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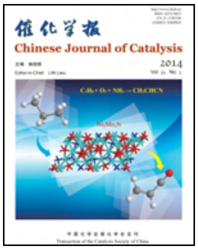

Article

Poly(vinyl chloride)-supported Pd(II) complex as an efficient catalyst for Heck and Cu-free Sonogashira reactions under aerobic conditions

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ABSTRACT

A novel poly(vinyl chloride)-supported Pd complex was found to be a highly active catalyst for the Heck and Sonogashira reactions of aryl halides under aerobic conditions. The complex is thermally stable, and can be easily recovered and reused. The catalyst was recycled for the Heck and Sonogashira reactions for five runs without appreciable loss of its catalytic activity, and with negligible metal leaching.

1. Introduction

Pd-catalyzed C–C-bond-forming reactions are established as one of the most important tools in organic synthesis [1]. Among these, the Mizoroki-Heck [2–7] and Sonogashira [8–12] reactions play important roles in modern synthetic chemistry.

These reactions are normally carried out homogeneously, using a Pd catalyst, a phosphine ligand, and a base. However, the reaction suffers from severe problems related to the separation, recovery, and instability of the homogeneous catalysts at high temperatures, and these have so far precluded its widespread industrial application.

These problems can be overcome, however, by the use of heterogeneous catalysts consisting of supported Pd complexes. These complexes include polymer-supported Pd catalysts, and Pd on clay [13], carbon nanofibers [14], montmorillonite (MMT) [15], magnetic mesoporous silica [16], zeolites [17], and metal oxides [18].

Recently, Singh et al. [19] reported the synthesis and characterization of a recyclable and recoverable MMT- exchanged ammonium-tagged carbapalladacycle catalyst for the Mizoroki-Heck and Sonogashira reactions in ionic-liquid media. Iranpoor group [20] used Pd nanoparticles supported on agarose as an efficient catalyst and a bioorganic ligand for C–C bond formation via solvent-free Mizoroki-Heck and Sonogashira reactions in polyethylene glycol (PEG 400). Wu group [21] described an ionic-liquid-functionalized phosphine-ligated Pd complex for the Sonogashira reaction under aerobic and Cu-free conditions.

Poly(vinyl chloride) (PVC) modified with a functional group can be directly prepared via a displacement reaction without chloromethylation, which makes it an inexpensive and practical support for heterogeneous catalysts. Cui et al. [22] described the synthesis and characterization of PVC-polyethylene-poly-

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amine-supported Pd complex catalysts for the Heck reaction of acrylic acid with aryl iodides in air at low temperature. Liu and co-workers [23] reported the synthesis and characterization of nano-Pd immobilized on the surface of a PVC-supported Schiff base, which had high catalytic activity in Suzuki-Miyaura cross-coupling reactions in 95% aqueous ethanol under atmospheric conditions. Above all, these methods provide good yields, although some of these reactions need harsh conditions.

Very recently, we reported the synthesis of a polystyrene-supported Pd(II) 1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone complex catalyst for the Heck and Suzuki reactions [24]. We have also developed successful Suzuki, Heck, and Cu-free Sonogashira reactions catalyzed by Pd(II) supported on 4-amino-5-methyl-3-thio-1,2,4-triazole-functionalized polystyrene resin under aerobic conditions in water [25]. However, to the best of our knowledge, no Heck and Sonogashira reactions catalyzed by a PVC-anchored Pd(II)-dithizone complex have yet been reported.

In this paper, we report the synthesis and characterization of a new PVC-supported Pd(II)-dithizone complex [PVC-dtz-Pd(II)], and the use of this complex in Mizoroki-Heck and Cu-free Sonogashira reactions under aerobic conditions. The ease of preparation of the complex, its long shelf life, its stability toward air, and its compatibility with a wide variety of aryl halides and alkynes make it ideal for these reactions.

2. Experimental

2.1. *Preparation of polymer-anchored PVC-dtz-Pd(II)*

PVC (3 g) and dithizone (7.0 mmol) were added to a 250-mL-round-bottomed flask equipped with a magnetic stirrer bar and containing dimethylformamide (DMF, 20 mL). The reaction mixture was stirred for 30 h at 100 °C, filtered, washed thoroughly with DMF, and dried in vacuo for 12 h. The dithizone-functionalized polymer **2** (3.0 g) was treated with ethanol (50 mL) for 30 min. An ethanolic solution of $PdCl_2(PhCN)_2$ (1.2 g) was added, and the resulting mixture was heated to 80 °C for 20 h. The resulting bright-yellow polymer, impregnated with the metal complex, was filtered and washed with ethanol to obtain PVC-dtz-Pd(II) **3** (Scheme 1).

2.2. *General procedure for Heck reaction*

A mixture of an aryl halide (1.0 mmol), alkyne (1.2 mmol), PVC-dtz-Pd(II) (0.01 mmol), and Et_3N (1.0 mmol) was stirred at 70 °C for 4 h. After completion of the reaction, the mixture was filtered to recover the catalyst. The polymer was washed with water and acetonitrile, vacuum dried, and stored for subsequent runs. After gas chromatographic (GC) analysis, the solvent was removed under vacuum, and the crude product was subjected to silica gel column chromatography, using $CHCl_3$-CH_3OH (97:3) as the eluent, affording the pure product.

2.3. *General procedure for Sonogashira coupling reaction*

An aryl halide (1.0 mmol) and a terminal alkyne (1.2 mmol) were added to a mixture of PVC-dtz-Pd(II) (0.01 mmol) and Et_3N (1.0 mmol) in a glass flask under vigorous stirring. The mixture was stirred at room temperature for 3 h under aerobic conditions. After completion of the reaction, the mixture was filtered to recover the catalyst. The polymer was washed with water and acetonitrile, vacuum dried, and stored for subsequent runs. After GC analysis, the solvent was removed under vacuum, and the crude product was subjected to silica gel column chromatography, using $CHCl_3$-CH_3OH (97:3) as the eluent, affording the pure product.

3. Results and discussion

The synthesis of the PVC-dtz-Pd(II) catalyst is shown in Scheme 1. To verify formation of the functionalized polymer and its corresponding Pd complex, infrared (IR) spectra were recorded separately at different stages of the preparation. The C–H vibrational stretching bands of PVC were observed at 2970, 2911, and 2851 cm^{-1} (Fig. 1). After addition of the ligand, these bands shifted to 2957, 2914, and 2869 cm^{-1}, indicating functionalization of PVC. The bands for the stretching vibrations of C=N appeared at 1600 cm^{-1} for PVC-dtz-Pd(II). Moreover, the spectrum of the PVC-supported Pd complex showed an absorption band at 3439 cm^{-1} attributed to N–H bonds. The N content of the catalyst was found to be 4.6%. The amount of Pd incorporated into the polymer, determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES), was

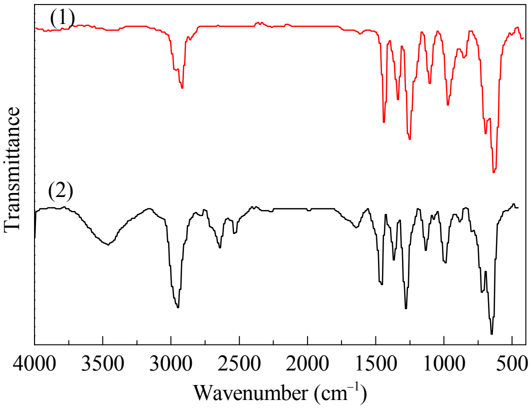
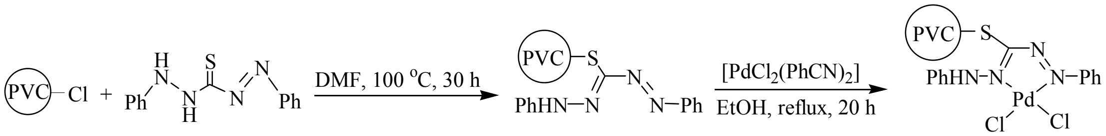


Fig. 1. Fourier-transform IR spectra of PVC (1) and PVC-dtz-Pd(II) complex (2).



1 **2** **3**

Scheme 1. Synthesis of PVC-dtz-Pd(II) catalyst.

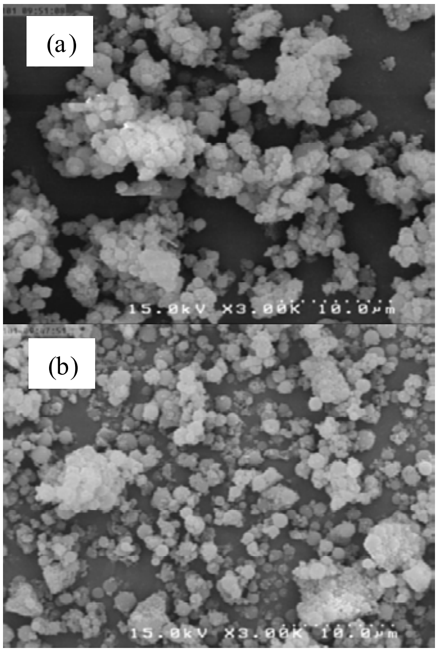


Fig. 2. SEM images of PVC (a) and PVC-dtz-Pd(II) complex (b).

4.9%.

Morphological changes were investigated by scanning electron microscopy (SEM) of a single bead of pure PVC and the polymer-anchored complex. As expected, the presence of Pd caused changes, namely changes in the polymer particle size and surface roughness (Fig. 2).

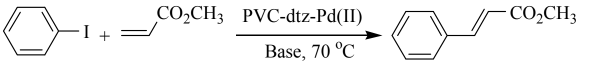
We used the PVC-dtz-Pd(II) complex **3** as the catalyst in Heck and Sonogashira reactions. In the initial investigations, we examined the Heck coupling reaction of iodobenzene (**4a**) with methyl acrylate (**5a**) at 70 °C for 4 h as a model reaction, using **3** (1%) as the catalyst (Table 1). As can be seen from Table 1, of the bases screened, Et_3N gave the best result, and the corresponding coupling product **6a** was obtained in 97% yield (Table 1, entry 2). The effect of temperature on the activity of the PVC-dtz-Pd(II) complex was also studied. As the temperature decreased from 70 to 25 °C, the yield of **6a** decreased from 97% to 55% (Table 1, entry 9). A low Pd concentration gave a decreased yield (Table 1, entry 10).

The optimal reaction conditions were therefore identified as the PVC-dtz-Pd(II) complex (1 mol%) as the catalyst, Et_3N (1.0 equiv.) as the base, and 70 °C. With the optimal reaction conditions in hand, we explored the scope and limitations of the reaction using a set of aryl iodides with methyl acrylate or styrene. It was found that all the reactions afforded the desired coupling products **6** in excellent yields within 4 h, and the substituents, either electron-donating groups such as methoxy groups or electron-withdrawing groups such as Cl or NO_2, on the phenyl ring of **4**, had no significant effect on these reactions (Table 2, entries 2–4). To extend the scope of our work, we next investigated the coupling reactions of aryl bromides with methyl acrylate or styrene. As shown in Table 2, activated aryl bromides such as *p*-nitrobromobenzene underwent the Heck reaction with methyl acrylate and styrene under similar conditions, affording the corresponding products in 90% and 92% yields, respectively (Table 2, entries 8 and 10). The reaction of bromobenzene with methyl acrylate and styrene gave products **6a** and **6e** in 97% and 88% yields, respectively (Table 2, entries 7 and 9).

We next investigated use of the PVC-dtz-Pd(II) complex catalytic system in the Cu-free Sonogashira cross-coupling reaction. The catalytic activity of the PVC-dtz-Pd(II) complex (1 mol%) was studied at room temperature under aerobic conditions in a Cu-free Sonogashira reaction using phenylacetylene and iodobenzene in the presence of various bases. Because no Cu salt was used, the undesired formation of the oxidative homocoupling product, a diyne, was avoided. When the reaction of phenylacetylene with iodobenzene was performed with Et_3N as the base, an excellent yield (99%) of the product was obtained (Table 3, entry 1). A low Pd concentration gave a decreased yield (Table 3, entry 9).

After the optimized conditions had been identified, we explored the general applicability of the PVC-dtz-Pd(II) complex as a catalyst for Cu-free coupling of different alkynes **7** with aryl halides **4** containing electron-withdrawing or electron-donating substituents. The results are shown in Table 4.

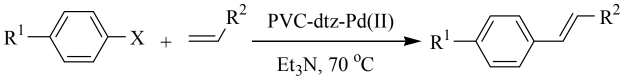
Table 1
Optimization of conditions for Heck reaction of iodobenzene with methyl acrylate.



Entry	Base	Cat (mol%)	GC yield (%)
1	DIPEA	1	81
2	Et_3N	1	97
3	pyridine	1	92
4	piperidine	1	78
5	pyrrolidine	1	83
6	KOH	1	84
7	Na_2CO_3	1	88
8	K_2CO_3	1	70
9[a]	Et_3N	1	55
10	Et_3N	0.5	76

Reaction conditions: iodobenzene 1.0 mmol, methyl acrylate 1.2 mmol, base 1.0 mmol, 4 h, 70 °C ([a] 25 °C).
DIPEA—diisopropylethylamine.

Table 2
Heck reactions of aryl halides with alkenes using PVC-dtz-Pd(II).



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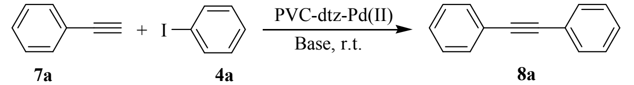
Entry	R¹	R²	X	Product	GC yield (%)
1	H	CO_2Me	I	**6a**	97
2	Cl	CO_2Me	I	**6b**	98
3	NO_2	CO_2Me	I	**6c**	99
4	MeO	CO_2Me	I	**6d**	91
5	H	Ph	I	**6e**	93
6	NO_2	Ph	I	**6f**	98
7	H	CO_2Me	Br	**6a**	97
8	NO_2	CO_2Me	Br	**6b**	90
9	H	Ph	Br	**6e**	88
10	NO_2	Ph	Br	**6f**	92

Reaction conditions: aryl halide 1.0 mmol, alkenes 1.2 mmol, Et_3N 1.0 mmol, PVC-dtz-Pd (II) **3** 0.01mmol, 4 h, 70 °C.

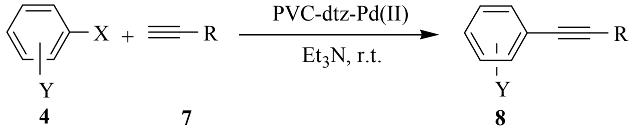
Table 3
Optimization of conditions for Sonogashira reaction of phenylacetylene with iodobenzene.



Entry	Base	Cat (mol%)	GC yield (%)
1	Et_3N	1.0	99
2	DIPEA	1.0	64
3	pyridine	1.0	85
4	piperidine	1.0	80
5	pyrrolidine	1.0	84
6	KOH	1.0	76
7	K_2CO_3	1.0	90
8	Na_2CO_3	1.0	87
9	Et_3N	0.5	80

Reaction conditions: phenylacetylene 1.0 mmol, iodobenzene 1.0 mmol, base 1.0 mmol, room temperature, 3 h.

Table 4
Copper-free Sonogashira reactions of terminal alkynes with aryl halides.



Entry	R	X	Y	Product	GC yield (%)
1	Ph	I	H	**8a**	99
2	Ph	I	4-NO_2	**8b**	100
3	Ph	I	3-NO_2	**8c**	100
4	Ph	I	4-$COCH_3$	**8d**	99
5	Ph	I	4-OCH_3	**8e**	95
6	*n*-C_6H_{13}	I	H	**8f**	91
7	*n*-C_6H_{13}	I	4-NO_2	**8g**	98
8	*n*-C_6H_{13}	I	4-OCH_3	**8h**	95
9	CH_2OH	I	H	**8i**	94
10	CH_2OH	I	4-NO_2	**8j**	97
11	CH_2OH	I	4-OCH_3	**8k**	95
12	Ph	Br	H	**8a**	96
13	Ph	Br	4-NO_2	**8b**	90
14	Ph	Br	3-NO_2	**8c**	95
15	Ph	Br	4-CN	**8l**	92
16	Ph	Br	4-OCH_3	**8e**	92
17	*n*-C_6H_{13}	Br	H	**8f**	90
18	*n*-C_6H_{13}	Br	4-NO_2	**8g**	95
19	*n*-C_6H_{13}	Br	4-OCH_3	**8h**	91
20	CH_2OH	Br	H	**8i**	92
21	CH_2OH	Br	4-NO_2	**8j**	99
22	CH_2OH	Br	4-OCH_3	**8k**	92
23	Ph	Cl	H	**8a**	50
24	Ph	Cl	4-NO_2	**8b**	64
25	Ph	Cl	4-OCH_3	**8e**	43

Reaction conditions: aryl halide 1.0 mmol, terminal alkyne 1.0 mmol, PVC-dtz-Pd(II) **3** 0.01 mmol, Et_3N 1.0 mmol, 3 h, room temperature, aerobic conditions.

The Sonogashira coupling of phenylacetylene with iodoanisole bearing an electron-donating group at the *para* position gave the corresponding diarylacetylene **8e** in 95% yield (Table 4, entry 5). *p*-Nitroiodobenzene and *m*-nitroiodobenzene containing electron-deficient aromatic rings also underwent Sonogashira coupling with phenylacetylene under similar conditions to afford the corresponding diarylacetylenes **8b** and **8c** in excellent yields (100%; Table 4, entries 2 and 3).

When the less-reactive acetylene, 1-octyne, and propargyl alcohol were used, the coupling products were produced efficiently. Coupling of iodobenzene with nitro and methoxy groups at the *para* positions took place with 1-octyne to give the corresponding products **8g** and **8h** in excellent yields (Table 4, entries 7 and 8). Propargyl alcohol also reacted efficiently with aryl iodides, providing excellent yields of the desired products (Table 4, entries 9–11).

To extend the scope of our work, we next investigated the coupling of various aryl bromides with terminal alkynes. As shown in Table 4, high catalytic activity was observed in the coupling reactions of activated aryl bromides such as nitrobromobenzenes (Table 4, entries 13, 14, 18, and 21) and *para*-substituted bromoanisoles (Table 4, entries 16, 19, and 22), as well as activated nitroiodobenzenes and *para*-substituted iodoanisole. *p*-Bromobenzonitrile also underwent Sonogashira coupling with phenylacetylene under similar conditions to afford the corresponding product in excellent yield (entry 15). The reactions of phenylacetylene with aryl chlorides performed under similar conditions afforded the corresponding products in low yields (Table 4, entries 23–25).

Reaction conditions: aryl halide 1.0 mmol, terminal alkyne 1.0 mmol, PVC-dtz-Pd(II) **3** 0.01 mmol, Et_3N 1.0 mmol, 3 h, room temperature, aerobic conditions.

One of the reasons for designing this heterogeneous catalyst is to enable recycling of the catalyst for use in subsequent reactions. The reusability of the catalyst was tested for the reaction of phenyl iodide with methyl acrylate (Heck reaction) and phenyl iodide with phenylacetylene (Sonogashira reaction), as representative reactions in the presence of 1 mol% PVC-dtz-Pd(II), to study the recyclability of this heterogeneous catalyst. The solid catalyst was recovered by separation of the organic compounds from the reaction mixture by extraction, and the recovered catalyst was used in subsequent runs of the reactions. The recycling process was repeated for five cycles; some decrease in the catalytic activity was observed (Table 5).

To determine the absolute amount of Pd species dissolved in solution by leaching, the crude reaction mixtures were evaporated to dryness and analyzed using ICP-AES. The amount of Pd leaching after five runs (for the Sonogashira reaction) was determined to be 6%; this shows that the average amount of leaching of Pd per cycle was around 1.2%.

Table 5
Heck and Sonogashira reactions catalyzed by recycled catalyst.

Cycle	GC yield (%)	
	Heck	Sonogashira
1	97	99
2	97	99
3	96	98
4	96	97
5	94	97

Reaction conditions: iodobenzene 1.0 mmol, methyl acrylate (Heck reaction) 1.2 mmol, iodobenzene 1.0 mmol, phenylacetylene (Sonogashira reaction) 1.0 mmol, PVC-dtz-Pd(II) **3** 0.01 mmol, base 1.0 mmol, 70 °C (for Heck reactions), room temperature (for Sonogashira reactions).

Graphical Abstract

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Poly(vinyl chloride)-supported Pd(II) complex as an efficient catalyst for Heck and Cu-free Sonogashira reactions under aerobic conditions

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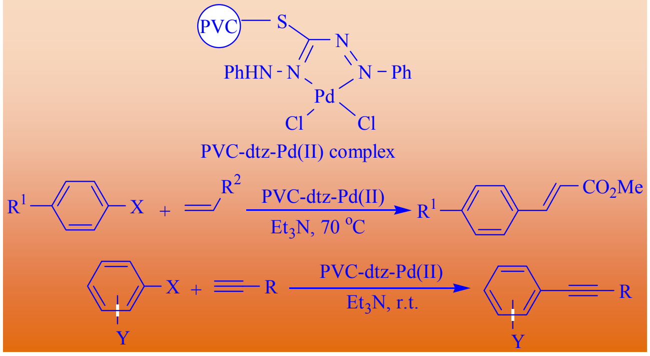

A novel poly(vinyl chloride)-supported palladium complex was found to be highly active in the Heck and Sonogashira reactions of aryl halides under aerobic conditions. The complex is thermally stable and can be easily recovered and reused for five runs without appreciable loss of catalytic activity.

4. Conclusions

We developed the first examples of Heck and Sonogashira reactions catalyzed by a cheap and air-stable PVC-dtz-Pd(II) complex. The ease of preparation of the complex, its indefinite shelf life, and its stability toward air make it an ideal complex for these transformations. The system works equally well for a wide range of aryl halides and alkynes, and tolerates a variety of functional groups. All the reactions were conducted in air without the use of an organic solvent. Moreover, the catalyst could be reused for five consecutive cycles without significant loss of its catalytic activity. These advantages make the process valuable from the synthetic and environmental points of view.

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