

Highly Efficient Palladium-Catalyzed Boronic Acid Coupling Reactions in Water: Scope and Limitations

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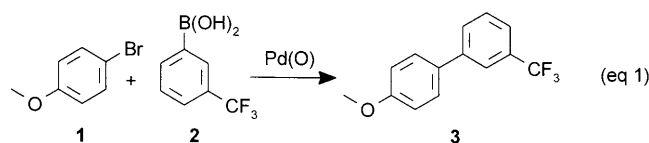
The "ligandless" palladium acetate-catalyzed Suzuki cross-coupling reaction of ArX with aryl- and vinylboronic acids in water without organic cosolvent in the presence of tetrabutylammonium bromide is reported. Aryl bromides give high yields and considerably accelerate the coupling. A wide variety of functional groups can be tolerated. Aryl iodides, however, give incomplete conversion and aryl triflate coupling shows no improvement over reported conditions.

Introduction

Palladium-catalyzed cross-coupling reaction of aryl halides or triflates with boronic acids (commonly referred to as the Suzuki reaction) is a powerful, versatile and popular tool for selective construction of carbon–carbon bonds.¹ The widely employed reaction protocol utilizes aqueous organic solvents in the presence of an inorganic base (typically carbonate, bicarbonate, or hydroxide) and triphenylphosphine as ligand. Novak and Wallow showed that phosphine ligand limits the catalytic efficiency of palladium.² "Ligandless" palladium catalytic species give fast coupling reactions,³ and the phosphine-related side reactions can be suppressed.⁴ We investigated the effects of various solvents and bases in optimal "ligandless" conditions and found that very fast reactions can be obtained with aryl bromides in the presence of 1 equiv of tetrabutylammonium bromide in water. The results of the extension of this protocol to aryl iodides and aryl triflates are described.

Results and Discussion

For initial studies we examined the coupling of **1** and **2** in the presence of 2% palladium acetate (eq 1).



All experiments were run at 70 °C with 0.9 M **1** and 2.5 equiv of base (Table 1). Triethylamine as base in DMF failed to produce any biaryl product **3**, and bromide **1** was recovered unchanged (entry 1). This is rather puzzling since Et₃N/DMF or Et₃N/EtOH systems have

been described for the Suzuki coupling of aryl halides,^{3a,5} but other authors report results in accordance with ours.⁶ The presence of electron-withdrawing substituents on aryl halide might be the decisive factor under these conditions.

Indeed, we found that with potassium carbonate in DMF a good yield of **3** was obtained, but the reaction stopped at about 80% conversion (entries 2–4). Other aprotic solvents were very inefficient (entries 5, 6, 7), and water played a key role in the coupling (cf. entries 7 and 8).

We then turned our attention to aqueous Suzuki aryl coupling of water soluble iodobenzoates and iodophenols, described by Bumagin *et al.*⁷ Coupling of **1** and **2** in water alone was not satisfactory (entry 10). A catalytic amount (10%) of tetrabutylammonium bromide did not achieve complete coupling (reaction stopped at about a 65:35 ratio of **1:3**, as in water alone, entry 11), but in the presence of 1 equiv of tetrabutylammonium bromide we obtained a very fast, high-yield reaction (entry 12). When only 0.2% of palladium acetate in the presence of 1 equiv of tetrabutylammonium bromide was employed with 1.1 equiv of **2** and 2.5 equiv of K₂CO₃ at 70 °C for 1 h, the reaction proceeded as well as with 2% of catalyst, yielding 95% of isolated pure **3** (entry 13).

Aryl Bromide Coupling. To evaluate the scope and limitations of this procedure, we performed a number of coupling reactions with several aryl bromides and aryl and vinyl boronic acids (Table 2). The results show that this coupling reaction is applicable to aryl bromides substituted with various functional groups: cyano, carbonyl, nitro, alcohol, acetal, and amido groups can be tolerated. Furthermore, an ester function survives the reaction, giving a high yield of ester-coupled product with no detectable traces of the corresponding carboxylic acid (entry 8). Reaction with an alkenylboronic acid gives a good yield of styrene derivative (entry 10).

This method also works in the biphasic system toluene/water, but the yields are lower than in water alone (Table 3). Both rate and yield change dramatically in the coupling of 4-bromoanisole with phenylboronic acid (entry 5 vs entry 6). As usual for standard Suzuki coupling, steric hindrance has little effect on the coupling reaction (entries 1 and 2).⁸

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Table 1. Effects of Solvent on Cross-Coupling of 1 and 2 Catalyzed by Ligandless Pd(OAc)₂.^a

entry	solvent	time (h)	1 (%) ^b	3 (%) ^b
1	DMF ^c	1	>95	<i>d</i>
2	DMF	1	20	80
3	DMF	2	20	80
4	DMF ^e	1	15	85
5	CH ₃ CN	1	>95	<i>d</i>
6	NMP	1	85	15
7	DMSO	1	95	5
8	DMSO + 4 equiv H ₂ O	1	60	40
9	EtOH	1	65	35
10	H ₂ O	3	65	35
11	H ₂ O + nBu ₄ NBr (10%)	3	65	35
12	H ₂ O + nBu ₄ NBr (1 equiv)	1	<i>d</i>	>95
13	H ₂ O + nBu ₄ NBr (1 equiv) ^f	1	<i>d</i>	>95

^a All couplings were carried out at 70 °C in the presence of 2% Pd(OAc)₂ and 2.5 equiv of K₂CO₃. ^b ¹H NMR yields determined by integration on the crude reaction mixture. ^c Et₃N employed as base instead of K₂CO₃. ^d None detected. ^e Carried out at 100 °C. ^f 0.2% Pd(OAc)₂.

Aryl Iodide Coupling. In the palladium-catalyzed Suzuki⁹ and Stille¹⁰ coupling of aryl halides, the order of reactivity is usually I > Br >> Cl. Under our conditions, aryl iodides gave incomplete conversion (Table 4). Reactions stopped after about 1 h.

The cross-coupling of 4-iodoanisole with phenylboronic acid under aqueous conditions with water-soluble Pd-TTPS (meta-sulfonated triphenylphosphine) catalyst has been reported to give good yields.¹¹ Moreover, it is well known that aryl iodides do not give complete conversion in simple displacement reactions (i.e. S_N2) in the LL-PTC system.¹² This suggests that an effective phase-transfer process is pivotal under our conditions.

Aryl Triflate Coupling. Suzuki coupling of aryl triflates with aryl boronic acids in a toluene/water biphasic system is reported to give high yields of biphenyl when an electron-withdrawing group is present on the aryl triflate.¹³ Lower yields and/or incomplete conversion are reported with nonactivated aryl triflates.¹⁴ No substantial improvement is observed in water in the presence of tetrabutylammonium bromide (Table 5). Low conversion is obtained with 4-acetamidophenyl triflate (entry 1). Cross-coupling proceeds rapidly with 4-acetylphenyl triflate, but there is significantly hydrolysis to phenol (entry 2).

The mechanism of the Pd-catalyzed Suzuki reaction of aryl halides with aryl boronic acids involves oxidative addition of Pd(0) to aryl halide, transmetalation of the Ar-Pd-X with Ar₂B(OH)₃⁻M⁺ and reductive elimination to give Ar-Ar₁.¹⁵ The high acceleration rate in the presence of tetrabutylammonium bromide is presumably due to the formation of an Ar₁B(OH)₃⁻Bu₄N⁺ species which partitions back into the organic phase, although the behavior observed with cosolvent (Table 3) suggests

that hydrophobic effects¹⁶ also play a role. Under "classical" conditions, the slow step when using aryl bromides has been shown to be the oxidative addition,¹⁷ whereas the transmetalation step seems to be rate-determining here.

In summary, we found that tetrabutylammonium bromide in water without organic cosolvent considerably enhances the rate of the Suzuki coupling of aryl bromides with aryl and vinyl boronic acids. A wide variety of functional groups, including base-sensitive ones (i.e. ester), can be tolerated.

Experimental Section

General. All reactions were carried out under argon. NMR spectra were recorded at 200 MHz using CDCl₃ or DMSO-*d*₆ as both solvent and reference. Coupling constants are given in hertz (Hz). IR spectra were recorded on a dispersion instrument. Elemental analysis was performed by the microanalytical laboratory of the Redox S.n.C. in Cologno Monzese, Italy.

Chemicals. Unless otherwise specified, all reagents were commercially available from Aldrich, Fluka, or Lancaster. Organic solvents were dried by distillation from CaH₂ and stored over molecular sieves (4 Å). Aryl triflates were prepared from the corresponding phenols by reported standard methods.¹⁸ (*E*)-1-octenyl-1-boronic acid was prepared as described by Brown.¹⁹

Representative Coupling Reactions. 6-Methoxy-2-phenylnaphthalene (Table 3, entry 4). To a 5 mL flask were added a stir-bar, 474.2 mg (2 mmol) of 2-bromo-6-methoxynaphthalene, 268 mg (2.2 mmol) of phenylboronic acid, 0.9 mg (0.2 mol %) of Pd(OAc)₂, 691 mg (5 mmol) of powdered K₂CO₃, and 644.8 mg (2 mmol) of Bu₄NBr. The flask was flushed with argon and equipped with a rubber septum. Water (2.2 mL) was added with a syringe, and the resulting suspension was energetically stirred and degassed to remove O₂. The mixture was stirred and heated for 1 h at 70 °C under argon. It was then cooled to room temperature, diluted with water, and extracted with EtOAc. The solution was dried (Na₂SO₄) and concentrated to yield a white solid. Chromatography on silica (1% EtOAc in hexane) afforded 465 mg (99% yield) of the title compound: mp 149–151 °C (lit.²⁰ mp 148 °C). Anal. Calcd for C₁₇H₁₄O: C, 87.14; H, 6.02. Found: C, 86.84; H, 6.00.

4-Methoxy-3'-(trifluoromethyl)-1,1'-biphenyl (Table 1, entry 13). Obtained as a colorless oil after flash-chromatography (5% EtOAc in cyclohexane). IR (film) 2839, 1337, 1263, 1166, 1124 cm⁻¹; ¹H NMR (CDCl₃) δ 7.81 (m, 1H), 7.72 (m, 1H), 7.6–7.5 (m, 4H), 7.01 (m, 2H), 3.88 (s, 3H). Anal. Calcd for C₁₄H₁₁F₃O: C, 66.67; H, 4.40. Found: C, 66.65; H, 4.38.

4-(2-Hydroxyethyl)-3'-(trifluoromethyl)-1,1'-biphenyl (Table 2, entry 3). Obtained as a colorless oil after flash-chromatography (10% EtOAc in cyclohexane). IR (film) 2941, 1336, 1166, 1128 cm⁻¹; ¹H NMR (CDCl₃) δ 7.88–7.71 (m, 2H), 7.67–7.50 (m, 4H), 7.40–7.28 (m, 2H), 3.92 (t, *J* = 6, 2H), 2.93 (t, *J* = 6, 2H). Anal. Calcd for C₁₅H₁₃F₃O: C, 67.67; H, 4.92. Found: C, 67.91; H, 4.91.

3-(2-Cyanomethyl)-3'-(trifluoromethyl)-1,1'-biphenyl (Table 2, entry 4). Obtained as a colorless oil after flash-chromatography (10% EtOAc in cyclohexane). IR (film) 2253, 1338, 1165, 1124 cm⁻¹; ¹H NMR (CDCl₃) δ 7.83–7.32 (m, 8H), 3.82 (s, 2H). Anal. Calcd for C₁₅H₁₀F₃N: C, 68.96; H, 3.86; N, 5.36. Found: C, 68.82; H, 3.85; N, 5.34.

3-(1,3-Dioxo-2-cyclopentyl)-3'-(trifluoromethyl)-1,1'-biphenyl (Table 2, entry 5). Obtained as a colorless oil after flash-chromatography (10% EtOAc in cyclohexane). IR (film)

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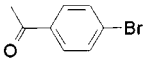
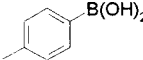
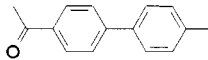
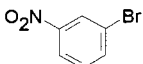
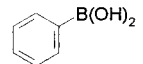
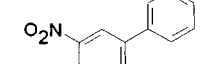
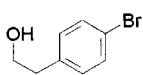
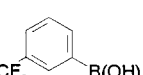
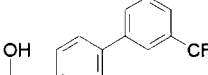
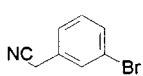
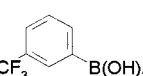
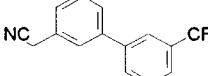
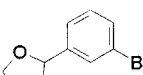
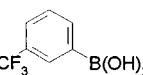
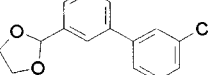
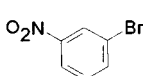
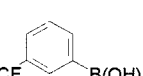
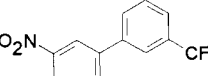
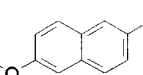
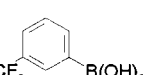
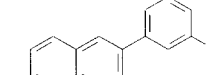
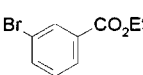
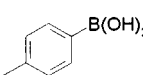
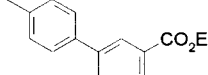
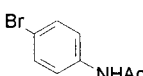
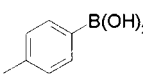
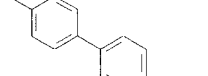
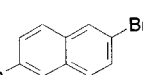
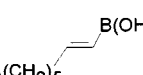
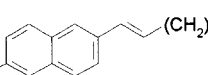
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
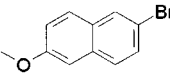
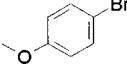
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Table 2. Suzuki Coupling of Aryl Bromides with Boronic Acids in Water in the Presence of Bu₄NBr^a

Entry	Aryl halide	Boronic acid	time(h)	Product(s)	yield(%) ^b
1			0.3		96
2			1		94
3			2		99
4			0.5		88
5			1		87
6			0.5		93
7			1		83
8			1		91
9			2		98
10			1.5		74

^a All couplings were carried out at 70°C with 1.05 equiv of boronic acid, 0.2% Pd(OAc)₂, 2.5 equiv of K₂CO₃ and 1 equiv of Bu₄NBr in water.^b Isolated yields.

Table 3. Cosolvent Effect in Coupling Reaction with Phenylboronic Acid in the Presence of Bu₄NBr^a

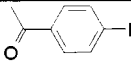
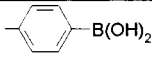

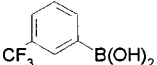
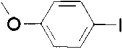
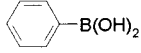
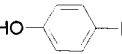
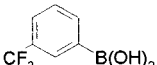
Entry	Aryl bromide	Solvent system	Time(h)	Isolated yield(%)
1		Toluene/H ₂ O	0.5	63
2		H ₂ O	0.5	70
3		Toluene/H ₂ O	1	75
4		H ₂ O	1	99
5		Toluene/H ₂ O	2	33
6		H ₂ O	1	95

^a All couplings were carried out at 70°C with 0.2% Pd(OAc)₂, 2.5 equiv of K₂CO₃ and 1 equiv of Bu₄NBr.

1338, 1165, 1125, 1076 cm⁻¹; ¹H NMR (CDCl₃) δ 8.0–7.7 (m, 3H), 7.67–7.48 (m, 5H), 5.99 (s, 1H), 4.22–4.0 (m, 4H). Anal. Calcd for C₁₆H₁₃F₃O₂: C, 65.31; H, 4.45. Found: C, 65.56; H, 4.46.

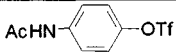

3-Nitro-3'-(trifluoromethyl)-1,1'-biphenyl (Table 2, entry 6). Obtained as a white solid after flash-chromatography (5% EtOAc in cyclohexane), mp 79–80 °C. IR (KBr) 1534, 1350, 1335, 1113 cm⁻¹; ¹H NMR (CDCl₃) δ 8.47 (m, 1H), 8.30–8.21

Table 4. Suzuki Coupling of Aryl Iodides with Arylboronic Acids in Water in the Presence of Bu₄NBr^a

Entry	Aryl iodide	Boronic acid	Time(h)	% convn. ^b
1			1	60
2			2	35
3			2	75
4			2	33

^a All couplings were carried out at 70 °C with 1.05 equiv of boronic acid, 0.2% Pd(OAc)₂, 2.5 equiv of K₂CO₃ and 1 equiv of Bu₄NBr. ^b Percent conversion is defined as [biaryl/(biaryl+aryl iodide)]·100. Determined by ¹H NMR of the crude reaction mixture.

Table 5. Suzuki Coupling of Aryl Triflates with Phenylboronic Acid in Water in the Presence of Bu₄NBr^a

Entry	Aryl triflate	Time(h)	Isolated yields (%)		
			ArOTf	ArOH	Ar-Ph
1		4	46	8	30
2		2	2	15	69

^a All couplings were carried out at 70 °C with 0.2% Pd(OAc)₂, 2.5 equiv of K₂CO₃ and 1 equiv of Bu₄NBr.

(m, 1H), 7.98–7.60 (m, 6H). Anal. Calcd for C₁₃H₈F₃NO₂: C, 58.44; H, 3.02; N, 5.24. Found: C, 58.58; H, 3.03; N, 5.25.

6-Methoxy-2-[3-(trifluoromethyl)phenyl]naphthalene (Table 2, entry 7). Obtained as a white solid after flash-chromatography (5% EtOAc in cyclohexane), mp 104–106 °C. IR (KBr) 1333, 1247, 1130, 1117 cm⁻¹; ¹H NMR (CDCl₃) δ 7.95–7.45 (m, 8H), 7.18–7.05 (m, 2H), 3.86 (s, 3H). Anal. Calcd for C₁₈H₁₃F₃O: C, 71.52; H, 4.33. Found: C, 71.23; H, 4.34.

3-Carboxy-4'-methyl-1,1'-biphenyl (Table 2, entry 8). Obtained as a colorless oil after flash-chromatography (5% EtOAc in cyclohexane).²¹ IR (film) 1720, 1305, 1242 cm⁻¹; ¹H NMR (CDCl₃) δ 8.29 (m, 1H), 8.0 (m, *J* = 8.2, 1H), 7.75 (m, *J* = 8.2, 1H), 7.60–7.45 (m, 3H), 7.26 (m, 2H), 4.40 (q, *J* = 7, 2H), 2.41 (s, 3H), 1.42 (t, *J* = 7, 3H). Anal. Calcd for C₁₆H₁₆O₂: C, 79.97; H, 6.71. Found: C, 80.15; H, 6.69.

(E)-6-Methoxy-2-oct-1-enylnaphthalene (Table 2, entry 10). Obtained as a white solid after recrystallization from MeOH, mp 68–70 °C. IR (KBr) 2920, 1602, 1464, 1243, 855, 816 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ 7.80–7.66 (m, 3H), 7.64–7.55 (m, 1H), 7.28 (m, 1H), 7.16–7.08 (m, 1H), 6.54–6.27 (m, *J* = 16, 2H), 3.87 (s, 3H), 2.29–2.12 (m, 2H), 1.52–1.20 (m, 8H), 0.92–0.80 (m, 3H). Anal. Calcd for C₁₉H₂₄O: C, 85.02; H, 9.01. Found: C, 84.69; H, 9.04.

2-(Trifluoromethyl)-1,1'-biphenyl (Table 3, entry 1). Obtained as a colorless oil after flash-chromatography (cyclo-

hexane). IR (film) 1317, 1129, 1111, 768, 701 cm⁻¹; ¹H NMR (CDCl₃) δ 7.80–7.72 (m, 1H), 7.61–7.30 (m, 8H); ¹³C NMR δ 141.4, 139.9, 132, 131.3, 128.9, 128.4, 127.7, 127.6, 127.3, 126, 124.2. Anal. Calcd for C₁₃H₉F₃: C, 70.27; H, 4.08. Found: C, 69.68; H, 4.53.

4-Acetyl-4'-methyl-1,1'-biphenyl (Table 2, entry 1). Obtained as a white solid, mp 118–120 °C (lit.²² mp 121–122 °C).

3-Nitro-1,1'-biphenyl (Table 2, entry 2). Obtained as a yellow solid, mp 58–60 °C (lit.²³ mp 61 °C).

4-Acetamido-4'-methyl-1,1'-biphenyl (Table 2, entry 9). Obtained as a white solid, mp 218–220 °C (lit.²⁴ mp 219–221 °C).

4-Methoxy-1,1'-biphenyl (Table 3, entry 6). Obtained as a white solid, mp 88–90 °C (lit.²⁵ mp 89–90 °C).

4-Acetamido-1,1'-biphenyl (Table 5, entry 1). Obtained as a white solid, mp 169–170 °C (lit.²⁶ mp 172 °C).

4-Acetyl-1,1'-biphenyl (Table 5, entry 2). Obtained as a white solid, mp 118–120 °C (lit.²⁷ mp 121 °C).

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