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Journal of Molecular Catalysis A: Chemical 273 (2007) 310–315
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
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Highly efficient Suzuki coupling using moderately bulky tolylphosphine ligands

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Received 27 February 2007; received in revised form 8 April 2007; accepted 16 April 2007
Available online 20 April 2007

Abstract

Tolylphosphines, P(*o*-tolyl)$_n$Ph$_{3-n}$ have been used in the palladium catalyzed Suzuki cross-coupling reactions of a series of aryl-bromides, chlorides and also two bromoarylphosphine oxides and a bromoarylphosphine with arylboronic acids. The effects of the phosphine, palladium source, base, solvent and promoter salt were investigated. In all studied phosphines, particularly P(*o*-tolyl)$_2$Ph high conversions and turnovers were seen compared to ortho-unsubstituted phosphines which indicates that other factors such as cyclometallation in addition to steric and electronic effects may be responsible.

Keywords: Suzuki coupling reaction; Tolylphosphine; Palladium catalyst

1. Introduction

Palladium-catalyzed Suzuki cross-coupling reactions of aryl halides with arylboronic acids have emerged as an extremely efficient and important tool in organic synthesis, as well as in a variety of industrial processes [1–20]. Commercially available PPh_3 has been used extensively for these reactions; however, it requires elevated reaction temperatures, tends to be inactive towards aryl chloride substrates, and produces phenyl-aryl by-products [21–23]. On the other hand, opposite activities have been reported using P(*o*-tolyl)$_3$ in the Suzuki cross-coupling reactions. Although many authors have reported P(*o*-tolyl)$_3$ to be a very active phosphine, Fu and co-worker have reported this ligand to be a relatively inactive phosphine [6]. In addition, Richards and co-workers have demonstrated a relationship between the steric and electronic effects of the phosphines as a plot where P(*o*-tolyl)$_3$ was placed in a lower activity zone [24]. This difference in activity results from the presence of many reaction steps, each of which may contribute in the rate of reaction (Scheme 1). The main components of the mechanism for the Suzuki coupling are believed to be an pre-dissociation and or reduction step in which the Pd(II) source is converted to the more active and coordinatively unsaturated Pd(O) catalyst. Sterically demanding and more electron-rich phosphines enforce this step (e.g., Wilkinson hydrogenation process) [23,25–27]. The next steps are an oxidative addition of aryl halide to the Pd(O) active catalyst followed by a transmetallation step in which the aryl group is transferred from boron to palladium, and finally a reductive elimination to release the product. More electron-rich and less bulky phosphines facilitate the oxidative addition step while more bulky and less electron-rich phosphines facilitate the reductive elimination step [28,29]. Therefore, the relative contribution of steric and electronic effects is very important, particularly for less reactive aryl chlorides [30–32]. Since the type and the number of substituents have an important effect on the bulkiness and electron density of the phosphines, and in continuation of our previous investigations on the

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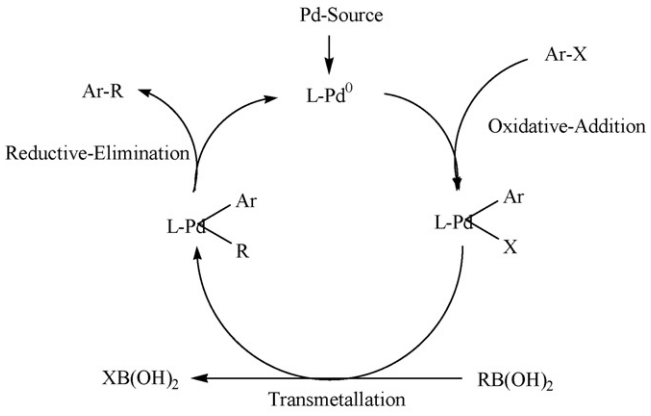
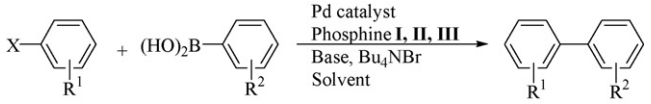
doi:10.1016/j.molcata.2007.04.022



Scheme 1. General mechanism for the Suzuki cross-coupling reactions.



I: P(o-toly)Ph_2, **II**: P(o-toly)$_2$Ph, **III**: P(o-toly)$_3$

Scheme 2. Screening the reaction of aryl halides with arylboronic acid.

application of mixed arylphosphines in the Suzuki coupling [33], we were encouraged to synthesize mixed phenyltolylphosphines, P(*o*-tolyl)$_n$Ph$_{3-n}$ **I–III** and investigate their activity in Suzuki cross-coupling (Scheme 2).

2. Experimental

2.1. Materials and techniques

All chemicals were purchased from Fluka and/or Merck companies. ^{1}H (400 MHz), ^{13}C (100 MHz) and ^{31}P (162 MHz) NMR spectra were recorded on a Bruker Avance Spectrometer. Shimadzu GC 14-A and thin layer chromatography on precoated silica gel fluorescent 254 nm (0.2 mm) were used for monitoring the reactions. Conversions were determined by GC, based on bromoacetophenone. Turnovers were defined as mole of product per mole of catalyst. Elemental analysis was performed using CHN Herause rapid model. The cross-coupling biphenyl product was characterized by its ^{1}H NMR spectrum and melting points.

2.2. Preparation of P(o-tolyl)$_3$ (*III*): typical procedure [34]

To a freshly prepared diethyl ether solution of 4-lithiotolyl (33 mmol, 3.23 g) at −78 °C was added freshly distilled PCl_3 (10 mmol, 1.38 g) in 5 mL of anhydrous diethyl ether dropwise with stirring over 20 min. After stirring at −78 °C (at this temperature organolithium reagent has sufficient stability and activity) for 30 min, the reaction mixture was allowed to warm to room temperature. After stirring at room temperature for 1.5 h, the reaction mixture was hydrolyzed with HCl (1N, 10 mL), followed by addition of chloroform and then, the organic solution was separated and dried over $MgSO_4$. The solvent was removed at reduced pressure. The residue was washed with methanol (4× 5 mL), to yield the crude product (2.42 g, 79.6%). The crude product was recrystallized from a chloroform/hexane (1/4) to yield desired pure product (2.15 g, 70.7%).

In order to prepare P(*o*-tolyl)$_2$Ph (**II**), and P(*o*-tolyl)Ph_2 (**I**), similar procedures were used using solutions of 4-tolyllithium (22 mmol, 2.16 g and 11 mmol, 1.08 g, respectively) in dry diethyl ether and solutions of PCl_2Ph (10 mmol, 1.78 g) or $PClPh_2$ (10 mmol, 2.25 g) in dry diethyl ether instead of PCl_3. The yields of pure products were 2.25 g (77.6%) for (**II**) and 2.08 g (75.4%) for (**III**), respectively.

Characterization data of phosphines: **I**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H), 6.7–7.4 (m, 14H); ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ 21.1, 125.8, 128.0, 128.2, 128.8, 129.5, 132.4, 133.1, 133.5, 135.5, 142.0, 142.5; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −12.35 (s); Anal. calcd. for $C_{19}H_{17}P$, C, 82.60, H, 6.16, Found C, 82.37, H, 6.11. mp = 74–75 °C; **II**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23 (s, 6H), 7.00–7.30 (m, 13H); ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ 21.0, 21.5, 126.7, 127.1, 128.0, 128.2, 128.8, 129.2, 134.5, 134.7, 134.9, 135.2, 135.5; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −21.77 (s); Anal. calcd. for $C_{20}H_{19}P$, C, 82.76, H, 6.55, Found C, 82.55, H, 6.48. mp = 85–86 °C; **III**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 9H), 6.60–7.30 (m, 12H); ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ 21.5, 22.1. 22.5, 126.0, 126.8, 128.4, 128.9, 129.3, 129.8, 132.5, 133.0, 134.0, 134.6, 143.0, 143.4, 144.0; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −31.13 (s); Anal. calcd. for $C_{21}H_{21}P$, C, 82.89, H, 6.90, Found C, 82.69, H, 6.84. mp = 121–123 °C.

2.3. Preparation of n-BuPyBF$_3$Cl: typical procedure

Pyridine (96 g, 1.2 mol) in 10% molar excess was refluxed with *n*-BuCl (105 g, 1.1 mol) for 72 h in dark. The reaction mixture was cooled and the solid obtained was recrystallized from MeCN/EtOAc, filtered under vacuum, washed with EtOAc and quickly transferred to a bottle while still moist with solvent. The excess solvent was then removed under vacuum. Then 1 mol BF_3 was added to *n*-BuPyCl (0.5) mol at room temperature under N_2 to give the desired ionic liquid.

2.4. General procedure for the Suzuki coupling of aryl halides (entry 1, Table 1)

Reaction tube was charged with $PhB(OH)_2$ (1.5 mmol), K_3PO_4 (2 mmol), and **II** (0.4 mol%) under a dry nitrogen atmosphere. A solution of 4-bromoacetophenone (1.0 mmol in 2 mL of freshly dried toluene) along with a solution of palladium acetate (0.1 mol% in 3 mL of dried toluene) was added through a rubber septum. After addition of water (1 mL), the resulting mixture was heated at 100 °C for 1 h. After extraction with ether, the organic phase was dried over $MgSO_4$. The solvent was evaporated and a crude product was obtained. For determination of conversions and yields by GC, a small portion of the crude product was added to a solution of hexadecane as internal standard in CH_2Cl_2 (1 mL). To isolate the product, the crude product was purified by chromatography with hexane/ethyl acetate

Table 1
Initial optimization of the system[a]

Entry	Catalyst (mol%)	Phosphine	Solvent	Base	Time (h)	Conversion (%)[b]
1	$Pd(OAc)_2$ (0.1)	**II**	Toluene	K_3PO_4	1	100
2	$Pd(OAc)_2$ (0.1)	**I**	Toluene	K_3PO_4	1	100
3	$Pd(OAc)_2$ (0.1)	**III**	Toluene	K_3PO_4	1	100
4	$Pd(OAc)_2$ (0.0001)	**II**	Toluene	K_3PO_4	10	95
5	$Pd(OAc)_2$ (0.0001)	**I**	Toluene	K_3PO_4	10	75
6	$Pd(OAc)_2$ (0.0001)	**III**	Toluene	K_3PO_4	10	70
7	$PdCl_2$ (0.1)	**II**	Toluene	K_3PO_4	1	95
8	$PdCl_2$ (0.0001)	**II**	Toluene	K_3PO_4	10	70
9	$Pd(dba)_2$ (0.1)	**II**	Toluene	K_3PO_4	1	100
10	$Pd(dba)_2$ (0.0001)	**II**	Toluene	K_3PO_4	10	90
11	$Pd_2(dba)_3$ (0.1)	**II**	Toluene	K_3PO_4	1	100
12	$Pd_2(dba)_3$ (0.001)	**II**	Toluene	K_3PO_4	10	95
13	Pd/C (0.1)	**II**	Toluene	K_3PO_4	1	95
14	Pd/C (0.0001)	**II**	Toluene	K_3PO_4	10	65
15[c]	$Pd(OAc)_2$ (0.1)	**II**	Toluene	K_3PO_4	1	50
16[d]	$Pd(OAc)_2$ (0.1)	**II**	Toluene	K_3PO_4	1	70
17	$Pd(OAc)_2$ (0.1)	**II**	Dioxane	K_3PO_4	1	90
18	$Pd(OAc)_2$ (0.1)	**II**	DMF	K_3PO_4	1	80
19	$Pd(OAc)_2$ (0.1)	**II**	THF	K_3PO_4	1	85
20	$Pd(OAc)_2$ (0.1)	**II**	DMSO	K_3PO_4	1	70
21	$Pd(OAc)_2$ (0.1)	**II**	DME	K_3PO_4	1	80
22	$Pd(OAc)_2$ (0.1)	**II**	$BuPyBF_3Cl$	K_3PO_4	1	95
23	$Pd(OAc)_2$ (0.1)	**II**	$BmimBF_3Cl$	K_3PO_4	1	100
24	$Pd(OAc)_2$ (0.1)	**II**	Toluene	KF	1	50
25	$Pd(OAc)_2$ (0.1)	**II**	Toluene	Cs_2CO_3	1	95
26	$Pd(OAc)_2$ (0.1)	**II**	Toluene	Na_2CO_3	1	75
27	$Pd(OAc)_2$ (0.1)	**II**	Toluene	NEt_3	1	65
28	$Pd(OAc)_2$ (0.1)	**II**	Toluene	K_2CO_3	1	75
29[e]	$Pd(OAc)_2$ (0.1)	**II**	Toluene	K_3PO_4	1	100
30[e]	$Pd(OAc)_2$ (0.0001)	**II**	Toluene	K_3PO_4	10	70

[a] Reaction conditions: 4-bromoacetophenone (1.0 mmol), $PhB(OH)_2$ (1.5 mmol), phosphine/palladium (4:1), base (2.0 mmol), Bu_4NBr (0.5 mmol), solvent (5 mL), water (1 mL), 100 °C.
[b] Determined by GC based on aryl halide (hexadecane standard).
[c] In the absence of water.
[d] In the presence of 0.5 mL water.
[e] In the absence of promoter.

(6:1). Yield 0.178 g (90.5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.65 (s, 3H, methyl of acetyl), 7.35–7.47 (m, 3H), 7.6–7.65 (m, 2H), 7.70 (d, 2H, $J = 8$ Hz), 8.0 (d, 2H, $J = 8$ Hz). mp = 119–120 °C.

2.5. General procedure for the Suzuki coupling of phosphine oxides (entry 1, Table 5)

Reaction tube was charged with $PhB(OH)_2$ (2.0 mmol), Na_2CO_3 (3.0 mmol), $OPPh_2(o\text{-}C_6H_4Br)$ (1.0 mmol), **II** (10 mol%) and $Pd_2(dba)_3$ (2.5 mol%) in freshly distilled DMF (10 mL) under a dry nitrogen atmosphere. After addition of water (1 mL), the resulting mixture was heated at 105 °C for 12 h. After cooling to room temperature, the mixture was diluted with water and extracted with chloroform (3× 10 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$. The solvent was evaporated and a crude product was obtained. The crude product was purified by flash chromatography (2:1 hexane/ethyl acetate) and crystallized to yield white crystals of product in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00–7.50 (m); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 28.9 (s); mp = 150–151 °C.

3. Results and discussion

3.1. Initial optimization

An initial screening was performed to discover the optimum catalyst, solvent, and base for the reaction between 4-bromoacetophenone and phenylboronic acid. All studied tolylphosphines showed excellent reactivity in relatively high catalyst concentration. However, with lower catalyst loading, the best results were found using $P(o\text{-tolyl})_2Ph$ **II** (Table 1, entries 1–6). In these phosphines, ligand **III** is the most electron donating (based on ^{31}P NMR chemical shifts [35]) and the bulkiest ligand (based on the Tolman's cone angles [36]) (Table 2); therefore, a critical optimum contribution of electronic and steric effects may be responsible for higher activity of **II**.

Readily available palladium species such as $Pd(OAc)_2$, $PdCl_2$, $Pd(dba)_2$, $Pd_2(dba)_3$, and Pd/C, showed similar reactivity (95–100% conversion) when used at relatively high catalyst loading (0.1 mol%) in the presence of 0.4 mol% phosphine **II** under identical conditions (Table 1, entries 1, 7, 9, 11, and 13). However, using low catalyst concentrations, $Pd(OAc)_2$, $Pd_2(dba)_3$, and $Pd(dba)_2$ showed higher reactivity. The slow

Table 2
Steric and electronic effects of the phosphines

Phosphine	θ[a] (°)	^{31}P chemical shift (ppm)
III	194	−31.13
II	177	−21.77
I	161	−12.35
PPh_3	145	−3.3

[a] From Ref. [36].

reaction of $PdCl_2$ (Table 1, entry 8) may be due to the difficult reduction of Pd(II) in the preparation of the active Pd(0) species. Being $Pd(PPh_3)_4$ as a less reactive catalyst may be due to existence of a slow pre-dissociation step and/or formation of by-products [21]. In the case of $Pd(OAc)_2$, preheating the palladium catalyst to 60 °C significantly increased the conversions obtained in the Suzuki reaction. This may be due to in situ formation of very active metallic particles.

Toluene was found to be the solvent of choice (Table 1, entries 1 and 17–21); moreover, the turnover of the reaction was optimized using a binary mixture of toluene/water (5:1). Using toluene/water (10:1) or dry toluene resulted in lower conversions (Table 1, entries 1, 15, and 16). Interestingly, reactions in the ionic liquids butylpyridinium chlorotrifluroborate, $BuPyBF_3Cl$, and butylimidazolium chlorotrifluroborate, $BmimBF_3Cl$, provided excellent conversions (Table 1, entries 22 and 23). These results are relevant from an environmental and industrial point of view [37–39]. Using an ionic liquid solvent, the active palladium catalyst can be recycled by simple extraction of the biphenyl product and inorganic salts from a triphasic system by addition of water and hexane. The catalyst can be reused at least three times. However, the catalyst activity was gradually declined in successive runs. Interestingly, adding 2 mol% of the phosphine in each run keep hold of the yield excellent.

3.2. Suzuki reaction of aryl-bromides and chlorides

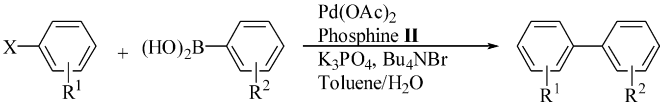
The efficiency of the optimized conditions was investigated in the Suzuki coupling of a series of aryl halides with arylboronic acids. The results show that the catalyst system obtained from $Pd(OAc)_2$/P(*o*-tolyl)$_2$Ph is very efficient for Suzuki cross-coupling reaction of activated and deactivated aryl halides with arylboronic acids (Table 3).

The additive Bu_4NBr has a beneficial effect on the cross-coupling of 4-haloacetophenone particularly, in low catalyst loading (Table 1, entries 1, 4 and 29–30; Table 3, entries 2 and 13). It is reported that Bu_4NBr stabilizes the anionic palladium species, facilitates the solvation of the organic substrates, activates the boronic acid, and stabilizes the colloidal palladium nanoparticles [40–46].

At high temperature, aryl bromides, and to a lesser extent aryl chlorides undergo reaction resulting in excellent conversion; however, 4-bromoacetophenone could also be employed under much milder conditions, although longer reaction times were required (Table 4). Again, the addition of Bu_4NBr salt increased the conversion significantly (Table 4, entries 6 and 7). As expected, increasing the amount of the catalyst also improved in the conversion (Table 4, entries 6 and 8).

The role of tolylphosphines in achieving excellent conversions compared to phenylphosphines [33] may be due to higher electron density and steric effects as well as other factors. One of the most probable factors is the formation of a monophosphine palladacycle intermediate, which is formed by in situ cyclopalladation. Cyclopalladation is carried out by C–H activation, which is easier for the H–C(sp^3) bond of methyl within the *o*-tolyl group than the H–C(sp^2) bond within the phenyl group [47–50]. In addition, the potential five-membered palladacycle produced by tolylphosphines would be more stable than the 4-membered palladacycle produced by phenylphosphines.

Table 3
Suzuki coupling of aryl halides with arylboronic acids[a]



Entry	X	$Pd(OAc)_2$ (mol%)	R^1	R^2	Time (h)	Conversion (%)[b]	TON
1	Br	0.1	4-COMe	H	1	100	1,000
2	Cl	0.1	4-COMe	H	6	90	900
3	Br	0.0001	4-COMe	H	8	80	800,000
4	Cl	0.0001	4-COMe	H	24	55	550,000
5	Br	0.1	H	H	1	100	1,000
6	Br	0.1	4-Me	H	1	90	900
7	Br	0.1	4-OMe	H	1	90	900
8	Br	0.1	4-Ph	H	1	85	850
9	Br	0.1	H	Me	1	100	1,000
10	Br	0.1	4-Me	Me	1	100	1,000
11	Br	0.1	4-OMe	Me	1	100	1,000
12	Br	0.0001	4-Me	Me	10	85	850,000
13[c]	Cl	0.1	4-COMe	H	6	55	550
14	Cl	0.0002	4-COMe	H	6	55	275,000

[a] Reaction conditions: aryl halide (1.0 mmol), $ArB(OH)_2$ (1.5 mmol), phosphine **II**/$Pd(OAc)_2$ (4:1), K_3PO_4 (2.0 mmol), Bu_4NBr (0.5 mmol), toluene (5 mL), water (1 mL), 100 °C.
[b] Determined by GC based on aryl halide (hexadecane standard).
[c] In the absence of promoter.

Table 4
The effect of temperature and time in the reaction of 4-bromoacetophenone with phenylboronic acid[a]

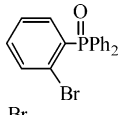
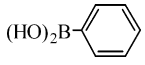
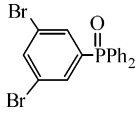
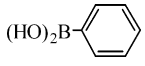
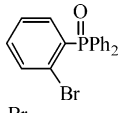
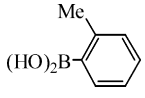
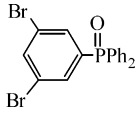
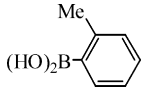
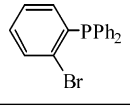
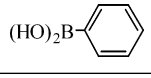
Entry	Temperature (°C)	Time (h)	Conversion (%)[b]	TON
1	100	1	100	1000
2	80	1	70	700
3	50	1	45	450
4	r.t.	1	30	300
5	r.t.	10	60	600
6	r.t.	24	75	750
7[c]	r.t.	24	40	400
8[d]	r.t.	24	95	475

[a] Reaction conditions: 4-bromoacetophenone (1.0 mmol), $ArB(OH)_2$ (1.5 mmol), $Pd(OAc)_2$ (0.1 mol%), **II** (0.4 mol%), K_3PO_4 (2.0 mmol), Bu_4NBr (0.5 mmol), toluene (5 mL), water (1 mL).
[b] Determined by GC based on aryl halide (hexadecane standard).
[c] In the absent of promoter.
[d] In the presence of 0.2 mol% of $Pd(OAc)_2$ and 0.8 mol% of **II**.

3.3. Suzuki reaction of bromoarylphosphine oxides

High conversions and turnovers of the above-mentioned classical Suzuki reactions and also growing interest in application of biaryl-based phosphines in a number of metal-catalyzed reactions encouraged us to investigate the coupling of arylboronic acids with bromoarylphosphine oxides using the phosphine **II**. Initial optimizations led us to use DMF, Na_2CO_3, and $Pd_2(dba)_3$ as solvent, base, and catalyst, respectively. Table 5 shows that this method is efficient to production of a biaryl- and terphenyl-based phosphine oxides (entries 2 and 4). Similar test using parent bromoarylphosphine instead of its oxide led to a lower yield indicating the importance of the electronic effects of phosphorus environment (Table 5, entry 5). Interestingly, the reaction does not need to loading of additional phosphine, which indicates the catalytic role of the obtained phosphines and/or starting bromoarylphosphine. The one-pot preparation of biaryl-based phosphines via this method simply negates the need for reduction of phosphine oxides to the corresponding phosphines.

Table 5
Suzuki coupling of bromoarylphosphine oxides and bromoarylphosphine[a]

Entry	Substrate	Arylboronic acid	Yield (%)[b]
1			95
2			88
3			78
4			55
5[c]			70

[a] Reaction conditions: phosphine oxide (or phosphine) (1.0 equiv.), $ArB(OH)_2$ (2.0 equiv.), $Pd_2(dba)_3$ (2.5 mol%), **II** (10.0 mol%), Na_2CO_3 (3.0 mmol), DMF (10 mL), water (1 mL), 100 °C, 12 h.
[b] Isolated yield according to ^{31}P NMR, not optimized.
[c] In the absence of phosphine **II**.

4. Conclusion

In conclusion, we reported a simple, efficient catalytic system for the Suzuki cross-coupling reaction of aryl halides, haloarylphosphines and phosphine oxides with arylboronic acids consisting of $Pd(OAc)_2$ and the moderately bulky electron-rich P(*o*-tolyl)$_2$Ph. These reactions occur at mild as well as elevated temperatures. In addition, the presence of water and Bu_4NBr leads to a significant increase in activity. Preparation of bulky biaryl-based phosphines is also one of the further advantages of this simple method.

Acknowledgements

The authors are grateful to the Kermanshah Oil Refining Company and the Razi University Research Council for the financial support of this work.

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