



A simple, efficient and recyclable phosphine-free catalytic system for Suzuki–Miyaura reaction of aryl bromides

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ABSTRACT

The Suzuki–Miyaura reaction of aryl bromides using 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium(II) complex [MCM-41-2N-Pd(II)] as an efficient heterogeneous catalyst is described. Developed catalytic system is found to be effective for the Suzuki–Miyaura reaction of aryl bromides with arylboronic acids providing good to excellent yield of the desired products. This heterogeneous palladium catalyst can be reused at least 10 times without any decrease in activity. Our system not only avoids the use of phosphine ligands, but also solves the basic problem of palladium catalyst recovery and reuse.

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1. Introduction

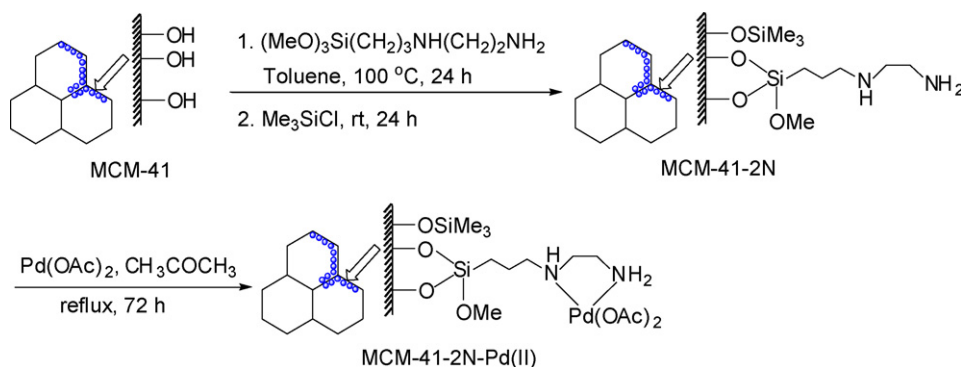
The importance of biaryl units as molecular components in pharmaceuticals, herbicides and natural products, as well as in engineering materials such as conducting polymers, molecular wires and liquid crystals, has attracted enormous interest [1,2]. The Suzuki reaction is proving to be increasingly popular method for the construction of unsymmetrical biaryl compounds as it represents an attractive alternative over other methods using organometallics because organoboranes are air- and moisture-stable with relatively low toxicity [3,4]. However, catalysts used in the Suzuki reaction have been traditionally based on homogeneous palladium complexes such as Pd(PPh₃)₄, Pd(PPh₃)₂Cl₂, which are rarely recoverable without elaborate and wasteful procedures that are commercially unacceptable [5]. In contrast, heterogeneous catalysts can be easily separated from the reaction mixture by simple filtration and reused in successive reactions provided that the active sites have not become deactivated. Heterogeneous catalysis also helps to minimize wastes derived from reaction workup, contributing to the development of green chemical processes [6–9]. From the standpoint of environmentally benign organic synthesis, development of immobilized palladium catalysts is challenging and important [10–12]. In an ideal system, they can be recovered from the reaction mixture by simple filtration and re-used infinitely, and

contamination of products by palladium is prevented. Despite the general use of the Suzuki reaction in organic synthesis, polymer-supported palladium catalysts have not been widely used for this reaction yet [13–19]. Study of new types of polymer-supported palladium catalysts which might be suitable for the Suzuki reaction has theoretical and practical significance. In the past, some of these studies have been related to polymer-supported phosphine palladium catalysts [13–16]. It is known that the catalysts containing phosphine ligands at higher temperatures are unstable [20–22]. Furthermore, the procedure for preparing the polymer-supported phosphine palladium complexes is rather complicated since the synthesis of the phosphine ligands requires multi-step sequences. Therefore, the development of phosphine-free heterogeneous palladium catalysts having a high activity and good stability is a topic of enormous importance.

Our approach was guided by three imperatives: the polymeric ligand should be easily accessible (1), starting from readily available and cheap reagents (2). The polymeric palladium catalyst should be air stable at room temperature, which should allow its storage in normal bottles with unlimited shelf life (3). Developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts [23]. MCM-41 has a regular pore diameter of ca. 5 nm and a specific surface area >700 m² g⁻¹ [24]. Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach to the surface of the channel [25–27]. It is generally believed that high surface area of heterogeneous catalyst results in high catalytic activity. Very recently, Yang

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Scheme 1. Preparation of the MCM-41-2N-Pd(II).

et al. have reported that palladium–guanidine complex immobilized on mesoporous materials [28,29] and *N*-heterocyclic carbene palladium complex supported on ionic liquid-modified SBA-16 [30] are highly active and recyclable catalysts for the Suzuki coupling. Considering the fact that the MCM-41 support has an extremely high surface area and the catalytic palladium species is anchored on the inner surface of the mesopore of MCM-41 support, we expect that MCM-41-supported palladium catalyst will exhibit high activity and good reusability. To date, a few palladium complexes on functionalized MCM-41 support have been prepared and used in organic reactions [31–34]. In continuing our efforts to develop greener synthetic pathways for organic transformations, our new approach, described in this paper, was to design and synthesize a new 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium(II) complex, which was used as an effective palladium catalyst for the Suzuki–Miyaura reaction of aryl bromides with arylboronic acids.

2. Experimental

All chemicals were reagent grade and used as purchased. The mesoporous material MCM-41 was prepared according to a literature procedure [35]. All reactions were performed under an inert atmosphere of dry argon using distilled dried solvents. All coupling products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were determined on a Perkin-Elmer 683 instrument. ^1H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard in CDCl_3 as solvent. ^{13}C NMR spectra were recorded on a Bruker AC-P400 (100 MHz) spectrometer in CDCl_3 as solvent. Palladium content was determined with inductively coupled plasma atom emission AtomsScan16 (ICP-AES, TJA Corporation). X-ray powder diffraction patterns were obtained on Damx-rA (Rigaku). X-ray photoelectron spectra were recorded on XSAM 800 (Kratos).

2.1. Preparation of MCM-41-2N

A solution of 1.54 g of 3-(2-aminoethylamino)propyltrimethoxysilane in 18 ml of dry chloroform was added to a suspension of 2.2 g of the MCM-41 in 180 ml of dry toluene. The mixture was stirred for 24 h at 100 °C. Then the solid was filtered and washed by CHCl_3 (2×20 ml), and dried in vacuum at 160 °C for 5 h. The dried white solid was then soaked in a solution of 3.1 g of Me_3SiCl in 100 ml of dry toluene at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone (3×20 ml) and diethyl ether (3×20 ml), and dried in vacuum at 120 °C for 5 h to obtain 3.49 g of hybrid material MCM-41-2N. The nitrogen content was found to be 1.84 mmol/g by elemental analysis.

2.2. Preparation of MCM-41-2N-Pd(II)

In a small Schlenk tube, 2.03 g of the above-functionalized MCM-41 (MCM-41-2N) was mixed with 0.137 g (0.61 mmol) of $\text{Pd}(\text{OAc})_2$ in 50 ml of dry acetone. The mixture was refluxed for 72 h under an argon atmosphere. The solid product was filtered by suction, washed with acetone, distilled water and acetone successively and dried at 70 °C/26.7 Pa under Ar for 5 h to give 2.12 g of a yellow palladium complex [MCM-41-2N-Pd(II)]. The nitrogen and palladium content was found to be 1.68 mmol/g and 0.27 mmol/g, respectively.

2.3. General procedure for Suzuki reaction of aryl bromides with arylboronic acids

A mixture of aryl bromide (1.0 mmol), arylboronic acid (1.5 mmol), potassium carbonate (2.0 mmol), xylene (3 ml) and the MCM-41-2N-Pd(II) complex (7 mg, 0.002 mmol of Pd) was stirred under Ar in an oil bath at 90 °C for 2–10 h. The mixture was cooled and filtered. The MCM-41-2N-Pd(II) complex was washed with distilled water (2×10 ml), dioxane (2×10 ml) and Et_2O (2×10 ml) and reused in the next run. The filtrate was poured into a saturated aqueous NaCl solution (50 ml) and extracted with methylene chloride (2×50 ml). The extracts were washed with water (3×30 ml) and dried over MgSO_4 . After removal of the solvent, the residue was purified by column chromatography on silica gel.

3. Results and discussion

Although the phosphine ligands stabilize palladium and influence its reactivity, the simplest and cheapest palladium catalysts are of course the phosphine-free systems, specifically when used in low loading. A novel 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium(II) complex [MCM-41-2N-Pd(II)] was very conveniently synthesized from commercially available and cheap 3-(2-aminoethylamino)propyltrimethoxysilane via immobilization on MCM-41, followed by reacting with palladium acetate (Scheme 1). X-ray powder diffraction (XRD) patterns of the parent MCM-41 and the modified material MCM-41-2N-Pd(II) are displayed in Fig. 1. Small angle X-ray powder diffraction of the parent MCM-41 gave the peaks corresponding to hexagonally ordered mesoporous phases. For MCM-41-2N-Pd(II), the (1 0 0) reflection of the parent MCM-41 with decreased intensity was remained after functionalization, while the (1 1 0) and (2 0 0) reflections became weak and diffuse, which could be due to contrast matching between the silicate framework and organic moieties which are located inside the channels of MCM-41. These results indicated that the basic structure of the parent MCM-41 was not damaged in the whole process of catalyst preparation.

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