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Modulating the electronics of palladium complexes supported by iminopyridine ligands as the catalysts in Suzuki-Miyaura and Heck-Mizoroki cross-coupling reactions.

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Abstract

Two bench stable palladium(II) complexes [κ^2-(PyCH=N(CHPh$_2$)PdCl$_2$)] (**1**) and [κ^3-(PyCH=N(CH(Ph$_2$)(C$_6$H$_4$))PdCl)] (**2**) supported by iminopyridine ligands (PyCH=NR) [R = CHPh$_2$, (**L1**) and R = CPh$_3$, (**L2**)] were synthesized and utilized as the competent catalysts in the formation of C-C coupling products for Suzuki-Miyaura and Heck-Mizoroki reactions. The palladium complex **1** was obtained by the κ^2 coordination of the ligand **L1** to the palladium precursor whereas complex **2** was achieved by ortho-

metallation of one of the phenyl groups present in ligand **L2** with the Pd metal under reaction conditions making the ligand κ^3-ligation to the metal. Complex **2** exhibited excellent catalytic efficiency at very low catalyst loading (0.5 mol%). The new C-C bond formations of the desired products were obtained in high yield at mild reaction conditions. Wide varieties of substrate scopes were explored for the C-C bond cross-coupling reactions.

Keywords

Palladium Catalysis • Suzuki-Miyaura Coupling • Heck-Mizoroki Coupling and one-pot synthesis.

Introduction

In 1991, Arduengo III isolated the stable N-heterocyclic carbenes (NHCs) which have transformed organometallic chemistry [1-3]. Especially, cross-coupling reactions developed by Richard F. Heck, Ei-ichi Negishi, and Akira Suzuki are dominant in the industry, optical devices, natural products, and in the synthesis of many drug molecules. NHCs-based metal complexes act as a catalyst and have attracted many researchers due to their wide applications in a variety of chemical reactions [4-10]. Palladium-catalyzed coupling reactions such as Suzuki-Miyaura, Negishi, Kumada-Tamao-Corriu, Hiyama, and Stille have gained a lot of interest owing to their facile formation of C-C bonds [11-18]. Further, cross-coupling reactions have found applications in chiral liquid crystals and chiral reagents [19]. To have excellent reactivity to form C-C cross-coupling reactions various ligands such as N-Heterocyclic carbenes (NHCs), cyclic (alkyl)(amino)carbenes (CAACs), and bicyclic (alkyl)(amino)carbenes (BiCAACs) were utilized to form palladium complexes [20-21]. In literature, various groups have developed palladium catalysts supported by NHCs as robust and extremely active in cross-coupling reactions [22].

Palladium catalysts supported by NHCs act as robust and extremely active in cross-coupling reactions. Nolan [23] and co-workers developed NHC stabilized palladium complex **I** (Figure 1), which catalyzed the Suzuki-Miyaura coupling reaction at room temperature, but relatively low yields (12%) were reported for the C-C coupled product (**I**, Figure 1). In 2004, the same group also reported palladium complex which is synthesized by the reaction of IMes·HCl and 1 equiv. of palladium acetate (**II**, Figure 1). The catalytic reactions of Suzuki-Miyaura and Heck-Mizoroki cross-coupling were studied using the palladium complex **II**, however, in both cases, the cross-coupling reactions at high temperatures were used for the formation of C-C coupled products. Later, in 2009 Huynh [24] *et al.* reported the Heck-Mizoroki cross-coupling reaction using trans-Diiodo-(2-methyl-1,3,5-triphenylpyrazolin-4-ylidene) (pyridine)palladium complex in which Heck-Mizoroki reaction to obtain good yields but the high temperatures are required for the complete conversion of the product. Further, Hong [25].and co-workers synthesized palladium complex **IV** (Figure 1) which catalyzed the Suzuki-Miyaura reaction using 2.5 mol% of the catalyst, 80 °C of temperature in 24 h of reaction time. Here, both the temperature and reaction times are significantly higher for the facile conversion of the product. Fukuzawa [26] and co-workers synthesized bis-1,4-dimesityl-1,2,3-triazol-5-ylidine-palladium complex **V** (Figure 1) catalyses the Heck-Mizoroki reaction with aryl bromides to give the corresponding alkenes in good to excellent yields, but the higher temperatures and reaction time are the disadvantages of this pathway. Later in 2016, Ghadwal [27] reported the palladium catalyst **VI** (Figure 1) which catalyzes the Suzuki-Miyaura coupling reactions in good yields, but the reaction time is here for the complete conversion of the product. In some catalytic systems, harsh conditions such as high temperatures and reaction time were used to attain the C-C bond coupling product. The dinitrogen-based ligands that supported palladium were developed for cross-coupling reactions to overcome the

drawbacks of using phosphine-based ligands. In 2005, Pelagatti [28] and co-workers reported pyridyl-imine palladium complex as a catalyst for the Heck coupling reaction in the presence of DMF using Et_3N as a base to form the desired C-C coupling product (**VII**, Figure 1).

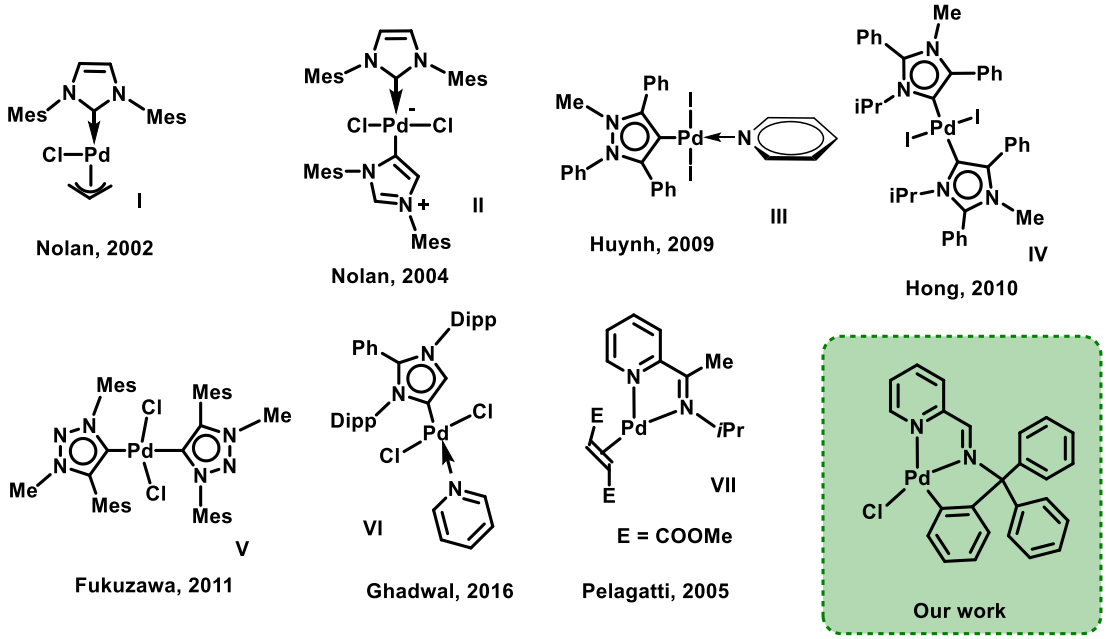
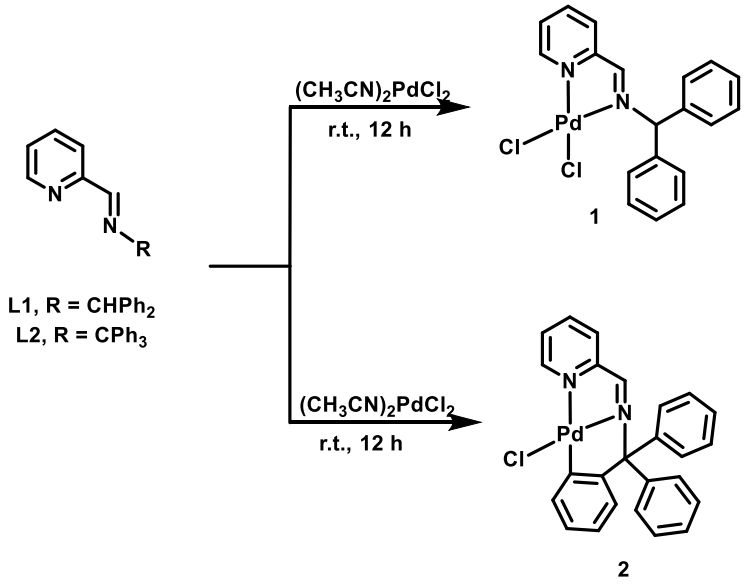


Figure 1. Selected examples for C-C coupling reactions in the presence of palladium catalyst.

Herein, we report the synthesis and structural characterization of two palladium complexes **1** and **2** supported by iminopyridine ligands PyCH=NR [R = $CHPh_2$, (**L1**) and R = CPh_3, (**L2**)]. Complex **2** is a cyclo-metallated palladium complex. The bench stable palladium complex **2** showed excellent reactivity for Suzuki-Miyuara reactions in the presence of aryl bromide, aryl iodide, and aryl chloride as a substrate to form the C-C coupling product at a shorter reaction time with low catalyst loading (0.5 mol%). Further, we also explored Heck-Mizoroki cross-coupling reactions under similar reaction conditions. The desired products were obtained in good to excellent yields.

Results and Discussion

Synthesis of Pd complexes **1** and **2**: The reaction of equimolar $(CH_3CN)_2PdCl_2$ with PyCH=NR [R = $CHPh_2$, (**L1**) in the presence of acetonitrile solvent afforded the palladium metal complexes [κ^2-(PyCH=N($CHPh_2$) $PdCl_2$)] (**1**) in 85% yield (Scheme 1). In contrast, an analogous reaction of ligand **L2** with $(CH_3CN)_2PdCl_2$ in a 1:1 molar ratio in acetonitrile gave a cyclo-metallated palladium complex [κ^3-(PyCH=N(CH(Ph_2)(C_6H_4)) PdCl)] (**2**) in 87% yield through ortho- C-H activation under reaction conditions (Scheme 1).



Scheme 1. Synthesis of palladium complexes **1** and **2** supported by (PyCH=NR) [R = $CHPh_2$, (**L1**) and R = CPh_3, (**L2**)].

Palladium complexes **1** and **2** were characterized by using multi-nuclear NMR spectroscopy and solid-state structures of the complexes were confirmed by single-crystal X-ray diffraction analysis. In the ^1H NMR spectrum of the metal complex **1** and **2**, which were recorded in CD_3CN and DMSO-d_6, the resonance signals for the *ortho* proton of the pyridine ring were obtained at δ_H 9.11 ppm and 8.92 ppm respectively, which is shifted downfield compared to that of ligands **L1** (8.63 ppm) and **L2** (8.61 ppm). Additionally, the δ_H imine proton of **1** is 8.00 ppm which shifted up field compared

to ligand **L1** which is 8.52 ppm, and, in the case, δ_H imine proton is 7.32 ppm which also shifted upfield compared with that of ligand **L2** (7.99 ppm). Crystals of palladium complex **1** were isolated from the slow evaporation of acetonitrile solution at room temperature. The solid-state structure of palladium metal complex **1** was confirmed by single-crystal X-ray diffraction analysis. The pertinent data are given in the electronic supporting information and the molecular structure of palladium complex **1** is given in Figure 2. Complex **1** crystallizes in a monoclinic system with a *C*2/c space group. The coordination polyhedron is formed by the chelation of the pyridine nitrogen and imine nitrogen atoms of the ligand **L1** to the palladium ion to form a five-member palladium metallacycle Pd1-N1-C5-C6-N2. Additionally, two chloride ions are bonded with a palladium ion adopting the metal centre square planar geometry around it. The bond distance of N2-Pd1 (2.031 Å) and N1-Pd1 (2.023 Å) are similar and slightly longer than those of our previously observed palladium complex [(κ^4- {1,2 C_6H_4(N=CH-$C_6H_4O)_2$}-Pd] [(1.968(7) and 1.949(10) Å]. [33].

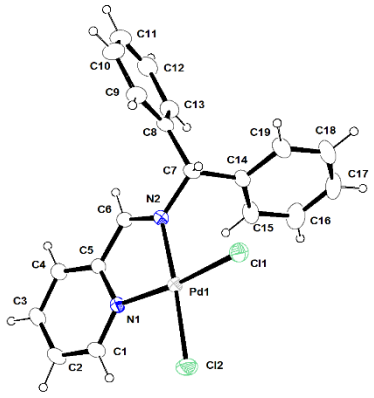


Figure 2. Solid-state structure of palladium metal complex **1**. Selected bond lengths (Å) and bond angles (°): Pd1-Cl1 2.270, Pd1-Cl2 2.278, Pd1-N2 2.031, Pd1-N1 2.023, N1-C5 1.359, N2-C6 1.272; Cl1-Pd1-Cl2 90.03, N2-Pd1-Cl1 95.14, N1-Pd1-Cl2 94.74, N1-Pd1-N2 80.15.

In the case of palladium complex **2**, single crystals were grown by the slow evaporation of acetonitrile solvent at room temperature. Dark red crystals appeared after two days

and the structure of palladium complex **2** was confirmed by a single-crystal X-ray diffractometer (Figure 3). The solid-state structure of palladium complex **2**, reveals that the steric repulsion from one of the phenyl groups of trityl amine favours the C(sp^2)-H bond activation with the abstraction of labile chlorine atom from the palladium centre to form the two five-membered metallacycles i.e., Pd1-N1-C10-C11-N2 and Pd1-N1-C3-C2-C1. Palladium metal complex **2** crystallizes in a triclinic system with a *P*-1 space group. The coordination geometry around the palladium metal is distorted square planar geometry. The central metal ion is coordinated by two nitrogen atoms, one chlorine atom, and one carbon atom from the phenyl ring. The bond distances between N1-Pd1 (1.968 Å) and Pd1-N2 (2.142 Å) are consistent and similar to the previously reported palladium complexes. [31] The Pd1-N2 bond distance of metal complex **2** is slightly longer compared with the Pd1-N2 of **1**, due to the presence of significant steric repulsions from three phenyl rings of tritylamine in metal complex **2** compared with that of two phenyl rings in metal complex 1. The Pd1-C1 bond distance in metal complex **2** is 1.970 Å, comparable to the previously reported palladium-carbon bonds. [31]

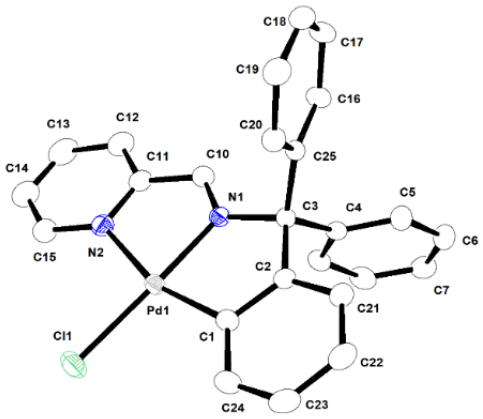
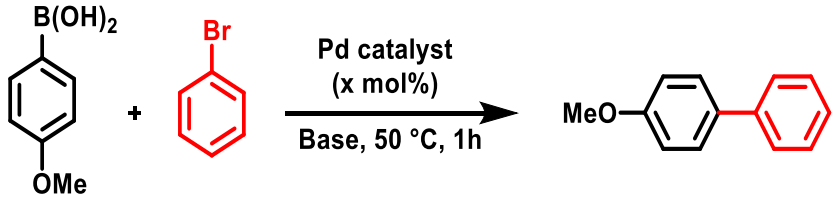


Figure 3. Solid-state structure of palladium metal complex **2**. Selected bond lengths (Å) and bond angles (°): Pd1-Cl1 2.3220, Pd1-C1 1.970, Pd1-N2 2.142, Pd1-N1 1.968,

N1-C3 1.504, N2-C11 1.348; C1-Pd1-Cl1 99.20, N1-Pd1-N2 79.42, N1-Pd1-C1 82.90, Cl1-Pd1-N2 98.49.

Catalysis: Cross-coupling reactions using palladium catalysts have gained a lot of interest due to their applications in various fields. In this regard, we have explored cross-coupling reactions of air and moisture-stable palladium catalysts **1** and **2** to form the C-C coupled products in the presence of air. Initially, the reaction of 4-methoxyphenylboronic acid with bromobenzene was investigated in the presence of palladium catalysts **1** and **2** under different reaction conditions which are depicted in Table 1.

Table 1. Optimization table for the Suzuki-Miyaura cross-coupling reactions[a].



Entry	Catalyst	Catalyst Mol%	Solvent	Base	Yield (%) [b]
1	Cat.1	0.5	*i*-PrOH	K_2CO_3	40
2	Cat.1	1.0	*i*-PrOH	K_2CO_3	85
3	**Cat.2**	**0.5**	***i*-PrOH**	**K_2CO_3**	**94**
4	Cat.2	0.5	Dioxane	K_2CO_3	72

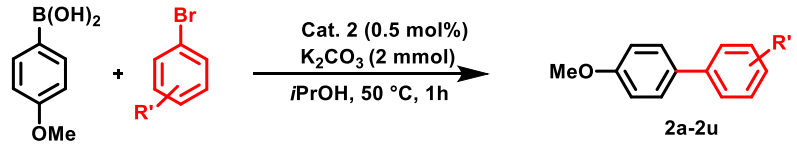
5	Cat.2	0.5	Toluene	K_2CO_3	15
6	Cat.2	0.5	EtOH	K_2CO_3	62
7	Cat.2	0.5	DMSO	K_2CO_3	0
8	Cat.2	0.5	THF	K_2CO_3	42
9	Cat.2	0.5	*i*-PrOH	KO^{t}Bu	68
10	Cat.2	0.5	*i*-PrOH	KOH	62
11	Cat.2	0.5	*i*-PrOH	Cs_2CO_3	80
12	Pd $(OAc)_2$	0.5	*i*-PrOH	K_2CO_3	67
13	$(CH_3CN)_2$ $PdCl_2$	0.5	*i*-PrOH	K_2CO_3	62

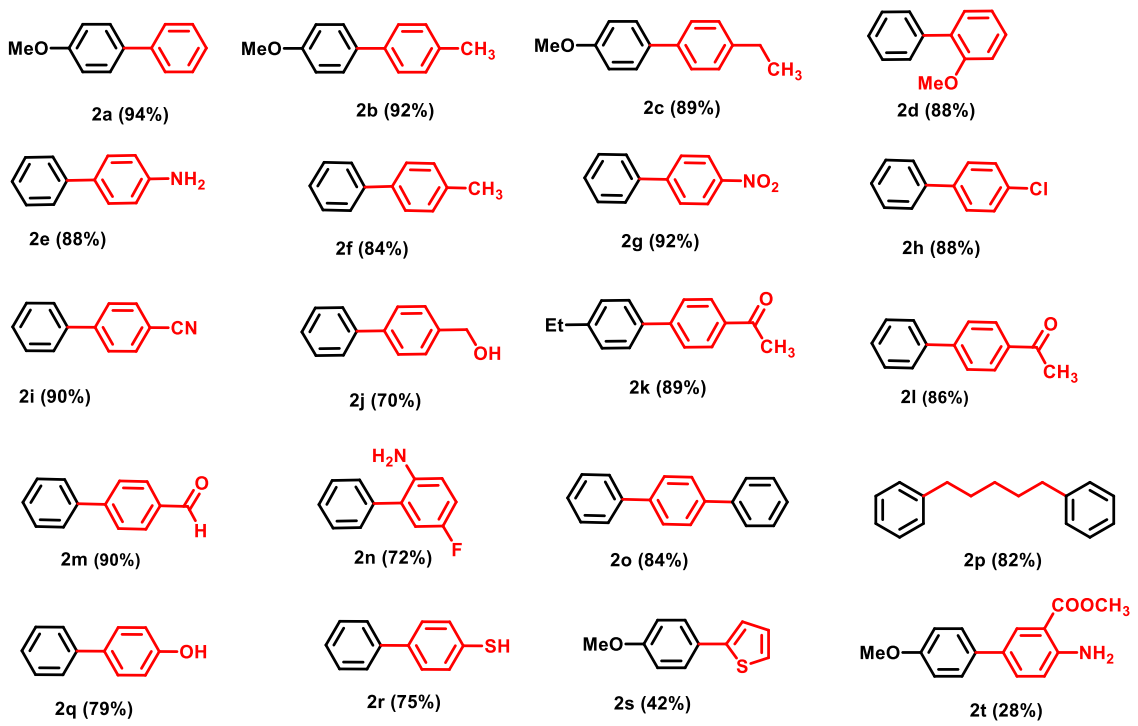
Reaction conditions: [a]Aryl bromide (0.80 mmol), Arylboronic acid (0.70 mmol) and base (2 mmol) at 50 °C temperature. [b]Isolated yields.

Primarily, palladium catalyst **1** (0.5 mol%) in isopropanol (*i*-PrOH) with K_2CO_3 (2 mmol) afforded the coupling product 4-methoxy-biphenyl in 40% yield (Table 1, entry 1). The variation in time and catalyst loading afforded the desired product in 85% yield (Table 1, entries 2). Later, the use of palladium catalyst **2** with 0.5 mol% loading in isopropanol (*i*-PrOH) with K_2CO_3 (1.5 mmol) afforded the coupling product 4-methoxy-biphenyl obtained 94% yield (Table 1, entry 3). Use of different solvent mediums such as 1,4-dioxane yielded the C-C coupled product in 72% yield and in the case of toluene 15% product was formed (Table 1, entries 4-5). The change of solvents to EtOH, DMSO and THF yielded in decrease in the formation of C-C coupled product (Table 1, entries 6-8). Subsequently, we performed the coupling reaction in the presence of different bases such as KO^{t}Bu and KOH under similar reaction conditions and concluded that K_2CO_3 is paramount for the cross-coupled C-C bond formation products (Table 1, entries 9-10). The use of Cs_2CO_3 yielded the C-C coupled product in 80% yield (Table 1, entry 11). The use of Pd $(OAc)_2$ yielded in 67% yield of C-C coupled product (Table 1, entry 12). Notably, the reaction was performed in $(CH_3CN)_2PdCl_2$ in 62 % yield of C-

C Coupled product (Table 1, entry 13). With the optimized conditions, 0.5 mol% loading of catalyst **2**, K_2CO_3 (2 mmol), and *i*-PrOH as solvent at 50 °C and one hour reaction time, the Suzuki-Miyaura coupling reactions were explored in the presence of various electron-donating and electron-withdrawing substituents on the aromatic rings (Table 2). Aryl iodides, aryl bromides, and aryl chlorides were used as a coupling reagents in the presence of aryl phenylboronic acid and palladium catalyst **2**. Further the reaction of 4-methoxyboronic acid with bromobenzene, 1-iodo-4-methylbenzene and 1-bromo-4-ethylbenzene gave the corresponding C-C coupled product in good yields (Table 2, entries **2a**-**2c**).

Table 2. Substrate scope for Suzuki-Miyaura cross-coupling reactions[a]





Reaction conditions: Aryl iodide/Aryl bromide/Aryl chloride (0.80 mmol), Arylboronic acid (0.70 mmol) and base (2 mmol) at 50 °C temperature. [b]Isolated yields.

The reaction between phenylboronic acid with electron-donating groups such as -OMe on aryl bromide, -NH_2 on aryl bromide/aryl chloride, and -Me on aryl iodide were smoothly converted to substituted biphenyl products in good yields (Table 2, entries **2d**-**2f**). Additionally, the electron-withdrawing substituents such as -NO_2, -Cl on aryl iodide, and -CN on aryl iodide/aryl chloride were also explored, which led to their corresponding coupled products in 90%, 88%, and 90% yields respectively, in the case of aryl chloride for -CN substituent the yield of the C-C coupled product is 88% (Table 2, entries **2g**-**2i**).The reaction between 4-bromobenzylalcohol and phenylboronic acid under similar reaction conditions effectively converted to biphenyl-4-methanol in 70% yield (Table 2, entry **2j**). Further, *p*-ethylphenylboronic acid was reacted to form the desired product 1-(4'-ethyl-[1,1'-biphenyl]-4-yl) ethan-1-one in good yield (Table 2, entry **2k**). Moreover, *p*-bromoacetophenone and *p*-bromobenzaldehyde also furnished their respective coupled products in the presence of palladium catalyst **2** (Table 2,

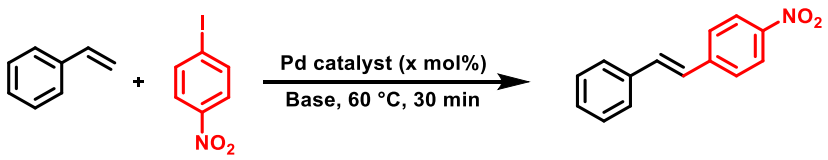
entry **2l**-**2m**). 2-Bromo-4-fluoroaniline and phenylboronic acid were coupled smoothly to 5-fluoro-[1,1'-biphenyl]-2-amine in 72% yield (Table 2, entry **2n**). Further, 1,4-dibromobenzene also reacted to form the desired product in 84% yield (Table 2, entry **2o**). 1,5-Dibromopentane also reacted with phenylboronic acid to form 1,5-diphenylpentane in the presence of palladium catalyst **2** (Table 2, entry **2p**) under similar reaction conditions. The reaction between *p*-chlorophenol with phenylboronic acid yielded the C-C coupled product in 79% yield (Table 2, entry **2q**). Similarly, *p*-chlororbenzenethiol reacted with phenylboronic acid under similar reaction conditions to form the [1,1'-biphenyl]-4-thiol in 75% yield (Table 2, entry **2r**). Further, the reaction of 4-methoxyboronic acid with 2-iodothiophenone and methyl-2-amino-5-bromobenzoate reacted to form the C-C coupled products in good yields (Table 2, entry **2s**-**2t**).

After the successful synthesis of Suzuki-Miyaura cross-coupling C-C products, we further studied the Heck-Mizoroki cross-coupling reactions under similar reaction conditions. Firstly, the reaction of styrene with 1-iodo-4-nitrobenzene was studied in the presence of palladium catalyst **1** and the results were depicted in Table 3. Initially, catalyst **1** (1.0 mol%) in DMF solvent was performed with K_2CO_3 (2 mmol) as a base obtained exclusively C-C coupled product in 88% yield (Table 3, entry 1). Further, a decrease in catalyst loading to 0.5 mol% yielded the product's 57% yield (Table 3, entry 2). Then, we performed the coupling reaction in the presence of palladium catalyst **2** (0.5 mol%) in DMF at 60 °C to afford the C-C coupling product exclusively in 90% yield (Table 3, entry 3). The use of different solvents such as THF, toluene, MeOH, and 1,4-dioxane yielded the C-C cross-coupling product in 40%, 52%, 45%, and 27% respectively (Table 3, entries 4-7). Further, the variation in the base to KO^{t}Bu under similar reaction conditions obtained the C-C coupled product with a 60% yield (Table

3, entry 8). The use of Pd $(OAc)_2$ yielded in 73% yield of C-C coupled product (Table 3, entry 9). The reaction of $(CH_3CN)_2PdCl_2$ yielded in 67 % yield of C-C coupled product (Table 3, entry 10).

Using 0.5 mol% of palladium catalyst **2**, K_2CO_3 (2 mmol) in DMF solvent at 60 °C, we explored the substrate scope for Heck-Mizoroki cross-coupling reactions and the C-C coupled products were obtained in excellent to moderate yields (Table 4). The catalytic reactions were explored by varying different substituents on the phenyl rings of olefin and aryl iodide/aryl bromide substituents. The reaction between styrene and 4-bromoaniline underwent smoothly in the presence of palladium catalyst **2** to form the C-C coupled product in 87% yield (Table 4, entry **3a**). Further, 1-iodo-4-nitrobenzene and 4-iodobenzonitrile also reacted under similar reaction conditions to form their C-C coupled products in good yields (Table 4, entry **3b**-**3c**). The use of 4-bromobenzaldehyde led to the formation of coupled product (*E*)-4-styrylbenzaldehyde in 86% yield (Table 4, entry **3d**). Next, we investigated 4-methoxystyrene as a coupling partner with 2-bromoaniline, 4-bromoaniline, and 4-bromo-2-methylaniline in the presence of palladium catalyst **2**, obtained the desired products in 88%, 90%, and 88% yield respectively (Table 4, entry **3e**-**3g**).

Table 3. Optimization table for the Heck-Mizorokicross-coupling reactions



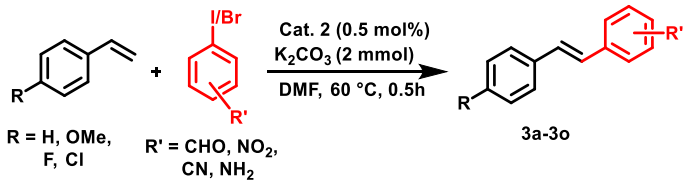
Entry	Catalyst	Catalyst Mol%	Solvent	Base	Yield (%) [b]

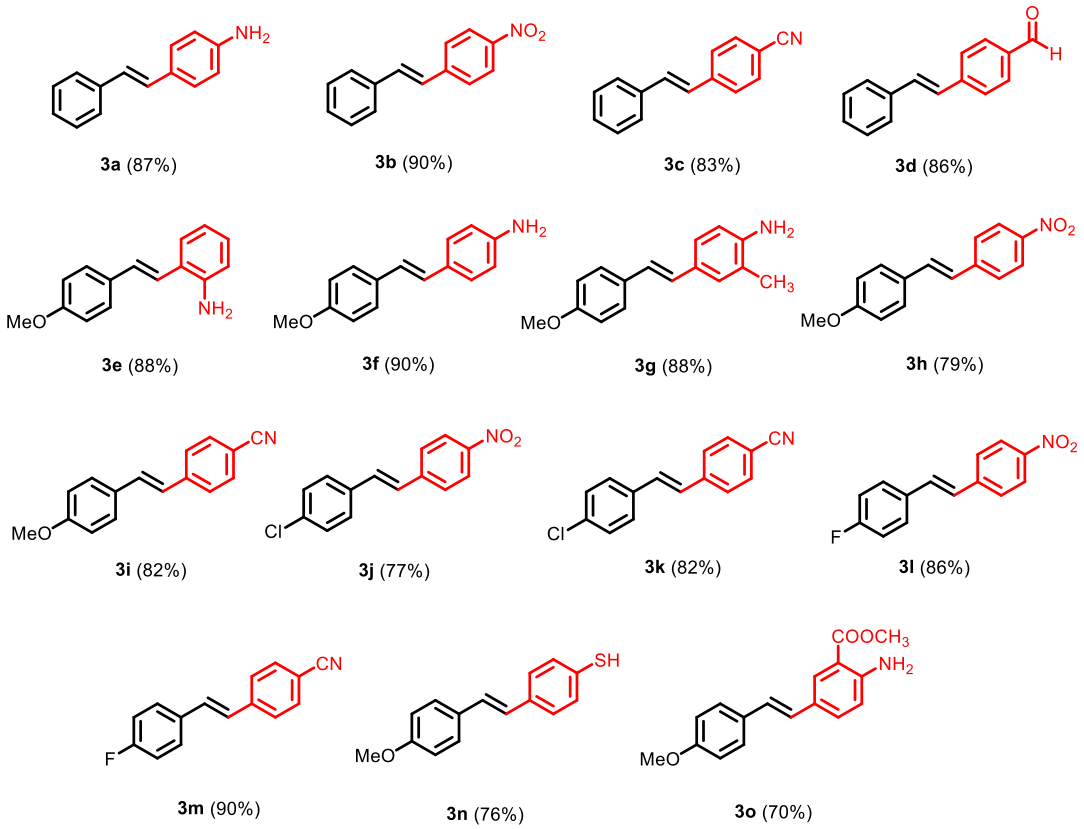
1	Cat.1	1.0	DMF	K_2CO_3	88
2	Cat.1	0.5	DMF	K_2CO_3	57
3	**Cat.2**	**0.5**	**DMF**	**K_2CO_3**	**90**
4	Cat.2	0.5	THF	K_2CO_3	40
5	Cat.2	0.5	Toluene	K_2CO_3	52
6	Cat.2	0.5	MeOH	K_2CO_3	45
7	Cat.2	0.5	Dioxane	K_2CO_3	27
8	Cat.2	0.5	DMF	KO^{t}Bu	60
9	Pd $(OAc)_2$	0.5	DMF	K_2CO_3	73
10	$(CH_3CN)_2PdCl_2$	0.5	*i*-PrOH	K_2CO_3	67

Reaction conditions: [a]Styrene (0.40 mmol), 1-iodo-4-nitrobenzene (0.60 mmol) and base (2 mmol) at 60 °C temperature. [b]Isolated yields.

Further, 4-methoxy styrene reacted with 1-iodo-4-nitrobenzene in which C-C coupled product (*E*)-1-methoxy-4-(4-nitrostyryl) benzene was obtained in 79% yield (Table 4, entry **3h**). In the case of 4-iodobenzonitrile, under similar reaction conditions, the C-C coupled product (*E*)-4-(4-methoxystyryl) benzonitrile was obtained in good yield (Table 4, entry **3i**). Next, we accomplished the cross-coupling reaction in the presence of 4-chlorostyrene with 4-iodonitrobenzene and 4-bromobenzonitrile which underwent smoothly to form the desired C-C coupled product in 77% and 82% yield respectively (Table 4, entries **3j**-**3k**).

Table 4. Substrate scope for Heck-Mizoroki cross-coupling reactions[a]





Reaction conditions: [a]Aryl iodide/ aryl bromide (0.60 mmol), substituted olefin (0.40 mmol) and base (2.0 mmol), solvent (1.0 mL) at 60 °C temperature. [b]Isolated yields.

The reaction between 1-fluoro-4-vinylbenzene and 1-iodo-4-nitrobenzene in the presence of 0.5 mol% loading of palladium catalyst **2**, the(*E*)-1-fluoro-4-(4-nitrostyryl) benzene obtained in 86% yield (Table 4, entries **3l**). Similarly, when 1-fluoro-4-vinylbenzene was reacted with 4-bromobenzonitrile under similar reaction conditions, the C-C coupled product obtained in 90% yield (Table 4, entries **3m**). Further, 1-methoxy-4-vinylbenzene also reacted smoothly with 4-bromobenzenethiol in the presence of palladium catalyst **2** (0.5 mol%) and K_2CO_3 to form the (*E*)-4-(4-

methoxystyryl) benzenethiol in 76% yield (Table 4, entries **3n**). Similarly, the reaction between 1-methoxy-4-vinylbenzene and methyl-2-amino-5-bromobenzoate also underwent smoothly to form the C-C coupled product in 70% yield (Table 4, entries **3o**). Thus, considering the Suzuki-Miyaura and Heck-Mizoroki coupling reactions, palladium catalyst **2** exhibits better efficiency with lower catalyst loading at lower temperatures and shorter reaction times than those of other NHC-supported palladium catalysts known in the literature. [23-29].

Conclusions

In summary, we have illustrated the synthesis of air and moisture-stable palladium complexes **1** and **2**. Complex **2** was achieved by ortho metalation of the phenyl group with Pd metal under reaction conditions. The cyclo-metallated palladium complex **2** acts as a robust catalyst in the cross-coupling of Suzuki-Miyaura and Heck-Mizoroki reactions with broad substrate scope. The substituted aryl bromides, aryl iodides, and aryl chlorides were converted to their C-C coupled products in excellent yields. The reactions were performed under mild conditions in the presence of a stable palladium complex **2** supported by a dinitrogen-based ligand. Thus, this protocol is a useful alternative to existing processes for synthesizing C-C coupled products with a wide-ranging substrate.

Experimental

Synthesis of ligands L1 and L2

A solution of pyridine-2-carboxyaldehyde (0.26 mL, 2.72 mmol) in EtOH and benzhydrylamine (500 mg, 2.72 mmol) or tritylamine (740 mg, 2.72 mmol) in ethanol was added to it. A few drops of glacial acetic acid (0.3 mL) were added to the reaction mixture. The solution was stirred at room temperature for 8 h. The precipitate was washed with cold ethanol. The ligands **L1** and **L2** were obtained as a white-colored solid.

Complex 1: $PdCl_2(CH_3CN)_2$ (65 mg, 0.36 mmol) was added to a solution of N-benzhydryl-1-(pyridine-2-yl) methenamine **L1** (100 mg, 0.36 mmol) in CH_3CN. The reaction mixture was stirred for 12 h. The solid was washed with Et_2O and recrystallized from CH_3CN to obtain orange crystals of palladium complex **1**.

Complex 2: $PdCl_2(CH_3CN)_2$ (50 mg, 0.28 mmol) was added to a solution of Py=NH(CPh_3) **L2** (100 mg, 0.28 mmol) in CH_3CN. The reaction mixture was stirred for 12 h. The solid was washed with Et_2O and recrystallized from CH_3CN to obtain orange crystals of palladium complex **2**.

Typical procedure for Pd (II) complex 2-catalyzed Suzuki-Miyaura cross-coupling reactions

Aryl boronic acid (0.70 mmol), K_2CO_3 (2.0 mmol), Aryl halide (0.80 mmol), and isopropanol (1.0 mL) were added to a Schlenk tube containing palladium catalyst **2** (2 mg, 0.5 mol%). The Schlenk tube was placed in a preheated (50 °C) oil bath and stirred for one hour. After completion of the reaction, the mixture was quenched with water, extracted with CH_2Cl_2, dried over Na_2SO_4, and filtered through a pad of celite. After rotary evaporation, the residue was purified by column chromatography (silica gel, petroleum ether/EtOAc) to give the desired product. All products were purified by

column (silica 60-120 mesh) chromatography and characterized by NMR spectroscopy (ESI Figures FS9–FS46).

Typical procedure for Pd (II) complex 2–catalyzed Heck-Mizoroki cross-coupling reactions

To 5 mL of DMF in a Schlenk tube, aryl halide (0.40 mmol), aryl olefin (0.60 mmol), K_2CO_3 (2 mmol), and palladium catalyst **2** (2 mg,0.5 mol %) were added subsequently. The solution was heated to 60 °C for 0.5 h. The reaction mixture was added to 20 mL of water and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was washed with water (2 × 20 mL), dried with anhydrous Na_2SO_4, and concentrated in a vacuum. After rotary evaporation, the residue was purified by column chromatography (silica gel, petroleum ether/EtOAc) to give the desired product. All products were purified by column (silica 60-120 mesh) chromatography and characterized by NMR spectroscopy (ESI Figures FS47–FS76).

Supporting information summary

Synthesis procedure and characterization data of ligands **L1** and **L2**, crystallographic data and ^{1}H, $^{13}C\{1H\}$ NMR spectra pertaining to complex **1** and **2**, the general procedure for catalytic Suzuki-Miyaura and Heck-Mizoroki cross-coupling reactions and characterization data of coupling products (**2a–2u** and **3a–3o**) are given in the electronic supporting information.

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