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Magnetic nanoparticle-supported Pd(II)-cryptand 22 complex: An efficient and reusable heterogeneous precatalyst in the Suzuki–Miyaura coupling and the formation of aryl–sulfur bonds

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In honor and memory of late Prof. Mathias Mertes

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ABSTRACT

In the present work, silica-coated magnetic nanoparticles [Fe_3O_4@SiO_2@C22–Pd(II)] were prepared and characterized by transmission electron microscopy, Fourier transform infrared spectroscopy, vibrating sample magnetometer, energy dispersive X-ray analysis, X-ray photoelectron spectroscopy, elemental analysis, inductively coupled plasma, thermogravimetric and differential thermal analysis. This heterogeneous catalyst is utilized as an effective catalyst for the Suzuki–Miyaura coupling of arylboronic acids and aryl halides, and the cross-coupling reaction of aryl halides and thiols. The catalyst was easily separated by magnetic decantation and the recovered catalyst was reused for five cycles without any significant loss of the catalytic activity.

1. Introduction

Transition metals catalyzed cross-coupling reactions for the construction of C_{aryl}–C_{aryl} and C_{aryl}–S bonds are among the most powerful organometallic transformations employed in organic synthesis for the preparation of various compounds that are of pharmaceutical, biological and material interest [1]. Among these, the coupling of aryl halides with aryl boronic acids (Suzuki–Miyaura coupling) or thiols represents the most successful method for the preparation of biaryls and aryl sulfides, respectively. Although some general methods are available for C_{aryl}–C_{aryl} bond formation, palladium-catalyzed Suzuki–Miyaura cross-coupling of boronic acids or esters with organic halides has proven to be one of the most common routes to form biaryl units which constitute an important class of compounds for pharmaceutical, materials and agricultural chemistry [2]. Besides the mild reaction conditions associated with this method, some of the key assets for this preference are the commercial availability of diverse boronic acids as well as their air and water stability, non-toxicity and the easy handling and removal of boron-containing by-products when compared to other organometallic reactants. One of their most significant drawbacks is the presence of homogeneous palladium species on the final product, and the high cost and difficultly of preparing and handling ligands, such as carbenes or phosphanes, and additives, such as organic ammonium salts. In fact, different heterogeneous systems have been proposed to overcome the first drawback [3]. However, many of them use different grafted-ligands to anchor the palladium atoms, maintaining the second drawback. Transition-metal catalyzed formation of C_{aryl}–sulfur bond has received much attention because aryl sulfides and their derivatives are of great significance to the pharmaceutical industry [4]. Conservative methods used in the formation of C_{aryl}–S bonds often require severe reaction conditions, such as strong bases, polar solvents, such as HMPA and high temperature around 200 °C [5]. Compared to C—C bond formation, C—S bond formation reaction is less studied because of the chances of thiols to undergo oxidative coupling to disulfides along with the possibility of the organosulfur compound to bind with the metal, leading to the catalyst deactivation [6]. Various transition-metals, including Cu [7], Ni [8], Pd [6], Fe [9], Co [10], In [11], and Zn [12] have been used to catalyze cross-coupling reactions of aryl halides with arenethiols or alkanethiols for the formation of carbon–sulfur bonds.

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Although significant developments have been achieved in the area of C_{aryl}–S coupling reactions, still there are some limitations. For example, some palladium-catalyzed couplings use environmentally unfriendly and air-sensitive organophosphane ligands; other synthetic protocols have common problems, such as metal toxicity, low turnover numbers, excess reagents, nonrecyclability of catalysts, high catalyst loading and reaction temperatures. Due to the inherent properties of silica-coated magnetic nanoparticles (Fe_3O_4@SiO_2), such as biocompatibility, easy renewability and recovery by magnetic separation, thermal stability against degradation, large surface area, low toxicity and higher loading of the active sites, these magnetic particles have emerged as a useful group of heterogeneous catalysts [13].

The design and/or utilization of organic ligands with carefully-placed binding sites offers enormous potential for the fabrication of complexes with novel architectures. In this regard, the macrocycles, such as crown ethers are of a high interest on account of the complexation and the chelation with their inner molecular cavities. Although cyclic crown ethers have the significant property of forming stable complexes with metal ions, they are only seldom employed as ligands for the construction of heterogeneous catalysts. In comparison to oxygen-donor crown ethers, azacrown ether analogues show a superior tendency to form a complex with metal ions. The origin of this higher tendency and stability is discussed in terms of ligand structural features (topology and binding sites). In others words, the stronger σ-donation of the nitrogen atoms favors both the oxidative addition step and the slow reductive elimination step in the catalytic cycle; also, ligands of the N,N-type show superior properties as compared to P,P-type ligands in terms of both the palladium complexation and the catalysis of cross-coupling reactions [14].

Very recently, as part of our attempts to identify a robust and easily prepared system to catalyze carbon–carbon and carbon–heteroatom bond-forming reaction of terminal alkynes, we demonstrated that the complexes of Pd(II) and Cu(I) with the commercially available diazacrown ether, 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (Kryptofix® 22 or cryptand-22) operate as an active homogeneous catalyst under aerobic conditions [15]. We thought that the flexible macrocyclic and chelating effect of N-and O-containing ligand may assist in stabilizing the reactive palladium and copper intermediates. In an effort to find an efficient catalyst for C_{aryl}–C_{aryl} and C_{aryl}–S coupling reactions, herein, we have introduced a new heterogeneous, recyclable, heat- and air-stable silica-coated magnetic nanoparticle (MNP)-supported palladium(II)-cryptand 22 complex [Fe_3O_4@SiO_2@ C22–Pd(II)] (4) catalyst (Scheme 1), as a highly efficient catalytic system for performing the Suzuki–Miyaura reaction and *S*-arylation of thiols.

2. Experimental

2.1. General

All chemicals were purchased from Merck, Aldrich and Fluka Chemical Companies. Melting points were determined on a Büchi melting point B-540 apparatus. Fourier transform infrared (FT-IR) spectra were recorded on an ABB Bomem Model FTLA 2000 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded at 300 (^1H) and 75.4 (^{13}C) MHz, on a commercial Bruker DMX-300 instrument using $CDCl_3$ as solvent. Thermogravimetric and differential thermal analyses (TG-DTA) were carried out, using a thermal gravimetric analysis instrument (NETZSCH STA 409 PC/PG). The energy dispersive X-ray analysis (EDX) for the elements' valuation was performed using an environmental scanning electron microscope Philips XL30 analyzer. The transmission electron microscope, TEM (Philips CM-10) was also used to obtain TEM images. The magnetic measurement of samples was carried out in a vibrating sample magnetometer (VSM) (4 in., Daghigh Meghnatis Kashan Co., Kashan, Iran) at room temperature. The X-ray photoelectron spectroscopy (XPS) data were recorded with 8025-BesTec twin anode XR3E2 X-ray source system. The inductively coupled plasma (ICP) analyses were carried out on a Varian Vista-MPX instrument. The CHN analysis was performed on a PerkinElmer 2004 (II) analyzer.

2.2. Preparation of Fe_3O_4 NPs

The synthesis of Fe_3O_4 was accomplished, using the reported procedure [13][13d]. In a typical preparation procedure, ferric chloride hexahydrate $FeCl_3{\cdot}6H_2O$ (11.0 g, 40.7 mmol) and ferrous chloride tetrahydrate $FeCl_2{\cdot}4H_2O$ (4.0 g, 20.1 mmol) were dissolved in deionized water (250 mL) under N_2 atmosphere with a mechanical stirrer at 85 °C. The pH value of the solution was adjusted to 9–11, using aqueous NH_3 (25%). After continuous stirring for 4 h, the magnetite precipitates were washed with distilled water until the pH value was descended to 7.0. The black precipitate (Fe_3O_4) was collected with a permanent magnet at the bottom of the reaction flask (Scheme 1a).

2.3. Preparation of Fe_3O_4@SiO_2 (**1**)

The preparation procedure involved a synthetic strategy based on the hydrolysis and the condensation of tetraethoxysilane (TEOS) on the surface of the prepared Fe_3O_4 magnetic nanoparticles. These silica coated core–shell magnetic nanoparticles (Fe_3O_4@SiO_2 MNPs) were prepared by an ultrasonic premixture of a dispersion of the above black precipitate (2.0 g) with ethanol (400 mL) for approximately 30 min at room temperature. Then, NH_3 (25%, 12 mL) and TEOS (4.0 mL) were slowly added successively. The resulting solution was mechanically stirred continuously for 24 h. Then, the dark brown precipitate, Fe_3O_4@SiO_2, (1), was collected by magnetic separation, washed with ethanol (3 × 15 mL), and dried under vacuum overnight at room temperature (Scheme 1a).

2.4. Preparation of Fe_3O_4@SiO_2@C22–Pd(II) (**4**)

A solution of Kryptofix® 22 or cryptand-22 (C22, 0.262 g, 1 mmol) and triethylamine (0.202 g, 2 mmol) in dry CH_2Cl_2 (10 mL) was treated with 3-(chloropropyl)-trimethoxysilane (CPTMS, 0.496 g, 2.5 mmol) and stirred, under N_2 atmosphere, at 25 °C for 24 h to obtain 2 (Scheme 1b). Then, the solution of dispersed $PdCl_2$ (0.195 g, 1.1 mmol) in anhydrous THF (5 mL) was added and the mixture was heated at reflux for 45 min to give $[(MeO)_3Si–Pr]_2$–C22–Pd(II) complex 3 (Scheme 1b). Subsequently, this product (3) was treated with silica-coated MNPs 1 (1 g) in refluxing THF for 24 h. The resulting mixture was separated by an external magnet, washed several times with THF, and dried under vacuum at room temperature overnight to give the final product (4, Scheme 1b).

2.5. General procedure for the Suzuki–Miyaura coupling reaction

Aryl halide (1 mmol), arylboronic acid (1.2 mmol), Et_3N (1.2 mmol), and the supported palladium catalyst (Fe_3O_4@SiO_2@C22–Pd(II), 0.5 mol%) were mixed in DMF/H_2O (1:1) (1 mL). The mixture was shaken at 75 °C in air atmosphere for an appropriate time. The progress of the reaction was monitored by thin-layer chromatography (TLC, silica gel), using *n*-hexane as eluent. After the completion and magnetic separation of the catalyst, the reaction mixture was treated with ethyl acetate