Journal of Molecular Catalysis A: Chemical 358 (2012) 112–120

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

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

Development of an efficient solvent free one-pot Heck reaction catalyzed by novel palladium (II) complex-via green approach

Parasuraman Karthikeyan, Prashant Narayan Muskawar, Sachin Arunrao Aswar, Pundlik Rambhau Bhagat*, Suresh Kumar Sythana

Organic Chemistry Division, School of Advanced Sciences, VIT University, Vellore 632 014, India

ARTICLE INFO

Article history:
Received 19 December 2011
Received in revised form 8 February 2012
Accepted 4 March 2012
Available online 13 March 2012

Keywords:
Palladium complex
Heck reaction
Aryl halide
Alkene
Ambient temperature

ABSTRACT

A novel 1-glycyl-3-methyl imidazolium chloride–palladium (II) complex [[Gmim]Cl–Pd (II)] was found to be a heterogeneous catalyst for an efficient Heck reaction with good to excellent yield under solvent free condition. Tetra-coordinated palladium complex was prepared by reacting $PdCl_2$ with 1-glycyl-3-methyl imidazolium chloride and its catalytic function invented for the C—C bond formation. Spectroscopic evidence of complex has been proved by powder XRD, SEM, FT-IR and AFM. This protocol provides a simple strategy for the generation of a variety of new C—C bonds under environmentally benign condition.

1. Introduction

In recent years, Ionic liquids have emerged as a set of green solvent with unique properties such as tunable polarity, high thermal stability and immiscibility with a number of organic solvents, negligible vapor pressure and recyclability. Their non-volatile character and thermal stability makes the metal complexes potentially attractive alternatives to environmentally unfavorable organic co-solvents, notably chlorinated hydrocarbons. They are particularly promising as solvents for the immobilization of transition metal catalysts, Lewis acids and enzymes [1–6]. As a result of their green credential and potential to enhance reaction rate and selectivities, ionic liquids are finding increasing application in organic synthesis.

The Mizoroki–Heck synthesis is an important task due to their valuable applications in both laboratory and industry. The significance of these compounds exist in the organic synthesis, polymerization processes, UV screens, preparation of hydrocarbons and in advanced enantioselective synthesis of natural products and pharmaceutically active heterocyclic compounds [7]. In general, palladium catalysts suffer the problems concerning extraction from the reaction mixture, waste production, high toxicity and price, air-sensitivity and leaching [8]. Hence, we felt it would be keen interest to eradicate these negative aspects of palladium complex. In this regard, we have developed stable, selective, suitable ligand that leads to efficient heterogeneous palladium complex with high turnover and reprocessibility.

In last two years, Petrovi et al. was described the synthesis of N, N-diethyl ethanolamine ionic liquid in green Heck reaction [9] and Liu et al. was reported efficient palladium-catalyzed Heck reaction by the diol-functionalized imidazolium ionic liquid [10]. Furthermore, Vaultier et al. have synthesized binary task specific ionic liquid and an efficiency of palladium nano particle catalyzed Heck cross-coupling [11]. However, Salunkhe et al. was illustrated multi-functional ionic liquid for Pd (II) catalyzed Heck reaction [12]. Li et al. was exemplified the Pd-TPPTS catalyzed Mizoroki–Heck coupling in halogen-free ionic liquid [13]. Above all the methods provide good yield, but some have drawbacks such as lengthy work-up procedure, harsh reaction conditions (organic co-solvents) and require absolutely dry and inert media. Herein, we report a protocol based on palladium functionalized 1-glycyl-3-methyl imidazolium chloride (Fig. 1), which proved to be highly efficient at ambient temperature for C—C bond formation under solvent free condition.

However, recovery and leaching can occur in the extractive work up leading to a loss of the catalyst in the reaction mixture on the one hand and requests additional effort to purify the extracted product. To overcome such problems, novel complex was developed [14] by covalent linking of organo catalytic unit with an ionic liquid moiety (often chloroglycine). This imparts a low solubility of catalyst in the solvents used for extraction of the product on the one hand and high solubility in the reaction medium on the other hand [15–19].

* Corresponding author. Tel.: +91 9047289073; fax: +91 4162240411.
E-mail address: drprbhagat111@gmail.com (P.R. Bhagat).

1381-1169/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2012.03.004

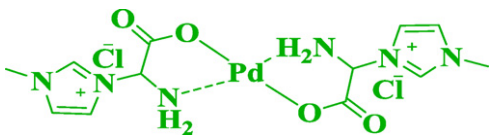

Fig. 1. 1-Glycyl-3-methyl imidazolium chloride–palladium (II) complex [Gmim]Cl–Pd (II).

This strategy was applied to Heck reaction providing high yield and good recyclability of the organocatalyst.

The objectives of the present study are to: (i) prepare tetra coordinated 1-glycyl-3-methyl imidazolium chloride–palladium (II) complex and to explore its application as catalyst, (ii) develop an efficient synthetic process for the facile conversion of Heck reaction. The present method developed for the Heck reaction offer many advantages including high conversion, short duration and the involvement of non-toxic reagents.

2. Experimental

2.1. Materials and methods

All solvents and chemicals were commercially available and used without further purification unless otherwise stated. [Gmim]Cl–Pd (II) complex was characterized by powder X-ray diffraction (P-XRD) diffractometer, a Bruker D8 (advance model); Germany and lynx eye detector operating with nickel filtered Cu-K radiation. The ^{1}H NMR spectra was record on a Bruker 500 MHz using $CDCl_3$/DMSO-d_6 as the solvent and mass spectra were recorded on JEOL GC MATE II HRMS (EI) spectrometer. FT-IR was recorded on AVATRA 330 Spectrometer with DTGS detector. Column chromatography was performed on silica gel (200–300 mesh). Analytical thin-layer chromatography (TLC) was carried out on precoated silica gel GF-254 plates. AFM and SEM was analyzed by (Nano Surf Easy Scan-2 Switzerland), (Carl Zeiss EVO MA 15(model)) respectively.

2.2. Preparation of [Gmim]Cl–Pd (II) complex

2.2.1. Protection of amino group using di. tert butyl pyrocarbonate (Boc)

A solution of the glycine (10 mmol) in a mixture of dioxane (10 mL), water (5 mL) and 0.5 N NaOH (5 mL) was stirred and cooled in an ice-water bath. Boc (8 mmol) was added and agitation continued at ambient temperature for 30–45 min. The resulting solution was concentrated in vacuo, cooled in an ice-water bath, covered with a layer of ethyl acetate (15 mL). Then, the reaction mixture was acidified to pH 2–3 using $KHSO_4$. The aqueous phase was extracted with ethyl acetate (3×10 mL). The ethyl acetate extract washed with water, dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was recrystallized using ethanol [20,21].

2.2.2. Protection of acid group using methyl ester

Boc-glycine (10 mmol) was suspended in 2, 2-di methoxypropane (DMP) (50 mL) and concentrated HCl (5 mL) was added. The mixture was allowed to stand at ambient temperature over night. The volatile reactants were removed in vacuo at 60 °C, the residue dissolved in a minimum amount of dry methanol and the solution diluted with dry ether (50 mL). The crystalline methyl ester hydrochloride was collected on a filter, washed with ether and dried in vacuo over NaOH. Recrystallization from methanol–ether (9:1 mL) affords the analytically pure ester [22].

2.2.3. Chlorination of protected glycine

In 100 mL RB, thionyl chloride (6 mmol) was added and cooled in an ice-water bath. The protected glycine (4 mmol) was dissolved in ethanol and added to RB drop wise at (0 °C) and stirred at ambient temperature for 48 h. The resulting solution was concentrated under vacuo, cooled in an ice-water bath to get the desired precipitate. Recrystallization of the product using ethanol–ether affords the analytically pure chloroglycine.

2.2.4. Removal of protecting groups

An about 33% (10 mL) solution of HBr in acetic acid is placed in a 100 mL RB flask and protected chloroglycine (4 mmol) was added with stirring. The flask was closed with a cotton filled drying tube and swirled to effect complete dissolution of the protected chloroglycine. The deprotection occurred with evolution of CO_2 and heat. When the gas evolution ceases, dry ether (50 mL) was added with swirling and the reaction mixture was stored in an ice-bath. The precipitated chloroglycine ester was collected on a filter, washed with ether and dried over NaOH in vacuo.

Furthermore, a solution chloroglycine ester (4 mmol) in methanol (10 mL) was surrounded by water bath at ambient temperature and NaOH (20 mL) was added with stirring. The mixture was stored at ambient temperature for overnight. Dilute HCl (10 mL) was added and methanol removed in vacuo. The aqueous solution was cooled in ice-water for 2 h. Chloroglycine was collected on a filter, washed with ether and dried in air [23–25].

2.2.5. Synthesis of 1-glycyl-3-methyl imidazolium chloride [Gmim]Cl

First, chloroglycine (0.01 mol) reacted with N-methylimidazole (0.11 mol) in 50 mL acetonitrile at 70 °C for 24 h to generate chloroglycine ligand modified by imidazole salt (3-(amino(carboxy)methyl)-1-methyl-1H-imidazol-3-ium chloride) [Gmim]Cl. The solvent (acetonitrile) was removed under reduced pressure at 80 °C (water bath temperature). Then the residue was mixed with 50 mL water and extracted with ethyl acetate (3×5 mL). Further, the water phase was evaporated under reduced pressure at 80 °C until the mass of the residue did not change. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.2 (s, 1H), 3.3 (s, 3H), 5.0 (s, 2H), 6.92 (d, 1H), 7.0 (d, 1H), 7.6 (s, 1H), 9.1 (s, 1H). HRMS (EI): $C_6H_{10}ClN_3O_2$ (found: 191.10), cal (191.05). FT-IR (KBr, cm^{-1}): 3429, 3372, 2933, 2855, 1628, 1526 and 1382.

2.2.6. Synthesis of 1-glycyl-3-methyl imidazolium chloride–palladium (II) complex [Gmim]Cl–Pd (II)

In RB, [Gmim]Cl (0.02 mmol) was stirred with $PdCl_2$ (0.01 mol) in 100 mL methanol at 50 °C for 12 h to deliver the [Gmim]Cl modified by palladium complex [Gmim]Cl–Pd (II). The solvent (methanol) was removed under reduced pressure at 80 °C (water bath temperature). Finally, white [Gmim]Cl–Pd (II) complex was obtained with 95% [26].

2.3. Procedure for Heck reaction

In a conical flask (50 mL), a mixture of 1-bromo-4-methoxybenzene (1 mmol), styrene (1.2 mmol), triethylamine (1 mmol) and [Gmim]Cl–Pd (II) (0.1 mmol) was added and stirred at ambient temperature for a period as indicated in Tables 5 and 6 (The reaction was monitored by HPLC and TLC). The resulting heterogeneous mixture was extracted with ethyl acetate or diethyl ether (3×5 mL). The organic phase was separated and dried over anhydrous Na_2SO_4 and evaporated. The resulting crude was purified by flash chromatography to give the desired pure product with excellent yield.