



cis-Fashioned palladium (II) complexes of 2-phenylbenzimidazole ligands: Synthesis, characterization, and catalytic behavior towards Suzuki–Miyaura reaction

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ABSTRACT

Reaction of 2-arylbenzimidazole with $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ in CH_2Cl_2 affords benzimidazole palladium (II) complexes in high yields. The structure of complexes **C1**, **C2**, and **C3** has been confirmed by X-ray structure analysis. The configuration of complexes depends on the substituent on the 2-position of benzimidazole. Phenyl affords the complexes in *cis*-fashion due to π – π stacking of phenyl and benzimidazole. Tolylyl affords the complex in *trans*-fashion. The catalytic studies show that *cis*-configured 2-phenylbenzimidazole palladium (II) complexes are highly efficient catalysts in the Suzuki–Miyaura reaction.

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1. Introduction

Palladium-catalyzed cross-coupling reaction between aryl halides or triflates and organometallic reagents (Sn, Mg, B, Li, Zn, etc.) has been developed as a versatile and efficient method for a variety of synthetic transformations [1,2]. Among these reactions, the Suzuki–Miyaura reaction represents one of the most powerful methods for the construction of diversified biaryls, and they have a myriad of applications in pharmaceutical, material, and agricultural chemistry [3,4]. Consequently, the development of a new type palladium catalyst is vital. It has been recognized that the ligand with appropriate steric/electronic natures has a significant impact on the outcome of the reactions. In the past decades, phosphine ligands based palladium catalysts were extensively used due to their extreme donor ability. Despite their toxicity, Pd(II) catalysts with phosphine ligands have shown very high TONs [5]. Recently, Pd(II) catalysts with diversified N-donor ligands became attractive for catalytic application, because these ligands possess the low toxicity and are easy to handle [6,7]. Although a variety of ligands have been introduced, an important factor that imparts a high catalytic performance is the π -systems of the aromatic groups on the ligands which interact with the Pd center. These factors may orient the structure and activity of the catalyst. Herein, we report synthesis, characterization, and catalytic application of

cis-fashioned palladium (II) complexes with 2-phenylbenzimidazole ligands. This diversified ligand scaffold offers remarkable tunability in steric/electronic natures and configuration.

2. Results and discussion

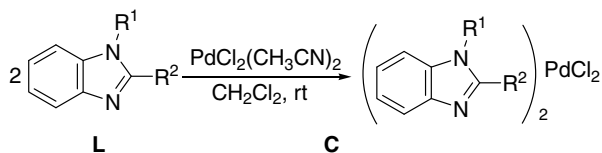
2.1. Synthesis of complexes

All the 2-substituted benzimidazole ligands were prepared according to the literature method [8]. Palladium (II) dichloride complexes **C1–C3** were obtained by the reaction of the corresponding ligands with $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ in dichloromethane at room temperature (Scheme 1). All complexes tended to precipitate from the reaction solution, and optimized yields were obtained by adding excessive amount of Et_2O in the reaction solution. The complexes **C1–C3** are pale yellow solids. These complexes are thermally stable. When the complexes **C1**, **C2**, and **C3**, were refluxed in DMSO for 1 h, respectively, the same NMR spectra were observed. In addition, they are remarkably stable towards moisture and air.

2.2. Structural features

The single crystals of complexes **C1**, **C2**, and **C3** suitable for X-ray crystallography were grown by diffusing Et_2O into the toluene for complex **C1**, dichloromethane for complex **C2**, and 1-methyl-2-pyrrolidinone (NMP) for complex **C3**, respectively. Crystallographic

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- C1.** R¹ = Me, R² = Ph, Yield: 97%
C2. R¹ = *i*-Pr, R² = Ph, Yield: 76%
C3. R¹ = Me, R² = *m*-Toly, Yield: 90%

Scheme 1.

data and refinement residuals are summarized in Table 1. The ORTEP diagrams of the complexes are presented in Figs. 1–3 with their corresponding bond lengths and angles in the coordination palladium frame. As shown in Figs. 1 and 2, the palladium atom is coordinated by two benzimidazole molecules *via* their nitrogen atoms and two chloride atoms in a square-planar fashion. The two 2-phenylbenzimidazoles are arranged in *cis* to each other with an angle of 90.10(2)° for complex **C1** and 90.23(1)° for complex **C2**, respectively. It appears that the complex contains an intramolecular π – π interactions between benzene ring and benzimidazole (centroid to face distance 3.355 Å and 3.284 Å for complex **C1** and 3.430 Å and 3.232 Å for complex **C2**, respectively) (Figs. 1C1–b

Table 1
Selected X-ray data for complexes **C1**, **C2**, and **C3**.

Empirical formula	C1	C2	C3
	C ₂₈ H ₂₄ Cl ₂ N ₄ Pd · C ₇ H ₈	C ₃₂ H ₃₂ Cl ₂ N ₄ Pd · 2CH ₂ Cl ₂	C ₃₀ H ₂₈ Cl ₂ N ₄ Pd · 2C ₅ H ₆ NO
Formula weight	685.97	819.77	820.13
Crystal color	Yellow	Yellow	Yellow
Temperature (K)	293(2)	293(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P2</i> ₁ / <i>c</i>	<i>Cc</i>	<i>P</i> -1
<i>a</i> (Å)	16.418(3)	11.005(2)	9.4704(2)
<i>b</i> (Å)	12.096(2)	16.632(3)	9.6986(2)
<i>c</i> (Å)	15.922(3)	20.470(4)	10.946(2)
α (°)	90	90	101.45(3)
β (°)	90.78(3)	99.25(3)	105.01(3)
γ (°)	90	90	92.41(3)
Volume (Å ³)	3161.7(1)	3697.7(1)	947.1(3)
<i>Z</i>	4	4	1
<i>D</i> _{calc} (g cm ⁻³)	1.441	1.473	1.438
μ (mm ⁻¹)	0.787	0.965	0.674
<i>F</i> (000)	1400	1664	424
Crystal size (mm)	0.31 × 0.25 × 0.18	0.35 × 0.24 × 0.19	0.26 × 0.18 × 0.16
θ Range (°)	1.24–27.48	2.02–27.39	1.97–27.33
Limiting indices	–21 ≤ <i>h</i> ≤ 21, –15 ≤ <i>k</i> ≤ 15, –20 ≤ <i>l</i> ≤ 20	–14 ≤ <i>h</i> ≤ 14, –21 ≤ <i>k</i> ≤ 21, –26 ≤ <i>l</i> ≤ 26	–11 ≤ <i>h</i> ≤ 12, –12 ≤ <i>k</i> ≤ 12, –14 ≤ <i>l</i> ≤ 14
Reflections collected	12945	12030	7725
Unique reflections	7251	7804	4251
Completeness to θ (%)	100.0 (θ = 27.48)	99.1 (θ = 27.39)	99.6 (θ = 27.33)
Absorption correction	None	None	None
Number of parameters	349	406	232
Goodness-of-fit on <i>F</i> ²	1.138	1.085	1.173
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0681, <i>wR</i> ₂ = 0.1564	<i>R</i> ₁ = 0.0536, <i>wR</i> ₂ = 0.1366	<i>R</i> ₁ = 0.0495, <i>wR</i> ₂ = 0.1273
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1054, <i>wR</i> ₂ = 0.1762	<i>R</i> ₁ = 0.0583, <i>wR</i> ₂ = 0.1404	<i>R</i> ₁ = 0.0539, <i>wR</i> ₂ = 0.1336
Largest differences in peak and hole (e Å ⁻³)	1.563 and –0.759	1.102 and –0.510	1.654 and –0.795

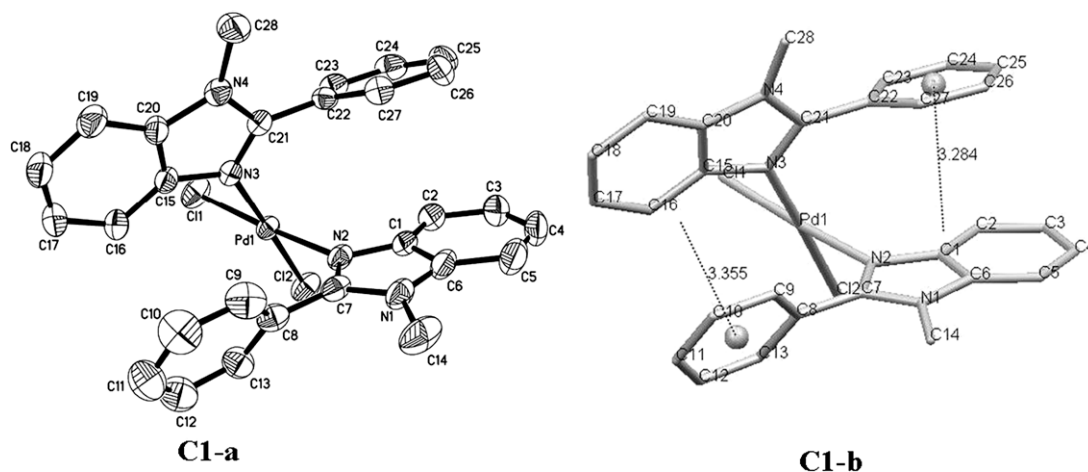


Fig. 1. Molecular structure of **C1**. **C1-a**: Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent have been omitted for clarity. Selected bond lengths (Å) and angles (°) are Pd1–N3, 2.020(4); Pd1–N2, 2.027(4); Pd1–Cl1, 2.2832(2); Pd1–Cl2, 2.2918(2); N3–Pd1–N2, 90.10(2); N3–Pd1–Cl1, 88.91(1); N2–Pd1–Cl1, 176.84(1); N3–Pd1–Cl2, 178.31(1); N2–Pd1–Cl2, 88.99(1); Cl1–Pd1–Cl2, 92.07(6). **C1-b**: Two pairs of intra-molecular π – π interactions.

and **2C2-b**). The distances between the arene planes are taken as the criterion to suggest π -stacking and these lie between 3.3 and 3.8 Å [9]. The dihedral angles of the benzene ring and the benzimidazole is 14.5° and 11.8° for complex **C1** and 19.6° and 15.8° for complex **C2**, respectively. This type of interaction leads to two 2-phenylbenzimidazoles in *cis*-fashion. When tolyl was introduced into 2-position of benzimidazole, as shown in Fig 3, the palladium atom is also coordinated by two 2-tolylbenzimidazoles *via* their nitrogen atoms and two chloride atoms. However, the two 2-tolylbenzimidazoles are arranged *trans* to each other with an angle of 180.0°, which is different from complexes **C1**–**C2**. These results may be attributed to the effect of substituent on the phenyl.

2.3. Suzuki–Miyaura reaction

The complexes **C1**–**C3** have been tested as catalysts in the model Suzuki–Miyaura reaction of 1-bromo-4-methoxybenzene with phenylboronic acid to ascertain the optimum condition (Table 2). Although the catalysts **C1**–**C3** were all effective for the Suzuki–Miyaura reaction, the use of **C1** as a catalyst led to higher yield for this reaction (entry 1). In general, the difference in reactivity of these palladium complexes can be attributed to the effect of the substituent on 2-position of benzimidazoles. With phenyl on the benzimidazole, the catalysts gave higher yields. With tolyl on the benzimidazole, the catalyst gave moderate yield. With methyl on the nitrogen of benzimidazole ring, the catalysts showed higher yield. Reducing the catalyst loading to 0.01 mol% or mixture of the $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ and ligand **L1** also afforded high yields, respectively (entries 4–5).

Since the proper combination of base and solvent is extremely important, we have examined several different bases and solvents for the Suzuki–Miyaura reaction (Table 3). Initially many commonly available bases were used with toluene as solvent. K_2CO_3 , Cs_2CO_3 , KOH, and $\text{K}_3\text{PO}_4 \cdot 7\text{H}_2\text{O}$ as a base produced higher yields (entries 1–4), respectively. The use of NaOAc, NEt_3 , and pyridine as bases gave inferior results (entries 5–7), respectively. In the reaction, several commonly used solvents were also tested. Solvents, such as *N,N'*-dimethylformamide (DMF) and THF were not effective (entries 8–9) for this reaction. NMP was less effective (entry 10). Therefore, we found the optimized conditions as follow:

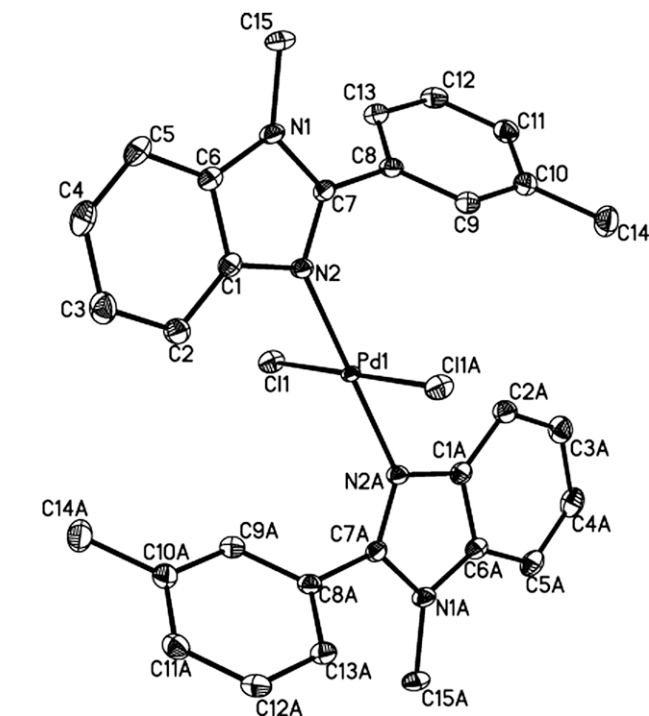


Fig. 3. Molecular structure of complex **C3**. Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent have been omitted for clarity. Selected bond lengths (Å) and angles (°) are Pd1–N2, 2.011(3); Pd1–N2A, 2.011(3); Pd1–Cl1, 2.3032(1); Pd1–Cl1A, 2.3032(1); N2A–Pd1–N2, 180.000(1); N2A–Pd1–Cl1A, 89.04(9); N2–Pd1–Cl1A, 90.96(9); N2A–Pd1–Cl1, 90.96(9); N2–Pd1–Cl1, 89.04(9); Cl1A–Pd1–Cl1, 180.00(3).

using the complex **C1**, the reaction proceeded with 99% yield in toluene with K_2CO_3 at 100 °C for 1 h.

In order to gauge the further potential of **C1** towards the Suzuki–Miyaura coupling methodology, we choose substituted aryl bromides, as shown in Table 4, for the reaction with phenylboronic acid. The results show that both activated and deactivated aryl bromides are efficiently converted to biaryl (entries 1–5). Aryl chlorides substrates were also examined. Using K_2CO_3 as a base, toluene as a solvent and 0.1 mol% of the catalyst, the reaction of

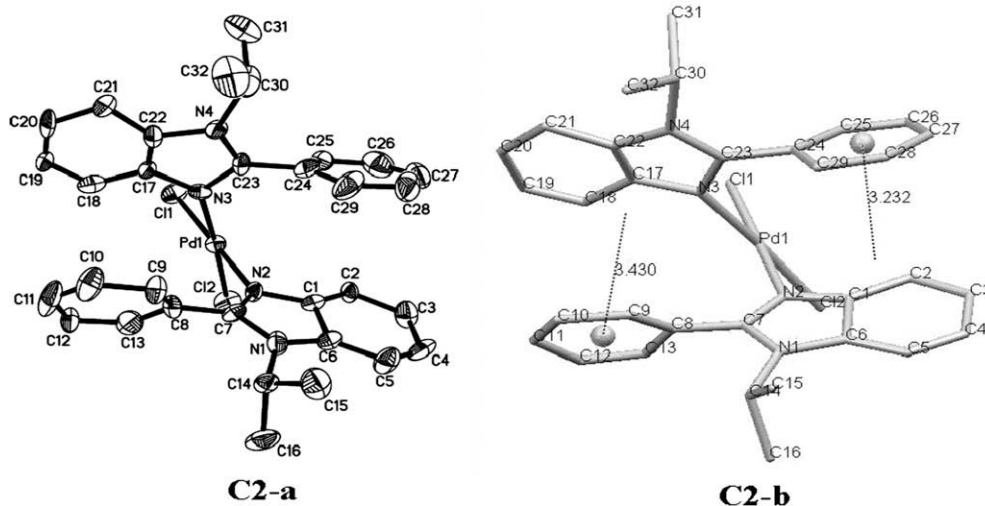
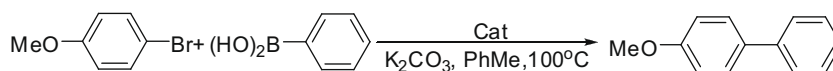


Fig. 2. Molecular structure of **C2**. **C2-a**: Thermal ellipsoids are shown at 30% probability; hydrogen atoms and solvent have been omitted for clarity. Selected bond lengths (Å) and angles (°) are Pd1–N2, 1.997(8); Pd1–N3, 2.057(6); Pd1–Cl1, 2.296(2); Pd1–Cl2, 2.302(3); N2–Pd1–N3, 90.23(1); N2–Pd1–Cl1, 179.3(2); N3–Pd1–Cl1, 89.2(2); N2–Pd1–Cl2, 88.7(2); N3–Pd1–Cl2, 176.2(2); Cl1–Pd1–Cl2, 91.87(5). **C2-b**: Two pairs of intra-molecular π – π interactions.

Table 2
2-Substituted benzimidazole-palladium catalyst for Suzuki–Miyaura reaction.^a



Entry	Cat	mol % cat	Time (h)	Yield (%)
1	C1	0.1	1	99
2	C2	0.1	1	93
3	C3	0.1	1	57
4	C1	0.01	24	82
5	Pd + L1	0.1 ^b	1	81

^a Reaction conditions: 4-bromoanisole (0.5 mmol), benzeneboronic acid (0.6 mmol), K₂CO₃ (1 mmol), PhMe (2.5 mL), catalyst was dissolved in NMP.

^b 0.1 mol% (CH₃CN)₂PdCl₂ + 0.2 mol% **L1**.

Table 3
Effect of base and solvent on the Suzuki–Miyaura reaction of 4-bromoanisole with benzeneboronic acid and **C1**.^a

Entry	Base	Solvent	Temperature (°C)	Yield (%) ^b
1	K ₂ CO ₃	PhMe	100	99(95)
2	Cs ₂ CO ₃	PhMe	100	99
3	KOH	PhMe	100	97
4	K ₃ PO ₄ · 7H ₂ O	PhMe	100	96
5	NaOAc	PhMe	100	Trace
6	NEt ₃	PhMe	100	Trace
7	Pyridine	PhMe	100	Trace
8	K ₂ CO ₃	THF	65	Trace
9	K ₂ CO ₃	DMF	110	6
10	K ₂ CO ₃	NMP	140	33

^a Reaction conditions: 4-bromoanisole (0.5 mmol), benzeneboronic acid (0.6 mmol), base (1 mmol), solvent (2.5 mL), catalyst was dissolved in NMP.

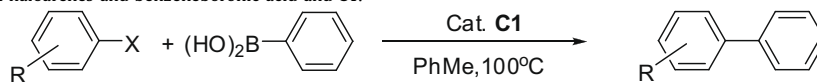
^b NMR yield, isolated yield was given in parentheses.

ArCl with PhB(OH)₂ gave inferior yields after 24 h (entry 6). The change of bases and catalyst loading, activated aryl chlorides (entries 7–9) gave 27%, 32%, and 60% yield, respectively, under the similar reaction conditions.

3. Conclusion

A series of palladium complexes containing 2-arylbenzimidazole ligands have been synthesized and characterized along with their single-crystal X-ray analysis. With phenyl on 2-position of benzimidazole, the palladium atom is coordinated by two benzimidazoles *via* their nitrogen atoms and two chloride atoms in *cis*-fashion. With tolyl on 2-position of benzimidazole, the complexes are in *trans*-fashion. The *cis*-fashion catalyst show highly catalytic activity for Suzuki–Miyaura reaction. The further study of supra-molecular approach to chelate ligands is in progress.

Table 4
Suzuki–Miyaura reactions between haloarenes and benzeneboronic acid and **C1**.^a



Entry	R	X	Base	mol% Cat. C1	Time (h)	Yield (%) ^b
1	<i>p</i> -Me	Br	K ₂ CO ₃	0.1	1	96(93)
2	<i>o</i> -Me	Br	K ₂ CO ₃	0.1	1	97(95)
3	H	Br	K ₂ CO ₃	0.1	1	98(96)
4	<i>p</i> -CHO	Br	K ₂ CO ₃	0.1	1	99(94)
5	<i>p</i> -Ac	Br	K ₂ CO ₃	0.1	1	99(95)
6	<i>p</i> -CHO	Cl	K ₂ CO ₃	0.1	24	Trace
8	<i>p</i> -CHO	Cl	Cs ₂ CO ₃	0.5	24	27
9	<i>p</i> -Ac	Cl	Cs ₂ CO ₃	0.5	24	32
10	<i>p</i> -NO ₂	Cl	Cs ₂ CO ₃	0.5	24	60(37)

^a Reaction conditions: haloarenes (0.5 mmol), benzeneboronic acid (0.6 mmol), base (1.0 mmol), PhMe (2.5 mL), the catalyst **C1** was dissolved in NMP.

^b NMR Yield or GC Yield, isolated yields are given in parentheses.

4. Experimental section

4.1. General

All manipulations were conducted in Schlenk tube and carried out in the air unless especially indicated. GC analyses were performed on a gas chromatograph equipped with a flame ionization detector using a capillary column (CBP1-M25-025). The NMR yields were determined using mesitylene as an internal standard. Unless otherwise noted, all starting materials were commercially available and were used without further purification. ¹H NMR and ¹³C NMR spectra were recorded on JOEL 300 NMR spectrometer with TMS as internal standard. Elemental analyses were performed on a Flash EA 1112 instrument. The IR spectra were obtained on a Perkin–Elmer FT-IR 2000 spectrophotometer by using the KBr disc in the range of 4000–400 cm⁻¹.

4.2. General procedure for the synthesis of palladium complexes **C1–C3**

All the benzimidazole ligands were synthesized according to the literature method [6]. Herein, only the synthesis of 1-isopropyl-2-phenylbenzimidazole is described as an example in detail. 276 mg (2 mmol) K₂CO₃ was added to a solution of 194 mg (1 mmol) 2-phenylbenzimidazole in 20 mL CH₃CN. Heated to 80 °C, the mixture was stirring for half an hour. Then the mixture was cooled to room temperature and 150 μL (1.5 mmol) isopropyl iodide was added dropwise in 3 min. After that, the mixture reacted overnight in the oil bath with a temperature of 50 °C. The brown solution was distilled under reduced pressure to about 2 mL and then diluted with 20 mL water and extracted with dichloromethane (3 × 10 mL). The combined extracts were dried over MgSO₄. The crude product was purified on silicon gel column chromatography using petroleum ether/ethyl acetate/Et₃N mixture

(15/1/1) and 1-isopropyl-2-phenylbenzimidazole **L2** was obtained in 44% yield (104 mg). White solid, m.p. 147–149 °C. ¹H NMR (300 MHz, CDCl₃, Me₄Si) δ 7.83 (m, 1H), 7.64 (m, 3H), 7.51 (m, 3H), 7.27 (m, 2H), 4.82 (sep, ³J_{HH} = 6.9 Hz, 1H), 1.65 (d, ³J_{HH} = 6.9 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 153.7, 143.9, 133.6, 131.2, 129.7, 129.6, 128.7, 122.3, 122.1, 120.4, 112.4, 48.9, 21.5. IR (KBr; cm⁻¹): 3064, 3031, 2979, 2934, 1776, 1678, 1612, 1601, 1523, 1453, 1377, 1282, 1134, 1102, 1018, 904, 850, 827, 779, 750, 703, 631.

All benzimidazole-coordinated palladium complexes were prepared in the similar method of our reported article [8e]. The synthesis of complex **C1** is described as an example here. To ligand **L1** (45.6 mg, 0.22 mmol) and PdCl₂(CH₃CN)₂ (25.9 mg, 0.1 mmol) was added 2 mL dichloromethane at room temperature and stirred overnight. Then 15 mL diethyl ether was added to precipitate the complex completely. Pale yellow powder **C1** was obtained in 97% isolated yield. ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.26 (m, 1H), 8.20 (m, 1H), 7.91–7.22 (m, 16H), 3.89 (s, 6H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 155.3, 148.5, 139.4, 131.7, 130.4, 129.3, 128.8, 124.2, 122.3, 118.9, 110.6, 31.7. IR (KBr; cm⁻¹): 3053, 3029, 2940, s1669, 1611, 1532, 1478, 1448, 1401, 1335, 1106, 927, 825, 780, 740, 697. Elem. Anal. Calc. for C₂₈H₂₄Cl₂N₄Pd · 2/3CH₂Cl₂: C, 52.93; H, 3.93; N, 8.61. Found: C, 52.60; H, 3.97; N, 8.35%.

4.2.1. Complex **C2**

Yellow powder in 76% isolated yield. ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.22–7.98 (m, 18H), 4.69 (sep, ³J_{HH} = 7.5 Hz, 2H), 1.59 (d, ³J_{HH} = 6.9 Hz, 12H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 156.1, 144.5, 139.5, 133.2, 129.4, 128.9, 128.6, 112.1, 121.6, 119.5, 112.7, 48.5, 20.9. IR (KBr; cm⁻¹): 3059, 2977, 2932, 2875, 1613, 1581, 1528, 1458, 1412, 1294, 1190, 1133, 1108, 1022, 915, 885, 831, 741, 683. Elem. Anal. Calc. for C₃₂H₃₂Cl₂N₄Pd · 1/4CH₂Cl₂: C, 57.71; H, 4.88; N, 8.35. Found: C, 57.92; H, 4.84; N, 8.39%.

4.2.2. Complex **C3**

Pale yellow powder in 90% isolated yield. ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.26 (m, 2H), 8.06 (m, 2H), 7.80–7.22 (m, 10H), 7.08–6.97 (m, 2H), 3.59 (s, 6H), 2.43(s, 6H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 153.1, 142.1, 138.7, 136.5, 130.4, 130.3, 129.9, 128.6, 126.4, 123.8, 122.4, 118.8, 110.7, 30.7, 21.1. IR (KBr; cm⁻¹): 3029, 2864, 1610, 1590, 1483, 1463, 1392, 1335, 1256, 1099, 919, 799, 744, 696. Elem. Anal. Calc. for C₃₀H₂₈Cl₂N₄Pd · 1/4H₂O: C, 56.49; H, 4.47; N, 8.71. Found: C, 56.17; H, 4.47; N, 8.71%.

4.3. X-ray crystallographic studies

Single-crystal X-ray diffraction studies for **C1**, **C2**, and **C3** were carried out on a Bruker SMART 1000 CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on *F*². All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package [10].

4.4. General procedure for Suzuki–Miyaura reaction

Aryl halide or substituted aryl halide (0.5 mmol), Benzeneboronic acid (0.6 mmol), base (1.0 mmol), catalyst in NMP and solvent (2.5 mL) were added to the Schlenk tube and stirred. After the reaction was completed, the mixture was diluted with 3–5 mL water, and extracted with ethyl ether (3 × 3 mL). The solvents were removed under reduced pressure. The crude product was

purified on silicon gel column chromatography using petroleum ether–ethyl acetate mixture and then detected by NMR, GC or TLC. Solids of the catalysts **C** are quite soluble in NMP. To get in quantity for the reaction, the catalyst was prepared in 100 mmol/L NMP solution.

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Appendix A. Supplementary material

CCDC 703079, 703080 and 703081 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. Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.042.

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