Journal of Organometallic Chemistry 740 (2013) 78–82

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

A phenyldithiocarbazate-functionalized polyvinyl chloride resin-supported Pd(II) complex as an effective catalyst for solvent- and copper-free Sonogashira reactions under aerobic conditions

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ARTICLE INFO

Article history:
Received 15 March 2013
Received in revised form
28 April 2013
Accepted 30 April 2013

Keywords:
Phenyldithiocarbazate
Supported catalyst
Sonogashira reactions
Aryl halides

ABSTRACT

The PVC-supported phenyldithiocarbazate palladium complex was prepared and characterized. The catalyst exhibits excellent catalytic activity and stability for the Sonogashira coupling reaction under ambient conditions. Various terminal alkynes were coupled with a number of aryl halides in the presence of 1.0 mol% of the catalyst to afford the corresponding products in high yields. Furthermore, the heterogeneous catalyst can be readily recovered by simple filtration and reused for several times without a significant loss in its activity.

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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].

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. These problems can be overcome, however, by the use of heterogeneous catalysts, made up of supported palladium complexes.

The use of heterogeneous catalysts for the Sonogashira coupling reaction has paid much attention to reducing waste, thus working toward an environmentally benign chemical process.

Macquarrie and co-workers have reported the effectiveness of N, P-chelated Pd(II) complexes immobilized on silica gel under solvent-free conditions [19]. Choudary et al. have proposed layered double hydroxide supported nanopalladium works as the Heck-type reactions including Sonogashira coupling [20]. Singh et al. have described the synthesis and characterization of recyclable and recoverable MMT-clay exchanged ammonium tagged carbapalladacycle catalyst for the Mizoroki–Heck and Sonogashira reactions in ionic liquid media [21]. Wu et al. have reported the ionic liquid functionalized phosphine-ligated palladium complex for the copper-free Sonogashira reactions under aerobic conditions [22]. Furthermore, Komura et al. have reported the copper-free Sonogashira coupling reaction of terminal alkynes with aryl halides catalyzed by a quinoline-2-carboimine palladium complex immobilized on MCM-41 under aerobic conditions [23].

Polyvinyl chloride modified by a functional group can be prepared *via* displacement reaction directly without chloromethylation which makes it inexpensive and a practical support for a heterogeneous catalyst. Nevertheless, only a few examples of Sonogashira reactions using polyvinyl chloride as a support have been reported in the literature. Cui et al. have described the synthesis and characterization of polyvinyl chloride–polyethylene–polyamine supported palladium complex catalysts for the Heck reaction of acrylic acid with aryl iodides in air at low temperature [24]. Liu and co-workers have reported the synthesis and characterization of nanopalladium immobilized on the surface of PVC-supported Schiff base for the Suzuki–Miyaura cross-coupling reactions in 95% aqueous ethanol under atmospheric conditions [25].

As part of our continuing interest in heterogeneous palladium-catalyzed carbon–carbon cross-coupling reactions [26–28], we have recently reported a mild protocol for the solvent-free Heck and copper-free Sonogashira coupling reactions catalyzed by a polystyrene-anchored Pd(II) phenyldithiocarbazate complex under

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http://dx.doi.org/10.1016/j.jorganchem.2013.04.058

aerobic conditions [29]. However, to the best of our knowledge, no Sonogashira reaction catalyzed by the PVC-anchored Pd(II) phenyldithiocarbazate complex has yet been reported.

Herein, we report the synthesis and characterization of a new polyvinyl chloride-supported palladium(II) phenyldithiocarbazate complex, and the application of this complex in the copper-free Sonogashira reactions under aerobic conditions.

2. Results and discussion

A PVC resin functionalized with phenyldithiocarbazate group was formed by heating a mixture of PVC with phenylhydrazine and carbon disulfide in the presence of KOH in DMF at 80 °C to produce the corresponding PVC-anchored phenyldithiocarbazate ligand **1**, which was then reacted with $PdCl_2(PhCN)_2$ in DMF at 80 °C to yield the PVC-anchored Pd(II) phenyldithiocarbazate complex **2** (Scheme 1). Catalyst **2** was characterized by the FT-IR, scanning electron micrograph (SEM), and inductively coupled plasma (ICP) techniques.

Presence of the phenyldithiocarbazate ligand on polyvinyl chloride was confirmed by FT-IR spectra. The stretching vibrations of the C=C band appeared at 1598 cm^{-1} for the PVC-phenyldithiocarbazate ligand. The NH group in PVC-phenyldithiocarbazate appeared, in the IR spectrum, at 3432 cm^{-1} (Fig. 1). The N content of the resin was obtained to be 2.3%. The amount of palladium incorporated into the catalyst **2** was also determined by ICP, which showed a value of about 2.5%.

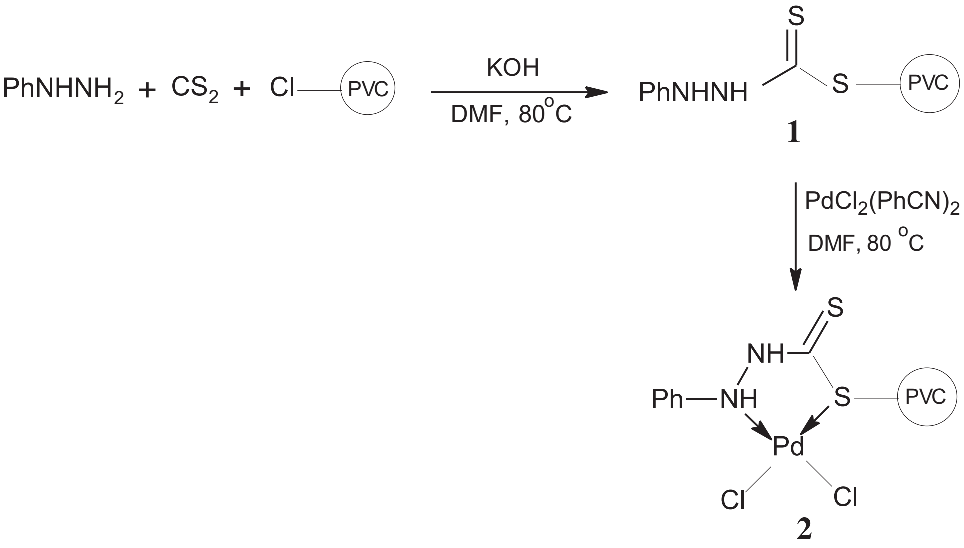
SEM was also recorded to understand the morphology of the surface of the support and catalyst. It can easily be seen in Fig. 2 that the resin beads have different size and roughness. The presence of Pd has caused changes, demonstrated by change in the polymer particle size and roughness of the surface.

To check the potency of the polyvinyl chloride resin supported phenyldithiocarbazate palladium catalyst, it was used in a solvent- and copper-free Sonogashira coupling reaction. The coupling between iodobenzene and phenylacetylene was chosen as the model reaction. Our optimization data is shown in Table 1. Out of the bases screened, pyridine gave the best results, and the corresponding coupled product **5a** was obtained in 98% GC yield (Table 1, entry 3). The inorganic bases KOH, K_2CO_3, and Na_2CO_3 were less effective. A low palladium concentration gave a decreased yield (entry 12). 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 an 80% yield of diphenylacetylene **5a** (entry 15). However, by changing the base to ethanolamine, bromobenzene could be smoothly coupled with phenylacetylene resulting in a high yield (95%) of diphenylacetylene (entry 20).

After the optimized conditions were found, we explored the general applicability of the PVC-anchored Pd(II) phenyldithiocarbazate complex **2** as a catalyst for the copper- and solvent-free coupling of different alkynes **3** with aryl halides **4** containing electron-withdrawing or donating substituents. The results obtained are shown in Table 2. The electron-neutral, electron-rich or electron-poor aryl iodides reacted with phenylacetylene to generate the corresponding cross-coupling products in high yields under the standard reaction conditions (Table 2, entries 1–7). The Sonogashira coupling of the less reactive acetylene, 1-hexyne, and propargyl alcohol with aryl iodides bearing electron-donating or electron-withdrawing groups all gave the corresponding products in high yields (entries 8–14). 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 aryl iodides appeared to be less significant than in aryl bromides. However, as shown in Table 2, high catalytic activity was observed in the coupling of activated aryl bromides such as *p*-nitrobromobenzene (entries 16, 21, and 25) and unactivated aryl bromides such as *p*-bromoanisole (entries 19 and 23) as well as *p*-nitroiodobenzene and *p*-iodoanisol. It should be noted that the coupling reactions of the aryl chlorides (entries 27–29), also took place under similar copper-free conditions, though the reactivity was much lower than their iodo and bromo counterparts.

The recovery and reusability of the catalyst were investigated using the reaction of iodobenzene with phenylacetylene as a model system. After completion of the reaction, $CHCl_3$ was added. The mixture from the first-run reaction was filtered, and the solid substance obtained was washed alternately with water, methanol, and acetonitrile. After drying under vacuum for 15 h, the recovered catalyst was reused in the same reaction under identical conditions.

The recycling process was repeated for five cycles with some decrease in the catalytic activity of the catalyst. We found that the product yield decreased slightly over five recycling runs (Table 3). The ICP analysis shows that the palladium content of the catalyst does not change after catalysis, indicating that no significant



Scheme 1. Preparation of the supported Pd–phenyldithiocarbazate complex.

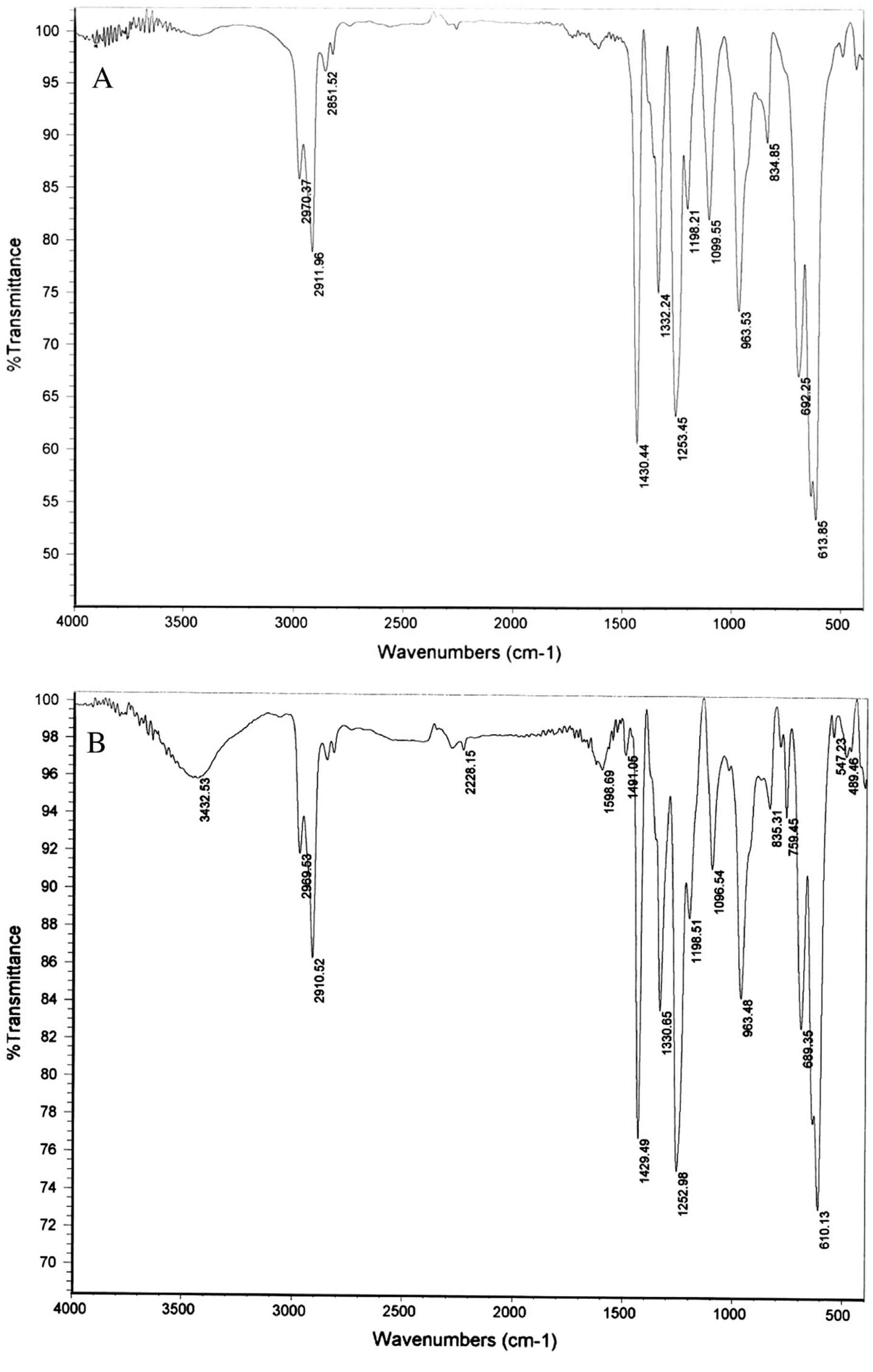


Fig. 1. FT-IR spectra of A) polyvinyl chloride; B) supported Pd–phenyldithiocarbazate complex.

leaching of palladium to the solution occurs during the catalytic processions.

3. Conclusion

We successfully prepared the polyvinyl chloride-anchored Pd(II) phenyldithiocarbazate complex, which was used as a heterogeneous catalyst for the room-temperature Sonogashira coupling reaction. The catalyst showed a high catalytic activity for the reaction affording a diverse range of aryl halides in good to excellent yields within 3 h, and could be easily recovered by simple filtration and reused for 5 times without a significant loss in its activity. These advantages make the process highly valuable from the synthetic and environmental points of view.

4. Experimental

*4.1. Preparation of polymer-anchored PVC-anchored Pd(II) phenyldithiocarbazate complex **2***

To a 250-ml round bottomed flask equipped with a magnetic stirrer bar and containing DMF (30 ml), were added polyvinyl

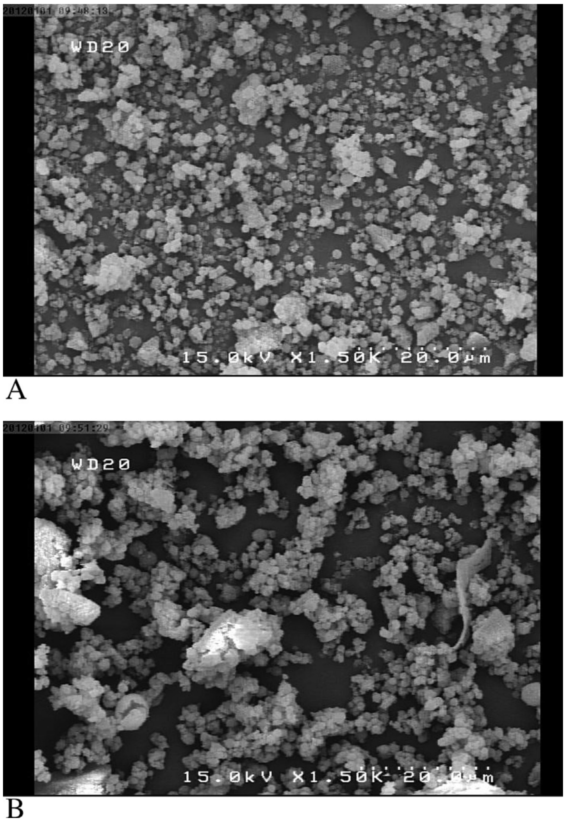
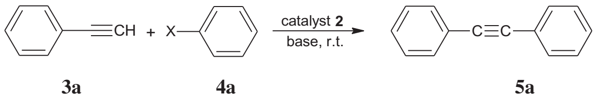


Fig. 2. Scanning electron micrograph of A) polyvinyl chloride; B) supported Pd–phenyldithiocarbazate complex.

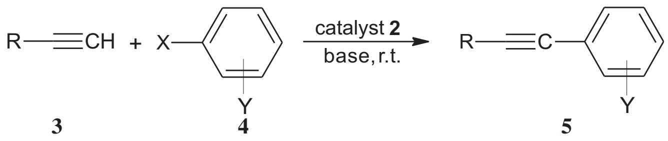
Table 1
Copper- and solvent-free coupling reaction of phenylacetylene with aryl halides in the presence of different bases.[a]



Entry	X	Base	Cat (mol%)	Yield[b] (%)
1	I	Et_3N	1	75
2	I	DIEA	1	80
3	I	Pyridine	1	98
4	I	Piperidine	1	71
5	I	Pyrrolidine	1	88
6	I	Diethylamine	1	40
7	I	Butylamine	1	55
8	I	Ethanolamine	1	64
9	I	KOH	1	55
10	I	K_2CO_3	1	57
11	I	Na_2CO_3	1	70
12	I	Pyridine	0.5	93
13	Br	Et_3N	1	70
14	Br	DIEA	1	83
15	Br	Pyridine	1	80
16	Br	Piperidine	1	78
17	Br	Pyrrolidine	1	90
18	Br	Diethylamine	1	40
19	Br	Butylamine	1	45
20	Br	Ethanolamine	1	95
21	Br	KOH	1	50
22	Br	K_2CO_3	1	68
23	Br	Na_2CO_3	1	52
24	Br	Ethanolamine	0.5	90

[a] Reaction conditions: phenylacetylene (1.0 mmol), aryl halides (1.0 mmol), base (1.0 mmol), catalyst **2** (0.01 mmol), room temperature, 3 h, aerobic conditions.
[b] GC yield.

Table 2
Copper- and solvent-free Sonogashira reactions of terminal alkynes with aryl halides.[a]



Entry	R	X	Y	Base	Product	Yield[b] (%)
1	Ph	I	H	Pyridine	**5a**	98 (96)
2	Ph	I	4-NO_2	Pyridine	**5b**	99
3	Ph	I	3-NO_2	Pyridine	**5c**	98
4	Ph	I	4-Br	Pyridine	**5d**	96 (93)
5	Ph	I	4-Cl	Pyridine	**5e**	97
6	Ph	I	4-$COCH_3$	Pyridine	**5f**	98
7	Ph	I	4-OCH_3	Pyridine	**5g**	92 (88)
8	n-C_4H_9	I	H	Pyridine	**5h**	90
9	n-C_4H_9	I	4-NO_2	Pyridine	**5i**	97 (93)
10	n-C_4H_9	I	4-$COCH_3$	Pyridine	**5j**	96
11	n-C_4H_9	I	4-OCH_3	Pyridine	**5k**	90
12	CH_2OH	I	H	Pyridine	**5l**	93
13	CH_2OH	I	4-NO_2	Pyridine	**5m**	98 (95)
14	CH_2OH	I	4-$COCH_3$	Pyridine	**5n**	94
15	Ph	Br	H	Ethanolamine	**5a**	95
16	Ph	Br	4-NO_2	Ethanolamine	**5b**	97 (95)
17	Ph	Br	3-NO_2	Ethanolamine	**5c**	91
18	Ph	Br	4-CN	Ethanolamine	**5o**	89
19	Ph	Br	4-OCH_3	Ethanolamine	**5g**	88 (85)
20	n-C_4H_9	Br	H	Ethanolamine	**5h**	88
21	n-C_4H_9	Br	4-NO_2	Ethanolamine	**5i**	97
22	n-C_4H_9	Br	4- Cl	Ethanolamine	**5p**	90 (86)
23	n-C_4H_9	Br	4-OCH_3	Ethanolamine	**5q**	87
24	CH_2OH	Br	H	Ethanolamine	**5l**	96
25	CH_2OH	Br	4-NO_2	Ethanolamine	**5i**	98 (94)
26	CH_2OH	Br	4-$COCH_3$	Ethanolamine	**5n**	69
27	Ph	Cl	H	Ethanolamine	**5a**	45
28	Ph	Cl	4-NO_2	Ethanolamine	**5b**	50
29	Ph	Cl	4-OCH_3	Ethanolamine	**5g**	28

[a] Reaction conditions: **3** (1.0 mmol), **4** (1.0 mmol), catalyst **2** (0.01 mmol), base (1.0 mmol), 3 h, room temperature, aerobic conditions.
[b] GC yield. Isolated yields are given in parentheses.

chloride (3 g), phenylhydrazine (5.0 mmol), KOH (5.0 mmol), and carbon disulfide (5.0 mmol). The mixture was stirred for 10 h at 80 °C, and was subsequently filtered and washed thoroughly with DMF, and dried in vacuo for 12 h. The phenyldithiocarbazate-functionalized polymer **1** (2.0 g) was treated with $PdCl_2(PhCN)_2$ (2.0 g) in DMF, and the resulting mixture was heated at 80 °C for 15 h. The resulting bright yellow colored polymer, impregnated with the metal complex, was filtered and washed with acetonitrile to give the catalyst **2** (Scheme 1).

4.2. General procedure for the Sonogashira coupling reaction

Under air atmosphere, around-bottomed flask was charged with an aryl halide (1.0 mmol), a terminal alkyne (1.0 mmol), a base

Table 3
The Sonogashira reactions catalyzed by the recycled catalyst.[a]

Entry	Cycle	Yield[b]
1	1	98
2	2	98
3	3	97
4	4	95
5	5	93

[a] Reaction conditions: iodobenzene (1.0 mmol), phenylacetylene, (1.0 mmol), catalyst **2** (0.01 mmol), Et_3N (1.0 mmol), room temperature.
[b] GC yield.

(1.0 mmol), and the catalyst **2** (1 mol%). 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, methanol, and acetonitrile, vacuum-dried, and stored for a new run. 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 eluent to afford the pure product.

Acknowledgments

We gratefully acknowledge the financial support of the Research Council of Shahrood University of Technology.

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