



# Dinuclear NHC–palladium(II) complexes: synthesis, characterization and application to Suzuki–Miyaura cross-coupling reactions

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## Abstract

Four dinuclear *N*-heterocyclic carbene–palladium(II) complexes **1–4** were prepared and characterized by elemental analysis and spectroscopic methods. The X-ray crystal structure of complex **2** showed a dinuclear framework in which *N*-heterocyclic ligands bridge between two square planar palladium(II) units. Each palladium center is surrounded by an imidazolylidene, a nitrogen atom from the central linking ligand, and two trans-chloride ligands. These dinuclear NHC–palladium(II) complexes exhibited efficient catalytic activities for the Suzuki–Miyaura coupling of aryl and benzyl chlorides with arylboronic acids.

## Introduction

During recent decades, transition-metal-catalyzed coupling reactions have contributed greatly to the straightforward construction of carbon–carbon and carbon–heteroatom bonds. Among such reactions, the palladium-catalyzed Suzuki–Miyaura coupling of aryl halides and organoboron reagents have attracted much attention in organic synthesis [1–11]. Consequently, considerable efforts have been made toward the discovery of more active catalysts for the Suzuki–Miyaura coupling reaction. Recently, *N*-heterocyclic carbene (NHC)–palladium complexes [12–20], which often show advantages such as higher air, moisture, and thermal stability, have been found to be good catalysts for the Suzuki–Miyaura coupling of aryl halides. For example,

the PEPPSI NHC–palladium complexes [21–24] show high levels of activity in the Suzuki–Miyaura coupling of aryl chlorides with arylboronic acids. Shao and Lu have prepared a well-defined *N*-heterocyclic carbene–Pd(II)-1-methylimidazole [NHC–Pd(II)–Im] [25–28] complex, which acted as a highly effective pre-catalyst for the Suzuki–Miyaura coupling of aryl as well as benzyl chlorides with arylboronic acids under mild conditions. Meanwhile, the NHC–Pd(II)-2-phenylimidazole complexes [29] have been found to catalyze the Suzuki cross-coupling of aryl as well as benzyl chlorides with a series of boronic acids in excellent yields, using a very low catalyst loading of 0.05 mol%. The use of imine–Pd–NHC complexes as active catalysts for the more challenging Suzuki–Miyaura cross-couplings of aryl chlorides have also been reported [30]. Recyclable supported *N*-heterocyclic carbene–palladium complexes have attracted recent interest for Suzuki–Miyaura coupling reactions [31]. Despite the impressive progress made so far in the use of *N*-heterocyclic carbene–palladium complexes as catalysts, very little research has been reported on dinuclear or multi-nuclear carbene–palladium complexes bearing bidentate or multidentate bridging ligands [32–35]. We have recently reported a simple route to the synthesis of trinuclear NHC–palladium complexes with bridging tridentate *N*-heterocyclic ligands [36]. These trinuclear palladium(II) complexes proved to be effective catalyst precursors for the Suzuki–Miyaura coupling of both aryl and benzyl chlorides with arylboronic acids. Moreover, the trinuclear NHC–Pd(II) complexes were found to exhibit a much higher activity than the analogous mononuclear NHC–Pd(II) complexes under the same reaction conditions. Encouraged by these

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results, and also in continuation of our interest [37–39] in the construction of functionalized complexes that can enter an array of di- and multi-nuclear systems, herein we have extended the methodology to the introduction of bidentate bridging *N*-heterocycles into NHC–palladium complexes. In this paper, we report the facile synthesis and characterization of four dinuclear NHC–Pd(II) complexes (Scheme 1). Furthermore, the catalytic applications of these dinuclear NHC–Pd(II) complexes in the Suzuki–Miyaura coupling of aryl and benzyl chlorides with a range of arylboronic acids have been explored.

## Experimental

### General

Both the procedures preparations of the dinuclear *N*-heterocyclic carbene–palladium(II) complexes and all the catalytic reactions were carried out under a nitrogen atmosphere. 1,4-bis(pyrid-4-yl)benzene was prepared according to the literature method [40]. Solvents were dried by standard methods and freshly distilled prior to use. All other chemicals were used as purchased. Melting points were measured on a XT4A melting point apparatus and are uncorrected. IR spectra were collected on a Bruker VECTOR22 spectrophotometer using KBr pellets.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX 400 instrument using TMS as an internal standard. Elemental analyses were measured on a Thermo Flash EA 1112 elemental analyzer.

### General procedure for synthesis of the complexes

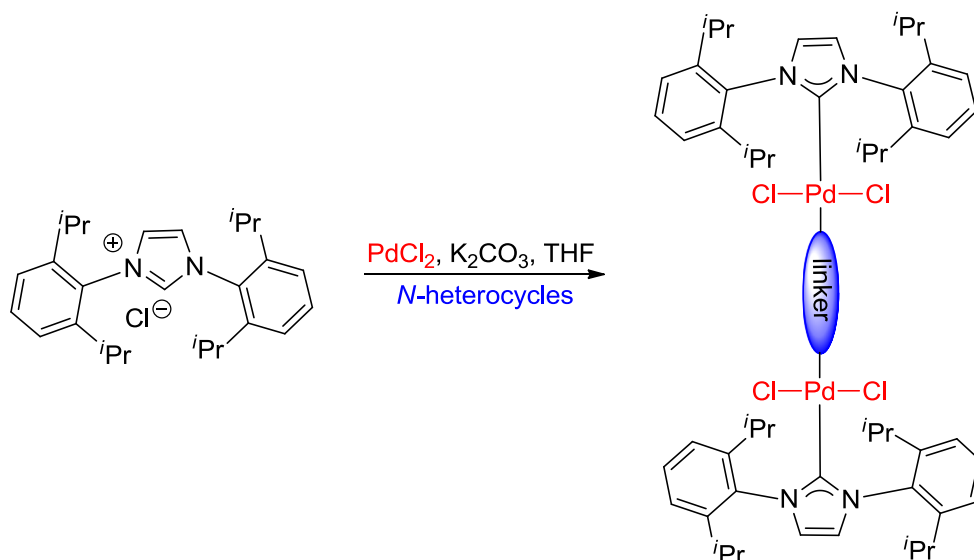
Under an  $\text{N}_2$  atmosphere, a mixture of the imidazolium salt (1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-3-ium chloride, 2.2 mmol), the required *N*-heterocycle (1.0 mmol),  $\text{PdCl}_2$  (2.2 mmol) and  $\text{K}_2\text{CO}_3$  (2.2 mmol) was stirred in anhydrous THF (10 mL) under reflux for 12 h. After cooling, filtration and evaporation, the residue was purified by preparative TLC on silica gel plates, eluting with  $\text{CH}_2\text{Cl}_2$  to afford the corresponding dinuclear *N*-heterocyclic carbene–palladium(II) complexes **1–4**.

#### Complex (1)

Yield: 39%, pale yellow solid. mp: 229–231 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45 (t,  $J$  = 7.7 Hz, 2H, ArH), 7.30–7.26 (m, 4H, ArH), 7.03 (s, 2H, NCH=), 5.29 (s, 1H, NH), 2.99–2.93 (m, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 2.64–2.59 (m, 2H,  $\text{CH}_2$ ), 2.37–2.35 (m, 2H,  $\text{CH}_2$ ), 1.36 (d,  $J$  = 6.6 Hz, 12H,  $\text{CH}_3\text{CHCH}_3$ ), 1.04 (d,  $J$  = 6.8 Hz, 12H,  $\text{CH}_3\text{CHCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.1, 146.6, 135.0, 130.1, 124.7, 123.8, 47.0, 28.6, 26.2, 23.1. IR(KBr,  $\text{cm}^{-1}$ ): 2966(s), 2867(s), 1467(s), 1412(s), 1383(s), 1079(m), 1012(s), 944(s), 887(m), 801(s), 755(m), 707(s). Anal. Calcd. for  $\text{C}_{58}\text{H}_{82}\text{Cl}_4\text{N}_6\text{Pd}_2$ : C, 57.20; H, 6.79; N, 6.90. Found: C, 57.38; H, 6.98; N, 6.70%.

#### Complex (2)

Yield: 64%, pale yellow solid. mp: 198–201 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.63 (d,  $J$  = 6.5 Hz, 2H, ArH), 7.48



**Scheme 1** Synthesis of the dinuclear *N*-heterocyclic carbene–palladium(II) complexes **1–4**. **1** linker = piperazine (39% yield); **2** linker = 4,4'-bipyridine (64%, yield); **3** linker = 1,2-bis(4-pyridyl)ethane (58%, yield); **4** linker = 1,4-bis(pyrid-4-yl)benzene (41% yield)

(t,  $J = 7.7$  Hz, 2H, ArH), 7.33 (d,  $J = 7.7$  Hz, 4H, ArH), 7.15 (d,  $J = 6.6$  Hz, 2H, ArH), 7.13 (s, 2H, NCH=), 3.17–3.11 (m, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.46 (d,  $J = 6.6$  Hz, 12H,  $\text{CH}_3\text{CHCH}_3$ ), 1.11 (d,  $J = 6.8$  Hz, 12H,  $\text{CH}_3\text{CHCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.4, 148.0, 136.3, 131.6, 126.4, 125.3, 123.0, 30.0, 27.6, 24.5. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  2964(s), 2866(s), 1609(s), 1530(m), 1488(s), 1456(m), 1411(s), 1382(s), 1280(s), 1223(m), 1132(s), 934(s), 863(m), 801(s), 755(m), 746(s), 703(s). Anal. Calcd. for  $\text{C}_{64}\text{H}_{80}\text{Cl}_4\text{N}_6\text{Pd}_2$ : C, 59.68; H, 6.26; N, 6.52. Found: C, 59.78; H, 6.48; N, 6.30%.

### Complex (3)

Yield: 58%, pale yellow solid. mp: 237–240 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.42 (d,  $J = 6.3$  Hz, 2H, ArH), 7.48 (t,  $J = 7.7$  Hz, 2H, ArH), 7.34 (d,  $J = 7.7$  Hz, 4H, ArH), 7.11 (s, 2H, NCH=), 6.86 (d,  $J = 6.2$  Hz, 2H, ArH), 3.20–3.13 (m, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 2.59 (s, 2H,  $\text{CH}_2$ ), 1.47 (d,  $J = 6.6$  Hz, 12H,  $\text{CH}_3\text{CHCH}_3$ ), 1.11 (d,  $J = 6.8$  Hz, 12H,  $\text{CH}_3\text{CHCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.0, 151.3, 151.2, 146.6, 135.1, 130.2, 125.0, 124.0, 123.8, 35.2, 28.7, 26.3, 23.3. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  2965(s), 2868(s), 1593(s), 1467(m), 1412(s), 1383(s), 1331(m), 1208(s), 1120(s), 1012(m), 886(s), 801(m), 756(m), 707(s). Anal. Calcd. for  $\text{C}_{66}\text{H}_{84}\text{Cl}_4\text{N}_6\text{Pd}_2$ : C, 60.23; H, 6.43; N, 6.39. Found: C, 60.33; H, 6.60; N, 6.20%.

### Complex (4)

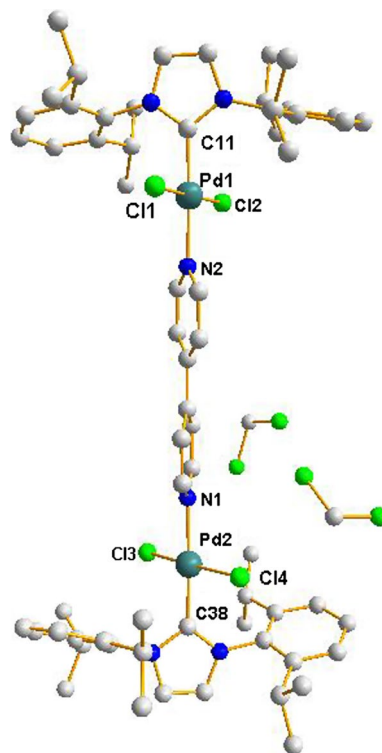
Yield: 41%, pale yellow solid. mp: 219–222 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.60 (d,  $J = 6.6$  Hz, 2H, ArH), 7.51–7.47 (m, 4H, ArH), 7.35 (d,  $J = 7.7$  Hz, 4H, ArH), 7.29–7.26 (m, 2H, ArH), 7.13 (s, 2H, NCH=), 3.21–3.15 (m, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.49 (d,  $J = 6.6$  Hz, 12H,  $\text{CH}_3\text{CHCH}_3$ ), 1.12 (d,  $J = 6.8$  Hz, 12H,  $\text{CH}_3\text{CHCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  154.9, 151.7, 148.7, 146.7, 138.2, 135.1, 130.3, 127.9, 125.1, 124.0, 121.8, 28.8, 26.3, 23.3. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  2966(s), 2867(s), 1612(s), 1466(m), 1410(s), 1383(s), 1346(m), 1280(s), 1223(m), 1120(s), 1059(m), 944(s), 815(s), 757(m), 705(s). Anal. Calcd. for  $\text{C}_{70}\text{H}_{84}\text{Cl}_4\text{N}_6\text{Pd}_2$ : C, 61.63; H, 6.21; N, 6.16. Found: C, 61.68; H, 6.25; N, 6.10%.

### General procedure for the Suzuki–Miyaura reaction

A Schlenk flask was charged with the required aryl chloride (0.50 mmol), arylboronic acid (0.75 mmol), dinuclear NHC–palladium(II) complex (1.0 mol%),  $\text{KO}^t\text{Bu}$  (2.0 equiv),  $^i\text{PrOH}$  (0.4 mL) and  $\text{H}_2\text{O}$  (0.8 mL). The mixture was stirred at 80 °C for 4 h under  $\text{N}_2$ . After cooling, the reaction mixture was evaporated, and the product was isolated by preparative TLC on silica gel plates.

### Crystal structure determination and data collection

Crystals of complex **2** (CCDC 1570267) were obtained by recrystallization from  $\text{CH}_2\text{Cl}_2/n$ -hexane at ambient temperature. Data were collected on an Oxford Diffraction Gemini E diffractometer with graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.7107$  Å). The structure was solved by direct methods using the SHELXS-97 program, and all non-hydrogen atoms were refined anisotropically on  $F^2$  by the full-matrix least-squares technique, using the SHELXL-97 crystallographic software package [41, 42]. The hydrogen atoms were included but not refined. Details of the crystal structure determination are summarized in Table 4. The crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Fig. 1** Molecular structure of the dinuclear *N*-heterocyclic carbene–palladium(II) complex **2**· $2\text{CH}_2\text{Cl}_2$ . Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) in complex **2**· $2\text{CH}_2\text{Cl}_2$ : Pd1–C11 1.970(5), Pd1–N2 2.110(5), Pd1–C11 2.2950(17), Pd1–Cl2 2.2883(17); C11–Pd1–C11 88.80(16), N2–Pd1–C11 92.18(15), C11–Pd1–Cl2 90.72(16), N2–Pd1–Cl2 88.46(15), C11–Pd1–N2 176.6(2), C11–Pd1–Cl2 177.17(9); Pd2–C38 1.972(5), Pd2–N1 2.107(5), Pd2–Cl3 2.2940(19), Pd2–Cl4 2.294(2); C38–Pd2–Cl3 89.02(18), N1–Pd2–Cl3 91.70(16), C38–Pd2–Cl4 90.59(18), N1–Pd2–Cl4 88.94(17), C38–Pd2–N1 176.8(2), Cl3–Pd2–Cl4 175.24(7)

## Results and discussion

### Synthesis and characterization of the complexes

Following the synthetic route reported previously [38], the required dinuclear *N*-heterocyclic carbene–palladium(II) complexes **1–4** were easily synthesized in a one-step reaction from the commercially available imidazolium salts, palladium chloride, and the bridging *N*-heterocycle ligands, as shown in Scheme 1. Complexes **1–4** were isolated in fair yields (39–64%) after purification and characterized by elemental analysis, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and IR spectroscopy. Additionally, the X-ray crystal structure of complex **2** was obtained. All four complexes isolated as pale yellow and air-stable solids.

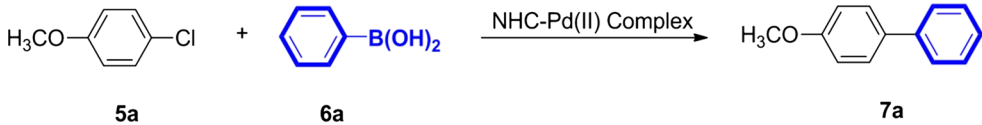
The X-ray crystal structure of complex **2** is shown in Fig. 1. Two dichloromethane molecules from the recrystallization solvent were found in the lattice unit of complex **2**. The crystal structure of **2** reveals a dinuclear framework

with the *N*-heterocyclic ligand bridging between two square planar palladium(II) units. Each palladium center is coordinated by a carbene, a nitrogen atom and two chloride ligands in a slightly distorted square planar geometry. The values of bond lengths and angles compare well with those of related dinuclear NHC–palladium(II) complexes [32–35]. The Pd(1)–C<sub>carbene</sub> bond length of 1.970(5) Å in complex **2** is shorter than that of Pd(1)–N(2) (2.110(5) Å). The C<sub>carbene</sub>–Pd(1)–N(2) and Cl(1)–Pd(1)–Cl(2) bond angles are close to 180° (see caption to Fig. 1), while the C<sub>carbene</sub>–Pd(1)–Cl(1), C<sub>carbene</sub>–Pd(1)–Cl(2), N(2)–Pd(1)–Cl(1) and N(2)–Pd(1)–Cl(2) angles are all close to 90°. The coordination environment around Pd(2) is very similar to that of Pd(1).

### Catalytic studies

In order to investigate the catalytic activities of the present dinuclear NHC–Pd(II) complexes, initial experiments were carried out using 1-chloro-4-methoxybenzene and

**Table 1** Optimization of reaction conditions for Suzuki–Miyaura coupling of 1-chloro-4-methoxybenzene with phenylboronic acid catalyzed by the dinuclear NHC–Pd(II) complexes

				
Entry	Cat.	Base	Solvent	Yield (%) <sup>a</sup>
1	<b>1</b>	KO <sup>t</sup> Bu	EtOH/H <sub>2</sub> O (1/3)	85
2	<b>1</b>	Cs <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O (1/3)	60
3	<b>1</b>	Na <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O (1/3)	65
4	<b>1</b>	NaO <sup>t</sup> Bu	EtOH/H <sub>2</sub> O (1/3)	75
5	<b>1</b>	K <sub>3</sub> PO <sub>4</sub>	EtOH/H <sub>2</sub> O (1/3)	21
6 <sup>b</sup>	<b>1</b>	KO <sup>t</sup> Bu	EtOH/H <sub>2</sub> O (1/3)	89
7 <sup>b</sup>	<b>1</b>	KO <sup>t</sup> Bu	<sup>i</sup> PrOH/H <sub>2</sub> O (1/3)	95
8 <sup>c</sup>	<b>1</b>	KO <sup>t</sup> Bu	<sup>i</sup> PrOH/H <sub>2</sub> O (1/2)	> 99
9 <sup>c,d</sup>	<b>1</b>	KO <sup>t</sup> Bu	<sup>i</sup> PrOH/H <sub>2</sub> O (1/2)	> 99
10 <sup>c,e</sup>	<b>1</b>	KO <sup>t</sup> Bu	<sup>i</sup> PrOH/H <sub>2</sub> O (1/2)	99
11 <sup>c,f</sup>	<b>1</b>	KO <sup>t</sup> Bu	<sup>i</sup> PrOH/H <sub>2</sub> O (1/2)	79
12 <sup>c,e</sup>	<b>2</b>	KO <sup>t</sup> Bu	<sup>i</sup> PrOH/H <sub>2</sub> O (1/2)	97
13 <sup>c,e</sup>	<b>3</b>	KO <sup>t</sup> Bu	<sup>i</sup> PrOH/H <sub>2</sub> O (1/2)	91
14 <sup>c,e</sup>	<b>4</b>	KO <sup>t</sup> Bu	<sup>i</sup> PrOH/H <sub>2</sub> O (1/2)	93
15 <sup>c,e</sup>	PdCl <sub>2</sub>	KO <sup>t</sup> Bu	<sup>i</sup> PrOH/H <sub>2</sub> O (1/2)	15

All reactions were carried out using **5a** (0.50 mmol), **6a** (0.75 mmol), base (2.0 equiv), Catalyst (1.0 mol%) in solvent (2.0 mL) at 80 °C for 12 h

<sup>a</sup>Isolated yields

<sup>b</sup>Solvent (1.0 mL)

<sup>c</sup>Solvent (1.2 mL)

<sup>d</sup>Reaction time was 8 h

<sup>e</sup>Reaction time was 4 h

<sup>f</sup>Reaction time was 2 h

**Table 2** Catalytic Suzuki–Miyaura reactions of aryl chlorides using complex **1** as the catalyst

$\text{Ar}^1\text{—Cl} \quad + \quad \text{Ar}^2\text{—B(OH)}_2 \xrightarrow{\text{NHC-Pd(II) Complex}} \text{Ar}^1\text{—Ar}^2$				
	<b>5a-j</b>	<b>6a-i</b>	<b>7a-r</b>	
Entry	<b>5</b> (Ar <sup>1</sup> )	<b>6</b> (Ar <sup>2</sup> )	Product	Yield (%) <sup>a</sup>
1	<b>5a</b> (4-MeO-C <sub>6</sub> H <sub>4</sub> )	<b>6a</b> (Ph)	<b>7a</b>	99
2	<b>5b</b> (3-MeO-C <sub>6</sub> H <sub>4</sub> )	<b>6a</b> (Ph)	<b>7b</b>	98
3	<b>5c</b> (2-MeO-C <sub>6</sub> H <sub>4</sub> )	<b>6a</b> (Ph)	<b>7c</b>	90
4	<b>5d</b> (4-Me-C <sub>6</sub> H <sub>4</sub> )	<b>6a</b> (Ph)	<b>7d</b>	> 99
5	<b>5e</b> (3-Me-C <sub>6</sub> H <sub>4</sub> )	<b>6a</b> (Ph)	<b>7e</b>	> 99
6	<b>5f</b> (2-Me-C <sub>6</sub> H <sub>4</sub> )	<b>6a</b> (Ph)	<b>7f</b>	99
7	<b>5g</b> (4-CH <sub>3</sub> CO-C <sub>6</sub> H <sub>4</sub> )	<b>6a</b> (Ph)	<b>7g</b>	99
8	<b>5h</b> (4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> )	<b>6a</b> (Ph)	<b>7h</b>	94
9	<b>5i</b> (2-Pyridyl)	<b>6a</b> (Ph)	<b>7i</b>	> 99
10	<b>5j</b> (3-Pyridyl)	<b>6a</b> (Ph)	<b>7j</b>	72
11	<b>5a</b> (4-OMe-C <sub>6</sub> H <sub>4</sub> )	<b>6b</b> (4-Me-C <sub>6</sub> H <sub>4</sub> )	<b>7k</b>	> 99
12	<b>5a</b> (4-OMe-C <sub>6</sub> H <sub>4</sub> )	<b>6c</b> (3-Me-C <sub>6</sub> H <sub>4</sub> )	<b>7l</b>	99
13	<b>5a</b> (4-OMe-C <sub>6</sub> H <sub>4</sub> )	<b>6d</b> (2-Me-C <sub>6</sub> H <sub>4</sub> )	<b>7m</b>	99
14	<b>5a</b> (4-OMe-C <sub>6</sub> H <sub>4</sub> )	<b>6e</b> (2,6-Me <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> )	<b>7n</b>	74
15	<b>5a</b> (4-OMe-C <sub>6</sub> H <sub>4</sub> )	<b>6f</b> (4-F-C <sub>6</sub> H <sub>4</sub> )	<b>7o</b>	98
16	<b>5a</b> (4-OMe-C <sub>6</sub> H <sub>4</sub> )	<b>6g</b> (4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> )	<b>7p</b>	99
17	<b>5a</b> (4-OMe-C <sub>6</sub> H <sub>4</sub> )	<b>6h</b> (1-Naphthyl)	<b>7q</b>	63
18	<b>5a</b> (4-OMe-C <sub>6</sub> H <sub>4</sub> )	<b>6i</b> (2-Naphthyl)	<b>7r</b>	71

All reactions were carried out using **5** (0.50 mmol), **6** (0.75 mmol), KO<sup>t</sup>Bu (2.0 equiv), **1** (1.0 mol%) in <sup>i</sup>PrOH/H<sub>2</sub>O (1.2 mL, V:V = 1:2) at 80 °C for 4 h

<sup>a</sup>Isolated yields

phenylboronic acid as the reactants in order to evaluate the catalytic properties of complex **1** in a solvent mixture consisting of ethanol (0.5 mL) and water (1.5 mL) (Table 1). When 1.0 mol% of complex **1** was used as catalyst, and either KO<sup>t</sup>Bu, Cs<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> or NaO<sup>t</sup>Bu as the base, the corresponding biaryl product **7a** was isolated in good yields (up to 85%) after 12 h (entries 1–4). K<sub>3</sub>PO<sub>4</sub> proved to be inferior as a base, affording the product in only 21% yield (entry 5). Thus, the choice of base is crucial to the yield of the reaction [43]. The yield did not increase significantly upon varying the amount of solvent (entry 6). However, when a solvent mixture of isopropanol and water was tested, the yield of the product improved to 95% (entry 7). When the ratio of isopropanol to water was changed to 1: 2, an almost quantitative yield was obtained (entry 8). Even when the reaction time was reduced to 4 h, the product **7a** was still obtained in 99% yield (entry 10). Further reduction of the reaction time to 2 h, afforded the product in 79% yield (entry 11). When the other three complexes **2–4** were used as catalysts,

excellent yields were still achieved (91–97%, entries 12–14). Meanwhile, in a control experiment with PdCl<sub>2</sub> as catalyst, only 15% yield was obtained.

With the optimized conditions in hand, the generality and limitations of the reaction for a variety of aryl chlorides and aryl boronic acids were evaluated. As shown in Table 2, most of the coupling reactions proceeded rapidly to provide the corresponding biaryl products in good to almost quantitative yields. Both electron-donating and electron-withdrawing substituents in the phenyl ring of the aryl chlorides were tolerated, giving good results (entries 1–8). In general, ortho-, para-, and meta-substituted aryl chlorides exhibited similar reactivities in this catalytic system. To our pleasure, when heteroaromatic chlorides such as 2-chloropyridine and 3-chloropyridine were used as the substrates, the corresponding products **7i–j** were obtained in good to high yields (entries 9–10). Next, the scope of the arylboronic acid component was examined (entries 11–18). A wide range of arylboronic acids containing various

**Table 3** Catalytic Suzuki–Miyaura reactions of benzyl chlorides using complex **1** as the catalyst

$  \begin{array}{ccc}  \text{Ar}^3\text{---CH}_2\text{Cl} & + & \text{Ar}^2\text{---B(OH)}_2 \\  \textbf{8a-f} & & \textbf{6a-h}  \end{array}  \xrightarrow{\text{NHC-Pd(II) Complex}}  \begin{array}{c}  \text{Ar}^3\text{---CH}_2\text{---Ar}^2 \\  \textbf{9a-l}  \end{array}  $				
Entry	<b>8</b> (Ar <sup>3</sup> )	<b>6</b> (Ar <sup>2</sup> )	Product	Yield (%) <sup>a</sup>
1	<b>8a</b> (Ph)	<b>6b</b> (4-Me-C <sub>6</sub> H <sub>4</sub> )	<b>9a</b>	> 99
2	<b>8a</b> (Ph)	<b>6c</b> (3-Me-C <sub>6</sub> H <sub>4</sub> )	<b>9b</b>	99
3	<b>8a</b> (Ph)	<b>6d</b> (2-Me-C <sub>6</sub> H <sub>4</sub> )	<b>9c</b>	95
4	<b>8a</b> (Ph)	<b>6e</b> (2,6-Me <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> )	<b>9d</b>	75
5	<b>8a</b> (Ph)	<b>6f</b> (4-F-C <sub>6</sub> H <sub>4</sub> )	<b>9e</b>	99
6	<b>8a</b> (Ph)	<b>6g</b> (4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> )	<b>9f</b>	99
7	<b>8a</b> (Ph)	<b>6h</b> (1-Naphthyl)	<b>9g</b>	99
8	<b>8b</b> (4- <sup>i</sup> Bu-C <sub>6</sub> H <sub>4</sub> )	<b>6a</b> (Ph)	<b>9h</b>	99
9	<b>8c</b> (4-Me-C <sub>6</sub> H <sub>4</sub> )	<b>6a</b> (Ph)	<b>9i</b>	99
10	<b>8d</b> (3-Me-C <sub>6</sub> H <sub>4</sub> )	<b>6a</b> (Ph)	<b>9j</b>	99
11	<b>8e</b> (2-Me-C <sub>6</sub> H <sub>4</sub> )	<b>6a</b> (Ph)	<b>9k</b>	99
12	<b>8f</b> (4-F-C <sub>6</sub> H <sub>4</sub> )	<b>6a</b> (Ph)	<b>9l</b>	99

All reactions were carried out using **8** (0.50 mmol), **6** (0.75 mmol), KO<sup>t</sup>Bu (2.0 equiv), **1** (1.0 mol%) in <sup>i</sup>PrOH/H<sub>2</sub>O (1.2 mL, V:V = 1:2) at 80 °C for 4 h

<sup>a</sup>Isolated yields

functional groups were well tolerated, giving the desired products **7k–7r** in good to almost quantitative yields. Nevertheless, the use of sterically hindered boronic acids such as 2,6-dimethylphenylboronic acid resulted in a significant decrease in yield (entry 14). Furthermore, the reactions of heteroaromatic boronic acids, such as 3-pyridinylboronic acid or 4-pyridinylboronic acid, did not occur (data not shown in Table 2). A possible reason for this observation would be their susceptibility to hydrolysis under the reaction conditions.

In order to further evaluate the catalytic activities of these complexes, the reactions of benzyl chlorides and arylboronic acids were investigated under the same reaction conditions. All of these reactions also proceeded smoothly to afford the corresponding diarylmethanes in good to almost quantitative yields (Table 3, entries 1–12). In general, the electronic effect of the substituent has no significant effect on the

reaction. However, a slightly lower yield (75%) of **9d** was obtained when the sterically hindered 2,6-dimethylphenylboronic acid was used (entry 4). Overall, these results indicate that these dinuclear NHC–Pd(II) complexes are highly efficient catalysts for the Suzuki–Miyaura coupling of both aryl and benzyl chlorides with arylboronic acids.

## Conclusion

In conclusion, a new set of dinuclear *N*-heterocyclic carbene–palladium(II) complexes have been prepared and used as catalysts for the Suzuki–Miyaura coupling of both aryl and benzyl chlorides with arylboronic acids. Studies on further modifications of such dinuclear NHC–Pd(II) complexes



**Table 4** Crystal data and structure refinement parameters for complex **2**

	<b>2·2CH<sub>2</sub>Cl<sub>2</sub></b>
Empirical formula	C <sub>66</sub> H <sub>84</sub> Cl <sub>8</sub> N <sub>6</sub> Pd <sub>2</sub>
Mr	1457.79
Temperature (K)	291.15
Wavelength (Å)	0.71073
Crystal system	Triclinic
Crystal size (mm)	0.20×0.20×0.20
<i>a</i> (Å)	12.6745(9)
<i>b</i> (Å)	18.1032(10)
<i>c</i> (Å)	18.3027(13)
$\alpha$ (°)	73.785(6)
$\beta$ (°)	75.626(6)
$\gamma$ (°)	75.932(6)
<i>V</i> (Å <sup>3</sup> )	3837.5(4)
<i>Z</i>	2
Space group	<i>P</i> – 1
<i>D</i> <sub>calcd</sub> (g cm <sup>−3</sup> )	1.262
$\mu$ (mm <sup>−1</sup> )	0.786
$\theta$ range (°)	3.16–26.37
<i>F</i> (000)	1500.0
No. of data collected	24,087
No. of unique data	15,053
<i>R</i> (int)	0.0702
Final <i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> <sub>1</sub> = 0.0762 <i>wR</i> <sub>2</sub> = 0.1960
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1169 <i>wR</i> <sub>2</sub> = 0.2196
Largest diff peak and hole (e <sup>−</sup> Å <sup>−3</sup> )	3.64 and −1.16

and their catalytic applications in other reactions are in progress in our laboratory (Table 4).

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