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Highly active Pd(II) catalysts with pyridylbenzoimidazole ligands for the Heck reaction

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Abstract

The air-, and thermo-stable palladium(II) complexes **C1**–**C10** are prepared by the reaction of $PdCl_2(CH_3CN)_2$ with pyridylbenzoimidazole. With various substituents on the pyridine ring, palladium atom was coordinated by two pyridylbenzoimidazole molecules *via* nitrogen atoms of benzoimidazole. The structure of complexes **C3**, **C4**, **C6**, and **C7** has been confirmed by X-ray diffraction analysis. Without substituents on the pyridine ring, palladium atom was directly coordinated with two nitrogen atoms of pyridine and benzoimidazole nitrogen *via* intramolecular chelation (**C10**). These complexes performed the Heck olefination of aryl bromides in a good to high yield under phosphine-free conditions.

Keywords: Heck reaction; Palladium; Pyridylbenzoimidazole; Catalysis

1. Introduction

Palladium-catalyzed olefination of aryl halides, known as the Heck reaction, have become one of the most powerful methods for carbon–carbon bond formation in organic synthesis [1,2]. The reactions are commonly carried out in the presence of phosphine ligands such as the reported works by the groups of Fu [3], Beller [4], and Hartwig [5] who have made use of sterically demanded electron-rich tertiary phosphines as catalyst modifiers as well as palladacycle formed by the reaction of $Pd(OAc)_2$ and tris(*o*-tolyl)-phosphine [6]. Considering the negative environmental effect, air-sensitivity, and cost of phosphine ligands, the development of phosphine-free catalysts for Heck reaction would be an important subject regarding academic and industrial application. Recently, some achievements have appeared in literature [7]. Among them, the low toxicity and stability of nitrogen-based ligands such as diimine [8], dipyridine [9], hydrazone [10] and imidazole [11] have attracted the interests of synthetic organic chemists. As examples, Hayashi et al. have reported the palladium-catalyzed Heck reaction that involved the simple catalytic system of $PdCl_2$-imidazole [11]. Mino et al. have reported the catalytic behavior of Pd(II) complexes that featured hydrazone on the Heck reaction [10]. Recently, we reported 2-iminopyridylpalladium dichloride as a highly active catalyst for the Heck reaction [12]. In this paper, we would like to report the synthesis of palladium(II) complexes from pyridylbenzoimidazole derivatives and their catalytic activity for the Heck olefination of aryl bromides. The resulting palladium(II) complexes are not only readily available, and inexpensive, but also the pyridylbenzoimidazole moiety allows the facile introduction of various substituents into the benzimidazole framework and pyridine framework.

2. Results and discussion

2.1. Synthesis and spectroscopic characterization

All the pyridylbenzoimidazole ligands were prepared according to the literature method [13–15]. Palladium(II)

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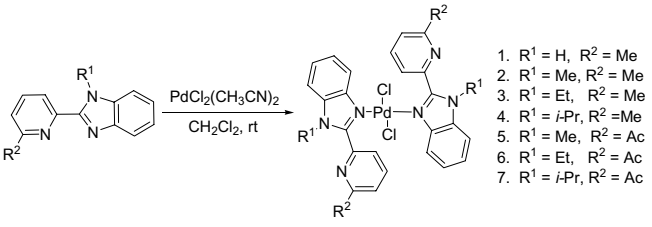
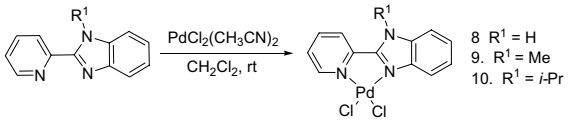
dichloride complexes **C1**–**C7** were obtained by the reaction of the corresponding ligands with $PdCl_2(CH_3CN)_2$ in dichloromethane at room temperature (Scheme 1). All complexes tended to precipitate from the reaction solution, and optimized yields were obtained by adding excessive amount of Et_2O in the reaction solution. The complexes **C1**–**C7** are pale yellow solids. Comparing their IR spectra, we noted that the palladium complexes **C1**–**C7** showed the suitable absorptions in the pyridine range, for example, 1594 cm^{-1} for **C2**, 1593 cm^{-1} for **C4**, 1586 cm^{-1} for **C7**, which are similar to **L2**, **L4**, **L7**, respectively. That means the pyridine did not have interaction with palladium. On the other hand, reaction of $PdCl_2(CH_3CN)_2$ with ligands **L8**–**L10** gave complexes **C8**–**C10** (Scheme 2), which are orange solids [16]. Comparing their IR spectra, we noted that the complexes **C8**–**C10** did not show the suitable absorptions in the pyridine range, such as 1604 cm^{-1} for **C10**. This observation is attributed to the infrared inactive pyridine vibration in the palladium complexes **C8**–**C10** [12,17]. Moreover, the shifts of the ^1H NMR peaks of the palladium complex **C10** tended to low field, which provided additional evidences for the existence of strong coordination of pyridine nitrogen and benzimidazole nitrogen to the palladium center. It is noteworthy that the reaction of **L4** with $PdCl_2(CH_3CN)_2$ was treated in the 1:1 ratio and **C4** was obtained in 41% isolated yield, while the reaction of **L10** with $PdCl_2(CH_3CN)_2$ was treated in 2:1 ratio, about 50% of the starting **L10** remained unreacted. These results further indicated that effect of substitutent on the pyridine led to formation of different type complexes. In addition, these complexes are thermally stable. When the complexes, such as **C4** and **C10**, were refluxed in DMSO for 1 h, respectively, the same NMR spectra were observed.

2.2. Structural features

The single crystals of complexes **C3**, **C4**, **C6**, **C7**, and **C10** suitable for X-ray crystallography were grown by diffusing Et_2O into the DMF solution. The ORTEP diagrams of the complexes are presented in Figs. 1–4 and their



Scheme 1.



Scheme 2.

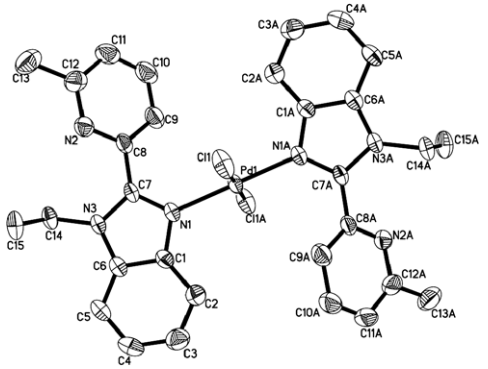


Fig. 1. Molecular structure of complex **3**. Thermalellipsoids are shown at 30% probability. Hydrogen atoms and solvent molecules have been omitted for clarity.

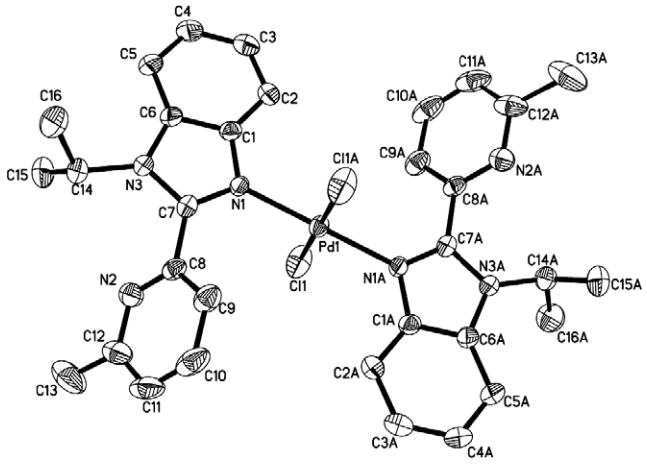


Fig. 2. Molecular structure of complex **4**. Thermalellipsoids are shown at 30% probability. Hydrogen atoms and solvent molecules have been omitted for clarity.

corresponding bond lengths and angles in the coordination palladium frame are shown in Table 1. As shown in Figs. 1–4, the palladium atom is coordinated by two benzimidazole molecules *via* their nitrogen atoms and two chloride atoms. The ORTEP diagrams of the complex **C10** is presented in Fig. 5 and its corresponding bond lengths and angles in the coordination palladium frame were shown in Table 2. The palladium atom was coordinated by pyridine nitrogen and benzimidazole nitrogen *via* chelation, which was different from complexes **C1**–**C7**. This result may be attributed to effect of substitutent on the pyridine.

2.3. Heck reaction

The complexes **C1**–**C10** have been tested as catalysts in the model Heck reaction of bromobenzene with *n*-butyl acrylate under nitrogen atmosphere to ascertain the most optimum conditions (Table 3). Although the catalysts **C1**–**C10** were all effective for the Heck reaction, the use of **C4** as catalyst led to higher yield for this reaction (entry 4). In general, the difference in reactivity of these palladium

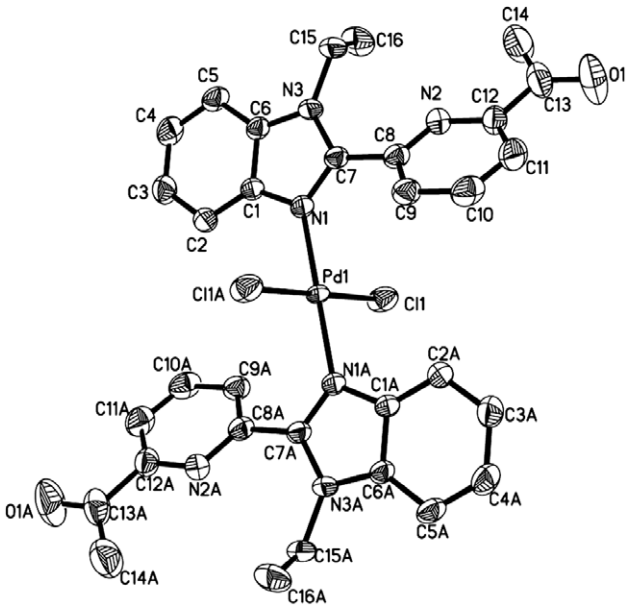


Fig. 3. Molecular structure of complex **6**. Thermalellipsoids are shown at 30% probability. Hydrogen atoms and solvent molecules have been omitted for clarity.

complexes can be attributed to the bulky effects of substituent of the nitrogen of benzimidazoles. In addition, it is no remarkable difference in the reactivity between methyl (electron-donating group) and acetyl (electron-withdrawing group) substitutent on pyridine ring. Without the substituent on the pyridine ring, the catalysts gave moderate yields. An investigation of the influence of the base suggested that K_2CO_3 was the reagent of choice. K_3PO_4 and NaOAc also affect the Heck coupling of bromobenzene with *n*-butylacrylate leading to low yields in 48 h (Table 3, entries 11 and 12). Piperidine (Pip), Et_3N, and CsF showed no activity under our conditions (Table 3, entries

Table 1
Selected bond lengths (Å) and angles (°) for complexes **C3**, **C4**, **C6**, and **C7**

	C3	C4	C6	C7
Bond lengths				
Pd1–N1	2.001(4)	2.035(4)	2.019(3)	2.013(2)
Pd1–N1A	2.001(4)	2.035(4)	2.019(3)	2.013(2)
Pd1–Cl1	2.2882(2)	2.2840(1)	2.2897(1)	2.2981(1)
Pd1–Cl1A	2.2882(2)	2.2840(1)	2.2897(1)	2.2981(1)
Bond angles				
N1–Pd1–N1A	180.0	180.000(1)	180.0	180.00(15)
Cl1–Pd1–Cl1A	180.00(7)	180.00(8)	180.00(7)	180.00(5)
N1–Pd1–Cl1	91.20(1)	90.82(1)	90.22(1)	90.45(8)
N1–Pd1–Cl1A	88.80(1)	89.18(1)	89.78(1)	89.55(8)
N1A–Pd1–Cl1	88.80(1)	89.18(1)	89.78(1)	89.55(8)
N1A–Pd1–Cl1A	91.20(1)	90.82(1)	90.22(1)	90.45(8)

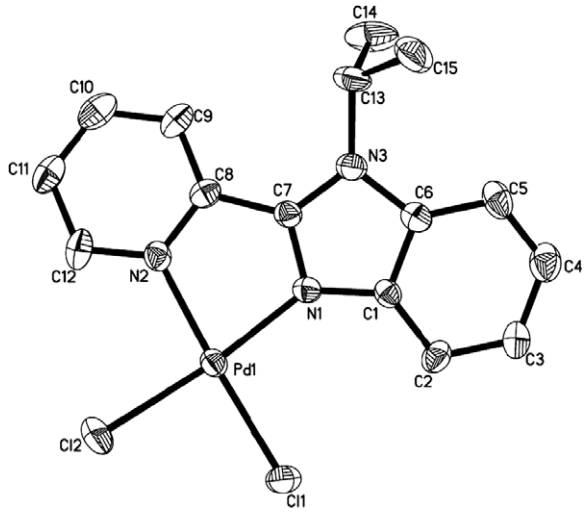


Fig. 5. Molecular structure of complex **10**. Thermalellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

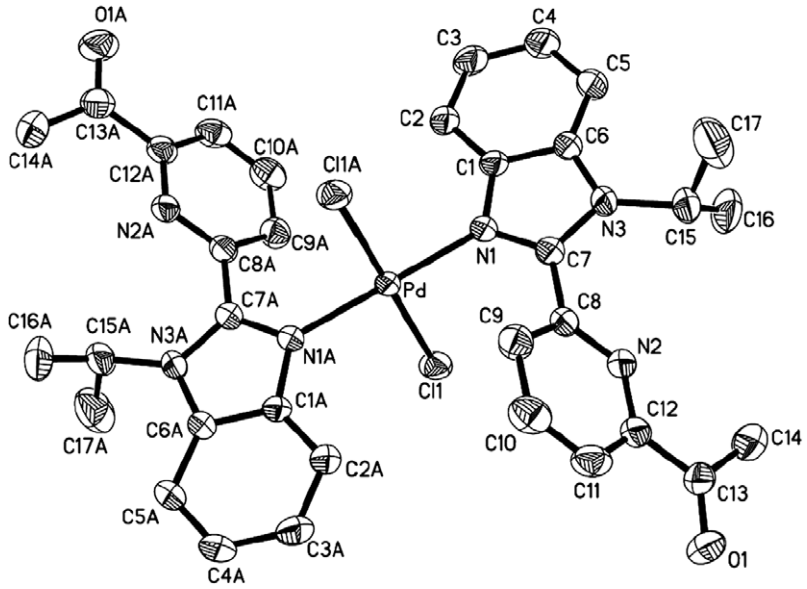
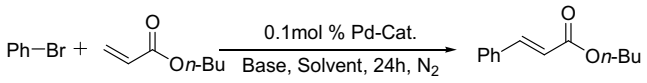


Fig. 4. Molecular structure of complex **7**. Thermalellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for complex **C10**

Bond lengths		Bond angles	
Pd1–N1	2.021(5)	N1–Pd1–N2	79.6(2)
Pd1–N2	2.040(5)	N1–Pd1–Cl2	172.59(2)
Pd1–Cl2	2.2849(2)	N2–Pd1–Cl2	94.07(2)
Pd1–Cl1	2.2926(2)	N1–Pd1–Cl1	97.12(2)
N1–C7	1.337(7)	N2–Pd1–Cl1	176.67(2)
C8–C7	1.456(8)	Cl2–Pd1–Cl1	89.22(7)
C8–C9	1.388(8)		
C8–N2	1.348(8)		

Table 3
Optimization of reaction conditions on Heck reaction of bromobenzene with butenyl acrylate[a]



Entry	Cat	Base	Solvent	Temperature (°C)	Yield[b] (%)
1	1	K_2CO_3	NMP	140	16
2	2	K_2CO_3	NMP	140	72
3	3	K_2CO_3	NMP	140	60
4	4	K_2CO_3	NMP	140	97
5	5	K_2CO_3	NMP	140	86
6	6	K_2CO_3	NMP	140	45
7	7	K_2CO_3	NMP	140	90
8	8	K_2CO_3	NMP	140	48
9	9	K_2CO_3	NMP	140	40
10	10	K_2CO_3	NMP	140	52
11	4	K_2PO_4	NMP	140	11
12	4	NaOAc	NMP	140	40
13	4	CsF	NMP	140	Trace
14	4	Pip	NMP	140	NR
15	4	K_2CO_3	NMP	140	NR
16	4	K_2CO_3	DMA	140	40
17	4	K_2CO_3	DMF	140	Trace
18	4	K_2CO_3	Toluene	110	NR
19	4	K_2CO_3	CH_3CN	50	Trace

[a] Reaction conditions: bromobenzene (1 mmol), butenyl acrylate (2.5 mmol), base (1.1 mmol), solvent (3 mL), catalyst (0.001 mmol).
[b] NMR yields.

13–15). In this reaction, several commonly used solvents were tested (Table 3, entries 16–19). Solvents, such as *N,N′*-dimethylformamide (DMF), toluene, and CH_3CN, were not effective (Table 3, entries 17–19) for this reaction. Dimethylacetamide (DMA) was less effective (Table 3, entry 16). Finally we found the optimized conditions as follow: using the complex **C4**, the reaction proceeded with 97% in NMP (NMP = 1-methyl-2-pyrrolidinone) with K_2CO_3 at 140 °C for 24 h under nitrogen atmosphere (Table 3, entry 4).

Heck couplings were carried out with catalyst **4** between aryl bromides and olefins. A summary of the results is shown in Table 4.

In the beginning, we investigated the activity of a group of olefins in the Heck reaction using 1-bromobenzene as substrate under the optimized reaction conditions (entries 1–6). Styrene or *para*-methyl styrene led to excellent yields of the desired products (entries 1 and 2). 4-Vinylpyridine also gave high yield of the Heck reaction product (entry 3). Using acrylate led to excellent yields of the desired product (entries 4 and 5). The above mentioned reactions proved highly regioselective (>99:1 *E* selectivity). This catalytic system was also active for simple linear alkenes such as oct-1-ene, although the yield was low (entries 6). We next investigated the effect of neutral and activated aryl bromides in the Heck reaction using styrene as substrate (entries 7 and 8). It is noteworthy that using 2-methyl-benzene bromides also led to excellent yields of the Heck reaction products (entry 7). Using 1-bromonaphthalene resulted in good yield of the desired product (entry 9).

3. Conclusions

A series of palladium complexes containing pyridylbenzoimidazole ligands have been synthesized and characterized along with their single-crystal X-ray analysis. With substitutent in the pyridine, the palladium atom is coordinated by two benzimidazole molecules *via* their nitrogen atoms and two chloride atoms. Without substitutent in the pyridine, the palladium atom is coordinated by pyridine nitrogen and benzimidazole nitrogen *via* chelation. Both showed catalytic activity for Heck coupling between aryl bromide and olefins. The investigation of the reactivity of the resulting palladium(II) complexes would provide a new catalyst system for the Heck reaction under phosphine-free conditions.

4. Experimental

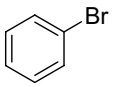
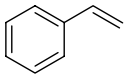
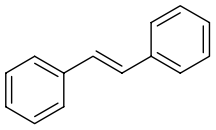
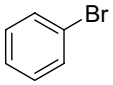
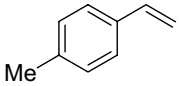
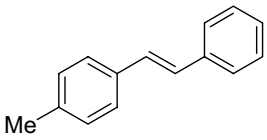
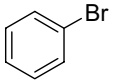
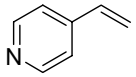
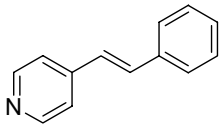
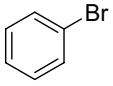
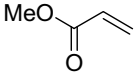
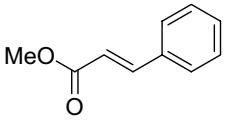
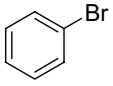
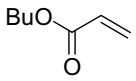
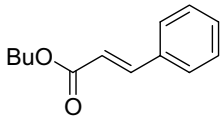
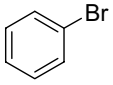
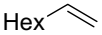
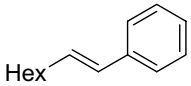
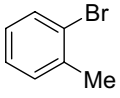
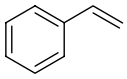
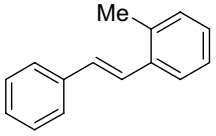
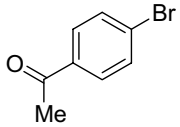
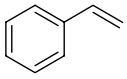
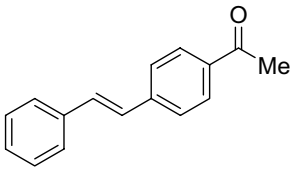
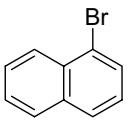
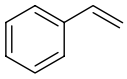
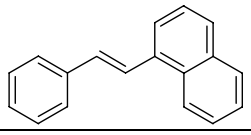
4.1. General

All manipulations were conducted in Schlenk tube and carried out under an atmosphere of nitrogen with a slightly positive pressure. 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 ^{13}C 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 *1–7*

All the benzimidazole based ligands were synthesized according to the literature method [13–15], and all palladium complexes were prepared by same procedure. Herein only the synthesis of palladium complex **4** is described as

Table 4
Heck reaction of aryl bromide with olefin using 2-benzimidazolylpyridine based catalyst **4**[a]

Entry	Aryl bromide	Olefin	Time (h)	Product	Yield[b] (%)	TON[c]
1			12		>99	990
2			12		90	900
3			12		>99	990
4			24		97	970
5			24		97	970
6			24		32	320
7			12		99	990
8			12		>99	990
9			12		88	880

[a] Reaction conditions: aryl bromide (1 mmol), olefin (2.5 mmol), K_2CO_3 (1.1 mmol), NMP (5 mL), catalyst **4** (0.001 mmol).
[b] NMR yields.
[c] TON = mol of product/mol of the catalyst.

an example in detail. To ligand **L4** (0.503 g, 2.0 mmol) and $PdCl_2(CH_3CN)_2$ (0.259 g, 1.0 mmol) was added 10 mL freshly distilled dichloromethane at room temperature and stirred overnight. Then 10 mL diethyl ether was added to precipitate the complex completely. *Trans*-di-[2-(1-isopropyl-2-benzimidazolyl)-6-methylpyridine]-dichloropalladium(**4**) (0.633 g, 0.93 mmol) light yellow powder was obtained in 93% yield. ^{1}H NMR (300 MHz, ppm, DMSO-d_6) δ 8.38–8.36 (d, 1H, –Py), 8.10–7.98 (m, 4H, Ar), 7.52–7.48 (m, 2H, –Ph), 5.30–5.25 (m, 1H, –CH–$(CH_3)_2$), 2.56 (s, 3H, –CH_3), 1.74–1.72 (d, 6H, –CH_3); ^{13}C NMR (75 MHz, ppm, DMSO-d_6) δ 158.7, 150.7, 147.8, 140.2, 138.5, 133.0, 125.7–124.1, 120.2, 114.8, 50.9, 24.8, 21.3. IR (KBr; cm^{-1}): 3082, 2979, 1593, 1462, 1420, 1302, 1248, 1203, 1139, 905, 815, 751. Anal. Calc. for $C_{32}H_{34}Cl_2N_6Pd \cdot 1.5H_2O$: C, 54.36; H, 5.27; N, 11.89. Found: C, 54.24; H, 5.11; N, 11.55%.

4.2.1. Complex *1*

Orange powder was produced in 92% yield ^{1}H NMR (300 MHz, ppm, DMSO-d_6) δ 10.5 (br, 1H, NH), 8.59–8.56 (m, 1H, –Py), 8.18–8.16 (m, 1H, –Py), 7.65–7.61 (m, 2H, –Ph), 7.46–7.44 (m, 1H, –Py), 7.30–7.26 (m, 2H, –Ph), 2.52 (s, 3H, –CH_3); ^{13}C NMR (75 MHz, ppm, DMSO-d_6) δ 158.8, 151.4, 150.6, 141.8, 138.3, 133.4, 125.5–123.8, 119.6, 113.7, 24.7. IR (KBr; cm^{-1}): 3111, 3053, 2976, 2928, 1597, 1510, 1471, 1438, 1396, 1341, 1295, 1202, 1159, 1137, 1112, 1066, 1026, 835, 782, 745, 686, 423. Anal. Calc. for $C_{26}H_{22}Cl_2N_6Pd \cdot 2.5H_2O$: C, 48.73; H, 4.25; N, 13.11. Found: C, 48.57; H, 3.95; N, 12.80%.

4.2.2. Complex *2*

Light yellow solid was produced in 90% yield ^{1}H NMR (300 MHz, ppm, DMSO-d_6) δ 8.48–8.45 (t, 1H, –Py), 8.24–8.22 (d, 1H, –Py), 7.95–7.93 (d, 1H, –Py), 7.80–7.77 (d, 1H, –Ph), 7.76–7.73 (d, 1H, –Ph), 7.51–7.44 (d, 2H, –Ph), 4.30 (s, 3H, –CH_3), 2.52 (s, 3H, –CH_3); ^{13}C NMR (75 MHz, ppm, DMSO-d_6) δ 158.0, 150.3, 147.1, 142.6, 140.7, 137.6, 135.1, 125.5–123.9, 119.4, 112.0, 33.1, 24.7. IR (KBr; cm^{-1}): 3053, 2953, 1594, 1571, 1483, 1436, 1406, 1341, 1248, 1161, 1084, 1002, 813, 750. Anal. Calc. for $C_{28}H_{26}Cl_2N_6Pd \cdot 1.5H_2O$: C, 51.67; H, 4.49; N, 10.89. Found: C, 51.49; H, 4.27; N, 12.75%.

4.2.3. Complex *3*

Light yellow solid was produced in 92% yield ^{1}H NMR (300 MHz, ppm, DMSO-d_6) δ 8.67–8.64 (d, 1H, –Py), 8.30–8.24 (t, 1H, –Py), 8.17–8.14 (d, 1H, –Py), 7.88–7.85 (m, 2H, –Ph), 7.49–7.43 (m, 2H, –Ph), 5.02–4.95 (q, 2H, –CH_2–), 2.56 (s, 3H, –CH_3), 1.61–1.57 (t, 3H, –CH_3); ^{13}C NMR (75 MHz, ppm, DMSO-d_6) δ 159.0, 151.9, 147.1, 144.4, 139.5, 133.5, 128.6, 124.6, 123.9, 122.4, 119.5, 111.8, 41.1, 26.6, 16.0. IR (KBr; cm^{-1}): 3063, 2976, 1585, 1475, 1426, 1354, 1298, 1255, 1081, 824, 747. Anal. Calc. for $C_{30}H_{30}Cl_2N_6Pd \cdot 0.75CH_2Cl_2$: C, 51.61; H, 4.44; N, 11.74. Found: C, 51.91; H, 4.33; N, 11.79%.

4.2.4. Complex *5*

Light yellow solid was produced in 88% yield ^{1}H NMR (300 MHz, ppm, DMSO-d_6) δ 8.62–8.59 (d, 1H, –Py), 8.30–8.25 (t, 1H, –Py), 8.13–8.11 (d, 1H, –Py), 7.86–7.83 (d, 2H, –Ph), 7.51–7.41 (m, 2H, –Ph), 4.37 (s, 3H, –CH_3), 2.79 (s, 3H, –CH_3); ^{13}C NMR (75 MHz, ppm, DMSO-d_6) δ 199.8, 153.2, 149.0, 147.9, 140.1, 139.7, 129.1, 125.3, 124.8, 123.0, 119.2, 113.1, 112.6, 34.2, 27.1. IR (KBr; cm^{-1}): 3387, 3063, 2947, 1703 ($\nu_{C=O}$), 1587, 1481, 1435, 1406, 1354, 1295, 1262, 1226, 1158, 1112, 1078, 993, 954, 824, 748, 591. Anal. Calc. for $C_{30}H_{26}Cl_2N_6O_2Pd \cdot 0.75CH_2Cl_2$: C, 49.67; H, 3.73; N, 11.30. Found: C, 49.57; H, 3.80; N, 11.26%.

4.2.5. Complex *6*

Light yellow solid was produced in 86% yield ^{1}H NMR (300 MHz, ppm, DMSO-d_6) δ 8.69–8.67 (d, 1H, –Py), 8.39–8.33 (t, 1H, –Py), 8.22–8.20 (d, 1H, –Py), 7.99–7.96 (d, 1H, –Ph), 7.92–7.90 (d, 1H, –Ph), 7.60–7.53 (m, 2H, –Ph), 5.04–5.00 (q, 2H, –CH_2–), 2.57 (s, 3H, –CH_3), 1.65–1.60 (t, 3H, –CH_3); ^{13}C NMR (75 MHz, ppm, DMSO-d_6) δ 199.6, 153.7, 147.3, 146.1, 140.6, 135.0, 126.5, 126.3, 124.0, 117.9, 113.3, 42.4, 27.0, 16.1. IR (KBr; cm^{-1}): 3418, 3063, 2976, 1700 ($\nu_{C=O}$), 1588, 1477, 1426, 1356, 1298, 1251, 1205, 1112, 824, 751, 594. Anal. Calc. for $C_{32}H_{30}Cl_2N_6O_2Pd \cdot 3H_2O$: C, 50.44; H, 4.76; N, 11.03. Found: C, 50.51; H, 4.38; N, 10.84%.

4.2.6. Complex *7*

Light yellow solid was produced in 90% yield. ^{1}H NMR (300 MHz, ppm, DMSO-d_6) δ 8.91–8.88 (d, 1H, –Py), 8.71–8.66 (t, 1H, –Py), 8.45–8.42 (d, 1H, –Py), 8.17–8.14 (d, 1H, –Ph), 8.04–8.01 (d, 1H, –Ph), 7.50–7.44 (m, 2H, –Ph), 5.94–5.90 (sep, 1H, –CH–$(CH_3)_2$), 2.48 (s, 3H, –CH_3), 1.69–1.66 (dd, 6H, –CH_3); ^{13}C NMR (75 MHz, ppm, DMSO-d_6) δ 196.5, 150.3, 147.4, 146.2, 136.7, 131.6, 129.0, 127.2, 121.6, 120.8, 117.9, 111.9, 48.7, 23.8, 19.0. IR (KBr; cm^{-1}): 3427, 3072, 2978, 1698 ($\nu_{C=O}$), 1586, 1458, 1423, 1357, 1297, 1248, 1203, 1163, 1136, 1112, 1062, 956, 818, 750, 598. Anal. Calc. for $C_{34}H_{34}Cl_2N_6O_2Pd \cdot CH_2Cl_2$: C, 51.21; H, 4.42; N, 10.24. Found: C, 51.47; H, 4.58; N, 10.25%.

4.3. General procedure for the synthesis of palladium complexes *8–10*

All the benzimidazole based ligands were synthesized according to the literature method [14,15], and all palladium complexes were prepared by same procedure. Herein only the synthesis of palladium complex **10** is described as an example in detail. To ligand **L10** (0.237 g, 1.0 mmol) and $PdCl_2(CH_3CN)_2$ (0.259 g, 1.0 mmol) was added 10 mL freshly distilled dichloromethane at room temperature and stirred overnight. Then 10 mL diethyl ether was added to precipitate the complex completely. (2-(Pyridin-2-yl)-1*H*-benzo[*d*]imidazol-1-yl)praseodymium palladium

dichloride **10** (0.357 g, 0.86 mmol) orange powder was obtained in 86% yield. ^{1}H NMR (300 MHz, ppm, DMSO-d_6) δ 9.24–9.22 (d, 1H, –Py), 8.87–8.84 (d, 1H, –Py), 8.33–8.32 (d, 2H, –Ph), 8.04–8.01 (d, 1H, –Py), 7.81–7.76 (q, 1H, –Py), 7.45–7.34 (m, 2H, –Ph), 5.55–5.42 (sep, 1H, N–CH–), 1.75–1.72 (d, 6H, –CH_3); ^{13}C NMR (75 MHz, ppm, DMSO-d_6) δ 151.7, 147.9, 141.8, 140.8, 133.3, 127.5, 125.9, 125.7, 125.1, 120.0, 115.2. IR (KBr; cm^{-1}): 3405, 2976, 1604, 1510, 1471, 1438, 1396, 1341, 1295, 1202, 1159, 1137, 1112, 1066, 1026, 835, 782, 745, 686. Anal. Calc. for $C_{15}H_{15}Cl_2N_3Pd \cdot H_2O$: C, 41.64; H, 3.96; N, 9.71. Found: C, 41.75; H, 3.61; N, 9.81%.

4.3.1. Complex *8*

Orange solid was produced in 75% yield. IR (KBr; cm^{-1}): 3161, 3092, 1611, 1590, 1542, 1482, 1459, 1447, 1327, 1308, 1151, 990, 822, 751, 657. Anal. Calc. for $C_{12}H_9Cl_2N_3Pd \cdot CH_2Cl_2$: C, 34.13; H, 2.42; N, 9.19. Found: C, 34.02; H, 2.39; N, 9.16%.

4.3.2. Complex *9*

Orange solid was produced in 90% yield. IR (KBr; cm^{-1}): 3133, 3044, 1608, 1531, 1485, 1456, 1410, 1350, 1224, 1170, 1028, 1015, 941, 829, 791, 760, 740. Anal. Calc. for $C_{13}H_{11}Cl_2N_3Pd$: C, 40.39; H, 2.87; N, 10.87. Found: C, 39.88; H, 2.89; N, 10.66%.

4.4. Heck reaction

4.4.1. General procedure

Under nitrogen atmosphere, K_2CO_3 (2.2 mmol), olefin (5 mmol), aryl bromide (2 mmol), and NMP (5 mL) were added in turn to a Schlenk tube equipped with a magnetic stirring bar. A 20 μL NMP solution containing 0.002 mmol of complex (about 1.1 mg) was added into the Schlenk tube. The mixture was stirred at 140 °C and monitored by GC. After 12–24 h, the mixture was diluted with ether and water. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica

Table 5
Crystal data and structure refinement for **C3**, **C4**, **C6**, **C7**, and **C10**

	C3	**C4**	**C6**	**C7**	**C10**
Empirical formula	$C_{60}H_{60}Cl_4N_{12}Pd_2 2CH_3CN$	$C_{32}H_{434}Cl_2N_6PdDMF$	$C_{32}H_{30}Cl_2N_6O_2Pd2DMF$	$C_{34}H_{34}Cl_2N_6O_2Pd$	$C_{15}H_{15}Cl_2N_3Pd$
Formula weight	1385.95	753.05	854.13	735.99	414.6
Crystal color	yellow	yellow	yellow	yellow	red
Temperature (K)	293(2) K	293(2) K	293(2) K	293(2) K	293(2) K
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073 A
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$	$P1$	Pc	$P2(1)/n$
a (Å)	9.4073(2)	16.7341(4)	9.3344(8)	7.3122(2)	11.2585(4)
b (Å)	11.658(2)	14.5875(4)	9.9752(9)	14.365(3)	10.2044(4)
c (Å)	15.631(3)	15.9854(4)	12.6714(1)	17.246(3)	13.6927(5)
α (deg)	100.63(3)	90	110.525(5)	90.0	90
β (deg)	91.46(3)	113.6640(1)	94.746(6)	98.67(3)	93.427(2)
γ (deg)	94.57(3)	90	110.388(6)	90.0	90
Volume (Å^3)	1678.1(5)	3574.06(2)	1007.14(2)	1790.8(6)	1570.29(10)
Z	1	4	1	2	4
D_{calc} (g cm^{-3})	1.371	1.399	1.408	1.365	1.754
μ (mm^{-1})	0.744	0.707	0.642	0.705	1.517
$F(000)$	708	1552	440	752	824
Crystal size (mm)	$0.32 \times 0.23 \times 0.15$	$0.35 \times 0.25 \times 0.18$	$0.30\times 0.20 \times 0.10$	$0.35 \times 0.25 \times 0.18$	$0.35 \times 0.25 \times 0.10$
θ Range (°)	1.33–27.49	1.93–28.29	3.29–28.37	1.85–27.47	1.81–28.30
Limiting indices	$-12 \leqslant h \leqslant 12$, $-15 \leqslant k \leqslant 15$, $-20 \leqslant l \leqslant 20$	$-18 \leqslant h \leqslant 22$, $-16 \leqslant k \leqslant 19$, $-21 \leqslant l \leqslant 20$	$-12 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $-16 \leqslant l \leqslant 16$	$-9 \leqslant h \leqslant 9$, $-18 \leqslant k \leqslant 18$, $-22 \leqslant l \leqslant 22$	$-11 \leqslant h \leqslant 15$, $-11 \leqslant k \leqslant 13$, $-18 \leqslant l \leqslant 18$
Reflections collected	12034	28564	19520	7469	13370
Unique reflections	7473	8844	4980	4058	3908
Completeness to (%)	97.0 ($\theta = 27.49°$)	99.5 ($\theta = 28.29°$)	99.0 ($\theta = 28.37°$)	98.8 ($\theta = 27.47°$)	99.9 ($\theta = 28.30°$)
Absorption correction	Empirical	Empirical	Empirical	Empirical	Empirical
Number of parameters	382	418	241	208	190
Goodness-of-fit on F^2	1.109	1.055	1.024	1.155	1.216
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0612$, $wR_2 = 0.1531$	$R_1 = 0.0681$, $wR_2 = 0.1233$	$R_1 = 0.0673$, $wR_2 = 0.1153$	$R_1 = 0.0422$, $wR_2 = 0.1027$	$R_1 = 0.0773$, $wR_2 = 0.1024$
R indices (all data)	$R_1 = 0.0855$, $wR_2 = 0.1672$	$R_1 = 0.1410$, $wR_2 = 0.1500$	$R_1 = 0.1037$, $wR_2 = 0.1297$	$R_1 = 0.0635$, $wR_2 = 0.1174$	$R_1 = 0.1071$, $wR_2 = 0.1099$
Largest difference in peak and hole (e Å^{-3})	0.850 and −0.614	0.553 and −0.521	0.654 and −0.513	0.468 and −0.630	0.499 and −1.241

gel using petroleum ether or mixture of petroleum ether and ethyl acetate.

4.5. X-ray crystal structural determination of complexes C3, C4, C6, C7, and C10

The single-crystal X-ray diffraction studies for complex **C3**, **C4**, **C6**, **C7** and **C10** were carried out on a Bruker SMART 1000 CCD diffractometer with graphite monochromated Mo Kα 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 of F^2. All non-hydrogen atoms were refined anisotropically. Structure solution and refinement were performed using the SHELXL-97 Package [18]. Crystal data and processing parameters were summarized in Table 5.

5. Supplementary material

CCDC 653044, 653045, 653046, 653047 and 653048 contain the supplementary crystallographic data for **C3**, **C4**, **C6**, **C7** and **C10**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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References

[1] (a) E. Negishi (Ed.), Handbook of Organopalladium Chemistry for Organic Synthesis, vol. 1, Wiley-Interscience, New York, 2002, p. 1133;
(b) N.J. Whitcombe, K. K Hii, S.E. Gibson, Tetrahedron 57 (2001) 7449;
(c) I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009;
(d) L.S. Hegedus, Transition Metals in the Synthesis of Complex Organic Molecules, 2nd ed., University Science Books, Sausalito, CA, 1999 (Chapter 4.6);
(e) S. Brase, A. de Meijere, in: F. Diederich, P.J. Stang (Eds.), Metal-Catalyzed Cross-coupling Reactions, Wiley-VCH, Weinheim, Germany, 1998 (Chapter 3);
(f) J.T. Link, L.E. Overman, in: F. Diederich, P.J. Stang (Eds.), Metal-Catalyzed Cross-coupling Reactions, Wiley-VCH, Weinheim, Germany, 1998 (Chapter 6);
(g) G.T. Crisp, Chem. Soc. Rev. 27 (1998) 427;
(h) W. Cabri, I. Candiani, Acc. Chem. Res. 28 (1995) 2;
(i) F. Alonso et al., Tetrahedron 61 (2005) 11771.
[2] (a) T. Mizoroki, K. Mori, A. Ozaki, Bull. Chem. Soc., Jpn. 44 (1971) 581;
(b) H.A. Dieck, R.F. Heck, J. Am. Chem. Soc. 96 (1974) 1133;
(c) H.A. Dieck, R.F. Heck, J. Org. Chem. 40 (1975) 1083.
[3] (a) A.F. Littke, G.C. Fu, J. Org. Chem. 64 (1999) 10;
(b) A.F. Littke, G.C. Fu, J. Am. Chem. Soc. 123 (2001) 6989.
[4] A. Ehrentraut, A. Zapf, M. Beller, Synlett 11 (2000) 1589.
[5] K.H. Shaughnessy, P. Kim, J. F Hartwig, J. Am. Chem. Soc. 123 (2001) 2123.
[6] (a) A.J. Spencer, Organomet. Chem. 258 (1983) 101;
(b) W.A. Herrmann, C. Brossmer, K. Öfele, C.T. Reisinger, T. Priermeier, M. Beller, H. Fischer, Angew. Chem., Int. Ed. Engl. 34 (1995) 1844;
(c) A. Zapf, M. Beller, Chem. Eur. J. 13 (2001) 2908.
[7] (a) W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Angew. Chem., Int. Ed. Engl. 34 (1995) 2371;
(b) M. Ohff, A. Ohff, D. Milstein, Chem. Commun. (1999) 357;
(c) A.A.D. Tulloch, A.A. Danopoulos, R.P. Tooze, S.M. Cafferkey, S. Kleinhenz, M.B. Hursthouse, Chem. Commun. (2000) 1247;
(d) A.S. Gruber, D. Zim, G. Ebeling, A.L. Monteiro, J. Dupont, Org. Lett. 2 (2000) 1287;
(e) E. Peris, J.A. Loch, J. Mata, R.H. Crabtree, Chem. Commun. (2001) 201;
(f) D.E. Bergbreiter, P.L. Osburn, Y.S. Liu, J. Am. Chem. Soc. 121 (1999) 9531;
(g) M.T. Reetz, E. Westermann, Angew. Chem., Int. Ed. 39 (2000) 165;
(h) M.T. Reetz, E. Westermann, R. Lohmer, G. Lohmer, Tetrahedron Lett. 39 (1998) 8449;
(i) A.H.M. Vries, J.M.C.A. Mulders, J.H.M. Mommers, H.J.W. Henderickx, J.G. Vries, Org. Lett. 5 (2003) 3285;
(j) J.A. Widegren, R.G. Finke, J. Mol. Chem. A: Chem. 198 (2003) 317.
[8] G.A. Grasa, R. Singh, E.D. Stevens, S.P. Nolan, J. Organomet. Chem. 687 (2003) 269.
[9] (a) W. Cabri, I. Candiani, A. Bedeschi, R. Santi, J. Org. Chem. 58 (1993) 7421;
(b) M.R. Buchmeiser, K. Wurst, J. Am. Chem. Soc. 121 (1999) 11101;
(c) J. Silberg, T. Schareina, R. Kempe, K. Wurst, M.R. Buchmeiser, J. Organomet. Chem. 622 (2001) 6;
(d) M.R. Buchmeiser, T. Schareina, R. Kempe, K. Wurst, J. Organomet. Chem. 634 (2001) 39;
(e) T. Kawano, T. Shinomaru, I. Ueda, Org. Lett. 4 (2002) 2545;
(f) C. Nájera, J. Gil-Moltó, S. Karlström, L.R. Falvello, Org. Lett. 5 (2003) 1451.
[10] T. Mino, Y. Shirae, Y. Sasai, M. Sakamoto, T. Fujita, J. Org. Chem. 71 (2006) 6834.
[11] S. Haneda, C. Ueba, K. Eda, M. Hayashi, Adv. Synth. Catal. 349 (2007) 833.
[12] W. Chen, C. Xi, K. Yang, Appl. Organometal. Chem. 21 (2007) 641.
[13] (a) P. Hao, S. Zhang, W.H. Sun, Q.S. Shi, A. Sherrif, X.M. Lu, P.Z. Li, Organometallics 26 (2007) 2439;
(b) W.H. Sun, P. Hao, S. Zhang, Q.S. Shi, W.W. Zuo, X.B. Tang, Organometallics 26 (2007) 2720.
[14] D.W. Hein, R.J. Alheim, J.J. Leavit, J. Am. Chem. Soc. 79 (1957) 427.
[15] J. Lu, H.G. Ge, Y.J. Bai, Chin. J. Org. Chem. 22 (2002) 782.
[16] (a) R.F. Carina, A.F. Williams, G. Bernardinelli, Inorg. Chem. 40 (2001) 1826;
(b) C. Mock, I. Puscasu, M.J. Rauterkus, G. Tallen, J.E.A. Wolff, B. Krebs, Inorg. Chim. Acta 319 (2001) 109;
(c) Z. Zhu, M. Kojima, K. Nakajima, Inorg. Chim. Acta 358 (2005) 476.
[17] (a) W. Zhang, W.H. Sun, B. Wu, S. Zhang, H. Ma, Y. Li, J. Chen, P. Hao, J. Organomet. Chem. 691 (2006) 4759;
(b) P. Pelagatti, M. Carcelli, M. Costa, S. Ianelli, C. Pelizzi, D. Rogolino, J. Mol. Catal. A: Chem. 226 (2005) 107.
[18] G.M. Sheldrick, SHELXTL-97. Program for the Refinement of Crystal Structures, University of Göttinge, Germany, 1997.