



A novel 1,2,4-triazine-functionalized polystyrene resin-supported Pd(II) complex: A copper- and solvent-free highly efficient catalyst for Sonogashira coupling reactions



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ABSTRACT

A polystyrene-supported triazine palladium complex was prepared and characterized. The catalyst exhibits excellent catalytic activity and stability for the Sonogashira coupling reaction under ambient conditions. Various aryl halides were coupled with a number of terminal alkynes under air in the presence of 0.1 mol% of the catalyst to afford the corresponding coupled 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

Palladium-catalyzed C–C forming reactions are of great interest in synthetic organic chemistry, and the Sonogashira coupling of aryl halides with terminal alkynes is one of the most important reactions [1,2]. These reactions have been widely employed in the synthesis of natural products, biologically active molecules, and material science [3,4].

In the Sonogashira coupling reaction, copper salts usually play an important role in assisting the oxidative addition of acetylene to palladium metal; this method has drawbacks, though, including waste production and the necessity of separation after the reaction. Recently, some successful examples of copper-free Sonogashira coupling reactions have been reported [5–8].

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 [9]. 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.

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.

Although homogeneous catalysts have many advantages [10–13], catalyst immobilization is a well-known methodology to allow efficient catalyst separation and to obtain metal-free products [14–17]. The successful methods include immobilizing or supporting the active homogeneous catalysts onto various inorganic supports such as zeolites, mesoporous materials, alumina, silica, clays, and high surface carbons [18–20] which assist in controlling reactivity and selectivity besides the advantage of easy workability.

Macquarrie and co-workers have reported the effectiveness of N, P-chelated Pd(II) complexes immobilized on silica gel under solvent-free conditions [21]. Choudary et al. have proposed layered double hydroxide supported nanopalladium works as the Heck-type reactions including the Sonogashira coupling [22]. Vasundhara Singh et al. have described the synthesis and characterization of the recyclable and recoverable MMT-clay exchanged ammonium tagged carbapalladacycle catalyst for the Mizoroki–Heck and Sonogashira reactions in ionic liquid media [6]. Haihong Wu et al. have reported the ionic liquid functionalized phosphine-ligated palladium complex for the copper-free Sonogashira reactions under aerobic conditions [8]. Furthermore, Kenichi Komura et al. have reported the copper-free Sonogashira coupling reaction of terminal

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alkynes with aryl halides catalyzed by a quinoline-2-carboimide palladium complex immobilized on MCM-41 under aerobic conditions [23].

Polystyrene is one of the most popular polymeric supports used in synthetic organic chemistry because of its inexpensive, ready availability, mechanical robustness, chemical inertness, and facile functionalization.

Polystyrene-supported palladium catalysts have successfully been used for the Heck [24] and Suzuki [25–27] reactions, and have shown lower levels of palladium leaching during cross-coupling. To date, a few palladium complexes on functionalized polystyrene support have been prepared and successfully used in the Sonogashira reaction.

S.M. Islam and co-workers have described synthesis and characterization of the reusable polystyrene anchored Pd(II) azo complex catalyst for the Suzuki and Sonogashira coupling reaction in water medium [28]. Moreover, Ying He et al. have developed a successful copper-free Sonogashira coupling reaction catalyzed by a reusable polystyrene-supported macrocyclic Schiff base palladium complex in water [29]. Although all the methods provide good yields, some of the reactions are sluggish, requiring high temperature for completion, and the reactions should be performed in the presence of relatively large amounts of palladium.

Our strategy for developing a versatile heterogeneous catalyst is based upon the concept of immobilizing an organometallic complex onto polystyrene. This is because the usage of polystyrene often offers enhanced catalytic activity due to its high surface area, and can be expected to have negligible leaching of precious metal species and high catalytic activity.

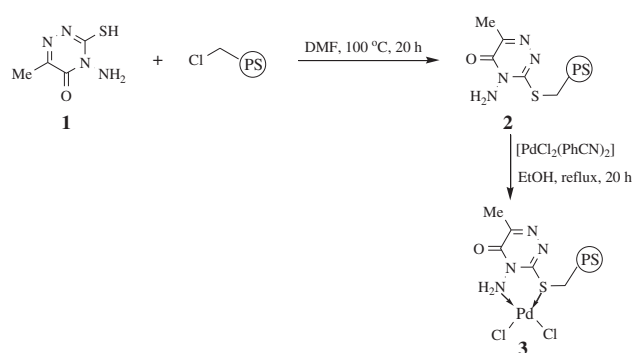
We have recently reported the synthesis and characterization of the polystyrene-supported bidentate phosphine palladium(0) complex and the polystyrene-supported palladium(II) 1-phenyl-1,2-propanedione-2-oxime thiosemi-carbazone complex, and found that these complexes are highly active and recyclable catalysts for the Sonogashira reaction of aryl halides with terminal alkynes under aerobic conditions [30,31]. Moreover, we have developed successful Suzuki, Heck, and copper-free Sonogashira reactions catalyzed by 4-amino-5-methyl-3-thio-1,2,4-triazole-functionalized polystyrene resin-supported Pd(II) under aerobic conditions in water [32]. However, to the best of our knowledge, no Sonogashira reactions catalyzed by PS-anchored Pd(II) triazine complex have yet been reported.

Thus we were encouraged to develop a further application toward the sophisticated chemical transformations, especially the carbon–carbon bond forming reactions.

Here, we report the heterogeneous copper-free Sonogashira coupling reaction of terminal alkynes with aryl halides catalyzed by the triazine-functionalized polystyrene resin-supported Pd(II) complex.

2. Results and discussion

We report here anchoring of 4-amino-5-methyl-1,2,4-triazine [33–35] on the cross linked polystyrene polymer (Scheme 1). The chelating polymeric matrix was further used for the Sonogashira reactions. A polystyrene resin (cross-linked with 2% divinylbenzene, 4–5% Cl content, 1.14–1.40 mmol/g Cl) functionalized with triazine groups was formed by heating a mixture of chloromethylated polystyrene and triazine in DMF at 100 °C for 24 h. PS-triazine prepared was characterized by elemental analysis. The nitrogen content of this resin was 3.67%. According to this value, the degree of triazine introduced to the polymer was 0.65 mmol/g of the support. This shows that only 46–57% of the total chlorine content was substituted by triazine. The reaction of polymer-bound triazine with a solution of PdCl₂(C₆H₅CN)₂ in ethanol under reflux



Scheme 1. Preparation of the supported Pd-triazine complex.

conditions resulted in the covalent attachment of palladium onto the functionalized polymer. The catalyst prepared, PS-triazine-Pd(II), was characterized by FT-IR and SEM. The amount of palladium incorporated into the polymer was also determined by inductively coupled plasma (ICP), which showed a value of 0.12 mmol/g of the heterogenized catalyst.

In order to ascertain the functionalized polymer and its corresponding Pd complex, IR spectra were recorded separately at different stages of preparation. As it can be seen in Fig. 1, the spectrum of chloromethylated polystyrene resin shows an absorption band at 1265 cm⁻¹, attributed to the C–Cl bond, and weakened after the introduction of 4-amino-5-methyl-1,2,4-triazine. Also the stretching vibrations of the C=O band appeared at 1697 cm⁻¹ for the PS-triazine-Pd(II). Moreover, the spectrum of polystyrene-supported palladium complex shows an absorption band at 3425 cm⁻¹, which is attributed to the N–H bond. Scanning electron micrographs (SEM) were reported for a single bead of pure chloromethylated polystyrene, and polymer-anchored complex to observe the morphological changes. 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 1,2,4-triazine-functionalized polystyrene resin-supported Pd(II) complex, it was used in the Sonogashira coupling reaction. The coupling between phenyl acetylene and iodobenzene was chosen as the model reaction. Initially, we examined the effects of bases on the copper- and solvent-free Sonogashira reaction at room temperature. The organic bases Et₃N, DIEA, pyridine, piperidine, and pyrrolidine were investigated (Table 1, entries 1–5). As shown in Table 1, Et₃N was the best base for the reaction with high TON 990. Also the inorganic bases KOH, K₂CO₃, and Na₂CO₃ were studied but unsatisfactory yields were obtained (Table 1, entries 6–8). Then different catalyst loadings were tested for the reaction. As illustrated in Table 1, 0.05 mol% of the catalyst gave rise to extremely high TON 1800 (Table 1, entry 9) but a lower yield was obtained. Thus we selected Et₃N as the base and 0.1 mol% of the catalyst as the optimal conditions for the reaction. 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 phenyl acetylene under the above conditions and found that it was not efficient since it afforded only a 50% yield of diphenyl acetylene **6a** (entry 10). However, by changing the base to piperidine, bromobenzene could be smoothly coupled with phenyl acetylene resulting in a high yield (98%) of diphenyl acetylene (entry 13).

After the optimized conditions were found, we explored the general applicability of the PS-triazine-Pd(II) complex **3** as a catalyst for copper-free coupling of different alkynes with aryl halides containing electron withdrawing or donating substituents.

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