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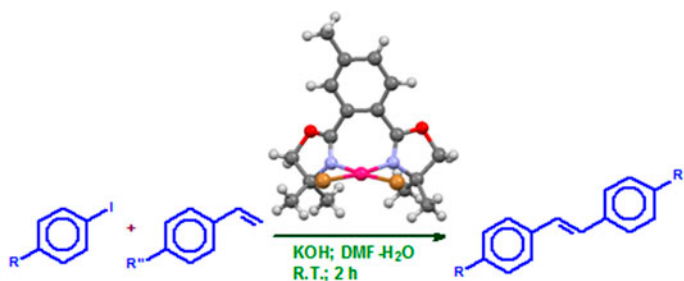
## Effective palladium(II)-bis(oxazoline) catalysts: synthesis, crystal structure, and catalytic coupling reactions

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New bis(oxazoline) ligands and their palladium complexes were synthesized and characterized. X-ray crystal structures of the two new complexes showed distorted square planar geometry with the palladium ion bonded to nitrogens of two bidentate heterocycles in addition to two bromides and two acetate ions for Pd-BOX-1 and Pd-BOX-2, respectively. The complexes adopt a chair structure with a rigid curvature inducing an inherent chirality. The complexes were effective catalysts for Suzuki–Miyaura, Mizoroki–Heck, and copper-free Sonogashira coupling reactions in aqueous dimethylformamide and under aerobic conditions. The reaction conditions were optimized for best solvent, base, and temperature. The substrate scope of the new catalytic system was evaluated for coupling reactions of a variety of aryl halides with aryl boronic acids, alkenes, and alkynes.

**Keywords:** Bis(oxazoline); Palladium; Crystal structure; Suzuki–Miyaura; Mizoroki–Heck; Sonogashira

### 1. Introduction

The synthetic utility of coupling reactions is illustrated by a wide variety of molecules produced and utilized either as starting materials, intermediates, or as final products [1].

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Coupling reactions have been extensively employed in the synthesis of important industrial raw materials [2], pharmaceuticals, and biologically active molecules [3]. Palladium complexes are primary catalysts for coupling reactions. They are particularly attractive due to their tolerance and compatibility with the reaction conditions and with a broad range of functional groups [4]. Most palladium-catalyzed coupling reactions are conventionally carried out in the presence of phosphine ligands and under rigorously dried organic solvents [5 (a)–(g)]. Methods have been reported using nitrogen-based ligands in palladium-catalyzed coupling in aqueous and organic solvents [6]. Although, some phosphine ligands have been reported to show stability toward air and moisture, the difficulty associated with their synthesis, the high production cost, and extreme toxicity restricted their applications [7–9]. Nitrogen ligands have been found to be easily accessible, air- and moisture-stable, modular, and less expensive [10].

In this article, we have developed new catalytic systems based on palladium-bis(oxazoline) (Pd-BOX) complexes. These catalytic systems have shown high catalytic activities in Suzuki–Miyaura [11], Mizoroki–Heck [12], and copper-free Sonogashira [13] coupling reactions using aqueous organic solvents and under aerobic conditions. The structure of BOX ligands allows formation of structurally constrained metal chelates with substituents on oxazoline rings in close proximity with the donor nitrogen, hence, providing strong directing effect and high activity in the reaction being catalyzed [14, 15]. The newly synthesized complexes were fully characterized using spectroscopic techniques and their molecular structures were established using X-ray structure analysis.

## 2. Experimental

### 2.1. Materials and instrumentation

Materials for synthesis of ligands and complexes were purchased from Sigma-Aldrich and used as received. All solvents (reagent grade) used in the synthesis were distilled before use. The products were purified using flash column chromatography packed with 60 F Silica gel from Fluka Chemie AG (Buchs, Switzerland).

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data were obtained using a 500 MHz NMR instrument (Jeol 1500 model). Chemical shifts were recorded in ppm using tetramethylsilane (TMS) as reference and  $\text{CDCl}_3$  as solvent. IR spectra were recorded in wave numbers ( $\text{cm}^{-1}$ ) using a FT-IR spectrometer (Perkin-Elmer 16F model). Elemental analyses were performed on a Perkin Elmer Series 11 (CHNS/O) Analyzer 2400. Merck 60 F<sub>254</sub> silica gel plates (250  $\mu\text{m}$  layer thickness) were used for thin-layer chromatography (TLC) analyses. A Varian Saturn 2000 GC–MS (30 m capillary column) was used to analyze the products. Agilent 6890 Gas chromatography (GC) was used to monitor the reactions and analyze the products.

### 2.2. Synthesis of bis(oxazoline) ligands (BOX-1 and BOX-2)

A 50 mL round bottom flask equipped with a reflux condenser was charged with the appropriate amount of the substituted phthalonitrile (4.0 mM), zinc triflate (5.0 M%, 0.20 mM), and chlorobenzene (30 mL) under argon. The mixture was stirred to dissolve the phthalonitrile and then 2-aminoalcohol (8.0 mM), dissolved in dry chlorobenzene, was slowly added. The temperature was raised to 135 °C and the reaction mixture was refluxed for 24 h. The

product of the reaction, which was obtained as an oily residue, was dissolved in 30 mL of dichloromethane and then extracted twice with distilled water (20 mL). The aqueous layer was separated and washed with dichloromethane. The separated organic layers were dried using anhydrous sodium sulfate. The dichloromethane was removed under vacuum on a rotary evaporator to give the crude product, which was then purified using silica gel column chromatography with dichloromethane/ether (4/1) as eluent [14, 16, 17].

**2.2.1. 2,2'-(4-Methyl-1,2-phenylene)bis(4,4-dimethyl-4,5-dihydrooxazole) (BOX-1).** Yellow oil, isolated yield 92%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.50 (d,  $J = 7.93$  Hz, 1H, C-5 arom), 7.41 (s, 1H, C-3 arom), 7.12 (d,  $J = 7.93$  Hz, 1H, C-6 arom), 3.92 (s, 4H,  $\text{OCH}_2 \times 2$ ), 2.24 (s, 3H,  $\text{CH}_3$  on arom), 1.25 (s, 12H,  $\text{NC}(\text{CH}_3)_2 \times 2$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 20.8 ( $\text{CH}_3$  on arom), 27.8 ( $\text{NC}(\text{CH}_3)_2 \times 2$ ), 67.5 ( $\text{NC}(\text{CH}_3)_2 \times 2$ ), 79.1 ( $\text{OCH}_2$ ), 79.2 ( $\text{OCH}_2$ ), 125.4, (C-2 arom), 128.2 (C-1 arom), 129.4 (C-3 arom), 130.0 (C-5 arom), 130.5 (C-6 arom), 140.3 (C-4 arom), 162.1 (C-4'), 162.4 (C-1'); IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu$  ( $\text{cm}^{-1}$ ) 2930, 1655, 1460, 1354, 1266, 1085, 969, 830, 735; GC-MS  $m/z$  287 ( $M + 1$ ). Anal. Calcd for  $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_2$  (%): C, 71.3; H, 7.7; N, 9.8. Found: C, 71.0; H, 7.7; N, 9.9.

**2.2.2. 2,2'-(4-Nitro-1,2-phenylene)bis(4,4-dimethyl-4,5-dihydrooxazole) (BOX-2).** Green solid, isolated yield 91%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.56 (s, 1H, C-3 arom), 8.28 (d,  $J = 6.1$  Hz, 1H, C-5 arom), 7.89 (d,  $J = 8.5$  Hz, 1H, C-6 arom), 4.09 (s, 4H,  $\text{OCH}_2 \times 2$ ), 1.38 (s, 12H,  $\text{NC}(\text{CH}_3)_2 \times 2$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 28.0 ( $\text{NC}(\text{CH}_3)_2 \times 2$ ), 68.5 ( $\text{NC}(\text{CH}_3)_2 \times 2$ ), 80.0 ( $\text{OCH}_2 \times 2$ ), 124.7 (C-3 arom), 124.9 (C-5 arom), 130.4 (C-2 arom), 131.1 (C-6 arom), 134.5 (C-1 arom), 148.5 (C-4 arom), 160.1 (C-4'), 160.5 (C-1'); IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu$  ( $\text{cm}^{-1}$ ) 2932, 1659, 1530, 1352, 1266, 1185, 1043, 968, 736; GC-MS  $m/z$  318 ( $M + 1$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_4$  (%): C, 60.5; H, 6.0; N, 13.2. Found: C, 60.6; H, 6.0; N, 13.3.

### 2.3. Synthesis of palladium bis(oxazoline) complexes (Pd-BOX-1 and Pd-BOX-2)

In a 25 mL round bottom flask flushed with nitrogen was charged 0.5 mM of the appropriate palladium(II) salt (in 8 mL DMF) and 0.5 mM of BOX ligand.  $\text{PdBr}_2$  was used with BOX-1 to prepare Pd-BOX-1, and  $\text{Pd}(\text{OAc})_2$  was used with BOX-2 for preparation of Pd-BOX-2. The reaction mixture was stirred at room temperature for 6 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed using a rotary evaporator. The crude product was dissolved in  $\text{CH}_2\text{Cl}_2$  and layered with hexane to obtain pure crystals. The crystals were separated and washed with ether and characterized with different spectroscopic techniques including  $^1\text{H}$  and  $^{13}\text{C}$  NMR, elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction [14].

**2.3.1. Dibromido(2,2'-(4-methyl-1,2-phenylene)bis(4,4-dimethyl-4,5-dihydrooxazole)-N, N')palladium(II) (Pd-BOX-1).** Brown solid; isolated yield 89%, m.p. 232 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.69 (d,  $J = 7.9$  Hz, 1H, C-5 arom), 7.59 (s, 1H, C-3 arom), 7.52 (d,  $J = 7.9$  Hz, 1H, C-6 arom), 4.31–4.23 (m, 4H,  $\text{OCH}_2 \times 2$ ), 2.49 (s, 3H,  $\text{CH}_3$  on arom), 1.77 (s, 6H,  $\text{NC}(\text{CH}_3)_2$ ), 1.58 (s, 3H,  $\text{NC}(\text{CH}_3)$ ), 1.55 (s, 3H,  $\text{NC}(\text{CH}_3)$ );  $^{13}\text{C}$  NMR

(125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm); 21.5 (CH<sub>3</sub> on arom), 28.9 (NC(CH<sub>3</sub>), 29.0 (NC(CH<sub>3</sub> x 2), 29.1 (NC(CH<sub>3</sub>), 71.1 (NC(CH<sub>3</sub>)<sub>2</sub>), 71.2 (NC(CH<sub>3</sub>)<sub>2</sub>), 80.9 (OCH<sub>2</sub>), 81.0 (OCH<sub>2</sub>), 123.1 (C-2 arom), 125.9 (C-1 arom), 130.1 (C-3 arom), 130.6 (C-5 arom), 133.3 (C-6 arom), 143.7 (C-4 arom), 164.0 (C-4'), 164.1 (C-1'); IR (KBr)  $\nu$  (cm<sup>-1</sup>) 2969, 2920, 1630, 1457, 1374, 1327, 1207, 1122, 1067, 961, 830, 722. Anal. Calcd for C<sub>17</sub>H<sub>22</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pd (%): C, 36.9; H, 4.0; N, 5.1. Found: C, 37.0; H, 4.0; N, 5.0; UV-vis:  $\lambda_{\max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm: 383;  $\epsilon$ /LM<sup>-1</sup> cm<sup>-1</sup>: 12,650.

**2.3.2. Diacetato(2,2'-(4-nitro-1,2-phenylene)bis(4,4-dimethyl-4,5-dihydrooxazole)-N,N') palladium(II) (Pd-BOX-2).** Green solid; isolated yield 92%, m.p. 149 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.72 (s, 1H, C-3 arom), 8.52 (d,  $J$  = 8.8 Hz, 1H, C-5 arom), 8.10 (d,  $J$  = 8.5 Hz, 1H, C-6 arom), 4.38–4.27 (m, 4H, OCH<sub>2</sub> x 2), 1.74 (s, 3H, NC(CH<sub>3</sub>), 1.73 (s, 3H, NC(CH<sub>3</sub>), 1.63 (s, 3H, NC(CH<sub>3</sub>), 1.61 (s, 3H, NC(CH<sub>3</sub>), 1.42 (s, 3H, OCOCH<sub>3</sub>), 1.41 (s, 3H, OCOCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm); 22.8 (OCOCH<sub>3</sub> x 2), 26.2 (NC(CH<sub>3</sub>), 26.3 (NC(CH<sub>3</sub>), 29.2 (NC(CH<sub>3</sub> x 2), 70.3 (NC(CH<sub>3</sub>)<sub>2</sub> x 2), 80.9 (OCH<sub>2</sub> x 2), 125.5 (C-3 arom), 126.0 (C-5 arom), 127.8 (C-2 arom), 131.5 (C-1 arom), 132.1 (C-6 arom), 149.5 (C-4 arom), 162.8 (C-4'), 163.1 (C-1'), 177.9 (OCOCH<sub>3</sub>), 178.0 (OCOCH<sub>3</sub>). IR (KBr)  $\nu$  (cm<sup>-1</sup>): 2980, 1651, 1605, 1533, 1500, 1376, 1329, 1222, 1172, 1129, 1063, 951, 713. Anal. Calcd for C<sub>20</sub>H<sub>25</sub>N<sub>3</sub>O<sub>8</sub>Pd (%): C, 44.3; H, 4.6; N, 7.8. Found: C, 44.3; H, 4.7; N, 7.7; UV-vis:  $\lambda_{\max}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm: 360;  $\epsilon$ /LM<sup>-1</sup> cm<sup>-1</sup>: 5926.

#### 2.4. General procedure for Suzuki–Miyaura coupling reaction

In a 25 mL round bottom flask, palladium complex (0.0020 mM) was dissolved in DMF (4 mL). Aryl halide (1.0 mM), aryl boronic acid (1.5 mM), potassium carbonate (2.0 mM), and distilled water (4.0 mL) were added. The mixture was stirred at room temperature for the required time. After complete reaction, the product was extracted three times with ethyl acetate (5 mL). The combined organic extract was dried with anhydrous sodium sulfate. The volume was reduced to 4 mL using a rotary evaporator. The product was analyzed by GC and GC–MS. The product was further purified using column chromatography with hexane–EtOAc (8 : 2) as eluent. The characterization data of **3a–3e** [14, 18] were in agreement with those observed in the literature.

#### 2.5. General procedure for Mizoroki–Heck coupling reaction

In a 15 mL round bottom flask, palladium complex (0.010 mM) was dissolved in DMF (2 mL). Aryl halide (1.0 mM), styrene (1.50 mM), KOH (2.0 mM), and distilled water (2 mL) were added. A condenser was attached and the mixture was stirred at 90 °C for the required time. After completion of the reaction, the product was extracted three times with ethyl acetate (5 mL). The combined organic extract was dried with anhydrous sodium sulfate. The volume was reduced to 4 mL using a rotary evaporator and the product was analyzed by GC and GC–MS. The product was further purified using column chromatography with hexane–EtOAc (7 : 3) as eluent. The characterization data of **5a–5e** [14, 18] were in agreement with those observed in the literature.

## 2.6. General procedure for Sonogashira coupling reaction

In a 15 mL round bottom flask, palladium complex (0.010 mM) was dissolved in DMF (2 mL). Aryl halide (1.0 mM), alkyne (1.5 mM), KOH (2.00 mM), and distilled water (2 mL) were added. A condenser was attached and the mixture was stirred at 70 °C for the required time. After completion of the reaction, the product was extracted three times with ethyl acetate (5 mL). The combined organic layer was dried with anhydrous sodium sulfate. The volume was reduced to 4 mL using a rotary evaporator. The product was analyzed by GC and GC–MS. The product was further purified using column chromatography with hexane–EtOAc (7 : 3) as eluent. The characterization data of **7a–7g** [14, 18, 19] were in agreement with those observed in the literature.

## 2.7. X-ray structure determination

Single-crystal data collection for **1** and **2** was performed at 120 and 296 K, respectively, on a Bruker-AXS Smart Apex system equipped with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The data were collected using SMART and the integration was performed using SAINT [20]. An empirical absorption correction was carried out using SADABS [21]. The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least squares on  $F^2$  using SHELXL-97 [22]. All nonhydrogen atoms were refined anisotropically. Hydrogens were placed at calculated positions using a riding model. Crystal data and details of the data collection are summarized in table 1. Selected bond lengths and angles are given in table 2.

Table 1. Crystallographic data for **1** and **2**.

Pd-BOX	<b>1</b>	<b>2</b>
Chemical formula	C <sub>17</sub> H <sub>22</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Pd	C <sub>21</sub> H <sub>27</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>8</sub> Pd
Formula weight	552.59	626.76
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Temperature (K)	120	296
Radiation		Mo K $\alpha$ ( $\lambda = 0.71073$ Å)
$\rho_{\text{Calcd}}$ (g cm <sup>-3</sup> )	1.872	1.551
$a$ (Å)	9.881(2)	11.0974(7)
$b$ (Å)	17.233(3)	18.991(1)
$c$ (Å)	11.612(2)	12.7396(8)
$\beta$ (°)	97.273(3)	91.926(1)
$V$ (Å <sup>3</sup> )	1961.2(6)	2683.3(3)
$Z$	4	4
Ref. collected/unique	25,922/4904	36,216/6665
Ref. observed [ $I > 2\sigma(I)$ ]	4004	4502
$R(\text{int})$	0.0449	0.0750
Data/restraints/parameters	4904/0/222	6665/0/322
Goodness-of-fit on $F^2$	1.123	1.111
R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0371$ ; $wR_2 = 0.0776$	$R_1 = 0.0536$ ; $wR_2 = 0.1109$
R indices (all data)	$R_1 = 0.0518$ ; $wR_2 = 0.0820$	$R_1 = 0.0799$ ; $wR_2 = 0.1270$
Largest diff. peak/hole (e Å <sup>-3</sup> )	1.289/−0.810	0.894/−0.802

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

Bond lengths		Bond angles	
<b>Pd-BOX-1</b>			
Pd1–N1	2.063(3)	N2–Pd1–N1	86.9(1)
Pd1–N2	2.045(3)	N2–Pd1–Br1	175.70(9)
Pd1–Br1	2.4158(7)	N1–Pd1–Br1	91.69(9)
Pd1–Br2	2.4162(7)	N2–Pd1–Br2	92.02(9)
		N1–Pd1–Br2	173.1(1)
		Br1–Pd1–Br2	88.85(2)
<b>Pd-BOX-2</b>			
Pd1–N1	2.020(3)	N1–Pd1–N2	88.0(1)
Pd1–N2	2.022(3)	O1–Pd1–N1	92.9(1)
Pd1–O1	2.001(2)	O1–Pd1–N2	177.6(1)
Pd1–O4	1.996(2)	O4–Pd1–O1	87.2(1)
		O4–Pd1–N1	172.9(1)
		O4–Pd1–N2	91.6(1)

### 3. Results and discussion

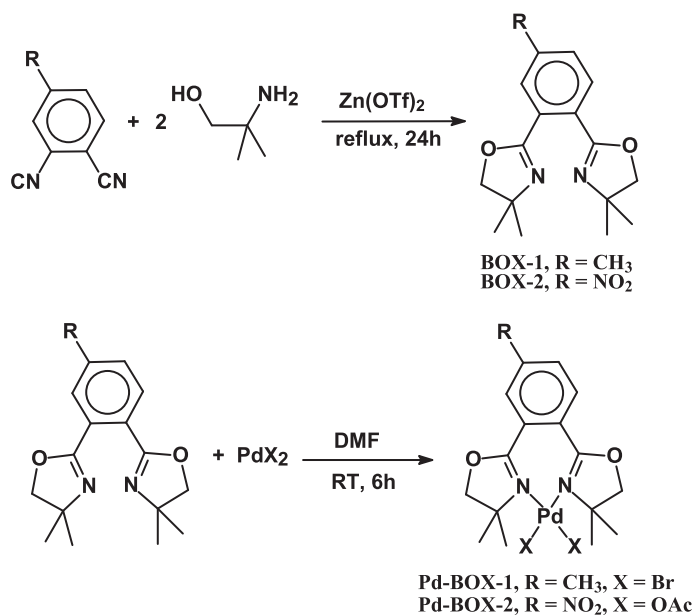
Our interest includes development of nonoptically active palladium bis(oxazoline) complexes and exploring their application as catalysts in coupling reactions. Although, a plethora of chiral metal-bis(oxazoline) complexes have been reported to be used efficiently in asymmetric catalysis [23], the use of nonoptically active palladium bis(oxazoline) complexes in coupling reactions is generally an underexplored area of research [24].

#### 3.1. Synthesis of BOX ligands and corresponding Pd(II)-BOX complexes

Treatment of phthalonitrile derivative with two equivalents of 2-amino alcohol in the presence of  $\text{Zn}(\text{OTf})_2$  afforded the corresponding bis(oxazoline) ligands BOX-1 and BOX-2 (scheme 1). The complexes Pd-BOX-1 and Pd-BOX-2 were obtained by reacting  $\text{PdBr}_2$  and  $\text{Pd}(\text{OAc})_2$  with BOX-1 and BOX-2 in DMF, respectively [14]. The Pd-BOX complexes were fully characterized using spectroscopic techniques and the molecular structures were determined using X-ray diffraction analysis.

#### 3.2. Molecular structures of Pd-BOX-1 and Pd-BOX-2

Pd-BOX-1 crystallizes in the  $P2_1/n$  space group. The palladium bonds to nitrogens of two oxazoline heterocycles in addition to two bromides with a distorted square planar geometry. The corresponding *cis*-angles are  $86.94(12)^\circ$ – $92.02(9)^\circ$  (figure 1). The Pd–N and Pd–Br bond distances (table 2) are similar to those reported for other bis(oxazoline)palladium complexes [14, 25] and dibromido(diimine)palladium(II) complexes [26, 27], respectively. Bonding to the metal ion results in tilting of the two oxazoline heterocycle planes from the benzene ring spacer. The dihedral angles between the mean planes of each of the two oxazoline heterocycles and the benzene ring spacer mean plane are  $38.0(3)^\circ$  and  $48.1(2)^\circ$ . The metal complex structure is reminiscent of a chair with the  $[\text{PdN}_2\text{Br}_2]$  moiety being the seat and the benzene ring spacer being the back of the chair (figure 1). The dihedral angle between the two moieties is  $88.1(1)^\circ$ . Despite the achirality of the ligand, this rigid chair curvature, together with the unsymmetrical substitution of the benzene spacer, generates an



Scheme 1. Synthesis of bis(oxazoline) ligands and their corresponding palladium complexes.

inherent chirality in the molecule and the complex crystallizes as racemic. We previously reported similar cases of inherent chirality in metal complexes of achiral bisoxazolines [14].

Pd-BOX-2 crystallizes in the  $P2_1/c$  space group. Similarly to Pd-BOX-1, the geometry around the palladium ion is distorted square planar with *cis*-angles of  $87.22(10)^\circ$ – $92.94(11)^\circ$  (figure 2). The Pd–N and Pd–O bond lengths are similar to those reported for bis(oxazoline)

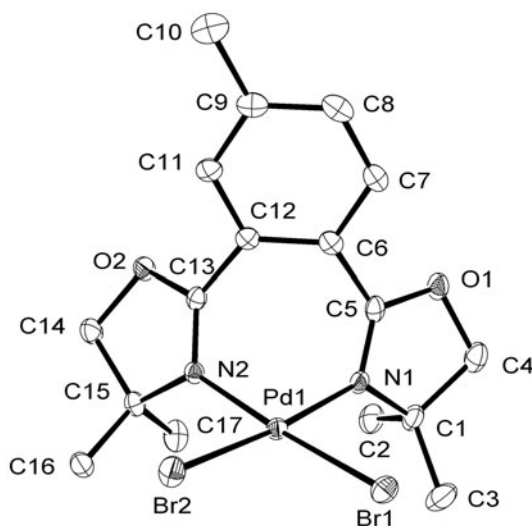


Figure 1. Molecular structure of Pd-BOX-1.



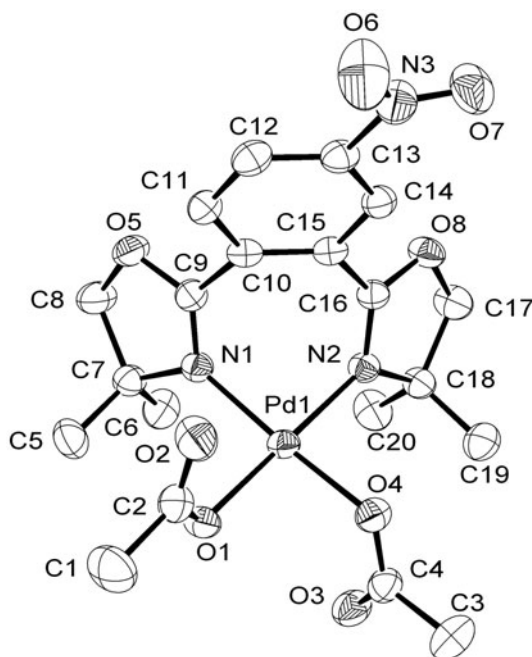


Figure 2. Molecular structure of Pd-BOX-2 (Dichloromethane has been omitted for clarity).

bis(trifluoroacetato)palladium(II) complexes [28] and the Pd–N bond lengths are significantly shorter than those of Pd-BOX-1 (table 2), likely due to the difference in  $\sigma$  and  $\pi$  donor effects of the acetate and bromide. As expected by steric effect, the two acetato acyl groups lie on opposite sides of the  $[\text{PdN}_2\text{O}_2]$  plane. The complex adopts a similar chair structure to Pd-BOX-1 with a rigid curvature inducing inherent chirality and the compound crystallizes as a racemic dichloromethane solvate.

### 3.3. Evaluation of the synthesized palladium-bis(oxazoline) complexes as catalysts in coupling reactions

We have investigated the use of Pd-BOX-1 and Pd-BOX-2 as catalysts for carbon–carbon bond formation, typically Suzuki–Miyaura [11], Mizoroki–Heck [12], and Sonogashira [13] coupling reactions in DMF–H<sub>2</sub>O and under aerobic conditions.

**3.3.1. Suzuki–Miyaura coupling reaction of phenylboronic acid and aryl halides using Pd-BOX-1 as a catalyst.** The palladium-catalyzed Suzuki–Miyaura coupling reaction of aryl boronic acids and aryl halides is a versatile method for synthesis of biaryls. We previously reported formation of biaryls at high temperature and for longer reaction time. However, we are delighted to achieve the formation of biaryls at room temperature with extremely short time using Pd-BOX-1 in aqueous organic media as a new catalytic system (table 3).

Table 3. Suzuki–Miyaura coupling reactions of 4-iodoacetophenone with phenyl boronic acid.<sup>a</sup>

Entry	Pd complex	Solvent	Base	Yield (%) <sup>b</sup>
1	Pd-BOX-1	Neat DMF	K <sub>2</sub> CO <sub>3</sub>	20
2	Pd-BOX-1	DMF–H <sub>2</sub> O (1 : 1)	K <sub>2</sub> CO <sub>3</sub>	98
3	Pd-BOX-1	Neat H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	16
4	Pd-BOX-1	Dioxane–H <sub>2</sub> O (1 : 1)	K <sub>2</sub> CO <sub>3</sub>	38
5	Pd-BOX-1	CH <sub>3</sub> CN–H <sub>2</sub> O (1 : 1)	K <sub>2</sub> CO <sub>3</sub>	28
6	Pd-BOX-1	DMF–H <sub>2</sub> O (1 : 1)	Et <sub>3</sub> N	20
7	Pd-BOX-1	DMF–H <sub>2</sub> O (1 : 1)	KOH	51
8	Pd-BOX-1	DMF–H <sub>2</sub> O (1 : 1)	KH <sub>2</sub> PO <sub>4</sub>	06
9	Pd-BOX-1	DMF–H <sub>2</sub> O (1 : 1)	K <sub>3</sub> PO <sub>4</sub>	95
10	Pd-BOX-2	DMF–H <sub>2</sub> O (1 : 1)	K <sub>2</sub> CO <sub>3</sub>	95
11	Pd-BOX-3	DMF–H <sub>2</sub> O (1 : 1)	K <sub>2</sub> CO <sub>3</sub>	98
12	Pd-BOX-4	DMF–H <sub>2</sub> O (1 : 1)	K <sub>2</sub> CO <sub>3</sub>	97
13	PdCl <sub>2</sub> -Bpy	DMF–H <sub>2</sub> O (1 : 1)	K <sub>2</sub> CO <sub>3</sub>	Traces
14	PdCl <sub>2</sub> -Phen	DMF–H <sub>2</sub> O (1 : 1)	K <sub>2</sub> CO <sub>3</sub>	40

<sup>a</sup>Reaction conditions: [Pd] (0.0020 mM), phenylboronic acid (1.5 mM), 4-iodoacetophenone (1.0 mM), base (2.0 mM), solvent (8 mL), 20 min, r.t.; <sup>b</sup>Isolated yield.

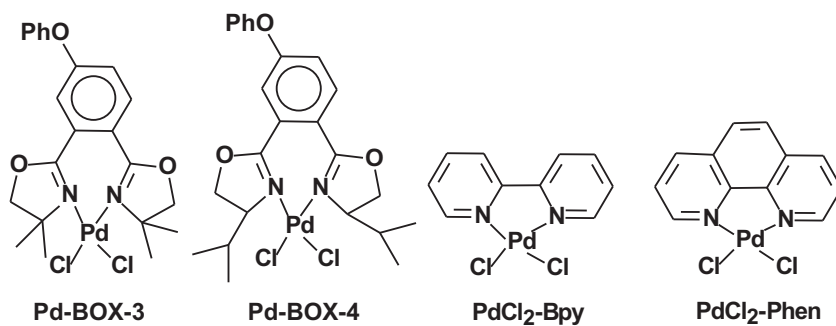
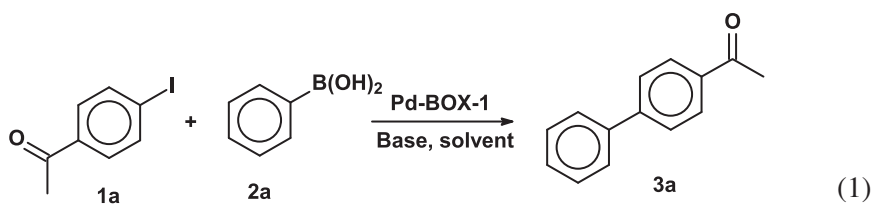


Figure 3. Palladium complexes having bidentate nitrogen donating ligands.

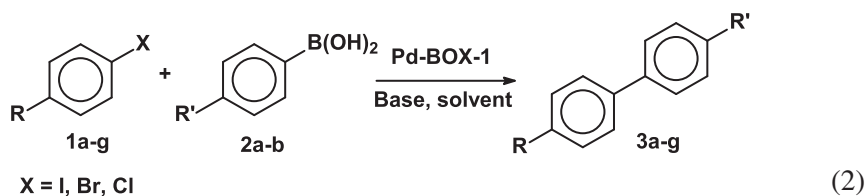
In order to determine the best conditions, a series of reactions were performed at room temperature and under aerobic conditions using 4-iodoacetophenone and phenyl boronic acid as model substrates. The effect of solvent was carefully investigated and the results are presented in table 3. Low conversion (20%) was observed when neat DMF was used as a solvent (table 3, entry 1). However, addition of water increases the yield of the coupling product. A full conversion was obtained with a ratio of 1 : 1 of DMF–water (table 3, entry 2); the reaction in neat water decreases significantly the yield of the product to 16% (table 3, entry 3). Other solvent systems such as dioxane–water and acetonitrile–water gave yields of 38 and 28%, respectively (table 3, entries 4 and 5).

We further screened various bases using the optimized solvent system. The use of triethylamine resulted in poor yield of coupling product (20%) (table 3, entry 6). However, potassium hydroxide gave moderate yield (50%) of the product (table 3, entry 7). The dibasic potassium hydrogen phosphate (table 3, entry 8) gave only traces of product, whereas excellent result (95%) was obtained with the tribasic potassium hydrogen phosphate (table 3, entry 9).

We further compare Pd-BOX-1 and Pd-BOX-2 with other palladium complexes (figure 3) [14, 19]. The palladium complexes were evaluated in the coupling reaction of 4-iodoacetophenone with phenylboronic acid, as model substrates, under the optimized reaction conditions (table 3). Pd-BOX-2, Pd-BOX-3, and Pd-BOX-4 gave isolated yields of 95, 98, and 97%, respectively (table 3, entries 10–12). Surprisingly, the reaction did not take place using PdCl<sub>2</sub>-Bpy (table 3, entry 13); however, PdCl<sub>2</sub>-Phen led to low yield of product (40%) (table 3, entry 14).

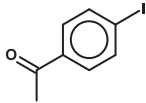
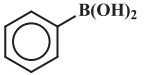
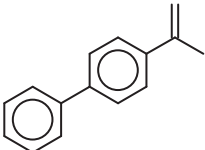
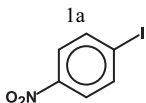
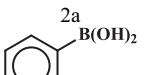
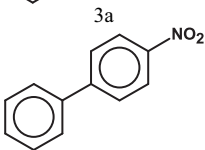
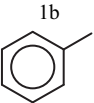
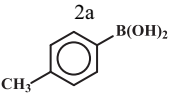
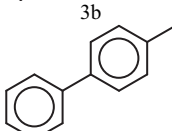
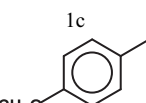
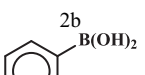
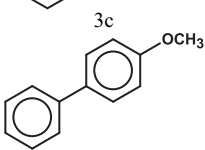
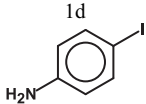
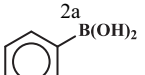
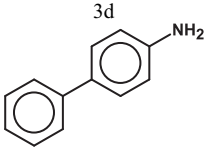
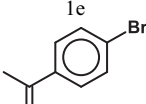
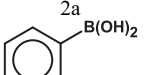
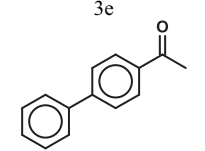
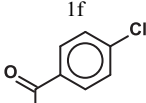
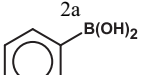
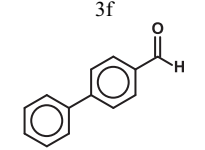
To explore the activity and versatility of the new catalysts, the optimized catalytic system was applied to various substrates. Aryl iodides having electron withdrawing groups such as COCH<sub>3</sub> and NO<sub>2</sub>, and electron donating groups such as OCH<sub>3</sub> and NH<sub>2</sub> coupled smoothly with the phenylboronic acids (table 4, entries 1–5) to give the corresponding coupling products in excellent yields (>90%). Despite the high activity of the new catalysts, the reaction rate depends on the type of substitution on the benzene ring. Aryl iodides having electron withdrawing groups (table 4, entries 1 and 2) reacted faster and full conversions were obtained within 20 min. Aryl iodides with electron donating substituents (table 4, entries 4 and 5) took 90 min to attain almost complete conversions. An aryl bromide and an aryl chloride as less activated halides were also considered in the Suzuki–Miyaura coupling reactions with phenyl boronic acid (table 4, entries 6 and 7). The reaction of the aryl bromide gave excellent yield (99%) of the coupling product but a longer reaction time (1 h) was required. The aryl chloride was less reactive at room temperature and a yield (90%) was obtained at 110 °C after 90 min of reaction.

The air- and moisture-stable Pd-BOX catalysts showed advantages in terms of the catalytic activity, the diversity of the substrates, the reaction temperature, or the reaction time as compared to catalysts based on palladium(II) complexes in the presence of phosphine ligands [5(a)–(c)] or nitrogen-based ligands [6].



(2)

Table 4. Suzuki–Miyaura coupling reactions of various aryl iodides with aryl boronic acids using Pd-BOX-1 as a catalyst.<sup>a</sup>

Entry	Iodobenzene 1a–g	Arylboronic acid 2a–b	Coupling product 3a–g	Time (min)	Yield (%) <sup>b</sup>
1				20	97
2				20	95
3				90	96
4				90	93
5				90	94
6				60	96
7 <sup>c</sup>				90	90
	1g	2a	3g		

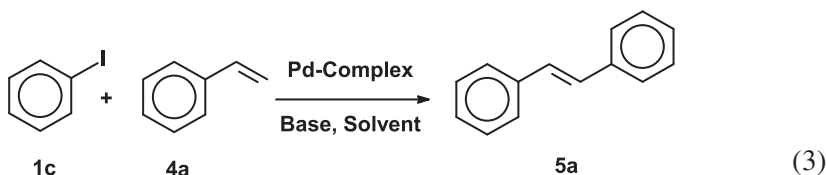
<sup>a</sup>Reaction conditions: Pd-BOX-1 (0.0020 mM), aryl boronic acid (1.5 mM), aryl halide (1.0 mM), K<sub>2</sub>CO<sub>3</sub> (2.0 mM), DMF (4.0 mL), H<sub>2</sub>O (4.0 mL), r.t.; <sup>b</sup>Isolated yield; <sup>c</sup>110 °C.

**3.3.2. Mizoroki–Heck coupling reactions of styrene derivatives with aryl iodides catalyzed by Pd-BOX-1.** The cross-coupling reactions of aryl halides with olefins, known as Mizoroki–Heck coupling, is a well-known and widely used methodology for the regioselective synthesis of various unsaturated compounds [12, 29]. The palladium bis(oxazoline) complexes were evaluated as catalysts in Mizoroki–Heck coupling reactions of styrene with different aryl iodides (equation 3). The reaction conditions were optimized as presented in table 5.

Table 5. Mizoroki–Heck coupling reactions of iodobenzene with styrene.<sup>a</sup>

Entry	Pd complex	Solvent	Base	Yield (%) <sup>b</sup>
1	Pd-BOX-1	Neat DMF	KOH	48
2	Pd-BOX-1	DMF–H <sub>2</sub> O (3 : 1)	KOH	99
3	Pd-BOX-1	Neat water	KOH	9
4	Pd-BOX-1	Dioxane–H <sub>2</sub> O (3 : 1)	KOH	20
5	Pd-BOX-1	DMF–H <sub>2</sub> O (3 : 1)	K <sub>2</sub> CO <sub>3</sub>	84
6	Pd-BOX-1	DMF–H <sub>2</sub> O (3 : 1)	Et <sub>3</sub> N	64
7	Pd-BOX-2	DMF–H <sub>2</sub> O (3 : 1)	KOH	97
8	Pd-BOX-3	DMF–H <sub>2</sub> O (3 : 1)	KOH	98
9	Pd-BOX-4	DMF–H <sub>2</sub> O (3 : 1)	KOH	96
10	PdCl <sub>2</sub> -Bpy	DMF–H <sub>2</sub> O (3 : 1 mL)	KOH	70
11	PdCl <sub>2</sub> -Phen	DMF–H <sub>2</sub> O (3 : 1)	KOH	56

<sup>a</sup>Reaction conditions: [Pd] (0.01 mM), iodobenzene (1.00 mM), styrene (1.5 mM), KOH (2.0 mM), solvent (4 mL), 90 °C, 2 h; <sup>b</sup>Isolated yield.



In the absence of water (neat DMF, table 5, entry 1), only moderate yield (50%) was achieved. However, in a mixture of DMF–water (3 : 1 mL) (table 5, entry 2), the coupling product was obtained in quantitative yield. The yield of product decreased sharply to traces in neat water (table 5, entry 3).

We have also evaluated other palladium bis(oxazoline) complexes and other commercially available palladium complexes of bidentate nitrogen donor ligands such as 2,2' bipyridine and 1,10-phenanthroline [19]. Pd-BOX-2, Pd-BOX-3, and Pd-BOX-4 yielded full conversions (entries 7, 8 and 9). PdCl<sub>2</sub>-Bpy and PdCl<sub>2</sub>-Phen gave lower isolated yields (70 and 56%, respectively) (entries 10 and 11).

The optimized catalytic system was then applied to substrates having either activating or deactivating substituents (table 6). As expected, the time required for completion of reactions depends on the type of substituent attached to the benzene ring on either the aryl halide and/or the styrene. However, some interesting results were observed (table 6, entries 2 and 3). An activating methoxy group attached to the styrene (table 6, entry 2) led to a full conversion in 1.5 h. However, when the same activating methoxy group is attached to the aryl halide (table 6, entry 3), a decrease in reaction rate was observed and full conversion was achieved in 2.5 h. Catalytic activities of the new Pd-BOX catalysts are higher in the Mizoroki–Heck coupling reactions at relatively milder conditions of temperature and reaction time as compared to palladium–phosphine [5(d) and (e)] or palladium–nitrogen catalyst

Table 6. Mizoroki–Heck coupling reactions of styrene derivatives with aryl iodides using Pd-BOX-1 as a catalyst.<sup>a</sup>

Entry	Aryl iodide 1a–d	Styrene derivative 4a–c	Coupling product 5a–e	Time (h)	Yield (%) <sup>b</sup>
1				2	99
2				1.5	95
3				2.5	94
4				2	97
5				2	96
6				1	98

<sup>a</sup>Reaction conditions: Pd-BOX-1 (0.010 mM), aryl iodide (1.0 mM), styrene derivative (1.50 mM), KOH (2.0 mM), DMF (3 mL), H<sub>2</sub>O (1 mL), 90 °C; <sup>b</sup> Isolated yield.

systems [6, 33], where higher temperatures (120–140 °C) and longer reaction times (6–24 h) are sometimes applied to obtain high yields of coupling products.

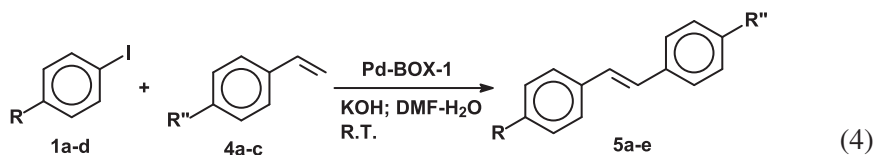


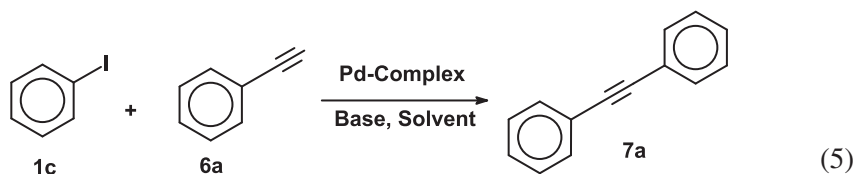
Table 7. Sonogashira coupling reaction of phenylacetylene with iodobenzene.<sup>a</sup>

Entry	Pd complex	Solvent	Base	Yield 7a (%) <sup>b</sup>
1	Pd-BOX-1	DMF	KOH	52
2	Pd-BOX-1	DMF-H <sub>2</sub> O (3 : 1)	KOH	96
3	Pd-BOX-1	Water	KOH	20
4	Pd-BOX-1	DMF-H <sub>2</sub> O (3 : 1)	NaOH	94
5	Pd-BOX-1	DMF-H <sub>2</sub> O (3 : 1)	K <sub>2</sub> CO <sub>3</sub>	82
6	Pd-BOX-1	DMF-H <sub>2</sub> O (3 : 1)	Et <sub>3</sub> N	85
7	Pd-BOX-2	DMF-H <sub>2</sub> O (3-1 mL)	KOH	93
8	Pd-BOX-3	DMF-H <sub>2</sub> O (3 : 1)	KOH	94
9	Pd-BOX-4	DMF-H <sub>2</sub> O (3 : 1)	KOH	96
10	PdCl <sub>2</sub> -Bpy	DMF-H <sub>2</sub> O (3 : 1)	KOH	86
11	PdCl <sub>2</sub> -Phen	DMF-H <sub>2</sub> O (3 : 1)	KOH	64

<sup>a</sup>Reaction conditions: [Pd] (0.010 mM), iodobenzene (1.0 mM), phenylacetylene (1.5 mM), base (2.0 mM), solvent (4 mL), 70 °C, 1 h; <sup>b</sup>Isolated yield.

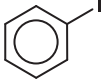
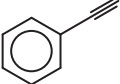
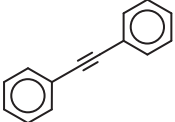
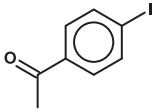
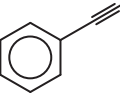
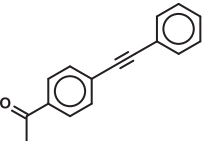
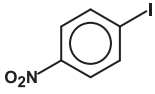
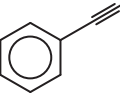
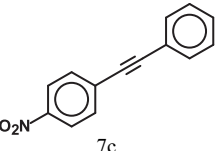
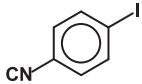
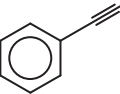
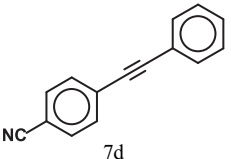
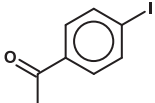
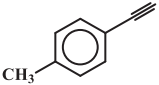
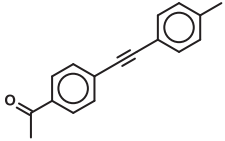
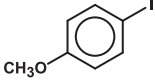
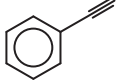
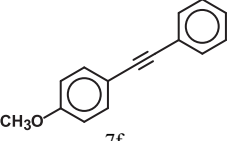
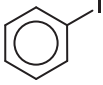
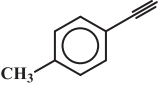
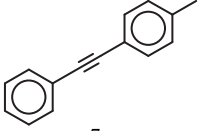
**3.3.3. Sonogashira coupling reactions of phenylacetylene with aryl iodides catalyzed by Pd-BOX-1.** An important method for the synthesis of alkyne derivatives is the Sonogashira cross-coupling reaction. Traditionally, the Sonogashira coupling reactions are catalyzed by palladium complexes in the presence of copper salt. Recently, active catalytic systems are being developed that make this reaction possible in the absence of copper [30–32]. In our research, the new Pd bis(oxazolines) complexes were also applied to copper-free Sonogashira coupling of aryl iodides with terminal alkynes in aqueous DMF and under aerobic conditions. The reaction conditions were also optimized and the results are summarized in table 7. Similar to the Heck reaction, the best solvent system was DMF-H<sub>2</sub>O (3 : 1 mL) (table 7, entry 2), and KOH was the most suitable base for the Sonogashira coupling reaction.

We have further evaluated the ligand effect by considering additional palladium-BOX complexes such as Pd-BOX-2, Pd-BOX-3, and Pd-BOX-4 [14], and two commercially available palladium complexes, PdCl<sub>2</sub>-Bpy and PdCl<sub>2</sub>-Phen. The palladium-BOX complexes synthesized in our laboratories (Pd-BOX-1, Pd-BOX-2, Pd-BOX-3, and Pd-BOX-4) were better than the commercially available palladium complexes (PdCl<sub>2</sub>-Bpy and PdCl<sub>2</sub>-Phen) (table 7, entries 6–11).



The excellent results encouraged us to extend our studies to a range of activated and deactivated substrates. The results are summarized in table 8. Most of the substrates studied

Table 8. Sonogashira coupling reactions of different aryl iodides with aryl alkynes.<sup>a</sup>

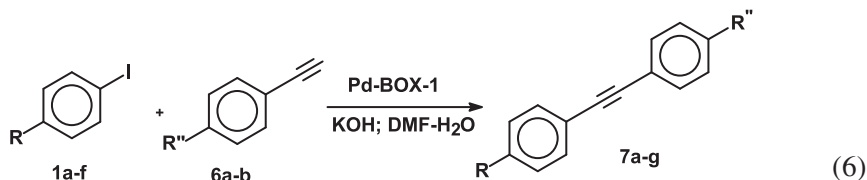
Entry	Aryl iodide 1a-f	Aryl alkyne 6a-b	Coupling product 7a-g	Time (h)	Yield 7a-g (%) <sup>b</sup>
1				2	94
	1c	6a	7a		
2				1	98
	1a	6a	7b		
3				1	96
	1b	6a	7c		
4				1	97
	1f	6a	7d		
5				1	99
	1a	6b	7e		
6				3	91
	1d	6a	7f		
7				2	93
	1c	6b	7g		

<sup>a</sup>Reaction conditions: Pd-BOX-1 (0.010 mM), aryl halide (1.0 mM), alkyne (1.5 mM), KOH (2.0 mM), DMF (3 mL), H<sub>2</sub>O (1 mL), 70 °C; <sup>b</sup>Isolated yield.

yielded excellent results. The reaction time depends on the type of substituent attached to the aryl iodide.



Again, Pd-BOX catalyst showed high catalytic activity in Sonogashira cross-coupling reactions at lower temperature (70 °C) and shorter reaction time (1–3 h) compared to reported palladium catalyst systems [5].



#### 4. Conclusion

The synthesis, characterization, crystal structure, and catalytic activities of new palladium-bis(oxazoline) complexes (Pd-BOX) have been described. The X-ray crystal structure reveals a square planar geometry and an inherent chirality in both new complexes. Highly active catalytic systems based on the new Pd-BOX complexes have been developed for Suzuki–Miyaura, Mizoroki–Heck, and copper-free Sonogashira coupling reactions in aqueous DMF and under aerobic conditions. Excellent catalytic activities were observed with Pd-BOX as compared to previously reported palladium–phosphine and palladium–dinitrogen catalysts applied for the same coupling reactions. In addition, the fact that Pd-BOX complexes are more active catalysts than other palladium(II)–dinitrogen complexes was confirmed from the results obtained with other palladium complexes having bidentate nitrogen donor ligands, such as PdCl<sub>2</sub>-Bpy and PdCl<sub>2</sub>-Phen, in the same catalytic coupling reactions. Almost complete conversions were observed with all palladium-bis(oxazoline) complexes. The observed increase in rate of the coupling reactions due to addition of water could be attributed to the possible formation of hydroxypalladium complexes [PdL<sub>2</sub>(OH)<sub>2</sub>], which are known to possess higher catalytic activity than their corresponding halopalladium complexes [6].

#### Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 902796 and 929605 for **1** and **2**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or <http://www.ccdc.cam.ac.uk>).

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