

Suzuki-Miyaura cross-coupling reaction catalyzed using highly efficient CN-dimeric *ortho*-palladated complex under microwave irradiation and conventional heating

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ABSTRACT

Suzuki cross-coupling reaction of different aryl halides with arylboronic acids was successfully carried out in methanol using *ortho*-palladated complex of 2-methoxyphenethylamine. All substrates afforded the corresponding products in good to high yields in the presence of low amounts of this complex as efficient and active catalyst. Application of microwave irradiation improved the yields of the reactions and reduced the reaction times some extent in comparison with traditional heating conditions.

Keywords: *Ortho-palladated complex, Suzuki-Miyaura reaction, Aryl halide, Arylboronic acid, 2-Methoxyphenethylamine.*

1. Introduction

Transition metal-catalyzed cross-coupling reactions are very versatile and useful in organic chemistry [1]. Since these reactions represent a powerful and popular method for carbon-carbon bond formations, they have been widely studied [2]. Among these methods, the Suzuki-Miyaura reaction between organoboronic acids and aryl halides or triflates is one of the most extensively used protocols for the synthesis of biphenyls [3]. The rapid growth of studies in this area is mainly due to good tolerance of various functional groups, low toxicity and high stability of organoboranes towards air and moisture [4] along with wide applications of Suzuki products in the synthesis of various useful intermediates [5-7]. Since their discovery in the 1970s, various Pd/ligand complexes have been used as catalysts in this coupling reaction [8]. Phosphines are used extensively as ligands (such as simple *tert*-phosphines, hemilabile-type phosphines, sterically crowded biphenyl type phosphines and other electron-rich phosphines), but their sensitivity to air and moisture limits their stability and shelf-life [9]. Therefore, designing the efficient and phosphine-free ligands is still an important issue at present [10-11].

Among different palladium catalysts, palladacycles are one of the most famous classes of organopalladium derivatives. Since Beller and Herrmann's initial report on the use of a palladacycle derived from (*o*-tol)₃P and Pd(OAc)₂ for the palladium catalyzed Heck and Suzuki-Miyaura reactions, palladacycles have attracted a great deal of attention [12,13].

One disadvantage of the Suzuki reaction, especially with sterically hindered coupling partners, is the rather long reaction times [14]. Modern techniques are focused on the design of new methodologies, which are able to make the already known chemical transformations simpler, faster, cheaper and more efficient processes [15]. In this regard, microwave-assisted heating under controlled conditions is an alternative way to the traditional heating with the possible advantages of reducing the reaction time, increasing the yield, selectivity and purity of the products [16,17]. The first microwave-assisted Suzuki cross-coupling reaction was reported in 1996 [18,19]. Suzuki couplings under microwave irradiation in either sealed or open vessels have been extensively investigated by Leadbeater and coworkers [20-26].

They used organic bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,1,3,3-tetramethyl-guanidine (TMG) [27], and potassium organotrifluoroborates instead of phenyl boronic acids

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[24]. They also prepared a series of bis-imidazolium salts and used them for forming metal-NHC complexes, which were screened as catalysts in the Suzuki reaction [28,29].

In the Following of our investigation on the synthesis and applications of palladacycles in C-C cross coupling reactions [30-36], herein we report the utilization of $[\text{Pd}\{\text{C}_6\text{H}_3(\text{CH}_2\text{CH}_2\text{NH}_2)\text{-4-OMe-5-}\kappa^2\text{-C,N}\}(\mu\text{-Br})_2]$ in Suzuki-Miyaura reaction of various aryl halides and arylboronic acids under microwave irradiation and conventional heating conditions.

2. Experimental

2.1. General

All melting points were determined in open capillaries with a Gallenkamp instrument. The FT-IR adsorption spectra were run on a spectrophotometer (Jasco-680, Japan) as KBr disks or as smears between salt plates. Vibrational transition frequencies were reported in wave number (cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometer at 400 and 100 MHz, respectively; using CDCl_3 as solvent at room temperature (TMS was used as an internal standard). We used GC (BEIFIN 3420 Gas Chromatograph equipped with a Varian CP SIL 5CB column- 30 m, 0.32 mm, 0.25 μm) for examination of reactions completion. All reactions were carried out in open reaction vessels of the Milestone Microwave (Microwave Labstation- MLS GmbH- ATC-FO 300). All reagents and solvents used in this study, obtained from commercial suppliers (Acros, Merck and Aldrich) and used without further purification.

2.2. Synthesis of Palladacycle Complex

In a 25 mL round-bottom flask equipped with a magnetic stir bar and a condenser, a mixture of 258 mg (1.7 mmol) of 2-methoxyphenethylamine and 382 mg (1.7 mmol) of $\text{Pd}(\text{OAc})_2$ was heated in acetonitrile (20 mL) for 6 h at 55 °C. After cooling, the resulting suspension was filtered through a plug of MgSO_4 and the filtrate was vaporated under reduced pressure on a rotary evaporator to give complex **2** as a yellow solid. Solid sodium bromide (165 mg, 1.6 mmol) was added to a suspension of complex **2** (500 mg, 0.79 mmol) in acetone (30 mL) and the mixture was stirred for 8 h. The solvent was removed and CH_2Cl_2 (10 mL) was added. The resulting suspension was filtered through a plug of MgSO_4 and the filtrate was concentrated to 2 mL under reduced pressure on a rotary evaporator and *n*-hexane (15 mL) was added to precipitate a yellow solid, which was collected, washed with water and *n*-hexane and air dried. ^1H NMR (400 MHz, CDCl_3): δ = 7.22 (t, 1H, C_6H_3), 6.89 (d, 1H, C_6H_3), 6.86 (d, 1H, C_6H_3), 3.82 (s, 3H, OMe), 3.09 (m, 2H, CH_2CH_2), 2.84 (m, 2H, CH_2CH_2), 2.24 (br s, 2H, NH_2) ppm. ^{13}C NMR

(100 MHz, CDCl_3): δ = 156.10, 129.37, 126.90, 126.79, 119.23, 109.14, 54.08, 43.63, 35.90 ppm. IR (KBr): $\bar{\nu}$ = 3228, 3225, 2936, 1599, 1571, 1494, 1460, 1244, 1031, 754 cm^{-1} .

2.3. General procedure for the Suzuki-Miyaura reaction of aryl halides with arylboronic acids

A mixture of the appropriate aryl halide (1 mmol), arylboronic acid (1.2 mmol), palladacycle complex (0.1 mol%, 0.0007 g), and K_2CO_3 (1 mmol, 0.138 g) was added to methanol (3 mL) in a round-bottom flask equipped with condenser and placed into the Milestone Microwave or an oil bath. Initially the microwave irradiation was set at 500 W, the temperature was ramped from room temperature to the desired temperature of 65 °C. Once this was reached, the reaction mixture was held at this temperature until the reaction was completed. During this time, the power was modulated automatically to keep the reaction mixture at 65 °C. After completion of the reaction, as indicated by TLC and GC, 20 mL water was added to the mixture and the product was extracted with *n*-hexane (20 mL). The organic phase was dried over CaCl_2 , filtered and the solvent was evaporated using rotary evaporator. The residue was purified by silica gel column chromatography (*n*-hexane:EtOAc, 9:1). All synthesized cross-coupled products were characterized by spectral data (IR, ^1H and ^{13}C NMR), their melting points and comparison with authentic samples [37-42].

Selected spectral data

4-Acetylbiphenyl (Table 3, entry 7):

m.p.= 117-118 °C [37], found 118-120 °C. ^1H NMR (500 MHz, CDCl_3): δ = 8.03 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 7.2 Hz, 2H), 7.47 (t, J = 7.8 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 2.62 (s, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 198.15, 146.21, 140.32, 136.31, 129.39, 128.67, 127.71, 127.66, 27.08 ppm. IR (KBr): $\bar{\nu}$ = 3073, 2916, 1680, 1600, 1262, 764 cm^{-1} .

Biphenyl-4-carbaldehyde (Table 3, entry 10):

m.p.= 60-63 °C [38], found 59-60 °C. ^1H NMR (500 MHz, CDCl_3): δ = 9.95 (s, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 7.2 Hz, 2H), 7.38 (t, J = 7.2 Hz, 2H), 7.32 (t, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 191.99, 147.20, 139.72, 135.20, 130.31, 129.05, 128.51, 127.71, 127.39 ppm. IR (KBr): $\bar{\nu}$ = 3029, 2835, 2744, 1697, 1602, 1562, 1215, 1171, 834, 763 cm^{-1} .

4-Phenylbenzophenone (Table 3, entry 18):

m.p.= 256-258 °C. ^1H NMR (500 MHz, CDCl_3): δ = 7.90 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 7.7 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.49 (dd, J = 7.8 Hz, 4H), 7.41 (t,

$J = 7.5$ Hz, 1H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 196.76, 145.67, 140.43, 138.22, 136.69, 132.79, 131.15, 130.43, 129.40, 128.74, 128.62, 127.74, 127.40$ ppm. IR (KBr): $\bar{\nu} = 3051, 1644, 1602, 1578, 1445, 1401, 1318, 1290, 940, 851, 769, 757$ cm^{-1} .

4,4'-Dimethoxybiphenyl (Table 3, entry 20):

m.p. = 178-179 °C [39], found 175-177 °C. ^1H NMR (500 MHz, CDCl_3): $\delta = 7.48$ (d, $J = 8.8$ Hz, 4H), 6.96 (d, $J = 8.76$ Hz, 4H), 3.84 (s, 6H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 159.14, 133.93, 128.16, 114.60, 55.77$ ppm.

3. Results and Discussion

Synthesis and application of $[\text{Pd}\{\text{C}_6\text{H}_2(\text{CH}_2\text{CH}_2\text{NH}_2)-(\text{OMe})_{2,3,4}\}(\mu\text{-Br})_2]$ complex as an efficient homogeneous catalytic system in the Suzuki-Miyaura coupling reaction was reported in our previous work [31]. In this complex, because of the presence of the electron-donating methoxy group *ortho* to the C-Pd bond, breaking of this bond is difficult leading to lower reaction rates. In order to conquer this problem, we successfully synthesized the $[\text{Pd}\{\text{C}_6\text{H}_3(\text{CH}_2\text{CH}_2\text{NH}_2)-4\text{-OMe}-5\text{-}\kappa^2\text{-C,N}\}(\mu\text{-Br})_2]$ complex that could act as a better catalyst compared to the previous one [30]. Another main advantage of this catalyst is its easier preparation method. Furthermore, although homoveratrylamine (3,4-dimethoxyphenethylamine) ligand has two positions for the formation of palladacycle, 2-methoxyphenethylamine has only one such position. The efficiency of this complex as a catalyst for the Suzuki reaction of various types of aryl halides with different arylboronic acids was examined (Scheme 1).

In order to optimize the reaction conditions, preliminary experiments were carried out for the reaction of 4-bromoanisole and phenylboronic acid in the presence of various solvents and bases using 0.3 mol% of catalyst. Several organic solvents such as toluene, acetonitrile, *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), 1,4-dioxane and methanol were examined.

According to given data in Table 1, methanol was the

best solvent for this reaction (Table 1, entry 7).

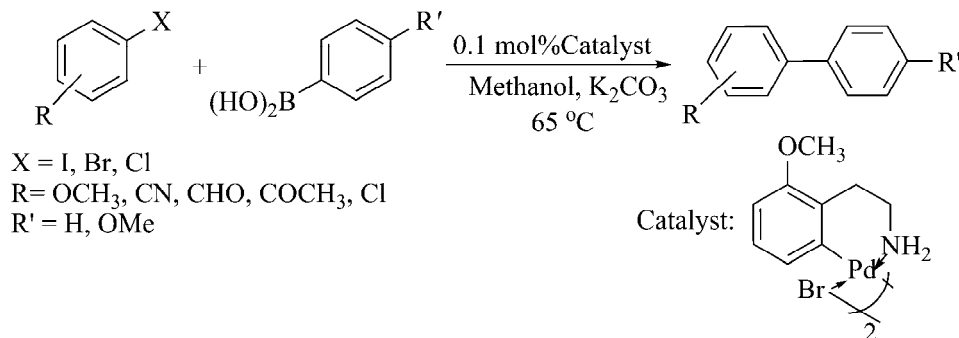
After choosing methanol as the solvent, we screened several different bases. An investigation on the effect of base indicated that the base was mandatory for the Suzuki-Miyaura cross-coupling reaction (Table 1, entry 9). As can be seen in Table 1, K_2CO_3 and Cs_2CO_3 have approximately the same efficiency, and since Cs_2CO_3 is more expensive, K_2CO_3 was chosen as the best (Table 1, entries 7 and 8).

Various amounts of catalyst were also tested for the reaction of 4-bromobenzonitrile and phenylboronic acid (Table 2). In this reaction, 0.1 mol% gave the best result, so it was chosen as the optimum amount.

Since this catalyst is not sensitive to oxygen, the reactions were carried out under atmosphere. The optimum reaction conditions were applied in the Suzuki reaction of different aryl halides and arylboronic acids under microwave irradiation (Table 3).

Reactions were performed with both electron donating and electron withdrawing groups and results clearly showed that there is not any sensitivity to substituents on the aryl ring. The chemoselectivity of the method was investigated using *ortho*-, *meta*- and *para*-bromochlorobenzene as the model substrates. In each case only Br as the better leaving group was substituted and Cl was not entered the reactions. It is worth mentioning that in Suzuki reactions 4-methoxyphenylboronic acid as boron reagent acted as good as unsubstituted phenylboronic acid.

As can be seen in Table 3, full conversions were achieved in all cases except for the reaction of 2-bromoacetophenone and 4-chlorobenzaldehyde, which did not proceed quantitatively in the definite time even by prolonging the reaction time (Table 3, entries 9 and 11). This can be due to the more steric hindrance in the vicinity of leaving group (Br) in the former and less reactivity of Cl as leaving group in the later. The reaction of 1,4-dibromobenzene as a difunctional aryl halide also proceeded quantitatively in a short reaction time using twofold amount of other substrates.



Scheme 1. The Suzuki cross-coupling reaction by *ortho*-palladated catalyst.

Table 1. Optimization of base and solvent in the Suzuki reaction using the *ortho*-palladated catalyst under microwave irradiation.^a

Entry	Base	Solvent	Temp. (°C)	Time (min)	Conversion (%) ^b
1	K ₂ CO ₃	DMF	130	2	98
2	Na ₂ CO ₃	DMF	130	2	90
3	NaOAc	DMF	130	2	80
4	Cs ₂ CO ₃	DMF	130	2	98
5	Et ₃ N	DMF	130	2	75
6	K ₂ CO ₃	THF	Reflux	2	65
7	K ₂ CO ₃	MeOH	Reflux	1	100
8	Cs ₂ CO ₃	MeOH	Reflux	1	100
9	-	MeOH	Reflux	2	0
10	K ₂ CO ₃	Toluene	Reflux	2	55
11	K ₂ CO ₃	CH ₃ CN	Reflux	2	70
12	K ₂ CO ₃	NMP	130	2	95
13	K ₂ CO ₃	1,4-Dioxane	Reflux	2	50

^aReactions conditions: 4-bromoanisole (1 mmol), phenylboronic acid (1.2 mmol), base (1 mmol), palladacycle (0.3 mol%), solvent (3.0 ml).

^bDetermined by GC.

Table 2. Optimization of catalyst concentration.^a

Entry	Catalyst (mol%)	Time (min)	Conversion (%) ^b
1	None	1	0
2	0.05	1	88
3	0.1	1	98
4	0.2	1	100
5	0.3	1	100

^aReactions conditions: 4-bromobenzonitrile (1.0 mmol), phenylboronic acid (1.2 mmol), K₂CO₃ (1 mmol) and various concentration of palladacycle in methanol (3.0 ml).

^bDetermined by GC.

A short glimpse to the results listed in Tables 3 and 4 indicates that using microwave irradiation not only reduces the reaction times, but also increases the yields of the reactions to some extent in comparison with traditional heating. Comparison of the efficiency of *ortho*-palladated catalyst with other catalytic systems, in the Suzuki coupling reaction of 4-bromoanisole using various catalytic systems under conventional heating conditions is presented in Table 5. The *ortho*-Palladated catalyst was found to be more active and efficient than the other catalysts. Concerning the reaction mechanism, the mercury drop test was carried

out. In the presence of a heterogeneous catalyst, mercury leads to amalgamation on the surface. In contrast, Hg(0) cannot have a poisoning effect on homogeneous palladium complexes, where the Pd(II) metal centre remains tightly bound to the ligand. When a drop of Hg(0) was added to the reaction mixture with 4-bromobenzonitrile and phenylboronic acid under the optimized conditions and heated, the complex lost its catalytic activity. The data obtained can be rationalized in terms of a Pd(0):Pd(II) cycle. We propose that 2-methoxyphenethylamine impedes the fast agglomeration of Pd(0) species.

Table 3. Suzuki reaction of various aryl halides under microwave irradiation.^a

Entry	Aryl halide	Arylboronic acid	Time (min)	Yield (%) ^b
1	Iodobenzene	Phenylboronic acid	0.5	96
2	Bromobenzene	Phenylboronic acid	0.75	95
3	Chlorobenzene	Phenylboronic acid	1	95
4	4-Iodoanisole	Phenylboronic acid	0.75	93
5	4-Bromoanisole	Phenylboronic acid	2	92
6	3-Bromoanisole	Phenylboronic acid	3	90
7	4-Bromoacetophenone	Phenylboronic acid	6	94
8	3-Bromoacetophenone	Phenylboronic acid	9	89
9	2-Bromoacetophenone	Phenylboronic acid	10	68
10	4-Bromobenzaldehyde	Phenylboronic acid	3	93
11	4-Chloroacetophenone	Phenylboronic acid	10	50
12	1-Bromo-4-chlorobenzene	Phenylboronic acid	1	95
13	1-Bromo-3-chlorobenzene	Phenylboronic acid	0.75	95
14	1-Bromo-2-chlorobenzene	Phenylboronic acid	2	94
15	4-Bromobenzonitrile	Phenylboronic acid	1	93
16	1-Bromonaphthalene	Phenylboronic acid	4	92
17	9-Bromophenanthrene	Phenylboronic acid	5	90
18	4-Iodobenzophenone	Phenylboronic acid	2	93
19	Bromobenzene	4-Methoxyphenylboronic	0.5	92
20	4-Bromoanisole	4-Methoxy phenylboronic	1	94
21	4-Bromoacetophenone	4-Methoxy phenylboronic	3	91
22	4-Bromobenzaldehyde	4-Methoxy phenylboronic	2	92
23	1-Bromo-4-chlorobenzene	4-Methoxy phenylboronic	0.5	93
24	1,4-Dibromobenzene	4-Methoxy phenylboronic	3	90
25	9-Bromophenanthrene	4-Methoxy phenylboronic	4	91

^aReaction condition: aryl halide (1 mmol), arylboronic acid (1.2 mmol), K₂CO₃ (1 mmol), palladacycle (0.1 mol%), methanol (3 ml), temperature 65 °C.

^bIsolated yield.

Table 4. Suzuki reaction of some of aryl halides under conventional heating in oil bath.^a

Entry	Aryl halide	Arylboronic acid	Time (min)	Yield (%) ^b
1	Bromobenzene	Phenylboronic acid	3	94
2	4-Iodoanisole	Phenylboronic acid	3	91
3	3-Bromoanisole	Phenylboronic acid	6	90
4	1-Bromo-4-chlorobenzene	Phenylboronic acid	2	92
5	9-Bromophenanthrene	Phenylboronic acid	8	88
6	4-Bromobenzonitrile	4-Methoxy phenylboronic	10	93

^aReaction condition: aryl halide (1 mmol), arylboronic acid (1.2 mmol), K₂CO₃ (1 mmol), palladacycle (0.1 mol%), methanol (3 ml), 65 °C.

^bIsolated yield.

Table 5. Comparison of the activity of various catalysts in the Suzuki coupling reaction of 4-bromoanisole with arylboronic acid.

Entry	Catalyst	Time (h)	Yield (%)	Ref.
1	<i>Ortho</i> -palladated catalyst	0.07	98	This work
2	Pd/C (10 mol %)	24	73	[43]
3	Pd(OAc) ₂ (3 mol %), DABCO (6 mol %)	16	90	[44]
4	(BeDABCO) ₂ Pd ₂ Cl ₆ (0.05 mol%)	0.7	98	[45]
5	Zeolite confined Palladium(0) nanoclusters (0.82 mol%)	6	99.6	[46]

4. Conclusions

The [Pd{C₆H₃(CH₂CH₂NH₂)-4-OMe-5-κ²-C,N} (μ-Br)]₂ complex of 2-methoxy-phenethylamine exhibited very good activity in the Suzuki reaction of aryl iodides and bromides and was partly less reactive in aryl chlorides. This catalyst was stable under microwave irradiation conditions without using inert atmosphere due to its inherent air and moisture resistances.

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