

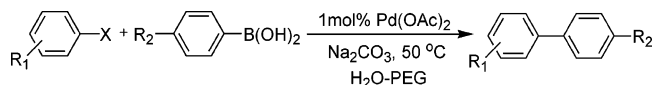
Phosphine-Free Palladium Acetate Catalyzed Suzuki Reaction in Water

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$\text{Pd}(\text{OAc})_2$ in a mixture of water and poly(ethylene glycol) (PEG) is shown to be an extremely active catalyst for the Suzuki reaction of aryl iodides and bromides. The reaction can be conducted under mild conditions (50 °C) without the use of a microwave or phosphine ligand in high yields. The isolation of the products is readily performed by the extraction of diethyl ether, and the $\text{Pd}(\text{OAc})_2$ -PEG can be reused without significant loss in activity.

The Suzuki coupling reaction is an important and versatile method for the generation of unsymmetrical biaryls from arylboronic acids and aryl halides in a single step.¹ As an intriguingly flexible reaction, it offers considerable potential in the synthesis of natural products, herbicides, pharmaceuticals, and conducting polymers.² The traditional Suzuki reaction usually proceeds using phosphine-based palladium catalysts, and there has been considerable recent interest in the development of new catalysts that are environmentally benign and efficient. Some significant advances have been made, including the use of palladium nanoparticles,³ water-soluble phosphines as ligands,⁴ microwave technology,⁵ nucleophilic carbene ligands,⁶ ionic liquids,⁷ and so on.⁸

Water has clear advantages as a solvent for use in chemistry because it is cheap, readily available, and nontoxic. The phosphine-free Suzuki reaction involving water as the cosolvent was reported by Wallow and Novak in 1994.^{9a,b} Later, Badone and co-workers developed an elegant method of Suzuki reaction by using water as the solvent and palladium acetate as the catalyst.^{9c} In their experiments, 1 equiv of tetrabutylammonium bromide (TBAB) was required as the promoter for the

complete conversion of aryl bromides, albeit aryl iodides delivered moderate yields in the same conditions. Very recently, the Suzuki coupling reaction catalyzed by the $\text{Pd}(\text{OAc})_2$ - H_2O -TBAB system was investigated under conventional thermal conditions and microwave irradiation.^{10,11} PEGs are known to be nontoxic, recoverable, and inexpensive media of phase-transfer catalysts.¹² The Suzuki reaction of PEG-bound aryl halides has been reported.^{13a} However, the Suzuki coupling reaction for non-PEG-bound aryl halides was only studied under microwave conditions, and the yields of the PEG-bound products were superior to those of non-PEG-bound transformations.¹³ We herein report the application of $\text{Pd}(\text{OAc})_2$ - H_2O -PEG system as an efficient catalytic medium for the Suzuki coupling reaction. We found that the ratio of water and PEG was pivotal to the Suzuki reaction of non-PEG-bound aryl halides, and the conventional thermal condition was more applicable to the $\text{Pd}(\text{OAc})_2$ - H_2O -PEG system than the microwave irradiation.

The effect of PEG on the Suzuki reaction in water was initially investigated. The coupling of 4-bromotoluene (1 mmol) and phenylboronic acid (1.5 mmol) was chosen as the model reaction. The reaction was carried out in water (3 g) in the presence of 1 mol % of $\text{Pd}(\text{OAc})_2$ using

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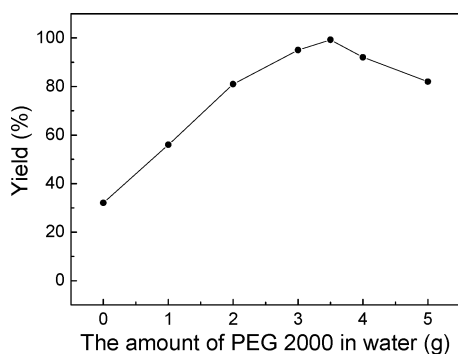


FIGURE 1. Effect of PEG 2000 on the Suzuki coupling of bromotoluene and phenylboronic acid in water.

Na_2CO_3 (2 mmol) as base at 50 °C for 0.5 h in air. In the absence of PEG 2000, the result was not promising, and a very low yield was obtained (Figure 1). However, the addition of incremental PEG 2000 led to a very rapid increase in activity, and a maximum (99.5%, GC yield) was observed when the amount of PEG 2000 was achieved 3.5 g. Further addition of PEG 2000 caused the decreasing of the yields. It was worthy of note that only trace of the desired 4-methyl-biphenyl produced using neat PEG 2000 as the solvent (Table 1, entry 1). The byproduct of biphenyl from the self-coupling of phenylboronic acid was not detected in all of the reactions.

To compare the effect of PEG in organic solvents, the Suzuki reaction was performed at the same conditions in the mixture of PEG 2000 and various solvents, including DMF, acetonitrile, acetone, toluene, dioxane, methanol, ethanol, 1-propanol, and 2-propanol (Table 1). The combination of PEG 2000 with nonpolar toluene and aprotic polar solvents, such as DMF, acetonitrile, acetone, and dioxane, afforded very little of the product (Table 1, entries 2–6). On the other hand, the mixture of PEG 2000 with polar protic solvents, such as water, methanol, ethanol, and 2-propanol, furnished the coupling product in various yields. The solution of PEG 2000-water and PEG 2000-methanol afforded the coupling product in excellent yields (Table 1, entries 7 and 8), whereas PEG 2000-ethanol only delivered a moderate yield (Table 1, entry 9). The very low yields were obtained in PEG 2000–2-propanol and PEG 2000–1-propanol (Table 1, entries 10 and 11). These results show a profound solvent effect on the reaction, and the water as well as methanol is good solvent for the Suzuki reaction in the presence of PEG.

Of the bases tested, NaOAc was a poor base for the coupling (Table 1, entry 14). The use of Na_2CO_3 , K_2CO_3 , and K_3PO_4 delivered the product in high yields (Table 1, entries 7, 12, and 13). KF, Et_3N and KOH gave moderate yields (Table 2, entries 15–17). We chose to use Na_2CO_3 for the remainder of the studies as it is less expensive. In addition, the efficiency of various chain length PEGs on the reaction was examined at the same reaction conditions (Table 1, entries 18–21). PEG 2000 was superior to PEG 600 and PEG 1000. The large chain length PEGs such as PEG 4000 and PEG 6000 were almost as good as PEG 2000.

The scope of the reaction was studied with various aryl halides (Table 2). It was seen that the catalytic system

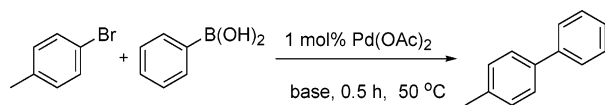
was applicable to various aryl bromides and tolerant to a broad range of functional groups, such as NO_2 , NH_2 , OMe, OH, COMe, and CN (Table 2, entries 1–10). Both the electron-rich and electron-deficient aryl bromides delivered the products with high yields, and the reaction was not affected by the aqueous conditions. Furthermore, sterically demanding aryl bromide also gave good yields (Table 2, entries 3 and 5). The coupling of phenylboronic acid with aryl iodides in the $\text{Pd}(\text{OAc})_2\text{-H}_2\text{O-PEG}$ system was superior and afforded almost quantitative yields (Table 2, entries 11–13). This new catalyst system toward the Suzuki reaction of aryl iodides is more efficient than the published $\text{Pd}(\text{OAc})_2\text{-H}_2\text{O-TBAB}$ system.^{9c} The high efficiency of $\text{Pd}(\text{OAc})_2\text{-H}_2\text{O-PEG}$ system is probably attributed to the properties of PEG as cosolvent¹⁴ and PTC.

Encouraged by these results, we studied the activity of aryl chlorides (Table 2, entries 14–19). The activated 4-nitrochlorobenzene was first applied as the Suzuki coupling partner. Surprisingly, the coupling reaction proceeded almost quantitatively and afforded the desired biaryl with high yield after the increase of the temperature to 120 °C for 3 h using 2 mol % of $\text{Pd}(\text{OAc})_2$ (Table 2, entry 14). The coupling yield of 4-chloroacetophenone as the substrate dropped to 52%, although the reaction time was prolonged to 28 h (Table 2, entry 15). In these cases, however, the biphenyl was formed as a byproduct from the self-coupling of phenylboronic acid as confirmed by GC–MS and ^1H NMR. To study the impact of reaction conditions to the formation of biphenyl, we performed the coupling reactions with bromotoluene and chlorotoluene respectively at various reaction conditions. The results showed that the excellent yield of Suzuki coupling product with bromotoluene was always obtained, and the increase of temperature (from 50 °C to 100 °C), reaction time (0.5–2 h), and the amount of $\text{Pd}(\text{OAc})_2$ (1–5 mol %) had a small influence to the formation of biphenyl. In contrast, a very low yield of the desired 4-methylbiphenyl was obtained in the case of deactivated chlorotoluene at 50 °C, and the byproduct of biphenyl was rapidly formed (Table 2, entry 16). The biphenyl in the coupling of chlorotoluene was markedly increased with the enhancement of temperatures and the prolongation of reaction times (Table 2, entries 17–19). These results illustrated that the self-coupling of the phenylboronic acid occurred rapidly when the Suzuki coupling reaction was slow in the $\text{Pd}(\text{OAc})_2\text{-H}_2\text{O-PEG}$ system.¹⁵

The effect of the arylboronic acid partner on the Suzuki reaction in water was also investigated (Table 3). It can be seen that both active arylboronic acid with an electron-donating group and deactivated arylboronic acid with an electron-withdrawing group exhibited excellent reactivity in high yields (Table 3, entries 1–12), although the prolonged reaction time was required for deactivated

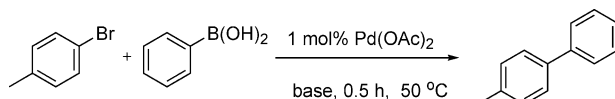
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TABLE 1. Suzuki Coupling Reaction of Bromotoluene with Phenylboronic Acid in Various Media^a

entry	base	solvent ^b	yield ^c (%)	entry	base	solvent ^b	yield ^c (%)
1	Na ₂ CO ₃	PEG	11	12	K ₂ CO ₃	PEG/H ₂ O	95
2	Na ₂ CO ₃	PEG/toluene	32	13	K ₃ PO ₄	PEG/H ₂ O	96
3	Na ₂ CO ₃	PEG/DMF	24	14	NaOAc	PEG/H ₂ O	47
4	Na ₂ CO ₃	PEG/CH ₃ CN	32	15	KOH	PEG/H ₂ O	70
5	Na ₂ CO ₃	PEG/dioxane	15	16	KF	PEG/H ₂ O	86
6	Na ₂ CO ₃	PEG/acetone	21	17	Et ₃ N	PEG/H ₂ O	76
7	Na ₂ CO ₃	PEG/H ₂ O	97	18	Na ₂ CO ₃	PEG600/H ₂ O	64
8	Na ₂ CO ₃	PEG/methanol	97	19	Na ₂ CO ₃	PEG1000/H ₂ O	75
9	Na ₂ CO ₃	PEG/ethanol	72	20	Na ₂ CO ₃	PEG4000/H ₂ O	94
10	Na ₂ CO ₃	PEG/propanol	40	21	Na ₂ CO ₃	PEG6000/H ₂ O	90
11	Na ₂ CO ₃	PEG/2-propanol	41				

^a Reaction conditions: bromotoluene (1.00 mmol), PhB(OH)₂ (1.5 mmol), base (2 mmol). ^b The amount of water or solvent was 3 mL, PEG was 3.5 g. ^c Isolated yields.

TABLE 2. Suzuki Reactions of Aryl Halides with Phenylboronic Acid Catalyzed by Pd(OAc)₂-H₂O-PEG^a

entry	X	R ₁	time (h)	yield ^d (%)	entry	X	R ₁	time (h)	yield ^d (%)
1	Br	4-OMe	0.5	95	11	I	4-OMe	0.5	97
2	Br	3-OH	0.5	98	12	I	H	0.4	99
3	Br	2-NH ₂	0.5	94	13	I	4-NO ₂	0.25	99
4	Br	4-NH ₂	0.5	98	14	Cl	4-NO ₂	3	98 ^b (23) ^c
5	Br	2-Me	0.5	95	15	Cl	4-COCH ₃	28	52 ^b (41) ^c
6	Br	4-Me	0.5	97	16	Cl	4-Me	28	22 ^b (43) ^c
7	Br	H	0.3	97	17	Cl	4-Me	0.5	4 ^b (8) ^c
8	Br	4-COCH ₃	0.3	98	18	Cl	4-Me	1	5 ^b (21) ^c
9	Br	4-CN	0.3	98	19	Cl	4-Me	3	7 ^b (23) ^c
10	Br	4-NO ₂	0.25	96					

^a Reaction conditions: aryl halide (1 mmol), PhB(OH)₂ (1.5 mmol), Na₂CO₃ (2 mmol), H₂O/PEG 2000 = 3:3.5 g. ^b The reaction temperature was 120 °C, and the amount of Pd(OAc)₂ was 2%. ^c The GC yield of biphenyl is shown in parentheses. ^d Isolated yields.

arylboronic acid (Table 3, entries 6–12). Homocoupled product of arylboronic acid was not detected under the reaction conditions, which made the isolation of the product easier.

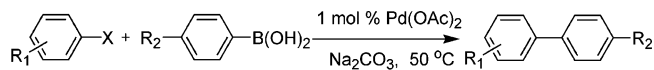
Data in the literature showed that microwave conditions were less efficient in the Suzuki reaction in PEG.¹³ To determine the effect of the Pd(OAc)₂-H₂O-PEG system under microwave conditions, the mixture of 4-bromotoluene (1 mmol), phenylboronic acid (1.5 mmol), Na₂CO₃ (2 mmol), water (3 g), and PEG 2000 (3.5 g) was subjected to microwave irradiation in the presence of 1 mol % of Pd(OAc)₂. In accordance with the results of Blettner et al.,^{13a} the conversion was very low (100 W, 4 min, 8%; 300 W, 8 min, 58%). It is known that PEG can serve as the PTC since the poly(ethylene oxide) chains in PEG can form complexes with the metal ions, similar to crown ethers.¹⁶ In the Pd(OAc)₂-H₂O-PEG system, it is possible that the PEG-metal cation complexes bring the activated ArB(OH)₃⁻ to maintain the electro-neutrality, which react with the palladium intermediates and thus make the Suzuki reaction in water proceed rapidly. However, if these large complexes are instable to microwave irradiation, the catalytic efficiency of the Pd(OAc)₂-H₂O-PEG system will decrease under microwave conditions. In the case of PEG-bound aryl halides, besides

the activating effect of the ester linkage, the direct bonding of the aryl halide with the PEG probably enhances the reactivity of the Suzuki coupling under microwave conditions.^{13a}

The reusability of PEG and catalyst was tested in the coupling reaction of bromotoluene with phenylboronic acid using 1 mol % of Pd(OAc)₂. The product was isolated by extraction with diethyl ether (4 × 15 mL), and the solidified Pd(OAc)₂-PEG was subjected to the second run by charging with the same substrates without any regeneration or addition of Pd(OAc)₂. The yields of the first three cycles were almost consistent (99%, 98%, 97%). In the fourth cycle, the yield dropped down to 89%.

In summary, we have shown that Pd(OAc)₂, in combination with PEG, can be used as a highly efficient catalyst for the Suzuki coupling reaction of aryl halides in water. The role of PEGs is extraordinary in the catalysis relative to classical phase transfer agent of

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TABLE 3. Suzuki Coupling Reaction of Various Arylboronic Acid with Aryl Halides^a

entry	X	R ₁	R ₂	time (min)	yield ^b (%)
1	Br	H	4-OCH ₃ (a)	20	94
2	Br	H	4-CF ₃ (b)	45	89
3	Br	4-CH ₃	(a)	25	94
4	Br	4-CH ₃	(b)	30	87
5	Br	2-CH ₃	(a)	30	96
6	Br	2-CH ₃	(b)	40	92
7	Br	4-OCH ₃	(a)	45	94
8	Br	4-OCH ₃	(b)	60	85
9	Br	4-COCH ₃	(a)	20	96
10	Br	4-COCH ₃	(b)	40	96
11	Br	4-NO ₂	(a)	15	97
12	Br	4-NO ₂	(b)	20	93
13	I	H	(a)	20	97
14	I	H	(b)	30	98
15	I	4-OCH ₃	(a)	30	95
16	I	4-OCH ₃	(b)	40	96
17	I	4-NO ₂	(a)	10	97
18	I	4-NO ₂	(b)	25	97

^a Reaction conditions: aryl halide (1 mmol), ArB(OH)₂ (1.5 mmol), Na₂CO₃ (2 mmol), H₂O/PEG 2000 = 3:3.5 g. ^b Isolated yields.

tetrabutylammonium bromide. The application of various aryl halides and arylboronic acids permits a number of biaryls to be produced in a short reaction time under mild conditions involving only air-stable chemicals.

Experimental Section

General Procedure for Suzuki Reaction. A mixture of Na₂CO₃ (0.212 g, 2 mmol), Pd(OAc)₂ (2 mg, 1 mol %), PEG 2000 (3.5 g), and water (3 g) was heated to 50 °C with stirring. Afterward, aryl halides (1 mmol) and arylboronic acid (1.5 mmol) were added to the solution, and the reaction was carried out at 50 °C for the indicated time. After the reaction solution was cooled to room temperature, the resulting suspension was extracted four times with diethyl ether (4 × 15 mL). The residue of the extraction was subjected to a second run of the Suzuki reaction by charging with the same substrates (bromotoluene, phenylboronic acid, water, and Na₂CO₃) under the same conditions without further addition of Pd(OAc)₂ or PEG. The combined ether phase was analyzed by GC/MS and then concentrated. Further purification of the product was achieved by flash chromatography on a silica gel column. All of the products prepared are known and were characterized by ¹H NMR and MS.

4-Methoxybiphenyl (Table 2, Entry 6). ¹H NMR (500 MHz, CDCl₃, TMS): δ 7.54 (q, 4 H, *J* = 6.7 Hz), 7.42 (t, 2 H, *J* = 7.7 Hz), 7.28 (t, 1 H, *J* = 14.8 Hz), 6.98 (d, 2 H, *J* = 4.3 Hz), 3.86 (s, 3 H). MS (EI) *m/z*: 184 (100) [M⁺], 169 (44), 141 (38), 115 (26), 63 (4).

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Supporting Information Available: Experimental procedure and spectroscopic data (¹H NMR and MS) for the products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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