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Highly efficient recyclable heterogeneous palladium catalyst for C–C coupling, amination and cyanation reactions

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ABSTRACT

An inexpensive, air–moisture stable and reusable PS–Pd(II)–anthra complex was synthesized by reacting chloro-methylated polystyrene with anthranilic acid to get polymer anchored ligand which was then reacted with $PdCl_2$ to get polymer anchored complex. This complex was characterized by different spectroscopic and elemental analyses. The activity of the Pd-complex as catalyst was tested for the Suzuki, Heck, Sonogashira cross-coupling and also for amination and cyanation reactions under various conditions. The catalyst exhibits high catalytic activities for the coupling of various aryl halides with organoboronic acid, alkene, alkyne and amine along with the cyanation of aryl halides providing excellent yields of desired product. Further, the catalyst can be easily recovered quantitatively by simple filtration and reused up to five times without sufficient loss of its catalytic activity.

1. Introduction

Transition metal-catalyzed carbon–carbon and carbon–nitrogen coupling reactions are probably among the most frequently employed methods of C–C and C–N bond formation in organic synthesis [1–6]. They have been applied to the synthesis of many organic compounds, especially those of complex natural products, supramolecular chemistry, and engineering materials such as conducting polymers, molecular wires, and liquid crystals [7–10]. With various metals being employed in coupling reactions, palladium probably is the most versatile metal in promoting or catalyzing reactions involving C–C and C–N bond formation due to its excellent catalytic efficiency in this type of reactions [11–14]. In recent years, various homogeneous palladium–phosphine catalysts [15–18] have been developed for the efficient cross-coupling reactions. However, these catalysts usually need to be handled under inert atmosphere or dry conditions. In addition, they sometimes suffer from significant P–C bond degradation at elevated temperatures, which leads to palladium aggregation and eventually affects the overall catalytic performance. Supported metal complexes continuously attract the interest of a growing part of the scientific community for the advantages that they offer with respect to their soluble counterpart. The use of heterogeneous catalysts in organic synthesis has now become a common practice [19–22], especially following the rapid development of combinatorial chemistry. Solid-supported palladium complexes having high activity and selectivity, offer several significant practical advantages in synthetic and industrial chemistry; among those, the ease of separation of the catalyst from the desired reaction products and the ease of recovery and re-use of the catalyst are most important. A large number of materials have been used to support, including activated carbon, silica gel, polymers containing covalently bound ligands, metal oxides, porous aluminosilicates, clays and other inorganic materials, and microporous and mesoporous supports [23–29].

Polystyrene is one of the most widely studied heterogeneous supports due to its environmental stability and good catalytic activity. Polymer-supported palladium catalysts derived from chloro-methyl polystyrene resin have been employed in various coupling reactions [30–38], and have shown lower leaching of palladium during cross-coupling. Suzuka et al. have reported PS–PEG resin-bound palladium complex for Sonogashira reaction [39]. Linear polystyrene-supported Pd nanoparticle was developed by Ohtaka et al. for the Suzuki–Miyaura cross-coupling reaction in water medium [40]. These results encouraged us to investigate the anthranilic acid-functionalized polystyrene resin-supported Pd(II) complex, PS–Pd(II)–anthra, for the coupling and cyanation reactions. We have already reported the use of an

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polystyrene anchored Pd(II) complexes as an air-stable, active, and reusable catalyst in C–C coupling reactions [41–43].

In the present work, we have prepared heterogeneous Pd(II) catalyst on polystyrene and used it in the Suzuki, Heck, Sonogashira, amination and cyanation reactions of aryl halides in the presence of inorganic or organic bases. The catalyst was characterized by various physicochemical and spectroscopic techniques. The effects of the various reaction parameters on the catalytic activity were studied. The key features of the catalyst include rapid reactions with excellent conversion without the use of phosphine ligands and total stability under the reaction conditions. Further this polymer-supported catalyst demonstrated outstanding reusability for these reactions.

2. Experimental

All the reagents were analytical grade and used as such without further purification. Solvents were purified and dried according to standard procedures. Chloro-methylated polystyrene was purchased from Aldrich and $PdCl_2$ was procured from Arora Matthey. Other reagents were purchased from Merck.

The palladium content was determined by Varian, USA, AA240 atomic absorption spectrophotometer (AAS). A Perkin–Elmer, USA, 2400C elemental analyzer was used to collect microanalytical data (C, H and N). Surface morphology of functionalized polystyrene ligand and metal complex were analyzed using a scanning electron microscope (ZEISS EVO40, England) equipped with EDX facility. Fourier transform infrared (FTIR) spectra for the catalyst and its precursors were recorded on a Perkin–Elmer, USA, FTIR 783 spectrophotometer using KBr pellets. UV–vis spectrum was taken using a Shimadzu, Japan, UV-2401PC double beam spectrophotometer having an integrating sphere attachment for solid samples. The thermal stability of the immobilized catalyst was determined using a Mettler Toledo, Switzerland, TGA/DTA 851e instrument. The reaction products were analyzed using a Varian, USA, 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a flame ionization detector. All reaction products were identified by using an Agilent, USA, GC–MS (QP-5050) equipped with a 30 m HP-5ms capillary column.

2.1. General experimental procedure for Suzuki coupling reaction

A mixture of aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), DMF (6 mL), n-dodecane (15–20 mg) as an internal GC standard and 0.5 mol% of catalyst was stirred at 70 °C in air. Progress of the reaction was monitored by withdrawing the reaction mixtures periodically and analyzed by GC/GC–MS. GC yields were based on the amount of aryl halide employed. At the end of the reaction, the catalyst was separated by simple filtration. Filtrate was dried over Na_2SO_4, filtered, concentrated and the residue was purified by flash column chromatography on silica gel. The product was analyzed by GC–MS. All the prepared compounds are known and compared with authentic sample.

2.2. General experimental procedure for Heck reaction

A mixture of aryl halide (1.0 mmol), styrene (2.0 mmol), K_2CO_3 (2.0 mmol), DMF (6 mL) n-dodecane (15–20 mg) and 0.5 mol% of catalyst was stirred at 90 °C under air. To study the progress of the reaction, the reaction mixtures were collected at different time interval and quantified by GC analysis. At the end of the reaction, the catalyst was separated by simple filtration. Filtrate was dried over Na_2SO_4, filtered, concentrated and the residue was purified by flash column chromatography on silica gel. The product was analyzed by GC–MS. All the prepared compounds are known and compared with authentic sample.

2.3. General experimental procedure for Sonogashira reaction

A round-bottomed flask was charged with aryl iodide (1.0 mmol), phenylacetylene (1.5 mmol), catalyst (1.0 mol% Pd), triethylamine (2.0 mmol) and DMF (6 mL) and n-dodecane (15–20 mg) as an internal GC standard. The resulting mixture was stirred at the appropriate temperature (90 °C). The reaction mixtures were withdrawn periodically and analyzed by GC/GC–MS. GC yields are based on the amount of aryl halide employed. Upon completion of the reaction, the reaction mixture was cooled and filtered to remove the catalyst which could be used for further reaction. The filtrate obtained was purified by flash column chromatography on silica gel to afford the desired product, which was confirmed by GC–MS. All the prepared compounds are known and compared with authentic sample.

2.4. General experimental procedure for amination reaction

A mixture of aryl halide (1.0 mmol), amine (1.0 mmol), KO^tBu (1.5 mmol), toluene (6 mL) n-dodecane (15–20 mg) and 1.0 mol% Pd of catalyst was stirred at 120 °C under nitrogen atmosphere. To study the progress of the reaction, the reaction mixtures were collected at different time interval and quantified by GC analysis. At the end of the reaction, the catalyst was separated by simple filtration. Filtrate was dried over Na_2SO_4, filtered, concentrated and the residue was purified by flash column chromatography on silica gel. The product was analyzed by GC–MS. All the prepared compounds are known and compared with authentic sample.

2.5. General experimental procedure for cyanation reaction

A mixture of $K_4Fe(CN)_6$ (1.0 mmol), aryl halides (1.5 mmol), catalyst (1.0 mol% Pd), triethylamine (2.0 mmol) and DMF (6 mL) was stirred for 24 h under air at 100 °C. The progress of reaction was monitored by gas chromatography. After completion, the reaction mixture was cooled and filtered to remove the catalyst which could be used for further reaction. The filtrate obtained was purified by flash column chromatography on silica gel to afford the desired product, which was confirmed by GC–MS. All the prepared compounds are known and compared with authentic sample.

2.6. Synthesis of catalyst

The synthetic procedure of polymer anchored palladium complex is illustrated in Scheme 1. The complex was prepared according to the literature procedure [44]. Firstly, the chloromethylated polystyrene (**1**) (1 g) was reacted with anthranilic acid (500 mg) in DMF (10 mL) under reflux condition for 36 h to afford polymer anchored ligand (**2**). This polymer anchored anthranilic acid ligand (1 g) subsequently reacted with palladium chloride (0.1 g) in methanol (10 mL) at 80 °C for 10 h to generate the corresponding polymer anchored Pd(II) complex (**3**).

3. Results and discussions

3.1. Characterization of the PS–Pd(II)–anthra complex

Due to insolubility of the polymer anchored Pd(II) complex in all common organic solvents, its structural investigations were limited only to its physicochemical properties, SEM–EDX, TGA–DTA, IR and UV–vis spectral data. The complete incorporation of the organic substructure in the material was confirmed by elemental analysis.