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Biphasic Suzuki coupling reactions of aryl or benzyl bromides employing cobalt-containing phosphine ligand coordinated palladium complex

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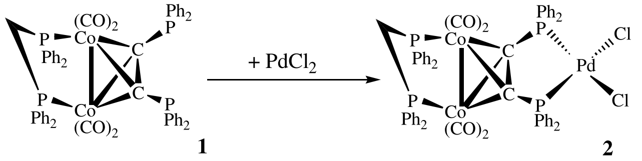
Abstract—Biphasic Suzuki-coupling reactions of aryl and benzyl bromides employing a cobalt-containing phosphine ligand chelated palladium complex **2** were carried out in various reaction conditions. Comparisons of the catalytic efficiencies in the presence/absence of a phase-transfer agent, TBAB, were presented. In addition, the effects of altering solvents, temperatures, catalysts, and substrates on the reactions were monitored and reported. Better yields were commonly observed while a phase-transfer agent TBAB was participated in the reactions. The factor of reaction time is more crucial than that of temperature in short reaction hour experiments. Obviously, an induction period for the reduction of Pd(II) to Pd(0) active species is needed for this type of reaction.

1. Introduction

Palladium-catalyzed Suzuki cross-coupling of haloarenes with arylboronic acid is among the most powerful C_{sp^2}–C_{sp^2} bond-formation available to synthetic organic chemists.[1] Although *N*-heterocyclic carbenes (NHC) have been emerged as potentially effective ligands for Suzuki reactions recently,[2] yet, phosphines remain the most employed ligands in accelerating or modifying the reactions.[3] Even though various synthetic methods have been extensively explored in searching of more versatile and efficient organic phosphine ligands in the palladium-catalyzed Suzuki–Miyaura cross-coupling reactions,[4] nevertheless, to our best knowledge, a systematical investigation of transition-metal-containing phosphines (TM-phosphines) has yet remained a relatively uncultivated territory.[5,6]

Our previous work had demonstrated the catalytic capacity of an unusual palladium complex **2**, which is coordinated by a cobalt-containing bidentate phosphine ligand [(μ-$Ph_2PCH_2PPh_2$)$Co_2(CO)_4$(μ-$PPh_2C{\equiv}CPPh_2$)] **1**, on Suzuki cross-coupling reactions (Scheme 1).[7] The reactions, using bromobenzene (or bromothiophene) with phenylboronic acid as reaction substrates, were carried out by employing **2** as catalyst in organic as well as biphasic media and results were satisfactory.[8]



Scheme 1.

The reactants of the catalytic processes under investigation were composed of 1.00 mmol of aryl halide, 1.5 equiv of phenylboronic acid, 1 mol% of **2** (based on aryl halide), 1 mL toluene (or mixed solvent: THF/H_2O = 5 mL/1 mL), and 2.0 equiv of K_3PO_4 (based on aryl halide). The reaction mixture was stirred at 65 °C for 16 h then workup followed. In most of the cases, the reactions carried out in biphasic media are more efficient than that in pure organic phase. The fact that high efficiency was achieved for an alkyl bromide is noteworthy.[8,9]

As known, Suzuki–Miyaura coupling reactions are more efficient in organic phase while employing $Pd(OAc)_2$ as catalyst; on the contrary, it is more efficient in biphasic media for using $PdCl_2$.[10] The idea of using biphasic media in Suzuki–Miyaura coupling reaction is attractive because of the ecological and safety reason for using water as a major component of the reaction solvent.[11] In addition, water-soluble reagent such as NaOH, K_3PO_4 (bases using in Suzuki reaction) and NaCl (side product of Suzuki reaction) can be dissolved extensively in water. Besides, the disadvantage of low solubility of the metal catalysts in

Keywords: Biphasic Suzuki reaction; Palladium complex; Cobalt-containing phosphine; Phase-transfer agent.

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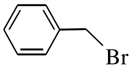
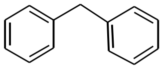
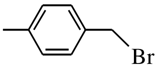
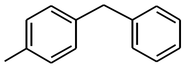
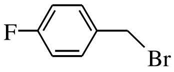
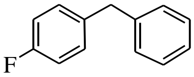
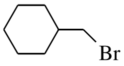
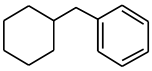
Table 1. Suzuki-coupling reactions of benzyl bromides employing catalyst **2**[a]

Entry	Halide	Product	Solvent	Yield (%)
1			THF–H_2O(5:1) Toluene	99.0 90.0
2			THF–H_2O(5:1) Toluene	79.2 64.9
3			THF–H_2O(5:1) Toluene	90.2 72.4
4			THF–H_2O(5:1) Toluene	NR NR

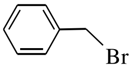
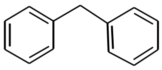
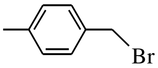
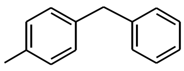
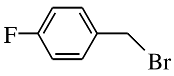
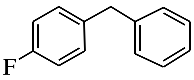
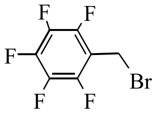
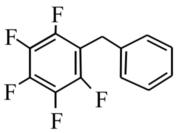
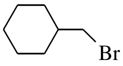
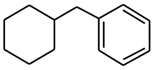
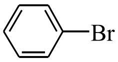
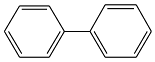
[a] Reactions were conducted in either THF with NaOH(aq) (3 M, 1.00 mL) or in toluene (1.00 mL) with K_3PO_4 (3 equiv) at 65 °C for 16 h employing 1 mol% of **1** with bromides (1.00 mmol) and phenylboronic acid (1.50 mmol).

biphasic media might be overcome either by employing phase-transfer agent or water-soluble phosphine ligands.[12] Phase transfer agent such as tetrabutylammonium bromide (TBAB) was reported frequently used in biphasic reactions.[13] Role played by the ammonium salt is thought to be two-folds. First, it facilitates the solvability of the organic substrates in the solvent medium. Second, it was thought to enhance the rate of the coupling reaction by activating the boronic acid through the formation of a boronate complex $[ArB(OH)_3]^-[R_4N]^+$. TBAB has been used recently in conjunction with a palladium oxime catalyst for the Suzuki coupling of aryl chlorides with phenylboronic acid in water[14] and as a promoter in the $Pd(PPh_3)_4$ catalyzed Suzuki coupling reaction of 4-bromobenzonitrile and phenylboronic acid in organic solvents.[15]

In principle, the carbon–halide bond, either C_{sp3}-, C_{sp2}-, or C_{sp}–X, are all subjected to the attack of deliberately chosen electrophiles while appropriate metal-containing catalysts were employed.[16] Nevertheless, difficulties are often encountered while inactivated alkyl halides and alkyl electrophiles are employed in Suzuki coupling reactions. First, alkyl halides (even CH_3I) react slowly with Pd^0 complexes, in contrast with the behavior observed for allyl, benzyl, alkenyl, and aryl halides.[17] Second, once the alkyl-Pd^{II} complex is formed, it should face the possibility of decomposition by a fast β-hydride elimination, which competes with the usually slower trans-metalation process. β-Hydride elimination process requires several conditions such as the existence of a vacant coordination site and the feasibility of arranging the M–C(α)–C(β)–H atoms in the same plane. This undesirable process may not be a problem in carbonylative couplings of C(sp^3) centers since the fast CO insertion prevents decomposition of the alkyl-Pd intermediate.[18] Third, the reductive elimination process is normally slow for σ-alkyl-σ-aryl-Pd^{II} or di-σ-alkyl-Pd^{II} complexes.[19]

Reported herein are some notable results from biphasic Suzuki–Miyaura coupling reactions of aryl or benzyl

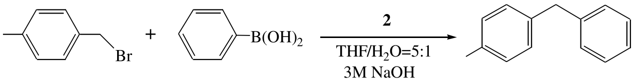
Table 2. Biphasic Suzuki-coupling reactions of benzyl bromides with phenylboronic acid employing catalyst **2** and adding TBAB[a]

Entry	Bromides	Product	Temperature (°C)	Time (h)	Yield (%)
1			40 65	0.5 16	98.2 99.0
2			40 65	0.5 16	72.0 86.8
3			40 65	0.5 16	74.2 90.2
4			40	0.5	47.8
5			40	0.5	37.4
6[b]			40	0.5	6.8

[a] Reactions were conducted in THF with 1 mol% of **2**, NaOH(aq) (3 M, 1.00 mL), bromides (1.00 mmol), TBAB (0.20 mmol) and phenylboronic acid (1.50 mmol).

[b] For comparison.

Table 3. Biphasic Suzuki coupling reactions employing **2** at various conditions[a]



Entry	TBAB (equiv)	Temperature (°C)	Time (h)	Yield (%)
1	—	65	16	>99
2	0.2	65	16	>99
3	—	65	0.5	10.8
4	0.2	65	0.5	16.2
5	—	40	16	75.4
6	0.2	40	16	87.5
7	—	40	0.5	10.5
8	0.2	40	0.5	6.8

[a] Reactions were conducted in THF with 1 mol% of **2**, NaOH(aq) (3 M, 1.00 mL), bromide (1.00 mmol) and phenylboronic acid (1.50 mmol).

bromides employing a cobalt-containing phosphine ligand coordinated palladium complex **2** in the presence/absence of a phase-transfer agent, TBAB.

2. Results and discussion

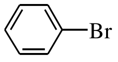
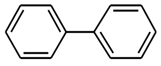
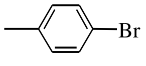
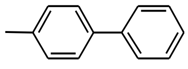
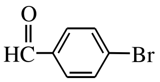
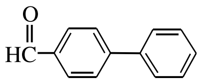
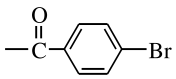
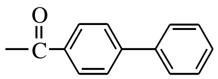
2.1. Suzuki reaction using cobalt-containing phosphine ligand chelated palladium complex 2

In our previous work,[8] an unusual high efficiency was achieved for a substituted alkyl bromide, benzylbromide, in a **2**-catalyzed Suzuki reaction. For comparison, the same reaction conditions were employed for several structural related substituted bromomethanes in either uni- or bi-phasic media (Table 1). The reactants of the catalytic reactions under investigation are consisted of 1.0 mmol of aryl halide, 1.5 equiv of phenylboronic acid, 1 mol% of **2** (based on aryl halide), 1.00 mL toluene (or mixed solvent: $THF/H_2O=5$ mL/1 mL), and 3.0 equiv of K_3PO_4. The reaction mixture was stirred at 65 °C for 16 h then workup followed. Encouraging results were obtained as shown (Table 1, entries 1–3). In these cases, reactions carried out in biphasic media are more efficient than that in pure organic solvent. Almost quantitative yield (99.0%) was obtained when bromobenzene is used as the halide source (entry 1). Nevertheless, the reaction was not very efficient (79.2% in THF/H_2O and 64.9% in toluene) when a less reactive 4-methyl-benzyl bromide, having a σ electron-donating group, was used (entry 2). The reaction with 4-fluoro-benzyl bromide, having a σ electron-withdrawing group at the *para*-position, gave a better yield, that is, 90.2% in THF/H_2O and 72.4% in toluene (entry 3). However, no reactivity was observed for using an aliphatic bromide as substrate (entry 4).

Biphasic Suzuki-coupling reactions, using benzyl bromides and phenylboronic acid as reaction substrates, were carried out employing catalyst **2** (Table 2, entries 1–5). A phase-transfer agent, TBAB, was intentionally added to enhance the reactivity of the reaction. Satisfactory results were obtained for using benzyl bromide or mono-substituted benzyl bromides as reaction substrates (entries 1–3). The substituent, either electron-withdrawing/donating, in the *para*-position does not affect the outcome notably (entries 2–3). Although having five strong σ electron-withdrawing groups at the *ortho*, *meta*, *para*-position for pentaflurobenzylbromide, as demonstrated in entry 4, the yield drops significantly, 47.8%. Obviously, the exceedingly strong electron-withdrawing effect from the five substituents as well as the steric effect caused by *ortho*-position substituent play major role in preventing the aryls from coupling. It is worthy of noting that the yield is improved from almost nothing (Table 1, entry 4) to 37.4% (Table 2, entry 5) while adding TBAB to the reaction system. On the contrary, the yield drops from 99.0% (Table 1, entry 1) to 6.8% (Table 2, entry 6) while the reaction time is shortened from 16 h to 30 min. It indicates that an induction period is needed before the reaction can be speeded up to a reasonable rate. In brief, the biphasic Suzuki coupling reactions are more efficient in the presence of phase-transfer agent TBAB than those without it.

Table 3 lists the results from the biphasic Suzuki coupling reactions, employing **2** as catalyst and with 4-methylbenzyl bromide and phenylboronic acid as substrates, in various reaction conditions. This study has shown the importance of two features. First, the yields are relatively lower for reactions without adding TBAB (entry 3 vs 4; 5 vs 6). Second, the factor of reaction time is more crucial than that of temperature. Low yield was observed commonly for short reaction time. Obviously, an induction period for the reduction of Pd(II) to Pd(0) active species is needed for this type of reaction.

Table 4. Biphasic Suzuki coupling reaction of aryl bromides employing catalyst **2** and adding TBAB[a]

Entry	Halide	Product	Yield (%)
1			6.8
2			Trace
3			12.3
4			27.2

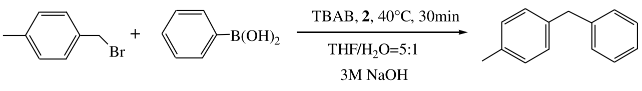
[a] Reactions were conducted in THF at 40 °C for 0.5 h employing 1 mol% of **2**, NaOH(aq) (3 M, 1.00 mL), bromides (1.00 mmol), TBAB (0.20 mmol) and phenylboronic acid (1.50 mmol).

The necessity of long reaction hours for this type of reaction is also demonstrated in the following experiments (Table 4). The following reactions were carried out for only 0.5 h rather than the commonly employed 16 h. A rather low yield, 6.8%, was obtained while bromobenzene is used as the halide source (Table 4, entry 1). By contrast, almost quantitative yield (99.0%) was obtained at higher temperature, 65 °C, and long reaction hours, 16 h (Table 1, entry 1). The account is also valid for entries 2–4 no matter which type of halides, with electron-withdrawing/donating substituents, are used. It is concluded here that longer reaction time is more crucial for aryl bromides (C_{sp^2} substituent) than benzyl bromides (C_{sp^3} substituent) to produce better yield in Suzuki coupling reaction employing the kind of catalyst like **2**.

2.2. Suzuki reactions using 3, 4, 5-chelated palladium complexes and 2

For comparison, biphasic Suzuki-coupling reaction of benzyl bromides employing a number of palladium catalysts were carried out (Table 5). Rather low yields were observed for using **3** as an acting diphosphine ligand in the cases or either $Pd(OAc)_2$ or $(COD)PdCl_2$ as the palladium source (entries 1–2). Slightly improved yields were obtained while a mono-dentate phosphine ligand **4** was used (entries 3–4). Better yields were seen while 2-(di-*tert*-butylphosphino)biphenyl **5**, the powerful phosphine ligand which was used by Buchwald,[20] were employed (entries 5 and 6). Not many differences were observed either using $Pd(OAc)_2$ or $(COD)PdCl_2$ as the palladium source. In summary, the catalytic efficiencies of these types of ligands are in the sequence of **5** > **4** > **3**. The best yield was found while **2** was used as the catalyst (entry 7).

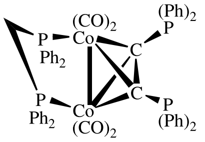
Table 5. Biphasic Suzuki-coupling reaction of benzyl bromides employing various palladium catalysts[a]



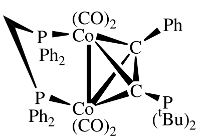
Entry	Pd	Ligand[b]	Isolated yield (%)
1	$Pd(OAc)_2$	3	6.4
2	$(COD)PdCl_2$	3	4.6
3	$Pd(OAc)_2$	4	12.9
4	$(COD)PdCl_2$	4	12.6
5	$Pd(OAc)_2$	5	43.5
6	$(COD)PdCl_2$	5	38.7
7	**2**	—	72.0

[a] Reactions were conducted in THF with 1 mol% of Pd catalysts, NaOH(aq) (3 M, 1 mL), bromides (1.00 mmol), TBAB (0.20 mmol) and phenylboronic acid (1.50 mmol).

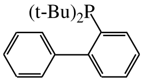
[b]



3



4



5

3. Concluding remarks

We have demonstrated the catalytic capacity of a novel cobalt-containing phosphine chelated palladium complex **2** in either uni- or bi-phasic Suzuki's reactions. It has shown that Suzuki-coupling reactions of benzyl bromides (substrates of C_{sp^3} substituent) employing catalyst **2** was performed better than using aryl bromides (substrates of C_{sp^2} substituent). In most cases, the reactions carried out in biphasic media were much efficient than that in pure organic phase. Better yields were commonly observed while a phase-transfer agent TBAB was added in the reactions. The factor of reaction time is more crucial than that of reaction temperature. Not many differences were observed either using $Pd(OAc)_2$ or $(COD)PdCl_2$ as the palladium source.

4. Experimental

4.1. General

All operations were performed in a nitrogen flushed glove box or in a vacuum system. Freshly distilled solvents were used. ^1H NMR spectra were recorded over Varian-400 spectrometer at 400.00 MHz. The chemical shifts are reported in ppm relative to internal standard $CDCl_3$.

4.2. General procedures for the Suzuki cross-coupling reactions

Suzuki cross-coupling reactions were performed according to the following procedures.

4.2.1. Method I (conducted in a THF–H_2O biphasic medium). Complex **2** (0.012 mg, 0.01 mmol) and boronic acid (0.183 g, 1.50 mmol) were charged into a 20 mL Schlenk flask. The flask was evacuated and backfilled with nitrogen before adding THF (5 mL), 3 M NaOH solution (1 mL), aryl halide (1.00 mmol) and (in the presence/absence of) tetrabutylammonium bromide (TBAB, 0.65 g, 0.20 mmol). The solution was stirred at 65 °C for 30 min–16 h. The mixture was washed with aqueous NaOH (1 M, 20 mL), and then the aqueous layer was extracted with ether (30 mL). The combined organic layers were washed with brine (20 mL), and dried over with anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel.

4.2.2. Method II (conducted in a toluene medium). Complex **2** (0.012 mg, 0.01 mmol), the boronic acid (0.183 g, 1.50 mmol), and K_3PO_4 (0.425 g, 2.00 mmol), were charged into a Schlenk flask. The flask was evacuated and backfilled with nitrogen before adding toluene (1 mL) and the aryl halide (1.00 mmol). The solution was stirred at 65 °C, 16 h. The same procedures as Method I were followed from here accordingly.

4.2.3. Method III (conducted in a THF–H_2O biphasic medium). Ligand **1** (1.00 mmol), boronic acid (0.183 g, 1.50 mmol) and 1 mol% of Pd complex ($Pd(OAc)_2$ or $PdCl_2$), were charged into a Schlenk flask. The flask was evacuated and backfilled with nitrogen before adding THF (5 mL), 3 M NaOH solution (1 mL), tetrabutylammonium bromide (TBAB, 0.065 g, 0.20 mmol) and aryl halide (1.00 mmol). The flask was sealed with Teflon screw cap, and the solution was stirred at 40 °C for 0.5 h. The same procedures as Method I were followed from here accordingly.

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