

2-Aminophenyl diphenylphosphinite as an easily accessible ligand for heterogeneous palladium-catalyzed Suzuki–Miyaura reaction in water in the absence of any organic co-solvent

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ABSTRACT

In this article, we have introduced application of 2-aminophenyl diphenylphosphinite as an easily accessible ligand for heterogeneous palladium-catalyzed Suzuki–Miyaura reaction in water in the absence of any organic co-solvent. By using 2-aminophenyl diphenylphosphinite as a ligand and Pd(OAc)₂ as the pre-catalyst, structurally different aryl halides (I, Br, Cl) were reacted efficiently with phenylboronic acid in water to produce their corresponding biphenyl products in good to excellent yields under heterogeneous conditions. The catalyst is recyclable and was recycled for seven runs for the reaction of bromobenzene with phenylboronic acid without appreciable loss of its catalytic activity.

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1. Introduction

Transition metal-catalyzed organic reactions are important achievements in organic synthesis [1–10]. One of most important transition metal-catalyzed reactions is one in which palladium is used as catalyst [11–18]. The palladium-catalyzed sp²–sp² cross-coupling reaction between aryl halides and arylboronic acids has found wide applications in laboratory and industries. Over the past two decades, the impact of the Suzuki–Miyaura reaction upon academia and industries has been considerable and is one of the most efficient ways for the generation of biaryl moieties which are found in building blocks of polymers, ligands and a wide range of natural products [11–18].

Nowadays, environmental consciousness encourages more environmentally sustainable chemical processes. In response to these important demands, industries have started implementing green chemistry practices such as waste prevention rather than its treatment, using new recyclable or heterogeneous catalysts and the use of less toxic materials as solvents and reagents. Organic solvents disposal in pharmaceutical industries is their major problem nowadays and composing around 80% of their wastes. Substitution

of expensive, not recyclable, flammable and toxic organic solvents with water is a challengeable subject and is of importance from different views. The use of water as the reaction media has several benefits; water is a cheap and plentiful, nontoxic, nonflammable compound and is a green solvent. On the other hand, water with its chemical and physical properties imposes selectivity and reactivity in reactions conducted in this media which cannot be attained using organic solvents. In addition, in water, phase separation is facile because most of the organic compounds are not soluble in water therefore, can easily be separated from aqueous phase. However, the heat capacity of water is not favorable, which causes isolation and drying of the products sometimes difficult especially, when large-scale operation is of concern [19–32].

Using water [33–41], ionic liquids [42,43] and PEG [44,45] as green media has been of our interest in recent years. Some of the examples are; regioselective iodination of aromatic compounds [33,34], ring opening of epoxides with varieties of nucleophiles [35], oxidation of sulfides to their sulfoxides with H₂O₂ [36], Michael addition of indoles and pyrroles to α,β -unsaturated electron-deficient compounds [37], conversion of epoxides to thiranes and amino alcohols [38], C–S Bond formation [39,44,45] and Michael addition of amines and thiols to α,β -unsaturated ketones in aqueous media [40].

In the articles appeared in recent years dealing with Suzuki–Miyaura reactions, the following subjects are considered as

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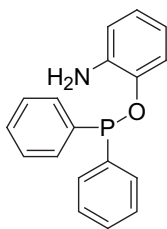


Fig. 1. 2-Amino diphenyl phosphinite (L).

challenges for investigation [11]. a) Shortening of the reaction times, b) using efficient ligands, c) easy separation of the catalyst from the reaction mixture, d) the stability of the catalysts in air, their recycling and e) use of low loading catalysts [46–48]. In addition, improving the low reactivity of aryl bromides and chlorides by changing solvents, ligands, palladium salts etc. should be also considered as an important subject for investigation and worthy of attention [11].

Phosphorous based ligands such as phosphines, phosphinites [PPh₂(OR)] and related compounds have been employed as ligands for C–C bond formation using palladium salts as the pre-catalysts [49–76]. For this purpose, we have recently introduced 2-aminophenyl diphenylphosphinite as an easily prepared and cheap phosphinite ligand for Heck–Mizoroki and Sonogashira–Hagihara reactions in neat water with success [41,77].

Now in this article, we have presented another important application of 2-aminophenyl diphenylphosphinite as a ligand for efficient Suzuki–Miyaura cross-coupling reactions using palladium acetate as the pre-catalyst in neat water.

2. Experimental

2.1. General remarks

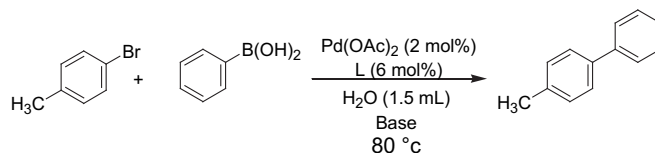
NMR spectra were recorded on a Bruker Avance DPX-250. The purity of the products and the progress of the reactions were accomplished by TLC on silica–gel polygram SILG/UV254 plates or GC analysis using a 3-m length column packed with DC-200 stationary phase.

2.2. General experimental procedure for the Suzuki–Miyaura reaction

In a 5 mL flask, a mixture of Pd(OAc)₂ (0.02 mmol, 4.5 mg) and 2-aminophenyl diphenylphosphinite (0.06 mmol, 17 mg) in distilled water (1.5 mL) was stirred for 10 min at 80 °C producing a black heterogeneous mixture. To the resulting mixture, aryl halide (1 mmol), phenylboronic acid (1.5 mmol, 180 mg) and NaOH (2 mmol, 80 mg) in distilled water (1.5 mL) were added and stirred at 80 or 95 °C. The progress of the reaction to completion was monitored by TLC or GC. The resulting heterogeneous aqueous mixture was filtered and the aqueous layer was extracted with ethyl acetate or diethyl ether (5 × 1 mL). Organic extracts were combined together and dried over anhydrous Na₂SO₄. Evaporation

Table 1

The effect of different bases upon the reaction of 4-bromotoluene with phenylboronic acid.



Entry	Base	Time (h)	Yield%
1	0	24	0
2	NaOH	2	90
3	K ₂ CO ₃	10	80
4	K ₃ PO ₄	9	82
5	CS ₂ CO ₃	10	86
6	Et ₃ N	9	85
7	DBU	9	60

of the solvent gave the crude product residue which was further purified by flash chromatography using *n*-hexane/EtOAc to give the desired coupling product in 70–94% isolated yields (Table 3).

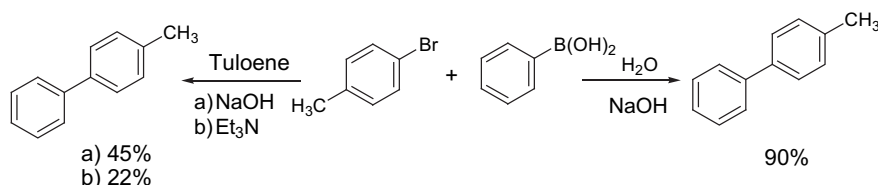
2.3. Recycling of the catalyst

In a 5 mL flask, bromobenzene (2 mmol, 0.2 mL) was reacted with phenylboronic acid (3 mmol, 360 mg) in neat water (3 mL) in the presence of Pd(OAc)₂ (0.04 mmol, 9 mg), 2-aminophenyl diphenylphosphinite (0.12 mmol, 34 mg) and NaOH (4 mmol, 160 mg) at 80 °C. After completion of the reaction (GC), the black solid catalyst was separated by centrifugation, washed with diethyl ether and charged into another batch of the reaction. This recycling was repeated for seven runs without appreciable loss of the activity of the catalyst.

3. Results and discussion

Phosphinites denote an interesting alternative to phosphines as ligands for metal ions used as catalysts in organic synthesis [43,73–76]. In this study, we have introduced 2-aminophenyl diphenylphosphinite (L) for Suzuki–Miyaura reaction which is easily prepared from the reaction of commercially available chlorodiphenyl phosphine with 2-aminophenol in a high yield (Fig. 1).

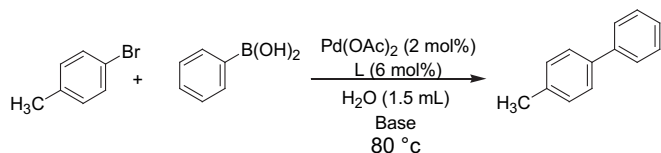
2-Aminophenyl diphenylphosphinite (L) is a water and air stable compound and shows a good stability towards hydrolysis and tolerates excess amounts of NaOH solution at reflux conditions. The formation of active Pd(0) catalysts was produced by mixing pre-catalyst [Pd(OAc)₂] with 2-aminophenyl diphenylphosphinite in water at 80 °C which produces a black heterogeneous solid mass after a few minutes in aqueous media. The SEM image of the black solid indicates the shape of particles varying from needle to spherical, uniformly dispersed sized particles which is characteristic of the formation of Pd(0) complex [41]. The XRD patterns of the



Scheme 1. Comparison of water and toluene as the media for the reaction 4-bromotoluene with phenylboronic acid.

Table 2

Comparison of 2-aminophenyl diphenylphosphinite (L) with Ph_3P and ligand-free reactions upon the reaction of 4-bromotoluene and phenyl boronic acid.



Entry	Ligand	Time (h)	Yield%
1	—	2	29
2	PPh_3	2	66
3	P(OPh)_3	2	64
4	L	2	90

black solid showed the characteristic bands for the formation of Pd (0) at (111), (200), (220) and (311) crystallographic planes for the complex [41]. The molar ratio of the ligands with respect to Pd has been determined to be ML_2 by employing the mole ratio method [41].

In order to show the effect of solvents upon the reaction, the reaction of 4-bromotoluene (1 mmol) reacted with phenylboronic acid (1.5 mmol) in toluene (1.5 mL) or in water (1.5 mL) in the presence of 6 mol% of 2-aminophenyl diphenylphosphinite (L), 2 mol% of $\text{Pd}(\text{OAc})_2$, and NaOH (2 mmol) at 80 °C. The results show that the reaction proceeded in a higher yield in water (90%) than in toluene (45%) after 2 h. We have also investigated the similar reaction using Et_3N as a soluble base in toluene. We found that only 22% of the desired product was isolated after 2 h. Therefore, water was recognized to be a more suitable reaction media for this reaction. The results are shown in Scheme 1.

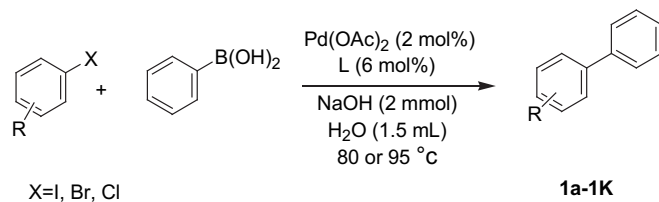
The effect of different bases upon the reaction of 4-bromotoluene with phenylboronic acid was also studied. The results show that NaOH was the most suitable base for this reaction. The results are tabulated in Table 1.

The role of 2-aminophenyl diphenylphosphinite (L) in comparison with Ph_3P , $(\text{PhO})_3\text{P}$ and also under ligand-free conditions has been disclosed for the reaction of 4-bromotoluene and phenylboronic acid. The results are presented in Table 2, which shows the advantage of using 2-aminophenyl diphenylphosphinite (L) in comparison with Ph_3P , $(\text{PhO})_3\text{P}$ and under ligand-free conditions (Table 2).

By using the above mentioned information and the optimized conditions, we applied this catalytic system for the reaction of structurally different aryl halides (I, Br, Cl) with phenylboronic acid in neat water at two different temperatures (80 and 95 °C) in the presence of NaOH. By this protocol, the reaction of aryl iodides proceeded smoothly to produce the desired biphenyl compounds in high to excellent yields (Table 3, entry 1–5). Since aryl iodides are more expensive than their corresponding bromides and chlorides, the use of iodides for large-scale reactions are not economically encouraged. Therefore, we applied this catalytic system for the reaction of aryl bromides and chlorides with phenylboronic acid. As it is evident from the results tabulated in Table 3, different aryl bromides were reacted with phenylboronic acid at 80 °C in appropriate reaction times. The desired biphenyl compounds were isolated in 70–90% yields. We have also shown the utility of the method for using aryl chlorides for this reaction. For this purpose, chlorobenzene, 4-chlorotoluene and 4-chloronitrobenzene were subjected to the reaction at 95 °C in the presence of 2 mol% of $\text{Pd}(\text{OAc})_2$, 6 mol% of the ligand in neat water (1.5 mL) in the presence of NaOH. The reactions proceeded well under this condition and the

Table 3

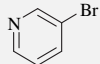
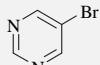


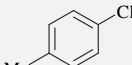
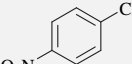
Suzuki–Miyaura coupling reactions of different aryl halides with phenyl boronic acid in neat water.



Entry	Ar-X	T °C	Time	Product	Isolated yield%
1		80	0.25	1a [78]	90
2		80	0.5	1b [78]	83
3		80	0.20	1c [78]	94
4		80	2	1d [79]	91
5		80	1	1e [78]	86
6		80	0.3	1a [78]	90
7		80	2	1e [78]	90
8		80	2	1f [78]	70
9		80	8	1g [78]	84
10		80	2	1h [80]	90
11		80	1.5	1c [78]	89

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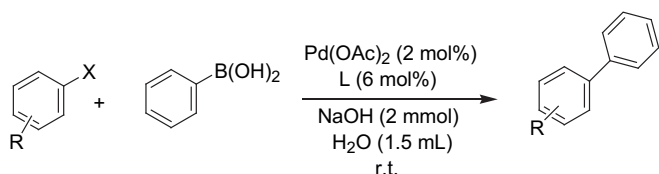
Table 3 (continued)

Entry	Ar-X	T °C	Time	Product	Isolated yield%
12		80	1	1i [78]	85
13		80	1.15	1j [81]	85
14		80	3	1k [81]	84
15		95	1	1a [78]	88
16		95	2	1e [78]	86
17		95	3	1c [78]	89 ^a

^a Reactions were performed in 15 mol% TBAB in order to facilitate the solubility of the solid and high melting point substrates.

Table 4

Room temperature Suzuki–Miyaura coupling reactions of different aryl halides with phenylboronic acid in neat water in the presence of 2-aminophenyl diphenylphosphinite ligand (L) and NaOH as a base.




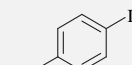
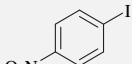
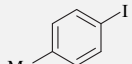

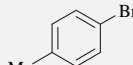

Entry	Ar-X	Time (h)	Product [73]	Isolated yield %
1		7	1a	90
2		20	1b	84 ^a
3		15	1c	88 ^a
4		12	1e	83

Table 4 (continued)

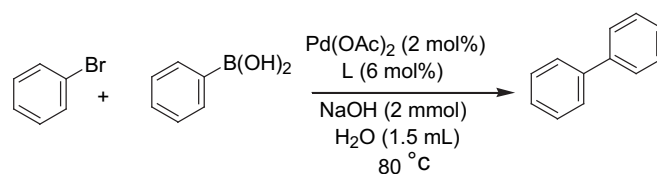
Entry	Ar-X	Time (h)	Product [73]	Isolated yield %
5		20	1a	90 ^b
6		24	1e	52 ^a
7		24	1j	78

^a The reaction was performed in 15 mol% TBAB in order to facilitate the solubility of the substrate in water.

^b GC Conversion, *n*-octane has been used as an internal standard.

Table 5

Recycling of the catalyst for the Suzuki–Miyaura reaction of bromobenzene with phenyl boronic acid.



Run	Time (min)	GC conversion%
1	30	100
2	30	100
3	30	98
4	30	97
5	30	97
6	30	95
7	30	96

desired products were isolated in 82–89% within 1–3 h (Table 3, entries 15–17).

Suzuki–Miyaura transformation at room temperature is highly attractive from economical and environmental views [82–87]. In order to evaluate the scope of this catalytic system for room temperature reactions, we have performed the reaction of some aryl iodides and bromides (1 mmol) with phenylboronic acid (1.5 mmol) in the presence of 2 mol% of Pd(OAc)₂, 6 mol% of the ligand and 2 mol% of NaOH in the presence or absence of tetrabutylammonium bromide (TBAB) as a phase-transfer agent (Table 4). The results of this study showed that the structurally different aryl iodides and bromides were reacted with phenylboronic acid to produce the desired biphenyl compounds in 52–90% yields (Table 4).

At the end, we have also studied the recycling of the catalyst for the reaction of bromobenzene with phenylboronic acid at 80 °C. For this purpose, the heterogeneous solid catalyst was separated by simple filtration or centrifugation and was charged into another batch of the reaction for seven consecutive runs without appreciable loss of its catalytic activity. The results are shown in Table 5.

4. Conclusions

In this study, we have successfully applied 2-aminophenyl diphenylphosphinite (L) as a cheap and easily prepared ligand for

Suzuki–Miyaura reactions using different aryl halides (I, Br, Cl), phenylboronic acid, palladium acetate in neat water under heterogeneous conditions at 80 and 90 °C. Arylation of aryl iodides and arylbromides with phenylboronic acid was also proceeded at room temperature using this catalytic system in the presence or absence of TBAB. The heterogeneous catalyst is easily separated from the reaction mixture and has been recycled for several runs without appreciable loss of its catalytic activity significantly. We believe addition of this catalytic system to the class of the available methods for carbon–carbon bond formation reactions is a useful addition to the category of organic synthetic methods.

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Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.05.016.

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