

SYNTHESIS OF N-(2'-IMIDAZOLYL)-2- AMINOPYRIDYL PALLADIUM DICHLORIDE AND ITS APPLICATION AS CATALYST IN SUZUKI-MIYAURA CROSS COUPLING REACTION.

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Abstract

The ligand N-(2'-imidazolyl)-2- aminopyridine **9** was prepared from imidazole. Compound **9** forms complex with Na₂PdCl₄ in methanol. The complex **10** (1.5 mmol %) was utilized in Suzuki-Miyaura cross-coupling reaction to prepare substituted biphenyls, terphenyls, and heterobiaryls in good to excellent yields.

Keywords: N-(2'-imidazolyl)-2-aminopyridine ligand/Palladium Complexes/ Palladacycles/ Suzuki-Miyaura Cross Coupling/Biaryls/Terphenyls/Heterobiaryls/Suzuki-reaction.

Introduction

The last half-century has witnessed enormous growth in transition metal- organometallic chemistry, both as scientific discipline and as a subject for research and applications in industry. Organopalladium compounds have a very rich chemistry and are among the readily available and easily prepared and handled of the plethora of known transition-metal complexes. The facile redox interchange between the two stables Pd (II)/Pd (0) oxidation states is mainly responsible for the rich chemistry enjoyed by palladium compounds. Palladacycles have various activities in the field of Catalysis¹⁻⁷, Medicinal and Biological Chemistry⁸⁻⁹, Liquid Crystals (Mesogenic Palladacycles)¹⁰ and as Photo luminescent material¹¹.

Recent advances in metal catalyzed coupling methods have allowed increasing usage of cross-coupling reactions in synthetic organic chemistry, for example, the Suzuki-Miyaura (SM)¹² cross-coupling reaction. Transition-metal-catalyzed cross-coupling reactions have had a major impact on the construction of C-C bonds in functionalized biaryl and hetero-biaryl system¹³.

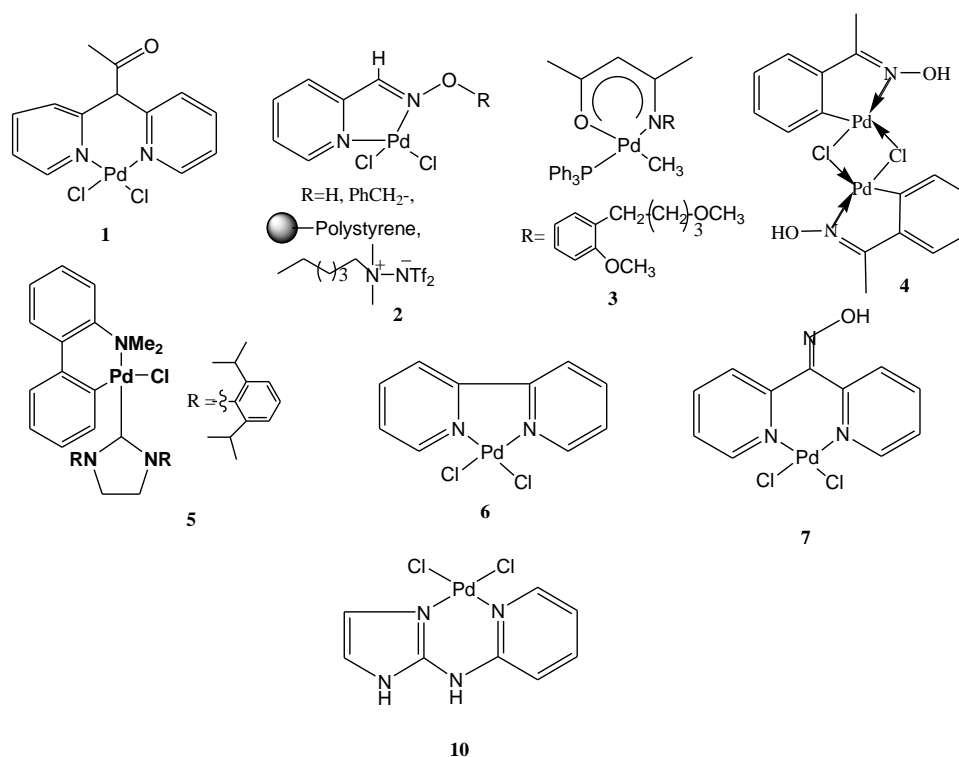
Although many different types of ligands have been discovered for these types of reactions, there is still a need for creative innovations. For example, the development of catalysts not including phosphane ligands is of special interest due to environmental concerns. As reported in several scientific papers, it is very difficult to separate the remaining phosphane moiety during work-up process¹⁴. Moreover, many ligands are often air-sensitive or expensive, which places significant limits on their synthetic applications.

In recent years, palladacycles as catalyst in cross-coupling reactions have been

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described¹⁵. There are also homogeneous catalysts, which are reusable, very stable and their enhanced activity has been reported¹⁶. The complexes of palladium (II) salts with the dipyridine-based ligands of type **1**, have shown to be efficient catalysts for C-C bond forming reactions¹⁷. Recently, we have reported a new pyridine oxime ligands-based palladium catalyst **2**, for the C-C coupling reactions¹⁸. (β -Oxoiminato)(phosphanyl) palladium complexes¹⁹ **3** have been found to be very active as catalyst in Suzuki-Miyaura coupling reactions. Recently, A. Kirschning and others²⁰ have developed a number of new palladacycles (complex **4** & **5**). The dipyridyl-palladium complexes **6** & **7**, which are easily prepared in good yield and with high purity promote the Suzuki-Miyaura cross-coupling reaction in the preparation of substituted biphenyls, terphenyls, heterobiaryls in good to excellent yields²¹.

In continuation of our work on palladacycles we synthesized more new palladacyclic catalysts based on the derivatives of primary and secondary heteroaromatic amines and the halogen substituted imidazole that can promote carbon-carbon, carbon-nitrogen bond formation. For this purpose we report a new palladacyclic catalyst **10** based on the derivative secondary heteroaromatic amine. Our future aim will be to test the biological activity of prepared new palladacyclic catalyst.



Scheme 1

Experimental

¹H-NMR & ¹³C-NMR Spectra of some samples were recorded using a Bruker WH 400MHz Spectrometer in the Bangladesh Council of Scientific and Industrial Research (BCSIR) Laboratories, Dhaka and by using 300 MHz NMR-Spectrometer in Leibniz Institute of Plant Biochemistry, Weinberg-3, D-06120 Halle (Saale), Germany and also by using 400 MHz NMR-Spectrometer in Academia Sinica, Nankang, Taipei, Taiwan, Republic of China. The spectra were recorded in CD₃OD, DMSO and mostly in CDCl₃ with TMS as internal standard. The chemical shifts were expressed in δ-values. Mass spectra were recorded on LC-ESI-MS system in Leibniz Institute of Plant Biochemistry, Weinberg-3, D-06120 Halle (Saale), Germany. The thin layer chromatography (TLC) was performed on precoated aluminium plates (Merck 60 F₂₅₄ silica gel) and detected by uv light and in Iodine chamber. Column chromatography was performed with Merck silica gel 60, 70-230 mesh ASTM. Yields of the products are the isolated yield after column chromatography. All solvents were dried and purified by usual techniques.

Preparation of 2-Bromoimidazole, 8

Imidazole (30 mmol) was treated with NBS (30 mmol) in dichloromethane (10 mL) in presence of silica gel (2.40 g) under nitrogen at room temperature for 2 hours. After reaction, the product was taken in 10mL MeOH and it was filtered to remove silica gel. The methanolic solution was then evaporated in rotary evaporator to get the solid product. The crude was washed twice with 10mL distilled water. After drying in desiccator it gave pure crystals. An ash grey colored crystal of 2-bromoimidazole was obtained after removal of solvent.

Preparation of the ligand, N-(2'-imidazolyl)-2-aminopyridine, 9

A reaction of 2-bromoimidazole (6 mmol), 2-aminopyridine (1.410 g ≈15 mmol), and cesium carbonate (5.09 g), palladium catalyst, **6** (10 mmol) in dioxane (40 mL) was carried out at 100°C for 25 hours. Then the reaction mixture was shaken with water (20 mL) and ethyl acetate (10 mL) and filtered to remove catalyst. Organic layer was collected by extraction with ethyl acetate (20 mL) and dried over anhydrous magnesium sulfate over night. A red solid was obtained on removal of the solvent in rotary evaporator.

The crude product was chromatographed over a column of silica gel 60 (70-230 mesh) using EA: MeOH (9.8:0.2) as eluent. The eluting solvent was collected in several test tubes and the fractions having the same TLC behavior were combined. Compound **9** was obtained as a red solid having melting point 79-80°C.

General procedure for the preparation of N-(2'-imidazolyl)-2-aminopyridyl palladium dichloride complex 10

N-(2'-imidazolyl)-2-aminopyridine, **9** (3-6 mmol) and Na₂PdCl₄ (3.2-6.3 mmol) were dissolved in methanol and stirred for 16 hours at room temperature. The solids formed

were filtered in a sintered crucible. The solids were further washed with methanol to obtain an orange-yellow solid. The complex **10** was dried over conc. H₂SO₄/P₂O₅ in a vacuum desiccator until constant weight.

General procedure of Suzuki-Miyaura cross-coupling with the complex 10

Arylboronic acid (1.5 mmole), Arylhalide (1.0 mmole), base, K₂CO₃ (2 mmole) and toluene (3-4 mL) were mixed together. The mixture was refluxed at 105°C for 2-4 hours. The mixture was cooled to room temperature, then H₂O (10 mL) and ethyl acetate (10 mL) were added; any residual solids present were filtered. To the filtrate ethyl acetate was added again and shaken well. The two layers were separated. The aqueous layer was again extracted with either ethyl acetate or dichloromethane and combined with the original organic layer. The organic phase was dried over anhydrous sodium sulphate. The solvent was removed in rotary evaporator. The crude product was column chromatographed over a silica gel eluting with petroleum ether-ethyl acetate solvent mixture to obtain pure product. Yields were calculated from this isolated products.

Table-1: Spectral data for compounds 8, 9 and 10

Compound	¹ H-NMR (δ, ppm)	¹³ C-NMR (δ, ppm)	MASS m/z
8	(In CD ₃ OD): 7.19(2H, s, H-4, 5), 8.02(1H, s, N-H)	135.9(C-2), 121(C-4, 5) DEPT-135°- 121(C-4, 5)	ESI (+ve): m/z: 165 [M+NH ₄] ⁺ ESI (-ve): m/z: 294 [2M-H] ⁻
9	(In CDCl ₃): 8.67 (2H, broad, 2N-H), 8.37(2H,d, J=7.98 Hz, H-4', 5'), 7.80(2H, dd, J=7.7 Hz, 1.7 Hz, H-3, 6,), 7.29 (2H, ddd, J=7.7 Hz, 7.3 Hz, 1.7 Hz, H-4, 5)	121.19, 123.23, 136.99, 149.15, 156.11	—
10	(In DMSO-d ₆): 9.13 (2H, broad, 2N-H), 8.60 (2H,d, J=8.1 Hz, H-4', 5'), 8.35 (2H, dd, J=7.7 Hz, J=1.7 Hz, H-3, 6), 7.82 (2H, ddd, J=7.7 Hz, 7.3 Hz, 1.7 Hz, H-4, 5)	157 (C-2, 2'), 150 (C-3, 6), 140 (C-4), 127 (C-5), 124 (C-4', 5') DEPT-135°-150 (C-3, 6), 140 (C-4), 127 (C-5), 124 (C-4', 5')	ESI (+ve): m/z: 360, 362, 364 [M+Na] ⁺

Table-2: Spectral data for compounds 11-12

Compound	¹ H-NMR (CDCl ₃), (δ, ppm)	¹³ C-NMR (CDCl ₃), (δ, ppm)	MASS m/z
11	7.62 (4H, dd, J _o =7.2 Hz, J _m =1.6 Hz, H-2, 2', 6, 6'), 7.46 (4H, dd, J _o =7.6 Hz, 7.2 Hz, H-3, 3', 5, 5'), 7.36 (2H, dt, J _o =7.6 Hz, J _m =1.6 Hz, H-4, 4').	141.20 (C-1, 1'), 128.72 (C-2, 2', 6, 6'), 127.22 (C-4, 4'), 127.14 (C-3, 3', 5, 5') DEPT-135°-128.72 (C-2, 2', 6, 6'), 127.22 (C-4, 4'), 127.14 (C-3, 3', 5, 5')	ESI (+ve): m/z: 177.2 [M+Na] ⁺ , 193.2 [M+K] ⁺ ESI (-ve): m/z: 307 [2M-H] ⁻ , 213.2 [M+OAc] ⁻ .
12a	7.57 (2H, dd, J _o =8 Hz, J _m =1.2 Hz, H-2', 6') , 7.48 (2H, d, J _o =7.6 Hz, H-3, 5) , 7.41 (2H, dd, J _o =8 Hz, J _m =1.2 Hz, H-3', 5') , 7.31 (1H, t, J _o =8.0 Hz, H-4') , 7.24 (2H, d, J _o =7.6 Hz, H-2, 6) , 2.38 (3H, s, CH ₃) ,	145.70(C-1), 139.6(C-4), 135.4(C-1'), 128.83 (C-2, 6), 128.56(C-3, 5), 128.22(C-2', 6'), 127.27(C-4'), 127.18(C-3', 5'), 26.55(C-7, CH ₃) DEPT-135°-128.83 (C-2, 6), 128.56(C-3, 5), 128.20(C-2', 6'), 127.24(C-4'), 127.19(C-3', 5'), 26.65(C-7, CH ₃)	ESI (+ve): m/z: 191 for [M+Na] ⁺ ESI (-ve): m/z: 227 [M+OAc] ⁻ .
12b	8.02 (2H, d, J _o =8.4 Hz, H-2, 6) , δ 7.68 (2H, d, J _o =8.4 Hz, H-3, 5) , 7.63 (2H, dd, J _o =7.2 Hz, J _m =1.2 Hz, H-2', 6') , δ 7.46 (2H, dt, J _o =7.2 Hz, J _m =1.2 Hz, H-3', 5') , 7.39 (1H, dt, J _o =7.2 Hz, J _m =1.2 Hz, H-4') , δ 2.63 (3H, s, CH ₃)	197.74 (C-7, C=O), 145.74(C-1), 139.8(C-4), 135.8(C-1'), 128.93 (C-3, 5), 128.66(C-2, 6), 128.20(C-2', 6'), 127.24(C-4'), 127.19(C-3', 5'), 26.65(C-8, CH ₃) DEPT-135°-128.93 (C-3, 5), 128.66(C-2, 6), 128.20(C-2', 6'), 127.24(C-4'), 127.19(C-3', 5'), 26.65(C-8, CH ₃)	ESI (+ve): m/z: 414[2M+Na-H] ⁺ , 219.1 [M+Na] ⁺ ESI (-ve): m/z: 255.3 [M+OAc] ⁻
12c	8.29 (2H, d, J _o =8.8 Hz, H-2, 6), 7.73 (2H, d, J _o =8.8 Hz, H-3, 5) , 7.62 (2H, dd, J _o =7.2 Hz, J _m =1.6 Hz, H-2', 6') , 7.49 (2H, dd, J _o =7.2 Hz, 7.6 Hz, H-3', 5') , 7.45 (1H, dt, J _o =7.6 Hz, J _m =1.6 Hz, H-4').	147.59 (C-1), 147.02(C-4), 138.72(C-1'), 129.12(C-2, 6), 128.89(C-3, 5), 127.76 (C-2', 6'), 127.37(C-3', 5'), 124.07(C-4') DEPT-135°-129.12(C-2, 6), 128.89(C-3, 5), 127.76, (C-2', 6'), 127.37(C-3', 5'), 124.07(C-4')	ESI (+ve): m/z: 222.2 [M+Na] ⁺ ESI (-ve): m/z: 258.3[M+OAc] ⁻ , 199 [M] ⁻
12d	8.45 (1H, dd, , J _m =1.6 Hz, 2 Hz, H-2) , 8.19 (1H, dd, J _o =8.0 Hz, J _m =1.2 Hz, H-6) , 7.90 (1H, dd, J _o =7.6 Hz, J _m =1.2 Hz, H-4) , 7.58-7.63 (3H, m, H-5 & H-2', 6') , 7.49 (2H, t, J _o =7.2 Hz, H-3', 5') , 7.43 (1H, dt, J _o =7.2 Hz, J _m =1.2 Hz, H-4').	148 (C-1), 142 (C-3), 138 (C-1'), 133 (C-2), 129.67(C-6), 129.12 (C-4), 128.50 (C-5), 127.77(C-2', 6'), 121.99(C-3', 5'), 121.91(C-4') DEPT-135°-133 (C-2), 129.67(C-6), 129.12 (C-4), 128.50 (C-5), 127.77(C-2', 6'), 121.99(C-3', 5'), 121.91(C-4')	ESI (+ve): m/z: 222.2 [M+Na] ⁺ ESI (-ve): m/z: 258.3[M+OAc] ⁻

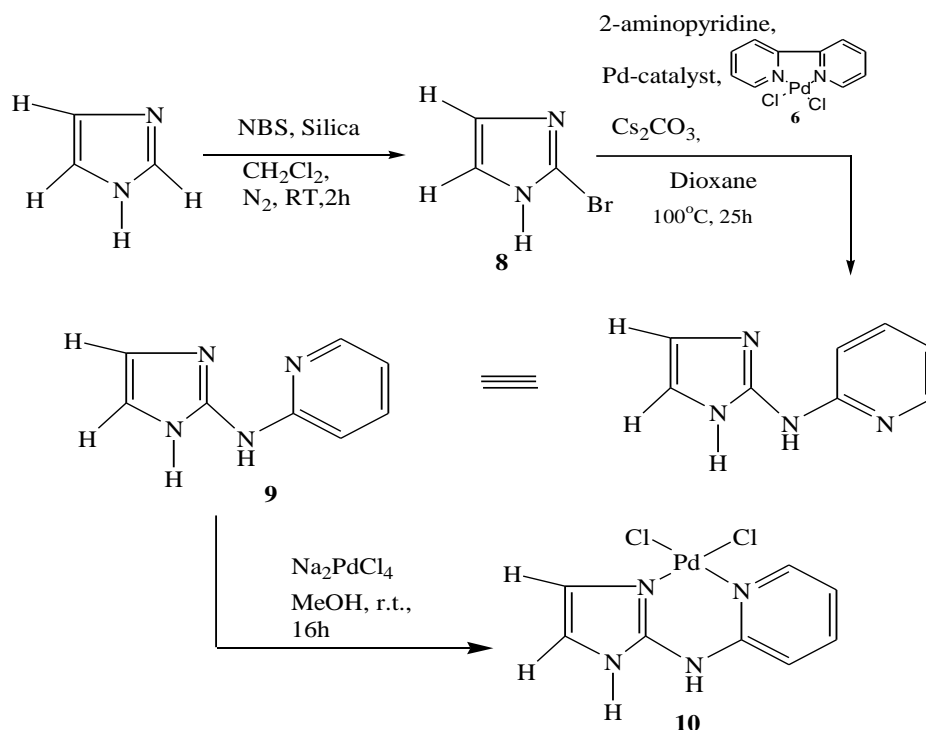
Compound	¹ H-NMR (CDCl ₃), (δ, ppm)	¹³ C-NMR (CDCl ₃), (δ, ppm)	MASS m/z
12e	7.50-7.62 (4H, m, H-2, 2', 6, 6'), 7.43 (2H, dd, J _o =7.2 Hz, J _o =7.5 Hz, H-3', 5'), 7.33 (1H, dt, J _o =7.5 Hz, H-4'), 7.12 (2H, dt, J _o =8.7 Hz, J _m =2.1 Hz, H-3, 5)	164 (C-1), 160.80 (C-4), 141.22 (C-1'), 138.97 (C-2, 6), 137.32(C-3, 5), 137.28 (C-2', 6'), 128.79 (C-3', 5'), 115.72(C-2, 6) DEPT-135°-128.97 (C-2, 6),137.32(C-3, 5), 137.28 (C-2', 6'), 128.79 (C-3', 5'), 115.72(C-2,6)	ESI (+ve): m/z: 193[M+Na] ⁺ ESI (-ve): m/z: 228.4[M+OAc-H] ⁻
12f	7.68 (4H, s (br), H-2, 3, 5, 6), 7.58 (2H, dt, J _o =6.9 Hz, J _m =1.8 Hz, H-2', 6'), 7.46 (2H, dt, J _o =6.9 Hz, J _m =1.8 Hz, H-3', 5'), 7.39 (1H, dt, J _o =7.2 Hz, J _m =1.8 Hz,H-4').	144.70 (C-4), 139.75 (C-1), 129.53 (C-3, 5), 128.97 (C-2, 6), 127.40(C-2', 6'), 127.26 (C-3', 5'), 129.71 (C-1'), 126.11(C-7), 125.77 (C-4') DEPT-135°-129.53 (C-3, 5), 128.97 (C-2, 6), 127.40(C-2', 6'), 127.26 (C-3', 5'), 125.77 (C-4')	ESI (+ve): m/z: 242.3 [M+Na] ⁺ ESI (-ve): m/z: 253.5[M+ ³⁵ Cl] ⁻ , 255.5[M+ ³⁷ Cl] ⁻

Table-3: Spectral data for compounds 13

Compound	¹ H-NMR (CDCl ₃), (δ, ppm)	¹³ C-NMR (CDCl ₃), (δ, ppm)	Mass m/z
13a*	7.81(1H, t, J _m =1.8 Hz, H-2), 7.65 (4H, dd, J _o =6.9 Hz, J _m =2.1 Hz, H-2', 2", 6', 6"), 7.59 (2H, m, H-4, 6), 7.52 (1H, dd, J=6.0 Hz, 5.4 Hz, H-5), 7.48 (4H, m, H-3', 3", 5', 5"), 7.37 (2H, dt, J _o =7.1 Hz, J _m =2.1 Hz, H-4', 4")	—	—
13b	7.63(4H, dd, J _o =6.9 Hz, J _m =1.5 Hz, H-2, 3, 5, 6), 7.55 (4H, dt, J _o =7.2 Hz, J _m =1.2 Hz, H-2', 2", 6', 6"), 7.44 (4H, dd, J _o =7.5 Hz, 7.2Hz, H-3', 3", 5', 5"), 7.35 (2H, dt, J _o =7.5 Hz, J _m =1.2 Hz, H-4', 4")	141 (C-1, 4), 140 (C-1',1"), 131.8 (C-2, 3, 5, 6), 128.7 (C-2', 2", 6', 6"), 127.5 (C-3', 3", 5', 5"), 126.9 (C-4', 4") DEPT-135°-131.8 (C-2, 3, 5, 6), 128.7 (C-2', 2", 6', 6"), 127.5 (C-3', 3", 5', 5"), 126.9 (C-4', 4")	ESI (+ve): m/z: 253.1 [M+Na] ⁺ ESI (-ve): m/z: 265.1[M+ ³⁵ Cl] ⁻ , 228.4 [M-2H] ²⁻
13c	8.05 (1H, s, H-1), 7.92 (1H, d, J _o =8.4 Hz, H-3), 7.90 (1H, d, J _o =8.4 Hz, H-4), 7.89 (1H, dd, J _o =6.8 Hz, 7.2 Hz, H-8), 7.88 (1H, d, J _o =6.8 Hz, H-7), 7.71-7.77(3H, m, H-5, 6, 7),7.46-7.54 (4H, m, H-2', 3', 5', 6'), 7.39 (1H, dt, J _o =6.8 Hz, 7.2 Hz, H-4')	141.1 (C-2), 138.53 (C-1'), 133.64 (C-9), 132.58 (C-10), 128.84, 128.39, 128.17, 127.62, 127.41, 127.33, 126.27, 125.91, 125.78, 125.58 DEPT-135°-128.84, 128.39, 128.17, 127.62, 127.41, 127.33, 126.27, 125.91, 125.78, 125.58	ESI (+ve): m/z: 247 [M+42+H] ⁺ ESI (-ve): m/z: 206 [M-H] ⁻

Results and Discussion

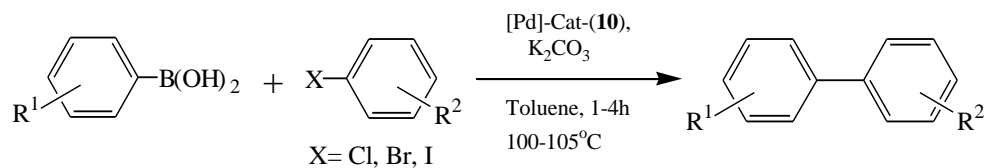
The Pd catalyst was easily prepared from N-(2'-imidazolyl)-2-aminopyridine by the reaction with Na_2PdCl_4 in MeOH at room temperature (Scheme 2). Complex **10** was obtained with high purity as orange-yellow powder.



Scheme 2: Synthesis of Pd complex **10**

The Pd-complex **10** was characterized from the ^1H NMR, ^{13}C -NMR and Mass spectral data analysis (table 1). In the complex **10** each of the protons shifts to downfield by about 0.3-0.6 ppm than that of the ligand indicating the complex formation. The molecular mass for $[\text{M}+\text{Na}^+]$ confirms the molecular structure of **10** with dichloro pattern (peak ratio 9: 6: 1).

With the Pd catalyst **10**, we tested the Suzuki-Miyaura coupling to obtain the product 1,1-biphenyl, **11** from the reaction of different halobenzenes (Scheme 3, table-4, entry **1, 2, 3**) with phenylboronic acid in the presence of K_2CO_3 . The reaction was done in toluene at 100-105°C.

**Scheme 3**

All the three reactions resulted in the formation of the same compound 1, 1'- biphenyl, **11** having melting point 68-70°C with yields of 34%, 97% and 90% with chloro, bromo and iodo benzene respectively. The reaction of chlorobenzene is most time consuming and the yield is very poor. To facilitate the reaction, the amount Pd [cat] needed is higher than the other two reactions.

Table 4: Suzuki-Miyaura coupling of aryl halides with arylboronic acid to synthesize 1, 1'- biphenyl, 11

Entry	Arylboronic acid R ¹ = Substituent	Aryl halides (R ² = H) X	T (°C)	6 (mmole %)	Time (h)	Yield (Product 11) (%)
1	H	Cl	105	3	12	34
2	H	Br	105	1	2	97
3	H	I	105	1	1.5	90

Then we tested the Suzuki-Miyaura (SM) coupling reaction of 4-Bromotoluene with phenylboronic acid in the presence of K₂CO₃ as a model reaction. The reaction was done in toluene at 100-105°C with 1 mmol % of **10**. The reaction led to 97% of the product, 4-methylbiphenyl, **12a** in 2 hrs. and all of the starting material was converted into the product (Scheme 3, table 5, entry 1). We repeated the SM coupling reaction of phenyl boronic acid with electron withdrawing substituents (-COCH₃, -NO₂ & F) in bromides (table 5, entry 2, 3, 4 & 5), the coupling was very easy and the yields were excellent. The catalyst **10** was also used for the coupling of phenyl boronic acid with 4-trifluoromethyl iodobenzene (table 5, entry 6), the product, **12f** was obtained in excellent yield.

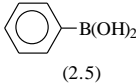

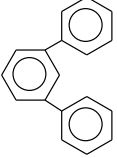
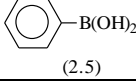
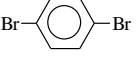

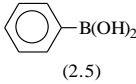
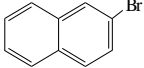
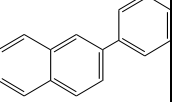
We also tested the catalyst, **10**, with the dibromides and naphthylbromides. The coupling with dibromides led to the production of terphenyls, **13a** and **13b** in good yield (table 6, entry 1 & 2). The naphthylbromide gave phenyl naphthalene, **13c** (table 6, entry 3), in quantitative yield.

From the above results we found that Pd complex **10** showed outstanding performance. The complex **10** was very stable to oxygen and moisture: no change in its activity was observed, when it was exposed to air or water.

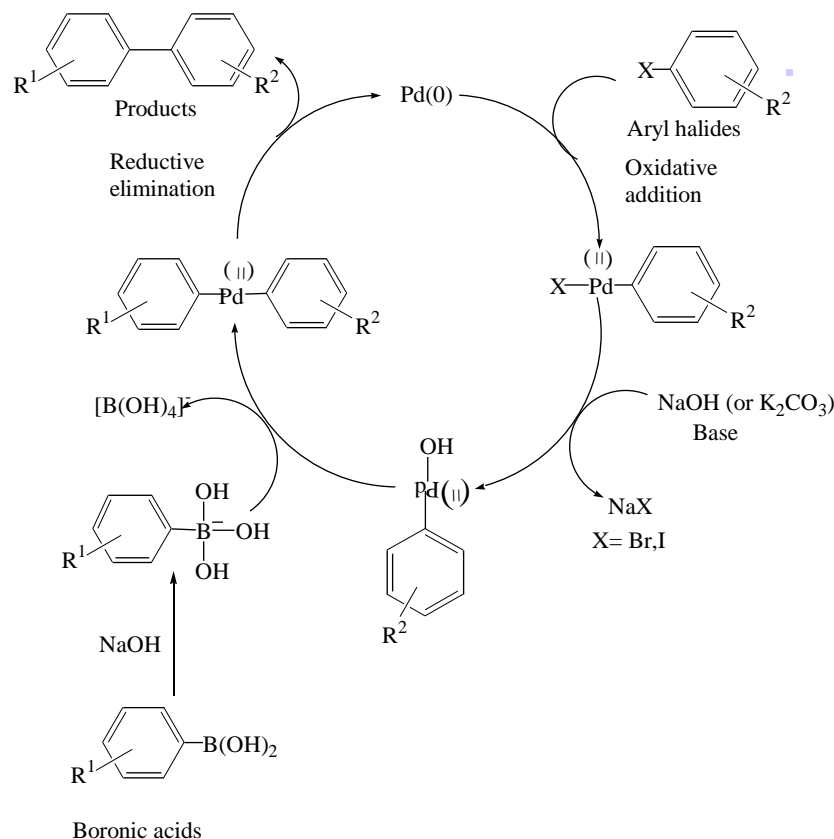
Table 5: Suzuki-Miyaura coupling of substituted aryl halides with arylboronic acid

Entry	Arylboronic acid, R ¹	Aryl halides R ² -Substituent X= Br, I	T (°C)	6 (mmole %)	Time (h)	Product 12	Yield (%)
1	H	4-Me	105	1	2	a	97
2	H	4-COCH ₃	105	1	2	b	91
3	H	4-NO ₂	105	1	1.5	c	100
4	H	3-NO ₂	105	1	1.5	d	100
5	H	4-F	105	1	3.5	e	96
6	H	4-CF ₃	105	1	1.5	f	91

Table 6: SM coupling of aryldibromides with phenyl boronic acid in presence of complex 10

Entry	Phenylboronic acid (equiv.)	Aryl halides (equiv.)	Coupling Product 13	Temp. (°C)	10 (mmole %)	Time (h)	Product 13	Yield (%)
1	 (2.5)			105	3	2.5	a	84
2	 (2.5)			105	3.5	2	b	90
3	 (2.5)			105	2	1	c	100

The plausible mechanism for the Suzuki coupling reaction of aryl boronic acids with aryl halides can be represented according to the literature²²⁻²⁵ as shown below:



Scheme 4: The mechanism of Suzuki-Miyaura cross coupling reaction.

Conclusions

On the basis of the reaction time, yield, and mechanistic pathway it was observed that the aryl halides substituted with electron withdrawing groups at para position were more reactive and had higher yield than the aryl halides substituted with electron donating group. Due to crowding effect aryl halides substituted with electron withdrawing groups at ortho position were less reactive to the coupling reaction than the para derivative.

In case of aryl halides the reaction of chloro derivatives were more time consuming and the yield was very poor. To facilitate the reaction, the amount [Pd] catalyst needed was higher than the bromo and iodo derivatives.

We have shown in the above results and discussion that the Pd- complex **10** is highly efficient catalyst in Suzuki-Miyaura coupling reactions. It is very stable in various reaction conditions.

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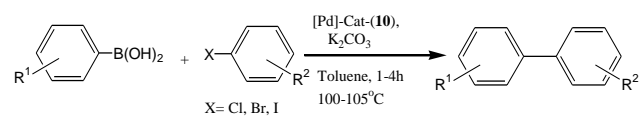
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Graphical Abstract

Synthesis of N-(2'-imidazolyl)-2-aminopyridyl palladium dichloride and its application as catalyst in Suzuki-Miyaura cross coupling reaction.

N-(2'-imidazolyl)-2-aminopyridyl palladium dichloride complex, **10** by Suzuki-Miyaura cross coupling led to the isolation of several substituted biaryls, triaryls and heterobiaryls derivatives by the reaction of substituted phenylboronic acids and substituted aryl chlorides, bromides and iodides in excellent yield.



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R¹ = H, X = Cl, Br, I
R² = Me, NO₂, Br, F, COCH₃, CF₃ etc.