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# Copper- and solvent-free Sonogashira coupling reactions of aryl halides with terminal alkynes catalyzed by 1-phenyl-1,2-propanedione-2-oxime thiosemi-carbazone-functionalized polystyrene resin supported Pd(II) complex under aerobic conditions

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# 1. Introduction

The palladium-catalyzed Sonogashira cross-coupling reaction [1-4] between aryl halides and terminal acetylenes serves as a powerful method for the preparation of internal acetylenes [5–11], heterocycles [12–14], and natural products [15–18]. Traditionally, the reaction is carried out in an aprotic, polar solvent such as DMF or DMAC, with a complex palladium catalyst in conjunction with CuX (X = Cl, Br, I) as a co-catalyst [19]. One of the major problems associated with this reaction lies in the reaction conditions, where the use of both a palladium catalyst and a copper reagent (co-catalyst) is frequently required to promote the reaction, resulting in contamination of the coupling products with metal residue. In addition, it has been well-documented that the Sonogashira coupling often suffers from the Glaser-type oxidative dimerization of the alkyne substrate [20,21] as a side-reaction in the presence of a Cu(I) cocatalyst. Moreover, one of the complications with the Sonogashira coupling reactions is that they need degassed solvents, and have to be carried out under an inert atmosphere [22,23]. This is particularly inconvenient when the reactions are carried out in multiple vessels for library generation. Therefore, the development of a convenient method is an important objective in this effort.

# ABSTRACT

A polystyrene-supported palladium(II) 1-phenyl-1,2-propanedione-2-oxime thiosemi-carbazone (PPDOT) complex is found to be a highly active catalyst for the Sonogashira coupling reactions of aryl halides with terminal alkynes. The reactions can be performed under copper- and solvent-free conditions in an air atmosphere. The palladium catalyst is easily separated, and can be reused for several times without a significant loss in its catalytic activity.

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In recent years numerous modifications have been reported for the Sonogashira coupling procedure such as reaction in ionic liquids [24], reaction in microemulsion [25], using Pd/C [26–29], zeolite-supported reaction system [30], fluorous biphasic system (FBS) using fluorous palladium catalysts [31–34], phase-transfer catalytic reaction conditions [35], various copper-free conditions [36–52], solvent-free reaction system [53–56], use of a variety of promoters [57–59] such as Zn, Mg, and Sn, and the use of microwave irradiation [60].

The original Sonogashira reaction generally proceeds in the presence of a homogeneous palladium catalyst, which makes the separation and recovery of the catalysts tedious, if not impossible, and might result in unacceptable palladium contamination of the products. A way to overcome these difficulties would be the use of a heterogeneous palladium catalyst.

From the standpoint of green chemistry, the development of more environmentally benign conditions for the reaction such as the use of a heterogeneous palladium catalyst would be desirable [61–64]. Particularly, there have been many efforts on the development of copper-free methodologies [65–69].

So far, polystyrene-supported palladium catalysts have successfully been used for the Heck [70] and Suzuki [71–74] reactions, and have shown lower levels of palladium leaching during crosscoupling. To date, a few palladium complexes on functionalized polystyrene support have been prepared and successfully used in Sonogashira reaction [75–81]. Recently, Suzuka et al. [82] have

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reported that the Sonogashira coupling reaction of aryl halides with terminal alkynes in water catalyzed by polystyrene-poly-(ethylene glycol) (PS-PEG) resin-supported palladium–phosphine complex under copper-free conditions. However, their methodology involved the use of 5 mol% of Pd, and the reactions were carried out at 40-100 °C for 6-24 h.

Islam et al. [83] have reported the polystyrene anchored Pd(II) azo complex catalyzed copper-free coupling reaction of aryl halide with terminal alkynes in water at 70 °C for 6–12 h. The advantages of this heterogeneous catalytic system are mild reaction conditions (0.5 mol% palladium catalyst), and reusability of the catalyst. Very recently, we have reported the synthesis of the polystyrene-supported bidenate phosphine palladium(0) complex [abbreviated as PS-dpp-Pd(0)], and found that this complex is a highly active and recyclable catalyst for Sonogashira reaction of aryl iodides or benzoyl chlorides with terminal alkynes [84,85]. However, to the best of our knowledge, no Sonogashira coupling reaction of aryl halides with terminal alkynes catalyzed by a polystyrene-supported palladium(II) 1-phenyl-1,2-propanedione-2-oxime thiosemi-carbazone complex [abbreviated as PS-ppdot-Pd(II)] has been reported.

In this paper, we wish to report the synthesis of PS-ppdot-Pd(II) and its catalytic properties in the copper- and solvent-free Sonogashira reaction of aryl halides with terminal alkynes catalyzed under aerobic conditions. The ease of preparation of the complex, its long shelf-life, stability toward air, and compatibility with a wide variety of aryl halides and alkynes make it ideal for the above mentioned reactions.

# 2. Experimental

All materials were commercial reagent grade. Chloromethylated polystyrene (4–5% Cl and 2% cross-linked with divinylbenzene) was a product of Merck. Alkyne and aryl halide compounds were obtained from Merck or Fluka.

# 2.1. Preparation of 1-phenyl-1,2-propanedione-2-oxime thiosemi-carbazone (PPDOT) **1**

The ligand PPDOT was prepared according to a previously reported procedure [86]. In a round-bottom flask, 1-phenyl-1,2-propanedione-2-oxime (5 g, 0.03 mol) in 100 ml of 1% HCl-ethanol and thiosemicarbazide (2.8 g, 0.03 mol) dissolved in hot water were mixed and refluxed for 3 h. On cooling, a pale yellow colored precipitate was formed, which was filtered off, washed with hot water and methanol, and dried in vacuo to afford the title compound.

Yield, 70%; m.p. 190–191 °C; <sup>1</sup>H NMR  $\delta$  (500 MHz, DMSO-*d*<sub>6</sub>): 2.20 (s, 3H, CH<sub>3</sub>), 7.0–7.50 (m, 5H, Ph), 8.50 (b, 2H, NH<sub>2</sub>); 10.75 (s, 1H, NH); 11.72 (s, 1H, OH); IR,  $\upsilon$  (KBr disc) cm<sup>-1</sup>: 3410 (OH), 3342 and 3245 (NH), 1615 (C=N), 1204 (C=S).

#### 2.2. Preparation of polymer-anchored PS-ppdot-Pd(II) 3

To a 250-ml round bottom flask equipped with a magnetic stirrer bar and containing DMF (100 ml), were added chloromethylated polystyrene (2 g, 1.25 mmol/g of Cl) and PPDOT (7.5 mmol), and the reaction mixture was stirred for 24 h at 100 °C. The reaction mixture was filtered and washed thoroughly with DMF, and dried in vacuo for 12 h. The PPDOT-functionalized polymer **2** (1.5 g) was treated with ethanol (50 ml) for 30 min. An ethanolic solution of 0.12 g of PdCl<sub>2</sub>(PhCN)<sub>2</sub> was added, and the resulting mixture was heated to 70 °C for 6 h. The resulting bright yellow colored polymer, impregnated with the metal complex, was filtered and washed with ethanol to obtain PS-ppdot-Pd(II) (Scheme 1).

#### 2.3. General procedure for the Sonogashira coupling reaction

An aryl halide (1.0 mmol) and a terminal alkyne (1.5 mmol) was added to a mixture of PS-ppdot-Pd(II) (0.01 mmol) and base (2 mmol) in a glass flask under vigorous stirring. The mixture was stirred at room temperature for 3 h under aerobic conditions. Upon completion of the reaction, the reaction mixture was dissolved in chloroform (10 ml). The palladium catalyst was separated from the mixture by filtration, washed with water (10 ml) and acetonitrile (10 ml), and reused in the next run. The chloroform solution was washed with water (10 ml) and dried over MgSO<sub>4</sub>, and toluene (1.0 mmol) was added as internal standard for GC analysis. After GC analysis, the solvent was removed under vacuum, and the crude product was subjected to silica gel column chromatography using CHCl<sub>3</sub>-CH<sub>3</sub>OH (97:5) as eluent to afford the pure product.

# 3. Results and discussion

#### 3.1. Characterization of PS-ppdot-Pd(II)

It is well known that chloromethylated polystyrene (2% DVB) as catalyst support is still one of the most popular polymeric materials used in synthesis due to its inexpensive, ready availability, mechanical robustness, and facial functionalization. In addition, this resin was swollen by a number of solvents such as benzene, pyridine, dioxane, methanol, and chloroform. The resin could



Scheme 1. Preparation of the heterogeneous catalyst [PS-ppdot-Pd(II)] 3.

easily be penetrated by various reagents [87]. The immobilized Schiff base palladium PS-ppdot-Pd(II) can be prepared easily from a commercially available chloromethylated polystyrene (2% DVB) polymer. In this approach, the Schiff base palladium complex is attached, *via* a covalent bond, to a pendant chloromethyl group on the surface of the polymer resin particles. Reaction of polystyrene resin with PPDOT 1 in DMF at 100°C and then treatment of the PPDOT-functionalized polymer 2 with a solution of PdCl<sub>2</sub>(PhCN)<sub>2</sub> in ethanol under reflux resulted in covalent attachment of the palladium complex to give the polymer-supported palladium(II) complex catalyst PS-ppdot-Pd(II) **3** (Scheme 1). Successful func-tionalization of the polymer was confirmed by elemental analysis. The N content of resin was obtained to be 4.77% (0.82 mmol/g), which indicates that only 65% of total chlorine was substituted by amine. The metal loading of the polymer-supported palladium complex, determined by inductively coupled plasma (ICP), was obtained to be 4.38% (0.41 mmol/g).

In the IR spectrum of the polymer-bound PPDOT obtained, the sharp C–Cl peak (due to–CH<sub>2</sub>Cl groups) at 1264 cm<sup>-1</sup> in the starting polymer was practically omitted or was seen as a weak band after introduction of PPDOT and palladium on the polymer. In addition, the IR spectrum of the polymer-anchored PPDOT showed new absorption band at 1678 cm<sup>-1</sup> (C=N), which was absent in the IR spectrum of pure polymer beads. This confirms the formation of metal complex on the surface of the polymer. Scanning electron micrographs (SEM) were recorded for a single bead of pure chloromethylated polystyrene and polymer-anchored complex to observe the morphological changes. As expected, the pure polystyrene bead had a smooth and flat surface, while the anchored complex showed roughening of the top layer (Fig. 1).

# 3.2. Application in copper- and solvent-free Sonogashira coupling reactions

The catalytic activity of the PS-ppdot-Pd(II) complex **3** (1 mol%) was studied at room temperature under aerobic conditions in a copper- and solvent-free Sonogashira reaction using pheny-lacetylene and iodobenzene in the presence of various bases. Our optimization data is shown in Table 1.



**Fig. 1.** Scanning electron micrograph of: (a) chloromethylated polystyrene; (b) [PS-ppdot-Pd(II)] complex.

#### Table 1

Copper- and solvent-free coupling reaction of phenylacetylene with aryl halides in the presence of different bases.<sup>a</sup>



Entry	Х	Base	Yield <sup>b</sup> (%)	
1	Ι	DIEA	73	
2	I	Et <sub>3</sub> N	97	
3	I	Pyridine	85	
4	I	Piperidine	95	
5	Ι	Pyrrolidin	80	
6	Ι	Diethylamin	39	
7	Ι	Butylamin	52	
8	I	Isobutylamin	83	
9	Ι	2-Methoxyethylamin	50	
10	Ι	Ethanolamin	30	
11	Br	DIEA	70	
12	Br	Et <sub>3</sub> N	60	
13	Br	Pyridine	93	
14	Br	Piperidine	78	
15	Br	Pyrrolidin	60	
16	Br	Diethylamin	36	
17	Br	Butylamin	48	
18	Br	Isobutylamin	58	
19	Br	2-Methoxyethylamin	31	
20	Br	Ethanolamin	42	

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<sup>a</sup> Reaction conditions: phenylacetylene (1.5 mmol), halobenzene (1.0 mmol), base (2.0 mmol), [PS-ppdot-Pd(II)] (0.01 mmol), room temperature, 3 h, aerobic conditions. <sup>b</sup> GC yield. When the reaction of phenylacetylene with iodobenzene was performed with  $Et_3N$  as base, an excellent 97% yield of the product was obtained (entry 2). Since bromoarenes are cheaper and more readily available than iodoarenes and hence are synthetically more useful as educts, we examined the reaction of bromobenzene with phenylacetylene under the above conditions, and found that it was not efficient since it afforded only a 60% yield of diphenylacetylene **6a** (entry 12). However, by changing the base to pyridine, bromobenzene could be smoothly coupled with phenylacetylene resulting in a high yield (93%) of diphenylacetylene (entry 13).

After the optimized conditions were found, we explored the general applicability of the PS-ppdot-Pd(II) complex **3** as a catalyst for copper- and solvent-free coupling of different alkynes **4** with aryl iodides and bromides **5** containing electron-withdrawing or donating substituents. The results are shown in Table 2. The coupling of phenylacetylene with iodobenzene took place smoothly at room temperature in the presence of Et<sub>3</sub>N (2 mmol) and 1 mol% palladium of the PS-ppdot-Pd(II) complex **3** to give a quantitative yield of diphenylacetylene (entry 1). The Sonogashira coupling of phenylacetylene save the corresponding biarylacetylenes **6f** in 80% yield, (entry 6). *p*-Nitroiodobenzene, meta-niroiodobenzene, *p*-chloroidobenzene, and *p*-acetoxyiodobenzene, having electron-deficient aromatic rings, also underwent the Sonogashira coupling

with phenylacetylene under similar conditions to afford the corresponding biarylacetylenes 6b, 6c, 6e, and 6g in excellent yield (99%) (entries 2, 3, 5, and 7). When the less reactive acetylene, 1-hexyne, and propargyl alcohol were used, the coupling product was produced efficiently. The coupling of para-substituted iodobenzene having nitro, bromo, chloro, methoxy, and acethoxy groups took place with 1-hexyne to give the corresponding products **6i-m** in 99%, 98%, 99%, 95%, and 85% yields, respectively (entries 9–13). Coupling reaction of propargyl alcohol with more reactive electron-withdrawing *p*-nitroiodobenzene gave good yield (97%) (entry 15). Under the same conditions, the less active electron-rich p-iodoanisol produced a lower yield (60%) (entry 16). Copper-free coupling reactions of aryl iodides with trimethylsilylacetylene also took place under similar conditions to give products 6n and 6o in 45% and 43% yields, respectively (entries 17 and 18).

To extend the scope of our work, we next investigated the coupling of various aryl bromides with terminal alkynes. As expected, aryl iodides were more reactive than aryl bromides, and the substituent effects in the aryl iodides appeared to be less significant than in the aryl bromides. However, as shown in Table 2, high catalytic activity was observed in the coupling of unactivated aryl bromides such as *p*-nitrobromobenzene (entries 20, 26, and 31) and *p*-bromoanisole (entries 24, 32, and 35) as well as activated

## Table 2

Copper- and solvent-free Sonogashira reactions of terminal alkynes with aryl halides.<sup>a</sup>

4		base, r. t.	6 Y	·/		
Entry	R	Х	Ŷ	Base	Product	Yield <sup>b</sup> (%)
1	Ph	I	Н	Et <sub>3</sub> N	6a	97 (94)
2	Ph	Ι	4-NO <sub>2</sub>	Et <sub>3</sub> N	6b	99
3	Ph	Ι	3-NO <sub>2</sub>	Et <sub>3</sub> N	6c	99
4	Ph	Ι	4-Br	Et <sub>3</sub> N	6d	95
5	Ph	Ι	4-Cl	Et <sub>3</sub> N	6e	99
6	Ph	Ι	4-OCH <sub>3</sub>	Et <sub>3</sub> N	6f	80
7	Ph		4-COCH <sub>3</sub>	Et <sub>3</sub> N	6g	99 (95)
8	$n-C_4H_9$	Ι	Н	Et <sub>3</sub> N	6h	85
9	n-C <sub>4</sub> H <sub>9</sub>	Ι	4-NO <sub>2</sub>	Et <sub>3</sub> N	<b>6</b> i	99 (96)
10	n-C <sub>4</sub> H <sub>9</sub>	Ι	4-Br	Et <sub>3</sub> N	6j	98
11	n-C <sub>4</sub> H <sub>9</sub>	Ι	4-Cl	Et <sub>3</sub> N	6k	99
12	$n-C_4H_9$	Ι	4-OCH <sub>3</sub>	Et <sub>3</sub> N	61	95 (92)
13	$n-C_4H_9$	Ι	4-COCH <sub>3</sub>	Et <sub>3</sub> N	6m	85
14	CH <sub>2</sub> OH	Ι	Н	Et <sub>3</sub> N	6p	75
15	CH <sub>2</sub> OH	Ι	4-NO <sub>2</sub>	Et <sub>3</sub> N	6q	97 (93)
16	CH <sub>2</sub> OH	Ι	4-0CH3	Et <sub>3</sub> N	6r	60
17	Me <sub>3</sub> Si	Ι	Н	Et <sub>3</sub> N	6n	45
18	Me <sub>3</sub> Si	Ι	4-OCH <sub>3</sub>	Et <sub>3</sub> N	60	43
19	Ph	Br	Н	Pyridine	6a	93
20	Ph	Br	4-NO <sub>2</sub>	Pyridine	6b	95 (91)
21	Ph	Br	3-NO <sub>2</sub>	Pyridine	6c	88
22	Ph	Br	4-F	Pyridine	<b>6s</b>	74
23	Ph	Br	4-CN	Pyridine	6t	90
24	Ph	Br	4-OCH <sub>3</sub>	Pyridine	6f	82
25	$n-C_4H_9$	Br	Н	Pyridine	6h	85
26	$n-C_4H_9$	Br	4-NO <sub>2</sub>	Pyridine	<b>6</b> i	98 (94)
27	$n-C_4H_9$	Br	4-F	Pyridine	6u	88
28	$n-C_4H_9$	Br	4-Cl	Pyridine	6k	92
30	CH <sub>2</sub> OH	Br	Н	Pyridine	6p	97
31	CH <sub>2</sub> OH	Br	4-NO <sub>2</sub>	Pyridine	6x	98 (95)
32	CH <sub>2</sub> OH	Br	4-OCH <sub>3</sub>	Pyridine	6r	65
33	Me <sub>3</sub> Si	Br	Н	Pyridine	6k	86 (82)
34	Me <sub>3</sub> Si	Br	4-F	Pyridine	6w	70
35	Me <sub>3</sub> Si	Br	4-OCH <sub>3</sub>	Pyridine	60	84
36	Ph	Cl	Н	Et <sub>3</sub> N	6a	35
37	Ph	Cl	4-NO <sub>2</sub>	Et <sub>3</sub> N	6b	50
38	Ph	Cl	4-0CH <sub>3</sub>	Et <sub>3</sub> N	6f	23

<sup>a</sup> Reaction conditions: 4 (1.5 mmol), 5 (1.0 mmol), [PS-ppdot-Pd(II)] (0.01 mmol), base (2 mmol), 3 h, room temperature, aerobic conditions.

<sup>b</sup> GC yield. Numbers in parentheses are isolated yields.

#### Table 3

Copper-free Sonogashira reaction of phenylacetylene with iodobenzene catalyzed by the recycled catalyst.<sup>a</sup>

Entry	Cycle	Yield (%) <sup>b</sup>	TOF
1	1	97	32
2	2	95	31
3	3	92	30
4	4	87	29

 $^a$  Reaction conditions: phenylacetylene (1.5 mmol), iodobenzene (1.0 mmol), [PS-ppdot-Pd(0)] (0.01 mmol), Et\_3N (2 mmol), room temperature, 3 h, aerobic conditions.

<sup>b</sup> GC yield.

*p*-nitroiodobenzene (entries 2, 9, and 15) and *p*-iodoanisol (entries 6, 12, and 16).

Moreover, *p*-chlorobromobenzene, *p*-bromobenzonitrile, and *p*-fluorobromobenzene having electron-deficient aromatic rings also underwent the Sonogashira coupling with terminal alkynes under similar conditions to afford the corresponding products in good to excellent yields.

It should be noted that the coupling reactions of the aryl chlorides (entries 36–38), also took place under similar copper-free conditions, though the reactivity was much lower than their iodo and bromo counterparts (entries 1, 2, 6, 19, 20, and 24).

Unsurprisingly, *p*-nitroiodobenzene and *p*-nitrobromobenzene were found to be the most reactive amongst the aryl halides studied (entries 2, 9, 15, 20, 26, and 31). In all reactions, only 1 mol% of PS-ppdot-Pd(II) based on the aryl halides was used, the turnover frequency (TOF) was larger than that in the corresponding coupling reaction catalyzed by other polystyrene-supported catalysts reported [82,83].

#### 3.3. Recycling of the catalyst

One of the purposes for designing this heterogeneous catalyst is to enable recycling of the catalyst for use in subsequent reactions. For the recycle experiment, we used phenylacetylene and iodobenzene as the representative reactants in the presence of 1 mol% PS-ppdot-Pd(II) to study the recyclability of this heterogeneous catalyst. After a reaction time of 3.0 h at room temperature, the mixture from the first-run reaction was centrifuged, and the solid obtained was washed alternately with ethanol and  $CH_3CN$ . After drying, the recovered PS-ppdot-Pd(0) was then reused in the same reaction under identical conditions. We found that the product yield decreased slightly from 97 to 87% over four recycling runs (Table 3).

In order to determine the absolute amount of the palladium species dissolved in solution caused by leaching, the crude reaction mixtures were evaporated to dryness and analyzed using ICP-AE. It was shown that less than 2% of the total amount of the original palladium species was lost into solution during the course of a reaction. This almost negligible leaching level, which is at the limit of detection of the ICP, accounts for the recoverability and reusability of the palladium resin catalyst.

### 4. Conclusion

In conclusion, we have developed a clean and safe protocol for the Sonogashira coupling of aryl iodides and bromides with terminal acetylenes using the PS-ppdot-Pd(II) catalyst to give various biarylacetylene derivatives. The reactions can be carried out under copper- and solvent-free conditions in an air atmosphere. The catalyst used is easily separated, and can be reused for several times without a noticeable change in activity. Further investigations for more favorable strategies and conditions for recycling PS-ppdot-Pd(II) as well as synthetic applications are currently in progress, and will be reported in due course.

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