

Synthesis, Structural Characterization and Catalytic Activities of Palladium(II) Schiff Base Complexes Containing Tetradentate N_2O_2 & N_2S_2 Donor Ligands

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Abstract

New family of palladium(II) tetradentate complexes of the general formula $[Pd(L_{1-4})]$ (L_1-L_3 ; tetradentate N_2O_2 donors & L_4 ; tetradentate N_2S_2 donors) have been synthesized by the reaction of $Pd(OAc)_2$ with tetradentate Schiff base ligands. The palladium(II) complexes were fully characterized by analytical, spectral (FT-IR, UV-Vis, 1H -NMR & ^{13}C -NMR) methods. Further, the new palladium(II) complexes were tested as catalyst for Suzuki-Miyaura and Sonogashira coupling reactions and exhibits very good catalytic activity.

Keywords: Palladium(II) Complexes, Schiff Base, Catalyst, Suzuki & Sonogashira Coupling Reaction

1. Introduction

Palladium catalyzed cross coupling reactions emerged as extraordinarily method to form carbon-carbon bonding in synthetic organic chemistry [1]. These coupling reactions have been intensively utilized in the production of polymers and biaryls which play a key role in various vital industrial applications thanks to their use in pharmaceutical intermediates, agrochemicals, biologically active, and natural products [2-5]. Thus, palladiums catalyzed cross coupling reactions have attracted green attention of researchers in recent years. Among these reactions, Suzuki coupling reactions, which have been performed by the reactions of aryl boronic acids with aryl halides, have been intensively preferred by many researchers because of their outstanding properties such as mild reaction conditions, ease of separation of by products from the reaction mixture, and high tolerance towards a wide range of functional groups [6]. Cross-coupling reactions are powerful and versatile tools in modern organic synthesis for the formation of mainly carbon-carbon bonds.

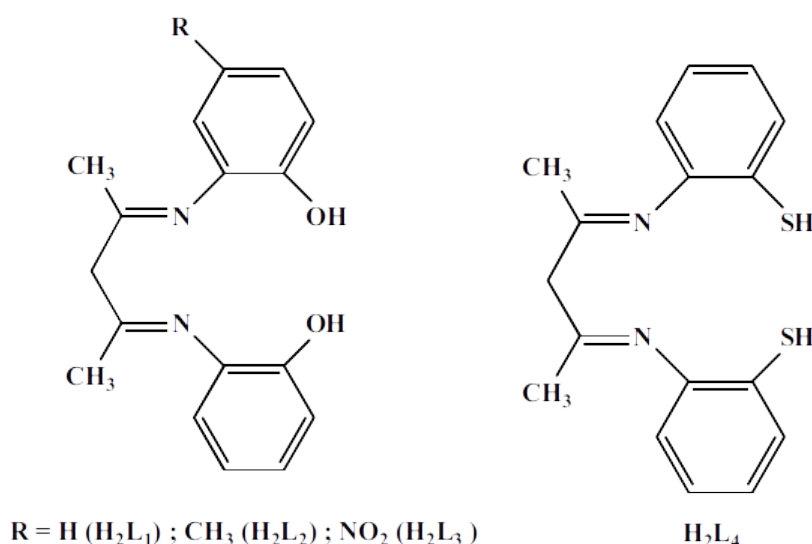
The palladium complexes have wide-spread applications in syntheses and become one of the most powerful and convenient C-C, C-N bond forming process in pharmaceutical chemistry; materials and synthetic chemistry [7]. Moreover, the metal complexes incorporating ortho substituted azo benzene ligands have versatile properties such as C-H activation [8,9], C-C activation [10], C-C coupling [11], -N=N- bond cleavage [12], electron transfer reaction [13, 14], hydroxylation [15], isomerization [16], photo isomerization [17], cyclo toxicity toward cancer cells and applications in catalytic transformations [18].

Palladium-catalyzed cross-coupling reactions for the formation of carbon-carbon bonds have recently emerged as a powerful method in an organic synthesis. The palladium-catalyzed coupling [19] of an aryl halide with aryl boronic acid (Suzuki coupling) or terminal alkynes (sonogashira coupling) is recognized as the most successful method for carbon-carbon bond formation reactions. Many catalytic systems have

been developed for the Suzuki-Miyaura and sonogashira cross coupling reactions using different palladium catalysts such as $\text{Pd}(\text{OAc})_2$, $\text{PdCl}_2(\text{PPh}_3)_2$ [20]. However, phosphine ligands used in these reactions are sensitive to air oxidation and thus require air-free conditions which pose significant inconvenience on synthetic applications [21]. Palladium(II) complexes containing nitrogen oxygen donor ligands showed high catalytic activity in C-C coupling reaction than commercially ligands are used phosphine containing metal complexes. Further, nitrogen based ligands are popular in coordination chemistry because they are easily modified both sterically and electronically [22-24].

In this research, I have reported palladium(II) complexes with various types of tetradentate Schiff base ligands. The palladium(II) Schiff base complexes were fully characterized by FT-IR, UV-Vis, ^1H -NMR and ^{13}C -NMR spectral studies. The catalytic activity in Suzuki and Sonogashira coupling reactions of various aryl halides by these complexes has also been examined. The following Schiff bases Figure 1 has been used to synthesise new palladium Schiff complexes.

Figure 1: Schiff Base Ligands



2. Experimental

2.1. Material and Methods

All the reagents used were pure and analytical reagent grade. Palladium(II) acetate, 2-aminophenol, 2-aminothiophenol, 2-amino-4-nitrophenol, 2-amino-4-methylphenol, triethylamine and all other chemicals were purchased from Aldrich and were used without further purification. The elemental analysis was determined using a thermo Finnigan CE125 CHN analyzer, Infrared (FT-IR) spectra of the synthesized complexes were recorded in an Agilent resolution pro spectrophotometer. Electronic spectra of the complexes in JASCO V-570 were recorded in CHCl_3 . The proton ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz instrument using tetramethylsilane (TMS) internal reference.

2.2. Synthesis of Tetradentate Schiff Base Ligands

The Schiff base ligands were prepared by according to reported literature procedure [25, 26]. The Schiff bases H_2L_1 - H_2L_4 were prepared by refluxing a methanolic solution of acetyl acetone (0.20-0.51, 5mmol) was slowly added corresponding 2-aminophenol, (0.06-1.06, 10 mmol) and 2-aminothiophenol (1.0699, 10 mmol) 20 ml of ethanol in a RB flask. The mixture was stirred for 3 hours to give yellow solution. Yellow solid was appeared when the solution was allowed to room temperature. The solid was filtered off washed with ethanol and dried in a vacuum. Recrystallization from ethanol afforded pure Schiff bases.

2.3. Synthesis of Palladium(II) Schiff Base Complexes

In a RB flask, Schiff base ligands ($H_2L_1 - H_2L_4$) (0.28-0.33 g; 1 mmol), few drops of Et_3N in 10 ml acetonitrile was added and $Pd(OAc)_2$ (0.1 g, 1 mmol). The reaction mixture was stirred for 5 h, and then concentrated to 2 ml, on the addition of hexane the complexes was precipitated and resulting precipitate was collected by filtration and washed with acetonitrile and dried. Following the same procedure all the complexes were prepared.

2.4. General Procedure for Suzuki-Miyaura Cross Coupling Reactions

Suzuki-Miyaura cross coupling reactions were achieved with a procedure described [27]. In a two-necked flask under an atmosphere of nitrogen was placed palladium complexes (1-4) (1 mol %), bromobenzene (0.5 mmol), aryl boronic acid (0.75 mmol) and K_2CO_3 (1 mmol). The mixture was then refluxed at $80^\circ C$ for 2 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure and the resulting product was diluted with water (10 ml) and Et_2O . The combined organic fraction was dried over $MgSO_4$. The crude product was purification by column chromatography by using hexane as eluent.

2.5. General Procedure for Sonogashira Coupling Reactions

To a slurry of aryl halide (0.5 mmol), palladium catalyst (0.3 mol %) in an appropriate solvent (5 ml), phenyl acetylene (0.75 mmol) and K_2CO_3 (1.25 mmol) were added and heated at required temperature. After completion of the reaction (monitored by TLC), the flask was removed from the oil bath and water (20 ml) added, followed by extraction with ether (4×10 ml). The combined organic layers were washed with water (3×10 ml), dried over anhydrous Na_2SO_4 and filtered, solvent was dissolved in hexane and analyzed by GC-MS using Elite-5 columns, which are fused silica capillary columns coated with 5% diphenyl and 95% dimethyl polysiloxane.

Table 1: Analytical Data of Palladium(II) Schiff Base Complexes

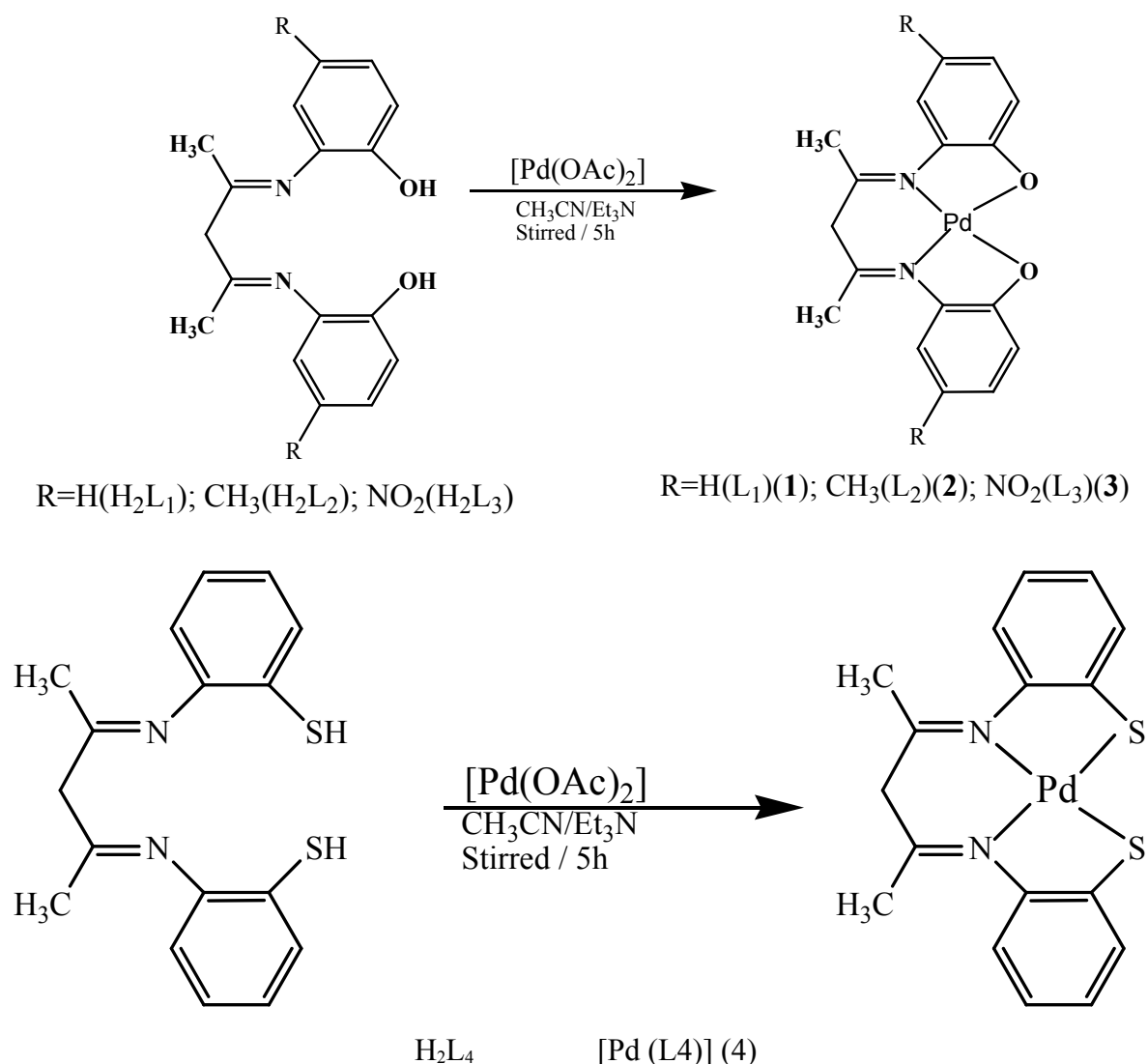
Complexes	colour	MP	Yield (%)	Analysis found (calculated%)		
				C	H	N
1	Brown	160 ^o c	38	52.79 (52.81)	4.14 (4.17)	7.24 (7.28)
2	Yellow	162 ^o c	35	42.82 (42.85)	2.93 (2.96)	11.75 (11.78)
3	Dark yellow	158 ^o c	43	55.01 (55.08)	4.82 (4.86)	6.75 (6.79)
4	Red	152 ^o c	40	48.75 (48.79)	3.82 (3.85)	6.69 (6.70)

3. Results and Discussion

3.1. Synthesis and Characterization

The yellow-red colored Pd(II) Schiff base complexes 1-4 were obtained by the reaction of $Pd(OAc)_2$ with equivalent moles of Schiff base ligands in acetonitrile. In this reaction, the Schiff base ligands behave as a tetradentate fashion by replacing acetate ion. The complexes are colored and insoluble in water, but slightly soluble in organic solvents like ethanol, methanol and completely soluble in chloroform, dichloroform etc., The solid Pd(II) Schiff base complexes were subjected to elemental analysis which are given Table 1, are in good agreement with those required by the proposed formula.

Scheme 2: Synthesis of Palladium(II) Schiff Base Complexes



3.2. IR Spectra

The IR data of the ligands (H_2L_1 - H_2L_4) and their complexes are summarized in Table 2. The IR spectra of the complexes are compared with those of the free ligands in order to determine the coordination sites that may be involved in chelation. The free Schiff bases (1-4) exhibit a broad band in the region 3030-3058 cm^{-1} , which is characteristic of the $\nu(\text{OH})$ functional group [28]. The azomethine $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O})$ stretching frequencies are assigned in the region around 1579-1591 cm^{-1} and 1337-1377 cm^{-1} respectively [29-32]. Upon coordination, the frequencies of the azomethine $\nu(\text{C}=\text{N})$ stretching shift toward lower frequencies at 1551-1573 cm^{-1} and phenolic $\nu(\text{C}-\text{O})$ stretching exhibit slight higher frequencies at 1264-1361 cm^{-1} as compared to their respective ligands. The participation of the phenolic OH atom in the shift in the position of this band to higher frequency [33]. Thus, the imine nitrogen and phenolic oxygen functionalities suggest the presence of a square planar environment around palladium(II) metal centre [34, 35]. Representative IR spectra of complexes 1-4 are given in figs S1-S4 (see supporting information).

3.3. Electronic Spectra

The electronic spectra of the Pd(II) complexes have been recorded in chloroform and showed intense absorption in the UV-Vis region. Representative UV-Vis spectra of complexes 1-4 are given in figs S5-

S8 (see supporting information). The absorption bands observed around 250-260 nm are assigned to the π - π^* transition in the Schiff base ligands, whereas the medium absorption bands, appearing at 325-350 nm, are assigned to the n - π^* transitions. The π - π^* and n - π^* transitions for the free ligands were shifted to higher wavelengths as a consequence of the coordination to the metal ions, indicating the formation of palladium(II) Schiff base complexes. In addition, these spectra showed a band around 350-450 nm, assigned to MLCT transition, which strongly favours the square planer geometry around the central metal ion [36, 37].

Table 2: Important IR and Electronic Spectral Data of the Pd(II) Schiff Base Complexes

Ligand/ Complex	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	max(nm)		
H ₂ L ₁	1590	1375			
H ₂ L ₂	1579	1337			
H ₂ L ₃	1591	1376			
H ₂ L ₄	1590	1377			
1	1588	1359	^a 400	^b 350	^c 240
2	1551	1320	^a 360	^b 325	^c 260
3	1569	1363	^a 390	^b 325	
4	1568	1360	^a 380	^b 320	

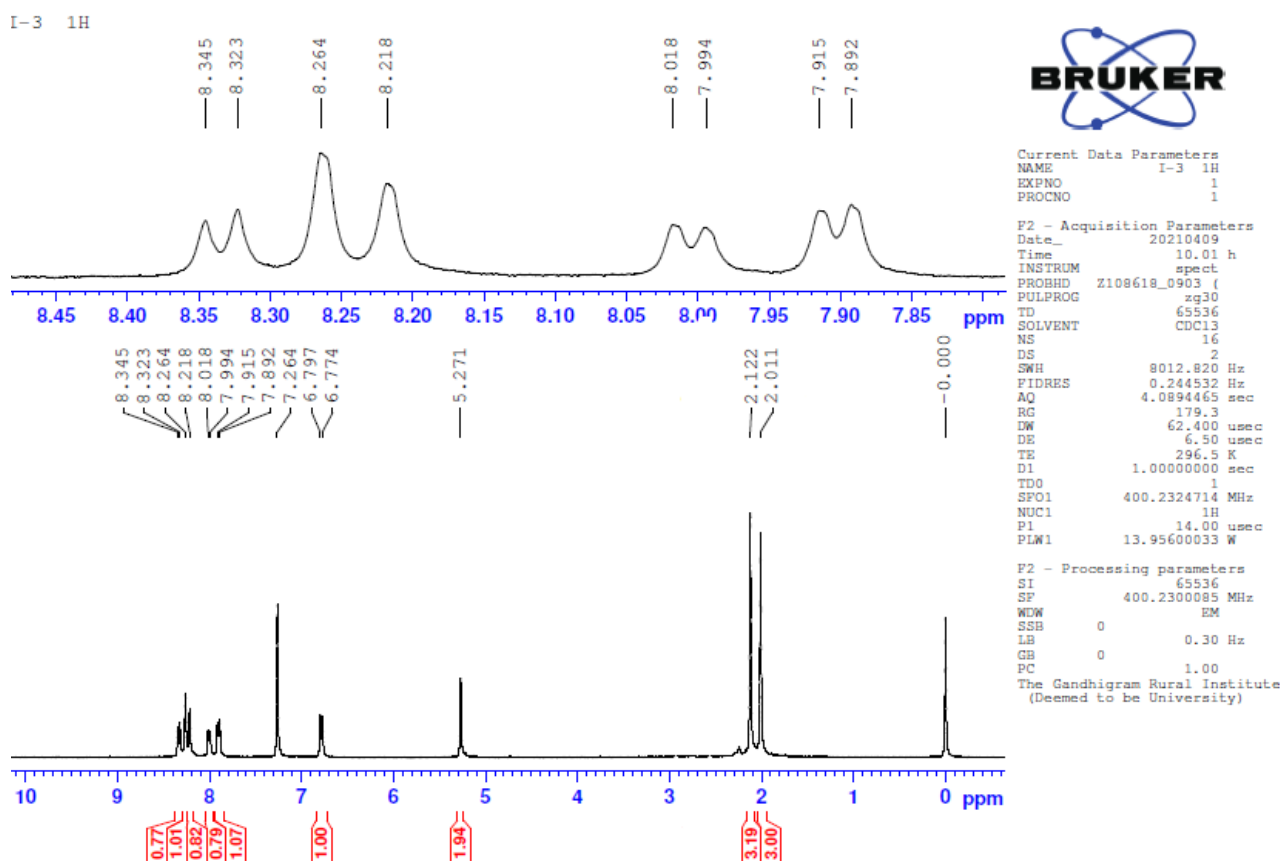
^a MLCT transition

^b n - π^*

^c π - π^*

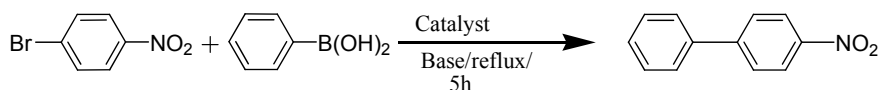
3.4. ¹H and ¹³C-NMR Spectra

The ¹H-NMR spectra of all the complexes were recorded in CDCl₃ to conform the coordination mode of Schiff base ligands to the palladium(II) ion. The multiplets of the aromatic proton of the complexes (1-4) were observed in the region 6.414-8.345 ppm. A sharp singlet at 2.028 - 2.076 ppm in the spectra was attributed to methyl groups for the complex 2. The singlet due to the -OH proton of the free ligand in the region around δ 12 ppm is absent in the complexes (1-4) supporting the coordination of the phenolate oxygen to the Pd(II) ion. Representative NMR spectra of complexes 1-4 are given in Fig S13-S16 (see supporting information).



3.5. Catalytic Suzuki-Miyaura Coupling Reaction

Initially, a brief screening of the base, catalyst loading and solvents was conducted by running a carbon-carbon coupling reaction of 4-bromonitrobenzene and phenylboronic acid (Table 3). After optimization, we found that 1 mol % catalyst, 1 mmol K_2CO_3 , DMF as solvent and a reaction time 5 h furnished a good yield of expected product.

Table 3: Optimization of the Reaction Condition


Entry	Catalyst (mol%)	Solvent	Base	Yield ^b (%)
1	1.0	DMF	K ₂ CO ₃	98
2	0.5	DMF	K ₂ CO ₃	89
3	0.2	DMF	K ₂ CO ₃	85
4	0.1	DMF	K ₂ CO ₃	60
5	0.01	DMF	K ₂ CO ₃	49
6	0.001	DMF	K ₂ CO ₃	41
7	0.0001	DMF	K ₂ CO ₃	33
8	1.0	Ethanol	K ₂ CO ₃	85
9	1.0	Toluene	K ₂ CO ₃	60
10	1.0	THF	K ₂ CO ₃	42
11	1.0	DCM	K ₂ CO ₃	35
12	1.0	H ₂ O	K ₂ CO ₃	NR ^c
13	1.0	DMF	NaOH	82
14	1.0	DMF	KOH	88
15	1.0	DMF	Na ₂ CO ₃	90
16	1.0	DMF	Et ₃ N	59

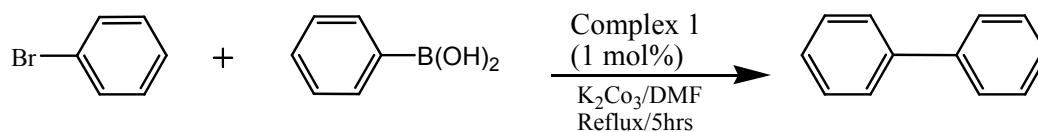
^aReaction conditions: 4-Bromo nitrobenzene (1mmol), Phenyl Boronic acid (1.2mmol), Base (1mmol), Catalyst, Solvent (5ml).

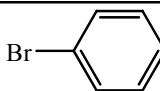
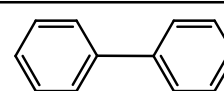

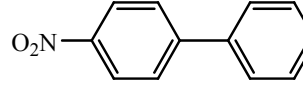
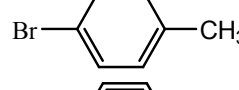
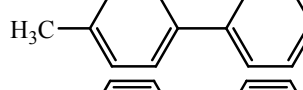
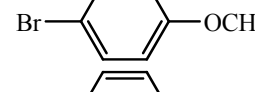
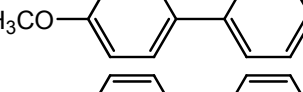
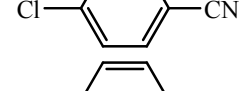
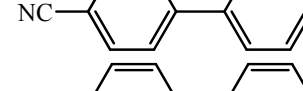
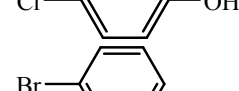
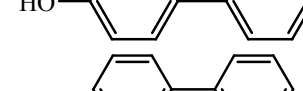
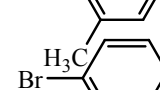
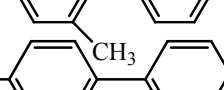
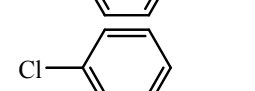
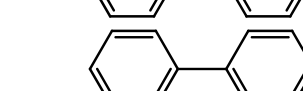
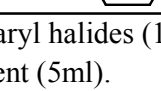
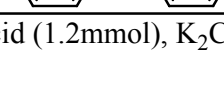
^b Isolated Yields.

^cNo reaction.

Upon lowering the catalyst loading, the yield of the reaction also decreased significantly. Different bases were tested and the coupling products were obtained in good yields when K₂CO₃ was used. Moderate yields were obtained in the cases of Na₂CO₃, KOH and NaOH and very low yield was obtained with Et₃N. Using K₂CO₃ as a base, different solvents were tested and the products were obtained in good yield in DMF.

A general catalytic cycle for the cross-coupling reaction of organo boron reagents with aryl halides involves an oxidative addition of the aryl halide, transmetalation, and reductive elimination steps (Table 4) [38, 39]. Aryl bromides with various functional groups efficiently reacted with boronic acids (entries 1-9) using K₂CO₃ and 5 ml of DMF at reflux temperature in the presence of palladium(II) complex 1 for 5 h to yield Suzuki-Miyaura products in good conversions. The conversion of 4-bromotoluene and 4-bromoanisole (entries 3 and 4) into their corresponding biaryls compounds are 94% and 90% respectively. Substrates with electron-withdrawing substituents such as NO₂ and CN (entries 2 and 5) gave excellent conversion 99% and 83% respectively. In addition, the complex efficiently catalyzes the 4-chlorophenol and 4-bromo benzaldehyde (entries 6 and 8) into corresponding C-C coupling products of 80% and 87% respectively.

Table 4: Suzuki–Miyaura Coupling of Aryl Halide with Phenylboronic Acid using Complex (1)^a


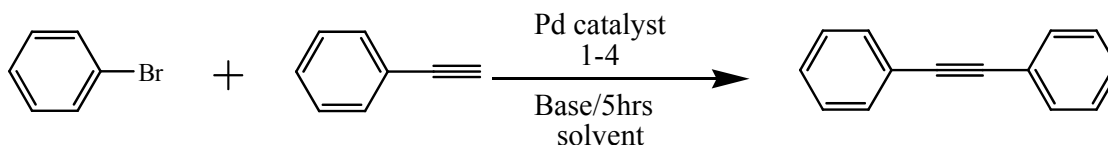
Entry	Substrate	Product	yield ^b (%)
1			95
2			99
3			94
4			90
5			83
6			80
7			85
8			87
9			60

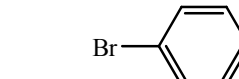
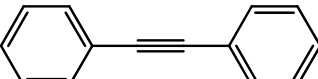
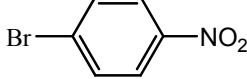
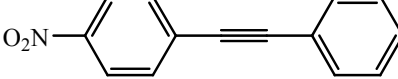
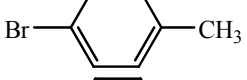
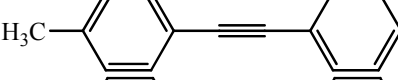
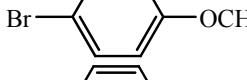
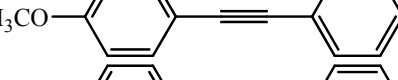
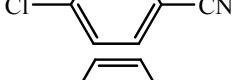
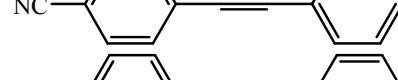
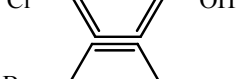
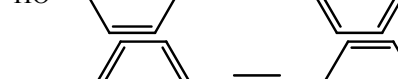
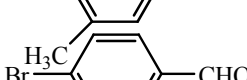
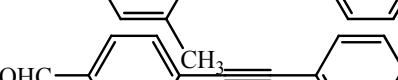
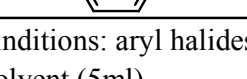
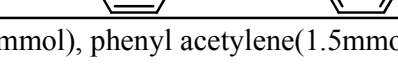
^aReaction conditions: aryl halides (1mmol), phenyl boronic acid (1.2mmol), K₂CO₃ (1mmol), catalyst (1mol%), DMF, Solvent (5ml).

^bIsolated yield after column chromatography.

3.6. Catalytic Sonogashira Coupling Reactions

To extend the scope of our work, we next investigated the coupling of various aryl bromides with terminal alkynes. The results are summarized in (Table 5). The electron donating groups such as -Me, -Ome, at the *para* position of aryl bromide couple smoothly with phenyl acetylene to give good to excellent yield of isolated cross coupling products Table 5, entries 3 and 4. The *p*-chlorobenzonitrile having electron-deficient aromatic rings, also underwent the Sonogashira coupling with terminal alkynes under similar conditions to afford the corresponding products in good yields entry 5. Bromobenzene could be smoothly coupled with phenyl acetylene resulting in a high yield of diphenyl acetylene 93% (entry 1). 2-bromotoluene (entry 7), gave the corresponding product in slightly lower yield 75%, which may be due to steric effects compare with *p*-bromotoluene (entry 6) found to be moderate yield 78%.

Table 5: Sonogashira Reaction of Aryl Halides with Phenyl Acetylene


Entry	Substrate	Product	Yield ^b (%)			
			complexes			
			1	2	3	4
1			93	80	90	93
2			91	85	88	83
3			92	80	90	88
4			97	92	94	90
5			90	88	80	93
6			86	79	75	78
7			85	82	80	75
8			90	86	92	78

^aReaction conditions: aryl halides (1mmol), phenyl acetylene(1.5mmol), K₂CO₃ (2mmol), Catalyst (1mol%), Solvent (5ml).

^bIsolated yield after column chromatography.

4. Conclusion

The present work describes the synthesis of new palladium(II) Schiff base complexes derived from the 1:2 molar ratio of Schiff base ligands H₂L₁, H₂L₂, H₂L₃ and H₂L₄ with [Pd(OAc)₂]. Further, these new palladium(II) Schiff base complexes were structurally characterized by analytical and spectral (IR, UV-Vis, ¹H-NMR and ¹³C-NMR) methods. These catalysts showed good catalytic activities towards Suzuki and Sonogashira cross coupling reactions of aryl halides with phenyl boronic acid and phenyl acetylene.

5. References

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