3, R_2= H, R_3= H, X= S
C30e: R_1= CF_3, R_2= H, R_3= F, X= S
C30f: R_1= OMe, R_2= H, R_3= H, X= S
C30g: R_1= H, R_2= H, R_3= H, X= N*n*-Bu

Scheme 15. Pyrazole and benzothiazole palladacycles for the Heck coupling and three-component cascade reactions.



C31a: R_1= H, R_2= H, R_3= H, R_4= H
C31b: R_1=H, R_2= H, R_3= NO_2, R_4= H
C31c: R_1= H, R_2= H, R_3= F, R_4= H
C31d: R_1= H, R_2= H, R_3= CF_3, R_4= H
C31e: R_1= H, R_2= H, R_3= OMe, R_4= H
C31f: R_1= Me, R_2= Me, R_3= Me, R_4= H
C31g: R_1= Me, R_2= Me, R_3= Me, R_4= H
C31h: R_1= Me, R_2= Me, R_3= H, R_4= Me
C31i: R_1= CF_3, R_2= Me, R_3= OMe, R_4= H
C31j: R_1= CF_3, R_2= Me, R_3= H, R_4= OMe

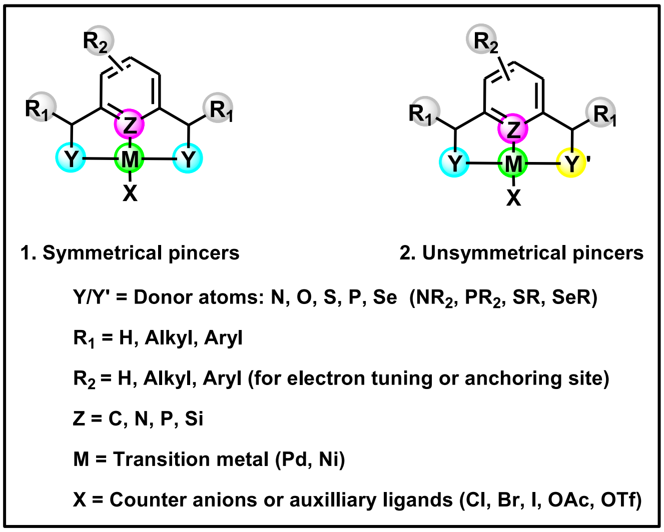
Scheme 16. Applications of cyclopalladated complexes based on substituted 8-methyl quinoline for the Heck coupling reaction.



Palladacycle	Imidate	Time (h)	Yield (%)	
			I	II
C32a	suc	22	82	0
C32d	suc	1.3	86	4
C32f	suc	1.5	95	4
C33a	pht	3.75	72	0
C33b	pht	6	99	0
C33c	pht	20	80	0
C33d (Py)	pht	2.75	63	3
C33e (p-$MeC_6H_4NH_2$)	pht	5.75	84	0
C33f (tht)	pht	1	81	0
C34a (PPh_3)	mal	21	53	0
C34d (Py)	mal	20	32	1
C34f (tht)	mal	3	70	0

Ligands	suc	pht	mal
PPh_3	C32a	C33a	C34a
$P(p\text{-}C_6H_4F)_3$	C32b	C33b	C34b
PBu_3	C32c	C33c	C34c
Py	C32d	C33d	C34d
p-$MeC_6H_4NH_2$	C32e	C33e	C34e
Tetrahydrothiphene	C32f	C33f	C34f

Scheme 17. Palladacyclopentadiene complexes with mono and bidentate imidato ligands for the Stille coupling reaction.



Y/Y' = Donor atoms: N, O, S, P, Se (NR_2, PR_2, SR, SeR)

R_1 = H, Alkyl, Aryl

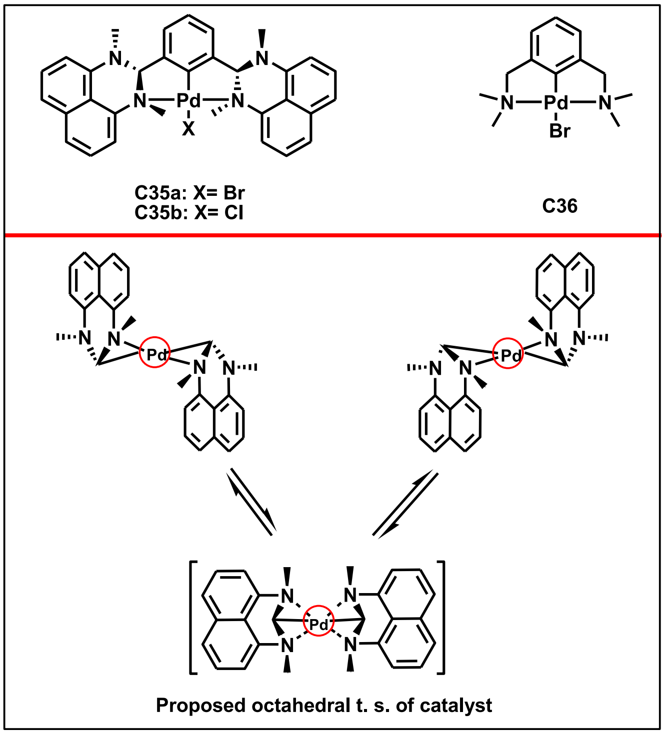
R_2 = H, Alkyl, Aryl (for electron tuning or anchoring site)

Z = C, N, P, Si

M = Transition metal (Pd, Ni)

X = Counter anions or auxilliary ligands (Cl, Br, I, OAc, OTf)

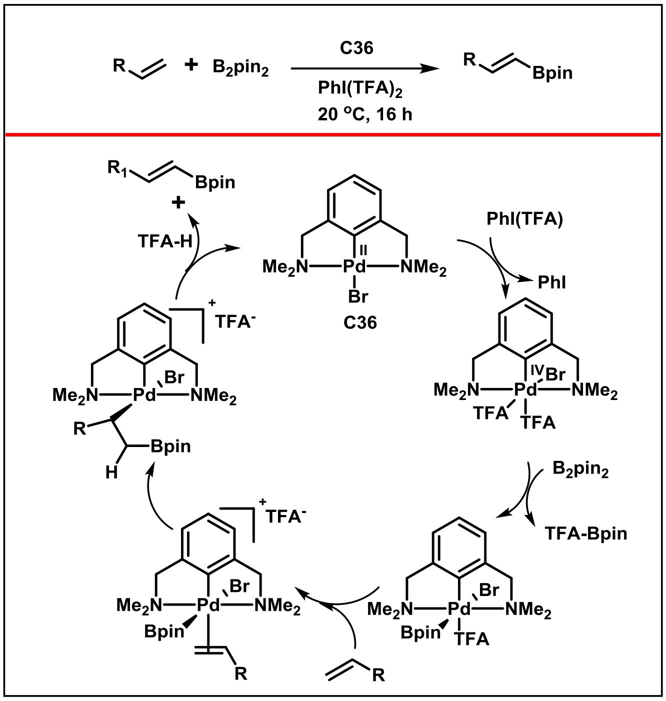
Fig. 7. Schematic representation of pincer architectures.



Scheme 18. Proposed octahedral transition state of the catalyst.

angle strain can allow conformational flexibility and minimizes the energy of structure. Thus, complex **C39a-b** has little bond angle strain around the metal center and the two pyridine rings are twisted with respect to each other by about 48°. The pincer complex **C39a** obtained from their corresponding ligand and K_2PdCl_4 in refluxing glacial acetic acid; otherwise it was not possible by other Pd sources [50]. The complex **C39a** was converted to **C39b** by treating with AgOTf. Though, both **C39a** and **C39b** complexes were effective in the catalytic Heck coupling between aryl halides and methyl acrylate in DMF and Et_3N under reflux, complex **C39b** was more reactive than **C39a**. Comparison of results with **C39a** indicated that pincer complexes based on the six-membered metallacycles are much more efficient than fine membered metallacycles (Scheme 20).

In 2015, Wang et al. [51] studied the effect of catalytic activity of substituents present on the diimino Pd (II) pincer complexes (**C40a-k**) on the Sonogashira coupling reaction (Scheme 21). The ligand synthesis involves the condensation of isophthalaldehydes and anilines followed by treatment with $Pd_2(dba)_3$ in toluene. Catalyst **C40i** exhibited the highest catalytic activity to the Sonogashira coupling reaction of phenyl acetylene with various halides in DMAc and KOAc in the presence of CuI at 90 °C. Thus the proposed



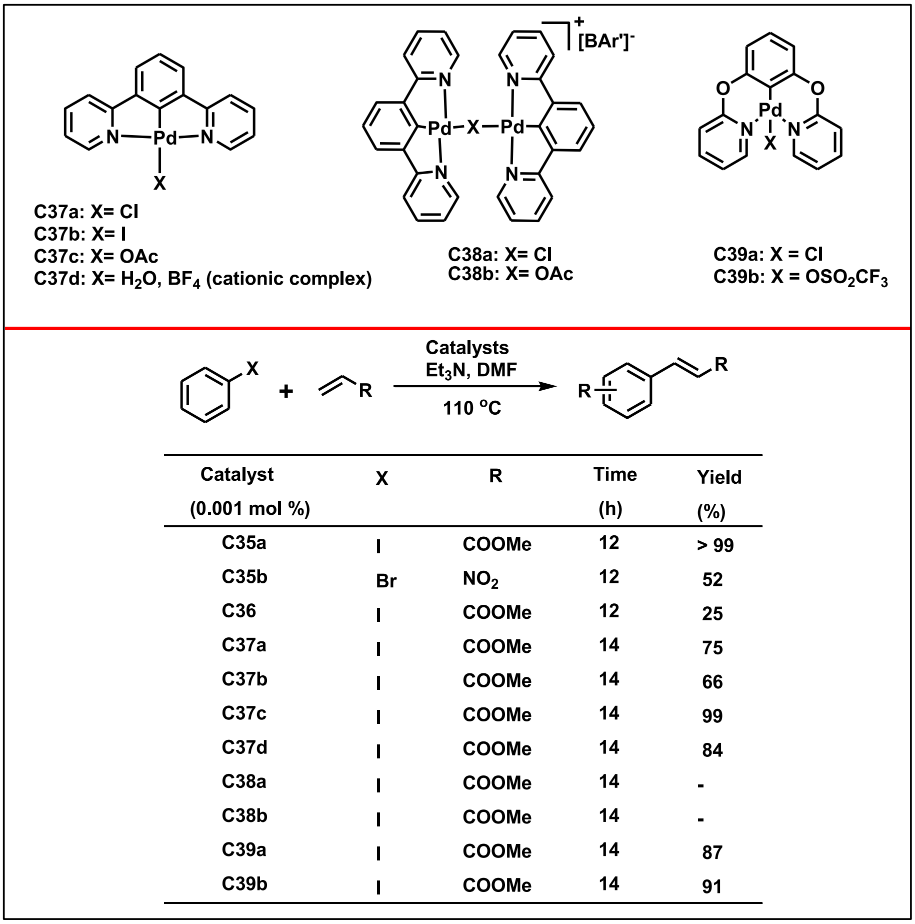
Scheme 19. Proposed catalytic cycle for the C–H borylation reaction.

mechanism shown in Scheme 21, indicated that the electron withdrawing group NO_2 in catalyst might favor the oxidative addition of aryl halides and accelerates its coupling with acetylene.

A series of chiral NCN pincer Pd complexes (**C41a-f**) were prepared by Uozumi and coworkers [52] from *trans*-(4-tert-butyl-2,6-diformylphenyl)chlorobis(triphenylphosphine)palladium *via* dehydrative introduction of the corresponding alkylimino ligands (ligand introduction route). The complexes (1 mol %) demonstrated high catalytic activity for the Heck coupling reaction of aryl iodides in NMP and Bu_3N at 100 °C (Scheme 21). Similarly, they used a novel amphiphilic pincer palladium complexes (**C42a-b**) having a self-assembling behavior for the Miyaura-Michael reaction in water [53] (Scheme 22).

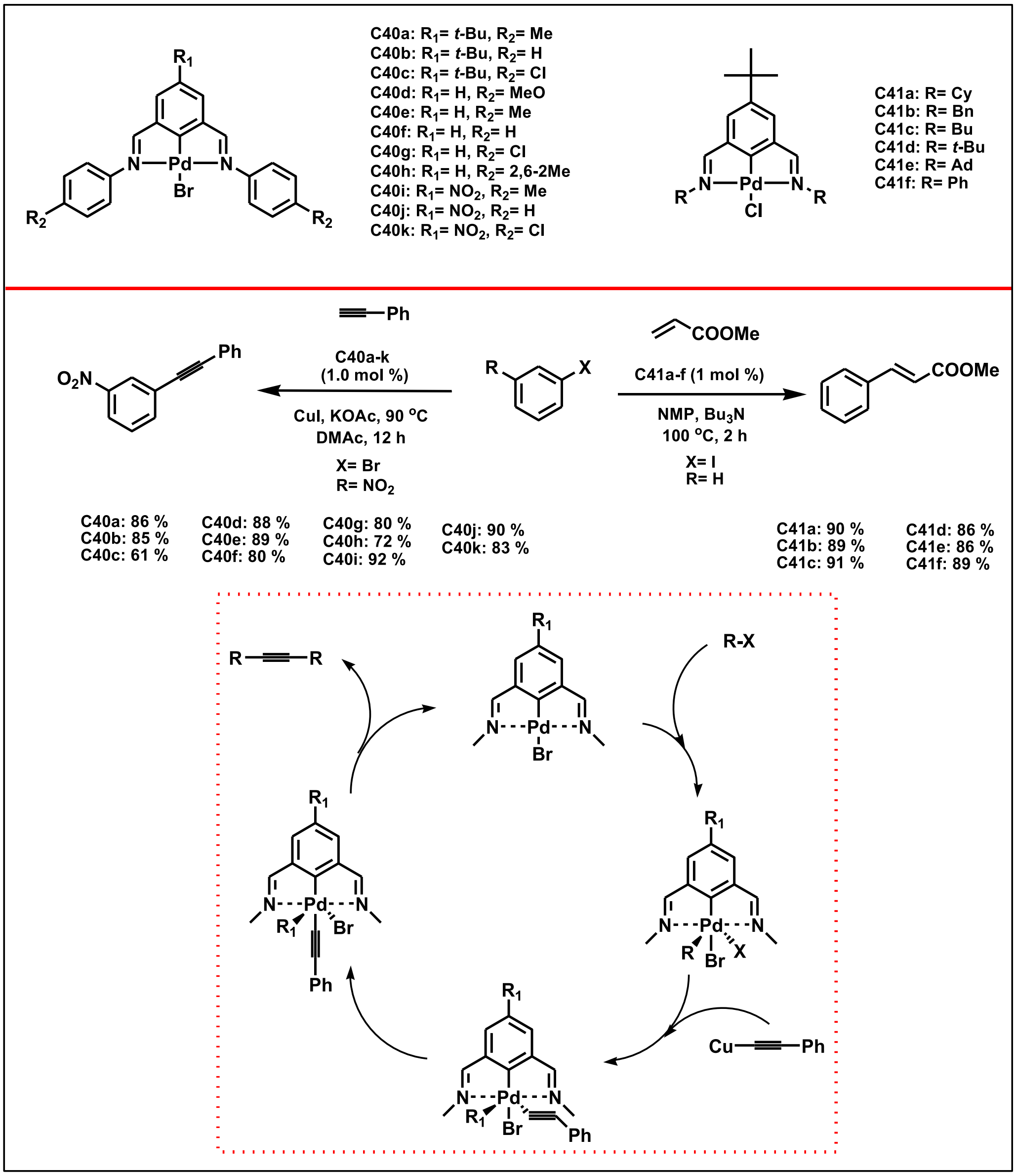
In 2009 Koten et al. [54a] immobilized Pd pincer catalysts (**C43a-b**) on functionalized silica materials through different spacers. The catalysts were applied for allylic stannylation, as well for sequentially two-step conversion of allyl chloride to allylic-alkylation reaction (Scheme 23) [54b].

Tejeda et al. [55a] demonstrated the catalytic activity of a 1,2,4-triazole-based NCN–Pd(II) pincer complex (**C44**) for the Heck coupling of aryl iodides, bromides and chlorides with butyl acrylate (Scheme 24). The tridentate and meridional complex bearing a 1,2,4-triazole ring on each of the pendant ligands was synthesized by reacting $Pd(OAc)_2$ to 1,3-bis(1H-1,2,4-triazol-1-ylmethyl)benzene followed by treatment with KI [55b]. The presence of a 1,2,4-triazole ring influence the metal binding stability and affects the catalytic activity. The catalyst (0.5 mol %) successfully coupled 4-bromobenzaldehyde with *n*-butyl acrylate giving an excellent



Catalyst (0.001 mol %)	X	R	Time (h)	Yield (%)
C35a	I	COOMe	12	> 99
C35b	Br	NO_2	12	52
C36	I	COOMe	12	25
C37a	I	COOMe	14	75
C37b	I	COOMe	14	66
C37c	I	COOMe	14	99
C37d	I	COOMe	14	84
C38a	I	COOMe	14	-
C38b	I	COOMe	14	-
C39a	I	COOMe	14	87
C39b	I	COOMe	14	91

Scheme 20. Symmetrical NCN–Pd pincer complexes used for the Heck coupling reaction.

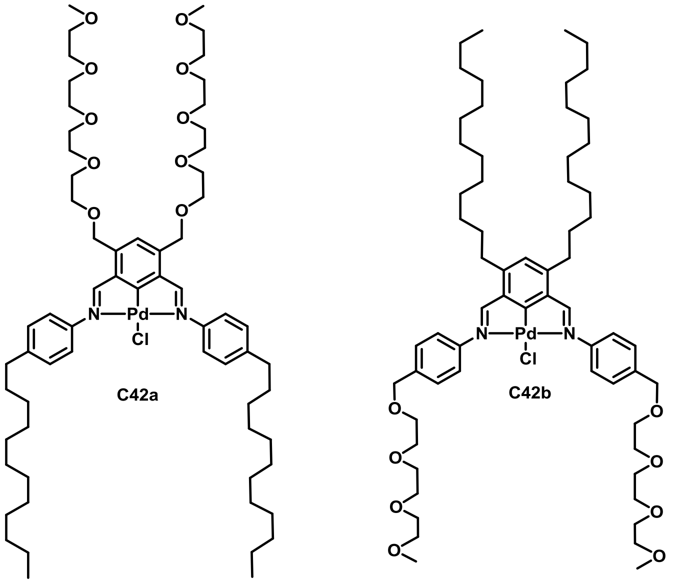


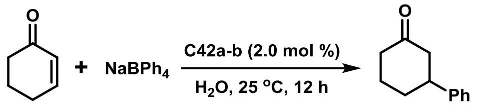
Scheme 21. Proposed catalytic cycle of NCN–Pd(II) pincer complexes in the Sonogashira coupling reaction.

yield (95%) in DMA in the presence of NaOAc at 125 °C in 15 h. The catalyst (1.0 mol %) was also active towards activated aryl chlorides only under 'Jeffery's' conditions (TBAB) giving 20–100% yield at 140 °C, while non-activated aryl chlorides were highly unreactive. They confirmed that an anionic (acetate) activation is responsible for an increase in the reaction rate by applying 'Jeffery's' protocol for the reaction of 4-bromobenzaldehyde in the presence of 18-crown-6 and TBAB as both have a positive effect on the reaction.

Valderrama et al. [56] obtained NCN–Pd(II) pincers (**C45a-b**) containing 3,5-bis(indazol-2-ylmethyl) toluene ligand from 3,5-bis(bromomethyl)toluene. The type of complex formed depends on the nature of Pd source used. The reaction of 3,5-bis(bromomethyl)toluene with $Pd(OAc)_2$ in refluxing acetic acid, followed by a metathetic reaction with LiCl gave pincer complex **C45a**, while reaction with $[PdCl_2(cod)]$ in refluxing MeCN gave complex **C45b**. The complex **C45a** was more active than **C45b** giving higher yields of desired coupling products for the Suzuki coupling reaction in toluene using Cs_2CO_3 as a base under MW irradiation (Scheme 25). Similarly, it was also tested for the Heck coupling reaction of 4-iodobenzene and methyl acrylate in refluxing DMF and Et_3N under MW irradiation (40 min, 150 °C, 150 W).

Xiao et al. [57] synthesized and characterized symmetrical NCN–Pd pincer complexes (**C46a**–**d**) (Fig. 8) containing bis(thiazole) motifs and studied their catalytic activity in the Suzuki coupling of aryl halides. The coupling of 4-methoxybromobenzene with phenylboronic acid in 1,4-dioxane and K_2CO_3 as base at 110 °C showed that the catalytic activity of complexes was in the order of **C46a** > **C46b** > **C46c** > **C46d**. The complexes **C46a** and **C46b** was of similar activity, but superior than **C46c** and **C46d**, indicated that the pincer complexes containing acetate ion had more impact on the catalytic activity than the bromide ion. It observed that, the **C46a** was the more robust catalyst for coupling various aryl halides and arylboronic acids with TON up to 1.9×10^8 and TOF up to 5×10^6 h^{-1} at a temperature >90 °C, and was better than that of the





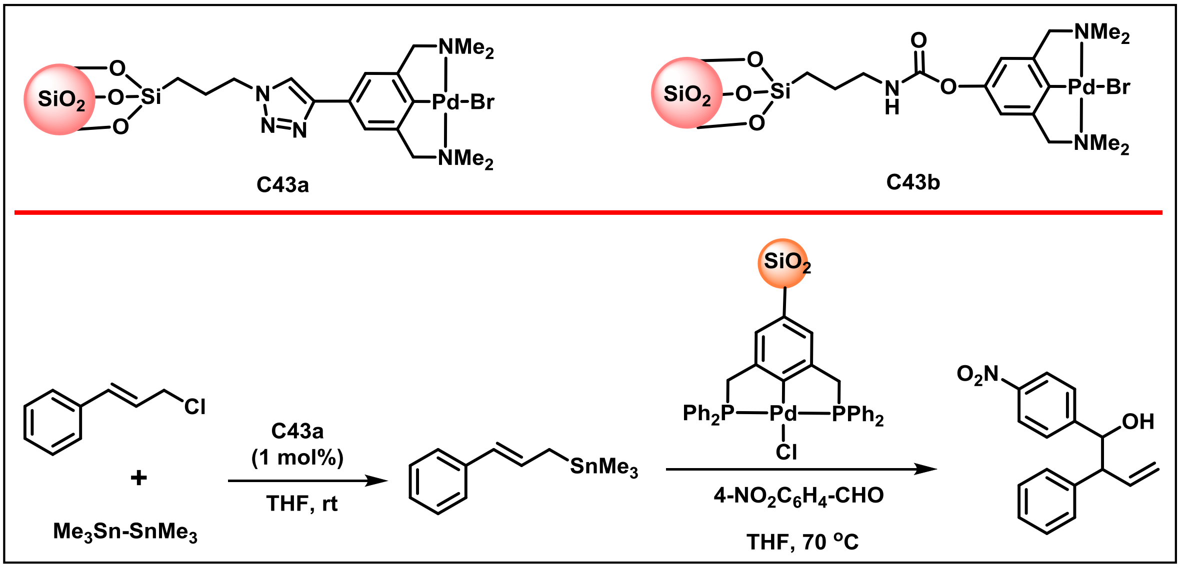
Catalyst	Conversion (%)	Yield (%)	Selectivity (%)
C42a	19	198	99
C42a	21	5	24
C42b	85	83	98
C42b	23	7	30

Scheme 22. Amphiphilic pincer Pd complexes for the Miyaura-Michael reaction.

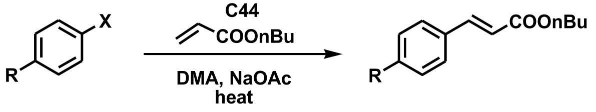
NHC type pincer Pd complexes. Deactivated aryl bromides undergo easy coupling in the presence of **C46a** (0.01–0.05 mol %) with excellent yields under aerobic conditions which was close to that of the phosphorus containing complexes and better than that of many NHC-type pincer complexes. Moreover, activated aryl chlorides gave TON up to 4400 as the same order of magnitude as PCP pincer complex, while non-activated aryl chlorides also worked well but with lower yields.

Uozumi et al. synthesized NCN pincer palladium complex (**C47**) (Fig. 8) from the corresponding alkylimino ligands and applied for the Heck coupling reaction using Bu_3N in NMP or a mixture of NMP:H_2O (7:3) with/without TBAB at 100/140 °C and attain TON up to 519.6×10^6 and TOF ca. 6500 sec^{-1} for the reaction of iodobenzene and methyl acrylate [58]. Considering the attractive feature of porphyrins Osuka et al. [59] applied porphyrin pincer Pd complexes (**C48a-d**) for the typical Heck coupling reaction (Fig. 8). Recently, Rafiee and Hosseini [59b] reported CNC–Pd pincer complex supported on magnetic chitosan (2×10^{-5} mol %) as highly efficient and recyclable nanocatalyst for the Suzuki coupling of aryl halides (I, Br and Cl) with phenylboronic acid in $NaHCO_3$, H_2O:EtOH (1:1) at 70 °C.

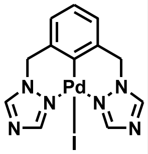
Iwasa et al. [60] synthesized C_2-symmetric NCN type bis(oxazolinyl)phenyl-Pd(II) complexes **C49a-b** (Phebox–Pd). They used an alternative approach for synthesis of these complexes that do not use organotin compounds. The complexes were obtained in high yields by the oxidative addition of $PdCl_2(PhCN)_2$ or $[Pd_2(dba)_3]$



Scheme 23. Sequential allylic-stannylation/allylic-alkylation using immobilized NCN–Pd complexes.

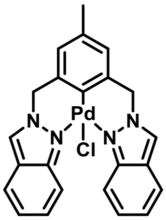


R	X	Additive	Time (h)	Conversion (%)	TON	TOF (h^{-1})
NO_2	Cl	TBAB	15	89	-	-
CH_3	Cl	TBAB	25	43		
OCH_3	Cl	TBAB	15	9		
CHO	Br	-	6	-	28000	4600
CHO	Br	TBAB	6	-	83000	13800
CHO	Br	18-crown-6	6	-	86000	14300

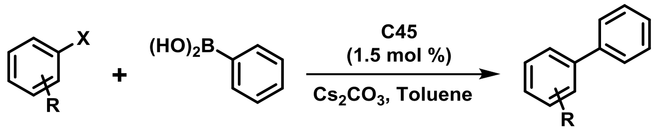


C44

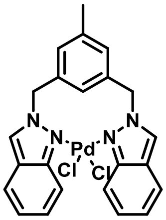
Scheme 24. 1,2,4-triazole-based NCN–Pd(II) pincer complex for the Heck coupling reaction.



C45a



Catalyst	R	X	Reaction conditions	Yield (%)
C45a	H	Br	80 °C, 24 h	31
C45b	H	Br	80 °C, 24 h	14
C45a	H	Br	MW, 150 W, 100 °C, 40 min	36
C45a	H	Cl	MW, 150 W, 100 °C, 40 min	29
C45a	Me	Cl	MW, 150 W, 100 °C, 40 min	-



C45b

Scheme 25. NCN–Pd(II) pincer for the Suzuki coupling under microwave irradiation.

$CHCl_3$ on 1-chloro-2,6-bis(oxazolinyl)benzene in toluene at 80 °C. The complexes (0.011 mmol, S/C = 20) gave the corresponding biaryl products in high yields for the Suzuki coupling reactions of aryl halides and aryl boronic acids with TON 900,000 and TOF 45,000 h^{-1} in *i*-PrOH at 90 °C using K_2CO_3 as a base (Scheme 26). Moreover the catalyst can be recovered quantitatively. Furthermore, chiral inductions were observed in the case of asymmetric Suzuki coupling reactions of different 1-naphthylboronic acid and 2-alkyl/methoxy-1-iodonapthalene with the formation of the *R* enantiomer using **C49b** catalyst.

4.2. Unsymmetrical pincers

A several asymmetrical Pd pincers of different combinations like NCN, CNN, CCN, and CNC were synthesized and applied to various coupling reactions.

4.2.1. NCN pincers

Song et al. [61] used unsymmetrical oxazolinyl containing achiral and chiral NCN Pd(II) pincer complexes (**C50a-d** and **C51**) (0.1 mol %) for the Suzuki coupling reaction of aryl bromides and activated aryl chlorides with phenylboronic acid using K_2CO_3 as a base in dioxane at 110 °C under air (Scheme 27). In continuation of this, they reported NCN Pd(II) pincer complex (**52a**) with *N*-isopropyl-1-aminomethyl-3-(2-pyridyloxyl)benzene for the allylation of aldehydes as well as for three component allylation of aldehydes, arylamines and allyltributyltin [62]. Avila-Sorrosa et al. [63] synthesized a non-symmetric NCN–Pd(II) pincer complex (**C52b**) by a tandem reaction of 3-[(2,4,6-trimethyl-phenylimino)-methyl]-phenol with $[Pd(NCPh)_2Cl_2]$ in toluene in the presence of a Na_2CO_3 (Scheme 27). This complex (0.1 mol %) exhibited good activity to the Suzuki coupling reaction of phenylboronic acid with activated and deactivated *p*-substituted aryl bromides using Na_2CO_3 as a base in DMF at 120 °C.

4.2.2. CNN pincers

Though a large number of symmetric pincer ligands (PCP and NCN) have been demonstrated for various bond activation processes like C–C, C–H and C-X, but the reports on unsymmetrical ligands are scare. In this connection, Broring et al. [64] synthesized unsymmetrical CNN–Pd complex (**C53**) based on 1-(arylimino)-3-(2-hetarylimino)isoindolines and applied for the Heck and Stille coupling reactions (Scheme 28). The catalyst showed decreased activity as I > Br > Cl, while steric repulsion has minor effect. The catalyst was highly active as compared to $Pd(OAc)_2$ for the Heck coupling reaction. Similar results were obtained for the Stille

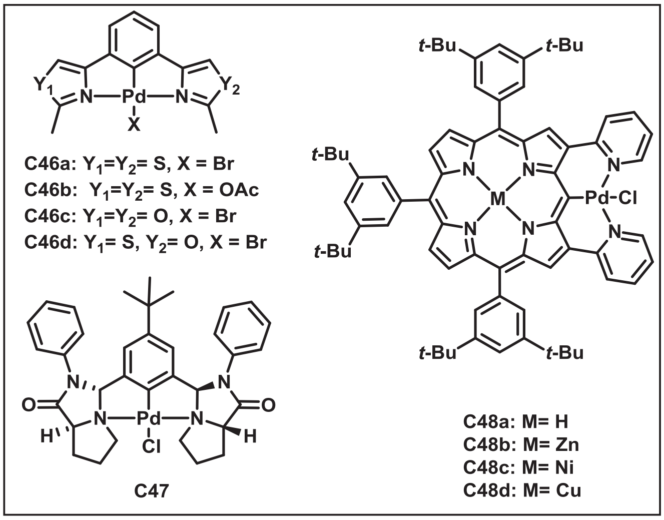


Fig. 8. Various NCN Pd pincer complexes used in the Suzuki and Heck coupling reactions.

coupling reaction. Actual active species are elemental Pd, as analyzed by Hg experimentation.

The CNN Pd(II) pincers **C54a**–**e** and **C55** were prepared from a series of chiral 2-aryl-6-(oxazolinyl)pyridine (aryl = phenyl or 1-naphthyl) ligands *via* aryl C–H bond activation [65]. The catalysts showed high yields with good enantioselectivity (up to 86% *ee*) of 3-allyl-3-hydroxyoxindoles in the asymmetric allylation of isatins with allyltributyltin. Optimization of all the pincers (5.0 mol %) for the asymmetric Suzuki coupling of 1-iodonaphthalene with 1-naphthaleneboronic acid showed that **C55c** gave a good yield (71%) with 50% *ee* in 24 h using K_2CO_3 as a base in DCE at 80 °C (Scheme 29). The catalyst **C55c** (5 mol %) also showed good enantioselectivity and yield for the reaction of various 1-iodo-2-alkoxynaphthalenes and bulky arylboronic acids using K_2CO_3 as a base in DCE at 80 °C. The CNN Pd(II) pincer complexes (**C56a-c**) with N-substituted-2-aminomethyl-6-phenylpyridines also applied for allylation of benzaldehyde with allyltributyltin and synthesis of homoallylic amines by three-component allylation reaction [62].

Chen et al. [66] tested a series of CNN pincer type palladacycles **C57a-b** and **C58a-e** (1.0 mol %) for the Suzuki coupling reaction of 4-bromoacetophenone with phenylboronic acid at room temperature. It was observed that catalysts **C58c** and **C58d** exhibited better activities using K_3PO_4/KF as a base in THF/DMA/toluene at room temperature (Scheme 30). The activity of these catalysts was further studied for the Heck coupling reaction of aryl halides and styrene using different bases and solvents at different temperatures.

Pramanik and coworkers [67] explored the catalytic activity of the luminescent bisazoaromatic CNN pincer palladacycles **C59a-d** (0.01–0.001 mol %) in the Suzuki coupling reaction using K_2CO_3 in toluene at 70–110 °C (Scheme 31). The catalysts also showed good activity in the Heck coupling reaction of aryl iodides and bromides using K_2CO_3 in DMF at 135 °C. While, bishydrazone-Pd-complex (**C59e**) was showed good activity in the Suzuki coupling reaction [68]. The CNN–Pd pincer complex **C60a** efficiently catalyzed allylic arylation at parts per billion levels [69a], while **C60b** acts as a good catalyst precursor for the Heck coupling reaction [69b].

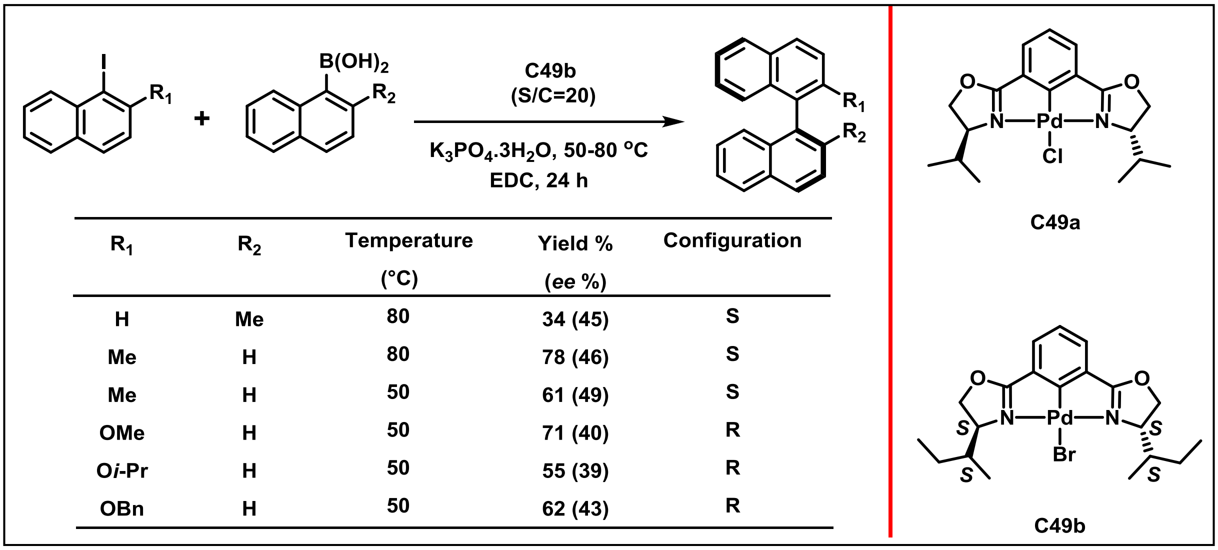
4.2.3. CCN pincers

Sun et al. [70] reported Pd(II) bisimino functionalized dibenzo [a,c]acridine pincer frameworks for the Heck coupling reaction (Scheme 32). A conjugated ligands 10-[1-(arylimino)ethyl]-14-[(arylimino)methyl]dibenzo[a,c]acridine incorporating aldimine and ketimine units was prepared from phenanthrene-9,10-dione, which on cyclopalladation with $PdCl_2(MeCN)_2$ afford pincer complexes **C61a-b**, while **C61c-d** were obtained by hydrolysis of the pendant aldimine units. Out of all the catalysts, **C61c** (0.002 mol %) was efficiently mediate the Heck coupling of aryl halides and various olefins using Na_2CO_3 as a base in DMF at 140–200 °C with TON up to 1,74,000.

4.2.4. CNC pincers

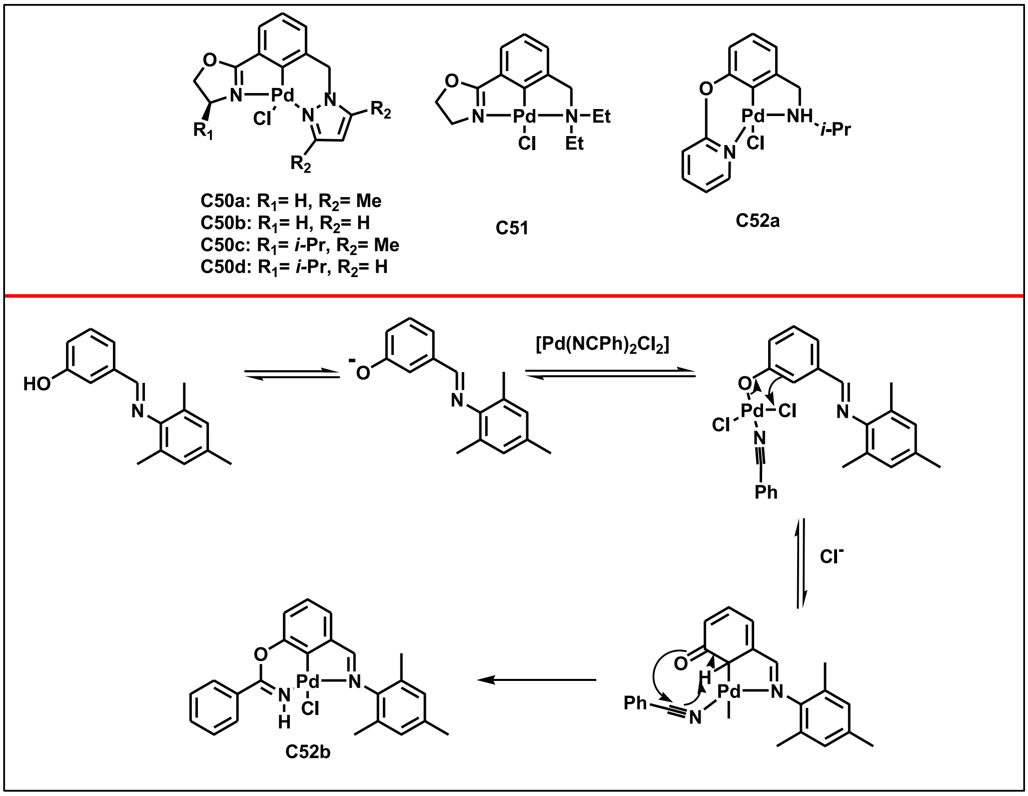
Chen et al. [71] reported palladacycles (**C62a-f)** containing pendant benzamidinate ligands (CNC) for the Suzuki and Heck coupling reactions (Scheme 33). Due to the good activity and solubility **C62c** was applied to the Heck coupling reaction.

Urriolabeitia et al. [72] synthesized C,N (**C63a-b**) and CNC (**C63c-**



R_1	R_2	Temperature (°C)	Yield % (*ee* %)	Configuration
H	Me	80	34 (45)	S
Me	H	80	78 (46)	S
Me	H	50	61 (49)	S
OMe	H	50	71 (40)	R
O*i*-Pr	H	50	55 (39)	R
OBn	H	50	62 (43)	R

Scheme 26. C_2-symmetric NCN type bis(oxazolinyl)phenyl-Pd(II) complexes for asymmetric Suzuki coupling reaction.



Scheme 27. Mechanism of the formation of **C52b** *via* a tandem process.

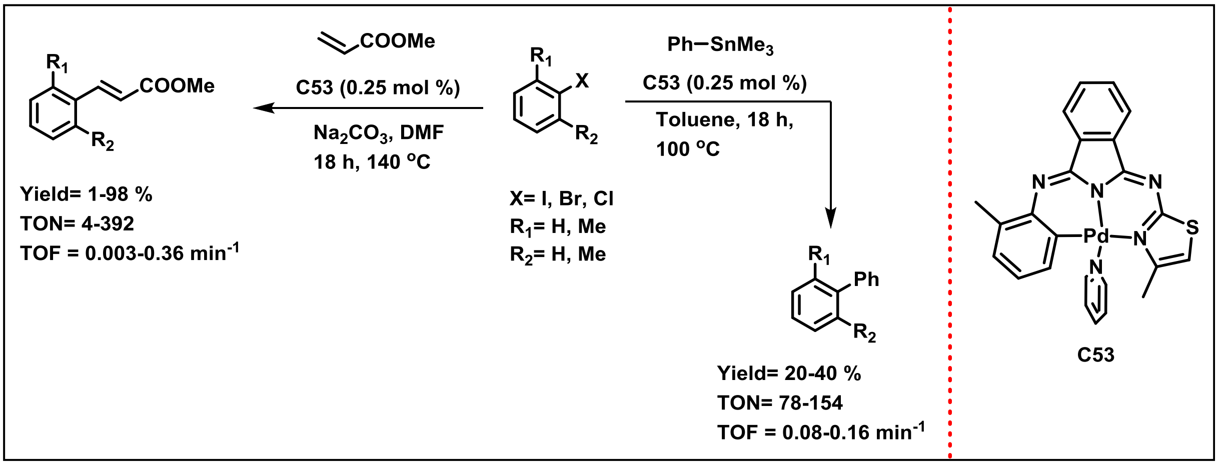
d) *ortho*-palladated iminophosphoranes that showed moderate to good activity in the Heck coupling reaction of methyl acrylate with different arylhalides using Et_3N as a base in DMF at reflux (Scheme 34).

5. Nstabilized NHC complexes

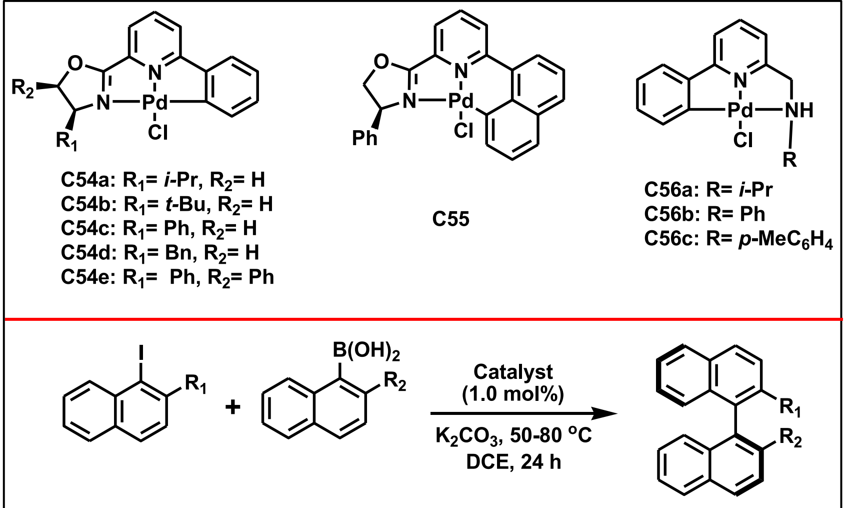
The success behind the popularity of 'N-heterocyclic carbenes (NHCs)' for metal catalyzed cross-coupling reactions lays its strong σ-donating ability that facilitates strong ligand-metal bonds and prevents catalyst leaching. The σ-donating ability also enhances the efficiency and lifetime of the catalysts. Hence NHC is called as "spectator" ligands and are becoming increasingly popular as a substitute for phosphine substitutes [73].

The electron density and consequently the σ-donation to metal centers in NHC can be increased by following ways;

1. The introduction of different substituents on NHC (which has limited effect on the electronic density).
2. Alteration of steric bulk on NHCs by bulky substituents.
3. Introduction of one/more heterocycles at N-position which acts as a 'hemilabile' ligand which influence the electronic density of metal through coordination. This hemilabile ligand creates an unsaturated coordination site and stabilizes the active species



Scheme 28. Pd–CNN pincer based on 1-(arylimino)-3-(2-hetarylimino)isoindolines for the Heck and Stille coupling reactions.



C54a: R_1= *i*-Pr, R_2= H
C54b: R_1= *t*-Bu, R_2= H
C54c: R_1= Ph, R_2= H
C54d: R_1= Bn, R_2= H
C54e: R_1= Ph, R_2= Ph

C55

C56a: R= *i*-Pr
C56b: R= Ph
C56c: R= *p*-MeC$_6$H$_4$

R_1= H and R_2= OMe		
Catalyst	Yield (%)	*ee* (%)
C54a	69	45
C54b	76	32
C54c	71	50
C54d	73	31
C54e	78	48
C55	72	44

Scheme 29. Chiral CNN–Pd (II) pincer complexes for enantioselective allylation and Suzuki coupling reactions.

after reductive elimination in the catalytic cycle. It also stabilizes *in situ* generated active Pd species.

Recently, a development in transition metal complexes of bis-NHC ligands containing a heteroarene spacer was reviewed by Chen and coworkers [74]. The NHC functionalized with N/O/P facilitates complexation to metals through chelation with enhanced activity for transition metal catalysts. It imparts additional stability to the metal complexes due to the presence of polar functional groups by long range hydrogen bonding or electrostatic interactions [75]. This would also enhance the catalyst stability and inhibits catalyst leaching that affects the catalyst efficiency as well as lifetime. It has been reorganized that the oxidative addition involving the cleavage of a C–X bond is the key step in Pd catalyzed cross coupling reactions. The catalyst with an electron rich metal center would significantly influence the oxidative addition and consequently facilitate the C–C cross-coupling reactions. Thus, there are many reports that investigated the correlation between the electron richness of a metal center with catalytic efficiency. Considering these effects number of groups has reported a systematic approach towards designing N functionalized NHC with improved catalytic efficiency.

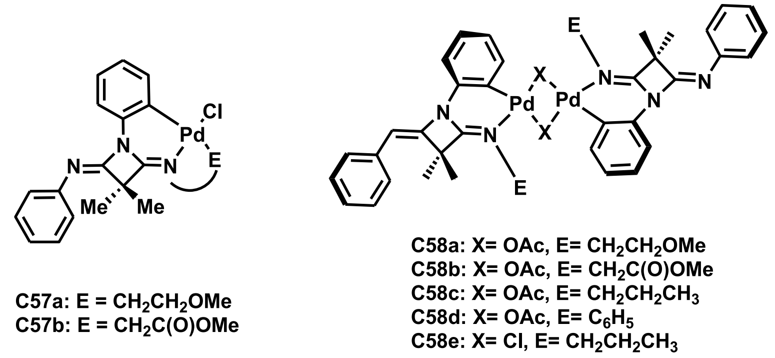
The hemilabile arm present in palladacycle/pincer/NHC ligands undergoes reversible dissociation from the metal center and will produce vacant coordination sites that allow complexation of substrates during the catalytic cycle, and the strong donor moiety remains connected to the metal center. Thus functionalized NHC containing N makes them suitable for the generation of hemilabile ligands. In addition the increased steric bulk in the NHC, also leads to a lower coordination number around the Pd center that facilitates a more facile oxidative addition [76]. Recently, Pape and Teichert [77] reviewed bidentate NHC bearing anionic substituents (tethered NHCs) in transition-metal-catalyzed reactions. Such chelating ligands can have following potential advantages.

(i) In such complexes the corresponding transition metal complexes can be better stabilized by chelation.
(ii) The chiral group can be placed within the heterocyclic backbone that enables to carry out stereoselective catalytic transformations.
(iii) Such catalysts can be acts as cooperative (bifunctional) catalysts.

For simplification, we grouped all the N stabilized Pd–NHCs complexes into the following groups.

5.1. Amine stabilized NHC complexes

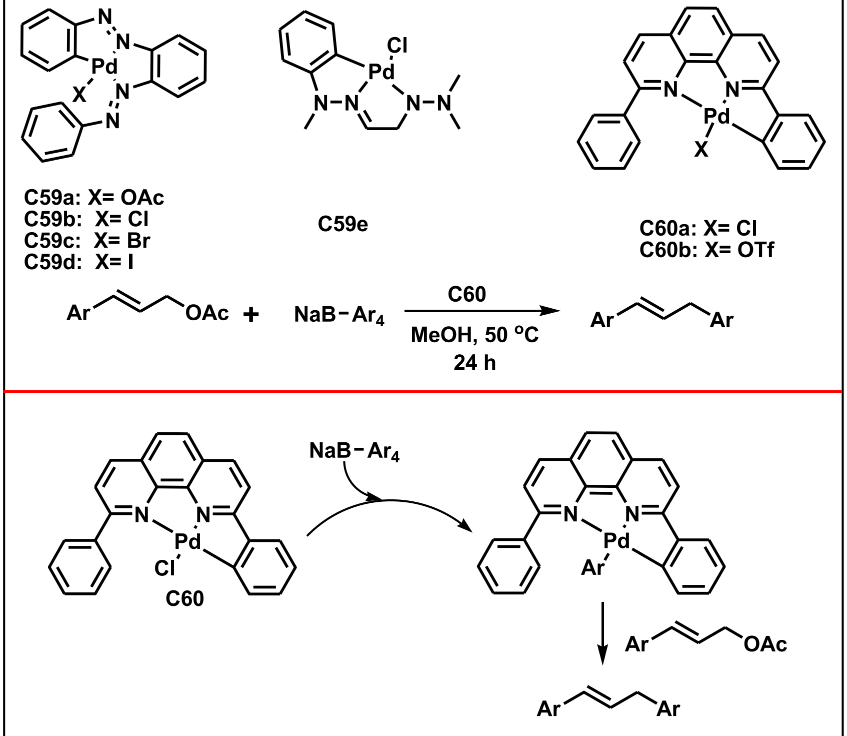
Considering the intermediate σ-donor capabilities, between 3-Cl-pyridine and P(OR)$_3$, and the low steric demand Navarro and coworkers reported participation of TEA as an inexpensive and easily removable ligand called “throw-away”ligand in the catalytic cycle. In this concept, a conversion of the stable Pd(II) complex to the active Pd(0) species is occur with the loss of the ligands attached to the metal center (“throw-away”ligands) (Scheme 37). They reported synthesis of a new complexes **C64a, C64c** and **C65a**



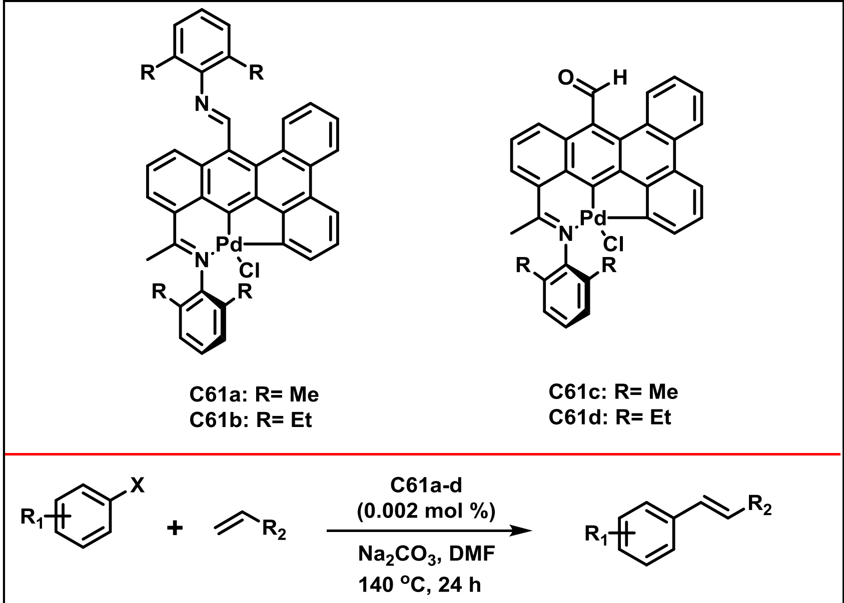
4-Bromoacetophenone + Phenylboronic acid $\xrightarrow[\text{solvent, base, 80 °C, 1 h}]{\text{Catalyst (1 mol \%)}}$ Suzuki coupling product

Catalyst	Base	Solvent	Conversion (%)	Yield (%)
C57a	K_3PO_4	DMA	99	94
C57b	K_3PO_4	Toluene	67	-
C58a	K_3PO_4	DMA	84	79
C58b	K_3PO_4	Toluene	99	91
C58c	KF	THF	99	95
C58d	K_3PO_4	THF	99	96
C58e	K_3PO_4	Toluene	99	93

Scheme 30. CNN pincer palladacycles used for the Suzuki coupling reaction.



Scheme 31. CNN type palladacycle used in the Suzuki and Heck coupling reactions.



C61a: R= Me
C61b: R= Et

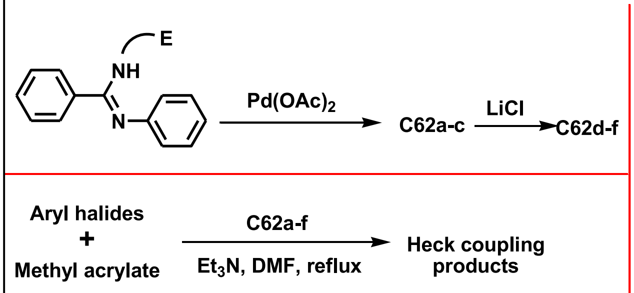
C61c: R= Me
C61d: R= Et

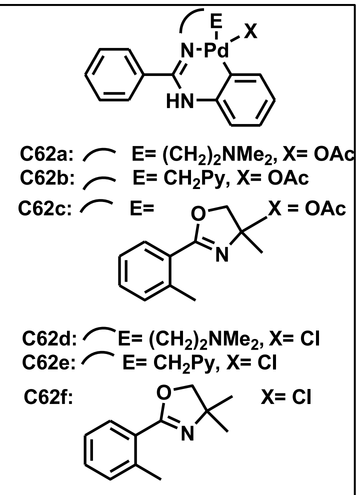
X= Br, R_1= H, R_2= Ph

Catalyst	Yield (%)	TON
C61a	67	33500
C61b	62	31000
C61c	70	35000
C61d	66	33000
$PdCl_2$	20	200

X = I, Br
R_1 = H, Me, COMe, OMe, NH_2, CN
R_2 = Ph, CONH*t*-Bu,
Yield = 12-93 %
TON = 9500-49500

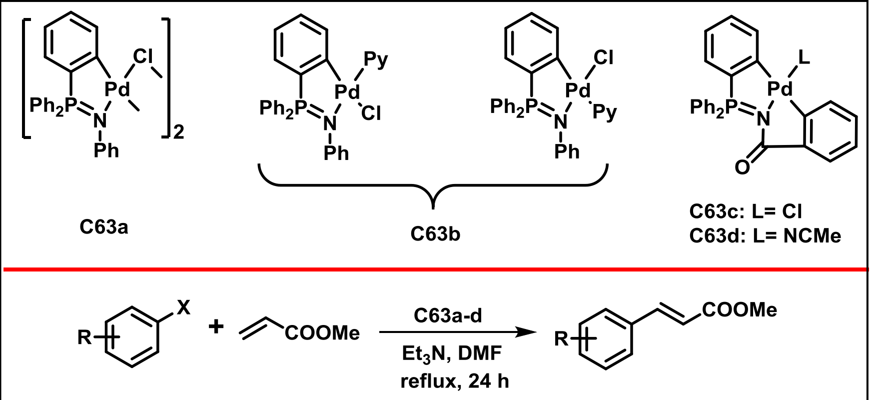
Scheme 32. Heck coupling reaction using Pd(II)-bisimino-functionalized dibenzo[a,c]acridine pincer complexes.





Catalyst	Base	Conversion (%)	Yield (%)
C62a	KF	78	70
C62b	K_3PO_4	86	79
C62c	K_3PO_4	99	91
C62d	KF	81	74
C62e	K_3PO_4	86	78
C62f	K_3PO_4	98	91

Scheme 33. Palladacycles containing pendant benzamidinate ligands for the Suzuki and Heck coupling reactions.



Catalyst	X	R	Yield (%)	TON
C63a (0.0001 %)	I	H	43.4	434000
C63a (1.0 %)	Br	CHO	8.9	9
C63b (0.0001 %)	I	H	52.6	526000
C63b (1.0 %)	Br	CHO	47.0	47
C63c (0.0001 %)	I	H	11.4	114000
C63c (1.0 %)	Br	CHO	14.4	14
C63d (0.0001 %)	I	H	45.6	456000
C63d (1.0 %)	Br	CHO	15	15

Scheme 34. *Ortho* palladated iminophosphoranes for the Heck coupling reaction.

from the corresponding [(NHC)–PdCl$_2$]$_2$ dimer using TEA (Fig. 9). The activity of catalyst **C64a** (1.0 mol %) was found to be high in the Suzuki coupling reaction of aryl chlorides and phenylboronic acid using NaOH as a base in ethanol at 25/50 °C [78a]. The complexes **C64b** and **C65a** (1.0 mol %) were also applied for the Buchwald-Hartwig reactions of aryl chlorides and different amines using KO*t*-Bu as a base in DME at 50 °C/room temperature [78b]. Furthermore, the complexes **C64a** and **C65a** (1 mol %) enabled coupling of activated aryl chlorides and deactivated aryl bromides with various olefins in Heck coupling using K$_2$CO$_3$ and TBAB in DMF at 140 °C [78c].

Similarly, Organ et al. [79] synthesized the [(IPent)PdCl$_2$(morpholine catalysts)] (**C64c-e, C65b** and **C66**) containing *trans*-oriented morpholine ligand from [(NHC)PdCl$_2$]$_2$ dimers with a slight excess of morpholine in CH$_2$Cl$_2$ at room temperature (Fig. 9). Of all the catalysts tested, complex **C64d** was acting as a highly efficient

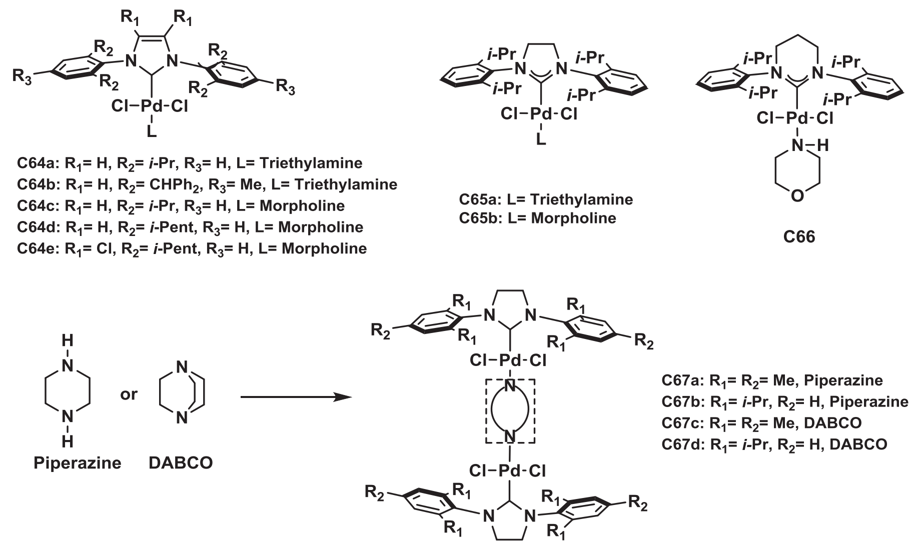
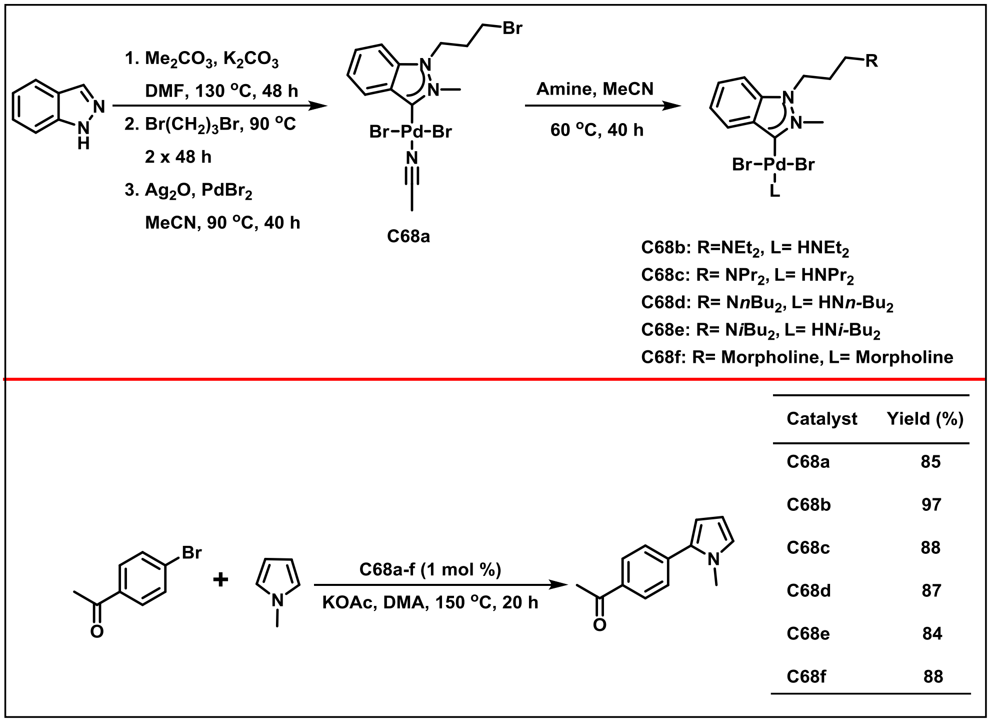


Fig. 9. Triethylamine, Morpholine, DABCO and Piperazine as the “throw-away” ligands used in coupling reactions.



Catalyst	Yield (%)
C68a	85
C68b	97
C68c	88
C68d	87
C68e	84
C68f	88

Scheme 35. Direct arylation of 1-methylpyrrole using amine functionalized *trans*-[$PdBr_2$(amine)(indyl)] complexes.

precatalyst for sulfination of sterically and electronically deactivated aryl bromides and chlorides with aryl sulfide partners using K*t*-OBu in toluene at 24 °C.

The piperazine and DABCO bridged dinuclear NHC–Pd(II) complexes (**C67a-d**) (Fig. 9) (0.25 mol %) also showed good activity for the Hiyama coupling reaction of various aryl chlorides with phenyltrimethoxysilane using *n*-Bu_4NF in toluene at 110 °C [80].

Huynh et al. [81] prepared a series of amine functionalized *trans*-[$PdBr_2$(amine)(indy)] complexes (**C68a-e**) by post coordinate modification of a single bromo alkyl functionalized precursors. All the complexes were applied as precatalysts for the direct arylation of 1-methylpyrrole using 4-bromoacetophenone in KOAc and DMA at 150 °C. It was observed that the least bulky diethylamine containing complex **C68b** gave excellent yields of the desired product (Scheme 35).

The complexes containing benzoxazole or benzothiazole (**C69a-d**) (Fig. 10) were also prepared from the corresponding imidazolium salts, $PdCl_2$, and benzoxazole or benzothiazole in the presence of

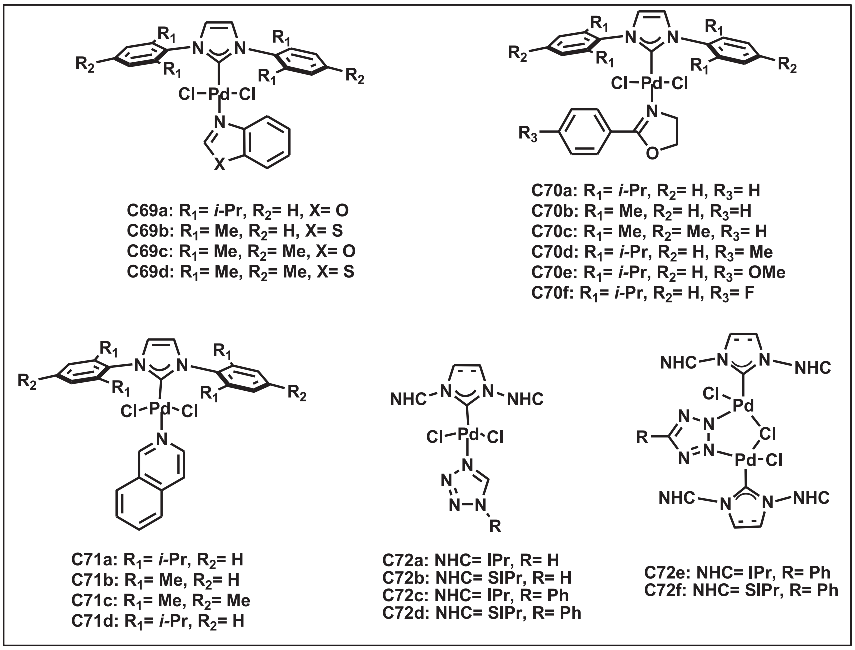
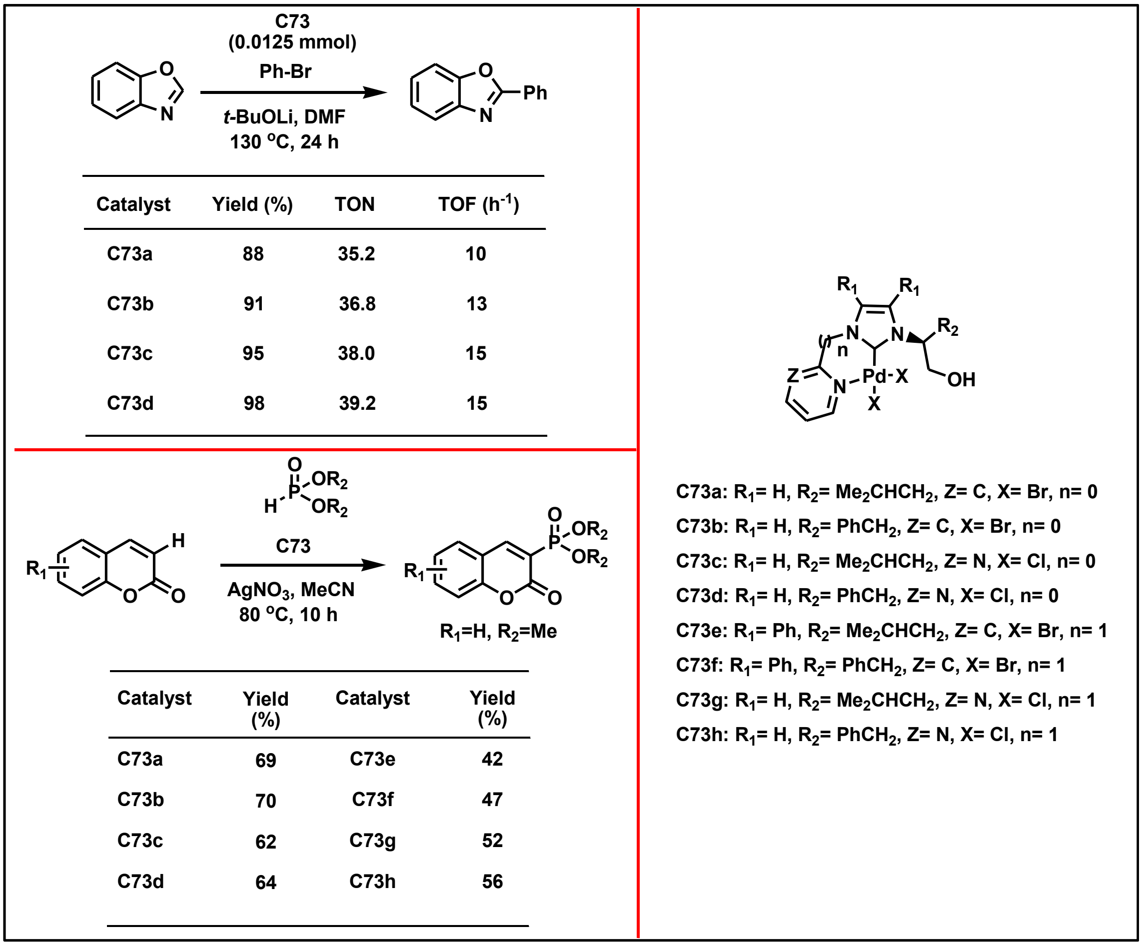


Fig. 10. NHC–$PdCl_2$-oxazole, thiazole, quinoline and tetrazole complexes for the coupling reactions.



Catalyst	Yield (%)	TON	TOF (h^{-1})
C73a	88	35.2	10
C73b	91	36.8	13
C73c	95	38.0	15
C73d	98	39.2	15

Catalyst	Yield (%)	Catalyst	Yield (%)
C73a	69	C73e	42
C73b	70	C73f	47
C73c	62	C73g	52
C73d	64	C73h	56

C73a: R_1= H, R_2= Me_2CHCH_2, Z= C, X= Br, n= 0
C73b: R_1= H, R_2= $PhCH_2$, Z= C, X= Br, n= 0
C73c: R_1= H, R_2= Me_2CHCH_2, Z= N, X= Cl, n= 0
C73d: R_1= H, R_2= $PhCH_2$, Z= N, X= Cl, n= 0
C73e: R_1= Ph, R_2= Me_2CHCH_2, Z= C, X= Br, n= 1
C73f: R_1= Ph, R_2= $PhCH_2$, Z= C, X= Br, n= 1
C73g: R_1= H, R_2= Me_2CHCH_2, Z= N, X= Cl, n= 1
C73h: R_1= H, R_2= $PhCH_2$, Z= N, X= Cl, n= 1

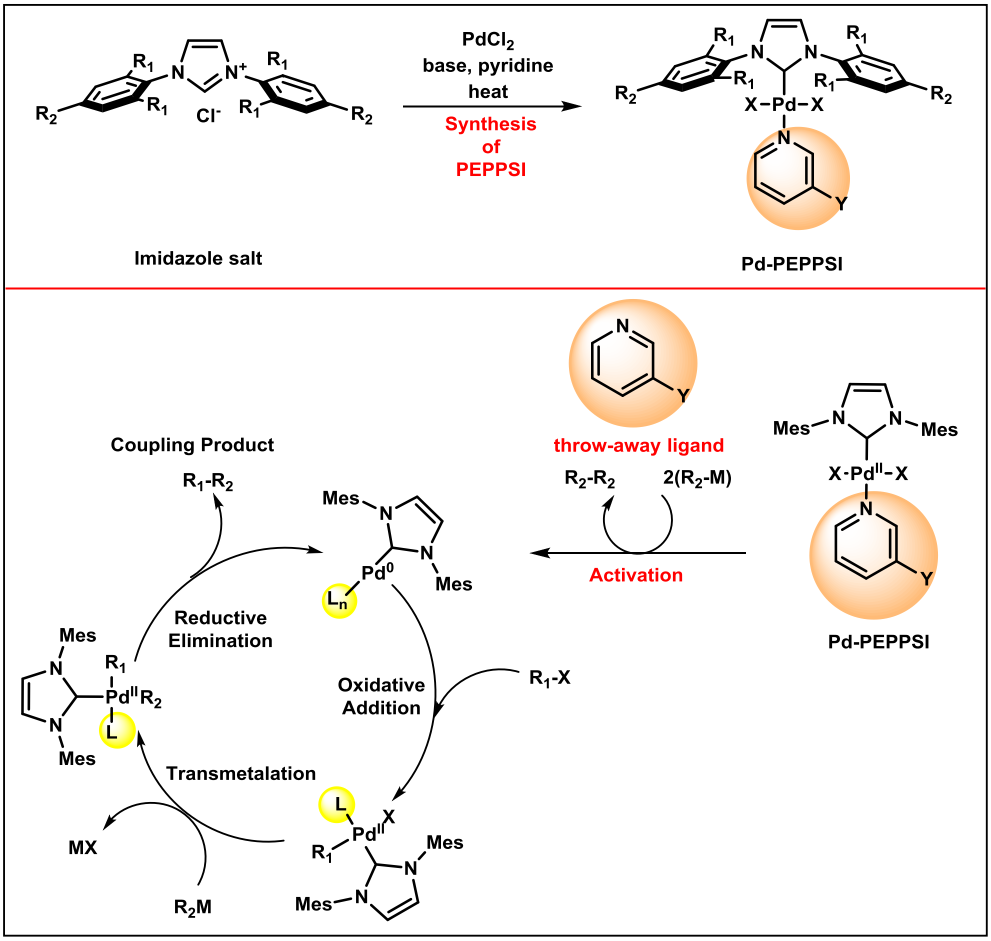
Scheme 36. C–H functionalization using Pd–NHC complexes containing pyridine/pyrimidines.

K_2CO_3 in THF at 65 °C in good yields [82]. The complexes showed good activity in the Suzuki coupling reactions of aryl as well as benzyl chlorides with arylboronic acids. The complex **C69a** (2.0 mol %) was successfully coupled various aryl chlorides with aryl boronic acids in KO*t*-Bu and *i*-PrOH:H_2O (1:1) at 80 °C.

The Pd(II)–NHC complexes of 4,5-dihydrooxazoles (**C70a-f**) [83] and NHC–$PdCl_2$-(iso)quinoline complexes (**C71a-d**) [84] were applied for the amination reaction using K*t*-OBu in dioxane at 90 °C and 110 °C respectively.

Yang et al. [85] synthesized mono and dinuclear Pd(II)–NHC complexes (**C72a-f**) stabilized by tetrazole ligands from the dimeric $[Pd(m\text{-}Cl)(Cl)(NHC)]_2$ compound and tetrazoles in different solvents at room temperature (Fig. 10). The activity of all the catalysts (0.25–0.5 mol %) were investigated for the Hiyama coupling of various aryl chlorides with phenyltrimethoxysilane using TBAF in toluene at reflux. They also synthesized a chelated NHC–Pd complexes (**C73a-h)** containing pyridine/pyrimidine hydroxyalkyl functionalized ligands [86a] *via* direct metallation of the corresponding imidazolium salts by $Pd(OAc)_2$ (Scheme 36). All the catalysts efficiently carried out the direct C–H bond arylation of various benzoxazoles using aryl bromides and *t*-BuOLi in DMF at 130 °C. They also reported the catalytic activity of these complexes towards selective phosphorylation of coumarins [86b].

The Pd catalysts (**C74a-c**) (Fig. 11) containing acyclic imino-NHC prepared from the corresponding imidoyl chlorides with 1-methylimidazole and $Pd(COD)Cl_2$ also reported for the aqua-phase Suzuki coupling reaction of aryl halide (Br and Cl) with arylboronic acids using KOH at 100 °C [87]. A copper and amine-free Sonogashira coupling reaction was carried out by using Pd complexes of N-functionalized NHC (**C74d**) in a mixed aqueous medium [88]. Recently, highly active 1,10-Phenanthroline NHC complexes (**C75a-b**) (Fig. 11) were applied to room temperature, the Suzuki coupling reaction of aryl chlorides in aqueous media [89]. Gade et al. [90a] reported oxazoline based NHC (**C76**) (Fig. 11) for the Heck and Suzuki coupling reactions, while Hor et al. [90b] used benzenimidazole functionalized Pd–NHC (**C77**) (Fig. 11) for the Suzuki coupling reaction. Hursthouse et al. [91] reported the pyridine functionalized hemilabile NHC–Pd complexes (**C78a**-**b**) for the Heck coupling and amination reactions of aryl iodides and bromides with olefins using various bases in NMP at 65–140 °C with good to excellent TON. Shreeve et al. [92] reported the synthesis and characterization of pyrazolyl functionalized imidazolium based ILs and hemilabile carbene Pd (II) complexes (**C79a-b**) (Fig. 11) for the Heck coupling reaction. Similarly, the pyrazolyl functionalized NHC–Pd complexes (**C80a-c**) based on 1-[2-(pyrazol-1-yl)phenyl]imidazole (Fig. 11) obtained by the carbene transfer reaction of the corresponding NHC–Ag complexes with $Pd(CH_3CN)_2Cl_2$ also applied for the Suzuki (*i*-PrOH:H_2O (1:1), Cs_2CO_3) and Heck (DMF:H_2O (1:1), K_2CO_3) coupling reactions of aryl iodides and bromides in aqueous medium [93]. The Triazole based NHC–Pd (**C81a-b**) also works well in Suzuki coupling reaction as reported by Ruzicka et al. [94].



Scheme 37. Synthesis and proposed 'throw-away' ligand mechanism of Pd-PEPPSI catalysts.

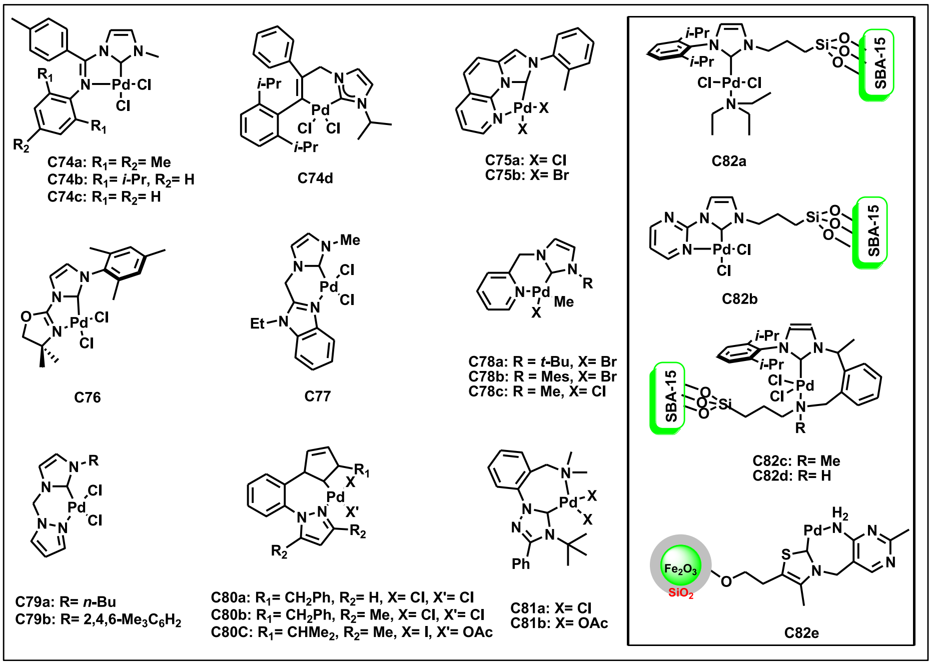


Fig. 11. Amine stabilized hemilabile NHC–Pd(II) complexes used in coupling reactions.

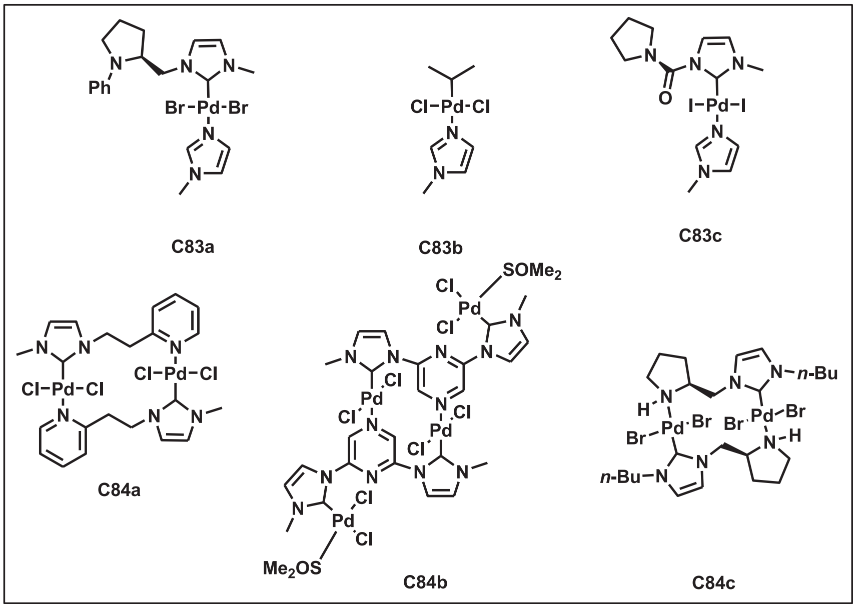


Fig. 12. Imidazole and pyridine stabilized hemilabile carbene Pd(II) complex.

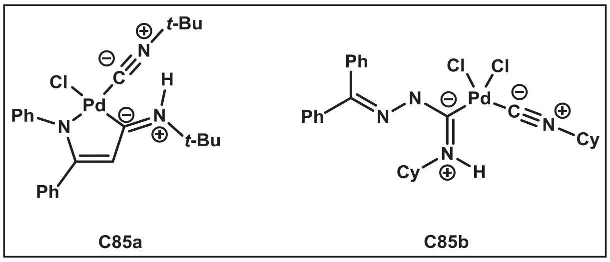


Fig. 13. Chelating and non-chelating Pd(II) diaminocarbene complexes.

The Pd—NHC catalysts **C82a-d** stabilized by different N ligands and immobilized on mesoporous SBA-15 silica (1.0 mol %) efficiently catalyzed the Suzuki coupling reaction of aryl chlorides and arylboronic acids using KOH as a base in *i*-PrOH at 82 °C (Fig. 9) [95a]. Recently, a similar Pd—NHC (**C82e**) based on Vitamin B1 supported on silica coated Fe_3O_4 NPs was reported for C—C coupling reactions [95b].

Considering the strong acidity of the H-2 proton, Batey et al. [96] investigated the formation of metal carbene complexes (**C83a**) (Fig. 12) derived from carbamoyl imidazolium salts for the Sonogashira coupling reactions. Shao et al. [97] reported Pd(II)—NHC-1-methylimidazole complex (**C83b**) for the Suzuki coupling of aryl sulfonates with arylboronic acids, while imidazole-coordinated monodentate NHC—Pd(II) complex (**C83c**) derived from proline was highly efficient for coupling arylboronic acids with carboxylic acid anhydrides in water at room temperature [98]. The Pd(II) complexes (**C84a**) containing mono, di and tridentate carbene ligand was also applied as a catalyst in C—C coupling reactions [99]. The theoretical studies of Pd(II)—NHC complex (**C84b**) based on multitopic pyrazine for the Suzuki coupling reaction was carried out by Roymahapatra et al. [100]. The proline containing dinuclear Pd(II)—NHC complex (**C84c**) showed good activity for the Heck coupling reaction in water [101].

The chelating (**C85a**) and non-chelating (**C85b**) Pd(II) diaminocarbene complexes exhibited a good catalytic activity for the Sonogashira and Suzuki coupling reactions than the traditional phosphine based catalysts (Fig. 13) [102].

5.2. PEPPSI themed analogues

Recently, NHC ligands have been found to be the best alternative to phosphane ligands as it can be acted as strong σ-donors. But its high instability towards air is the main obstacle to its use in metal catalysis. Hence, the NHCs are often generated *in situ* by the reaction of imidazolium salts with base. Alternatively, it can be stabilized by the use of additional pyridine ligand in the form of PEPPSI. Thus ‘Pyridine Enhanced Precatalyst Preparation, Stabilization and Initiation (PEPPSI)’ themed analogues have been attracted as a great attention for many transition metal catalyzed reactions [103]. The general procedure for preparation of Pd-PEPPSI involves the direct C—H insertion of the corresponding imidazolium salts with $PdCl_2$, in the presence of a base in neat pyridine derivatives (Scheme 37). PEPPSI is a Pd(II) precatalyst that can be reduced to active Pd(0). These catalysts showed outstanding air and moisture stability, so that it can be readily used in air and aqueous conditions.

These catalysts showed excellent catalytic activity in many cross-coupling reactions with high TON and TOF, due to non-coordinating and non-bulky ‘throw-away’ ligands, as demonstrated in the following general mechanism (Scheme 37). The role of pyridine is to attach and detach from the highly active Pd(0)—NHC complex in solution [103]. It involves a sequential double transmetalation of an organometallic reagent with the PEPPSI catalyst. The reductive elimination provides the catalytically active NHC—Pd(0)(L)n complex through dissociation of pyridine prior to oxidative addition into the aryl halide.

5.2.1. Imidazole based PEPPSI catalysts

The Organ's research group reported a series of air-stable, user-friendly and highly active imidazole based Pd-PEPPSI complexes (**C86**) as precatalysts (Fig. 14) for a different cross-coupling reaction. They introduced Pd-PEPPSI precatalysts with bulky NHC ligands as an alternative to Pd phosphine complexes [103].

In their first report they applied **C86a-c** precatalysts for the

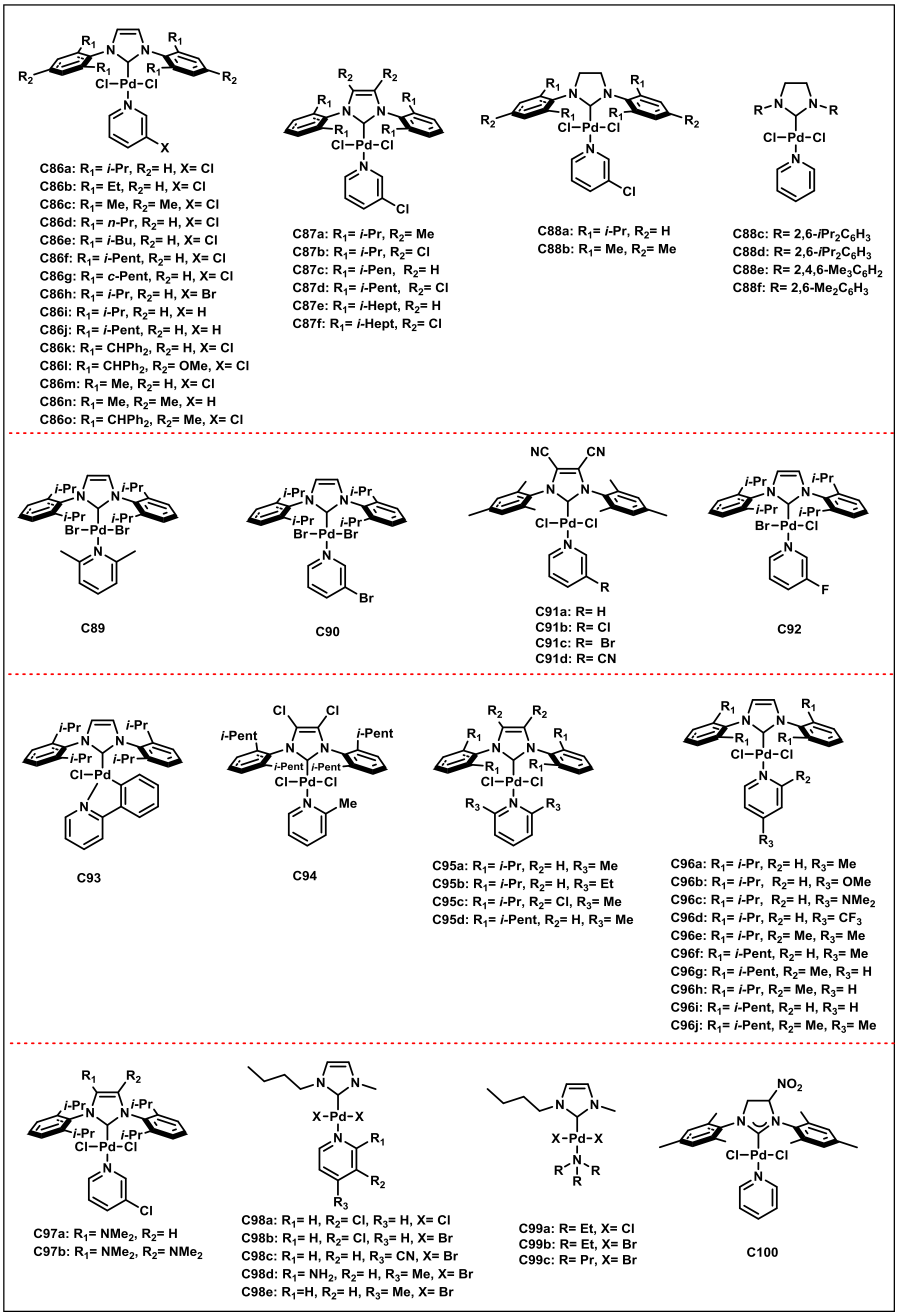
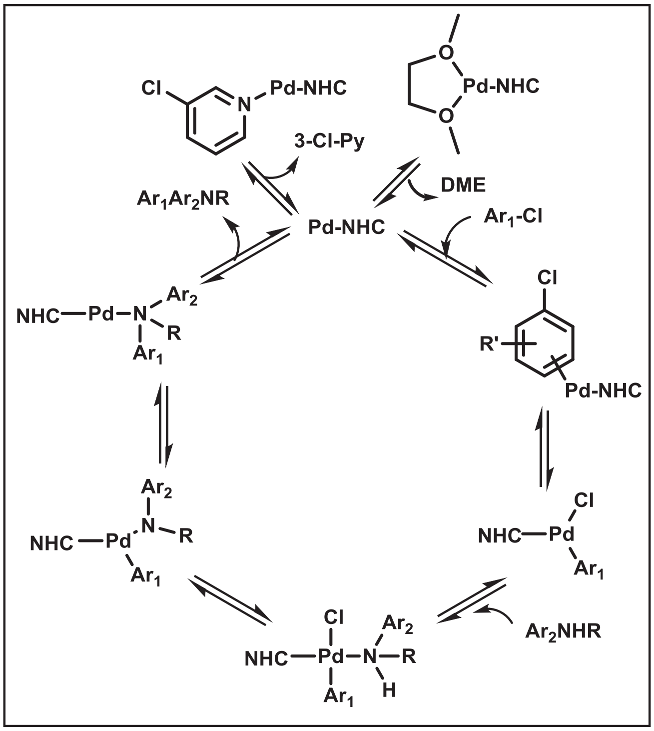


Fig. 14. Variety of Pd-PEPPSI scaffolds used as precatalysts in different coupling reactions.

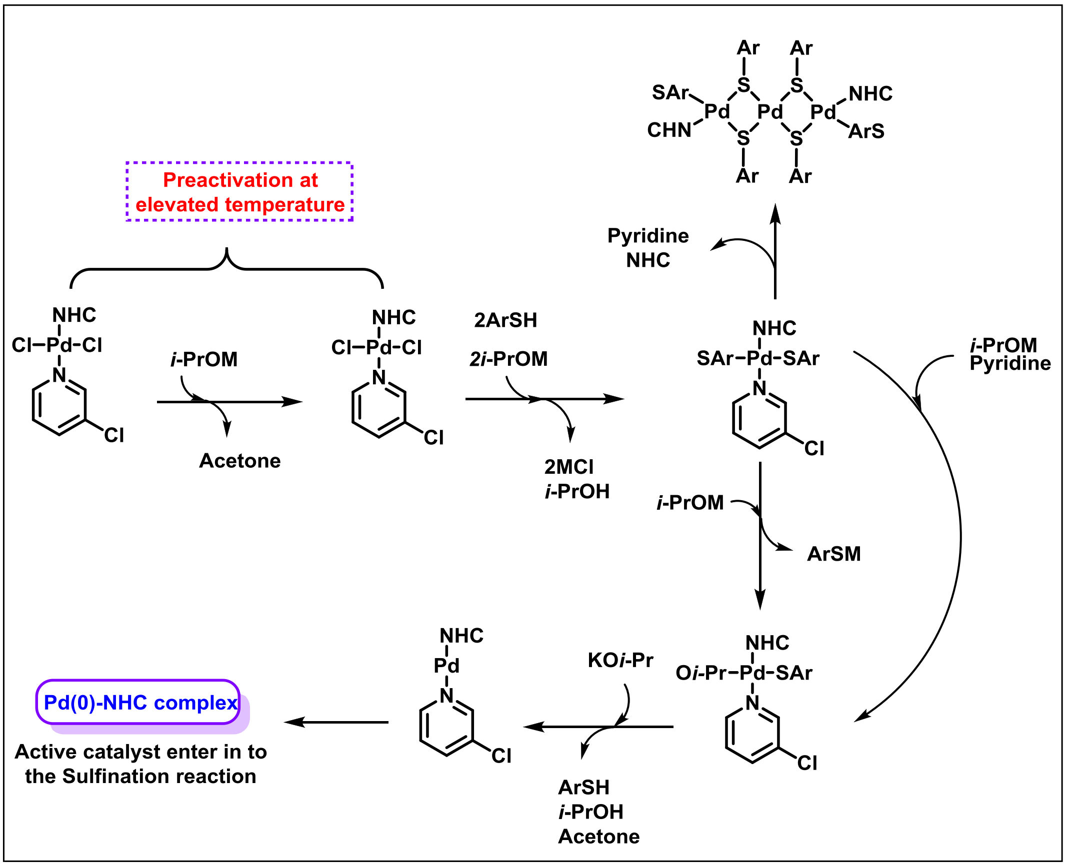


Scheme 38. The Proposed mechanism of NHC–Pd catalyzed amination of aryl chlorides with amines.

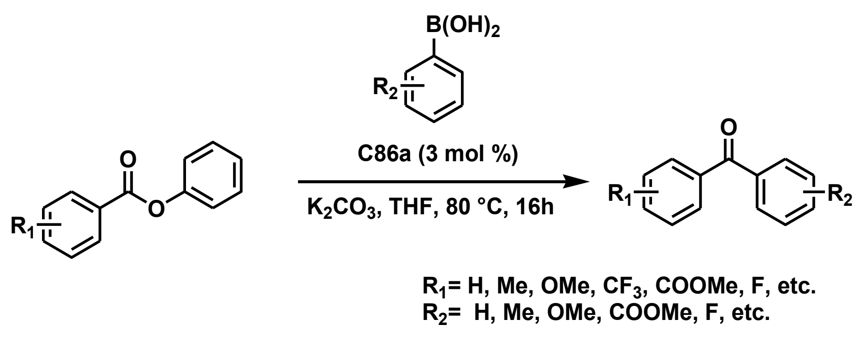
Suzuki coupling reaction of large variety of sterically hindered aryls and heteroaryls under four different methods (Method A: **C86a** (1 mol %), K*t*-OBu, *i*-PrOH, RT. Method B: **C86a** (2 mol %), dioxane, 60 °C. Method C: **C86a** (2 mol %), K_2CO_3, MeOH, 60 °C. Method D: **C86a** (2 mol %), KOH, dioxane, RT) [104].

As an extension, the catalysts **C86a, C86c** and **C86e-g** were successfully used for the synthesis tetra *ortho* substituted biaryls by Suzuki coupling reactions of *ortho* substituted sterically hindered aryl bromides and chlorides with aryl boronic acids in good yields under mild reaction conditions [105]. These results showed that for effective cross-coupling reactions there is essential of “flexible steric bulk” in the vicinity of the metal center. They also developed the first user friendly Negishi protocol (sp^3-sp^3) for coupling various alkyl and aryl partners in THF:DMI (2:1 or 1:3 or 1:2) or THF:NMP (2:1 or 1:2) mixture catalyzed by **C86a** (1 mol %) at room temperature to 65 °C in the presence of LiBr or LiCl [106a]. As an extension they compared, the activity of **C86f**, and **C87d-f** for the coupling of a variety of five-membered-ring heterocycles and 2-propylzinc bromide in THF or toluene [106b]. The catalysts **C86a**, **C86c-d**, **C86f**, **C87a-b**, **C87d**, and **C88a-b** also applied for the synthesis of biaryls under Kumada coupling reaction at room temperature [107]. In 2010, they introduced the exhaustive report on the structure activity relationship analysis of a range of Pd-PEPPSI complexes (**C86a**, **C86c**, **C86d**, **C86h**, **C86i**, **C86m**, **C88a-b**, **C89**, **C92** and **C93**) for different coupling reactions and developed the detailed catalytic cycle and the precatalyst activation model [108].

As an extension they carried out the rate and computational studies for the Buchwald-Hartwig amination reaction of substituted anilines using **C86a**, **C86f, C86j**, **C87a-b** and **C87g** complexes in the presence of Cs_2CO_3 in DME at 80 °C as well as in

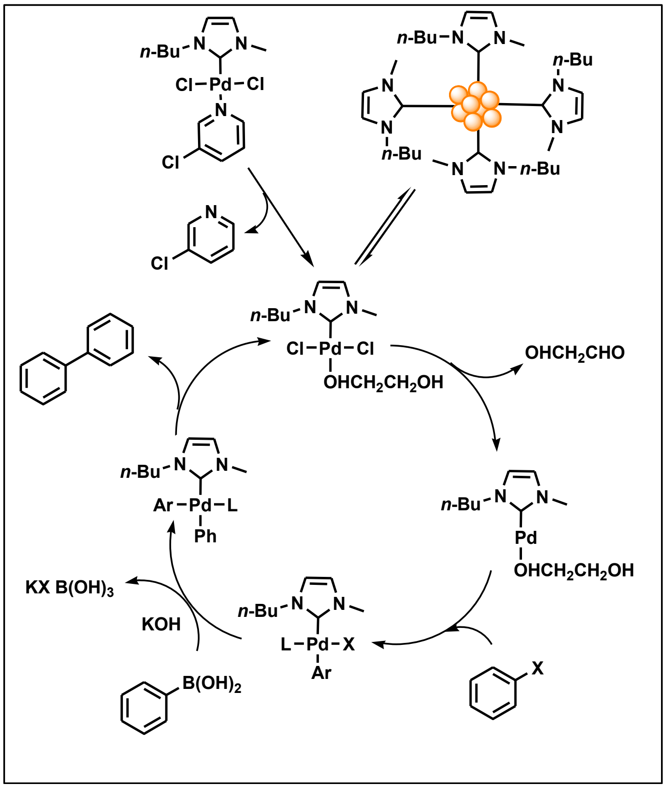


Scheme 39. Proposed NHC–Pd catalyzed sulphination of aryl chlorides.



Catalyst (3 mol %)	Yield (%)
C86a	84
C86c	45
C86f	42
C86l	71

Scheme 40. The Suzuki coupling of esters by C—O cleavage catalyzed by Pd-PEPPSI catalysts.



Scheme 41. Proposed mechanism for non-bulky NHC ligand for the Suzuki coupling reaction.

toluene at 110 °C [109]. The proposed NHC—Pd catalyzed amination of aryl chlorides with amines is shown in Scheme 38 [109a].

They also studied the effect of cation, solvent and the role of butoxide base in the Sulfination reaction by using various Pd-PEPPSI complexes (**C86a**, **C86i**, **C95a-c** and **C96a-j**) (Scheme 39) [110,103c].

Lavigne et al. [111a] studied the effect of the NMe$_2$ group present on the Pd-PEPPSI complexes (**C97a-b)** on the catalytic efficiency for the Buchwald–Hartwig amination reaction. Similarly, a novel and efficient Pd-PEPPSI precatalysts **C86o**, **C87b-d** and **C97a-b** [111b-c] were applied for C–N coupling reactions. Holdt et al. [112] studied the activity of **C86n** and **C91a-d** catalysts (0.01 mol %) with the structure [PdCl$_2${(CN)$_2$IMes}(3-R-py)] bearing the maleonitrile based NHC for the Suzuki coupling reaction in the presence of Na$_2$CO$_3$, TBAB in EtOH:CHCl$_3$ (39:1) at 80 °C. A Pd-PEPPSI catalysts **C86a** also showed good activity for the Suzuki coupling of esters by C—O cleavage (Scheme 40) [113]. A nitro based Pd-PEPPSI precatalyst (**C100**) was also active towards the Suzuki coupling of aryl chlorides and arylboronic acids at room temperature in aqueous solution [114].

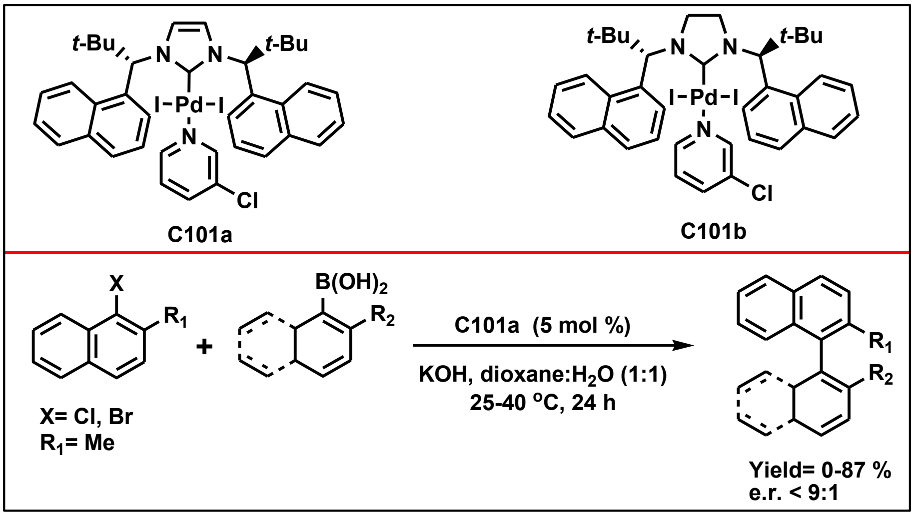
Trzeciak et al. [115] applied various Pd-PEPPSI type complexes (**C88a**, **C88b**, **C98a-e** and **C99a-c**) with non-bulky NHC ligands for the Suzuki and Hiyama coupling reactions. The proposed mechanism for non-bulky NHC ligand for the Suzuki coupling reaction is depicted in Scheme 41. The Hg(0) test suggests the homogeneous reaction pathway of the reaction that involves participation of active soluble palladium species.

Kundig et al. [116] synthesized new chiral Pd-PEPPSI complexes containing chiral NHC ligands based on 2,2-dimethyl-1-(o-substituted aryl)-propan-1-amines (**C101a-b)** for asymmetric Suzuki coupling reaction giving atropisomeric biaryl products (Scheme 42). It was observed that complex **C101a** (5 mol %) achieved best results in the asymmetric Suzuki coupling of 1-halo-2-substituted naphthalenes with sterically hindered boronic acids in the presence of KOH in dioxane:water (1:1) mixture at 25–40 °C giving modest to good enantiomeric ratio.

A series of new highly active unsymmetrically substituted Pd-PEPPSI catalysts (**C102**–**C106**, 0.5 mol %) (Fig. 15) synthesized from Pd-isonitriles were applied to the Suzuki coupling reaction of chlorobenzene and 2,5-dimethylphenylboronic acid using KO*t*-Bu as a base in EtOH at room temperature [117]. The catalysts (2 mol %) were also applied to the Negishi coupling of chloro or bromobenzenes, mesityl magnesium bromide and ZnCl$_2$ in NMP at 70 °C. Similarly, Yang et al. [118] synthesized a novel chiral NHC—Pd complexes (**C107a-d**) and applied in copper-free Sonogashira coupling reaction.

Shi et al. [119] prepared a series of Pd-PEPPSI catalysts (**C108a-f**) with alkyl bridges of different chain lengths (n = 2–10) by refluxing corresponding imidazolium salt, with PdCl$_2$ in pyridine and K$_2$CO$_3$. The catalysts **C108a-c** (0.5 mol %) were successfully tested in the Heck coupling reaction of aryl bromides and styrene with good activity (yield = 66–77%, *E*:*Z* = 5.2–10.0:1) in toluene and K$_2$CO$_3$ at 110 °C, while complexes **C108c-f** (0.5 mol %) showed excellent activity (yield = 87–95%, *E*:*Z* = 5–29:1) in DMF under similar reaction condition (Scheme 43).

Recently, Organ et al. [120] immobilized Pd-PEPPSI complex onto silica gel (**C109**) (Fig. 16) and successfully applied as a heterogeneous catalyst for the Negishi coupling reaction of heteroaryl chlorides under both batch and continuous flow operation. The similar catalyst immobilized on silica (**C110a**) was reported by



Scheme 42. Chiral Pd-PEPPSI complexes used for asymmetric Suzuki coupling reaction.

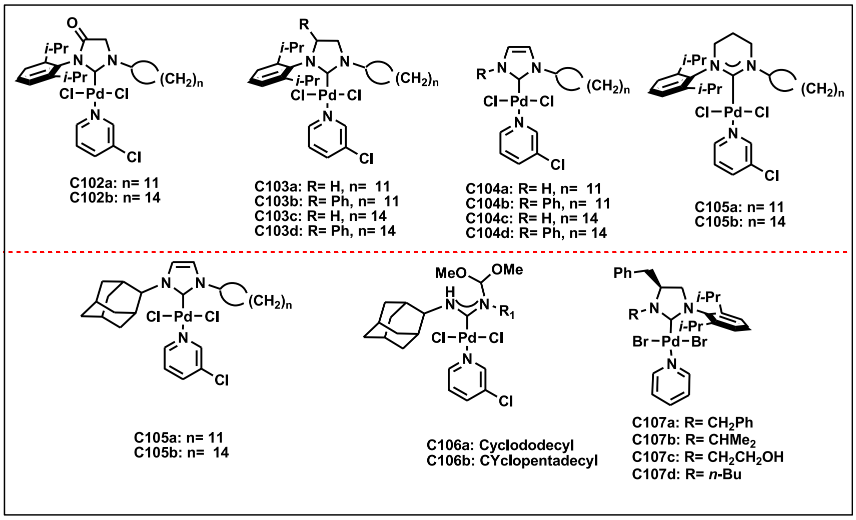
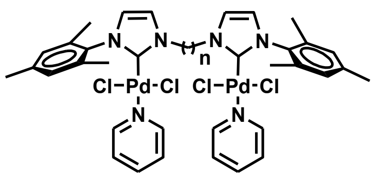


Fig. 15. Unsymmetrically substituted Pd-PEPPSI catalysts used for various coupling reactions.

Reaction conditions	Catalyst (0.5 mol %)	Yield (%)	*E:Z*
Ph-Br, Styrene, K_3CO_3 Toluene, 110 °C, 18 h	C108a	77	8.6:1
	C108b	66	10:1
	C108c	75	5.2:1
Ar-Br, Styrene, K_3CO_3 DMF, 110 °C, 23 h, (Ar = C_6H_5, p-OMeC_6H_4, p-FC_6H_4	C108c	93-95	17-25:1
	C108d	89-91	5-29:1
	C108e	91-93	11-23:1
	C108f	87-89	12-23:1



C108a: n=2
C108b: n=3
C108c: n=4
C108d: n=5
C108e: n=6
C108f: n=10

Scheme 43. Heck reaction using Pd-PEPPSI with alkyl bridges of different chain lengths (n = 2–10).

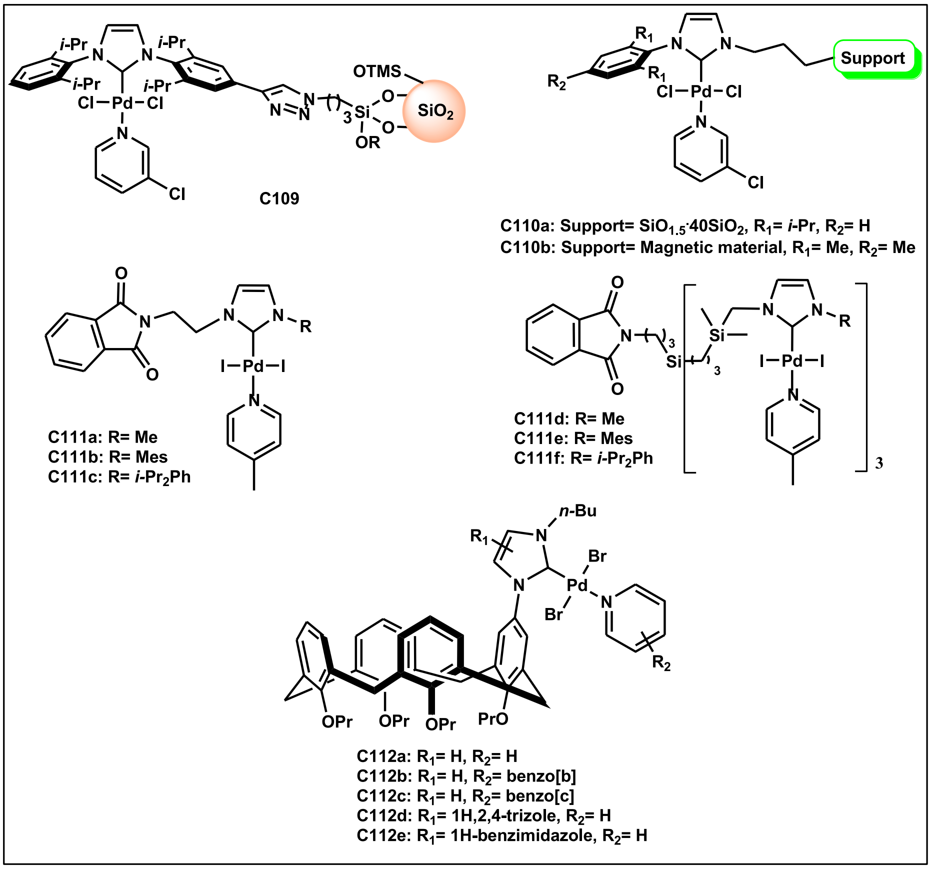
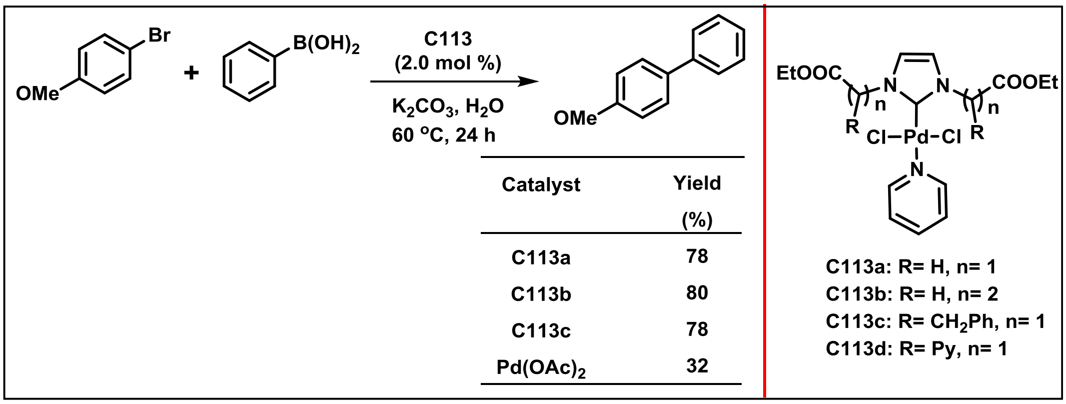


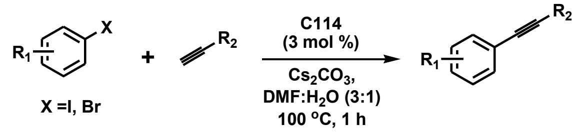
Fig. 16. Recyclable Pd-PEPPSI-NHC catalysts used for the Heck coupling reaction.



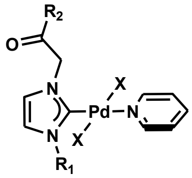
Catalyst	Yield (%)
C113a	78
C113b	80
C113c	78
Pd(OAc)$_2$	32

Scheme 44. Amino acid derived PEPPSI-type Pd—NHC complexes used in coupling reactions.

Pleixats et al. [121] and used as recyclable catalysts for the Heck, Suzuki and Sonogashira coupling reactions. The Pd-PEPPSI complex supported on magnetic material (**C110b**) also applied to the Suzuki coupling reaction of aryl bromides and phenylboronic acid in the EtOH:H$_2$O mixture with TON > 87000 [122]. The catalyst also showed good performance for aryl chlorides at 100 °C and could be recycled 21 runs. Flories et al. [123] applied recyclable heterogeneous and homogeneous trimetallic Pd-PEPPSI-NHC catalysts (**C111a-f**) (0.5 mol %) for the Heck coupling reaction of aryl iodides and methyl acrylate using Et$_3$N in DMF at 65 °C. Considering the attached set of podand arms on calixarene skeleton and wide functional groups tolerance, Darbost et al. [124] attached Pd-PEPPSI-NHC complexes (**C112a-e**) on calix [4]arenes. The catalysts were prepared starting from monobromide calix [4]arene-imidazolyl, triazolyl and benzimidazolyl salts by Ullmann type coupling in the presence of CuI/DMEDA and Cs$_2$CO$_3$ in DMF followed by quaternization using *n*-BuBr. Direct C—H insertion of salts in PdCl$_2$ in pyridine at 80 °C in the presence of K$_2$CO$_3$ and KBr afforded the results complexes in good to excellent yields. In addition, the corresponding quinoline or isoquinoline derivatives **C112b** and **C112c** obtained in dioxane. After extensive optimization of all the catalysts, complex **C112d** (0.08 mol %) was applied for the Suzuki

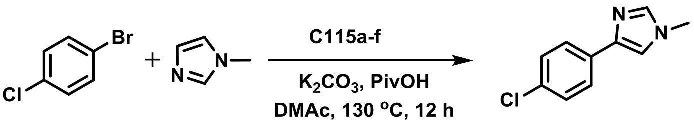


Catalyst (3 mol %)	R_1	R_2	Yield (%)
C114a	H, COMe, Me, Br	Ph, Py etc.	4-76
C114b			11-66
C114d	H, COMe, Me, CN, NO_2, CHO	H, NMe_2	23-96
C114c			25-99

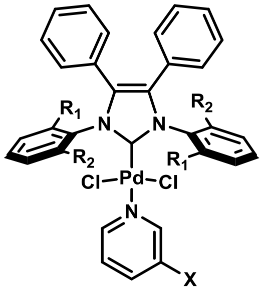


C114a: R_1= CH_2Ph, R_2= *t*-Bu, X= Br
C114b: R_1= CH_2Ph, R_2= NH*t*-Bu, X= Cl
C114c: R_1= Mes, R_2= NHPh, X= Cl
C114d: R_1= *i*-Pr, R_2= 2,6(*i*-Pr)$_2C_6H_3$, X= Cl

Scheme 45. N-functionalized Pd-PEPPSI-NHC catalysts for the Sonogashira coupling reaction.



Catalyst (1 mol %)	Yield (%)	Selectivity (%)
C115a	73	97
C115b	83	97
C115c	88	98
C115d	71	98
C115e	66	97
C115f	86	97



C115a: R_1= Me, R_2= H, X= Cl
C115b: R_1= Me, R_2= Me, X= Cl
C115c: R_1= Et, R_2= Et, X= Cl
C115d: R_1= Me, R_2= H, X= H
C115e: R_1= Me, R_2= Me, X=H
C115f: R_1= Et, R_2= Et, X= H

Scheme 46. Pd-PEPPSI catalysts containing tetraarylimidazolium carbenes for regioselective C5-arylation of imidazoles.

coupling of various aryl bromides with arylboronic acids in K_3PO_4 and dioxane at 100 °C.

The amino acid derived (glycine, *β*-alanine and phenylalanine) PEPPSI-type Pd—NHC complexes (**C113a-c**) (2 mol %) successfully coupled aryl/benzyl halides with phenylboronic acid/pinacol ester in the presence of K_2CO_3 and TBAB in H_2O at 60 °C (Scheme 44) [125].

Similarly, Ghosh et al. [126a-b] introduced series of N/O functionalized Pd-PEPPSI-NHC catalysts (**C114a-b**) for various coupling reactions. The catalysts (3 mol %) were applied to amine-free Sonogashira coupling reaction of aryl iodides with substituted acetylenes in Cs_2CO_3, CuBr (10 mol %), DMF:H_2O (3:1) at 100 °C. Whereas, **C114c-d** were applied for the fluoride-free Hiyama, as well as Cu and amine-free Sonogashira couplings in aqueous medium (Scheme 45) [126c].

Recently, Liu et al. [127] prepared Pd-PEPPSI catalysts containing tetraarylimidazolium carbenes (**C115a-f**) by the condensation of anilines and benzyl (Scheme 46). The obtained α-diimines subsequently cyclizes with chloromethyl ethyl ether followed by a one-pot reaction with $PdCl_2$ in pyridine or 3-chloropyridine in the presence of K_2CO_3 to afford the **C115a-f**. After optimization of various parameters, catalysts **C115f** (1.0 mol %), was applied for regioselective C5-arylation of imidazole with aryl bromides in PivOH, K_2CO_3 and DMAc at 130 °C (Scheme 46).

5.2.2. *Benzimidazole based PEPPSI catalysts*

Organ and coworkers [107] applied the benzimidazole based Pd-PEPPSI catalysts **(C116a-c** and **C118)** for the synthesis of biaryls under Kumada coupling reaction at room temperature (Fig. 17). Similar catalysts based on (benzimidazolin-2-ylidene) (**C117**) was synthesized by Baker et al. [128] and applied for the Heck and Suzuki coupling reactions of aryl halides using K_2CO_3 as a base in DMF. Yasar et al. [129] reported Pd(II)-PEPPSI complexes based on benzimidazole (**C119a-f**) (1 mol %) for the Suzuki coupling reactions of electron-rich and electron-poor aryl chlorides in aqueous DMF using K_2CO_3 at 80 °C. Pd-PEPPSI type complexes (**C120** and **C121**) bearing abnormal and normal NHC ligands based on benzimidazole were also applied to the Heck, direct C—H arylation, and decarboxylative coupling reactions [130]. Pd—NHCs of symmetrically and unsymmetrically substituted benzimidazolium salts of different 9-alkylfluorenyls (**C122a-c**) were applied to the Suzuki coupling reaction of aryl chlorides [131].

5.2.3. *Acenaphthyl, pyrene and phenanthroline based PEPPSI catalysts*

Liu et al. [132] reported Pd-PEPPSI complexes (**C123a-b**) containing bulky [(1,2-di-(*t*-butyl)acenaphthyl)] (DtBu-An) group for the Suzuki coupling reaction of heteroaryl chlorides with arylboronic acids using K_3PO_4 as a base in EtOH at 80 °C. Recently they

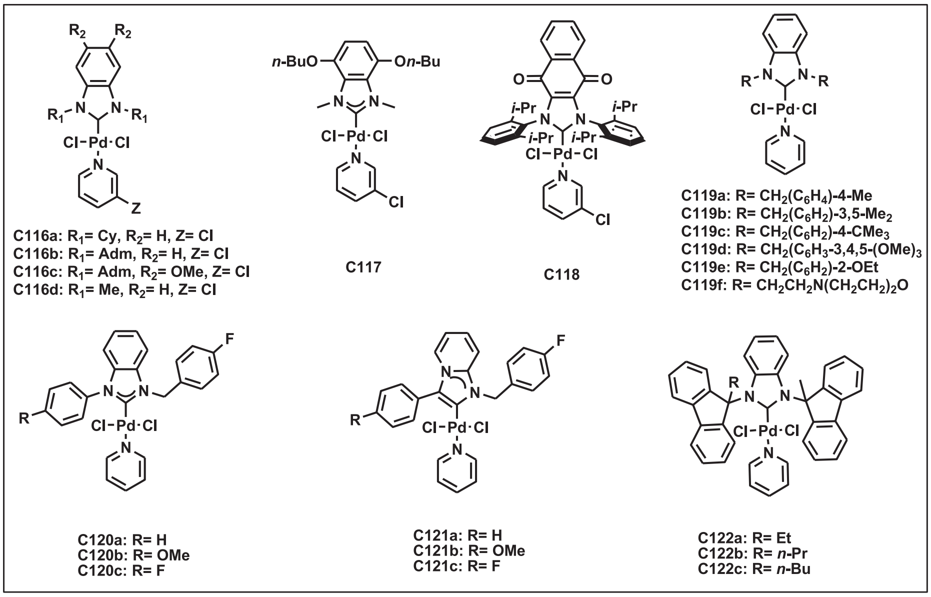


Fig. 17. Benzimidazole based Pd-PEPPSI catalysts used in coupling reactions.

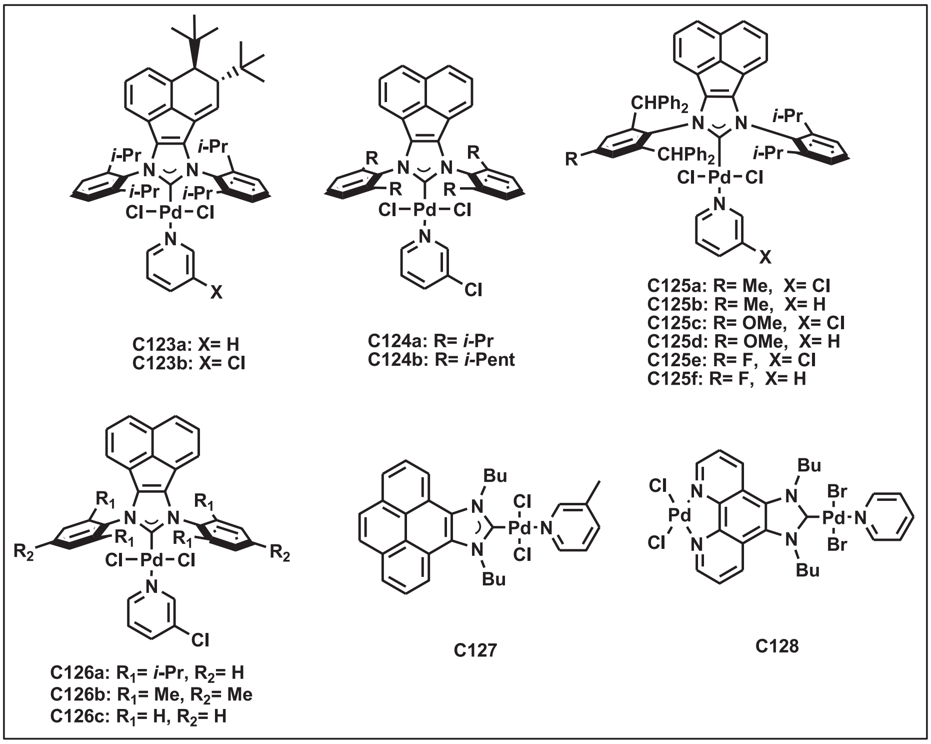
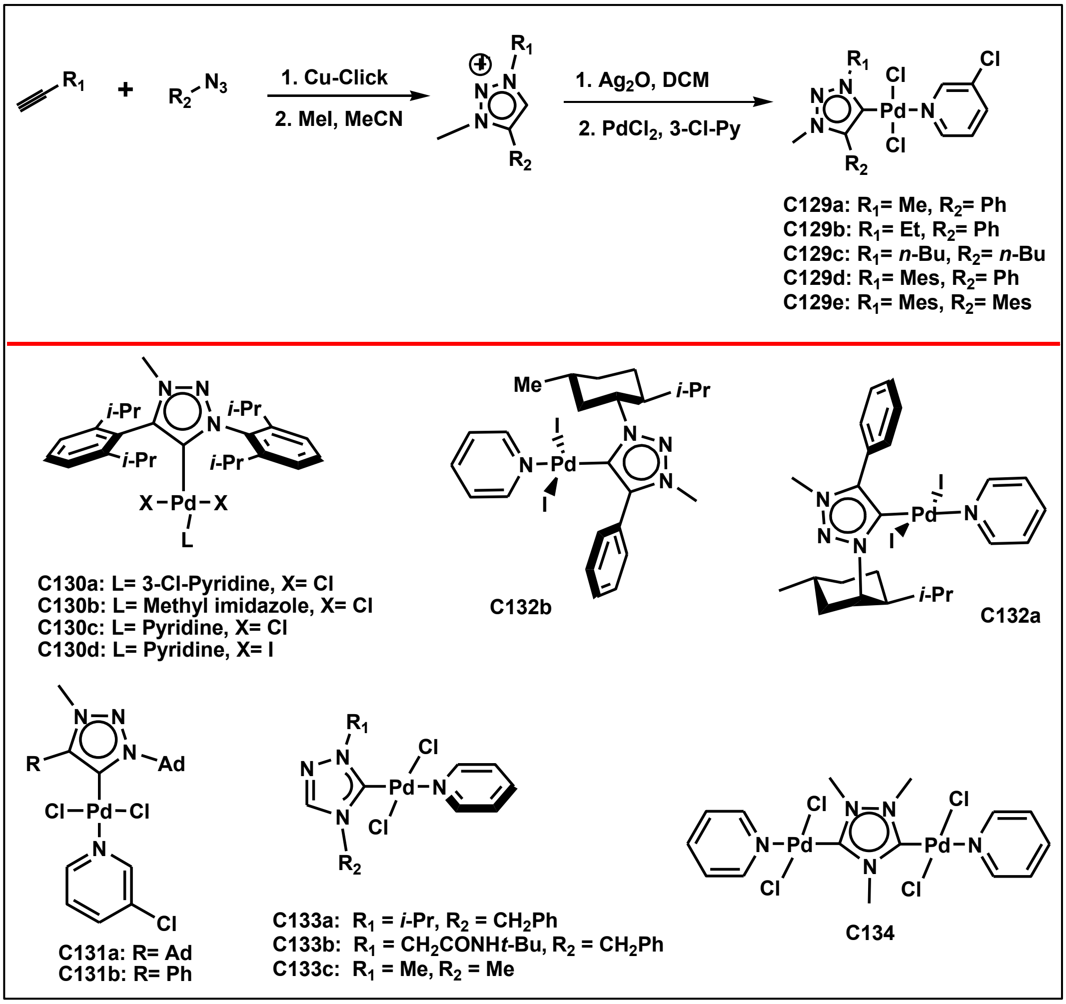


Fig. 18. Acenaphthyl, pyrene and phenanthroline based Pd-PEPPSI catalysts used in coupling reactions.

used bulky and flexible Pd-PEPPSI-IPentAn complexes (**C124a-b**) for the synthesis of sterically hindered biaryls in air [133] and flexible sterically bulky bis(imino)acenaphthene (BIAN)-supported Pd—NHC catalysts (**C125a-f**) in Buchwald-Hartwig amination in the air [134]. Highly efficient acenaphthoimidazolylidene palladium complexes (**C126a-c**) were also applied for the Suzuki and amination reaction of aryl chlorides [135]. NHC-based on pyrene—imidazolylidene catalyst (**C127**) was tested in the Suzuki coupling and α-arylation of ketones (Fig. 18) [136]. Türkmen et al. [137] used the imidazo{ [4,5-f] [1,10]-phenanthrolin}l-2-ylidene based Pd— PEPPSI complex (**C128**) for the Suzuki (aryl chlorides, phenylboronic acid, Cs_2CO_3, DMF/H_2O at 100 °C) and Heck (aryl bromide, styrene/*n*-butyl acrylate, Na_2CO_3, DMF 100 °C) coupling reactions.

5.2.4. Triazol based PEPPSI catalysts

The triazole NHCs are more basic than classical imidazole-2-ylidene NHCs due to the presence of one additional nitrogen



Scheme 47. Triazol based Pd-PEPPSI used in coupling reactions.

adjacent to the carbon bonding site that have remarkable impact on the working mode of the catalyst due to the decreased Pd-carbene bond stability [138]. In this connection, Albrecht et al. [139] synthesized a series of C5-bound 1,4-di(2,6-diisopropylphenyl)-1,2,3-triazol-5-ylidene (tzIPr) based PEPPSI type Pd complexes (**C129a-e**) and applied to the Suzuki coupling reaction (Scheme 47). The activity of these complexes depends upon the steric effects. Thus the catalyst having less bulky substituents showed better activity than bulkier substituents in the *ortho* positions, which is in contrast to the trends observed with the imidazole-2-ylidene congeners. It was observed that 35% conversion was attained after 15 min by catalyst **C129a**, while 60 min required for catalyst **C129e**.

Hong and coworkers [140a] synthesized 1,4-di(2,6-diisopropylphenyl)-1,2,3-triazol-5-ylidene (tzIPr) based PEPPSI type Pd complexes (**C130a-b**) for the Suzuki coupling reaction of various types of aryl chlorides and aryl boronic acids. The complex **C130b** showed excellent activity than **C130a** in the Suzuki coupling reaction of 1-chloro-2,6-dimethylbenzene and phenylboronic acid in ethanol at room temperature, due to slower dissociation of the imidazole ligand as compared to pyridine [140b].

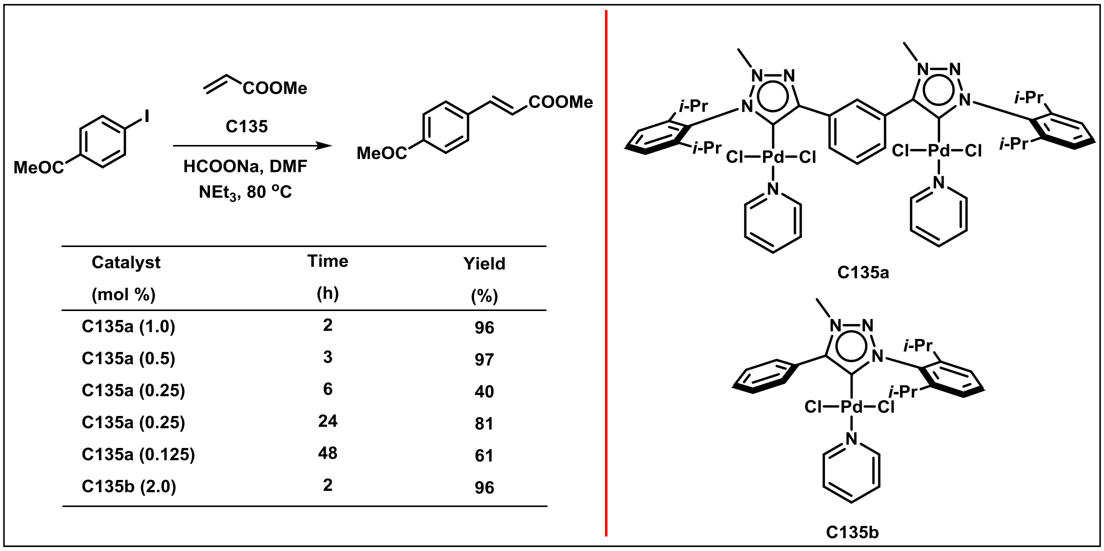
The PEPPSI type Pd-complexes (**C131a-b**) containing bulky mesoionic 1,2,3-triazolium carbenes (tzNHC) based on the adamantyl groups were prepared from 1-azidoadamantane and 1-ethynyladamantane. It was observed that catalysts gave good product yields for the Hiyama (NaOH, 1,4-dioxane, H_2O, 80 °C) and Suzuki (*t*-BuOK, EtOH, 50 °C) coupling reactions of aryl bromides [141].

Sankararaman et al. [142] synthesized menthyl and neomenthyl substituted enantiopure bis(1,2,3-triazol-5-ylidene)PdI_2 complexes and PEPPSI type (1,2,3-triazol-5-ylidene) (pyridine)PdI_2 complexes (**C132a-b**) for the Suzuki coupling reaction of aryl bromides and arylboronic acids in the presence of *t*-BuOK in ethanol at room temperature.

The **C133a-b** (2 mol %) and **C88c-f** were applied for fluoride-free Hiyama as well as copper and amine free Sonogashira coupling of aryl halides with phenyltrimethoxysilane using NaOH, in dioxane:H_2O (2:1) at 80 °C [126c]. Mata et al. [143] synthesized benzofurans by domino approach through the sequential Sonogashira/Hydroalkoxylation couplings catalyzed by **C133c** and **C134** catalysts.

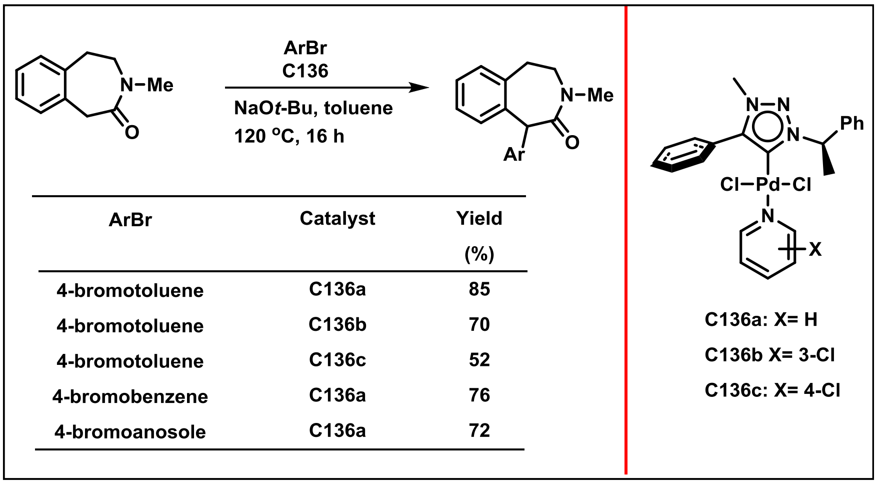
Crudden et al. [144] applied a PEPPSI type mono and bimetallic 1,2,3-triazol-5-ylidene mesoionic carbene (MIC)–Pd complexes (**C135a-b**, 2.0 mol %) for the Heck coupling reaction of aryl halides (I and Br) and methyl acrylate using HCO_2Na (10 mol %), Et_3N as a base in DMF at 80–125 °C (Scheme 48).

Similarly, Sarkar et al. [145] synthesized PEPPSI type mesoionic carbene (MIC)–Pd complexes (**C136a-c**) (5.0 mol %) that enabled α-arylation by using a 4-bromotoluene in the presence of NaO*t*-Bu in



Catalyst (mol %)	Time (h)	Yield (%)
C135a (1.0)	2	96
C135a (0.5)	3	97
C135a (0.25)	6	40
C135a (0.25)	24	81
C135a (0.125)	48	61
C135b (2.0)	2	96

Scheme 48. Mono and bimetallic 1,2,3-triazol-5-ylidene mesoionic carbene (MIC)–Pd complexes for the Heck coupling reaction.



ArBr	Catalyst	Yield (%)
4-bromotoluene	C136a	85
4-bromotoluene	C136b	70
4-bromotoluene	C136c	52
4-bromobenzene	C136a	76
4-bromoanosole	C136a	72

Scheme 49. 1,2,3-triazol-5-ylidene mesoionic carbene (MIC)–Pd complexes for α-arylation and methylation.

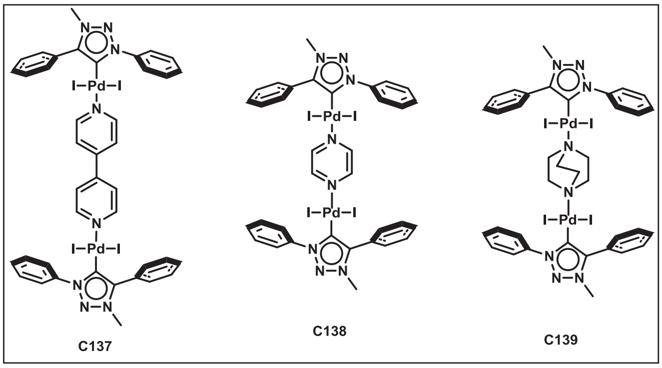


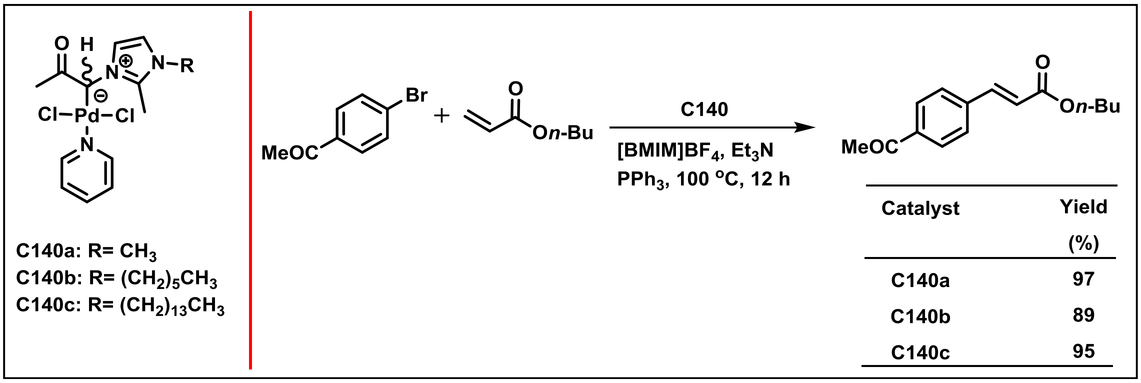
Fig. 19. Bipyridine, pyrazine and DABCO bridged Pd-PEPPSI complexes used in coupling reactions.

toluene at 120 °C. All the catalysts (2.5 mol %) were also highly active in the Suzuki coupling reaction of aryl halides and phenylboronic acid in K_2CO_3 and H_2O:dioxane (3:2) at room temperature (Scheme 49).

Sankararaman et al. [146] prepared a series of 1,2,3-triazolylidene based mononuclear and PEPPSI type Pd(II) diiodo complex (**C130d**), bridged 4,4′-bipyridine (**137**), pyrazine (**138**) and DABCO (**139**) PEPPSI complexes (Fig. 19). The catalyst **C130d** (1.0 mol %) efficiently carried out the Suzuki coupling of aryl halides with phenylboronic acid in *t*-BuOK and EtOH at room temperature.

5.2.5. Miscellaneous PEPPSI catalysts

The zwitterionic Pd complexes (**C140a-c**) synthesized by the reaction of 1-alkyl-2-methyl-1H-imidazoles and $PdCl_2$ in DMF in the presence of pyridine and Cs_2CO_3 at room temperature were acts as a recyclable catalyst for the Heck coupling reaction of aryl halides with *n*-butyl acrylate in the presence of PPh_3 (4.0 mol %) and Et_3N in [bmim][BF_4] at 100 °C (Scheme 50) [147].



Catalyst	Yield (%)
C140a	97
C140b	89
C140c	95

Scheme 50. Zwitterionic Pd-PEPPSI complexes for the Heck coupling reaction in IL.

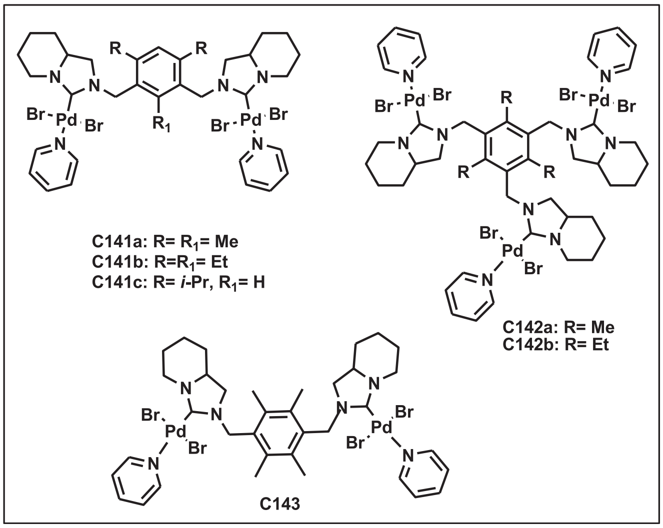


Fig. 20. Di and tri nuclear Pd complexes bearing piperidoimidazolin-2-ylidenes anchored to benzene ring for coupling reactions.

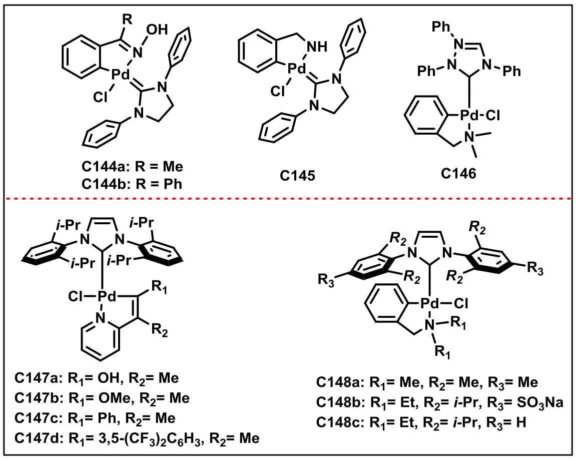
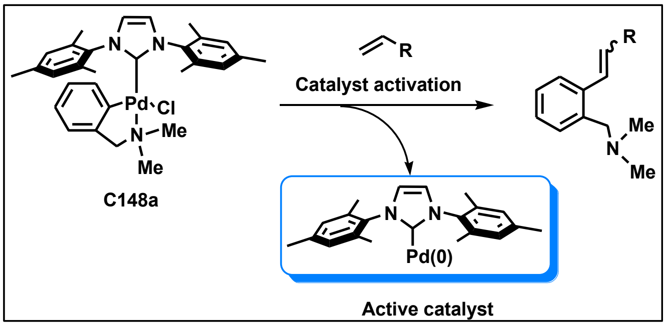


Fig. 21. Monoligated imine-Pd–NHC palladacycles used in coupling reactions.



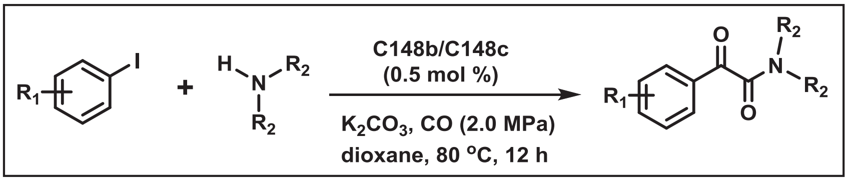
Scheme 51. Release of NHC–Pd(0) catalyst.

The di and tri nuclear Pd complexes (**C141**–**C143**) bearing piperidoimidazolin-2-ylidenes (Fig. 20) anchored to benzene ring *via* methylene spacers were synthesized by Turkmen et al. [148]. The tri-nuclear Pd(NHC) complexes (**C142b**, 0.33 mol %) was highly active than the corresponding mono and di-nuclear complexes towards the Suzuki coupling reaction of aryl chlorides, and phenylboronic acid using KOH in *i*-PrOH at 80 °C. A similar trend was also observed in the Heck coupling reaction of aryl bromides and styrene in the presence of Na$_2$CO$_3$ as a base in DMF at 100 °C.

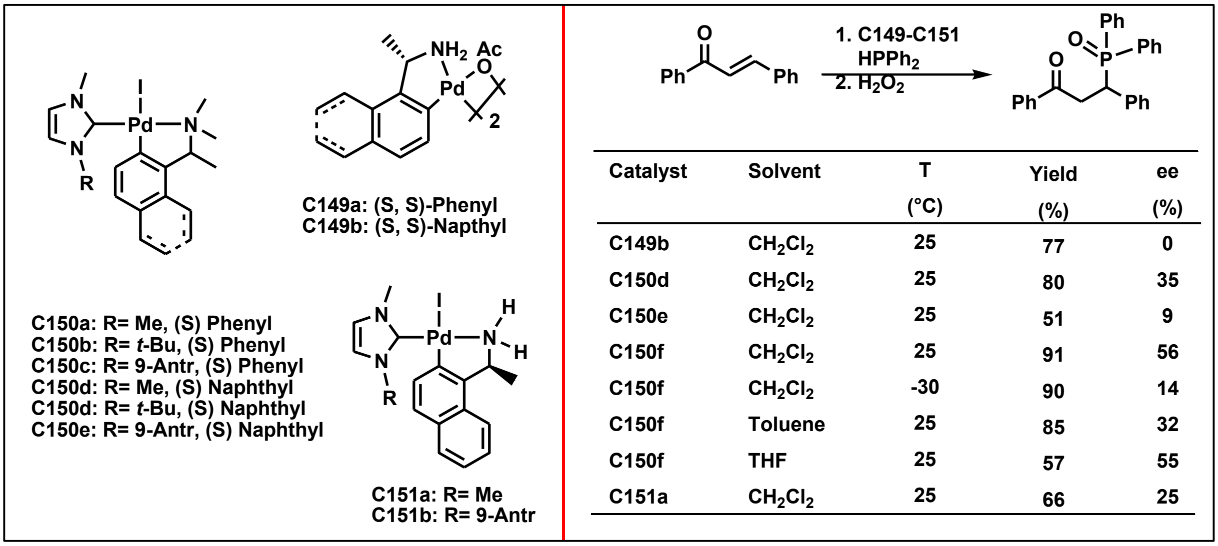
5.3. NHC-palladacycles

The *ortho*-palladated aryl oxime and amine NHC palladacycles (**C144a-b** and **C145**) (Fig. 21) also showed moderate to excellent activity for the Heck coupling of aryl bromides and chlorides with olefins in NMP using NaOAc at 130–150 °C with TON 1705–91950 [149]. The catalyst **C144b** also worked efficiently for the Suzuki coupling reaction of aryl bromides and chlorides with phenylboronic acid in DMF and K$_3$PO$_4$ at 120 °C with TON 185–2313. The NHC palladacycle **C146** also applied in the Heck coupling reaction [150]. The monoligated imine-Pd–NHC complexes (**C147a-d**) obtained from acetophenone oxime and PdCl$_2$ successfully used as precatalysts (0.005 mol %) for the Suzuki coupling of aryl chlorides using KOH in *i*-PrOH:H$_2$O (10:1) mixture at 80 °C [151].

Ying and coworkers [152] prepared cyclopalladated N,N-dimethylbenzylamine (dmba) ligated NHC (IMes) catalyst (**C148a**) with a one-pot, three-component reaction in multi-gram amount by reacting PdCl$_2$ with benzylamine in acetonitrile in the presence of K$_2$CO$_3$ followed by the addition of IMes·HCl. The catalyst (2 mol %) showed excellent activity for a wide range of substrates including electron rich deactivated arylbromides, functionalized aryl and heteroaryl bromides and iodides with a variety of olefins using K$_2$CO$_3$ in NMP at 140 °C. An excellent activity of the catalysts can be ascribed on the basis of the release of Pd(0) catalyst in the reaction mixture (Scheme 51).



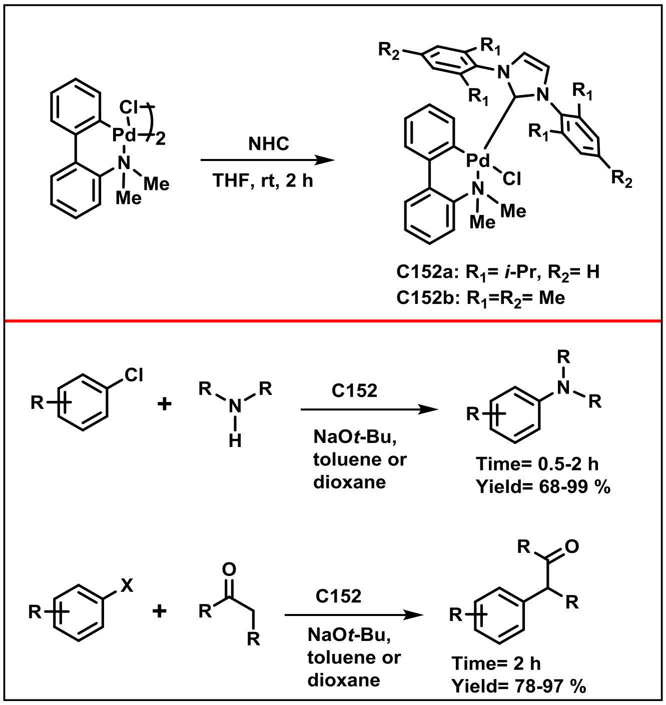
Scheme 52. Water-insoluble and water-soluble NHC–amine Pd complexes used in double carbonylation.



Catalyst	Solvent	T (°C)	Yield (%)	ee (%)
C149b	CH_2Cl_2	25	77	0
C150d	CH_2Cl_2	25	80	35
C150e	CH_2Cl_2	25	51	9
C150f	CH_2Cl_2	25	91	56
C150f	CH_2Cl_2	-30	90	14
C150f	Toluene	25	85	32
C150f	THF	25	57	55
C151a	CH_2Cl_2	25	66	25

Scheme 53. *Ortho*-palladated aryl oxime and amine NHC palladacycles used in the phosphination reactions.

The water-soluble SO_3-Ipr-Pd(deba)Cl (**C148b**) and water-insoluble Ipr-Pd(deba)Cl (**C148c**) NHC–amine Pd complexes also showed good activity in double carbonylation of aryl iodides with various amines using KO*t*-Bu, CO (2.0 Mpa) in water at 80 °C. The catalysts were highly selective due to the intramolecular ligation of amine ligand to Pd (Scheme 52) [153].



Scheme 54. A monomeric NHCs containing palladacycle complexes.

Similarly, chiral palladacycles with NHC ligands (**C149**–**C151**) was reported for the 1,4-addition of diarylphosphines to α,β-unsaturated ketones (Scheme 53) [154].

Nolan and coworkers prepared palladacycle complexes (**C152a-b**) containing NHCs by the reaction of NHC and a dimeric palladacycle in THF at room temperature (Scheme 54). The single crystal diffraction study showed a distorted square-planar coordination around the Pd center in which the NHC ligand is *trans* to the amine. The complexes were found to be equally active in aryl amination and α-arylation of ketones [155a-b] as well as the Suzuki coupling reactions [155c].

Holdt et al. [156] reported the NHC palladacycles **C153** and **154** (Fig. 22) for the Heck coupling reactions of various aryl halides with *n*-butyl acrylate. Precatalyst **C153** showed the best catalytic activity in the Heck coupling of simple, sterically hindered and electronically deactivated substrates with the formation of desired products in moderate yields in Na_2CO_3 and DMF at 140 °C. As an extension, they [157] reported catalytic activity of a 2-phenylidenepyridine Pd(II) complexes (**C155a-b**) bearing 1,3-bis(mesityl)imidazole-2-ylidene in the Heck coupling reaction of aryl bromides with *n*-butyl acrylate using Na_2CO_3 and TBAB in DMF at 140 °C.

Kim et al. [158a] applied dinuclear azido-palladacycles (**C155c**, **C156a-b**, **C157** and **C158**) for the Suzuki coupling reaction of activated and nonactivated aryl bromides in MeOH at room temperature and aryl chlorides using Cs_2CO_3 as a base in EtOH at 80 °C. The catalyst **C156a** (1.0 mol %) also coupled aryl chlorides and potassium aryl trifluoroborates in EtOH using Cs_2CO_3 and TBAB at 120 °C. The NHC-palladacycle **C159** obtained from di-μ-hydroxopalladacycles also applied for the Suzuki arylation of 9-

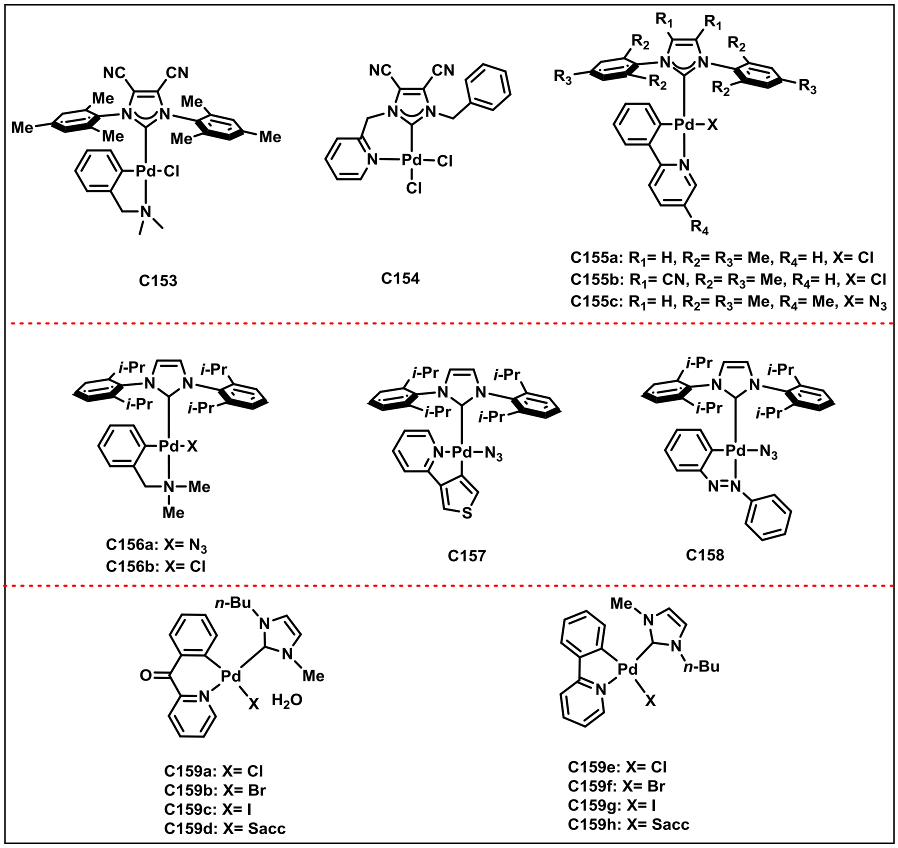


Fig. 22. NHC palladacycles used in various coupling reactions.

bromophenanthrene using Na_2CO_3 as a base in PhMe:H_2O mixture (1:2) at 80 °C with excellent yields [158b].

5.4. NHC-pincers

The pincer complexes have high thermal stability due to chelate effects such complexes are the choice of ligands for high temperature Heck coupling reaction.

5.4.1. NHC-pincers with single carbene unit

Palladium complexes **C160a-h** (Fig. 23) of pyridyl supported pyrazolyl-NHC ligands were synthesized and structurally characterized by Zeng and Yu [159]. The catalysts were used in the Suzuki coupling reaction of phenyl or *p*-tolylboronic acid with aryl halides (I and Br) and activated aryl chlorides under mild conditions using K_2CO_3/Cs_2CO_3 as a base in DMF:H_2O (20:1)/(10:1) mixture at 80/120 °C. Screening of catalysts showed that the **C160e** showed excellent activity for coupling bromobenzene and *p*-tolylboronic acid using Cs_2CO_3 in DMF:H_2O (10:1). Similarly, Pd(II) complexes of pyrazolyl-pyridyl containing NHC (**C161a-d**) were also applied for the Suzuki coupling reaction in the presence of Cs_2CO_3 in DMF:H_2O (10:1) mixture at 80 °C [160]. While, similar Pd–CNN pincer type complexes **C162a-g** and **C163** were tested in the Suzuki coupling of aryl bromides using K_2CO_3 in methanol and H_2O at RT/90 °C [161]. The authors showed that the complexes generated from the hydrolytic ring opening coordination, exhibit excellent catalytic activity as compared to complexes with normal coordination.

Symmetric NCN–Pd pincer complexes **C164** and **C165** stabilized by pyridine [162] were applied to the Suzuki coupling reaction. The 1,3-dipicolyl-3,4,5,6-tetrahydropyrimidin-2-ylidenes based NCN–Pd pincer complexes **C166a-b** also acts as a good catalyst for

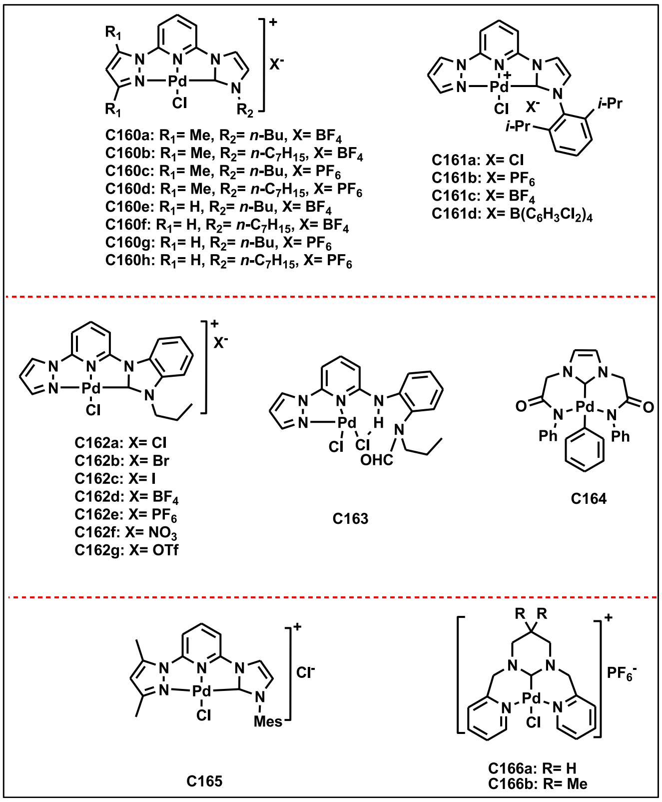


Fig. 23. NHC-Pd-pincers with single carbene unit used in coupling reactions.

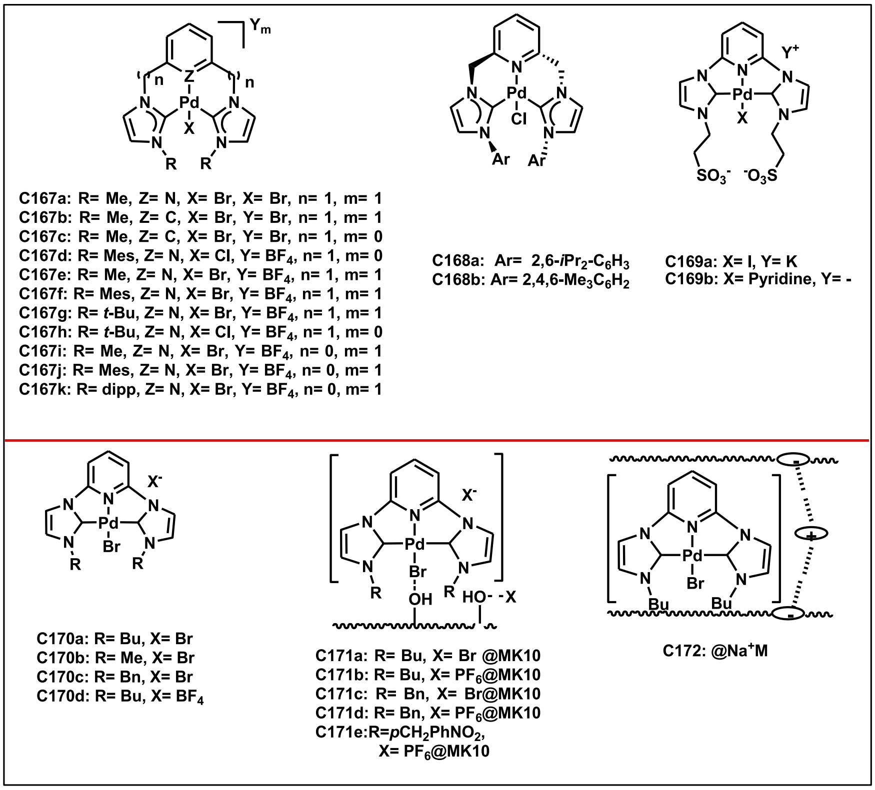


Fig. 24. NHC-Pd-pincers with two carbene units used in coupling reactions.

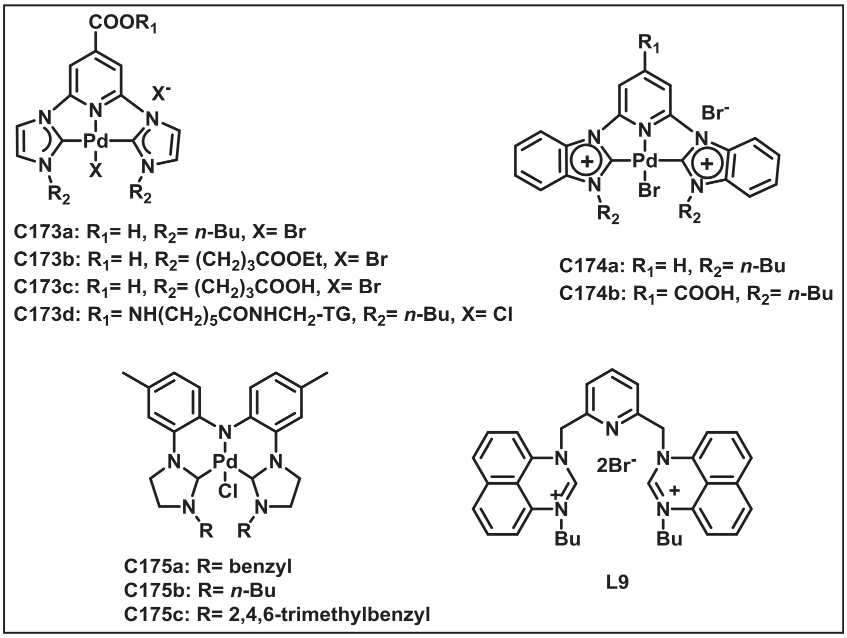
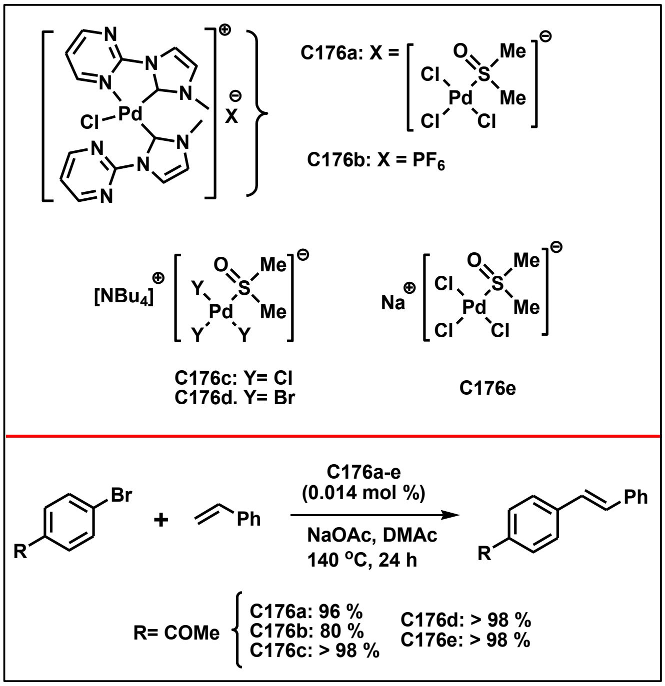


Fig. 25. NHC-Pd-pincers with two carbene units used in coupling reactions.

the Heck coupling reactions of aryl bromides with acrylate/styrene using Et_3N as a base in DMA at 135 °C [163].

5.4.2. NHC-pincers with two carbene units

Crabtree and coworkers prepared tridentate CNC-bis—NHC—Pd complexes **C167a-c** (Fig. 24) from the corresponding carbene precursors and $Pd(OAc)_2$ at 160 °C. The complex **C167a** was highly active towards the Heck coupling reaction of aryl halides (Br and Cl) in DMA at reflux using NaOAc as a base [164]. The complex **C167a** is flat and has low solubility. Hence, they synthesized complexes



Scheme 55. Anionic palladium complexes for the in the Heck coupling reaction.

C167b and **C167c** containing CH_2 spacer between the rings, which enhances solubility with twisted geometry. Both the complex **C167b** and **C167c** were highly active towards the Heck coupling reaction of aryl halides under similar reaction conditions. The identical NHC-pincer complexes (**C167d-k**) were reported for the Heck coupling reaction by White et al. [165]. A similar CNC-bis–NHC–Pd complexes **C168a-b** containing two chiral tridentate 2,6-lutidinyl units with helical C_2 symmetrical structures was reported by Danopoulos et al. [166]. Both the complexes were prepared by the reaction of analogous silver complexes with (COD) $PdCl_2$ in dichloromethane. Catalyst **C168b** was more active than **C168a** for the Heck coupling of aryl chlorides due to the steric crowding at the reactive site. A sulfonate functionalized Pd–NHC pincer catalysts (**C169a-b**) also applied to the Suzuki coupling reaction of aryl halides and phenylboronic acid in water and in *i*-PrOH:H_2O mixture [167]. As clay offers immobilization of catalytic systems *via* adsorption/cation exchange, Fernandez et al. [168] prepared homogeneous as well as clay immobilized Pd-NCC pincer complexes **C170**–**C172** for the Heck and Sonogashira coupling reactions. The immobilization procedure involves impregnation of complex onto the montmorillonite K-10 and bentonite (Na^+) clays in CH_2Cl_2. In first catalyst there is interaction of counter anion and cation with MK-10 by hydrogen bonding, while second catalyst involves electrostatic attraction between counter cation with bentonite layers. This different type of interaction ultimately causes the difference in the activity of two catalysts for the Heck coupling reaction.

In 2009, Domínguez et al. [169] reported COOH functionalized hydrophilic CNC-pincer Pd complexes **C173a-c** (Fig. 25) for the Suzuki, Heck and Sonogashira coupling reactions. Insertion of the hydrophilic carboxyl functional group in ligand provides tuning of the catalytic activity and increases its solubility in water. All the catalysts were obtained by the treatment of 2,6-dibromo-4-carboxy pyridine with the corresponding N-substituted imidazoles which was palladated with $Pd(OAc)_2$/DMSO. All the complexes (0.01 mol %) were highly active towards the Suzuki coupling reaction of aryl bromides and arylboronic acids in water at 100 °C using K_2CO_3 as a base, giving an excellent yield of the desired coupling products in 2 h (92–99% for **C173a**, 24–99% for **C173b**, 50–99% for **C173c**). They also evaluated the activity of **C173b** and **C173c** for the Heck and Sonogashira coupling reactions. Catalyst **C173c** was inefficient in the water, but highly efficient in DMF, while catalyst **C173c** worked best in both water and DMF. Both **C173b** and **C173c** catalysts were highly active for the Sonogashira coupling in the water and pyrrolidone at 50 °C. The catalysts **C173b** and **C173c** were also applied tor the Sonogashira coupling reaction in organic and aqueous media [170]. Steel et al. [171] derived CNC-bis–NHC–Pd pincer complexes from dichloroisonicotinic acid. It showed that the incorporation of an amide unit at C-4 of the pyridine ring allows its easy immobilization on suitable supports (**C173d**) had little effect on the overall yield in both the Heck and Suzuki coupling reactions. The complex was supported on amino terminated Tenta Gel® resin (0.26 mmol/g) and showed excellent recyclability (14 times) for coupling aryl iodides but less effective for aryl bromides in DMA at 165 °C. The arene fused six-membered heterocycles provide a novel type of NHC framework having stronger σ-donor ability in comparison with NHC derived from benzimidazolium salts. Similarly, the hydrophilic pyridine-bridged bis-benzimidazolylidene Pd pincer complex (**C174a**) was reported by Tu et al. [172]. The complex showed excellent catalytic activity towards the Suzuki coupling reaction of a variety of aryl bromides and arylboronic acids in water as well as H_2O:MeOH (1:1) mixture with a catalyst loading down to the ppm scale (0.005 mol %). They also used lutidine-bridged bis-perimidinium dibromide salt **L9** for the Heck and Suzuki coupling reactions using K_2CO_3 in NMP at 140 °C in the presence of equimolar amounts of $Pd(OAc)_2$ in very low Pd loading [173]. The new CNC pincer type Pd(II) complexes **C175a-c** also found to be active catalysts (1.0 mol %) for the Suzuki coupling reaction of aryl bromides in the presence of Na_2CO_3 as a base in dioxane at 90 °C [174].

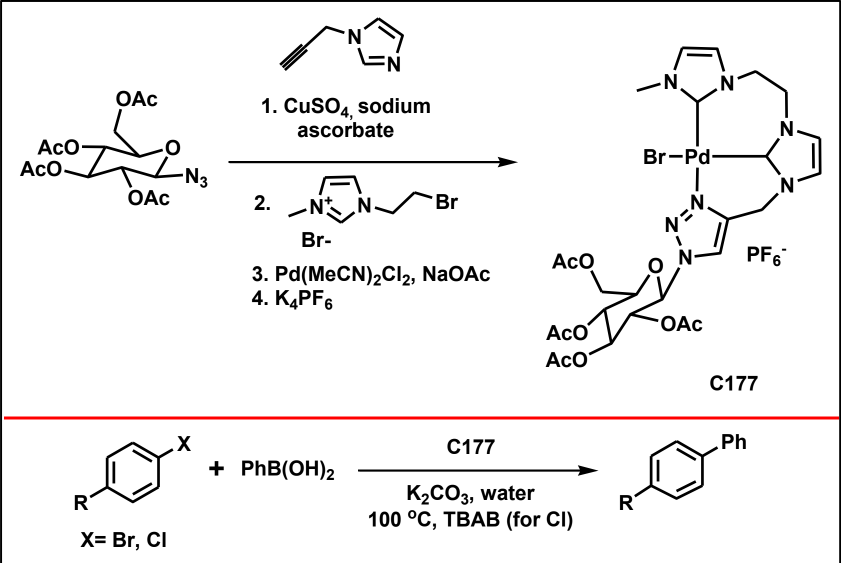
Recently, anionic palladium complexes **C176a-e** [(pym-Im-Me)$_2$PdCl]PF_6 was synthesized by Strassner et al. [175] for the Heck coupling reaction of aryl bromides with styrene in DMAc at 140 °C in the presence of NaOAc as a base and TBACl (Scheme 55). Thus the complex **C176a** (0.014 mol %) showed superior activity as compared to the other complexes in the Heck coupling reaction of 4-bromoacetophenone and styrene, in the presence of NaOAc in DMAc at 140 °C for 24 h. The actual catalytic species are anionic "ligandless" [NBu_4][Pd-(DMSO)Cl_3] complex.

Nishioka et al. [176] synthesized Pd-pincer complex (**C177**) containing two NHC and one triazole moiety holding a sugar unit incorporated by 'click' chemistry. The complex (0.5 mol %) showed excellent activity for the Suzuki coupling reaction of 4-chloroacetophenone and phenylboronic acid in the presence of K_2CO_3 and TBAB in water at 100 °C with TON up to 76000 (Scheme 56).

5.4.3. Tetra coordinated Pd–NHC complexes

A pyridine functionalized monomeric and dimeric NHC–Pd complex **C178** (Fig. 26) was also applied for the Heck, Suzuki, and Sonogashira coupling reactions under different reaction conditions [177]. The dinuclear palladacyclic complexes **C179** and **C180** also showed good activity in the Heck and Suzuki coupling reactions of activated aryl bromides [178].

Chen et al. reported the synthesis of complexes, [Pd(L)Cl](PF_6) (**C181**) containing 3-butyl-1-(1,10-phenanthrolin-2-yl)imidazolylidene ligand for Cu-free Sonogashira coupling reaction of aryl iodides at room temperature and aryl bromides at 80 °C in water [179a]. They also reported two Pd–NHC catalysts, in which complex



R= COMe				
X	C177 (mol %)	Time (h)	Yield (%)	TON
Br	1	16	94	94
Br	10-2	16	98	9800
Br	10-3	16	76	76000
Br	10-4	16	6.5	65000
Cl	0.5	17	46	92
Cl	0.5	17	32	64
Cl	0.5	17	53	106
Cl	0.5	41	51	103
Cl	0.5	41	54	109

Scheme 56. Sugar based Pd-pincer complex for the Suzuki coupling reaction.

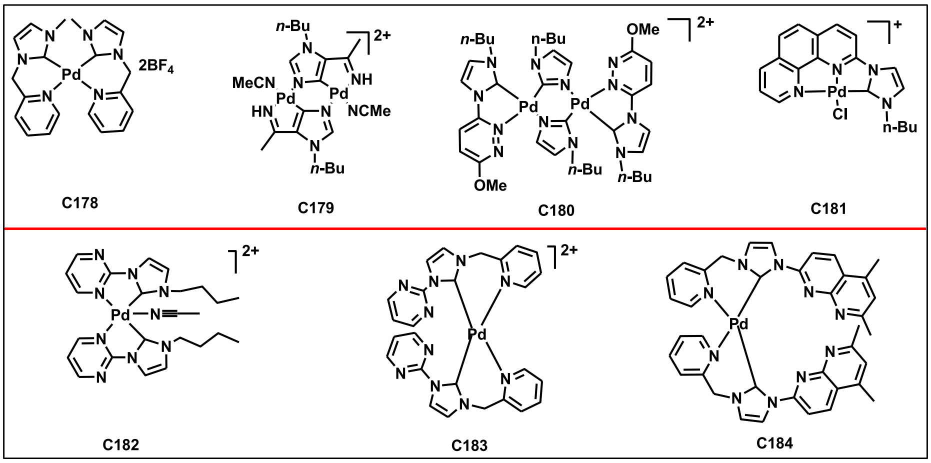
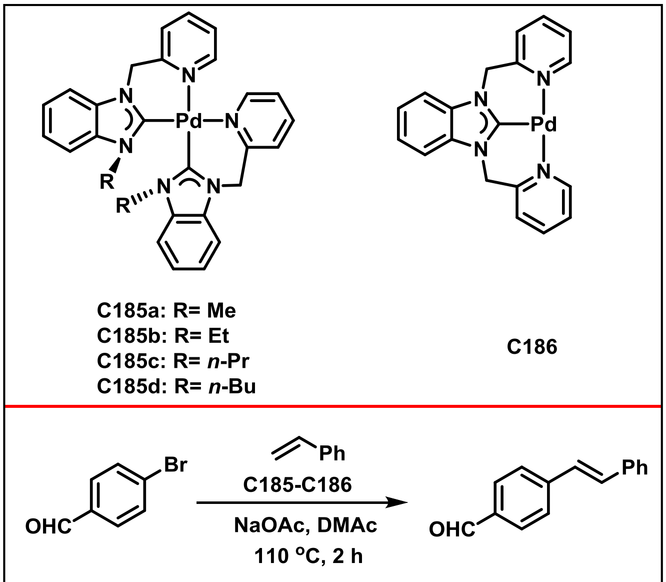


Fig. 26. NHC-Pd-pincers with tetra coordinated carbene units.



Catalyst (1 mol %)	Yield (%)
185a	30
185b	28
185c	32
185d	27
186	82

Scheme 57. Picoline functionalized benzimidazolin-2-ylidene Pd complexes for the Heck coupling reaction.

C182 and **C183** in the Heck coupling reaction of aryl bromides and activated aryl chlorides using NaOAc and DMAc at 80–140 °C with/without TBAB [179b]. Similarly, the complex **C184** having a helical structure in which Pd located in a square-planar environment with two carbene ligands and two pyridines in a *cis* arrangement for the Heck coupling of aryl halides with *n*-butyl acrylate in DMF/DMAc using NaOAc as a base at 140 °C [179c].

Han et al. [180] used picoline functionalized benzimidazolin-2-ylidene Pd complexes **C185a-d** and **C186** for the Heck coupling reaction. It was observed that the complex **C186** (1 mol %) exhibited highest catalytic activity in the Heck coupling reaction of activated aryl bromides with styrene or *n*-butyl acrylate using NaOAc in DMAc at 120 °C. Whereas, all the complexes are less active in coupling reactions of aryl chlorides or deactivated aryl bromides (Scheme 57).

Similarly, benzimidazole functionalized NHC–Pd(II) complexes **C187a-b** (Fig. 27) [181] and bis-benzimidazolium NHC–Pd (**C188)** [182] were also effective for Suzuki, Heck and Sonogashira coupling reactions.

Kosmrlj et al. [183] reported a water soluble mesoionic bis(Py-tzNHC) Pd(II) complex **C189** for Cu, amine, phosphine and additive-free Sonogashira alkynylation of aryl bromides in water. The catalyst was prepared through direct metallation of the appropriate triazolium cation with Pd(OAc)$_2$ in the presence of a Cs$_2$CO$_3$. The complex (1 mol %) was highly active for the alkynylation of electron-poor and electron-rich aryl bromides with various acetylenes using Cs$_2$CO$_3$ in water under two different reaction conditions (A and B) (Scheme 58). The catalyst also furnished optically pure intermediate in good yield (82%) which is one of the intermediate compounds involved in the synthesis of SIB–1508Y (Altinicline), a potential drug for neurodegenerative diseases. They showed that the catalysis proceeds along two connected catalytic cycles containing Pd(0) and Pd(II) species, as demonstrated by electrospray ionization mass spectrometry.

Lee and coworkers [162,184] applied *cis* Pd–NHC complexes **C190a-b** and its *trans*-analogues **C191a-b** (Fig. 28) for the Heck coupling reaction of activated aryl chlorides in TBAB. The complex **C190a** (3 mol %) was more effective for coupling deactivated aryl chlorides and bulky aryl bromides and mediates one-pot sequential Heck-Heck and Suzuki-Heck couplings of 4-bromochlorobenzene in TBAB at 140 C. Similarly, a reaction of PdCl$_2$, 3-(trifluoromethyl)-5-(2-pyridyl)pyrazole (fppzH) and corresponding imidazolium carbene precursors gave complex **C192a-c** (0.5 mol %) in the presence of K$_2$CO$_3$ [185] and showed excellent activity in the Heck coupling reaction of aryl halides with alkenes using NaOAc, TBAB, at 120–160 °C.

6. Conclusion

The past few decades perceived the growing progress of the phosphine as well as NHC based ligands in many cross-coupling reactions. Concerning on the economic and environmental point of view the major use of the Pd–N especially, Pd–C–N based catalytic system is a very imperative substitute to phosphine ligands. In the near future more and more NHC, palladacycles, symmetric and non-symmetrical pincers, PEPPSI type catalysts containing C–N ligands will come forth due to its high activity and selectivity towards Pd catalyzed coupling reactions of aryl chlorides, which otherwise not possible without using phosphine ligands. The advantages of these ligands and catalysts include high activity with

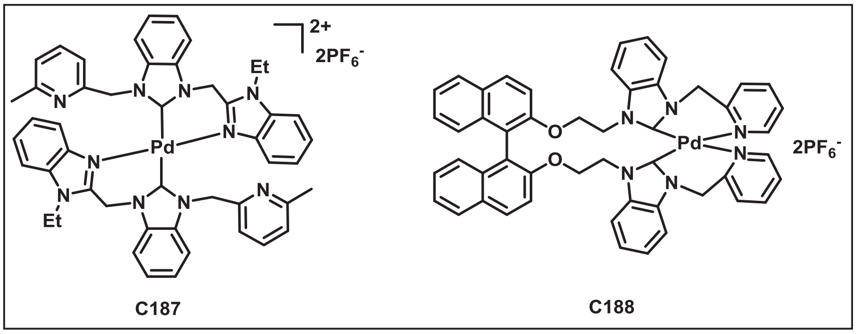
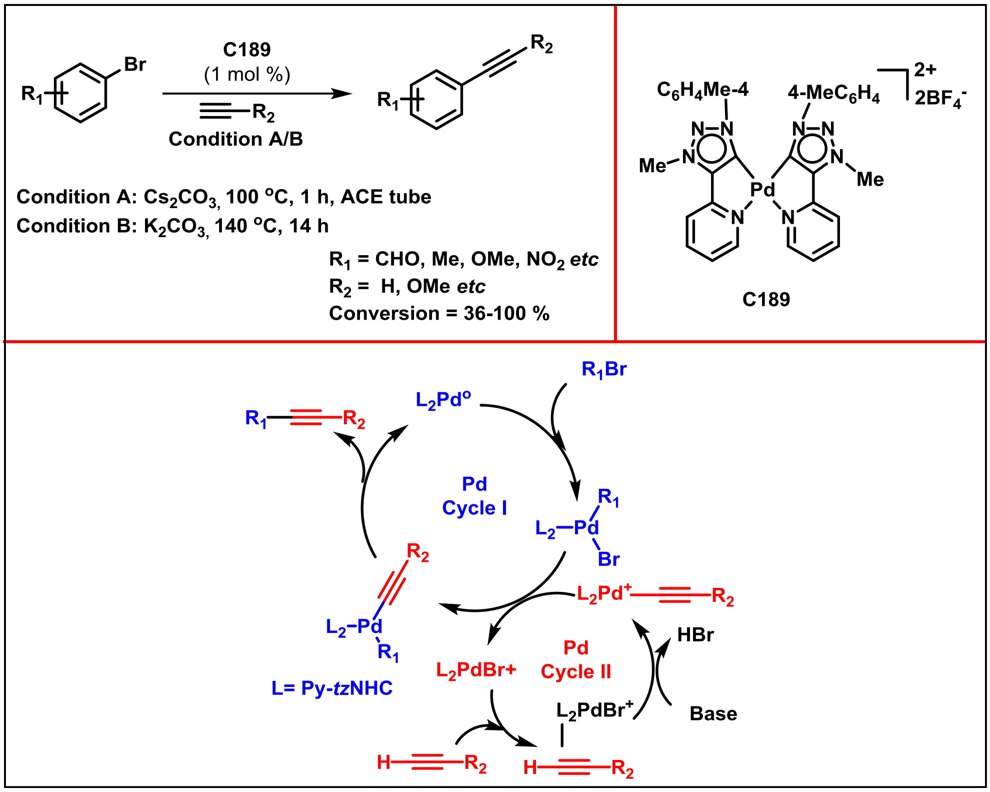


Fig. 27. Benzimidazole functionalized tetracoordinated NHC–Pd(II) complexes used in coupling reactions.



Scheme 58. A water soluble mesoionic bis(Py-tzNHC) Pd(II) complex used for the Sonogashira coupling reaction.

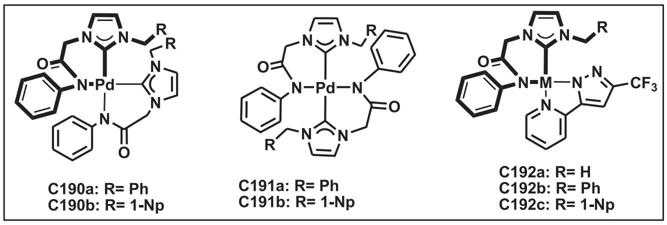


Fig. 28. Tetracoordinated NHC–Pd(II) complexes used in coupling reactions.

enhanced selectivity, low toxicity, moisture, air as well as thermal stability. Most importantly, such complexes have broad applications in catalysis under ambient conditions. We hope this review inspires further uses of N ligands as a sustainable ligand for many other transition metal catalyzed transformations.

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