



Polymer anchored ruthenium complex: A highly active and recyclable catalyst for one-pot azide–alkyne cycloaddition and transfer-hydrogenation of ketones under mild conditions



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ABSTRACT

A new polymer supported Ru(III) complex has been synthesized and characterized. The catalytic performance of the complex has been tested for the first time azide–alkyne cycloaddition reaction in water and transfer-hydrogenation reaction of ketones in open air. 1,4-disubstituted-1,2,3-triazoles were obtained in excellent yields from azides and terminal alkynes in aqueous medium in the presence of the above catalyst. Aromatic ketones have been converted to their corresponding alcohols using the polymer supported Ru(III) catalyst. The effects of solvents, reaction time, catalyst amount for the azide–alkyne cycloaddition reaction and transfer-hydrogenation reaction were studied. This catalyst showed excellent catalytic activity and recyclability. The polymer supported Ru(III) catalyst could be easily recovered by filtration and reused more than five times without appreciable loss of its initial activity. There was no evidence of leached Ru from the catalyst during the course of reaction has been observed, suggesting true heterogeneity in the catalytic process.

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Introduction

The copper-catalyzed azide–alkyne cycloaddition (CuAAC) yielding 1,2,3-triazoles is a powerful one pot click reaction [1]. 1,2,3-triazoles are five-membered nitrogen heterocyclic compounds that are widely used in various research fields including synthetic organic, medicinal, materials, and biological chemistry [2–5]. Most azide–alkyne cycloaddition (AAC) have been carried by homogeneous copper catalysts [6–10]. Homogeneous catalysts have some disadvantages, such as they may easily be destroyed during the course of the reaction and they cannot be easily recovered after the reaction for reuse and the use of copper salt is restricted as it often leads to the formation of undesired homo-coupled product of alkyne [11–13].

To get rid from these serious issues various solid-supported copper catalysts were also reported. The supports employed to date are activated carbon, inorganic materials, such as zeolites, amine-bound silica, superparamagnetic mesoporous silica, AlO(OH), metal oxide, hydrotalcite, an ionic liquid, a ligand-bound organic polymer, and polysaccharide [14–23]. Most of these reported CuAAC studies are on two component reaction systems using organic azides which are synthesized in advance. These organic azides are potential hazards especially in the isolation or the purification process and thus can be problematic. To overcome these drawbacks some copper catalysts were reported where organic azides were synthesised in situ to avoid the handling of such hazardous materials [24–27]. But these methodologies suffer from several drawbacks like use of long reaction time and elevated temperature.

It is thus desirable to develop an efficient one-pot methodology to avoid all these difficulties. More recently, it has been disclosed that (pentamethylcyclopentadienyl) ruthenium chloride complexes can effectively catalyze the facile cycloaddition of a wide range of azides and terminal alkynes (RuAAC) to afford regioselectively the complementary 1, 5-disubstituted 1,2,3-triazoles

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[28,29]. But Pei et al. reported that ruthenium complexes lacking cyclopentadienyl ligands, can catalyze the cycloaddition of terminal acetylenes and azides to give selectively 1, 4-substituted triazole regioisomers rather than 1, 5-disubstituted 1,2,3-triazoles [30,31].

In our present work, we have synthesized a polymer anchored ruthenium(III) complex and utilized it to catalyze the azide–alkyne cycloaddition reaction. During the course of our effort to develop ruthenium mediated cycloaddition of azides and alkynes, we have found that polymer anchored ruthenium(III) complex not only catalyze the three component cycloaddition of terminal acetylenes, sodium azide and alkyl halides to give selectively 1,4-substituted triazole regioisomers but also catalyze the transfer-hydrogenation reaction under mild conditions.

Amongst the many catalytic applications of Ru(III) in organic synthesis transfer-hydrogenation has become very popular in the last decade. It is indeed a very powerful tool for the reduction of ketones to their corresponding alcohols. The catalytic transfer-hydrogenation of ketones represents a viable method, not only in the laboratory but also on a commercial scale, because of its ease of handling, lower cost and safety compared with the typically used expensive, hazardous and dangerous reagents such as borane reagents, high-pressure hydrogen gas [32–37]. Among the different metal catalyzed transfer-hydrogenation reactions, ruthenium-based catalytic systems are found to be effective in the transfer-hydrogenation of ketones [38].

Herein we report the synthesis and characterization of a polymer supported ruthenium catalyst and illustrate its application for the synthesis of 1,4-disubstituted triazoles via three-component coupling of alkynes, azides and alkyl halides in water medium and transfer-hydrogenation reaction of various ketones in open air.

Experimental section

Materials

Analytical grade reagents and freshly distilled solvents were used throughout the experiments. All reagents and substrates were purchased from Merck. Liquid substrates were predistilled and dried by molecular sieve and solid substrates were recrystallized before use. Distillation, purification of the solvents and substrate were done by standard procedures. 5.5% crosslinked chloromethylated polystyrene and ruthenium trichloride were purchased from Sigma Aldrich and used as without further purification.

Physical measurements

The FT-IR spectra of the samples were recorded from 400 to 4000 cm^{-1} on a Perkins Elmer FT-IR 783 spectrophotometer using KBr pellets. UV–vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e. Surface morphology of the samples was measured using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility. Ruthenium content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS). NMR spectra were recorded on a Varian Mercury plus NMR spectrometer (^1H NMR at 300 and 500 MHz and ^{13}C NMR at 75 MHz and 125 MHz) in pure deuterated solvents.

Synthesis of the metal complex

The synthesis of the immobilized polymer supported ruthenium(III) catalyst is illustrated in Scheme 1. It was readily prepared through a two-step procedure. First, 0.2 g of chloromethylated

polystyrene (5.5 mmol Cl/g of resin) was treated with 0.979 g of β -alanine in DMF to produce the corresponding polymer supported ligand (PS-L). Then, the polymer was washed thoroughly with DMF to remove excess β -alanine. Finally, it was washed with double distilled water, dried and stored at room temperature for further use.

In the second step, the polymer supported β -alanine ligand (1 g) in DMF (20 mL) was treated with 5 mL 1% (w/v) DMF solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ over a period of nearly 30 min under constant stirring. The reaction mixture was refluxed for 24 h. The deep grey coloured ruthenium complex thus formed was filtered and washed thoroughly with ethanol and dried in room temperature under vacuum.

General procedure for the formation of triazoles

Polymer supported metal catalyst (25 mg, 21×10^{-3} mmol) in water (5 mL) was taken in a 50 mL round bottom flask. Then phenylacetylene (1 mmol), sodium azide (1.2 mmol) and benzyl bromide (1 mmol) were added and stirred at room temperature for 180 min. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried in oven. The filtrate was extracted with ethyl acetate (3×20 ml) and the combined organic layers were dried with anhydrous Na_2SO_4 by vacuum. All the prepared compounds were confirmed by ^1H and ^{13}C NMR.

General procedure for the catalytic transfer hydrogenation reaction

The substrate (ketone) (2.4 mmol), ruthenium catalyst (2.5 μmol), and propan-2-ol (5 mL) were introduced into a two necked round-bottomed flask fitted with a condenser and heated at 80 $^\circ\text{C}$ for 15–20 min in an open air atmosphere. Then, a solution of KOH (0.05 mmol) in 2-propanol (5 mL) was introduced to initiate the reaction and it was heated at 80 $^\circ\text{C}$. The progress of the reaction was monitored by GC analysis of the samples.

Results and discussion

Characterization of the polymer supported catalyst

Due to insolubilities of the polymer supported ruthenium catalyst in all common organic solvents, its structural investigation was limited to its physicochemical properties, chemical analysis, SEM, TGA, IR and UV–vis spectroscopic data. Table 1 provides the data of elemental analysis of polymer supported ligand and the polymer supported ruthenium catalyst. Ruthenium content in the catalyst determined by AAS suggests 8.50 wt% Ru in the catalyst.

Various frameworks bonding present in the polymer supported metal catalyst were obtained from the FT-IR spectrum (Fig. 1). The sharp C–Cl peak due to $-\text{CH}_2\text{Cl}$ group in polymer (Fig. S1, supporting information) at 1264 cm^{-1} had disappeared in the polymer anchored ligand. A new strong band appeared at 3426 cm^{-1} showed the presence of a secondary ($-\text{NH}-$) amine group in the ligand. The ($\text{C}=\text{O}$), ν_{asym} (COO) and ν_{sym} (COO) stretching vibrations are observed at 1733, 1667 and 1513 cm^{-1} for polymer anchored bidentate ligand [39] bound to the central metal ion through the carboxylic OH and the secondary amino group; ($-\text{NH}-$). The bands at 1667 and 1513 cm^{-1} , due to ν_{asym} (COO) and ν_{sym} (COO) of the amino acids, appear at 1663 and 1510 cm^{-1} in the complex. The shifting of these two bands suggests the involvement of the carboxylic group of the polymer supported ligand in the complex formation [40,41]. The participation of OH group in bonding was confirmed from the shift in the position of the C–O stretching vibration of the free ligand (1424 cm^{-1}) in the spectra of the complex. The decrease in the intensity of N–H stretching frequency of the

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