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Room Temperature Suzuki Reactions in Aqueous Media under Air by Palladium(II) Complexes with Pyrazole Derived Ligands

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Two new palladium complexes with pyrazole derived ligands **2a**–**2b** have been easily prepared and well characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, and IR spectra. Their detailed structures are determined by a single-crystal X-ray analysis of **2a**. The two compounds were successfully applied to the Suzuki coupling reactions of aryl bromides with phenylboronic acid, in aqueous solution at room temperature under air, giving the desired coupled products in good to excellent yields with catalyst loadings as low as 0.01–0.05 mol-%.

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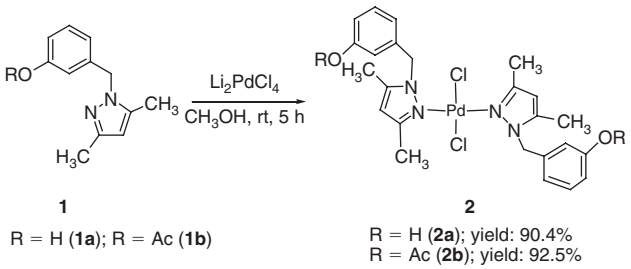
Introduction

The palladium-catalyzed Suzuki reaction of aryl halides with boronic acids is one of the most widely studied transition metal catalyst reactions for the formation of C–C bonds.[1–5] A plethora of palladium catalysts, usually simple palladium salts or palladium complexes with appropriate ligands have been successfully used in this C–C coupling reaction under various reaction conditions. Among them, phosphine ligand-based palladium catalysts; especially those with bulky, electron-rich phosphine ligands; have proved to be highly efficient for the activation of notoriously unreactive aryl chlorides.[6–9] However, the high price usually associated with phosphines along with their negative environmental effect and air-sensitivity, have encouraged researchers to explore alternatives for phosphines. In this regard, Pd(II) complexes with nitrogen-containing ligands became attractive due to their low cost and toxicity, easy accessibility, and insensitivity to oxygen under aerobic conditions. Some recent examples of such complexes are monodentate *N*-coordinated palladium-amine complexes[10] and palladium-benzimidazole complexes[11,12] or bidentate *N*-coordinated palladium complexes.[13,14] Particularly, the benzimidazolium-pyrazole-palladium complexes are found to be active catalysts for the Suzuki reaction of unactivated aryl bromides with arylboronic acids at room temperature under aerobic conditions with turnover frequencies (TOF) reaching as high as 60000 h^{-1}.[14] During our continuous research on Suzuki reactions,[15–20] we have been interested in the development of highly stable and also active palladium catalysts that can be used in aqueous solution at room temperature under air. For this purpose, we synthesized two new palladium complexes with pyrazole derived ligands **2a**–**2b** (Scheme 1) and investigated their catalytic activity in room temperature Suzuki reactions. The introduction of a hydroxy group in the benzene ring in complex **2a** was enlightened by the literature results that room temperature Suzuki couplings in MeOH/H_2O proceeded much more quickly with a *p*-hydroxyacetophenone-oxime derived palladacycle as a catalyst, than with acetophenone-oxime derivative (5 h versus 4 days to afford similar turn over numbers), although the two palladacycles promoted the reactions at comparable speed in refluxing water.[21] Complex **2b** with AcO-group in the benzene ring was prepared for comparison with **2a**.



1

R = H (**1a**); R = Ac (**1b**)

2

R = H (**2a**); yield: 90.4%
R = Ac (**2b**); yield: 92.5%

Scheme 1.

Results and Discussion

Synthesis and Characterization of Complexes 2a–2b

The pyrazolyl-containing *m*-phenol derivative **1a** was prepared from commercially available 3-hydroxybenzaldehyde in three steps by reduction of the aldehyde, bromination, and nucleophilic substitution with 3,5-dimethyl pyrazole. Acetylation of hydroxy group in ligand **1a** by acetyl chloride easily afforded ligand **1b**. Then **1a** or **1b** was reacted with Li_2PdCl_4 in MeOH at room temperature for 5 h (Scheme 1). The resulting yellow precipitate was collected and washed with CH_2Cl_2 to provide the corresponding Pd(II) complexes **2a** or **2b** in excellent yields. The two new palladium complexes are stable towards moisture and air. They were each characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, and IR spectra. The molecular structure

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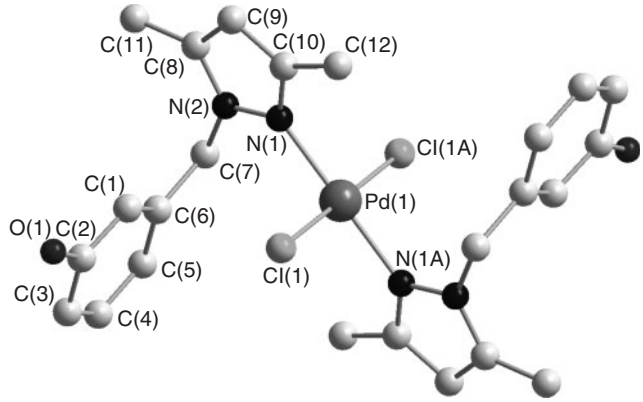


Fig. 1. Molecular structure of complex **2a**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] are as follows: Pd(1)–N(1) 2.011(2), Pd(1)–N(1A) 2.011(2), Pd(1)–Cl(1) 2.3073(9), Pd(1)–Cl(1A) 2.3073(9), N(1)–N(2) 1.360(3), N(1)–C(10) 1.339(4), N(2)–C(8) 1.353(4), N(2)–C(7) 1.458(4) and N(1A)–Pd(1)–N(1) 180.000(1), N(1A)–Pd(1)–Cl(1A) 89.63(8), N(1)–Pd(1)–Cl(1A) 90.37(8), N(1A)–Pd(1)–Cl(1) 90.37(8), N(1)–Pd(1)–Cl(1) 89.63(8), Cl(1A)–Pd(1)–Cl(1) 180.0.

of **2a** was further confirmed by a single-crystal X-ray analysis. Although X-ray analysis clearly indicates that complex **2a** adopts a *trans*-geometry in the solid state with the two chlorine atoms being in a *trans*-position (see Fig. 1), the ^{1}H NMR and ^{13}C NMR spectra of **2a** as well as **2b** are more complicated than the expected *trans*-structure, suggesting the existence of other isomers in solution. For example, the ^{1}H NMR spectrum of **2a** exhibits two singlets at δ 6.14 and 5.88 ppm, for the benzyl–CH_2 protons. The signals for the pyrazole proton are observed at δ 6.11 and 6.09 ppm as two singlets, and four singlets at δ 2.76, 2.54, 2.09, and 2.07 ppm are assigned to the –CH_3 in the pyrazole ring. For complex **2b**, the corresponding singlets appear at 6.18 and 5.75 ppm, 5.92 and 5.89 ppm as well as 2.88, 2.55, 2.09, and 2.05 ppm, respectively. The ^{13}C NMR spectra of **2a** and **2b** also exhibited more signals than expected. The complex NMR spectra of **2a** and **2b** are most likely due to the presence of both *trans*- and *cis*- structures in solution. Another possibility is that all species are *trans*-, whereas the benzyl groups may be in a *syn*- and *anti*- configuration.

Crystal Structure

The molecular structure of complex **2a** is shown in Fig. 1. The Pd atom has a square-planar coordination geometry, which is bonded to two chlorine atoms and two nitrogen atoms from two ligands of pyrazolyl-containing *m*-phenol derivative **1a**. Each of the chlorine and nitrogen atoms are in the *trans*-position, with bond angles of N(1A)–Pd(1)–N(1) being 180.000(1)° and Cl(1A)–Pd(1)–Cl(1) being 180.0°. All the bond distances and angles around Pd(II) centre are similar to those observed in the related monodentate *N*-coordinated palladium-benzimidazole[12,22] or pyrazole complexes.[23]

In complex **2a**, chlorine atom forms hydrogen bond with the adjacent –OH group of aryl ring (Cl1···H1E = 2.356 Å, Cl1···H1E-O1 = 167.7°). Intermolecular π-stacking interactions involving the neighbouring benzene rings are also evident in the crystal structure. The interplane distance and angle are ~3.5107 Å and 0°, respectively. Owing to the π-π stacking effects and OH···Cl hydrogen bonds, the crystal structure of **2a** is extended into a 2D architecture (Fig. 2).

Suzuki Coupling Reactions

Many *N*-based compounds have been reported to be efficient ligands for the Suzuki reactions, in most cases the reactions were carried out in organic solvent at elevated temperature (60–110°C) and/or under an inert atmosphere.[12,17,24–26] Room temperature Suzuki reactions under aerobic conditions could be accomplished by using a simple amine/$Pd(OAc)_2$[10] or glyoxal bis(*N*-methyl-*N*-phenylhydrazone)/$Pd(OAc)_2$ system[13] with a Pd loading as high as 2 mol-%. The catalyst loadings could be lowered to 0.01–0.5 mol-% with benzimidazolium-pyrazole-palladium(II) complexes[14] or *N*-phenylurea-palladium(II) complexes[27] as catalysts with the coupling of aryl bromides and boronic acids at room temperature in alcohol-water media under aerobic conditions. Very recently, phosphine free diaminodiol based palladium catalysts were also demonstrated to be effective in room temperature Suzuki reactions in MeOH under aerobic conditions with typical catalyst loadings ranging 0.5–1 mol-%.[28] Based on the literature results and our own experience with Suzuki reactions,[15–20] we tested the catalytic activity of complexes **2a** and **2b** in the Suzuki reactions by performing the reactions at room temperature in EtOH-water media, under air in the presence of *n*-Bu_4NBr (TBAB), with K_2CO_3 as a base. It was believed that TBAB would act as a phase-transfer catalyst under aqueous conditions and could also stabilize catalytically active palladium nanoparticles, thereby avoiding aggregation.[29] The results are shown in Table 1. At the beginning 0.5 mol-% of complex **2a** was used as the catalyst. It was found that a variety of electronically and structurally diverse aryl bromides coupled efficiently with phenylboronic acid giving the corresponding biaryl products in excellent yields after 12 h. These aryl bromides included electron-neutral *para*- and *ortho*-bromotoluene, electron-rich *para*-, and *ortho*-bromoanisole as well as electron-deficient *para*- and *meta*-bromonitrobenzene (Table 1, entries 1, 5, 9, 17, 21, 24). Surprisingly, the electron-deficient *ortho*-bromonitrobenzene only gave a 35% yield under the same reaction conditions (entry 25). When a heteroaryl bromide, such as 2-bromothiophene, was used as the coupling partner, a moderate yield was obtained (66%, entry 26). Further studies indicated that the catalyst loading could be lowered to 0.05 mol-% without obvious loss of activity except in the case of 2-bromothiophene. The two complexes **2a** and **2b** exhibited comparable activity under the same conditions, with complex **2b** being slightly more active in most cases. Good yields could be achieved in a shorter reaction time of 4.5 h with 0.05 mol-% of **2b,** or after 12 h with only 0.01 mol-% of **2b** in the coupling of *para*-bromoanisole with phenylboronic acid (85% and 76% yields, respectively; Table 1, entries 15, 16). The effect of TBAB in the same coupling reaction was also investigated. Excellent yields could also be obtained in the presence of 0.5 mol-% of **2b** without the addition of TBAB (92%, entry 10). While a moderate yield was obtained with 0.05 mol-% of **2b** in the absence of TBAB (79%, entry 14), indicating that TBAB could accelerate the coupling especially at lower catalyst loadings. The above results indicated that complexes **2a** and **2b** were much more active than the related pyrazole-based bidentate ligand-palladium complexes shown in Fig. 3.[30] It was reported that ligand **3**, in combination with Pd, did not catalyze the Suzuki coupling reaction at all. The deposition of Pd black commenced after 1 h at room temperature or within a few minutes at 65–70°C. Although ligands **4a** and **4c** could promote the

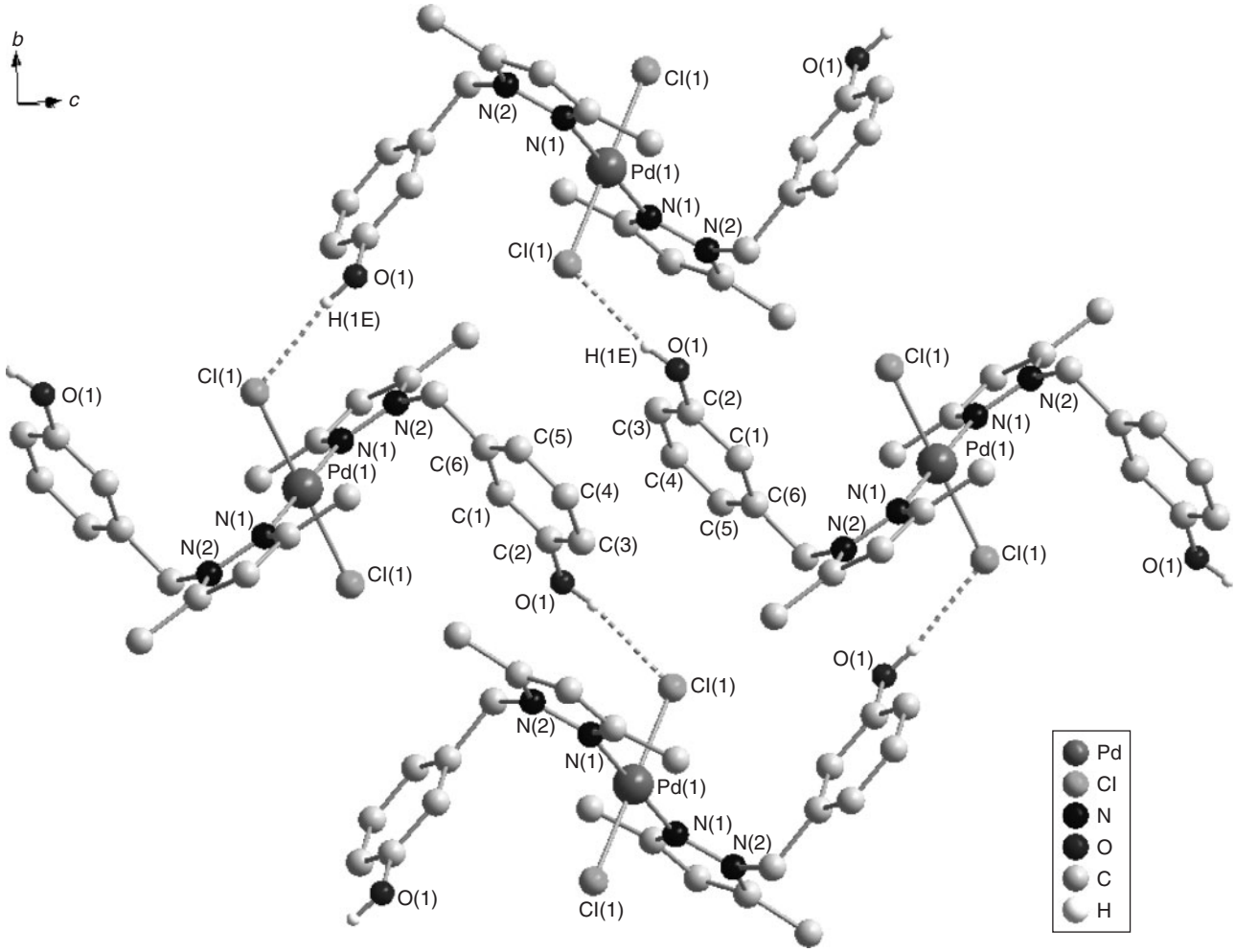


Fig. 2. 2D lamellar structure of complex **2a** formed by hydrogen bonds and π–π interactions. Non-hydrogen bonding H atoms have been omitted for clarity.

coupling of *para*-bromoanisole with phenylboronic acid at 45°C, affording the coupled product in moderate yields (around 70%), in the presence of 1 mol-% of $Pd_2(dba)_3$, neither of them were effective at room temperature. The same coupling was observed at room temperature when ligand **4b** or **4d** with 1 mol-% of $Pd_2(dba)_3$ were used. In this case, the catalyst loading was obviously high and the yields of the products were moderate (77–78% after 10 h).[30]

The coupling of non-activated and activated aryl chlorides with phenylboronic acid, as catalyzed by **2**, was also investigated. Unfortunately, formation of the coupled products was not observed in any appreciable amounts with a catalyst loading of 1 mol-%, under the same reaction conditions as those applied to the aryl bromides at room temperature (data not shown in Table 1).

In conclusion, we have demonstrated that easily accessible and stable palladium complexes **2** are highly active catalysts for the Suzuki coupling of aryl bromides with phenylboronic acid in aqueous media at room temperature under air. The present catalytic process is easy to handle and the reaction conditions are mild, affording the desired coupled products in high yields.

Experimental

General

3,5-dimethylpyrazole[31] and pyrazolyl-containing *m*-phenol derivative **1a**[18] were prepared according to literature methods. Li_2PdCl_4 (0.1 mol L^{-1} in CH_3OH) was obtained by stirring $PdCl_2$ and two equivalent of anhydrous LiCl in CH_3OH at room temperature for 20 h. All other chemicals were used as purchased. Melting points were measured using a WC-1 microscopic apparatus and were uncorrected. Elemental analyses were determined with a Thermo Flash EA 1112 elemental analyzer. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer, with TMS as an internal standard.

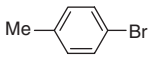
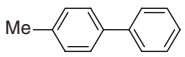
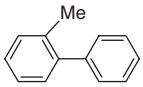
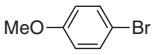
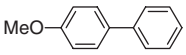
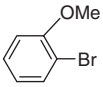
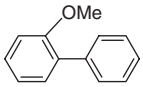
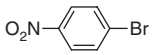
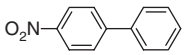
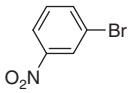
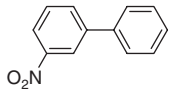
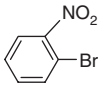
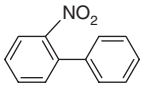
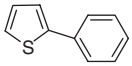
General Method for the Synthesis of Palladium(II) Complexes *2a–2b*

A mixture of pyrazolyl-containing *m*-phenol derivative **1a** (202 mg, 1.0 mmol), acetyl chloride (85 μL, 1.2 mmol), and sodium hydride (48 mg, 2.0 mmol) in 10 mL of CH_2Cl_2 was stirred at room temperature for 12 h. Then the reaction was quenched with water. The aqueous layer was extracted with dichloromethane, and the organic layers were dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by preparative TLC on silica gel plates eluting with CH_2Cl_2/AcOEt (1:1) to afford **1b** as an oil (150 mg, 61.5% yield).

1b: δ_H (400 MHz, $CDCl_3$) 7.31 (t, $J = 7.9$ Hz, 1H, Ar–H), 6.98 (dd, $J = 1.9$, 7.9 Hz, 1H, Ar–H), 6.93 (d, $J = 7.9$ Hz, 1H, Ar–H), 6.79 (s, 1H, Ar–H), 5.85 (s, 1H, Pz–H), 5.21 (s,

Table 1. Suzuki coupling reactions of aryl bromides with phenylboronic acid catalyzed by complexes 2a–2b

Reaction conditions: aryl bromide (0.5 mmol), $PhB(OH)_2$ (0.6 mmol), K_2CO_3 (1.0 mmol), *n*-Bu_4NBr (0.5 mmol), C_2H_5OH/H_2O 2 mL (v/v = 1:1), at room temperature under air for 12 h

Entry	Aryl bromide	Cat. [mol-%]	Product	Yield[A] [%]	Turn over numbers[B]
1		**2a** (0.5)		>99	198
2		**2a** (0.1)		>99	990
3		**2a** (0.05)		94	1880
4		**2b** (0.05)		>99	1980
5		**2a** (0.5)		>99	198
6		**2a** (0.1)		92	920
7		**2a** (0.05)		87	1740
8		**2b** (0.05)		>99	1980
9		**2a** (0.5)		>99	198
10[C]		**2b** (0.5)		92	184
11		**2a** (0.1)		>99	990
12		**2a** (0.05)		>99	1980
13		**2b** (0.05)		>99	1980
14[C]		**2b** (0.05)		79	1580
15[D]		**2b** (0.05)		85	1700
16		**2b** (0.01)		76	7600
17		**2a** (0.5)		97	194
18		**2a** (0.1)		97	970
19		**2a** (0.05)		93	1860
20		**2b** (0.05)		>99	1980
21		**2a** (0.5)		>99	198
22		**2a** (0.05)		96	1920
23		**2b** (0.05)		92	1840
24		**2a** (0.5)		96	192
25		**2a** (0.5)		35	70
26		**2a** (0.5)		66	132
27		**2a** (0.1)		43	430
28		**2a** (0.05)		39	780
29		**2b** (0.05)		45	900

[A]Isolated yields based on aryl bromide.
[B]TON = mol of product/mol of the catalyst.
[C]*n*-Bu_4NBr was not added.
[D]Reaction time 4.5 h.

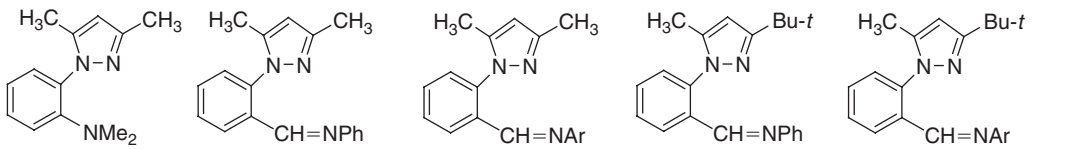


Fig. 3. Pyrazole-based bidentate ligands for the palladium-catalyzed Suzuki reaction reported in ref. [30].

2H, CH_2), 2.27 (s, 3H, Ac), 2.24 (s, 3H, CH_3), 2.15 (s, 3H, CH_3). δ_C (100 MHz, $CDCl_3$): δ 169.3, 150.9, 147.7, 139.2, 139.1, 129.7, 123.9, 120.7, 119.7, 105.6, 52.1, 21.1, 13.5, 11.1. ν_{max}(KBr)/cm^{-1} 2927, 1764, 1601, 1554, 1451, 1376, 1308, 1205, 1142, 1018, 786, 704.

To a stirred solution of ligand **1a** (101 mg, 0.5 mmol) or **1b** (122 mg, 0.5 mmol) in CH_3OH (10 mL) was added dropwise a solution of Li_2PdCl_4 in CH_3OH (0.1 mol L^{-1}, 5 mL) at room temperature. The reaction mixture was stirred at rt for 5 h. The resultant yellow precipitate was collected and washed with

CH_2Cl_2 to give **2a** (263 mg, 90.4% yield) or **2b** (308 mg, 92.5% yield).

2a: m.p. >270°C. δ_H (400 MHz, DMSO-d_6): The complex exists as a mixture of isomers in solution with a ratio of ~1.1:1. 9.45 (s, 1H, Ar–OH), 9.37 (s, 1H, Ar–OH), 7.14 (t, $J = 7.8$ Hz, 1H, Ar–H), 7.01 (t, $J = 7.8$ Hz, 1H, Ar–H), 6.85 (d, $J = 7.6$ Hz, 1H, Ar–H), 6.73–6.64 (m, 4H, Ar–H), 6.50 (s, 1H, Ar–H), 6.14 (s, 2H, CH_2), 6.11 (s, 1H, Pz–H), 6.09 (s, 1H, Pz–H), 5.88 (s, 2H, CH_2), 2.76 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.07 (s, 3H, CH_3). δ_C (100 MHz, DMSO-d_6): δ 157.3, 148.8, 148.7, 143.5, 137.0, 136.9, 129.4, 129.2, 117.6, 117.5, 114.4, 114.3, 113.9, 113.7, 107.6, 107.5, 53.0, 52.8, 14.6, 14.4, 11.3. ν_{max}(KBr)/cm^{-1} 3349, 2958, 1725, 1620, 1591, 1553, 1476, 1402, 1307, 1215, 1152, 1071, 1036, 957, 867, 801, 767, 685, 610. Found: C 48.90, H 4.84, N 9.48%. Calcd for $C_{24}H_{28}Cl_2N_4O_2Pd$: C 49.54, H 4.85, N 9.63%.

2b: m.p. 192–193°C. δ_H (400 MHz, $CDCl_3$): The complex exists as a mixture of isomers in solution with a ratio of ~1.2:1. The ratio changed to ~2:1 after the sample solution was placed at room temperature for 3–4 days. 7.39 (t, $J = 8.0$ Hz, 1H, Ar–H), 7.28–7.26 (m, 1H, Ar–H), 7.24–7.18 (m, 2H, Ar–H), 7.06 (d, $J = 8.0$ Hz, 1H, Ar–H), 6.98–6.93 (m, 3H, Ar–H), 6.18 (s, 2H, CH_2), 5.92 (s, 1H, Pz–H), 5.89 (s, 1H, Pz–H), 5.75 (s, 2H, CH_2), 2.88 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 2.28 (s, 3H, Ac), 2.27 (s, 3H, Ac), 2.09 (s, 3H, CH_3), 2.05 (s, 3H, CH_3). δ_C (100 MHz, $CDCl_3$): δ 169.5, 151.0, 150.9, 150.5, 150.4, 143.7, 137.0, 136.9, 129.9, 129.5, 124.7, 124.3, 121.3, 121.0, 120.6, 120.3, 108.3, 108.1, 53.4, 52.8, 21.2, 15.2, 14.9, 12.0, 11.9. ν_{max}(KBr)/cm^{-1} 2925, 1764, 1591, 1558, 1443, 1373, 1318, 1205, 1144, 1014, 952, 891, 817, 791, 720, 692. Found: C 50.43, H 4.84, N 8.30%. Calcd for $C_{28}H_{32}Cl_2N_4O_4Pd$: C 50.50, H 4.84, N 8.41%.

General Procedure for the Suzuki Reactions

A tube was charged with aryl bromide (0.5 mmol), phenylboronic acid (0.6 mmol), K_2CO_3 (1.0 mmol), the catalyst **2** (0.0025 mmol, 0.5 mol-%) or a catalyst solution in EtOH (0.00005 or 0.00025 mmol mL^{-1}), *n*-Bu_4NBr (0.5 mmol), and EtOH-H_2O (2 mL, v/v = 1:1) under air. The reaction mixture was stirred at room temperature for 12 h (time not optimized). Water was subsequently added, and the aqueous phase was extracted with dichloromethane. The combined organic layers were washed with water, dried over $MgSO_4$, filtered, and evaporated. The products were isolated by flash chromatography on silica gel (the purified products were identified by comparison of melting points with the literature values or by ^{1}H NMR spectra).

X-ray Crystallography

The crystals of **2a** were obtained by recrystallization from dimethylsulfoxide at room temperature. The crystallographic data of **2a** was measured on a Rigaku-Raxis-IV X-ray diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 291(2) K. The hydrogen atoms were included but not refined. The full-matrix least-squares calculations on F^2 were applied on the final refinement. The structure was solved by direct methods. All non-hydrogen atoms were described anisotropically. Its raw data were corrected and the structure was solved using the *SHELXL-97* program. Crystal data for **2a**: $C_{24}H_{28}Cl_2N_4O_2Pd$: $M = 581.80$, monoclinic, space group: P2(1)/n, $a = 8.7926(18)$ Å, $b = 12.601(3)$ Å, $c = 11.494(2)$ Å, $\alpha = 90°$, $\beta = 101.43(3)°$, $\gamma = 90°$, $V = 1248.2(4)$ Å^3, $Z = 2$, $D_c = 1.548$ g cm^{-3}, $\mu = 0.986$ mm^{-1}, $F(000) = 592$, *hkl* ranges: $0 \le h \le 10$, $-15 \le k \le 15$, $-14 \le l \le 13$, θ range: 2.43° to 26.00°, 4187 reflections, 2380 unique ($R_{int} = 0.0284$), completeness to θ 26.00° 97.4%, max. and min. transmission 0.8582 and 0.8272, data/restraints/parameters 2380/0/156, goodness-of-fit on F^2 1.097, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0350$, $wR_2 = 0.0898$, R indices (all data): $R_1 = 0.0412$, $wR_2 = 0.0931$, extinction coefficient 0.0184(15), largest diff. peak and hole 0.460 and −0.476 e Å^{-3}. CCDC reference number 748824.

Accessory Publication

The Accessory Publication contains ^{1}H NMR and ^{13}C NMR spectra of ligand **1b** as well as those of palladium complexes **2a** and **2b**. It is available from the Journal's website.

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