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A phosphine-free, atom-efficient cross-coupling of aryl iodides with triarylindiums or trialkynylindiums catalyzed by immobilization of palladium(0) in MCM-41

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The first phosphine-free heterogeneous atom-efficient cross-coupling reaction of aryl iodides with triarylindiums or trialkynylindiums was achieved in THF at 68 °C by using 1 mol% of MCM-41-immobilized palladium(0)-Schiff base complex [MCM-41-N,N-Pd(0)] as catalyst, yielding a variety of unsymmetrical biaryls and arylalkynes in good to excellent yields. The heterogeneous palladium(0) catalyst could easily be prepared via a simple procedure from commercially readily available reagents, and recovered by filtration of the reaction solution and recycled at least 10 times without significant loss of activity.

1. Introduction

Biaryl compounds are widely used as chiral phosphine ligands [1], monomers of functional polymers [2–4], and as important building blocks for a large number of natural products, agrochemicals, and pharmaceutics [5–9]. Among many methods for construction of biaryl structures [10], the palladium-catalyzed cross-coupling reaction of organometallic reagents with aryl halides or triflates such as the Suzuki-Miyaura [11–13], Stille [14–16], and Hiyama [17–19] coupling reactions is one of the most important synthetic tools for the construction of unsymmetrical biaryls. Although various organometallic compounds such as organoboron, -tin, -silicon, -magnesium, and -zinc reagents have been successfully used for these cross-coupling reactions, the development of novel transition-metal-catalyzed cross-coupling reactions with high degrees of conversion of the organometallic species and high chemoselectivity is still of great interest. In addition, the minimization of byproduct formation [20] and the choice of processes with little or no risk associated to humans or the environment are major contemporary concerns in the chemistry community [21,22]. Organoindium compounds are potentially useful candidates for environmentally benign reagents since both indium metal and its derivatives are known to be less toxic or even nontoxic [23,24]. Besides, the byproduct generated after the reaction of organoindium compounds, normally indium(III) halides, are also nontoxic. Triorganoindiums (R_3In) can be easily prepared as solutions in THF by reaction of $InCl_3$ with readily available organolithium or Grignard reagents [25,26]. Importantly, triorganoindium compounds, unlike organoboron, organotin, and other organometallic compounds, can react with three equivalents of an electrophilic reagent [27,28]. Recently, palladium-catalyzed cross-coupling reaction [29–33] and carbonylative cross-coupling reaction [34,35] of triorganoindium compounds with a variety of organic electrophiles for C–C bond formation have been reported. Among the limited successful examples for the construction of C–C bonds, homogeneous palladium complexes such as $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, and $Pd(dppf)Cl_2$ are usually used as catalysts for these cross-coupling reactions. However, the problem with homogeneous catalysis is the difficulty to separate the expensive palladium catalyst from the reaction mixture and the impossibility to reuse it in consecutive reactions. In addition, homogeneous catalysis might result in unacceptable heavy metal contamination of the desired isolated product due to the leaching of the metal. These problems may have

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a very serious negative impact on their possible industrial applications, especially the pharmaceutical industry. In contrast, heterogeneous catalysts can be easily separated from the reaction mixture by a simple filtration of the reaction solution and reused in successive reactions provided that the active sites have not become deactivated. Heterogeneous catalysis also helps to reduce wastes derived from reaction workup, contributing to the development of green and sustainable chemical processes [36,37]. Therefore, from the viewpoints of economical and environmental concern, the development of recyclable immobilized palladium catalysts showing a high catalytic activity without leaching is highly desirable. So far, supported palladium catalysts have successfully been used for the Heck coupling, the Suzuki-Miyaura coupling, the Sonogashira coupling, the Hiyama coupling, and the Stille coupling, etc [38–41]. In spite of the significant advances in this area, to the best of our knowledge, no example of a heterogeneous palladium-catalyzed cross-coupling reaction of triorganoindiums with organic electrophiles has been described until now. The discovery of mesoporous MCM-41 materials has provided a new possible candidate for an ideal solid support to immobilize homogeneous catalysts and given an enormous stimulus to research in heterogeneous metal catalysis [42–44]. The hexagonally ordered MCM-41 material possesses large and uniform pore size, ultrahigh surface area, big pore volume and rich silanol groups in the inner walls [45]. To date, some functionalized MCM-41-supported palladium [46–49], rhodium [50], molybdenum [51,52], gold [53–55] and copper [56,57] complexes have been successfully used as potentially green and sustainable catalysts in organic reactions. In continuation of our efforts to develop greener synthetic pathways for organic transformations [48,49,55–57], we herein report the synthesis of an MCM-41-supported palladium(0)-Schiff base complex [MCM-41-N,N-Pd(0)] and its successful application to the atom-efficient cross-coupling of aryl iodides with triarylindiums or trialkynylindiums leading to unsymmetrical biaryls and arylalkynes in good to excellent yields (Scheme 1). This new phosphine-free heterogeneous palladium(0) catalyst exhibits high catalytic activity in the reaction and can easily be separated from the reaction mixture by a simple filtration of the reaction solution, and its catalytic efficiency remains unaltered even after recycling ten times.

2. Experimental

2.1. General remarks

All chemicals were reagent grade and used as purchased. The mesoporous material MCM-41 [45] and triorganoindium compounds [26] were prepared according to literature methods. The products were purified by flash chromatography on silica gel. Light petroleum ether (30–60 °C) or a mixture of light petroleum ether and ethyl acetate was generally used as eluent. All products were characterized by comparison of their spectra and physical data with authentic samples. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer in $CDCl_3$ as solvent. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer. Melting points are uncorrected. Palladium content was determined with inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation). X-ray powder diffraction was obtained on Damax–γA (Rigaku). The BET surface area and pore analysis were performed on ASAP2010 (micromeritics) by N_2 physical adsorption-desorption at 77.4 K. X-ray photoelectron spectra was recorded on XSAM 800 (Kratos).

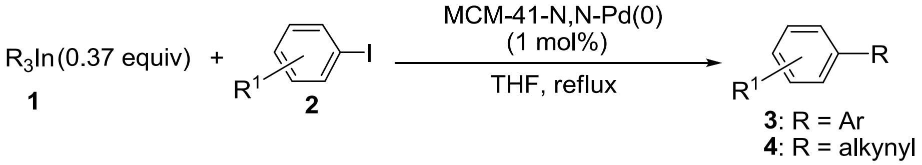
2.2. Preparation of MCM-41-N,N-Pd(0) complex

A solution of 2.2 g of 3-aminopropyltriethoxysilane in 15 mL of dry chloroform was added to a suspension of 2.8 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 product was then soaked in a solution of 4.5 g of Me_3SiCl in 80 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. The dried white solid (3.3 g) was then reacted with pyridine-2-carboxaldehyde (0.502 g, 4.7 mmol) in 20 mL of dry ethanol at 80 °C for 12 h. The solid product was filtered, washed with ethanol (3 × 20 mL) and diethyl ether (20 mL), and dried in vacuum at 120 °C for 5 h to obtain 3.45 g of hybrid material MCM-41-N,N. The nitrogen content was found to be 2.42 mmol/g by elemental analysis.

In a small Schlenk tube, 2.50 g of the above-functionalized MCM-41 material (MCM-41-N,N) was mixed with 0.216 g (1.22 mmol) of $PdCl_2$ 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 under vacuum at 80 °C for 5 h to give 2.63 g of a light yellow palladium(II) complex [MCM-41-N,N-$PdCl_2$]. The mixture of MCM-41-N,N-$PdCl_2$ (2.2 g) and hydrazine hydrate (1.5 g) in EtOH (30 mL) was then stirred at 30 °C for 3 h under Ar. The resulting product was filtered, washed with EtOH (3 × 20 mL) and Et_2O (2 × 20 mL) and dried under vacuum at 60 °C for 3 h to afford 2.15 g of the MCM-41-N,N-Pd(0) complex as a gray powder. The nitrogen and palladium content was found to be 2.27 mmol/g and 0.42 mmol/g, respectively.

2.3. General procedure for preparation of triarylindium and trialkynylindium reagents

A 25 mL round-bottomed flask containing a stirrer bar was charged with $InCl_3$ (0.37 mmol) and dried under vacuum with a heat gun. The flask was cooled, a positive argon pressure was established and anhydrous THF (2 mL) was added. The resulting solution was cooled to −78 °C and a solution of ArMgBr or RC≡CMgBr (1.1 mmol, 1.5 M in THF) was slowly added (15–30 min). The reaction mixture was stirred for 30 min, the cooling bath was removed, and the mixture was warmed to room temperature over 30 min.



Scheme 1. Heterogeneous phosphine-free palladium(0)-catalyzed cross-coupling of aryl iodides with triarylindiums or trialkynylindiums.