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Semi-hydrogenation of alkynes using Ru/TPPTS as a biphasic recyclable catalyst in ethylene glycol-toluene solvent system

Samadhan Ashok Jagtap, Bhalchandra Mahadeo Bhanage*

Department of Chemistry, Institute of Chemical Technology, Matunga, Mumbai, 400019, India

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ABSTRACT

The chemoselective semi-hydrogenation of alkynes into *E* and *Z*-alkenes was studied by using Ru/TPPTS as a biphasic and recyclable catalyst in ethylene glycol-toluene solvent system. Current protocol is atom efficient and gives selectivity up to 98%. This protocol is alternative to the classical Lindlar catalyst (Pd/$CaCO_3$) for Z-alkenes and also Birch reduction process (Li/Na/K in liq. NH_3) used for the synthesis of *E*-alkenes. A variety of alkynes with different functional group can be tolerated efficiently transformed into corresponding *E* and *Z* alkenes. This catalytic system has been effectively recycled up to five consecutive cycles without appreciable loss in its activity and selectivity.

1. Introduction

Chemoselective synthesis of *E* and *Z*-olefins *via* semi-hydrogenation of alkynes is one of the valuable organic transformations in synthetic organic chemistry [1]. *E* and *Z*- olefins are fundamental building blocks used in the several pharmaceutical drug moieties, flavours, natural products and biological active compounds [2]. Styrene and its derivatives are used as a raw material for the synthesis of polystyrenes, synthetic rubbers and the various organic commodities [3]. Alkenes are used in many synthetic organic reactions such as Markovnikoffs addition, epoxidation, metathesis, ozonolysis, hydroboration, hydrogenation, hydroformylation and hydroamination reactions [4]. *trans*-Stilbene is highly valuable intermediate employed in dyes, fluorescent whitener, liquid crystals and organic light-emitting diodes [5]. *Z*-alkenes are present in many biologically and pharmaceutically active compounds and are produced in numerous bulk and fine chemical processes [6].

According to literature survey, a variety of transition metal catalysts Pd [7], Rh [8], Ru [9], Cu [10], Au [11], Ni [12] and Co [13] have been reported for the semi-hydrogenation of alkynes. Lindlar catalyst (Pd/$CaCO_3$) is used as heterogeneous catalyst for *Z*-selective semi-hydrogenation of alkynes [14]. Despite the potential utility of Lindlar catalyst (Pd/$CaCO_3$) treated with $Pb(OAc)_2$ suffers from drawbacks such as use of poisonous lead (Pb) salt and use of excess quinoline to control the over-hydrogenation, which also limits its substrate scope and selectivity. The Birch-type reduction of alkynes by alkali metals (Li, Na) in liquid ammonia is conventional and powerful method for the synthesis of *E*-alkenes [15]. Birch reduction also have some limitations, as it requires the stoichiometric amount of a base and harsh reductive reaction conditions along with the use of alkali metals in liquid ammonia. This reagent was incompatible with functionalized alkynes containing base-labile or reducible moieties.

Aqueous biphasic organometallic catalysis is a greener method for the synthesis of organic chemicals [16]. The novel synthesis of sodium salt of trisulfonated triphenylphosphine (TPPTS) in 1974 helped to the development of the field of aqueous biphasic systems [17]. Ruhrchemie and Rhone-Poulenc commercialized the Rh-TPPTS based aqueous biphasic catalytic system in 1984 for the hydroformylation of propene [18]. Recently, we have reported the Rh-TPPTS catalyzed aqueous biphasic hydroformylation of biorenewable eugenol [19]. TPPTS ligand is highly robust and reusable using biphasic catalysis due to its highly solubility in water as well as it can interact with hydrophilic organic solvents like ethylene glycol [20]. We have recently reported efficient semi-hydrogenation of alkynes catalyzed by rhodium in the presence of various phosphine ligands [8(b)]. In spite of the good activity and selectivity of the catalyst used in this protocol was the homogeneous in nature and cannot be recycled. In view of these drawbacks, the development biphasic catalytic system for this reaction is highly desirable for recyclability of expensive metal catalyst.

In 2011, Hua [21] and co-workers reported ruthenium catalysed stereo-divergent transfer semi-hydrogenation using DMF and water as a hydrogen source. The use of acetic acid and trifluoroacetic acid (TFA) as additives is one of the drawbacks of this protocol. Recently, Rafał [22] et. al reported homogeneous ruthenium catalyzed olefin

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* Corresponding author.
E-mail address: bm.bhanage@ictmumbai.edu.in (B.M. Bhanage).

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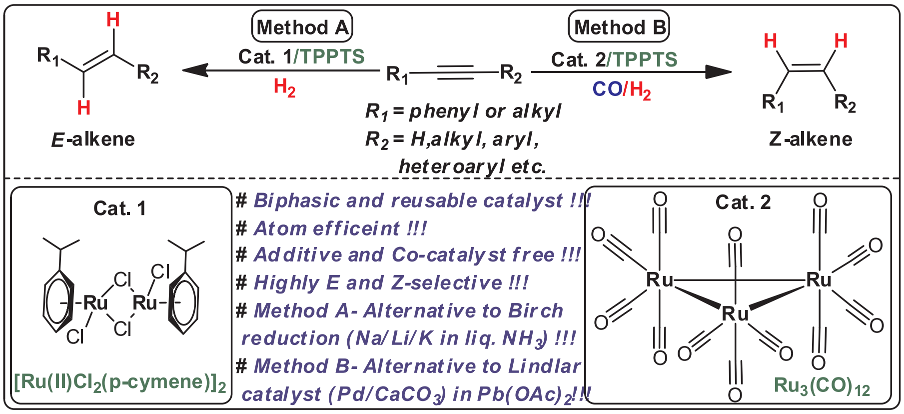

Scheme 1. *E* and *Z*- selective semi-hydrogenation of alkynes using Ru/TPPTS as a biphasic and recyclable catalyst.

metathesis for *E* and *Z* selective semi-hydrogenation of alkynes. In 2013, Niu [23] et al. described the recyclable ruthenium nanoparticles as catalysts for the semi-hydrogenation of alkynes using thermo regulated PEG as biphasic system. This catalyst works only for terminal alkynes. Considering all above these issues; highly efficient, recyclable, additive free and co-catalyst free catalytic system is highly desirable.

Herein, we report the Ru-TPPTS as a biphasic and reusable catalyst for the selective *E* and *Z* semi-hydrogenation of alkynes in ethylene glycol-toluene as a solvent system under syngas and molecular hydrogen (Scheme 1). Syngas containing carbon monoxide acts as a mild poison which inhibits the over-hydrogenation and provides selectively towards Z-alkenes as a major product by the syn addition of hydrogen [7(a)]. Selective formation of *E* product formed may be due to the steric hindrance caused by *p*-cymene ligand used in ruthenium **catalyst 1**. The developed protocol tolerates wide range of internal as well as terminal alkynes which affords the respective alkenes with 85–98% selectivity. This catalytic system was reusable up to five recycles without affecting the activity and selectivity.

2. Experimental

2.1. Materials and methods

All the experiments were performed under nitrogen atmosphere by using 100 mL stainless steel autoclave purchased from M/s Amar Equipments Pvt. Ltd, Mumbai. All the chemicals *e.g.* alkynes, [$RuCl_2$(*p*-cymene)]$_2$, [$Ru_3(CO)_{12}$] and TPPTS were purchased from Sigma Aldrich and Alfa Aesar. All other reagents and solvents (Ethylene glycol and Toluene) were purchased form Sigma Aldrich, S.D. Fine and commercial suppliers in Mumbai Area. The reagents of analytical grade were used without further purification. Syngas (CO and H_2 in the 1:1 ratio) with a purity of 99.9%, was procured from Rakhangi Gases Ltd, Mumbai, India. The progress of reaction was monitored by using PerkinElmer Clarus 400 gas chromatograph equipped with flame ionization detector using capillary column (Elite-1, 30 m × 0.32 mm × 0.25 m). GCMS-QP 2010 instrument (Rtx-17, 30 m × F5 mm ID, film thickness (*df*) = 0.25 m) was used for the mass analysis of the products. Organic compounds (products) were purified by column chromatography on silica (120–200 mesh). Nuclear magnetic resonance (NMR) spectra were taken on Bruker in $CDCl_3$ solvent (^1H, 400 MHz; ^{13}C, 100 MHz) spectrometer using tetramethylsilane (1 H) as an internal standard. Chemical shifts values are reported in parts per million (δ) relative to tetramethylsilane as an internal standard. The *J* (coupling constant) values were described in Hz. Splitting patterns of proton are denoted as *s* (singlet), *d* (doublet), *t* (triplet) and *m* (multiplet). Products were assured by the comparison of their GC, GC–MS, ^1H and ^{13}C NMR spectra with those of authentic data.

2.2. Typical experimental procedure for the synthesis of alkenes via semi-hydrogenation of alkynes

All the chemicals were added to a high pressure reaction using two different methods. For method A: alkyne (0.5 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (0.02 mmol), TPPTS (0.08 mmol), in a 10 mL biphase solvent (5 mL Toluene + 5 mL Ethylene glycol) were taken. The reactor was flushed three times with nitrogen, then pressurized with 5 bar of H_2 and heated at 80 °C with constant stirring (600 rpm) for 8 h. For method B: alkyne (0.5 mmol), $Ru_3(CO)_{12}$ (0.02 mmol), TPPTS (0.08 mmol), Solvent (5 mL Toluene + 5 mL Ethylene glycol) syngas (10 bar) were added to the reaction. After the completion of reaction, the reactor was cooled to room temperature and remaining gas vented out carefully. The obtained biphasic mixture was separated using simple decantation process. The separated organic product from biphasic solution was dried over sodium sulfate to remove moisture if present. The organic product was collected for purification and then it is subjected for further analysis such as GC, GC–MS, ^1H & ^{13}C NMR and matched with those of authentic data.

2.3. Typical experimental procedure for recycling of Ru-PPTS catalyst

In the catalyst recycling experiments, the Ru-TPPTS catalyst system was easily separated from the reaction mixture by simple phase separation as shown in Fig. 1. The biphasic solution has two phases, the upper phase of toluene containing reactant and product while lower phase of ethylene glycol contains Ru-TPPTS catalyst. The separated Ru-TPPTS catalyst in ethylene glycol was recovered and used for the next reaction cycle.

3. Results and discussion

The semi-hydrogenation of diphenylacetylene (DPA) was tested as a model reaction to estimate the feasibility of present catalytic system in toluene-ethylene glycol biphasic solvent at 80 °C for 10 h. Various reaction parameters such as loading of ruthenium catalyst, the influence of syngas and hydrogen pressure, effect of reaction time and temperature, and effect of solvent were screened. The obtained results are summarized in Tables 1–3. Various ruthenium precursors such as $Ru_3(CO)_{12}$, $RuCl_3.6H_2O$, [$RuCl_2$(*p*-cymene)]$_2$, [CpRu(COD)Cl], [Ru(COD)Cl_2], $Ru(PPh_3)_3Cl_2$, 10% Ru/C were tested as shown in Table 1. Among them $Ru_3(CO)_{12}$ and [$RuCl_2$(*p*-cymene)]$_2$ gives high conversion of **1a** with admirable selectivity towards the formation of *Z* and *E* stilbene **(2a)** respectively (Table 1, entries 2 and 4). As we increase the loading of catalyst (Ru_3CO_{12}) from 0.02 mmol to 0.03 mmol then conversion increases significantly, but the hydrogenation increases and selectivity of **2a** decreases (Table 1, entry 3). Furthermore, we studied [CpRu(COD)Cl], [Ru(COD)Cl_2] and $Ru(PPh_3)_3Cl_2$ catalyst precursors