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Ferrocenylimidazoline palladacycles: Syntheses, crystal structures and applications as catalysts for Suzuki cross coupling reaction in water

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Abstract

The air and moisture stable triphenylphosphine (PPh_3) adducts of cyclopalladated ferrocenylimidazoline complexes **2a** and **2b** have been synthesized and structurally characterized by single crystal X-ray diffraction. The catalytic studies on **2a** and **2b** indicate that they are effective catalysts for the Suzuki reaction of activated aryl chlorides with phenylboronic acid in neat water under air atmosphere.

Keywords: Suzuki coupling; Cyclopalladated ferrocenylimidazolines; Triphenylphosphine adducts; Aryl chlorides; Boronic acids; Neat water

Palladium-catalyzed Suzuki–Miyaura reaction is one of the most important and versatile methods for the construction of carbon–carbon bonds [1]. With increasing environmental and economical concerns, there is considerable interest in the development of promising protocols that not only can use water as a media, which is cheap, nontoxic, nonflammable, and readily forms biphasic mixtures with a variety of organic materials, but also couple aryl chlorides due to the lower cost and greater availability of these substrates compared with their bromide or iodide counterparts [2]. Although the Suzuki couplings of aryl chlorides with boronic acids in neat water with the use of cationic 2,2′-bipyridyl palladium(II), Pd/C, N-heterocyclic carbene ligands and $Pd(OAc)_2$ as well as palladium acetate in a mixture of TBAB as catalysts have been described [3], using inert gas protection, high loading of catalyst or high temperature is not often avoided in these strategies. Therefore, the development of more effective catalysts is desired extraordinarily in order to provide more insight into this process. On the other hand, transition metal (Cu, Ir, Pd or Ru) complexes containing imidazoline scaffold have been proven to be highly active catalysts in a range of organic reactions, such as epoxidation, 1,4-additon reaction, copolymerization of carbon monoxide and styrene, hydrogenation of aromatic ketones and Heck reaction [4]. However, examples involving the ferrocenylimidazoline palladacycles are rare [5]. More recently, we have found that ferrocenylimidazoline palladacycles are competent for the catalyzed Suzuki reactions of a wide range of aryl bromides at room temperature under aerobic conditions [6]. As an extension of this study, we report herein the syntheses, characterizations and crystal structures of two representative triphenylphosphine adducts of dimeric cyclopalladated ferrocenylimidazoline complexes **2a** and **2b** as well as their catalytic reactivity in the Suzuki reaction of aryl chlorides with phenylboronic acid in neat water under air atmosphere.

The preparations of compounds **2a** and **2b** are as follows: cyclopalladated ferrocenylimidazoline chloro bridge dimer **1a** [6] was treated with two equivalents of PPh_3 in methanol at room temperature for 1 h (Scheme 1). The mixture was concentrated under reduced pressure and the residue was purified by silica gel chromatogram (dichloromethane) to give orange-yellow solid **2a** (yield: 88%) [7].

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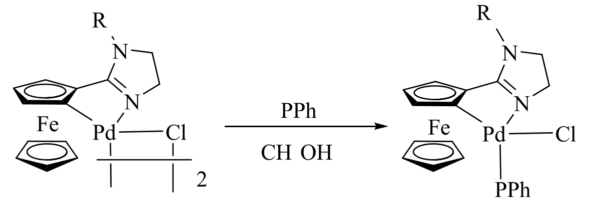

1 **2**

1a: R =n-C H ; **1b**: R =Ac **2a**: R =n-C H ; **2b**: R =Ac

Scheme 1.

Compound **2b** can similarly be obtained (red solid, yield: 84%) from **1b** [8].

Compounds **2a** and **2b** are identified by elemental analyses, IR, ^{1}H and ^{13}C NMR. Elemental analyses are in good agreement with the proposed formula. The IR spectra of **2a** and **2b** show strong signals at 1560 and 1567 cm^{-1}, respectively, assigned to the C=N stretching of the imidazoline ring, and this absorption shifts to lower energy by comparison with free ligand due to N → Pd coordination [9]. Two absorptions peaks around ν 1097 and 1000 cm^{-1} are also observed for each of the two compounds, which is indicative of unsubstituted cyclopentadienyl ring (Cp). In the ^{1}H NMR spectra of **2a** and **2b**, three proton signals appeared at 4.37, 3.97 and 3.25 ppm for **2a** and 5.27, 4.13 and 3.39 ppm for **2b** correspond to the substituted Cp ring, and the unsubstituted Cp proton is at 3.84 and 3.85 ppm, respectively. In ^{13}C NMR spectra, carbon signal displayed at 97.3 ppm for **2a** and 99.5 ppm for **2b** was assigned to the carbon of C–Pd, the signals at δ 70.2 ppm for **2a** and 70.4 ppm for **2b** were attributed to the unsubstituted Cp carbon. The signals at 76.2, 75.4, 68.4 and 64.8 ppm for **2a** and 77.2, 76.2, 70.6 and 69.9 ppm for **2b** were assigned to the substituted Cp carbons. The signal of the carbon from C=N appears at δ 174.6 ppm for **2a** and 171.5 ppm for **2b**. In **2b**, the peak at 167.1 ppm was assigned to the carbon from C=O.

The structures of compounds **2a** and **2b** were determined by X-ray crystallography and perspective views of their molecular structures are shown in Figs. 1 and 2, respectively [10]. Owing to the introduction of different substituents at N-1 position, the C–N and C=N bond lengths (1.468(3) Å, 1.309(3) Å) in **2a** are longer slightly than those in **2b** (C–N 1.465(3) Å, C=N 1.298(3) Å). The N–Pd bond length in **2a** (2.066(2) Å) is shorter than that in **2b** (2.0788(19) Å), whereas the bond length of C–Pd (2.016(3) Å) is longer compared to **2b** (2.003(2) Å). Meanwhile, compared with the N–Pd and C–Pd bond lengths found for the reported the triphenylphosphine adducts of cyclopalldated analogues, such as 2-(*N*-*p*-chlorophenyl-ethyl-1-imido) ferrocenyl-chloro-triphenylphosphine-palladium (2.132 Å, 1.992 Å) [11a], 2-(*N*-*p*-Tolyl-ethyl-1-imido)-ferrocenyl-chloro-triphenylphosphine-palladium (2.137 Å, 1.999 Å) [11b] and 2-(1-*N*-hydroxyiminoethyl)-ferrocenyl-chloro-triphenylphoshphin palladium (2.120 Å, 2.000 Å) [11c], the shorter N–Pd and longer C–Pd bond lengths have been observed in both compounds. In **2a**, the imidazoline ring is twisted with the dihedral angel between N1–C13–C12 and N1–C11–N2–C12 planes of 7.6°, while the imidazoline ring in **2b** is quasi-planar with all of the atoms deviating from their main plane by only 0.0152 Å. Each palladium atom in the two compounds adopts a distorted square planar configuration defined by atoms N1, C, P and Cl, and the angles around Pd center are in the range of 79.9–96.1° for **2a** and 79.6–95.9° for **2b**, respectively. The coordinated PPh_3 is *trans* to the imino nitrogen with a P–Pd–N angle of 170.0° for **2a** and 170.5° for **2b**, and the P–Pd bond length is 2.253 Å and 2.256 Å, respectively.

The intermolecular hydrogen bond between chlorine atom and the adjacent C–H group of imidazoline (C12

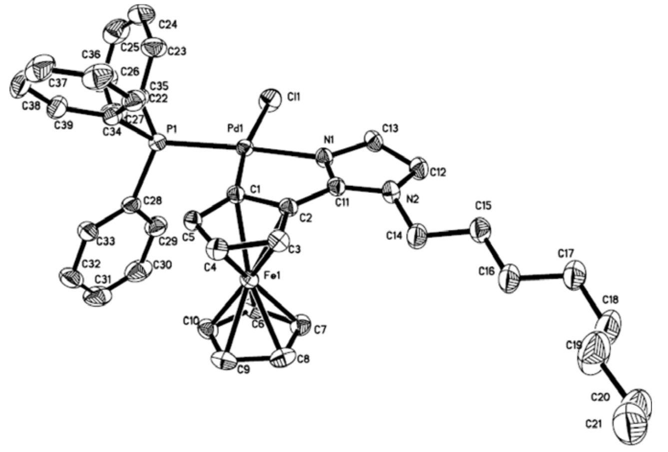

Fig. 1. Molecular structure of compound **2a**. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 2.016(3), Pd(1)–N(1) 2.066(2), Pd(1)–P(1) 2.2532(9), Pd(1)–Cl(1) 2.3888(10) and C(1)–Pd(1)–N(1) 79.86(9), C(1)–Pd(1)–P(1) 93.74(8), N(1)–Pd(1)–P(1) 173.58(6), C(1)–Pd(1)–Cl(1) 170.01(8), N(1)–Pd(1)–Cl(1) 90.28(6), P(1)–Pd(1)–Cl(1) 96.14(3).

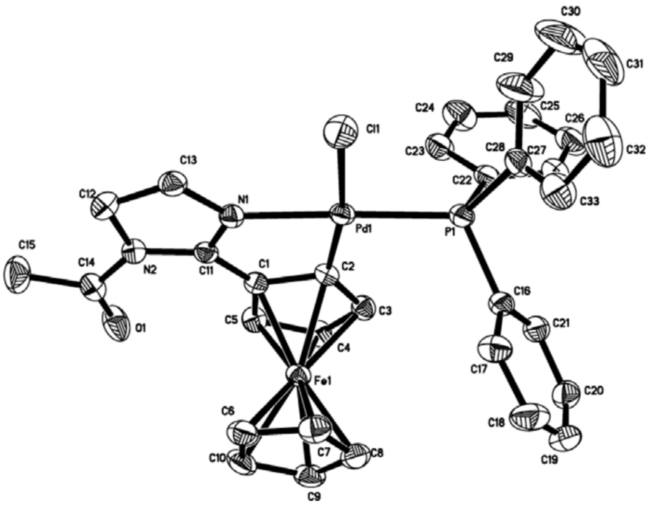

Fig. 2. Molecular structure of compound **2b**. Selected bond lengths (Å) and angles (°): Pd(1)–C(2) 2.003(2), Pd(1)–N(1) 2.0788(19), Pd(1)–P(1) 2.2562(7), Pd(1)–Cl(1) 2.3840(6) and C(2)–Pd(1)–N(1) 79.59(8), C(2)–Pd(1)–P(1) 93.60(7), N(1)–Pd(1)–P(1) 172.67(5), C(2)–Pd(1)–Cl(1) 170.46(7), N(1)–Pd(1)–Cl(1) 90.87(5), P(1)–Pd(1)–Cl(1) 95.92(2).

–H12A$\cdots$Cl1A = C12A–H12C$\cdots$Cl1 = 2.940 Å, 152.0°) and the C–H$\cdots\pi$ interaction between the C(3B)–H(3B) in the Cp ring and the adjacent Cp ring (C5–C10) (2.772 Å, 142.6°) are existed in **2a**. In **2b**, the chlorine atom (Cl1) is involved in hydrogen bonding to two different hydrogen atoms of two neighboring molecules, viz., to H(6) of the Cp of a neighboring molecule (C6–H6$\cdots$Cl1D = C6AB–H6AB$\cdots$Cl1 = 2.823 Å, 172.7°) and H(12) of the imidazoline ring from another neighboring molecule (C12–H12A $\cdots$Cl1D = C12D–H12I$\cdots$Cl1 = 2.884 Å, 133.1°). The O atom in acetyl group forms hydrogen bond with the adjacent C–H group of PPh_3 group (C14C–O1B$\cdots$H30D = C14D–O1AB$\cdots$H30E = 2.601 Å, 139.5°). In addition, there also exist the C–H$\cdots\pi$ interactions (2.787 Å, 141.0°) between C(9)–H(9) in the Cp ring and the adjacent Cp ring (see Figs. 3 and 4). Furthermore, we have examined the reactivity of compounds **2a** and **2b** for the coupling reaction of aryl chlorides with phenylboronic acids in the presence of tetrabutylammonium bromide (TBAB) in neat water at 100 °C under air atmosphere. In order to find out the optimum base, compound **2a** is employed as the catalyst in this transformation reaction. It is apparent that KF as base leads to the higher yield in 82% (Table 1 entry 6 vs entries 1–5) [12]. In the presence of KF, we compared catalytic efficiency of the title compounds, and find that **2b** gave higher yield of 88%. Subsequently, we extended the scope of substrates for Suzuki reaction catalyzed by **2b** and investigated the reactivity of various aryl chlorides in the same reaction condition. As can be seen in Table 1, 3-nitrochlorobenzene, 4-cyanochlorobenzene and 4-nitrochlorobenzene lead to good to excellent yields (entries 8–10), whereas the reactions of 4-chloroanisole, 4-chlorotoluene and chlorobenzene with phenylboronic acid gave low to moderate yields (entries 11–13). In the case of unactivated 4-chloroanisole, the desired product was obtained only in 37% or 41% yield even when prolonging the reaction time to 36 h or increasing the catalyst loading to 0.5 mol% (entries 15 and 16). 2-Chloropyridine could be coupled with phenylboronic acid and gave product in 43% yield (entry 14). All these results indicated that electronic effect of substituents on the aryl chlorides had great influence on the reaction and the electron-withdrawing substituents were more favorable for the coupling, which was analogous to those reported for other palladium catalysts [13].

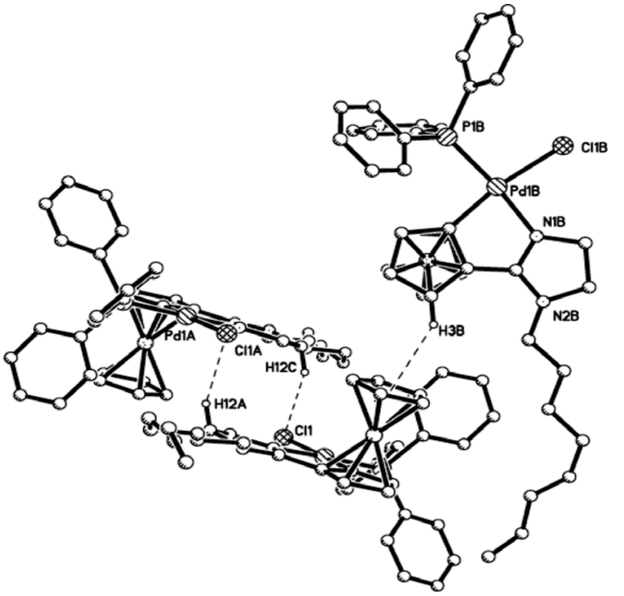

Fig. 3. The hydrogen bonds and C–H$\cdots\pi$ interactions of compound **2a** (H atoms are omitted for clarity).

In conclusion, we have designed and synthesized two new air and moisture stable triphenylphosphine adducts of cyclopalladated ferrocenylimidazoline complexes **2a** and **2b**. Compound **2b** is found to exhibit higher catalytic

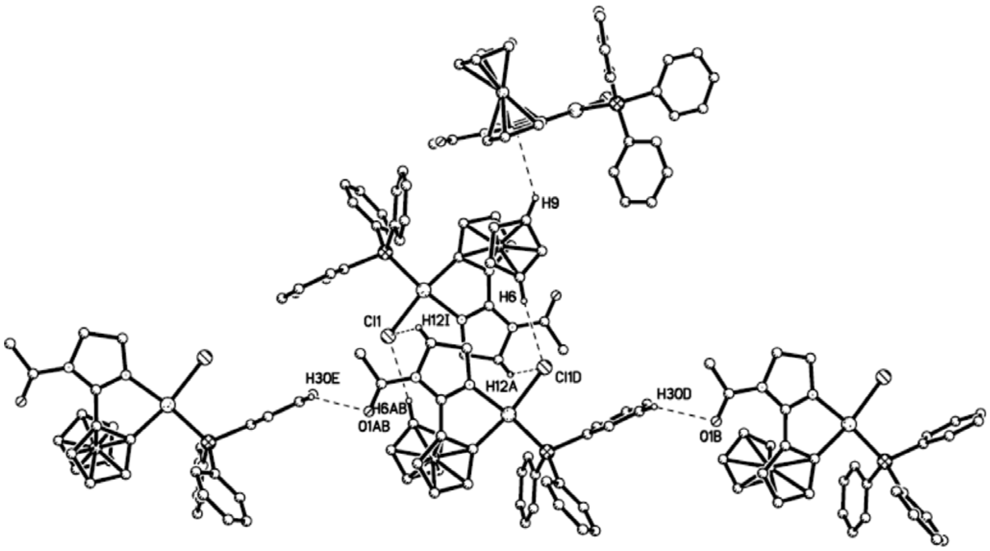

Fig. 4. The hydrogen bonds and C–H$\cdots\pi$ interactions of compound **2b** (H atoms are omitted for clarity).

Table 1
Suzuki reaction of aryl chloride with phenylboronic acid in neat water under air atomsphere[a]

$$\text{ArCl} + \text{PhB(OH)}_2 \xrightarrow[\substack{\text{Base (2 equiv)}\\ \text{water, 100°C, TBAB}}]{\text{0.1mol\% } \textbf{2a/2b}} \text{Ar-Ph}$$

Entry	ArCl	Catalyst	Base	T (h)	Product	Yield (%)[b]
1	4′-Chloroacetophenone	**2a**	K_2CO_3	20	4-Acetylbiphenyl	65
2	4′-Chloroacetophenone	**2a**	Na_2CO_3	20	4-Acetylbiphenyl	58
3	4′-Chloroacetophenone	**2a**	KOH	20	4-Acetylbiphenyl	40
4	4′-Chloroacetophenone	**2a**	NaOAc	20	4-Acetylbiphenyl	73
5	4′-Chloroacetophenone	**2a**	K_3PO_4	20	4-Acetylbiphenyl	67
6	4′-Chloroacetophenone	**2a**	KF	20	4-Acetylbiphenyl	82
7	4′-Chloroacetophenone	**2b**	KF	20	4-Acetylbiphenyl	88
8	4-Nitrochlorobenzene	**2b**	KF	12	4-Nitrobiphenyl	97
9	3-Nitrochlorobenzene	**2b**	KF	12	3-Nitrobiphenyl	78
10	4-Cyanochlorobenzene	**2b**	KF	20	4-Cyanobiphenyl	89
11	Chlorobenzene	**2b**	KF	24	Biphenyl	51
12	4-Chlorotoluene	**2b**	KF	24	4-Methylbiphenyl	34
13	4-Chloroanisole	**2b**	KF	24	4-Methoxylbiphenyl	22
14	2-Chloropyridine	**2b**	KF	24	2-Phenylpyridine	43
15	4-Chloroanisole	**2b**	KF	36	4-Methoxylbiphenyl	37
16	4-Chloroanisole	**2b**	KF	24	4-Methoxylbiphenyl	41[c]

[a] Reaction conditions: 1 equiv. of ArCl, 1.5 equiv. of $PhB(OH)_2$, 2 equiv. of base, 0.5 equiv. of TBAB, 0.1% equiv. of catalyst, water, 100 °C, under air atmosphere.

[b] Isolated yields, based on ArX, average of two runs.

[c] 0.5% equiv. of catalyst.

activity in the Suzuki reaction of activated aryl chlorides with phenylboronic acid in neat water under air atmosphere. Further studies using these compounds in palladium-catalyzed reactions are currently underway.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.03.018.

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[7] *Characterization data for* ***2a:*** yellow solid. Yield: 71%. mp 192-193 °C. Calcd for $C_{39}H_{44}ClFeN_2PPd$: C 56.74%, H 4.15%, N 4.27%; Found: C 56.97%, H 4.03%, N 4.46%. IR (KBr)/cm^{-1}: 3054, 2923, 2853, 1560, 1435, 1283, 1097, 1050, 999, 816, 747, 696. ^1H NMR ($CDCl_3$, ppm): $\delta = 7.81 - 7.77$ (m, 6H, ArH), 7.40-7.38 (m, 9H, ArH), 4.37 (s, 1H, C_5H_3), 3.97 (m, 3H, C_5H_3 and $C{=}NCH_2$), 3.84 (s, 5H, C_5H_5), 3.66 (m, 2H, $NCH_2C_7H_{15}$), 3.36 (m, 2H, NCH_2), 3.25 (s, 1H, C_5H_3), 1.68 (m, 2H, $CH_2C_6H_{13}$), 1.34 (m, 10H, $(CH_2)_5$), 0.89 (m, 3H, CH_3).

^{13}C NMR ($CDCl_3$, ppm): $\delta = 174.6$, 134.9, 134.8, 132.5, 132.0, 130.2, 128.1, 127.9, 97.3, 76.2, 75.4, 70.2, 68.4, 64.8, 52.4, 50.1, 47.6, 31.8, 29.4, 29.3, 28.7, 27.0, 22.6, 14.1.

[8] *Characterization data for* ***2b****:* red solid. Yield: 80%. mp 261–263 °C (dec.). Calcd for $C_{33}H_{30}ClFeN_2POPd$: C 56.68%, H 4.32%, N 4.01%; Found: C 56.41%, H 4.47%, N 3.84%. IR (KBr)/cm^{-1}: 3073, 1709, 1567, 1471, 1436, 1388, 1307, 1182, 1097, 1065, 1002, 821, 748, 696. ^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.79 - 7.75$ (m, 6H, ArH), 7.42-7.39 (m, 9H, ArH), 5.27 (s, 1H, C_5H_3), 4.13 (m, 5H, C_5H_3 and CH_2CH_2), 3.85 (s, 5H, C_5H_5), 3.39 (s, 1H, C_5H_3), 2.31 (s, 3H, CH_3CO). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 171.5$, 167.1, 134.9, 134.8, 131.9, 131.4, 130.4, 128.1, 128.0, 99.5, 77.2, 76.2, 70.6, 70.4, 69.9, 50.5, 49.8, 24.9.

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[10] Crystals of **2a** and **2b** were obtained by recrystallization from dichloromethane–methanol at room temperature. Crystal data for **2a**: $C_{39}H_{44}ClFeN_2PPd$, monoclinic, P2(1)/c, $a = 17.479(6)$ Å, $b = 10.149(3)$ Å, $c = 20.020(7)$ Å, $0.46 \times 0.35 \times 0.31$ mm^3, $\alpha = \gamma = 90°$, $\beta = 95.850(5)°$, $V = 3533(2)$ Å^3, $Z = 4$, $D_c = 1.477$ g/cm^3, $\mu = 0.71073$ mm^{-1}, $F(000) = 1584$, 13383 reflections measured, 6519 unique ($R_{int} = 0.0223$) which were used in all calculations, final $R_1 = 0.0291$, $wR_2 = 0.0697$ [$I > 2\delta(I)$]; Crystal data for **2b**: $C_{33}H_{30}ClFeN_2PPd$, monoclinic, P2(1)/c, $a = 13.6594(11)$ Å, $b = 9.9307(8)$ Å, $c = 22.2044(18)$ Å, $0.46 \times 0.31 \times 0.18$ mm^3, $\alpha = \gamma = 90°$, $\beta = 102.4440(10)°$, $V = 2941.2(4)$ Å^3, $Z = 4$, $D_c = 1.579$ g/cm^3, $\mu = 0.71073$ mm^{-1}, $F(000) = 1416$, 19745 reflections measured, 6701 unique ($R_{int} = 0.0223$) which were used in all calculations, final $R_1 = 0.0270$, $wR_2 = 0.0597$ [$I > 2\delta(I)$]. Crystal structure measurements for compounds **2a** and **2b** were performed on a Rigaku RAXIS-IV image plate area detector for study using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at 291(2) K using the $\omega - 2\theta$ scan technique. All data were corrected for Lorentz and polarization factors and for absorption by using empirical scan data. The structures were solved with the *SHELXTL* 97 program and refined by full-matrix least-squares methods based on F^2, with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were located theoretically and not refined.

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[12] *Catalyzed Suzuki reaction in water:* a mixture of aryl halide (1 mmol), catalyst **2a** or **2b** (0.1 mol%), phenylboronic acid (1.5 mmol), TBAB (0.5 mmol), base (2 mmol) and H_2O (3 mL) was stirred at 100 °C under air atmosphere. The reaction was monitored by TLC. Then the mixture was extracted with ethyl ether, and the organic phase was washed with water, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure to dryness. The residue was purified by flash column chromatography on silica gel.

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