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Structure–activity relationship of *N*-heterocyclic carbene–Pd(II)–imidazole complexes in Suzuki–Miyaura coupling between 4-methoxyphenyl chloride and phenylboronic acid

Huan Lv, Lei Zhu, Yi-Qiang Tang and Jian-Mei Lu*

A series of *N*-heterocyclic carbene–$PdCl_2$–imidazole [NHC–Pd(II)–Im] complexes were synthesized and the structure of most of them was unambiguously determined by X-ray single-crystal diffraction. The structure–activity relationship of these complexes was investigated for the Suzuki–Miyaura coupling between 4-methoxyphenyl chloride and phenylboronic acid, and the effect of the NHCs and Im moieties were fully discussed. The sterically hindered IPr-based complex showed the highest catalytic activity. Copyright © 2013 John Wiley & Sons, Ltd.

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Keywords: *N*-heterocyclic carbene; palladium complex; imidazole; structure–activity relationship; Suzuki–Miyaura coupling

Introduction

During the past decade, *N*-heterocyclic carbenes (NHCs) and their metal complexes have proven to be good catalysts for the formation of carbon–carbon and carbon–heteroatom bonds.[1] Recently, we developed a well-defined NHC–$PdCl_2$–1-methylimidazole [NHC–Pd(II)–Im] complex **1a** (Scheme 1) and found it to be an effective catalyst in the formation of carbon–carbon[2] and carbon–nitrogen[3] bonds using aryl chlorides as the substrates. In addition, compared to analogous structures with 3-chloropyridine,[1f,4] triethylamine,[5] diethylamine[6] and other N-donors involving structures as the 'throw-away' ligands,[7] complex **1a** showed similar catalytic activity. To understand the effect of imidazole and NHCs, we synthesized a number of NHC–Pd(II)–Im complexes, and their catalytic activities in the Suzuki–Miyaura coupling between 4-methoxyphenyl chloride **2** and phenylboronic acid **3** were investigated.

Results and discussion

Complexes **1** were prepared by a similar procedure to that previously reported.[3a] Under N_2 atmosphere, a mixture of an imidazolium (or imidazolinium) salt, $PdCl_2$, K_2CO_3 and imidazole was stirred in anhydrous THF under reflux for 20 h to provide the corresponding NHC–Pd(II)–Im complexes **1** in acceptable to good yields (Scheme 2).

Complexes **1a–1 k** are both air and moisture stable, and were fully characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, mass spectrometry, high-resolution mass spectrometry (HRMS) and/or elemental analysis. Crystals of **1a–1j** suitable for X-ray crystallography were grown in a mixture of ethyl acetate and dichloromethane (5:1), and the structures were unambiguously determined by X-ray crystallography. All complexes show a slightly distorted square-planar geometry of the Pd center with the two chloride ligands perpendicular to the plane of the NHC and the imidazole *trans* to it (for example, see ORTEP drawing of complex **1b** in Fig. 1) (see supporting information for more details).[8] (Crystals of **1 k** suitable for X-ray diffraction cannot be achieved at this stage, even though various methods were tried in this laboratory.)

Comparison of $\delta C_{carbene}$ and relevant bond distances are shown in Table 1. It can be seen that the nature of the NHC in **1** has some effect on the chemical shift of the carbene carbon. For example, the carbene carbon resonance of **1a** displays a downfield shift in the ^{13}C NMR spectrum due to sterically encumbered isopropyl groups at the *ortho* positions of the *N*-phenyl substituent compared to its methyl substituted counterparts **1c** and **1e**, implying a stronger σ-donation effect. Furthermore, the larger hindered substituents on the NHC moiety have a less *trans* influence than that of the smaller substituents, which would also account for the downfield shift of the corresponding ^{13}C NMR of the carbene carbon signal. Moreover, the same effect has been previously observed in Pd(II) complexes by Bedford and co-workers in 2010.[9] On the other hand, the imidazole moieties in the NHC–Pd(II)–Im complexes **1** have less effect on the chemical shift of the carbene carbon (Table 1, entry 1 vs. entries 7–11).

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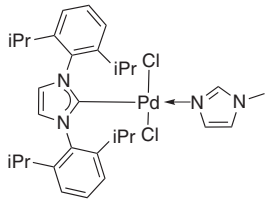
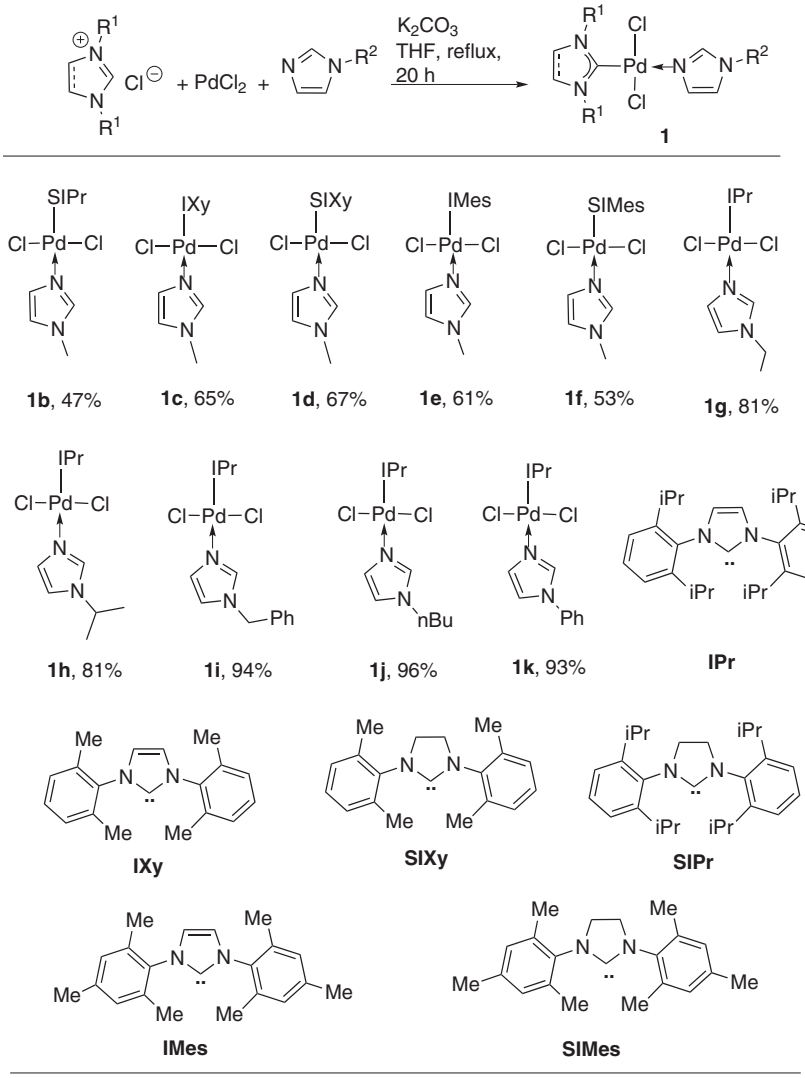
The carbene carbon chemical shift was shown to be more downfield in complex **1a** compared to its analogues **1c** and **1e**, due to the increasing steric bulk on the NHC moiety. This may suggest that a more electron-deficient metal center was formed. Table 2 compares catalytic activity of complexes **1** for the Suzuki–Miyaura coupling between 4-methoxyphenyl chloride **2** and phenylboronic acid **3**. Under the same reaction conditions, there is a clear difference in the catalytic activity between complexes **1a–1f**, which can be only attributed to the different NHC skeletons. The most bulky NHC-Pd(II)-Im complex **1a** showed the best catalytic activity (Table 2, entry 1), whereas complexes **1b–1f** showed lower activity (Table 2, entries 2–6). This illustrates that more σ-donating ligands on the metal center may facilitate the oxidative addition, and the more hindered ligands may facilitate the reductive elimination.[10] Complexes **1** with different imidazole moieties were also tested (Table 2, entries 7–11). Similar results were observed when complexes **1 g**, **1 h** and **1i** were used as the catalysts (Table 2, entries 7–9) suggesting that the imidazole moieties in **1** have less effect on their catalytic activities. Nevertheless, somewhat lower yields were observed when complexes **1j** and **1 k** were employed (Table 2, entries 10 and 11), which may be partially attributed to their solubility in the mixture solvent of THF and H_2O because both of them are more lipophilic than their counterparts such as **1a**, **1 g**, **1 h** and **1i**.



Scheme 1. NHC–Pd(II)–Im complex **1a**.



Scheme 2. Synthesis of NHC–Pd(II)–Im complexes **1**.

Conclusions

A few NHC–Pd(II)–Im complexes have been synthesized and were fully characterized by ^{1}H NMR, ^{13}C NMR, MS, HRMS and/or elemental analysis. The structures have been confirmed by X-ray single-crystal diffraction. The structure–activity relationship was investigated in the Suzuki–Miyaura coupling between 4-methoxyphenyl chloride and phenylboronic acid. The sterically bulky, unsaturated IPr–Pd(II) complexes demonstrated the highest activity, while the imidazole moieties in the complexes have less effect on the catalytic activity.

Experimental

General Remarks

Melting points are uncorrected. NMR spectra were recorded at 300/500 (for ^{1}H NMR) or 75/125 MHz (for ^{13}C NMR), respectively. ^{1}H NMR and ^{13}C NMR spectra recorded in $CDCl_3$ solutions were referenced to tetramethylsilane (TMS) (0.00 ppm) and the residual solvent peak (77.0 ppm), respectively. *J*-values are in Hz. Organic solvents used were dried by standard methods. Other commercially obtained reagents were used without further purification. Flash column chromatography was performed on silica gel (300–400 mesh).

General Procedure for the Synthesis of NHC–Pd(II)–Im Complexes 1

Under N_2 atmosphere, a mixture of imidazolium salt (1.2 mmol), $PdCl_2$ (1.0 mmol), K_2CO_3 (1.0 mmol) and 1-methylimidazole (4.0 mmol) was stirred in anhydrous THF (6.0 ml) under reflux for 20 h. The solvent was then removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (CH_2Cl_2) to give the pure NHC–Pd(II)–Im complex **1b** as a yellow solid (47%). The single crystal for X-ray diffraction was obtained by recrystallization from CH_2Cl_2 and ethyl acetate.

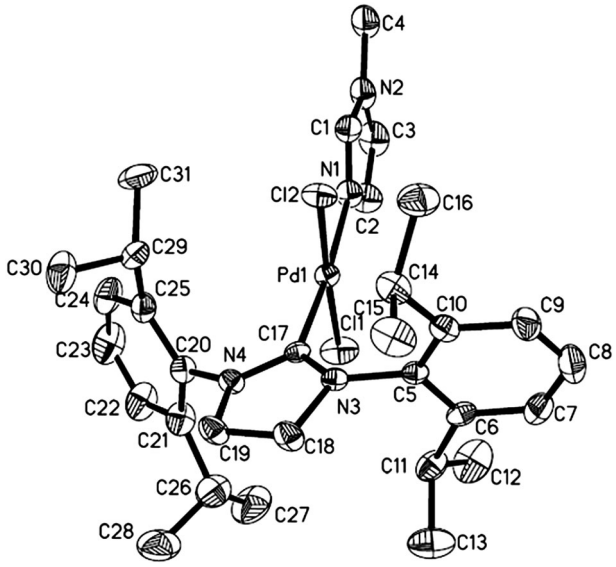
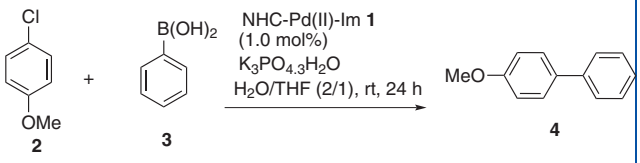


Figure 1. ORTEP drawing of complex **1b** with thermal ellipsoids at the 30% probability level and anisotropic displacement parameters. H atoms have been omitted. Selected bond distances (Å) and angles (deg.): Pd1—C17 = 1.962(3) Å, Pd1—N1 = 2.110(3) Å, Pd1—Cl1 = 2.301(1) Å, Pd1—Cl2 = 2.303(1) Å, C17—Pd1—N1 = 174.97(12)°, C17—Pd1—Cl2 = 86.74(9)°, N1—Pd1—Cl2 = 90.28(10)°, C17—Pd1—Cl1 = 92.52(9)°, N1—Pd1—Cl1 = 90.66(10)°, Cl1—Pd1—Cl2 = 177.04(4)°.

Table 1. Comparison of $\delta C_{carbene}$ and Pd—$C_{carbene}$ and Pd—N bond distances

Entry	Complexes	$\delta C_{carbene}$	Pd—$C_{carbene}$ (Å)	Pd—N (Å)
1[2a]	**1a**	156.5	1.954(5)	2.088(4)
2	**1b**	187.3	1.962(3)	2.110(3)
3	**1c**	154.2	1.986(3)	2.117(3)
4	**1d**	185.6	1.965(2)	2.092(2)
5[2a]	**1e**	154.0	1.971(3)	2.097(3)
6	**1f**	185.4	1.957(6)	2.089(5)
7	**1g**	156.5	1.969(4)	2.092(4)
8	**1h**	156.6	1.953(4)	2.084(4)
9	**1i**	156.3	1.965(2)	2.098(2)
10	**1j**	156.3	1.964(4)	2.091(4)
11	**1k**	156.0	—	—

Table 2. Catalytic activity of complexes **1** with the Suzuki–Miyaura coupling between 4-methoxyphenyl chloride **2** and phenylboronic acid **3** as the model



Entry[a]	Complexes **1**	Yield (%)[b]
1[2a]	**1a**	91
2	**1b**	53
3	**1c**	50
4	**1d**	48
5[c]	**1e**	70
6	**1f**	41
7	**1g**	84
8	**1h**	80
9	**1i**	86
10	**1j**	66
11	**1k**	55

[a]All reactions were carried out using **2** (0.5 mmol), **3** (0.6 mmol), **1** (1.0 mol%), $K_3PO_4.3H_2O$ (2.0 equiv.) in H_2O (2.0 ml) and THF (1.0 ml) at room temperature for 24 h.

[b]Isolated yields.

Compounds **1a**,[3a] **1e**[3a] and **4**[2a] are all known and were fully determined according to previously reported data.

Compound **1b**: a yellow solid; m.p. 270 °C (decomposed). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.25 (d, J = 6.6 Hz, 12H, 2CH(CH_3)$_2$), 1.55 (d, J = 6.6 Hz, 12H, 2CH(CH_3)$_2$), 3.45 (s, 3H, NCH_3), 3.59 (hept, J = 6.6 Hz, 4H, 4CH(CH_3)$_2$), 4.02 (s, 4H, NCH_2CH_2N), 6.52 (s, 1H, CH CH—NCH_3 in the imidazole moiety), 7.15 (s, 1H, CH CH—NCH_3 in the imidazole moiety), 7.27 (d, J = 6.6 Hz, 4H, 2C—CH CH—CH C in the phenyl moiety), 7.38 (t, J = 6.6 Hz, 2H, 2C—CH CH—CH C in the phenyl moiety), 7.66 (s, 1H, N CH—N in the imidazole moiety). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.2 (CH_3), 26.8 (CH_3), 28.7 (CH(CH_3)$_2$), 33.9 (NCH_3), 53.8 (NCH_2CH_2N), 118.9 (N—CH CH—NCH_3 in the imidazole moiety), 124.4 (Ar), 128.5 (N—CH CH—NCH_3 in the imidazole moiety), 129.2 (Ar), 135.5 (Ar), 138.2 (N CH—N in the imidazole moiety), 147.5 (Ar), 187.3 (carbene atom). IR (neat) ν 2961, 2862, 2331, 2087, 1673, 1583, 1533, 1448, 1358, 1325, 1262, 1189, 1103, 1053, 932, 801, 753, 730 cm^{-1}. HRMS (ESI): calcd for $C_{31}H_{44}Cl_2N_4NaPd$ $[M+Na]^+$: 671.1876; found: 671.1876. Anal. calcd for $C_{32}H_{44}Cl_2N_4Pd$ requires C, 57.28%; H, 6.82%; N, 8.62%; found: C, 57.27%; H, 6.82%, N, 6.83%.

Compound **1c**: a yellow solid; m.p. 287 °C (decomposed). ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 2.41 (s, 12H, 4CH_3), 3.44 (s, 3H, NCH_3), 6.53 (s, 1H, CH CH—NCH_3 in the imidazole moiety), 7.07 (s, 2H, CH CH), 7.18 (s, 1H, CH CH—NCH_3 in the imidazole moiety), 7.21 (d, J = 7.5 Hz, 4H, 2C—CH CH—CH C in the phenyl moiety), 7.31 (t, J = 7.5 Hz, 2H, 2C—CH CH—CH C in the phenyl moiety), 7.72 (s, 1H, N CH—N in the imidazole moiety). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.2 (CH_3), 33.9 (NCH_3), 118.9 (N—CH CH—NCH_3 in the imidazole moiety), 123.9 (CH CH), 128.5 (N—CH CH—NCH_3 in the imidazole moiety), 129.3 (Ar), 136.7 (Ar), 137.7 (Ar), 138.4 (N CH—N in the imidazole moiety), 154.2 (carbene atom). IR (neat) ν 2968, 1534, 1467, 1361, 1278, 1219, 1103, 1090, 940, 773, 741, 730, 700 cm^{-1}. HRMS (ESI): calcd for $C_{23}H_{26}Cl_2N_4NaPd$ $[M+Na]^+$: 557.0465; found: 557.0502. Anal. calcd for $C_{23}H_{26}Cl_2N_4Pd$ requires C, 51.56%; H, 4.89%; N, 10.46%; found: C, 51.78%; H, 4.99%, N, 10.32%.

Compound **1d**: a yellow solid; m.p. 256 °C (decomposed). ^{1}H NMR ($CDCl_3$, 500 MHz TMS) δ 2.62 (s, 12H, 4CH_3), 3.43 (s, 3H, NCH_3), 4.03 (s, 4H, NCH_2CH_2N), 6.51 (s, 1H, CH CH—NCH_3 in the imidazole moiety), 7.12 (s, 1H, CH CH—NCH_3 in the imidazole moiety), 7.17 (d, = 7.5 Hz, 4H, 2C—CH CH—CH C in the phenyl moiety), 7.22 (t, = 7.5 Hz, 2H, 2C—CH CH—CH C in the phenyl moiety), 7.67 (s, 1H, s, 1H, N CH—N in the imidazole moiety). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.5 (CH_3), 33.9 (NCH_3), 50.9 (NCH_2CH_2N), 118.9 (N—CH CH—NCH_3 in the imidazole moiety), 128.4 (N—CH CH—NCH_3 in the imidazole moiety), 128.6 (Ar), 128.7 (Ar), 137.55 (Ar), 137.57 (Ar y), 138.3 (N CH—N in the imidazole moiety), 185.6 (carbene atom). IR (neat) ν 1534, 1484, 1448, 1404, 1305, 1272, 1252, 1103, 947, 775, 738, 728 cm^{-1}. HRMS (ESI): calcd for

$C_{23}H_{28}Cl_2N_4NaPd$ $[M+Na]^+$: 559.0621; found: 559.0590. Anal. calcd for $C_{23}H_{28}Cl_2N_4Pd$ requires C, 51.36%; H, 5.25%; N, 10.42%; found: C, 51.34%; H, 5.24%, N, 10.40%.

Compound **1f**: a yellow solid; m.p. 251 °C (decomposed). ^{1}H NMR ($CDCl_3$, 500 MHz TMS) δ 2.30 (s, 6H, 2CH_3), 2.57 (s, 12H, 4CH_3), 3.44 (s, 3H, NCH_3), 3.99 (s, 4H, NCH_2CH_2N), 6.52 (s, 1H, CH C*H*—NCH_3 in the imidazole moiety), 6.98 (s, 4H, C*H* in the phenyl moiety), 7.15 (s, 1H, C*H* CH—NCH_3 in the imidazole moiety), 7.70 (s, 1H, N C*H*—N in the imidazole moiety). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.3 (CH_3), 21.1 (CH_3), 33.9 (NCH_3), 51.0 (NCH_2CH_2N), 118.8 (N—C*H* CH—NCH_3 in the imidazole moiety), 128.4 (N—CH C*H*—NCH_3 in the imidazole moiety), 129.4 (Ar), 135.1 (Ar), 137.1 (Ar), 138.1 (Ar), 138.4 (N C*H*—N in the imidazole moiety), 185.4 (carbene atom). IR (neat) ν 1968, 1530, 1484, 1448, 1262, 1229, 1103, 945, 851, 740 cm^{-1}. HRMS (ESI): calcd for $C_{25}H_{32}Cl_2N_4NaPd$ $[M+Na]^+$: 587.0935; found: 587.0891. Anal. calcd for $C_{25}H_{32}Cl_2N_4Pd$ requires C, 53.06%; H, 5.70%; N, 9.90%; found: C, 53.07%; H, 5.68%, N, 9.94%.

Compound **1 g**: a yellow solid; m.p. 263 °C (decomposed). ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 1.11 (d, J = 6.5 Hz, 12H, 2CH(CH_3)$_2$), 1.27 (t, J = 7.5 Hz, 3H, CH_2CH_3), 1.47 (d, J = 6.5 Hz, 12H, 2CH(CH_3)$_2$), 3.18 (hept, J = 6.5 Hz, 4H, 4C*H*(CH_3)$_2$), 3.75 (q, J = 7.5 Hz, 2H, NCH_2CH_3), 6.59 (s, 1H, CH C*H*—NCH_2CH_3 in the imidazole moiety), 7.09 (s, 2H, C*H* C*H*), 7.17 (s, 1H, C*H* CH—NCH_2CH_3 in the imidazole moiety), 7.33 (d, J = 8.0 Hz, 4H, 2C—C*H* CH—C*H* C in the phenyl moiety), 7.47 (t, J = 8.0 Hz, 2H, 2C—CH C*H*—CH C in the phenyl moiety), 7.72 (s, 1H, N C*H*—N in the imidazole moiety). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.7 (CH_2CH_3), 23.2 (CH_3), 26.2 (CH_3), 28.6 (C*H*(CH_3)$_2$), 42.5 (NCH_2CH_3), 117.2 (N—C*H* CH—NCH_2CH_3 in the imidazole moiety), 123.9 (Ar), 124.8 (Ar), 128.5 (N—CH C*H*—NCH_2CH_3 in the imidazole moiety), 130.0 (Ar), 135.2 (Ar), 137.2 (N C*H*—N in the imidazole moiety), 146.6 (Ar), 156.5 (carbene atom). IR (neat) ν 2968, 1527, 1461, 1441, 1262, 1109, 1086, 1056, 942, 834, 799, 760, 733, 703 cm^{-1}. HRMS (ESI): calcd for $C_{32}H_{44}Cl_2N_4NaPd$ $[M+Na]^+$: 683.1876; found: 683.1872. Anal. calcd for $C_{32}H_{44}Cl_2N_4Pd$ requires C, 58.05%; H, 6.70%; N, 8.46%; found: C, 58.32%; H, 6.90%, N, 8.28%.

Compound **1 h**: a yellow solid; m.p. 296 °C (decomposed). ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 1.11 (d, J = 7.0 Hz, 12H, 2CH(CH_3)$_2$), 1.30 (d, J = 7.0 Hz, 6H, NCH(CH_3)$_2$), 1.47 (d, J = 7.0 Hz, 12H, 2CH(CH_3)$_2$), 3.19 (hept, J = 7.0 Hz, 4H, 4C*H*(CH_3)$_2$), 4.11 (hept, J = 7.0 Hz, 1H, NC*H*(CH_3)$_2$), 6.63 (s, 1H, CH C*H*—$NCH(CH_3)_2$ in the imidazole moiety), 7.09 (s, 2H, C*H* C*H*), 7.17 (s, 1H, C*H* CH—$NCH(CH_3)_2$ in the imidazole moiety), 7.33 (d, J = 7.5 Hz, 4H, 2C—C*H* CH—C*H* C in the phenyl moiety), 7.47 (t, J = 7.5 Hz, 2H, 2C—CH C*H*—CH C in the phenyl moiety), 7.74 (s, 1H, N C*H*—N in the imidazole moiety). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.2 (CH_3), 26.2 (CH_3), 28.6 (C*H*(CH_3)$_2$), 49.9 (NC*H*(CH_3)$_2$), 115.3 (N—C*H* CH—$NCH(CH_3)_2$ in the imidazole moiety), 123.9 (Ar), 124.8 (Ar), 128.4 (N—CH C*H*—$NCH(CH_3)_2$ in the imidazole moiety), 130.0 (Ar), 135.2 (Ar), 136.0 (N C*H*—N in the imidazole moiety), 146.6 (Ar), 156.6 (carbene atom). IR (neat) ν 2961, 2862, 1514, 1461, 1404, 1341, 1265, 1202, 1113, 1083, 1056, 940, 800, 756, 733 cm^{-1}. HRMS (ESI): calcd for $C_{33}H_{46}Cl_2N_4NaPd$ $[M+Na]^+$: 697.2033; found: 697.2013. Anal. calcd for $C_{33}H_{46}Cl_2N_4Pd$ requires C, 58.63%; H, 6.86%; N, 8.29%; found: C, 58.72%; H, 7.31%, N, 7.96%.

Compound **1i**: a yellow solid; m.p. 198–199 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 1.11 (d, J = 6.5 Hz, 12H, 2CH(CH_3)$_2$), 1.47 (d, J = 6.5 Hz, 12H, 2CH(CH_3)$_2$), 3.18 (hept, J = 6.5 Hz, 4H, 4C*H*(CH_3)$_2$), 4.86 (s, 2H, NCH_2Ph), 6.51 (s, 1H, CH C*H*—NCH_2Ph in the imidazole moiety), 7.04–7.06 (m, 2H, C*H* in the phenyl moiety), 7.09 (s, 2H, C*H* C*H*), 7.21 (s, 1H, C*H* CH—NCH_2Ph in the imidazole moiety), 7.27–7.29 (m, 3H, C*H* in the phenyl moiety), 7.32 (d, J = 7.5 Hz, 4H, 2C—C*H* CH—C*H* C in the phenyl moiety), 7.47 (t, J = 7.5 Hz, 2H, 2C—CH C*H*—CH C in the phenyl moiety), 7.85 (s, 1H, N C*H*—N in the imidazole moiety). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.3 (CH_3), 26.2 (CH_3), 28.7 (C*H*(CH_3)$_2$), 51.5 (NCH_2Ph), 117.9 (N—C*H* CH—NCH_2Ph in the imidazole moiety), 124.0 (Ar), 124.9 (Ar), 127.7 (Ar), 128.5 (N—CH C*H*—NCH_2Ph in the imidazole moiety), 128.8 (Ar), 128.9 (Ar), 130.1 (Ar), 134.7 (Ar), 135.2 (Ar), 138.0 (N C*H*—N in the imidazole moiety), 146.7 (Ar), 156.3 (carbene atom). IR (neat) ν 2961, 2862, 1517, 1454, 1341, 1103, 1083, 1056, 969, 942, 801, 755, 732, 703 cm^{-1}. HRMS (ESI): calcd for $C_{37}H_{46}Cl_2N_4NaPd$ $[M+Na]^+$: 745.2034; found: 745.2031. Anal. calcd for $C_{37}H_{46}Cl_2N_4Pd$ requires C, 61.37%; H, 6.40%; N, 7.74%; found: C, 61.35%; H, 6.68%, N, 7.17%.

Compound **1j**: a yellow solid; m.p. 279 °C (decomposed). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.86 (t, J = 7.5 Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.11 (d, J = 6.9 Hz, 12H, 2CH(CH_3)$_2$), 1.19–1.29 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.47 (d, J = 6.9 Hz, 12H, 2CH(CH_3)$_2$), 3.19 (hept, J = 6.9 Hz, 4H, 4C*H*(CH_3)$_2$), 3.69 (t, J = 7.5 Hz, 2H, NCH_2CH_2CH_2CH_3), 6.57 (s, 1H, CH C*H*—NC_4H_9 in the imidazole moiety), 7.08 (s, 2H, C*H* C*H*), 7.18 (s, 1H, C*H* CH— NC_4H_9 in the imidazole moiety), 7.32 (d, J = 7.5 Hz, 4H, 2C—C*H* CH—C*H* C in the phenyl moiety), 7.47 (t, J = 7.5 Hz, 2H, 2C—CH C*H*—CH C in the phenyl moiety), 7.72 (s, 1H, N C*H*—N in the imidazole moiety). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4 ($NCH_2CH_2CH_2CH_3$), 19.7 ($NCH_2CH_2CH_2CH_3$), 23.3 (CH(CH_3)$_2$), 26.3 (CH(CH_3)$_2$), 28.7 (C*H*(CH_3)$_2$), 32.5 ($NCH_2CH_2CH_2CH_3$), 47.5 ($NCH_2CH_2CH_2CH_3$), 117.7 (N—C*H* CH—NC_4H_9 in the imidazole moiety), 124.0 (Ar), 124.8 (Ar), 128.4 (N—CH C*H*—N C_4H_9 in the imidazole moiety), 130.0 (Ar), 135.3 (Ar), 137.6 (N C*H*—N in the imidazole moiety), 146.7 (Ar), 156.3 (carbene atom). IR (neat) ν 2954, 2915, 2855, 1520, 1457, 1404, 1345, 1109, 1086, 1053, 969, 939, 843, 801, 756, 748, 740, 733 cm^{-1}. HRMS (ESI): calcd for $C_{34}H_{48}Cl_2N_4NaPd$ $[M+Na]^+$: 711.2190; found: 711.2158. Anal. calcd for $C_{34}H_{48}Cl_2N_4Pd$ requires C, 59.17%; H, 7.01%; N, 8.12%; found: C, 59.21%; H, 7.20%, N, 7.81%.

Compound **1 k**: a yellow solid; m.p. 196–197 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, TMS) δ 1.12 (d, J = 7.0 Hz, 12H, 2CH(CH_3)$_2$), 1.48 (d, J = 7.0 Hz, 12H, 2CH(CH_3)$_2$), 3.20 (hept, J = 7.0 Hz, 4H, 4C*H*(CH_3)$_2$), 6.95 (s, 1H, CH C*H*—NPh in the imidazole moiety), 7.11 (s, 2H, C*H* C*H*), 7.20 (d, J = 7.0 Hz, 2H, CH in the phenyl moiety), 7.32–7.40 (m, 8H, CH in the phenyl moiety and imidazole moiety), 7.47 (t, J = 7.5 Hz, 2H, 2CH C*H*—CH C in the phenyl moiety), 8.10 (s, 1H, N C*H*—N in the imidazole moiety). ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.3 (CH_3), 26.3 (CH_3), 28.7 (C*H*(CH_3)$_2$), 117.3 (N—C*H* CH—NPh in the imidazole moiety), 121.7 (Ar), 124.0 (Ar), 124.9 (Ar), 128.1 (N—CH C*H*—NPh in the imidazole moiety), 129.3 (Ar), 129.8 (Ar), 130.1 (Ar), 135.2 (Ar), 136.6 (N C*H*—N in the imidazole moiety), 136.7 (Ar), 146.7 (Ar), 156.0 (carbene atom). IR (neat) ν 2961, 2862, 1511, 1461, 1302, 1262, 1202, 1056, 801, 735, 702 cm^{-1}. MS (ESI): 731 $[M+Na]^+$; HRMS (ESI): calcd for $C_{36}H_{44}Cl_2N_4NaPd$ $[M+Na]^+$: 731.1877; found: 731.1847.

General Procedure for the Suzuki–Miyaura Coupling between 4-Methoxyphenyl Chloride 2 and Phenylboronic Acid 3

Under N_2 atmosphere, phenylboronic acid **3** (0.6 mmol), NHC–Pd (II)–Im complex **1a** (1.0 mol%), $K_3PO_4.3H_2O$ (2.0 equiv.), H_2O (2.0 ml), and THF (1.0 ml) were added to a Schlenk reaction tube, then 4-methoxyphenyl chloride **2** (0.5 mmol) was added. The mixture was stirred at room temperature for 24 h. The mixture was then extracted with EtOAc, dried over anhydrous Na_2SO_4 and purified by flash column chromatography to give pure product **4** as a white solid.

Crystal Structure Determination of NHC–Pd(II)–Im Complexes 1

Single-crystal data were collected on a Bruker Smart APEX CCD diffractometer and graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Structure solution and refinement were carried out with the program package SHELXTL-PLUS version 5.1.[11] All the non-hydrogen atoms were refined with anisotropic displacement parameters using full-matrix, least-squares technique.

The crystallographic data for complexes **1b–d** and **1f–j** have been included in the supporting information.

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Supporting Information

Additional supporting information may be found in the online version of this article at the publisher's web site.

The crystal data of compounds **1** can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ (fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk), reference numbers CCDC-808377, -818903, -808367, -808368, -819946, -824878, 818754, -828919 and -882158.