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吖啶作为辅助配体的 N-杂环卡宾-钯(II)化合物: 合成、表征和催化应用

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摘要 以咪唑鎓盐、氯化钯和吖啶等为起始原料, 经一锅法反应方便地合成了两种新颖的 N-杂环卡宾-钯(II)化合物. 新化合物通过 ^{1}H NMR, ^{13}C NMR 和元素分析等手段进行了结构表征, 结构通过 X 射线单晶衍射进行了确定. 此外, 所获得的钯(II)化合物可以作为芳基或苄基氯化合物与芳基硼酸的 Suzuki-Miyaura 偶联反应高效催化剂. 在优化的反应条件下, 所有拓展的底物都能成功地发生反应, 并得到较好的收率.

关键词 N-杂环卡宾; 钯; 吖啶; Suzuki-Miyaura 偶联反应

N-Heterocyclic Carbene-Palladium(II) Complexes with Acridine Ligand: Synthesis, Characterization and Catalytic Applications

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Abstract Two novel *N*-heterocyclic carbene-palladium(II) complexes were conveniently synthesized through one-pot reactions of imidazolium salts, palladium chloride and acridine. The new complexes have been fully characterized by ^{1}H NMR, ^{13}C NMR, elemental analysis, and X-ray single-crystal diffraction. Moreover, the obtained palladium(II) complexes were the effective catalyst precursors for the Suzuki-Miyaura coupling of aryl as well as benzyl chlorides with arylboronic acids. Under the optimal conditions, all reactions proceeded successfully to give the desired products in good to almost quantitative yields.

Keywords N-heterocyclic carbene; palladium; acridine; Suzuki-Miyaura cross-coupling

The cross-coupling of organic halides and organoboron reagents, known as the Suzuki-Miyaura coupling stands out as one of the most powerful, convenient, and versatile methods to create carbon-carbon bonds and thus has found widespread applications in advanced materials, natural products and organic synthesis.[1~9] Most published examples concern the use of aryl iodides and bromides in the reaction, but the application of aryl chlorides[10~13] has recently attracted much attention mainly due to their economic reason of low cost, availability and stability. Recently, N-heterocyclic carbene (NHC)-palladium complexes,[14~18] as an important and fascinating subclass of palladium catalysts, have been developed and shown good catalytic activity in the Suzuki-Miyaura coupling of aryl chlorides. For example, the PEPPSI (pyridine, enhanced, precatalyst, preparation, stabilization, initiation) NHC-palladium complexes[19~22] readily catalyzed the Suzuki-Miyaura coupling reaction of aryl chlorides with arylboronic acids in good yields. The NHC-Pd(II)-Im complexes[23~28] acting as highly effective pre-catalysts can perform the Suzuki-Miyaura coupling of aryl as well as benzyl chlorides with arylboronic acids under mild conditions. Strassner *et al.*[29] have explored the applications of the NHC-Pd(II)-2-phenylimidazole complexes for the Suzuki-Miyaura cross-coupling reaction of aryl chlorides and the reaction was found to tolerate a wide range of substrates at low catalyst loadings. The catalytic activities of imine-Pd-NHC complexes were evaluated for more chal-

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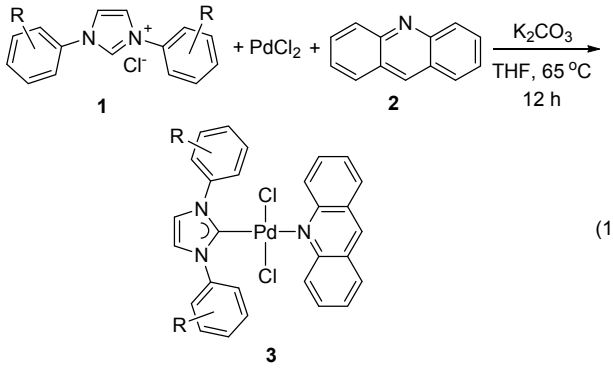
lenging Suzuki-Miyaura cross-coupling reaction of aryl chlorides.[30] Dinuclear NHC-palladium complexes containing various bridging ligands have also been reported to be active catalyst precursors for the coupling reactions.[31~33] In our previous work, the N-heterocyclic carbene-palladium(II) complexes with benzoxazole or benzothiazole ligands were developed, which were used as effective catalysts for the Suzuki-Miyaura coupling of aryl as well as benzyl chlorides with arylboronic acids.[34] Although these species have been found to be particularly useful as catalysts in the Suzuki-Miyaura coupling of aryl chlorides, the development of easily prepared, and highly reactive NHC-Pd(II) complexes still constitutes a challenging endeavor in current organometallic chemistry. Encouraged by the results mentioned above and also in continuation of our interest in the construction of functionalized complexes, herein we would like to report the synthesis and structural characterization of N-heterocyclic carbene palladium(II) complexes with acridine as ancillary ligands (Eq. 1). The application of the obtained complexes in the Suzuki-Miyaura coupling of aryl and benzyl chlorides with arylboronic acids is also presented below.



(1)

a: R = *o*,*o*′-(*i*-Pr)$_2$ (67%); **b**: R = *o*,*p*,*o*′-Me$_3$ (55%)

1 Results and disscussion

1.1 Synthesis and characterization of the palladium(II) complexes

According to our previous report,[34] the synthesis of the required N-heterocyclic carbene-palladium(II) complexes **3** was easily done in a one-step sequence from commercially available imidazolium salts, palladium chloride, and acridine as shown in Eq. 1. The expected palladium(II) complexes **3** were isolated in good yields after purification and fully characterized by ^{1}H NMR, ^{13}C NMR, and elemental analysis. The molecular structures of Pd complexes **3a** and **3b** were unambiguously determined by X-ray single crystal analysis. The molecules are illustrated in Figures 1 and 2, respectively. Complexes **3a** and **3b** showed slightly distorted-square-planar configuration for the central palladium atom. The two chloride anions perpendicular to the plane of the NHC ligands and the acridine is *trans* to it. All of the bond lengths and angles around the Pd(II) center in the two complexes are similar. The values of bond lengths and angles also compare well to those of the related NHC-Pd(II) complexes with N-containing compounds.[34] The Pd—N bond lengths (around 2.100 Å) in complexes **3a** and **3b** are slightly longer than that of Pd—C$_{carbene}$ (around 1.975 Å), the Pd—Cl(1) and Pd—Cl(2) bond lengths are nearly identical. The angles of C$_{carbene}$—Pd—N and Cl(1)—Pd—Cl(2) are almost close to 180°, while the C$_{carbene}$—Pd—Cl(1) angles, C$_{carbene}$—Pd—Cl(2) angles, N—Pd—Cl(1) angles and N—Pd—Cl(2) angles are almost close to 90°.

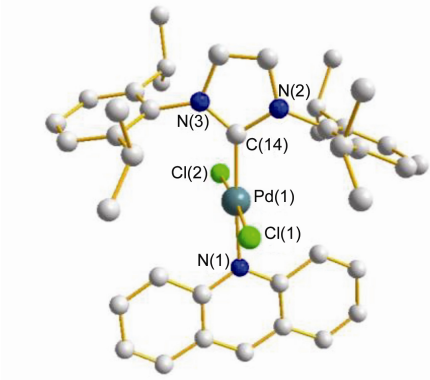


Figure 1 Molecular structures of the Pd(II) complexes **3a**
Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°) in complex **3a**: Pd(1)—C(14) 1.981(10), Pd(1)—N(1) 2.109(10), Pd(1)—Cl(1) 2.313(3), Pd(1)—Cl(2) 2.290 (3); C(14)—Pd(1)—Cl(1) 91.6(3), N(1)—Pd(1)—Cl(1) 88.7(3), C(14)—Pd(1)—Cl(2) 90.2(3), N(1)—Pd(1)—Cl(2) 89.7(3), C(14)—Pd(1)—N(1) 176.7(4), Cl(1)—Pd(1)—Cl(2) 175.73(13).

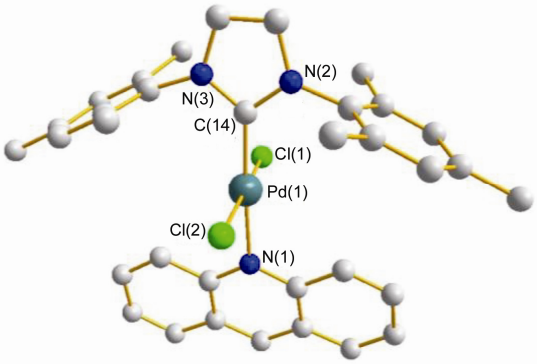


Figure 2 Molecular structures of the Pd(II) complexes **3b**
Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°) in complex **3b**: Pd(1)—C(14) 1.972(4), Pd(1) — N(1) 2.095(3), Pd(1) — Cl(1) 2.3005(12), Pd(1) — Cl(2) 2.2993(12); C(14) — Pd(1) — Cl(1) 90.30(11), N(1) — Pd(1) — Cl(1) 87.54(10), C(14) — Pd(1) — Cl(2) 93.16(11), N(1) — Pd(1) — Cl(2) 89.11(10), C(14) — Pd(1) — N(1) 176.66(15), Cl(1) — Pd(1) — Cl(2) 175.81(5).

1.2 Suzuki-Miyaura coupling reaction

In order to test the catalytic activities of the N-heterocyclic carbene-palladium(II) complexes **3a** and **3b**, initial experiments were carried out using 1-chloro-4-methoxybenzene and phenylboronic acid as the reactants, plus complex **3a** as the catalyst, in *i*-PrOH-H$_2$O at 80 ℃, with the results shown in Table 2. The choice of base proved to have an important influence on the reaction (Table 2, Entries 1～9).[35] Cs$_2$CO$_3$ was found to be the most effective among the

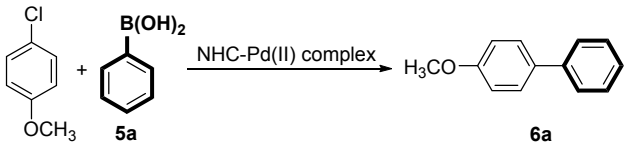
Table 1 Summary of crystallographic details for complexes **3a** annd **3b**

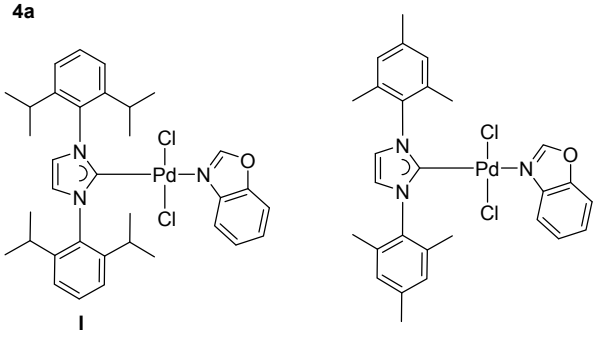
	3a•CH_2Cl_2	**3b**•CH_2Cl_2
Empirical formula	$C_{41}H_{47}Cl_4N_3Pd$	$C_{35}H_{35}Cl_4N_3Pd$
M_r	830.02	745.86
Temperature/K	301(2)	298(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Cryst size/mm^3	0.35×0.32×0.28	0.28×0.26×0.13
a/Å	13.3144(17)	12.6455(4)
b/Å	14.7975(18)	16.2574(5)
c/Å	21.804(3)	17.324(6)
α/(°)	90	90
β/(°)	103.742(4)	96.6480(10)
γ/(°)	90	90
V/Å^3	4172.8(9)	3537.2(2)
Z	4	4
Space group	$P2(1)/n$	$P2(1)/c$
D_{calcd}/(g•cm^{-3})	1.321	1.401
μ/mm^{-1}	0.732	0.854
θ range/(°)	2.92～25.00	2.98～26.00
F(000)	1712	1520
No. of data collected	46724	55414
No. of unique data	7313	6923
R(int)	0.0827	0.0613
Final R indices [$I>2\sigma(I)$]	R_1=0.1047	R_1=0.0517
R indices (all data)	R_1=0.1342	R_1=0.0763

tested bases in this case (Table 2, Entries 6 and 9). When 1.0 mol% complex **3a** was tested, the yield decreased (Table 2, Entry 10). In addition, *i*-PrOH mixed with an equal volume of water was found to be the most appropriate solvent, giving the biaryl product in a ＞99% yield (Table 2, Entry 6 vs. Entries 11～13). The complex **3b** was less efficient than **3a** under identical conditions (Entry 6 vs. Entry 14). Fortunately, in this system, the N-heterocyclic carbene- palladium(II) complexes **3** were found to exhibit better catalytic activity compared with a related NHC-Pd(II) catalyst (complex **I** or **II**) in the Suzuki-Miyaura coupling reaction. For example, in the presence of 2.0 mol% N-heterocyclic carbene-palladium(II) complex **I**, very low yield of the corresponding product **6a** was obtained (Entry 15). While similar results were also observed when the palladium(II) complex **II** was used as the catalyst (Entry 16). We speculate that the possible reasons were ascribed to the different coordination ability acridine and benzoxazole. However, the other N-heterocyclic carbene-palladium(II) complex **III** was examined, and similar yield was also achieved (95% yield, Entry 17).

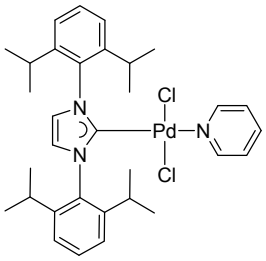
With the optimized conditions in hand, a series of aryl chlorides were first used as reactants with phenylboronic acid to test the generality of the reaction. As shown in Table 3, most of the coupling reactions proceeded efficiently to give the corresponding biaryl products **6a**～**6j** in good to excellent yields. Both electron-donating and withdrawing substitutets on the aryl chlorides were tolerated and yields

Table 2 Optimization of reaction conditions for Suzuki-Miyaura reaction of 1-chloro-4-methoxybenzene with phenylboronic acid catalyzed by the NHC-Pd(II) complexes[a]





I II



III

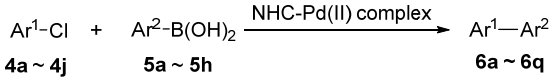
Entry	Cat.	Base	Solvent (V∶V)	Yield[b]/%
1	**3a**	KOBu-*t*	*i*-PrOH/H_2O (1∶1)	＞99
2	**3a**	K_2CO_3	*i*-PrOH/H_2O (1∶1)	89
3	**3a**	K_3PO_4	*i*-PrOH/H_2O (1∶1)	800
4	**3a**	Na_2CO_3	*i*-PrOH/H_2O (1∶1)	88
5	**3a**	NaOBu-*t*	*i*-PrOH/H_2O (1∶1)	97
6	**3a**	Cs_2CO_3	*i*-PrOH/H_2O (1∶1)	＞99
7	**3a**	$NaHCO_3$	*i*-PrOH/H_2O (1∶1)	31
8[c]	**3a**	KOBu-*t*	*i*-PrOH/H_2O (1∶1)	54
9[c]	**3a**	Cs_2CO_3	*i*-PrOH/H_2O (1∶1)	81
10[d]	**3a**	Cs_2CO_3	*i*-PrOH/H_2O (1∶1)	89
11	**3a**	Cs_2CO_3	*i*-PrOH/H_2O (1∶2)	74
12	**3a**	Cs_2CO_3	*i*-PrOH/H_2O (1∶3)	48
13	**3a**	Cs_2CO_3	EtOH/H_2O (1∶1)	85
14	**3b**	Cs_2CO_3	*i*-PrOH/H_2O (1∶1)	81
15	**I**	Cs_2CO_3	*i*-PrOH/H_2O (1∶1)	54
16	**II**	Cs_2CO_3	*i*-PrOH/H_2O (1∶1)	35
17	**III**	Cs_2CO_3	*i*-PrOH/H_2O (1∶1)	95

[a] All reactions were carried out using **4a** (0.20 mmol), **5a** (0.30 mmol), base (2.0 equiv.), Cat. (2.0 mol%) in solvent (2.0 mL) at 80 ℃ for 3 h. [b] Isolated yields. [c] Reaction time was 2 h. [d] Cat. (1.0 mol%).

of 79%～＞99% were obtained for **6a**～**6h**. Whilst the *ortho*-substituents showed some negative effect on the yields of the catalysis products **6c** and **6f**. To our pleasure, when heteroaromatic aryl chlorides such as 2-chloropyridine and 3-chloropyridine were used as the substrates, high

yields of the corresponding products were observed (**6i** and **6j**). Subsequently, the scope of complex **3a** catalytic system was further investigated with respect to arylboronic acids (Entries 11～17). In most cases, the reaction worked well and approached to corresponding products in good to almost quantitative yields under identical conditions. However, sterically hindered boronic acid such as 2,6-dimethylphenylboronic acid resulted in a significant decrease in yield (100% yield). In addition, in the case of 3-pyridinylboronic acid or 4-pyridinylboronic acid afforded trace amounts of product under the present reaction conditions (data not shown in Table 3). Overview, the results indicated that complex **3a** was still efficient in the catalytic process.

Table 3 Substrate scope for the catalytic Suzuki-Miyaura reaction of aryl chlorides using the NHC-Pd(II) complex **3a** as the catalyst[a]

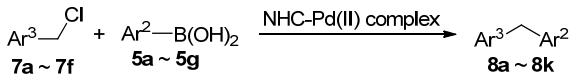


Entry	Ar^1	Ar^2	Product	Yield[b]/%
1	4-$MeOC_6H_4$	Ph	**6a**	＞99
2	3-$MeOC_6H_4$	Ph	**6b**	99
3	2-$MeOC_6H_4$	Ph	**6c**	93
4	4-MeC_6H_4	Ph	**6d**	99
5	3-MeC_6H_4	Ph	**6e**	95
6	2-MeC_6H_4	Ph	**6f**	79
7	4-$CH_3COC_6H_4$	Ph	**6g**	99
8	4-$O_2NC_6H_4$	Ph	**6h**	99
9	2-Pyridyl	Ph	**6i**	98
10	3-Pyridyl	Ph	**6j**	86
11	4-$MeOC_6H_4$	4-MeC_6H_4	**6k**	99
12	4-$MeOC_6H_4$	3-MeC_6H_4	**6l**	96
13	4-$MeOC_6H_4$	2-MeC_6H_4	**6m**	91
14	4-$MeOC_6H_4$	4-FC_6H_4	**6n**	99
15	4-$MeOC_6H_4$	4-$CF_3C_6H_4$	**6o**	98
16	4-$MeOC_6H_4$	1-Naphthyl	**6p**	91
17	4-$MeOC_6H_4$	2-Naphthyl	**6q**	99

[a]All reactions were carried out using **4** (0.20 mmol), **5** (0.30 mmol), Cs_2CO_3 (2.0 equiv.), Cat. **3a** (2.0 mol%) in *i*-PrOH/H_2O [V∶V=1∶1 (2.0 mL)] at 80 ℃ for 3 h. [b] Isolated yields.

Inspired by these successful results, we then turned our interest to such transformations using the benzyl chlorides as the substrates. As shown in Table 4, all reactions proceed smoothly to afford diarylmethanes in good to almost quantitative yields under identical conditions. Particularly, when sterically hindered boronic acids such as 2-methylphenylboronic acid were used as the substrates, high yield of the corresponding product was always observed (99% yield, Entry 3). Overview, the above results confirm that the present *N*-heterocyclic carbene-palladium(II) complexes are highly efficient catalysts for the Suzuki-Miyaura coupling of aryl as well as benzyl chlorides with arylboronic acids.

Table 4 Substrate scope for the catalytic Suzuki-Miyaura reaction of benzyl chlorides using the NHC-Pd(II) complex **3a** as the catalyst[a]



Entry	Ar^3	Ar^2	Product	Yield[b]/%
1	Ph	4-MeC_6H_4	**8a**	＞99
2	Ph	3-MeC_6H_4	**8b**	99
3	Ph	2-MeC_6H_4	**8c**	99
5	Ph	4-FC_6H_4	**8d**	99
6	Ph	4-$CF_3C_6H_4$	**8e**	98
7	Ph	1-Naphthyl	**8f**	96
8	4-*t*-BuC_6H_4	Ph	**8g**	99
9	4-MeC_6H_4	Ph	**8h**	99
10	3-MeC_6H_4	Ph	**8i**	99
11	2-MeC_6H_4	Ph	**8j**	99
12	4-FC_6H_4	Ph	**8k**	98

[a]All reactions were carried out using **7** (0.20 mmol), **5** (0.30 mmol), Cs_2CO_3 (2.0 equiv), Cat. **3a** (2.0 mol%) in *i*-PrOH/H_2O [V∶V=1∶1 (2.0 mL)] at 80 ℃ for 3 h. [b] Isolated yields.

2 Conclusion

In summary, the easily available, well-defined *N*-heterocyclic carbene-palladium(II) complexes **3a** and **3b**, being derived from the corresponding imidazolium salts, palladium chloride and acridine, showed good catalytic activity in the Suzuki-Miyaura coupling of aryl chlorides and benzyl chlorides with arylboronic acids. Further ex ploration of these *N*-heterocyclic carbene-palladium(II) complexes and their catalytic applications in other reactions is in progress.

3 Experimental

3.1 Apparatus and reagents

Melting points were measured on a XT4A melting point apparatus and uncorrected. ^{1}H NMR and ^{13}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. Reactions for the preparation of *N*-heterocyclic carbene-palladium(II) complexes were carried out under nitrogen atmosphere. Solvents were dried with standard methods and freshly distilled prior to use if needed. All other chemicals were used as purchased.

3.2 Synthesis of *N*-heterocyclic carbene-palladium (II) complexes

Under an N_2 atmosphere, the mixture of imidazolium salts (1.1 mmol), acridine (2.0 mmol, 358.4 mg), $PdCl_2$ (1.0 mmol, 177.3 mg) and K_2CO_3 (1.1 mmol, 152.0 mg) was stirred in anhydrous tetrahydrofuran (THF) (10 mL) under reflux for 16 h. After cooling, filtration and evaporation, the residue was purified by preparative thin layer chromatography (TLC) on silica gel plates eluting with CH_2Cl_2 to

afford the corresponding N-heterocyclic carbene-palladium(II) complexes **3a** and **3b**.

trans-[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]-(acridine)-palladium(II) dichloride (**3a**): 67% yield, orange solids. m.p. 143～145 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.17 (d, J=8.7 Hz, 2H, ArH), 8.61 (s, 1H, ArH), 7.77 (d, J=5.2 Hz, 2H, ArH), 7.71～7.67 (m, 2H, ArH), 7.55～7.54 (m, 6H, ArH), 7.40 (s, 2H, ArH), 7.29 (s, 2H, ArH), 3.32～3.30 [m, 4H, C**H**$(CH_3)_2$], 1.44 (d, J = 5.8 Hz, 12H, C**H**$_3$CHCH_3), 1.15 (d, J=6.1 Hz, 12H, CH_3CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.6, 147.6, 147.5, 138.7, 135.3, 131.2, 130.2, 128.9, 127.9, 127.2, 125.8, 124.8, 123.9, 29.0, 26.7, 22.6; IR (KBr) v: 3118, 3085, 2960, 2925, 2865, 1621, 1522, 1460, 1442, 1383, 1363, 1348, 1333, 1268, 926, 800, 756, 731, 707, 602, 499 cm^{-1}; MS (ESI$^+$) m/z: 708.1 (M－Cl). Anal. calcd for $C_{40}H_{45}Cl_2N_3Pd$: C 64.48, H 6.09, N 5.64; found C 64.43, H 6.10, N 5.66.

trans-[1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]-(acridine)-palladium(II) dichloride (**3b**): 55% yield, orange solids. m.p. 135～138 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.15 (d, J=8.7 Hz, 2H, ArH), 8.66 (s, 1H, ArH), 7.82 (d, J=8.0 Hz, 2H, ArH), 7.56 (t, J=7.4 Hz, 2H, ArH), 7.45 (t, J=6.9 Hz, 2H, ArH), 7.25 (s, 6H, ArH), 2.56 (s, 6H, CH_3), 2.46 (s, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.6, 147.7, 139.2, 138.8, 137.2, 135.2, 131.4, 129.2, 128.5, 128.0, 127.2, 125.9, 123.8, 21.4, 19.3; IR (KBr) v: 3160, 3127, 2917, 1620, 1570, 1521, 1484, 1460, 1411, 1369, 1339, 1279, 1231, 1154, 1038, 1010, 910, 861, 783, 733, 707, 601 cm^{-1}; MS (ESI$^+$) m/z: 624.0 (M－Cl)$^+$. Anal. calcd for $C_{34}H_{33}Cl_2N_3Pd$: C 61.78, H 5.03, N 6.36; found C 61.73, H 5.10, N 6.39.

3.3 General procedure for the catalytic Suzuki-Miyaura reaction

A Schlenk flask was charged with aryl chlorides (0.20 mmol), arylboronic acids (0.30 mmol), N-heterocyclic carbene-palladium(II) complex **3** (2.0 mol%), Cs_2CO_3 (2.0 equiv., 651.6 mg), *i*-PrOH (1.0 mL) and H_2O (1.0 mL). The mixture was stirred at 80 ℃ for 3 h. After cooling, the reaction mixture was evaporated and the product was isolated by preparative TLC on silica gel plates.

3.4 Crystal structure determination and data collection

Crystals of **3a** and **3b** were obtained by recrystallization from CH_2Cl_2/*n*-hexane at ambient temperature. Their data were collected on an Oxford Diffraction Gemini E diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The structures were 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, which used the SHELXL-97 crystallographic software package.[36,37] The hydrogen atoms were included but not refined. Details of the crystal structure determination of the Pd(II) complexes are summarized in Table S1 in the Supporting Information. CCDCs 1499311 and 1499312 contain the crystallographic data for complexes **3a** and **3b**, respectively.

Supporting Information ^{1}H NMR, ^{13}C NMR spectra of compounds **3a** and **3b** and the ^{1}H NMR spectra of catalysis products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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