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Suzuki–Miyaura cross-coupling reaction of aryl bromides catalyzed by palladium(II) pyridoxal hydrazone complexes

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ABSTRACT

The reaction of $[PdCl_2(PPh_3)_2]$ and substituted pyridoxal hydrazone ligands (H_2L) in methanol under reflux afford a series of palladium ONO coordinated complexes with general formula $[Pd(PPh_3)L]$ (where, L = dianionic terdentate pyridoxal hydrazones). All the palladium complexes are air stable and fully characterized by elemental analysis, spectral and X-ray diffraction methods. In chloroform solution all the metal complexes exhibit characteristic metal to ligand charge transfer (MLCT) absorptions and ligand based transitions. Molecular structure of one of the complexes (**3**) has been determined by X-ray crystallography indicates that the pyridoxal hydrazone ligands are coordinated to the palladium as a terdentate O, N, O donor and a distorted square-planar geometry is observed around palladium(II) metal center. Further, palladium-catalyzed protocol for Suzuki–Miyaura cross-coupling reactions by the complex (**3**) has been developed, enabling to obtain biaryl products in good to excellent conversions.

1. Introduction

Palladium-catalyzed reactions have become a powerful tool in chemical synthesis. Amongst them, palladium-catalyzed Suzuki–Miyaura cross-coupling reaction has become an important protocol for the synthesis of biaryls. The impact of the Suzuki–Miyaura reaction on academic and industrial research, as well as on production, has been immense [1–4]. In particular, the Suzuki–Miyaura reaction, employing organoboron compounds, represents an effective method for the construction of C–C bonds, and has potential applications in pharmaceutical, material, and agricultural chemistry [5–8]. Its impact on organic synthesis is largely attributed to the fact that it provides a general and applicable method for the formation of biaryls, which are found in polymers [9], biologically active compounds [10,11], ligands [12], and various materials [13]. As a consequence of its versatility, the chemical industry has been significantly involved in this area and numerous methods have been patented [14]. The key advantages of the Suzuki–Miyaura cross-coupling are the mild conditions under which it is conducted, the high tolerance toward functional groups that is observed, the commercial availability and stability of boronic acids to heat, oxygen, and water [15,16]. Important contributions to this field were made by Beller [17,18], Buchwald [19], Genet [20], Leadbeater [21], Miyaura [22], Plenio [23,24] and Shaughnessy [25,26]. Recently several reports are available on palladium complexes containing different ligands as efficient catalysts for Suzuki–Miyaura coupling reaction [27–29].

Generally, the coordination chemistry of pyridoxal hydrazones based ligands proved to be very interesting, because of their excellent complexation ability towards transition metals and the possibility of their analytical applications. These chelating ligands can exist in two different deprotonated forms such as neutral and anionic depending on pH. The most predominant coordination mode is tridentate, achieved through hydrazine nitrogen, phenolic oxygen and carbonyl oxygen atoms [30]. Metal complexes of hydrazones proved to have potential applications as catalysts [31], luminescent probes [32], and molecular sensors [33]. The availability of several publications in the literature clearly indicates the impact of the Suzuki–Miyaura cross-coupling reaction in organic synthesis in the past two decades (1981–2001). As such, there is an abundance of literature on this subject featuring several excellent reviews [34–37].

Previously, we have reported a number of ruthenium complexes bearing cyclometallated azophenol, pincer ligands, Schiff bases and thioamide ligands along with their catalytic applications [38–41]. Here in, we focus our interest on the synthesis and structural characterization of a series of palladium complexes (**1**–**5**) containing pyridoxal hydrazone ligands. All the synthesized complexes (**1**–**5**) were fully characterized by ^{1}H, ^{31}P in solution, electrospray

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mass spectroscopy and X-ray crystallography. The study of catalytic activity of palladium(II) pyridoxal hydrazone complexes containing triphenylphosphine in Suzuki–Miyaura coupling reaction is not known in the literature. As part of our endeavor to manifest the applicability of the complexes in catalysis, we explored the catalytic efficiency of the complex (**3**) in Suzuki–Miyaura C–C coupling of *para*-substituted aryl bromides with arylboronic acids derivatives in methanol medium.

2. Results and discussion

2.1. Synthesis of the complexes

The pyridoxal-*N*-substituted hydrazone derivatives were prepared according to a procedure described in the literature [42,43] employing the condensation reaction of the corresponding hydrazone derivative and 3-hydroxy-5-(hydroxymethyl)-2-methyl-4-pyridine carbaldehyde. All the ligands have been used in the present study are abbreviated in general as H_2L. Reaction of each of these ligands with $[Pd(PPh_3)_2Cl_2]$ in equal molar ratio and in presence of triethylamine proceeds smoothly in refluxing methanol under nitrogen atmosphere for 3 h (Scheme 1). Coordination was immediate, as a change of color from yellow to reddish orange solid formation. The solid residue thus obtained was filtered and washed with cold methanol and diethyl ether. Structural studies of palladium(II) complexes with pyridoxal hydrazone and analogs showed these diprotic ligands to act as tridentate, planar chelate ligands coordinating through the phenolic oxygen, amide oxygen and the imine nitrogen atom. All new complexes have been isolated as yellow or orange red colored air stable solids and non-hygroscopic in nature. The synthesized palldium(II) complexes are highly soluble in common solvents such as chloroform, dichloromethane. The analytical data (C, H, and N) are in good agreement with the compositions proposed for all the complexes and are presented in the experimental section.

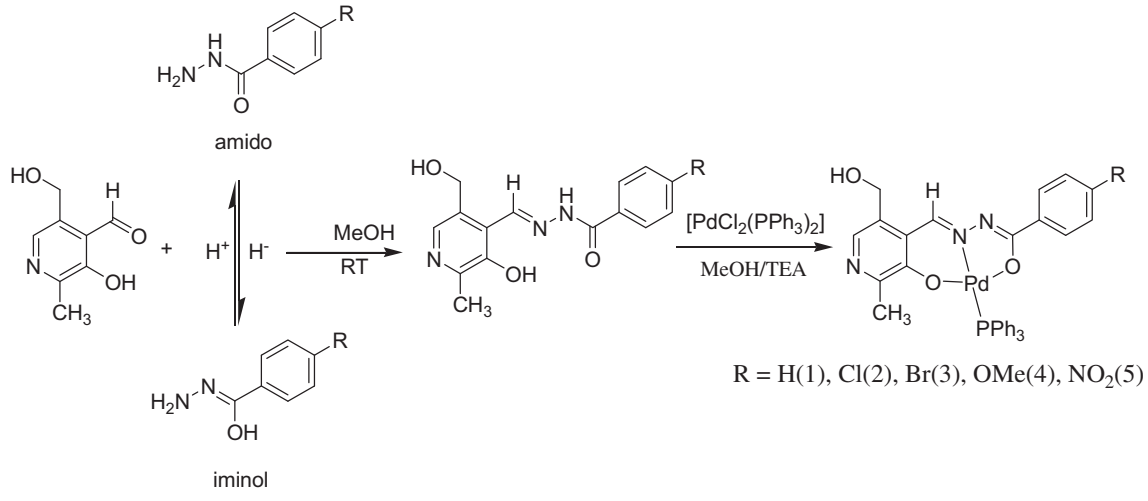
2.2. Spectral characterization

The $\upsilon_{C=O}$ and υ_{N-H} bands of ligands are disappeared upon complexation with palladium and the appearance of a new band in the region 1197–1260 cm^{-1} is assigned to the $\nu_{(C-Oiminol)}$ mode. Further, these complexes show new bands near 1660–1680 cm^{-1} and 1316–1325 cm^{-1} confirms the coordination of imine nitrogen ($\nu_{C=N}$) and phenolic oxygen (ν_{C-O}) to the palladium respectively. Electronic spectra of all the complexes have been recorded in dry chloroform solution in the range 200–800 nm (Table 1). The absorption spectra of the palladium pyridoxal hydrazone complexes exhibited very intense bands around 348–360 nm are assigned to ligand-centered (LC) $\pi \rightarrow \pi^*$ transitions, and moderately intense bands located in the visible region from 435 to 418 nm are ascribed to metal to ligand charge-transfer (MLCT) transitions.

^{1}H NMR spectra of the ligands and complexes were recorded to confirm the coordinating modes of the ligands. All the ligands show a broad signal at ca. 13.90 ppm due to phenolic –OH group. In the ^{1}H NMR spectra of complexes, the signal of the phenolic proton is absent due to deprotonation. The absence of a resonance for –NH suggests a predominance of the iminolate form in solution. The peak corresponding to the NH group and OH protons could not be located in the $\delta = 0$–15 ppm region in the spectra of the ligands. All the complexes show a clear pattern between 7.5 and 8.4 ppm is assigned to aromatic protons of the phenyl group of triphenylphosphine and the ligand aromatic protons. The methylene and methyl protons of the pyridoxal moiety of the ligands show a sharp peak at δ = 4.76 and 2.60 ppm respectively, and these signals appear in the complexes with slight shifts in their positions. The $-OCH_3$ protons from the hydrazide part appear as singlet at 3.8 ppm. The NMR spectral profiles of the palladium(II) complexes (**1**–**5**) are summarized in experimental section. The ^{31}P-{H}NMR spectra of all the complexes **1**–**5** showed a singlet around δ 21.8 which confirm that the one triphenylphosphine group is coordinated to palladium in the complexes. A representative ^{1}H and ^{31}P-{H}NMR spectra of complex (**1**) are given in the Supporting Information (Figs. S2 and S3). ESI-MS experiment supported the formation of palladium(II) pyridoxal hydrazone complexes by the appearance of prominent peaks corresponding to their molecular mass and the values are given in experimental section.

2.3. Molecular structure description

The crystal structure analysis of the complex $[Pd(PPh_3)(L^3)]$ (**3**) was performed by single crystal X-ray diffraction method and ORTEP view of the complex is shown in Fig. 1. The summery of single crystal X-ray structure refinement is shown in Table 2 and the selected bond angle and the bond length are given in Table 3. The pyridoxal hydrazone ligands coordinates to the palladium(II) ion with the phenolate oxygen, imine nitrogen, and keto oxygen



Scheme 1. Formation of palladium(II) pyridoxal hydrazone complexes.

Table 1
Electronic spectra of palladium(II) pyridoxal hydrazone complexes.

Complexes	λ_{max} (nm) ε (dm^3/mol/cm)
1	418(2744)[a], 352(3744)[b]
2	423(776)[a], 326(1192)[b]
3	421(1071)[a], 353(1850)[b]
4	435(2219)[a], 357(2211)[b]
5	425(2815)[a], 334(3918)[b]

[a] Ligand Centered Transition (LCT).
[b] Metal to Ligand Charge-Transfer (MLCT) transition.

donor atoms to form a square-planar geometry. The asymmetric unit consists of tridentate ONO dibasic ligand chelating the palladium atom together with one triphenylphosphine moiety. The palladium(II) complexes composed of one six-membered and one five-membered chelate ring with the bite angles around Pd(II) are O1–Pd1–N1 = 80.9(3); O2–Pd1–N1 = 94.2(3); P1–Pd1–O1 = 91.46(19); P1–Pd1–O2 = 93.5(2) summing up the in-plane angle to be exactly 360 °C. In the ligand, the pyridoxal nitrogen is deprotonated and this is confirmed by the narrow angle N3–C12–C15 of 117.7(10)° in protonated pyridoxal moieties, as said before, the reported angles are larger than 120° [44]. The Pd1–O1 (1.948(7)), Pd1–N1 (1.976(7)), Pd1–O2 (1.979(6)) and Pd1–P1 (2.283(2)) distances are all quite normal, as observed in structurally characterized other complexes of palladium containing these bonds [45,46]. The C1–O1, 1.295(12) Å, and N1–N2, 1.395(13) Å, bond distances are similar to the values found in non-co-ordinated hydrazone ligands [47].

2.4. Suzuki–Miyaura cross-coupling reactions by palladium complex

2.4.1. Effect of low catalyst loading

It is well established that palladium complexes containing triphenylphosphine group, which combine both good σ-donor strength and a π-accepting capacity, always have a high catalytic activity in Suzuki–Miyaura cross-coupling reactions [48,49]. Therefore we attempted to use one of our palladium(II) complex (**3**) as catalyst in Suzuki–Miyaura reaction. The ability to use small amounts of catalyst and still achieve high conversions is a great concern in cross-coupling reactions due to the high cost of metals and ligands. Low catalyst loading tests were performed to determine the catalytic efficiency of the catalyst in the presence of DMF and K_2CO_3. In order to optimize the reaction condition for the

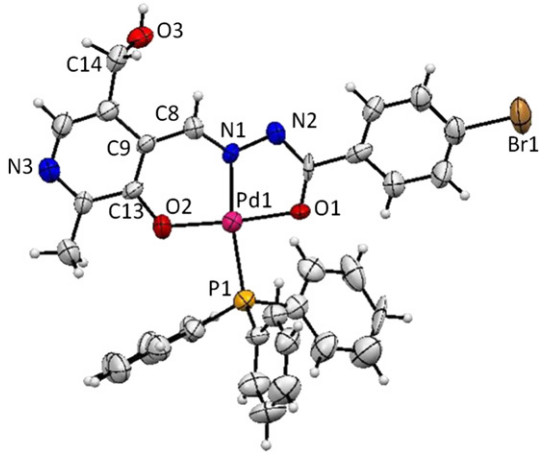


Fig. 1. X-Ray structure of complex [Pd(PPh_3)L3] (**3**).

Table 2
Crystal data refinement parameter of [Pd(PPh_3)L3] (**3**).

Formula	$C_{33}H_{27}BrN_3O_3PPd$
Formula weight	730.88
Crystal system	Monoclinic
Space group	*P*21/*c* (No. 14)
Unit cell dimensions	$a = 9.4194(3)$ Å, $\alpha = 90°$ $b = 9.9542(2)$ Å, $\beta = 92.354(2)°$ $c = 31.8707(9)$ Å, $\gamma = 90°$
Volume [$Å^3$]	2985.76(14)
Z	4
D(calc) [g/cm^3]	1.626
Mu (MoKα) [/mm]	2.053
F(000)	1464
Crystal size [mm]	0.30 × 0.26 × 0.22 mm
Temperature (K)	293(2)
Radiation [Å]	MoKα 0.71073
Theta Min-Max [°]	1.28, 18.89
Goodness-of-fit on F^2	1.223
R, *wR2*, *S*	0.0381, 0.1151, 1.223
R indices (all data)	0.0555, 0.0947, 1.223

coupling reactions different catalyst:substrate (C/S) ratios were taken and the results are summarized in Table 4. In the reaction optimization, we started the C/S ratios of 1:100, 1:300 and 1:500, the reaction proceeds with excellent conversions. When increasing the C/S ratio to 1:1000, 1:5000 and 1:10,000 the reaction still proceeds with a reasonable conversions. Although, only less cross-coupling products (entry 1:50%) was observed in 1:100 C/S ratio, when the reactions were carried out in room temperature. The high turnover number (TON) of 4000 was observed in the case of 1:10,000 C/S ratio. Thus, it was concluded that catalyst:substrate ratio of 1:500 is the best compromise between optimum reaction rate and C/S ratio.

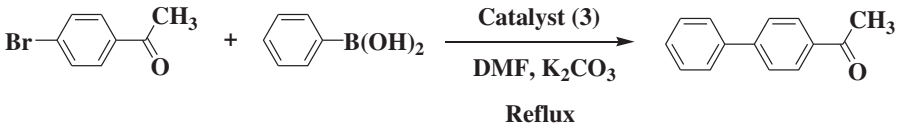
2.4.2. Effect of solvents

To study the effects of different solvents in our catalytic system, we have chosen the reaction between 4-bromoacetophenone with phenylboronic acid in presence of various solvents and K_2CO_3 base. In all instances the solvent was used as obtained commercially without further purification and the reactions were performed in air. After completion of the reaction, the 4-acetobiphenyl was isolated from the reaction mixture with diethyl ether. The results of the above reactions are summarized in Table 5. In the present study non-polar solvent like toluene gave moderate yield of 62% conversion (entry 4), whereas polar solvents such as methanol or DMF are found to be more efficient for the conversion of biaryl compounds to 99%, 99% respectively (entries 2 and 3). On the other hand aprotic solvents (entries 5–7) gave comparatively less yields. The lowest conversion (32%) was obtained with dichloromethane

Table 3
Selected bond angles and bond length of [Pd(PPh_3)L3] (**3**).

Bond length	Bond angles
Pd1–P1 2.283(2)	P1–Pd1–O1 91.46(19)
Pd1–O1 1.948(7)	P1–Pd1–O2 93.5(2)
Pd1–O2 1.979(6)	P1–Pd1–N1 172.2(3)
Pd1–N1 1.976(7)	O1–Pd1–O2 175.0(3)
N1–N2 1.395(13)	O1–Pd1–N1 80.9(3)
O1–C1 1.295(12)	O2–Pd1–N1 94.2(3)
N2–C1 1.324(13)	Pd1–P1–C16 110.9(4)
N1–C8 1.263(14)	Pd1–P1–C22 111.9(3)
	Pd1–P1–C28 114.9(3)
	Pd1–N1–N2 114.2(6)
	N2–N1–C8 120.8(8)
	Pd1–N1–C8 124.9(8)
	N1–N2–C1 108.5(7)

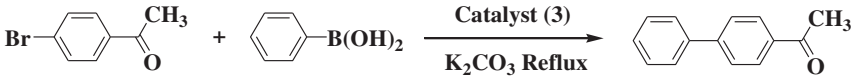
Table 4
Effect of low catalyst loading.[a]



Entry	C:S ratio	Time (h)	Conversion (%)[b]	TON
1	1:100 (RT)	24	50	250
2	1:100	6	>99	99
3	1:300	6	>99	297
4	1:500	6	>99	495
5	1:1000	8	81	810
6	1:5000	8	58	2900
7	1:10,000	10	40	4000

[a] Reaction conditions: 4-Bromoacetophenone (0.5 mmol), phenylboronic acid (0.75 mmol), base (1.5 mmol) and solvent (5 mL).
[b] Conversion to the coupled product was determined by ^{1}H NMR spectroscopy based on 4-bromoacetophenone; average of two runs.

Table 5
Effect of solvents.[a]



Entry	Solvents	Conversion (%)[b]
1	H_2O	NR[c]
2	Methanol	>99
3	DMF	>99
4	Toluene	62
5	Dioxane	40
6	THF	38
7	DCM	32

[a] Reaction conditions: 4-Bromoacetophenone (0.5 mmol), phenylboronic acid (0.75 mmol), catalyst (0.001 mmol), base (1.5 mmol) and solvent (5 mL).
[b] Conversion to the coupled product was determined by ^{1}H NMR spectroscopy based on 4-bromoacetophenone; average of two runs.
[c] No reaction.

solvent. In water the reaction is not progressing in room temperature as well as in reflux condition.

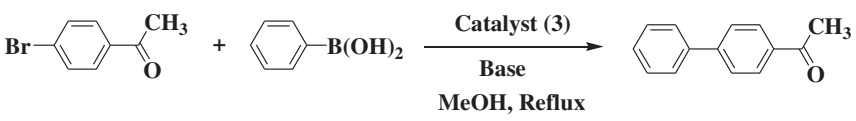
2.4.3. Effect of bases

Further, the effect of different mineral bases on this reaction was investigated by using the coupling of 4-bromoacetophenone with phenylboronic acid as a test case. First the reaction was conducted without any base and no reaction was observed. In presence of NaOH and KOH base shows a conversion of 80% and 89% respectively. Similarly Na_2CO_3 and K_2CO_3 did not significantly affect the reactions carried out at 70 °C (Table 6). Among the different bases used for our studies, the K_2CO_3 was the best choice of base, and the conversion of product could be increased to 99% (entry 4).

2.4.4. Suzuki–Miyaura cross-coupling reactions for aryl bromides

Under the optimized reaction conditions in hand, we have taken a series of aryl bromides and arylboronic acids and the conversions of the coupled products are given in Table 7. A general catalytic cycle for the cross-coupling reaction of organoboron reagents with aryl halides involves an oxidative-addition of the aryl halide, transmetalation, and reductive-elimination steps [50,1]. Aryl bromides with various functional groups efficiently reacted with boronic acids (entries 1–12) using K_2CO_3 and 5 mL methanol at reflux temperature in presence of palladium(II) catalyst for 6 h to yield Suzuki–Miyaura products in good to excellent conversions. The reaction of *p*-bromoacetophenone with boronic acid derivatives shows an excellent conversion (entries 1–4, 91–99%). In *p*-bromotoluene the conversions are good in all the cases (entries 5–8, 96–99%). *p*-Methoxy substrate also afforded an excellent conversion (entries 9–12, 92–99%). As expected, very satisfactory results were obtained with all the electron-deficient substrate in the boronic acid 2, 6, 10 shows a conversion of 91.7%, 99% and 93.7% respectively. The catalytic activity of the present complex is good when compared to palladium complexes containing Schiff bases

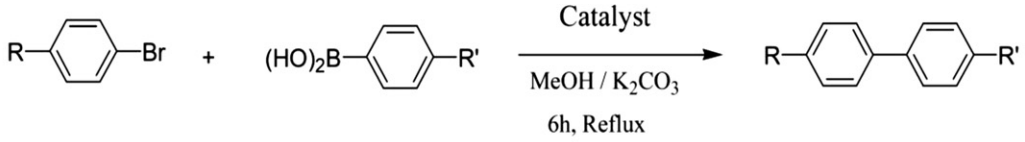
Table 6
Effect of bases.[a]

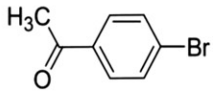
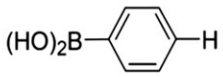
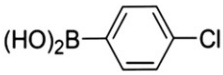
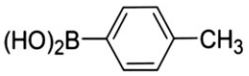
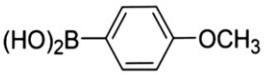
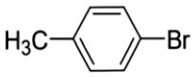
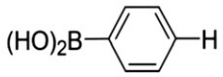
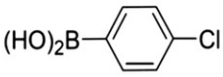
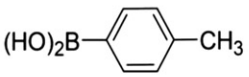
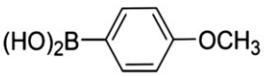
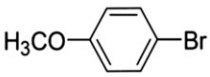
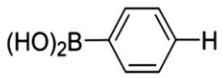
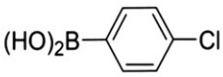
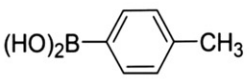
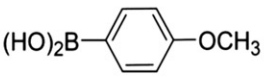


Sl. No	Base	Time (h)	Conversion (%)[b]
1	NaOH	6	80
2	KOH	6	89
3	Na_2CO_3	6	92
4	K_2CO_3	6	>99
5	NaOAc	6	42

[a] Reaction conditions: 4-Bromoacetophenone (0.5 mmol), phenylboronic acid (0.75 mmol), catalyst (0.001 mmol) and base (1.5 mmol), solvent (5 mL).
[b] Conversion to the coupled product was determined by ^{1}H NMR spectroscopy based on 4-bromoacetophenone; average of two runs.

Table 7
Suzuki–Miyaura coupling of aryl bromides with phenylboronic acid using catalyst (**3**).[a]



Entry	Aryl bromide	Boronicacid	Conversion (%) [b]	TON [c]
1			>99	495
2			92	409
3			>99	495
4			93	463
5			>99	495
6			>99	495
7			97	485
8			80	401
9			94	470
10			94	467
11			>99	495
12			93	464

[a]General conditions: ArBr (5 mmol), $PhB(OH)_2$ (7.5 mmol), catalyst (0.001 mmol), K_2CO_3 (1.5 mmol).
[b]All conversions determined by ^1H NMR spectroscopy, average of at least two runs.
[c]TON = Moles of product per mole of catalyst.

[51], carbenes [52–54] and metallocycles [55]. Although several catalytic systems have been reported to support Suzuki–Miyaura C–C coupling reaction, a catalyst of this type is novel for its ONO donor, PPh_3 ligand environment. This method proved successful in most cases to give the product in >95% purity as estimated by ^1H NMR spectroscopy. In all of the successful reactions, the ^1H NMR spectra of the products indicated no Suzuki–Miyaura coupling byproducts and the NMR data of all the Suzuki–Miyaura products are given in supporting information.

3. Conclusions

In this work we have synthesized five new palladium(II) pyridoxal hydrazone complexes bearing triphenylphosphine. The characterization of all the complexes was accomplished by analytical and spectral (IR, UV–vis and ^1H NMR, ^{31}P and ESI-MS) methods. X-ray analysis of complex (**3**) confirms the coordination mode of the ligand to the metal through O, N, O donors and reveals the presence of a square-planar geometry around the palladium

center. The catalytic efficiency of the one of the palladium(II) hydrazone complexes (**3**) was determined in Suzuki–Miyaura cross-coupling reaction and was found to be excellent. This facile, mild and general protocol represents, to a certain extent, a new advance in Suzuki–Miyaura cross-coupling reactions.

4. Experimental section

4.1. Reagents and materials

The ligands (**1**–**5**) were prepared as per the procedure previously reported [42,43]. Commercially available $Pd(PPh_3)_2Cl_2$ was purchased from Aldrich. pyridoxal hydrochloride, substituted benzoic acid hydrazide and aryl bromides, arylboronic acids were purchased from Aldrich. All the reagents used were chemically pure and analar grade. All solvents were distilled using the standard procedures [56].

4.2. Methods and instrumentation

Microanalytical (C, H, N) data were obtained with a Perkin–Elmer model 240C elemental analyzer. Melting Points were recorded in the Boetius micro heating table and are uncorrected. Infrared spectra of complexes were recorded in KBr pellets with a Perkin–Elmer 597 spectrophotometer in the range 4000–400 cm^{-1}. Electronic spectra were recorded on a Varian Cary 300 Bio UV–vis spectrophotometer using cuvettes of 1 cm path length. ^1H NMR spectra were recorded with a Bruker 400 MHz spectrometer. All ^1H, ^{31}P NMR spectra were taken in pure deuteriated DMSO solvents. Chemical shifts (δ) are given in ppm and refer to TMS as internal standard. The proton signals of the deuterated solvents were used as internal standards for the ^1H NMR spectra and 85% H_3PO_4 for the ^{31}P NMR spectra. Mass spectra were recorded using a Thermo Finnigan LCQ Advantage MAX 6000 ESI mass spectrometer.

4.3. General procedure for synthesis of palladium complexes

All Pd(II) complexes were prepared by a general method. An equimolar ratio of the ligand (1 mmol), $Pd(PPh_3)_2Cl_2$ (1 mmol) and triethylamine (0.2 mL) were mixed in dry methanol with constant stirring. The resulting yellow solution was stirred and heated under reflux for 3 h. The reactions were monitored by thin-layer chromatography. The solid was obtained from the above reaction are washed with cold methanol, ether and dried in vacuo. Single crystals of suitable for X-ray diffraction analysis were grown from mixture of chloroform–methanol solution at room temperature.

[$Pd(PPh_3)$L1] (**1**) Yield: 49 mg, 52%. M.p. 238 °C. $C_{33}H_{28}N_3O_3PPd$ (651.9): calcd. C 60.79, H 4.33, N 6.44; found C 60.72, H 4.38, N 6.49. MS (ESI): m/z = 651.8 [M^+]. IR (KBr, ν_{max}/cm^{-1}): 3178 (OH), 1607 ($C{=}N_{azomethine}$), 1372 (C–O). ^{31}P-{^1H} NMR in $CDCl_3$: δ 21.77 (s). ^1H NMR (400 MHz, $CDCl_3$, Me_4Si): 8.9 (1H, br s, OH py), 8.5 (1H, s, HC=N), 8 (2H, d, Ar–H) and 7.3 (2H, d, Ar–H), 7.4–7.8 (15H, m, PPh_3), 4.9 (2H, s, py CH_2O), 1.9 (3H, s, CH_3 py).

[$Pd(PPh_3)$(L2)]: Yield: 72 mg, 73%. M.p. 249 °C. $C_{33}H_{27}ClN_3O_3PPd$ (686.4): calcd. C 57.74, H 3.96, N 6.12; found C 57.76, H 3.93, N 6.20. MS (ESI): m/z = 687.7 [M^+]. IR (KBr, ν_{max}/cm^{-1}): 3179 (OH), 1610 ($C{=}N_{azomethine}$), 1368 (C–O). ^{31}P-{^1H} NMR in $CDCl_3$: δ 21.78 (s). ^1H NMR (400 MHz, $CDCl_3$, Me_4Si): 8.9 (1H, br s, OH py), 8.5 (1H, s, HC=N), 7.9 (2H, d, Ar–H), 7.3 (2H, d, Ar–H) and 7.4–7.8 (15H, m, PPh_3), 4.9 (2H, s, py CH_2O), 1.9 (3H, s, CH_3 py).

[$Pd(PPh_3)$(L3)]: Yield: 78 mg, 75%. M.p. 236 °C. $C_{33}H_{27}BrN_3O_3PPd$ (730.8): calcd. C 54.23, H 3.72, N 5.75; found C 54.29, H 3.66, N 5.71. MS (ESI): m/z = 731.6 [M^+]. IR (KBr, ν_{max}/cm^{-1}): 3310 (OH), 1623 ($C{=}N_{azomethine}$), 1398 (C–O). ^{31}P-{^1H} NMR in $CDCl_3$: δ 21.76 (s). ^1H NMR (400 MHz, $CDCl_3$, Me_4Si): 8.9 (1H, br s, OH py), 8.5 (1H, s, HC=N), 7.9 (2H, d, Ar–H), 7.4 (2H, d, Ar–H) and 7.4–7.8 (15H, m, PPh_3), 4.9 (2H, s, py CH_2O), 1.9 (3H, s, CH_3 py).

[$Pd(PPh_3)$(L4)]: Yield: 90 mg, 94%. M.p. 224 °C. $C_{34}H_{30}N_3O_4PPd$ (682.0): calcd. C 59.88, H 4.43, N 6.16; found C 59.95, H 4.48, N 6.23. MS (ESI): m/z = 681.7 [M^+]. IR (KBr, ν_{max}/cm^{-1}): 3256 (OH), 1675 ($C{=}N_{azomethine}$), 1371 (C–O). ^{31}P-{^1H} NMR in $CDCl_3$: δ 21.78 (s). ^1H NMR (400 MHz, $CDCl_3$, Me_4Si): 8.9 (1H, br s, OH py), 8.5 (1H, s, HC=N), 7.9 (2H, d, Ar–H), 7.3 (2H, d, Ar–H) and 7.4–7.8 (15H, m, PPh_3), 4.9 (2H, s, py CH_2O), 3.8 (3H, s, O–CH_3), 1.9 (3H, s, CH_3 py).

[$Pd(PPh_3)$(L5)]: Yield: 65 mg, 66%. M.p. 242 °C. $C_{33}H_{27}N_4O_5PPd$ (696.9): calcd. C 56.87, H 3.90, N 8.04; found C 56.93, H 3.86, N 8.09. MS (ESI): m/z = 696.7 [M^+]. IR (KBr, ν_{max}/cm^{-1}): 3208 (OH), 1685 ($C{=}N_{azomethine}$), 1346 (C–O). ^{31}P-{^1H} NMR in $CDCl_3$: δ 21.77 (s). ^1H NMR (400 MHz, $CDCl_3$, Me_4Si): 8.9 (1H, br s, OH py), 8.5 (1H, s, HC=N), 8.2 (2H, d, Ar–H), 7.4 (2H, d, Ar–H) and 7.4–7.8 (15H, m, PPh_3), 4.9 (2H, s, py CH_2O), 1.9 (3H, s, CH_3 py).

4.4. General procedure for Suzuki–Miyaura coupling reactions

In a typical run, an oven dried 25 mL flask equipped with a stir bar was charged with a known catalyst (0.001 mmol), base (1.5 mmol) and phenylboronic acid (0.75 mmol). To the above mixture methanol (5 mL) and aryl halide (0.5 mmol) were added. The reactions were allowed to reflux at 70 °C. After the specified time the flask was removed from the oil bath. The solvent was removed and water (10 mL) was added followed by extraction with diethyl ether (3 × 10 mL) and the catalyst was regenerated. The combined organic layers were washed with water (3 × 10 mL), dried over anhydrous Na_2SO_4, and filtered. The organic layers were evaporated under reduced pressure and the residue was analyzed by ^1H NMR. All the conversions were taken from ^1H NMR spectroscopy based on arylbromide methyl group [57,58] and the ^1H NMR data of all the products were given in supporting information.

4.5. X-ray crystallography

Single crystals of [$Pd(PPh_3)$(L3)] (**3**) were grown by slow evaporation of chloroform–methanol solution at room temperature. A crystal of dimensions 0.30 × 0.26 × 0.22 mm was selected and the data were collected. Significant crystal data collection and refinement parameters are listed in Table S1 (supporting information). A single crystal of suitable size was mounted on the top of a glass fiber, and transferred to a Stoe IPDS diffractometer using monochromated MoKα radiation. Corrections were made for Lorentz and polarization effects as well as for absorption (numerical). The structures were solved and refined by full-matrix least-squares techniques on $F2$ using the SHELX-97 program [59,60]. The absorption corrections were done by the multi scan technique. All data were corrected for Lorentz and polarization effects, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement process as per the riding model. CCDC 837648 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Appendix A. Supplementary material

CCDC 837648 for complex (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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