

An air stable and efficient palladium catalyst for Suzuki-Miyaura cross coupling reaction at room temperature

Raheleh Pourkaveh^a, Hirbod Karimi^{b,*}

^aLaboratory of Organic Synthesis and Natural Products, Department of Chemistry, Sharif University of Technology, Azadi Street, PO Box 111559516 Tehran, Iran.

^bYoung Researchers and Elite Club, Shahreza Branch, Islamic Azad University, Shahreza, Iran.

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ABSTRACT

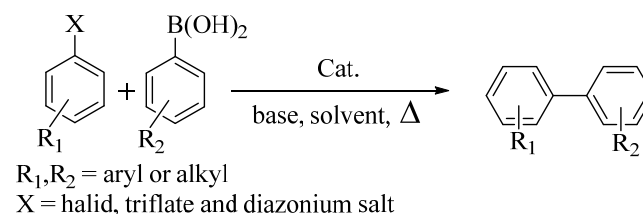
The cross-coupling reaction between phenylboronic acid and various types of aryl halides (Suzuki reaction) was carried out using a catalytic amount of a new palladium catalyst (1-benzyl-3-(1-benzyl-1-methylpyrrolidin-1-ium-2-yl) pyridin-1-ium palladium chloride [DBNT][PdCl₄]) in poly (ethylene glycol) (PEG-200) in the presence of KOH as the base. This new catalyst was synthesized and characterized by elemental analysis, NMR spectroscopy, UV-visible, and FT-IR spectra. This palladium catalyst is not sensitive to air and moisture, so reactions were carried out without using inert atmosphere at room temperature. The steric and electronic properties of the different substrates had a significant influence on the reaction conditions. This method for the synthesis of biaryls has several key advantages, including mild, environmentally friendly, and phosphine-free reaction conditions, excellent conversions as well as good to excellent yields, facile work-up.

Keywords: Palladium, Suzuki reaction, Phosphine-free, Room temperature, Arylboronic acid.

1. Introduction

Over the past 30 years, palladium-catalyzed cross-coupling reactions have gained popularity, especially as a suitable technique for the formation of carbon-carbon bonds. The palladium-catalyzed cross coupling reactions such as Stille [1,2] Suzuki [3-6] and Kumada-Hiyama [7] have become some of the most powerful methods for generating diversified biaryls which are used as building blocks for the synthesis of fine chemicals, functional materials and industrial starting materials. Specifically, the Suzuki-Miyaura cross-coupling reaction of aryl halides with arylboronic acids has emerged as the most important reaction and a reliable method for the construction of asymmetric biaryls [8-11]. During the past two decades, an exponential rise in the number of publications has been seen in the Suzuki-Miyaura reactions [12-14]. In this method, an organic electrophile and a nucleophilic organoboron derivative couple in the presence of a palladium catalyst (Scheme 1).

The special benefits of the Suzuki-Miyaura coupling are the straightforward synthesis of the wide tolerance compounds with vast functional groups under normal conditions, commercial availability of organoboron reagents, easy handling of these materials, use of aqueous inorganic bases, coupling of steric hindered substrates and removal of the nontoxic boron-containing byproducts [15-18]. Biaryls are considered as 'privileged structures' because of their prominence in pharmaceuticals. In many cases, one or both of the aryl groups contain a hetero atom. They have been found in many drugs like antibiotics, anticancer, antifungal and anti-hypertensive agents.



*Corresponding author email: h_karimi11x@yahoo.com
Tel.: +98 91 3304 6656

Scheme 1. Suzuki cross-coupling reaction.

Additionally, they are the integral part of some agrochemicals and liquid crystal displays, and have actively been incorporated into molecular machines, for example, catenanes [19-24]. In view of the importance of biaryls, a number of catalytic methods have been developed for forming these compounds in cross-coupling reactions. The key step in such syntheses is almost always the coupling of the two aromatics [25-29]. The Pd-catalyzed Suzuki reactions are well-known as influential methods to construct C-C bond in modern chemical transformations [30-33]. The high productivity of the palladium catalyst is due to the slow generation of low ligated Pd(0) complexes from a stable palladium(II) pre-catalyst [32,34]. Thus, in recent years, the development of new and efficient palladium catalytic systems has become a matter of wide interest. Although some of these methods have convenient protocols with good to high yields, the majority suffers from at least one of the following disadvantages: high temperature, the use of an appropriate ligand to accelerate the reaction and long reaction times.

In continuation of our recent investigations on the synthesis and application of efficient green catalysts, especially palladium catalysts in cross-coupling reactions, herein we report the application of a new, air and moisture-stable Pd(II) complex containing 1-benzyl-3-(1-benzyl-1-methylpyrrolidin-1-ium-2-yl)pyridin-1-ium with general formula [DBNT][PdCl₄] in Suzuki-Miyaura cross coupling reaction of various aryl halides with aryl boronic acids. This quaternary nicotinium cation stabilizes the Pd(0) species during the reaction process by preventing formation of unreactive palladium black. The validity of this catalyst performance was proved by the description of the effect of tetraalkylammonium salts on the activity and stability of palladium catalyst, which has been reported by Jeffery in 1996 [35]. With this new catalyst, the Suzuki cross-coupling reactions took place at room temperature in excellent conversions within short reaction times.

2. Experimental

2.1. General

NMR spectra were recorded at 400 MHz in DMSO solutions at room temperature (TMS was used as an internal standard) on a Bruker Avance 400 instrument (Rheinstetten, Germany). FT-IR spectra were recorded on a spectrophotometer (Jasco 680, Japan). Spectra of solids were carried out using KBr pellets.

Vibrational transition frequencies are reported in wave number (cm⁻¹). UV-visible spectra were recorded on a spectrophotometer

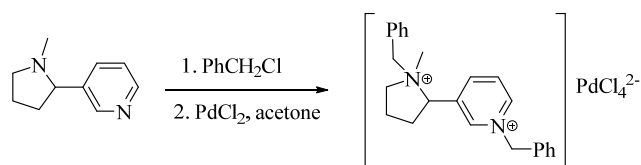
(Jasco V-570, Japan). The gas chromatography spectroscopy (GC) analyses were performed by the Agilent 5975C spectro-meter. Palladium acetate, aryl halides, and all chemicals were purchased from Merck and Aldrich and were used as received.

2.2. Catalyst synthesis

Amounts of 1 mmol (-)-nicotine with 4 mmol benzyl chloride were mixed under solvent-free conditions and the reaction mixture was heated at 70 °C for 6 hours. The reaction mixture was treated with dichloromethane (5×6 ml) to remove the unreacted materials and the dichloromethane phase was separated. The residue was obtained in 82% yields (0.340 g) and then was mixed with PdCl₂ (0.177 g PdCl₂: 0.415 g dibenzylated nicotinium salt) in acetone and refluxed for 12 hours. The supernatant was decanted and washed with acetone (3×5 ml) to produce the catalyst in 91% (0.530 g) yields as a brown powder [36] (Scheme 2).

2.3. General experimental procedure for Suzuki cross-coupling reaction

To a round-bottomed flask equipped with a magnetic stirring bar were added aryl halide (1 mmol), arylboronic acid (1.3 mmol), KOH (2 mmol), PEG-200 (1 ml), and the catalyst (0.5 mol%). As the catalyst is not sensitive to oxygen and moisture, the reactions mixture was stirred under air atmosphere for certain times (monitored by GC). The crude products were extracted with ethyl acetate (3×10 mL). The organic phases were separated and dried over CaCl₂. The solvent was removed under vacuum and when necessary the residual was purified by column chromatography on silica gel (silica gel 60, 70-230 mesh) with n-hexane / EtOAc (9:1) as eluent to afford the corresponding pure products. The biaryl products are known compounds and were characterized (See supplementary data) by comparing their IR, ¹H and ¹³CNMR spectra with those found in the literature [5,8,31].



Scheme 2. The catalyst ([DBNT][PdCl₄]) synthesis.

3. Results and discussion

3.1. Catalyst characterization

^{13}C NMR (100 MHz, DMSO): δ = 18.69 (C3'), 25.58 (C4'), 41.23 (CH_3 _{pyro}), 62.94 (CH_2 benzyl.pyro), 63.77 (CH_2 benzyl.py), 65.16 (C2'), 74.57 (C5'), 128.37 ($\text{C}_{\text{arom.phenyl}}$), 128.96 (C5), 129.22 ($\text{C}_{\text{arom.phenyl}}$), 129.48 ($\text{C}_{\text{arom.phenyl}}$), 130.30 ($\text{C}_{\text{arom.phenyl}}$), 132.47 ($\text{C}_{\text{arom.phenyl}}$), 132.91 ($\text{C}_{\text{arom.phenyl}}$), 133.82 (C3), 146.15 (C4), 147.56 (C2), 148.20 (C6) ppm. ^1H NMR (400 MHz, DMSO): δ = 1.27-1.32 (2H, m, H3'), 2.15-2.30 (2H, m, H4'), 2.50-2.74 (2H, m, H2'), 3.36 (3H, s, CH_3), 4.35 (1H, d, J = 12.0 Hz, $\text{CH}_{\text{benzyl.pyro}}$) 4.69 (1H, d, J = 12.0 Hz, $\text{CH}_{\text{benzyl.pyro}}$), 5.35 (1H, t, J = 10.8 Hz, H5'), 5.96 (2H, s, CH_2 benzyl.py), 7.47-7.63 (10H, m, H_{phenyl}), 8.43 (1H, dd, J_1 = 8.0 Hz, J_2 = 6.0 Hz, H5), 9.03 (1H, d, J = 8.0 Hz, H4), 9.39 (1H, d, J = 6.0 Hz, H6), 9.60 (1H, s, H2) ppm. FT-IR (KBr): $\bar{\nu}$ = 700, 900, 1468, 1632, 2945, 3018, 3412 cm^{-1} ; UV-Vis (DMSO): 267, 309 nm. Anal. Calcd. For $\text{C}_{24}\text{H}_{28}\text{Cl}_4\text{N}_2\text{Pd}$: C 48.63, H 4.76, N 4.73; Found C 48.10, H 4.35, N 4.33.

According to ^1H -NMR spectrum of the catalyst, dd peak appeared at 4.69 ppm which is attributed to benzylic position attached to the nitrogen of pyrrolidine. In addition, singlet peak appeared at 5.96 ppm which is related to benzylic position connected to the pyridine part of molecule. These observations indicate that both nitrogen atoms of (-) nicotine were successfully benzylated. Also, the presence of stretching mode for C-H vibrations at around 3000 cm^{-1} in FT-IR spectrum of the catalyst confirmed the structure of prepared catalyst.

UV absorbance spectra of (-) nicotine, 1-benzyl-3-(1-benzyl-1-methylpyrrolidin-1-ium-2-yl) pyridin-1-ium chloride (benzylated nicotine), PdCl_2 , and mono (1-benzyl-3-(1-benzyl-1-methylpyrrolidin-1-ium-2-yl) pyridin-1-ium) monopalladium (II) tetrachloride (catalyst) in dimethyl sulfoxide (DMSO) were recorded (Fig. 1). The 276 nm band corresponds to $\pi \rightarrow \pi^*$ transition of pyridine ring. Benzylated nicotine shows a 270 nm band which has hypsochromic shift relative to (-) nicotine due to having positive nitrogen atoms. In the electronic spectrum of PdCl_2 solution intense bands at 297 nm and 330 nm having a value of CTB from chloride ions to the metal. The electronic spectrum of the catalyst shows two bands at about 267 nm (associated with the $\pi \rightarrow \pi^*$ transition) and 309 nm. It seems coordination of chloride ion in PdCl_4^{2-} and involving in a complex makes the bond length shorter. So, the bonding energy increases, which results in shifting to lower wave length.

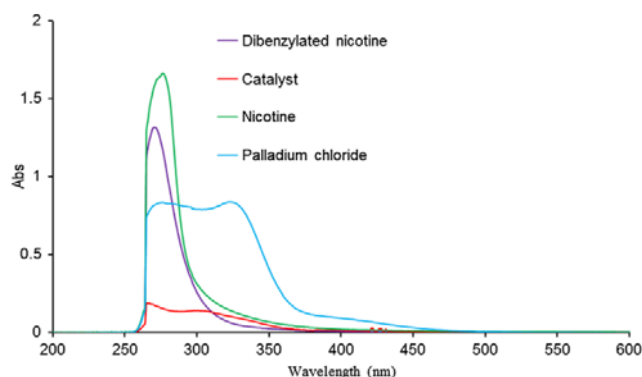


Fig. 1. Absorption spectra of catalyst and starting materials for its synthesis.

3.2. Catalytic activity in Suzuki cross coupling reaction

Initially, to optimize the reaction conditions, the effects of the solvents, bases, and the amount of the catalyst, on Suzuki cross coupling reaction was examined through the reaction of 4-iodoanisole and phenylboronic acid using $[\text{DBNT}][\text{PdCl}_4]$ complex as shown in Table 1.

As demonstrated in Table 1 (entry 2), KOH as the base and PEG-200 as the solvent gave the best results. Among organic and inorganic bases, KOH was chosen as the best choice. In case of other bases, crude starting materials remained intact and no significant desired product was detected. Exploring the effect of solvents on Suzuki reaction was also surveyed. Both polar and non-polar solvents were employed and among them PEG-200 gave the highest yield. Various catalyst concentrations were also tested and 0.5 mol% (Table 1, entry 2) gave the best result. As this catalyst is not sensitive to oxygen, the reactions were carried out under air atmosphere. The cross coupling reaction was also performed without a base or a catalyst (Table 1, entry 24-25). In both cases, no product was detected.

We applied the optimized conditions to the Suzuki cross-coupling reaction of different types of aryl halides with phenylboronic acids, as shown in Table 2. As it is demonstrated in Table 2, the $[\text{DBNT}][\text{PdCl}_4]$ complex catalyst can be used for cross-coupling reactions of aryl iodides, bromides, and even less reactive aryl chlorides with aryl boronic acids in good to excellent yields. In palladium catalyzed carbon-carbon bond formation reactions, it is commonly believed that better conversions are achieved for aryl halides with electron-withdrawing rather than electron-donating substituent [37,38]. We examined the electronic effects of various aryl halides bearing electron-donating and electron-withdrawing groups on the resulting yields and conversion times of the reactions.

Table 1. Optimization of reaction conditions on Suzuki reaction of 4-iodoanisole with phenylboronic acid.^a

Entry	Base	Solvent	Catalyst (mol%)	Time (min)	Conversion (%) ^b
1	K ₂ CO ₃	PEG-200	0.5	60	78
2	KOH	PEG-200	0.5	35	100
3	Na ₂ CO ₃	PEG-200	0.5	45	67
4	(CH ₃) ₃ COK	PEG-200	0.5	45	83
5	NaHCO ₃	PEG-200	0.5	50	68
6	CsF	PEG-200	0.5	40	66
7	Et ₃ N	PEG-200	0.5	45	80
8	Cs ₂ CO ₃	PEG-200	0.5	45	76
10	NaOAc	PEG-200	0.5	45	48
11	KOH	CH ₃ OH	0.5	75	34
12	KOH	CH ₃ OH / H ₂ O (2:1)	0.5	60	60
13	KOH	H ₂ O	0.5	60	70
14	KOH	NMP	0.5	90	15
15	KOH	Ethylene glycol	0.5	45	80
16	KOH	DMF	0.5	90	27
17	KOH	EtOH	0.5	60	76
18	KOH	THF	0.5	90	33
19	KOH	CH ₃ CN	0.5	90	57
20	KOH	PEG-200	0.1	45	72
21	KOH	PEG-200	0.25	40	83
22	KOH	PEG-200	0.75	35	95
23	KOH	PEG-200	1	35	91
24	-	PEG-200	0.5	60	-
25	KOH	PEG-200	-	60	-

^aReaction conditions: 4-iodoanisole (1 mmol), phenylboronic acid (1.3 mmol), base (3 mmol), solvent (2 mL) at r.t.

^bGC yield.

Aryl halides were substituted with electron-withdrawing groups and transformed into the corresponding coupled products with better conversions and shorter reaction times rather than an electron-donating substituent. The substituent effects in the aryl iodides emerged to be less significant than in the aryl bromides (Table 2, entries 1-6), and the reactivity of aryl bromides with electron-withdrawing substituent was higher than that of aryl bromides with electron-donating substituent (Table 3, entries 10–22). The steric hindrance of the procedure was examined using 2, 3 and 4-iodonitrobenzene, 3 and 4-iodoanisole, 2 and 4-bromonitrobenzene and 2, 3 and 4-bromoacetophenone as hindered substituted aryls (Table 3, entries 2-6, 12-16). Increased hindrance in the vicinity of the leaving group can cause a

decrease in the reaction conversion. Also, selectivity of the catalyst was examined by using ortho-, meta- and para-bromochlorobenzene (Table 2, entries 17–19 and 26, 27); in each case, only Br as the better leaving group was substituted and “Cl did not enter the reactions;” this means that the reaction acts chemoselectively and in comparison to Cl, Br is a better leaving group. These results prompt us to extend the optional process to less reactive and non-expensive aryl chlorides. The Suzuki reaction using aryl chlorides as substrate needs longer reaction times for completion under both reaction conditions (Table 3, entries 23-25). This catalytic complex was compatible with a wide range of functional groups such as nitro, cyano, methoxy, halogen, and carbonyl on aryl halides.

Table 2. Suzuki cross-coupling reaction using [DBNT][PdCl₄] as catalyst.

Entry	X	R ₁	R ₂	Time(min)	Conversion (%) ^b	Yield (%) ^c
1	I	H	H	15	100	90
2	I	2-NO ₂	H	60	92	88
3	I	3-NO ₂	H	45	100	95
4	I	4-NO ₂	H	30	100	95
5	I	2-OCH ₃	H	60	87	85
6	I	4-OCH ₃	H	45	95	93
7	I	H	4-OCH ₃	20	100	92
8	I	4-NO ₂	4-OCH ₃	45	100	93
9	I	3-NO ₂	4-OCH ₃	45	100	94
10	Br	H	H	25	100	87
11	Br	4-OCH ₃	H	60	93	83
12	Br	2-NO ₂	H	60	90	85
13	Br	4-NO ₂	H	30	100	90
14	Br	2-COCH ₃	H	75	87	75
15	Br	3-COCH ₃	H	60	94	83
16	Br	4-COCH ₃	H	45	100	92
17	Br	2-Cl	H	45	95	88
18	Br	3-Cl	H	30	100	93
19	Br	4-Cl	H	20	100	95
20	Br	4-CN	H	30	100	91
21	9-Bromophenanthrene		H	75	95	86
22	1-Br-Naphthalene		H	90	85	80
23	Cl	H	H	45	95	90
24	Cl	4-NO ₂	H	90	90	82
25	Cl	H	4-OCH ₃	90	90	78
26	Br	3-Cl	4-OCH ₃	40	90	82
27	Br	4-Cl	4-OCH ₃	30	100	92

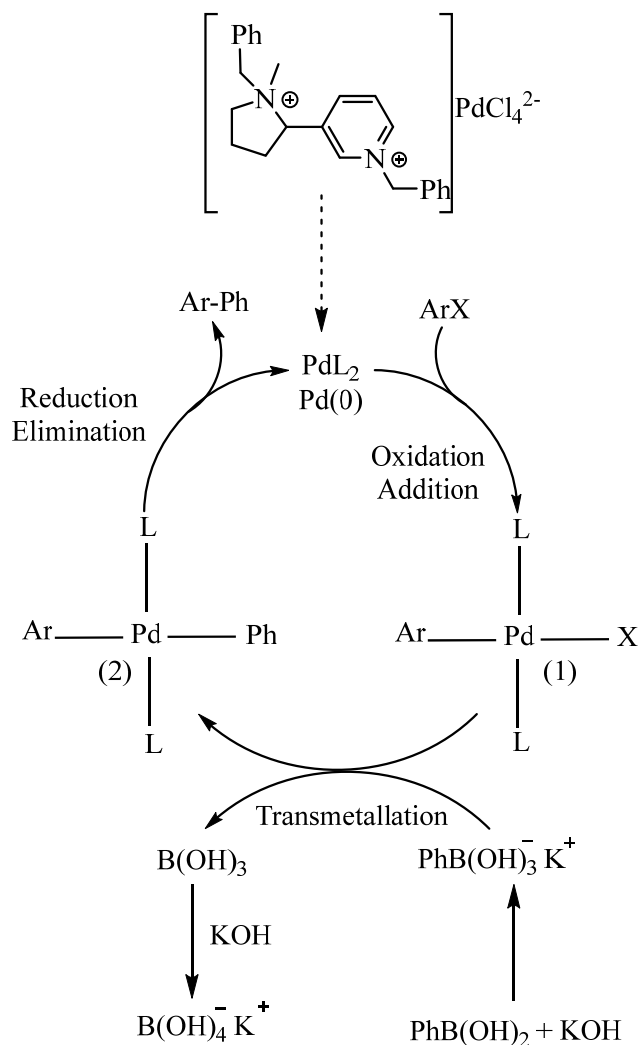
^aReaction conditions: 4-iodoanisole (1 mmol), phenylboronic acid (1.2 mmol), base (2 mmol), catalyst (0.5 mol %).^bGC yield.^cIsolated yield.

A mechanistic description of the Suzuki reaction has been presented in Scheme 3. Initially, Pd(II) converts to Pd(0) [37,39], followed by the oxidative addition of aryl halide to Pd(0) to form aryl palladium(II) intermediate 1. Phenylboronic acid which is activated

by KOH reacts with intermediate 1. After transmetalation reaction, the intermediate 2 obtains. Finally, reductive elimination of intermediate 2 produces the desired coupling products. To evaluate the suggested mechanism, the mercury drop test was

employed, since mercury leads to the amalgamation of the surface of a heterogeneous catalyst. In contrast, Hg(0) is not expected to have a poisoning effect on homogeneous palladium complexes, where the Pd(II) metal center is tightly bound to the ligand. When a drop of Hg(0) was added to the reaction mixtures of bromobenzene under mentioned optimized conditions at $t = 0$ min, no catalytic activity was observed for the catalyst. The obtained data confirm the Pd(0):Pd(II) cycle [34,40].

A comparison of the catalytic efficiency of [BMP][PdCl₄] with selected previously known catalysts is collected in Table 3. Of course, the reaction conditions are different, but the catalyst used in this study might be one of the best catalysts with regard to better yields, lower reaction time, and temperature.



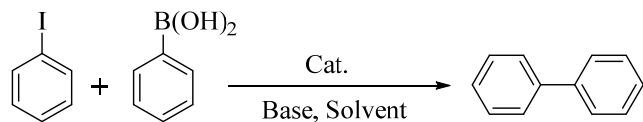
Scheme 3. Proposed mechanism for Suzuki reaction.

4. Conclusion

In summary, we have successfully synthesized and characterized [DBNT][PdCl₄] as an effective, not sensitive to air and moisture catalyst for room temperature Suzuki-Miyaura cross-coupling reaction of various aryl halides. The results clearly showed that the [DBNT][PdCl₄] shortened the required times for completion of the reactions from hours to minutes in comparison to the most conventional heating conditions. The yields were good to excellent, making this procedure a good synthetic route for biaryl synthesis.

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Table 3. Comparison of protocols for the Suzuki cross-coupling reaction.

Catalyst	Base	Solvent	Temp. (°C)	Time (min)	Yield %	Ref.
Cu-Pd/molecular sieve	K ₂ CO ₃	EtO	78	60	99	[8]
HT-Pd	K ₂ CO ₃	H ₂ O	100	10	92	[9]
PSPL-Pd	K ₂ CO ₃	DMF	80	100	96	[13]
Pd@g2Amino-Si(HIPE)	K ₂ CO ₃	Dioxane	Reflux	72 ^a	95	[15]
Pd@IRA-900	K ₂ CO ₃	EtOH/H ₂ O	70	60	99	[16]
Si-P4Vpy-Pd	K ₂ CO ₃	DMF	120	20	88	[18]
C-CeO ₂	K ₂ CO ₃	DMF	150	60	52	[25]
Pd(II) Schiff base	Cs ₂ CO ₃	H ₂ O	100	1	99	[27]
Pd(II)-NiFe ₂ O ₄	K ₂ CO ₃	EtOH/H ₂ O	80	180	86	[41]
Pd-NHC complex	Na ₂ CO ₃	DMF/water	80	120	83	[42]
PVC-EDA-SA-Pd	K ₂ CO ₃	EtOH	Reflux	240	84	[43]
[BMP][PdCl ₄]	KOH	PEG-200	RT	10	90	This work

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