



Recyclable palladium-catalyzed Sonogashira–Hagihara coupling of aryl halides using 2-aminophenyl diphenylphosphinite ligand in neat water under copper-free condition

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ABSTRACT

An efficient heterogeneous copper-free Sonogashira–Hagihara coupling reaction was performed in the presence of 2-aminophenyl diphenylphosphinite (L) as a ligand, Pd(OAc)₂ and a base in neat water at 25–95 °C. By this protocol, different aryl halides (Cl, Br, I) were reacted with phenylacetylene in good to excellent yields. The catalyst was recycled for the reaction of bromobenzene with phenylacetylene for six runs without appreciable loss of its catalytic activity.

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1. Introduction

In the past decade, much attention has been paid to research dedicated to the development of environmentally compatible processes [1–3]. Along with this awareness; industries have started implementing safer practices such as waste prevention, using new heterogeneous catalysts and the use of less toxic solvents and reagents. Nevertheless, discarding of organic solvents is the major problem in chemical industries which accounts around 80% of their wastes [1–8].

The application of water as a solvent in organic syntheses and in transition-metal catalyzed reactions has been gradually rising [9–17]. Without doubt, water is cheap, none toxic and not flammable which could be considered as an alternative to expensive organic solvents and also attractive media for the development of environmentally harmless chemical processes. Reactions in water are usually proceeded with higher selectivity than in organic solvents and in addition, separation of water-insoluble organic compounds from the aqueous phase is easy and not a time-consuming process [9–17].

Nowadays, transition-metal catalyzed reactions are recognized as important protocols in organic synthesis [9–24], among them,

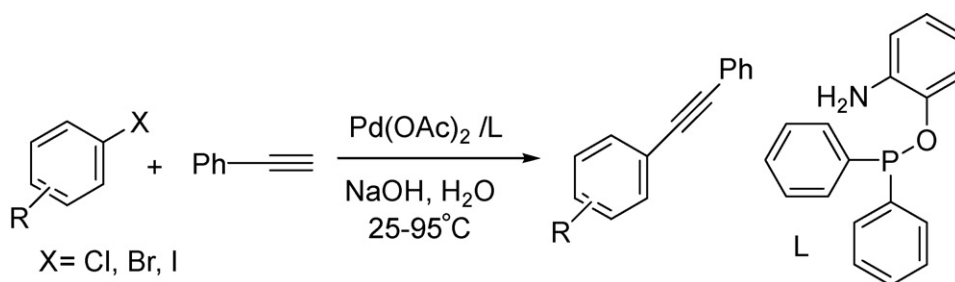
palladium-catalyzed reactions have occupied a special place. However, among fundamental types of palladium-catalyzed transformations, Sonogashira–Hagihara reaction which is a Csp²–Csp coupling reaction has found an important situation for the generation of C–C bonds by the reaction between aryl or alkenyl halides or triflates and terminal alkynes in the presence or absence of Cu(I) as a co-catalyst [25–33].

Aryl alkynes and conjugated enynes are precursors for the preparation of natural occurring compounds, pharmaceuticals and useful organic materials [25–33]. Because of the instability of the most catalysts and coupling reagent towards moisture and air, cross-coupling reactions are usually carried out under inert and anhydrous conditions. However, from an environmental and economic standpoint, it is desirable to avoid any use of hazardous and expensive organic solvents.

In recent years many modifications upon Sonogashira–Hagihara coupling reaction such as reaction in ionic liquids [34,35], reaction in microemulsion [36], zeolite-supported reaction system [37], fluorous biphasic system (FBS) using fluorous palladium catalysts [38–40], phase-transfer catalytic reaction conditions [41], various copper-free conditions [34,35,37,42–54], use of a variety of promoters [55–59], such as Zn, Mg, Sn, Au and Ag, the use of microwave irradiation [60] and polymer-supported catalysts [61,62] are reported. In addition, transition metals such as Fe [63,64], Co [65], Ni [66,67], Ru [68] and In [69] has been also reported for these reactions.

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Scheme 1. Shows the effect of water in comparison with toluene as solvents for the reaction of bromobenzene with phenylacetylene.

Development of aqueous-phase Sonogashira–Hagihara coupling reactions are of importance to chemists and industries from environmental protection issues. Reports regarding this coupling reaction in neat water and in a mixture of water and organic co-solvents are available in the literature [62–95].

The use of phosphines as ligands in the Pd-catalyzed Sonogashira–Hagihara coupling reaction provides efficient catalytic system for the formation of carbon–carbon bond in water [96–107]. Phosphinites are also interesting alternatives to phosphines for metal catalyzed organic synthesis. The preparation of phosphinites is usually simple and not a time-consuming process which is achieved by the reaction of commercially available compound such as PPh_2Cl with alcohols or phenols [108–114]. Reports on using palladium with phosphinites, phosphates, phosphoramidites, phosphinous acids and related compounds are also available for C–C bond formation [71,114–133].

Very recently; we have introduced and characterized 2-aminophenyl diphenylphosphinite as a new phosphinite ligand for the Heck–Mizoroki coupling reaction of structurally different aryl halides with styrene or *n*-butyl acrylate in water under heterogeneous conditions [133]. Herein, we describe another application of this aminophosphinite ligand for the copper-free Sonogashira–Hagihara coupling reaction in water in the absence of any organic co-solvent under heterogeneous conditions.

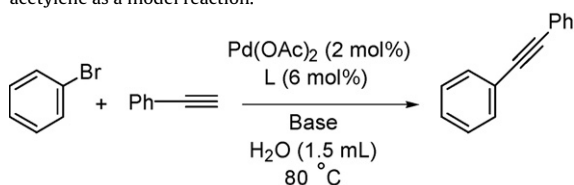
2. Experimental

2.1. General remarks

IR spectra were run on a PerkinElmer 781 Spectrophotometer. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 250 MHz Spectrometer in CDCl_3 or $\text{DMSO}-d_6$ solvents using TMS as an internal standard. Chemical shifts are reported in ppm (δ), and coupling constants (*J*), in Hz. Mass spectra were

Table 1

The effect of using different bases upon the reaction of bromobenzene with phenyl acetylene as a model reaction.



Entry	Base	Time (h)	Isolated yield (%)
1	0	24	0
2	NaOH	0.5	81
3	CS_2CO_3	2	79
4	K_3PO_4	4	77
5	K_2CO_3	4	78
6	Et_3N	6	73
7	DBU	6	68

obtained at 70 eV. The reaction monitoring were carried out on silica gel analytical sheets or by GC analysis using a 3-m length column packed with DC-200 stationary phase.

2.2. General experimental procedure for the Sonogashira–Hagihara reaction

In a 5 mL flask containing a stirring mixture of $\text{Pd}(\text{OAc})_2$ (0.02 mmol, 5 mg), L (0.06 mmol, 18 mg), and NaOH (2 mmol, 80 mg) in distilled water (1.5 mL) was added aryl halide (1 mmol) and alkyne (1.5 mmol) at 80 or 95 °C. The progress of the reaction was monitored by TLC or GC. After completion of the reaction, the mixture was washed with ethyl acetate or diethyl ether (5×1 mL) and the organic phase was separated and evaporated. Further purification was performed by column chromatography (EtOAc/n -hexane) to obtain the desired coupling product.

2.3. Recycling of the catalyst

After completion of the reaction of bromobenzene (1 mmol) with phenyl acetylene (1.5 mmol), the reaction mixture was centrifuged and the solid material was separated, washed with diethyl ether, dried and reused for the similar reaction. The recycling of the catalyst was repeated for six runs without appreciable loss of its catalytic activity.

2.4. 1-Chloro-4-(2-phenylethynyl)benzene (**1e**)

White solid, mp: 82–84 °C; ^1H NMR (250 MHz, CDCl_3) δ (ppm): 7.13–7.25 (m, 3H), 7.33–7.43 (m, 6H). ^{13}C NMR (62.9 MHz, CDCl_3) δ (ppm): 134.2, 132.8, 131.6, 128.7, 128.5, 128.4, 122.9, 121.8, 90.3, 88.2. Anal. Calcd for $\text{C}_{14}\text{H}_9\text{Cl}$: C, 79.06; H, 4.27. Found: C, 79.11; H, 4.25.

2.5. 1-Nitro-3-methyl-4-phenylethynyl-benzene (**1k**)

Yellow solid, mp: 90–92 °C; ^1H NMR (250 MHz, CDCl_3) δ (ppm): 8.01–7.91 (m, 2H), 7.53–7.45 (m, 3H), 7.31–7.7.28 (m, 3H), 2.50 (s, 3H). ^{13}C NMR (62.9 MHz, CDCl_3) δ (ppm): 146.8, 141.6, 132.3, 131.7,

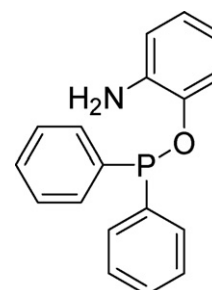
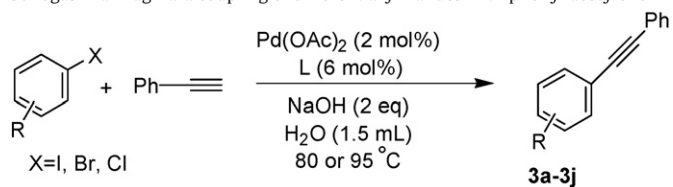


Fig. 1. 2-Aminodiphenyl phosphinite (L).

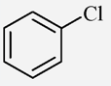
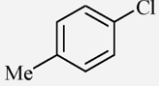
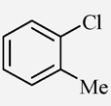
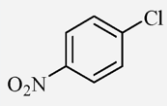
Table 2

Sonogashira–Hagihara coupling of different aryl halides with phenyl acetylene in water in the presence the catalyst using NaOH as a base.



Entry	Ar-X	T [°C]	Time (h)	Product [Refs.]	Isolated yield (%)
1		80	0.3	1a [134]	90
2		80	1	1b [134]	85
3		80	1	1c [134]	93
4		80	4	1d [135]	83
5		80	1	1a [134]	87
6		80	3.5	1e [134]	85
7		80	1.25	1f ^a	73
8		95	20	1g [134]	84 ^b
9		95	2	1h [134]	90 ^c
10		95	2	1c [134]	92 ^c
11		95	1	1i [134]	88 (10) ^d
12		95	1	1j [137]	90 ^c
13		80	2	1k [137]	88

Table 2 (Continued)

Entry	Ar-X	T [°C]	Time (h)	Product [Refs.]	Isolated yield (%)
14		95	15	1a [134]	71
15		95	9	1c [134]	67
16		95	24	1g [136]	36
17		95	24	1c [134]	73 (trace) ^d

^a Spectroscopic data are given in Section 2.

^b GC yields, *n*-octane was used as an internal standard.

^c The reaction of high melting point substrates was performed in the presence of TBAB (15 mol%) in order to facilitate the solubility of the substrate.

^d Yields in parenthesis show the reactions conducted in the absence of ligand.

130.0, 129.2, 128.5, 124.2, 122.3, 120.8, 98.5, 86.6, 20.8. IR (cm⁻¹): 2207.5, 1605.0, 1582.4, 1511.8, 1336.9, 1085.5, 757.8, 746.9, 685.4. Anal. Calcd for C₁₅H₁₁NO₂: C, 75.94; H, 4.67; N, 5.90. Found: 75.97; H, 4.65; N, 5.95.

3. Results and discussion

Phosphinites are potential ligands for the formation of complexes with metal ions that can be used as catalysts in organic synthesis. They are prepared easily from the reaction of commercially available compounds such as PPh₂Cl with alcohols or phenols.

In this study, 2-aminophenyl diphenylphosphinite (L) was obtained from the reaction of chlorodiphenyl phosphine with 2-aminophenol in high yields (Fig. 1).

2-Aminophenyl diphenylphosphinite is water and air stable, and the handling of its palladium complex does not need special precautions and inert atmosphere. The formation of active Pd(0) catalyst as a black insoluble mass was achieved by reacting Pd(OAc)₂ with 2-aminophenyl diphenylphosphinite (L) in water at 80 °C. At the start, the colour of the heterogeneous mixture was beige, which was changed to the dark brown colour and finally, a black heterogeneous mass was produced after a few minutes. The information about the formation of Pd(0) catalyst in the presence of this ligand was obtained by its XRD and SEM images. The molar ratio of the ligand with respect to Pd has been also determined to be ML₂ [133].

Sonogashira–Hagihara cross-coupling reactions of aryl bromides and chlorides at temperatures lower than 100 °C in neat water in the presence of heterogeneous catalysts are attractive from different views. However, we started to study the reaction in the presence of Pd(OAc)₂ and the ligand in neat water. The scope of the presented method has been shown by the reaction of aryl iodides, bromides and chlorides with phenylacetylene in neat water at 80 and 95 °C.

The effect of different bases upon the reaction of bromobenzene (1 mmol) with phenylacetylene (1.5 mmol) in the presence of Pd(OAc)₂ (2 mol%), and L (6 mol%) as a model reaction in water (1.5 mL) at 80 °C was studied. We have presented the results of this study in Table 1 which indicates NaOH was the most suitable base among the different bases studied for this purpose.

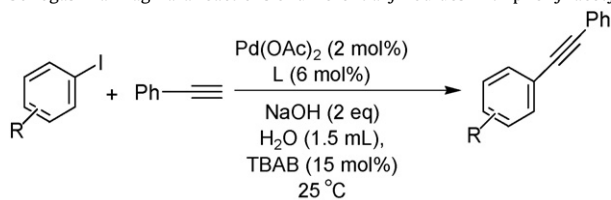
Also, in order to show the advantage of using water in comparison with organic solvents, we have studied the reaction of bromobenzene as a model compound with phenylacetylene in toluene at 95 °C and also in water at 80 °C in the presence of Pd(OAc)₂, the ligand and NaOH. As we have observed, this reaction proceeded more efficiently in a higher yield in water than in toluene as presented in Scheme 1.

The role of the ligand (L) in comparison with the ligand-free reactions and with Ph₃P in water has also been disclosed for the reaction of bromobenzene with phenylacetylene in the presence of Pd(OAc)₂ (2 mol%), NaOH (2 mmol) at 80 °C. The results of this study showed that in the presence of the ligand (L), the reaction proceeded well with the formation of the corresponding alkyne in 87% isolated yield. The similar reaction in the presence of PPh₃ proceeded in only 42% isolated yield and in the absence of the ligand, the desired product was isolated in only 15% yield.

Then, we successfully applied the optimized conditions for the Sonogashira–Hagihara cross-coupling reactions of structurally different aryl halides (Table 2). Iodobenzene, 4-iodoanisole, 4-nitroiodobenzene, 4-iodoaniline, bromobenzene, 4-bromotoluene, 1-bromo-4-chlorobenzene, and 3-bromothiophene (Table 2, entries 1–7, 13) were reacted with phenylacetylene using Pd(OAc)₂ and the ligand in water at 80 °C. The reactions proceeded well producing the desired products in high yields (73–93%). The reactions of 2-bromotoluene, 4-bromobenzonitrile, 1-bromo-4-nitrobenzene, 3-bromopyridine, 5-bromopyrimidine (Table 2, entries 8–12) with phenylacetylene proceeded at a higher temperature (95 °C) to give the desired products in high yields (84–92%). In all reactions, the corresponding homo-coupled products were also isolated in 5–8%. The reaction of chlorobenzene, 4-chlorotoluene, 2-chlorotoluene and 1-chloro-4-nitrobenzene with phenylacetylene proceeded well at 95 °C in neat water to yield the desired products in 36–73% isolated yields (Table 2, entries 14–17). For substrates with higher melting points such as 4-bromobenzonitrile, 1-bromo-4-nitrobenzene and 1-chloro-4-nitrobenzene use of a phase-transfer agent such as tetrabutylammonium bromide (TBAB) is necessary.

Sonogashira–Hagihara transformation at room temperature is highly desirable from economical and environmental views. In order to evaluate the scope of this new catalyst system for room temperature reactions, we have performed the reaction of some

Table 3
Sonogashira–Hagihara reactions of different aryl iodides with phenyl acetylene in water at room temperature.



Entry	Ar-X	Time (h)	Product [Refs.]	Isolated yield (%)
1		3	1a [134]	92
2		30	1b [134]	92 (35) ^a
3		12	1c [134]	92
4		24	1d [134]	90
5		24	1g [136]	70
6		11	1h [134]	90
7		14	1k [137]	87
8		15	1l ^b	86

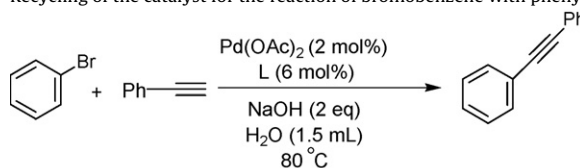
^a Isolated yield in the absence of ligand.

^b Spectroscopic data of these products are given in Section 2.

aryl iodides with phenylacetylene (1.5 mmol) in the presence of 2 mol% of Pd(OAc)₂, 6 mol% of the ligand, 2 mol% of NaOH, and 15 mol% of TBAB as a phase-transfer agent under copper-free conditions at room temperature (Table 3). The results of this study showed that structurally different aryl iodides were successfully reacted with phenylacetylene to produce the desired aryl alkynes in high to excellent yields. Aryl bromides and chlorides remain intact in the reaction mixture (GC).

We have also studied the recycling of the catalyst. For this purpose, bromobenzene as a model compound was reacted with phenylacetylene in the presence of 2 mol% of Pd(OAc)₂ and NaOH (2 mmol) in 80 °C in water. After completion of the reaction, the solid catalyst was separated by centrifugation and was reused for the subsequent reaction under the similar reaction conditions. This recycling was repeated for six runs without appreciable loss of the catalytic activity of the catalyst. The results are presented in Table 4.

Table 4
Recycling of the catalyst for the reaction of bromobenzene with phenyl acetylene.



Run	Time (h)	Isolated yield (%)
1	1	87
2	1	87
3	1	85
4	1	86
5	1	84
6	1	82

4. Conclusions

2-Aminophenyl diphenylphosphinite as an easily prepared compound has been applied as a ligand for Sonogashira–Hagihara coupling reaction of structurally different aryl halides with phenylacetylene in water under copper-free and heterogeneous conditions. Aryl iodides and bromides were reacted efficiently with phenylacetylene in the presence of Pd(OAc)₂, 2-aminophosphinite ligand and NaOH in water. Aryl iodides also react at room temperature in the presence of this catalyst with longer reaction times in the presence of TBAB. The heterogeneous catalyst has been easily separated and recycled for several runs without losing its catalytic activity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.02.010.

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