



## Heterogeneous Suzuki and copper-free Sonogashira cross-coupling reactions catalyzed by a reusable palladium(II) complex in water medium

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### ABSTRACT

A new polystyrene anchored Pd(II) azo complex has been synthesized and characterized. The present Pd(II) azo complex behaves as a very efficient heterogeneous catalyst in the Suzuki coupling and Sonogashira coupling reaction in water medium. Aryl halides, coupled with phenylboronic acids (Suzuki–Miyaura reaction) or terminal alkyne (Sonogashira reaction), smoothly afford the corresponding cross-coupling products in excellent yields (83–100% yield for Suzuki reaction and 68–96% yield for Sonogashira reaction of aryl halides) under phosphine-free reaction conditions in the presence of polystyrene anchored Pd(II) azo complex catalyst in water medium. Furthermore, the catalyst has shown good thermal stability and recyclability. This polymer-supported Pd(II) catalyst could be easily recovered by simple filtration of the reaction mixture and reused for more than six consecutive trials without a significant loss of its catalytic activity.

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Palladium-catalyzed cross-coupling reaction for the formation of carbon–carbon bonds has recently emerged as a powerful method in an organic synthesis.<sup>1</sup> The palladium-catalyzed coupling of an aryl halide with aryl boronic acid (Suzuki coupling)<sup>2</sup> or terminal alkyne (Sonogashira coupling)<sup>3</sup> is recognized as the most successful method for forming a C(sp<sup>2</sup>)–C(sp<sup>2</sup>) and C(sp)–C(sp<sup>2</sup>) carbon–carbon bond, respectively. These reactions have been widely employed in the synthesis of natural products, biologically active molecules and materials science.<sup>4</sup>

Although homogeneous catalysts have many advantages,<sup>5</sup> catalyst immobilization is a well-known methodology to allow efficient catalyst separation and to obtain metal-free products.<sup>6</sup> Several types of solid materials such as zeolites,<sup>7</sup> alumina,<sup>8</sup> silicas,<sup>9</sup> and polymers<sup>10</sup> have been used to support palladium species. From the standpoint of environmentally benign organic synthesis, the development of highly active and easily reusable immobilized catalysts and the use of water instead of organic compounds as solvent are of great interest to chemists. Solid-phase organopalladium metal complexes having high activity and selectivity offer several significant practical advantages in synthetic and industrial chemistry; among those, the ease of separation of the catalyst from the desired reaction products and the ease of recovery and reuse of the catalyst are most important. In addition, the use of water in palladium-catalyzed coupling reaction has become popular because water base synthetic processes are inherently safer as well as inexpensive.<sup>11</sup> Moreover, products can be isolated easily by extraction. Recently, a variety of aqueous catalytic systems<sup>12</sup> and

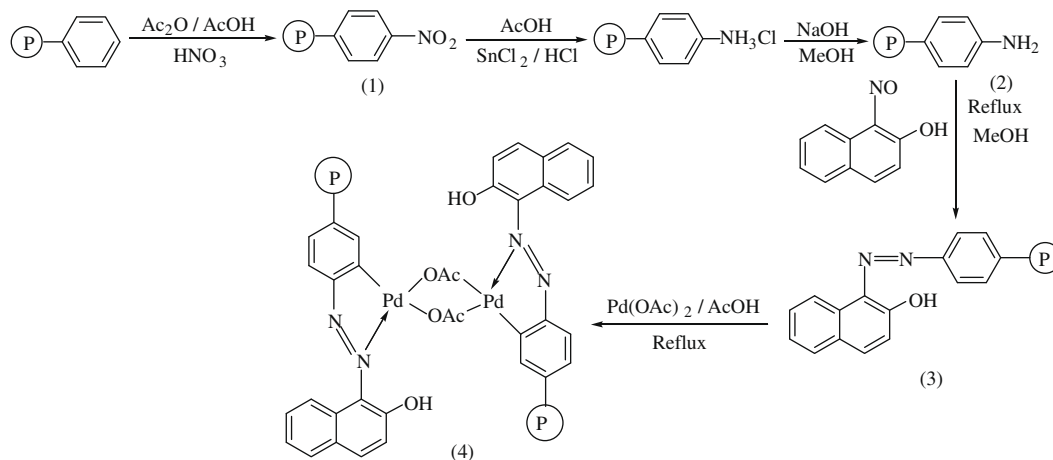
polymer-supported palladium catalysts<sup>13</sup> for the Suzuki and Sonogashira cross-coupling reactions have been reported.

Herein we report the synthesis and characterization of a new polystyrene anchored Pd(II) azo complex catalysts and illustrate its application for the Suzuki cross-coupling and Sonogashira cross-coupling reactions in water medium under aerobic condition. The catalyst shows a high catalytic activity in the coupling reactions of various aryl halides. Further easy catalyst recovery and excellent recycling efficiency of the catalyst make it an ideal system for coupling reactions in aqueous phase.

The preparation procedure followed to obtain the catalyst is indicated in Scheme 1. Polymeric amine was prepared according to the literature method.<sup>14</sup> The suspension of polymeric amine (3 g) treated with 1-nitroso-2-naphthol (1.0 g) in methanol (10 ml) to produce the corresponding polymer anchored azo ligand (**3**) which was then reacted with Pd(II) acetate (50 mg) in glacial acetic acid (10 ml) to yield the catalyst as light brown solid (**4**).

Due to insolubility of the different functionalized polystyrene and the corresponding polystyrene anchored Pd(II) complex in all common solvents, their structural investigations were limited only to their physico-chemical properties, SEM, TGA-DTA, IR, and UV–vis spectral data. Atomic absorption spectroscopy suggested 5.45% of Pd in the complex. The polystyrene anchored azo ligand shows a sharp peak at 1452 cm<sup>-1</sup> due to the N=N bond which on complexation with Pd disappears and appears as a band at 1440 cm<sup>-1</sup>. The lowering in frequency of N=N peak indicates an effective coordination interaction between the ligand and Pd center. The polystyrene anchored Pd(II) azo complex exhibited important IR peaks at 1585 cm<sup>-1</sup>, 1430 cm<sup>-1</sup> (ν COO bridged),<sup>15</sup> 520 cm<sup>-1</sup> (ν Pd–C), 722 cm<sup>-1</sup> (orthometallation),<sup>16</sup> and 455 cm<sup>-1</sup> (ν Pd–N),<sup>17</sup>

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Scheme 1. Preparation of polystyrene anchored Pd(II) azo complex.

The palladium-catalyzed Suzuki cross-coupling of aryl halides with arylboronic acids has become a general and convenient synthetic route in organic chemistry toward biaryls, which has been employed in many areas of organic synthesis, including natural product syntheses. To explore the catalytic activity, the Suzuki cross-coupling reaction of aryl halides with phenylboronic acid was conducted with the present catalyst. For optimization of the reaction conditions, we choose the cross-coupling of 4-iodotoluene with phenylboronic acid in water medium under aerobic condition as the model reaction, and the effects of the temperature and base on the reaction were examined. The results are presented in Table 1. At room temperature, low amount of coupled product was obtained. Increasing the temperature from 30 to 70 °C improved the conversion (Table 1, entries 1–3), while further increase in temperature to 80 °C, no such improvement in the conversion was obtained. We found that the reaction was highly dependent on the amount of base as well as its nature. The base-substrate ratio of 2:1 is the best for this catalytic system. Various bases such as Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, KOH, Et<sub>3</sub>N, NaO<sup>t</sup>Bu, and Na<sub>3</sub>PO<sub>4</sub> were examined for the reaction. The results revealed that the inorganic bases used were more effective than organic bases like NaO<sup>t</sup>Bu and Et<sub>3</sub>N (Table 1, entries 8 and 9) and hence the economically cheaper K<sub>2</sub>CO<sub>3</sub> was chosen as a base for these coupling reactions.

Next, to demonstrate versatility of the catalytic system for the Suzuki coupling reaction, aryl halides substituted with various electrons-withdrawing and electrons-donating groups were chosen. The results are summarized in Table 2. Both iodobenzene and bromobenzene showed excellent conversion in Suzuki reaction. The various substituted aryl iodides and bromides with deactivated (electron rich) and activated (electron poor) were

**Table 1**  
Effect of base on the Suzuki coupling reaction of 4-iodotoluene with phenylboronic acid in water medium

Entry	Base	Temp (°C)	Yield <sup>a</sup> (%)
1	K <sub>2</sub> CO <sub>3</sub>	30	35
2	K <sub>2</sub> CO <sub>3</sub>	50	87
3	K <sub>2</sub> CO <sub>3</sub>	70	96
4	K <sub>2</sub> CO <sub>3</sub>	80	96
5	Na <sub>2</sub> CO <sub>3</sub>	70	84
6	KOH	70	57
7	Na <sub>3</sub> PO <sub>4</sub>	70	48
8	Et <sub>3</sub> N	70	45
9	NaO <sup>t</sup> Bu	70	32

Reaction conditions: 4-iodo toluene (1.0 mmol), phenylboronic acid (1.5 mmol), catalyst (0.5 mol % Pd), base (2.0 mmol), water (6 ml).

<sup>a</sup> Yield determined by GC and GCMS analysis.

converted efficiently to the desired products in good to excellent yields within 6–8 h (entries 1–12). The less reactive chlorobenzene showed a moderate conversion. However, the activated aryl chloride, 4-acetylchlorobenzene gave the corresponding product in good yield using the present catalyst (entry 14). The sensitive heteroaryl halides bearing pyridyl moiety produced the corresponding aryl-heteroaryl coupled product in good yields (entry 12). Sterically hindered 2-nitrobromobenzene was found to react efficiently under the present reaction condition. However, the *ortho*-substituted aryl bromide required longer reaction times than *para*-substituted aryl bromide.

Another important Pd catalyzed coupling reaction is the alkanylation of aryl halides which is known as Sonogashira reaction. Application of this reaction is to be found in the synthesis of numerous natural products including enediyne antibiotics. In our present study, the Sonogashira coupling reactions of iodo and bromo arenes with phenyl acetylene in water medium was carried out under the copper-free and phosphine-free condition. Since no copper salt used, the undesired formation of oxidative homocoupling product, a diyne, was also avoided. The reaction was performed with Et<sub>3</sub>N as a base and TBAB as an additive. TBAB enhances the rate of the reaction by transferring haloarene to the aqueous phase and hence reaction with terminal alkyne is faster.<sup>18</sup> We employed the coupling reaction of iodo benzene with phenylacetylene as a model reaction to study the effect of base on the reaction (Table 3). Among various bases, triethylamine was found to be best. The reaction works well when organic bases are used. Inorganic bases, such as K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub>, and NaOH, were less effective to organic ones.

Next, several substituted iodo and bromoarenes were examined in Sonogashira reaction using polystyrene anchored Pd(II) azo catalyst to explore the catalytic activity of the present catalytic protocol. The results are summarized in Table 4. The aryl halides with electron-withdrawing substituents, such as nitro, (Table 4, entries 2 and 7) and acetyl, (Table 4, entries 3 and 8) gave excellent yields, while aryl halides with electron-donating groups, such as methyl and methoxy (Table 4, entries 4, 5, 9, and 10) gave the coupling products in slightly lower yield. The coupling reaction of aryl bromides required higher temperature and extended reaction time than aryl iodides. The heteroaromatic compound, 2-bromopyridine, also reacted with phenyl acetylene to give the desired product in good yield (entry 11). However, chloroarenes basically do not react under present reaction conditions, and yields are less than 6%.

In order to find out the effect of anchoring, the activity of the present polystyrene anchored Pd(II) azo complex catalyst was

**Table 2**

Suzuki coupling reaction of various aryl halides with phenylboronic acid catalyzed by polystyrene anchored Pd(II) azo complex

Entry	Arylhalide	Temp (°C)	Time (h)	Product	Yield <sup>a</sup> (%)
1	Iodobenzene	70	6	Biphenyl	100(98)
2	4-Nitroiodobenzene	70	6	4-Nitrobiphenyl	99(94)
3	4-Iodoacetophenone	70	6	4-Acetylbiphenyl	99(93)
4	4-Iodotoluene	70	6	4-Methylbiphenyl	96(87)
5	4-Iodoanisole	70	6	4-Methoxybiphenyl	98(94)
6	Bromobenzene	70	7	Biphenyl	99(96)
7	4-Nitrobromobenzene	70	6	4-Nitrobiphenyl	98
8	4-Bromoacetophenone	70	6	4-Acetylbiphenyl	99
9	4-Bromotoluene	70	8	4-Methylbiphenyl	94
10	4-Bromoanisole	70	8	4-Methoxybiphenyl	96
11	2-Nitrobromobenzene	70	10	2-Nitrobiphenyl	92
12	2-Bromopyridine	70	8	2-Phenylpyridine	90(82)
13	Chlorobenzene	85	12	Biphenyl	85
14	4-Chloroacetophenone	85	12	4-Acetylbiphenyl	90(84)
15	4-Chlorotoluene	85	12	4-Methylbiphenyl	83

Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), catalyst (0.5 mol % Pd), K<sub>2</sub>CO<sub>3</sub> (2.0 mmol), H<sub>2</sub>O (6 ml).<sup>a</sup> Yield determined by GC and GCMS analysis, based on aryl halides, average of two runs. Isolated yield are given in parentheses.**Table 3**

Effect of base on the Sonogashira coupling reaction of iodobenzene with phenylboronic acid in water medium

Entry	Base	Yield <sup>a</sup> (%)
1	K <sub>2</sub> CO <sub>3</sub>	49
2	Na <sub>2</sub> CO <sub>3</sub>	42
3	K <sub>3</sub> PO <sub>4</sub>	37
4	KOH	21
5	Et <sub>3</sub> N	94
6	Piperidine	79

Reaction conditions: iodobenzene (1.0 mmol), phenylacetylene (1.5 mmol), catalyst (0.5 mol % Pd), TBAB (1.0 mmol), base (2.0 mmol), water (6 ml), 70 °C.

<sup>a</sup> Yield determined by GC and GCMS analysis.

compared to that of the corresponding homogeneous analogue in the Suzuki coupling reaction. From the results it is seen that the present heterogeneous catalyst is more reactive than the corresponding homogeneous catalyst. The reaction using homogeneous catalyst with 4-iodo toluene and phenylboronic acid in H<sub>2</sub>O medium at 70 °C for 6 h results in 58% conversion, while the analogous heterogeneous reaction was performed successfully with 96% conversion by GC analysis. The activity of the catalyst was also superior with other reported heterogeneous catalysts for the reaction of aryl halides under aerobic condition.<sup>11a,19</sup> The catalytic activities are also comparable for copper-free Sonogashira coupling reaction in water medium under air atmosphere with other heterogeneous catalysts.<sup>20</sup>

An important point concerning the use of heterogeneous catalyst is its lifetime, particularly for industrial and pharmaceutical

applications of coupling reactions. To determine whether the catalyst is actually functioning in a heterogeneous manner, a hot-filtration test<sup>21</sup> was performed in the Suzuki coupling reaction of 4-iodo toluene and phenylboronic acid. During catalytic reaction, the solid catalyst was separated from the reaction mixture by filtration after 3 h and the determined conversion was 52%. The reaction was carried out for a further 2 h. The gas chromatographic analysis showed no increment in the conversion. Atomic absorption spectrometric analysis of the liquid phase of the reaction mixtures collected by filtration confirms that Pd is absent in the reaction mixture. These results suggested that no leaching of palladium takes place during the reaction and that the catalyst is purely heterogeneous in nature.

The reusability of this heterogeneous palladium catalyst was also examined for the Suzuki coupling reaction of 4-iodo toluene with phenylboronic acid using K<sub>2</sub>CO<sub>3</sub> as the base in water medium. After the first run, the catalyst was separated by simple filtration, washed thoroughly with water, methanol, and acetone, and dried in room temperature under vacuum for 8 h. The dried catalyst was then reused with a fresh reaction mixture without any further activation. The catalyst could be almost recovered and recycled for further reactions upto six runs without much loss of efficiency.

In summary, we have reported a polystyrene anchored Pd(II) azo complex which was efficiently used as a heterogeneous catalyst for Suzuki cross-coupling reaction and copper free Sonogashira cross-coupling reactions involving various aryl halides in water medium under aerobic condition. The catalyst shows not only high catalytic activity, but also offers many practical advantages such as oxygen insensitivity, thermal stability, and recyclability. The

**Table 4**

Sonogashira coupling reaction of various aryl halides with phenylacetylene catalyzed by polystyrene anchored Pd(II) azo complex

Entry	Arylhalide	Temp (°C)	Time (h)	Product	Yield <sup>a</sup> (%)
1	Iodobenzene	70	8	Diphenylacetylene	94(88)
2	4-Nitroiodobenzene	70	8	1-Nitro-4-(phenylethynyl) benzene	96(87)
3	4-Iodoacetophenone	70	8	1-Acetyl-4-(phenylethynyl) benzene	96(90)
4	4-Iodotoluene	70	10	4-(Phenylethynyl) toluene	87(82)
5	4-Iodoanisole	70	10	1-Methoxy-4-(phenylethynyl) benzene	90(85)
6	Bromobenzene	80	12	Diphenylacetylene	84
7	4-Nitrobromobenzene	80	12	1-Nitro-4-(phenylethynyl) benzene	91
8	4-Bromoacetophenone	80	12	1-Acetyl-4-(phenylethynyl) benzene	86
9	4-Bromotoluene	80	12	4-(Phenylethynyl) toluene	68(63)
10	4-Bromoanisole	80	12	1-Methoxy-4-(phenylethynyl) benzene	75(70)
11	2-Bromopyridine	80	12	2-Phenylethynyl pyridine	77(71)
12	Chlorobenzene	80	12	Diphenylacetylene	6

Reaction conditions: aryl halide (1.0 mmol), phenylacetylene (1.5 mmol), catalyst (0.5 mol % Pd), TBAB (1.0 mmol), Et<sub>3</sub>N (2.0 mmol), H<sub>2</sub>O (6 ml).<sup>a</sup> Yield determined by GC and GCMS analysis, based on aryl halides, average of two runs. Isolated yield are given in parentheses.

catalyst was reused for six consecutive cycles with consistent activity. The excellent catalytic performance in water medium and the easy preparation and separation of the catalyst make it a good heterogeneous system and a useful alternative to other heterogeneous palladium catalysts.

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### Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2010.02.079](https://doi.org/10.1016/j.tetlet.2010.02.079).

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