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Short Communication

PEG-anchored rhodium polyether diphosphinite complex as an efficient homogeneous and recyclable catalyst for hydroaminomethylation of olefins

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ABSTRACT

A recyclable rhodium polyether diphosphinite complex anchored in polyethylene glycol [RhPEGD] was studied for hydroaminomethylation of various olefins with primary and secondary amines. The protocol was optimized with respect to various reaction parameters and the general applicability of catalyst for hydroaminomethylation of different functionalized olefins with corresponding amines was investigated. During the course of reaction, catalyst was soluble with reactants/products while could be quantitatively separated from reaction media in biphasic form by addition of anti-solvent on completion of reaction. The catalyst exhibited remarkable activity and was subsequently recycled up to five consecutive cycles.

1. Introduction

The hydroaminomethylation reaction has attracted a great attention for synthesis of amines finding large applications in pharmaceutical and chemical industries [1,2]. It is a tandem reaction involving hydroformylation of an olefin to an aldehyde followed by the reaction of resulting aldehyde with a primary or secondary amine to provide the corresponding enamine or imine and finally the intermediate is hydrogenated to amine (Scheme 1).

From economical and environmental point of view, one pot synthesis of amines from inexpensive feedstock like alkenes sounds to be a superior method over conventional ones which comprises of usually multi-step and less atom-efficient processes [3].

In 1949, W. Reppe discovered the hydroaminomethylation using stoichiometric amount of $Fe(CO)_5$ as a catalyst. Till mid of 1990s, relatively harsh conditions were employed to obtain good yield of corresponding amines from simple olefins with the aid of hydroaminomethylation reaction [4–7]. However in the past two decades, several other catalysts comprising of rhodium, ruthenium and bimetallic complexes were developed [8–10]. It is also noteworthy to mention that, the several other methodologies developed for hydroaminomethylation using homogeneous catalytic system suffer with the limitation of catalyst-product separation and catalyst recyclability. However, some investigations have been made in this regard and the possible outcome includes anchoring of homogeneous catalyst, either by using a liquid–liquid two phase system or by supported liquid phase catalysis [11,12]. On other hand, Alper and co-workers employed ionic diamine rhodium complex for hydroaminomethylation reaction but the system fails to recover an expensive rhodium metal catalyst on completion of the reaction [13,14]. Hence, still there lies a great scope in development of an efficient and facile metal complex catalyst with an industrially feasible separation strategy for the hydroaminomethylation reaction.

Considering the above issues, the aim of present work highlights use of liquid phase catalyst soluble in organic solvent thus retaining the merits of homogeneous systems with an additional advantage of biphasic separation strategy. On completion of reaction, the catalyst can be quantitatively separated in liquid form from the reaction mixture by addition of a volatile anti-solvent such as *n*-hexane which forms two phases and thus the liquid phase catalyst can be subsequently reused (Fig. 1). In continuation to our interest in application of biphasic separation methodology [15], we herein report a facile and highly efficient protocol for homogeneous liquid phase catalytic system for hydroaminomethylation reaction.

2. Experimental methods

2.1. Materials

All chemicals like olefins, amines, chlorodiphenylphosphine, $[Rh(acac)(CO)_2]$ and Xantphos were purchased from Sigma-Aldrich and Alfa Aesar. PEG-600 was supplied by S. D. Fine Chemicals India. All other reagents were of analytical grade and were used without further purification. Syn gas (CO and H_2, 1:1), with a purity of 99.9% was obtained from Rakhangi Gases Ltd., Mumbai, India.

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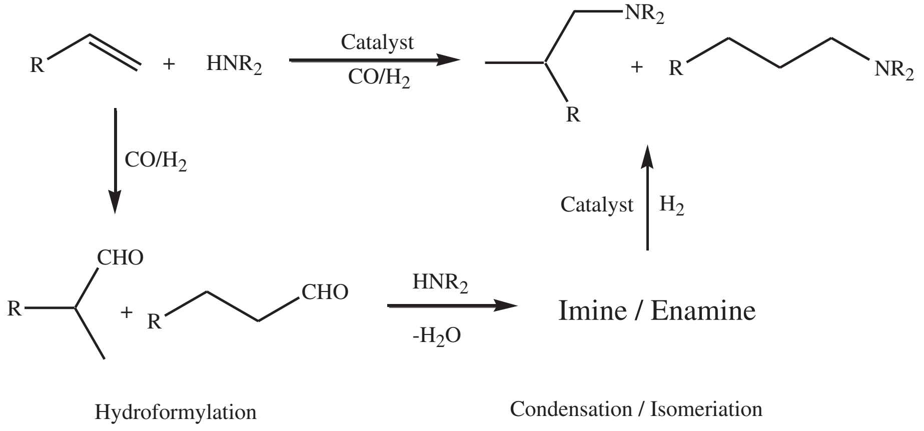

Scheme 1. Hydroaminomethylation of olefins.

2.2. General procedure for hydroaminomethylation

In a typical hydroaminomethylation procedure, to a high pressure reactor of 100 mL, olefin (2 mmol), amine (2 mmol) and toluene (10 mL) were added with polymeric RhPEGD-600 (2.5 µmol) (3.9 mg). The reactor was then flushed with nitrogen followed by syn gas (1:1 mixture of H_2 and CO gas) at room temperature; the reaction was then pressurized to 400 psi and was heated to 100 °C with stirring speed of 800 rpm. After completion of the reaction, the reactor was cooled to room temperature and remaining syn gas was carefully vented. The reaction mixture was analyzed by gas chromatography (Perkin Elmer, Clarus 400 GC) equipped with capillary column (30 m × 0.25 mm × 0.25 µm) and a flame ionization detector (FID). All the products obtained are well known in literature [8] and were confirmed by GC–MS analysis (Shimadzu, GCMSQP2010) equipped with Rtx wax capillary column (30 m length and 0.25 mm diameter).

2.3. Catalyst preparation and characterization

The polyether ligand α,ω-bis(diphenylphosphino)-poly(ethyleneglycol-200) [DPPPEG-200], α,ω-bis(diphenylphosphino)-poly(ethyleneglycol-400) [DPPPEG-400], α,ω-bis (diphenyl phosphino)-poly(ethyleneglycol-600) [DPPPEG-600], $Bu(OPPh_2)_2$ and Rh(I) carbonyl phosphinite complex [RhPEGD-600] were prepared by procedures reported in literature [15–19]. The complex $HRhCO(PPh_3)_3$ was also prepared by reported method [20,21]. ^{31}P NMR analysis of the diphosphinite ligand [DPPPEG-600] and polyether Rh metal complexes were carried out using a Varian 300 MHz instrument. Thermogravimetric analyses (TGA) of metal complex were performed using an SDT-Q600 instrument under N_2 atmosphere (refer supporting information).

2.3.1. Synthesis of α,ω-bis(diphenylphosphino)-poly(ethylene glycol) [DPPPEG-600] ligand

In an inert atmosphere, chlorodiphenylphosphine (2.3 g, 10.0 mmol) in THF (2.0 mL) was added slowly into a stirred solution of polyethylene glycol-600 (PEG-600) (5.0 mmol) and pyridine (Py) (0.8 g, 10.0 mmol) in THF (20 mL) at room temperature. The reaction mixture was stirred for 3 h at room temperature (30 °C). Precipitated Py.HCl was filtered off, and the THF solution was passed through a silica gel column to remove the dissolved Py.HCl. The ligand α,ω-bis(diphenylphosphino) poly(ethylene glycol-600) was obtained in 80% yield (4.0 g) after evaporation of THF under rotary evaporator.

^{31}P NMR (400 MHz, DMSO): δ 19.98 (s).

2.3.2. Synthesis of polyether phosphinite Rh (I) complex (RhPEGD-600)

A solution of $RhCl_3 \cdot H_2O$ (1 g, 3.8 mmol) in ethanol (30 mL) was added to a refluxing solution of polyether diphosphinite (11.4 mmol) in ethanol (150 mL). After 30 min, on dropwise addition of 40% aqueous formaldehyde (5 mL) the solution turned pale yellow. Further, addition of sodium borohydride (1 g) in ethanol to this hot mixture yielded the greenish yellow product, as described above with 70% yield.

^{31}P NMR (400 MHz, DMSO): δ 73.88 (d, $J_{(Rh,P)}$ 144 Hz).

2.4. Catalyst recyclability study

The catalyst was investigated for five consecutive recycles for hydroaminomethylation reaction using the above experimental procedure (described in Section 2.2). During recyclability study, additional PEG-600 (1 mL) was added for recovery of the catalyst. On completion of reaction, 20 mL *n*-hexane was added to the reaction mixture, which separated the lower catalyst-philic PEG phase from upper product phase. After phase separation PEG phase containing polyether Rh(I) catalyst was subjected to reuse by charging the same amount of substrate (2 mmol) in toluene as a solvent.

3. Results and discussion

The initial studies were conducted using RhPEGD-600 as a choice of catalyst for the hydroaminomethylation of cyclopentene with morpholine as a model reaction (Scheme 2).

Various reaction conditions for this transformation were extensively studied and the results obtained were summarized in Table 1. Initially, the reaction was studied at different temperatures in the

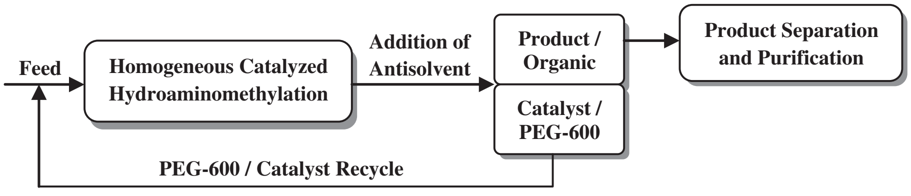

Fig. 1. Diagrammatic representation for catalyst separation and reusability.