



Palladium phosphine complex catalysts immobilized on silica via a tripodal linker unit for the Suzuki–Miyaura coupling reactions of aryl chlorides

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ABSTRACT

Silica-immobilized palladium phosphine complex catalysts bearing a tripodal linker unit were tested for their ability to facilitate the Suzuki–Miyaura coupling reactions of aryl chlorides. The catalyst containing the tripodal linker with a trimethylsilyl capping group on the residual surface silanol groups displayed better catalytic activities and lower palladium and phosphorus leaching levels than the catalysts bearing a conventional trialkoxy-type linker.

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1. Introduction

The Suzuki–Miyaura coupling reaction is a powerful and versatile tool for synthesizing organic compounds that can be utilized as organic electronic materials or intermediates for the preparation of pharmaceuticals and agricultural chemicals [1–5]. Over the last decade, studies of the coupling reactions have focused on the use of aryl chlorides as readily accessible and inexpensive substrates; however, aryl chlorides are much more difficult to activate than aryl bromides or aryl iodides. Soluble palladium complexes with electron-rich and bulky phosphine ligands have been widely and commonly used as catalysts for coupling reactions involving aryl chlorides [6–11]; however, these reactions tend to suffer from certain drawbacks. Homogeneous catalysts are generally connected with the problem of catalyst separation out from a reaction mixture. Electron-rich phosphine ligands and their palladium complexes can be difficult to handle because of their air-sensitive nature. They are also difficult to reuse after performing a reaction. Thus, the development of practical immobilized aryl chloride coupling catalysts

having a low susceptibility to oxidation remains an area of ongoing interest.

Previous investigations of immobilized Suzuki–Miyaura coupling catalysts for aryl chlorides have mainly focused on modifying the ligand structures of palladium complexes, such as bulky electron-rich phosphines, palladacycles, and N-heterocyclic carbenes, similar to the approaches used to develop homogeneous catalysts [12–21]. In this study, we adopted a different catalyst design strategy for promoting aryl chloride coupling reactions. Here, we demonstrate that the immobilized catalysts could be remarkably improved by modifying the structure of a linker [22–25] connecting the palladium complex to the silica support. This result is surprising in view of the use of a simple alkyldiphenyl phosphine ligand. Unlike most electron-rich phosphines, alkyldiphenyl phosphines are not very air-sensitive and, hence, they are easily handled.

2. Experimental

2.1. Materials

All chemicals were reagent-grade and were used without further purification. A potassium diphenylphosphide (KPPH₂) solution in tetrahydrofuran (THF) (0.5 mol/L) was purchased from Sigma–Aldrich Co. Ethoxytrimethylsilane was purchased

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from Shin-Etsu Chemical Co., Ltd. Palladium(II) acetate was supplied by N.E. Chemcat Co. Ordered mesoporous silica with a 2D hexagonal structure (TMPS-4) [26], used as a silica support, was supplied by Taiyo Kagaku Co., Ltd. The specific surface area, pore volume, and average pore size were 1039 m²/g, 1.46 cm³/g, and 3.8 nm, respectively. Mesoporous silica was dried in vacuo at 80 °C for 3 h prior to use.

2.2. Preparation of diphenylphosphino-functionalized silica

The structures of the organic-functionalized silica materials used in this study are summarized in Fig. 1. The diphenylphosphino-functionalized silica **1a**, in which the tripodal linker unit was used, was prepared by grafting 3-bromopropyltris[3-(allyldimethylsilyl)propyl]silane onto mesoporous silica. The resulting 3-bromopropyl-functionalized silica was reacted with KPPH₂ in THF according to a procedure described previously (the “bottom-up” method) [24].

The trimethylsilyl-capped diphenylphosphino-functionalized silica **1b** was prepared by capping the residual surface silanol groups of 3-bromopropyl-functionalized silica with ethoxytrimethylsilane, followed by phosphination using KPPH₂. The procedure to prepare **1b** was as follows: 3-bromopropyl-functionalized silica (1.0 g) and ethoxytrimethylsilane (20 mL) was stirred at 60 °C for 20 h. The resulting solid was filtered, washed with methanol, and dried in vacuo at 80 °C for 3 h. A THF solution of KPPH₂ (6 mL) was then added to a suspension of the trimethylsilyl-capped 3-bromopropyl-functionalized silica (1.0 g) in dry THF (30 mL), and the mixture was stirred for 20 h. The resulting solid was filtered, washed successively with THF, methanol, and hexane (five times for each solvent (10 mL)) to eliminate unreacted KPPH₂ as well as any by-products, and then dried in vacuo at 80 °C for 3 h to give **1b**.

For comparison, diphenylphosphino-functionalized silica bearing the conventional trialkoxy-type linker **2a**, its trimethylsilyl-capped derivative **2b**, or diphenylphosphino-functionalized silica bearing the conventional monoalkoxy-type linker **3** was prepared in a similar manner using the appropriate silane coupling reagents.

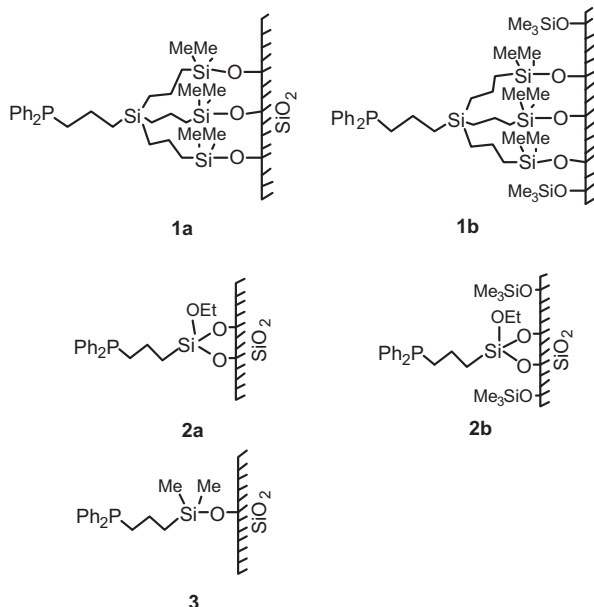


Fig. 1. Organic-functionalized silica materials.

2.3. Preparation of the palladium catalysts

Mesoporous silica-immobilized palladium phosphine complex catalysts were prepared by reacting the diphenylphosphino-functionalized silicas **1a–3** with palladium acetate (P/Pd molar ratio = 6/1) in THF at room temperature for 12 h. After the reaction, the resulting solid was filtered, washed with THF, and dried in vacuo at 80 °C for 3 h. ICP-MS analysis proved that the palladium concentrations in the filtrates obtained from the catalyst preparation procedure were less than the quantitative limit, and that all catalysts contained virtually all of the added palladium. Hereafter, the palladium catalysts will be referred to as **X-Pd**, where X is the type of diphenylphosphino-functionalized silica. The prepared catalysts were air- and moisture-stable and could, therefore, be easily stored and handled. The preparation procedures of **1a-Pd** and **1b-Pd** are summarized in Scheme 1.

A mesoporous silica-supported Pd(OAc)₂ catalyst **SiO₂-Pd** was prepared by impregnating mesoporous silica with a THF solution of Pd(OAc)₂ at room temperature for 12 h, followed by drying in vacuo at 80 °C for 3 h.

2.4. Characterization

Nitrogen adsorption/desorption isotherms were measured at –196 °C using a Bel Japan BELSORP-mini II analyzer. All Samples were heated under vacuum at 80 °C for 3 h prior to conducting the measurements. The specific surface areas were calculated using the BET method. The pore size distribution was obtained by applying the BJH method applied to the adsorption branch of the nitrogen adsorption/desorption isotherm. An elemental analysis of carbon was conducted using a CE Instruments EA 1112 elemental analyzer. The palladium concentrations in solution were determined using an Agilent 7500ce inductively coupled plasma-mass spectrometer (ICP-MS). The phosphorous content of the catalysts was determined using a Shimadzu EDX-800HS energy-dispersive X-ray fluorescence spectrometer (EDXRF). Scanning transmission electron microscopy (STEM) images were taken on a Hitachi HD-2000 microscope with an acceleration voltage of 200 kV. Solid-state ²⁹Si, ¹³C, and ³¹P cross-polarization/magic angle spinning (CP/MAS) NMR spectra were recorded on a Bruker AVANCE 400WB spectrometer operated at 79.5, 100.6, or 162.1 MHz for ²⁹Si, ¹³C, or ³¹P, respectively, and using a 4 mm CP/MAS probe head. A typical spinning rate was 12.5 kHz, and CP contact times were 3.5, 2.0, and 3.0 ms for ²⁹Si, ¹³C, and ³¹P CP/MAS, respectively.

2.5. Catalytic testing

The Suzuki–Miyaura coupling of aryl chloride and phenylboronic acid was carried out in a Schlenk tube (30 mL) under a nitrogen atmosphere. A typical experimental procedure was as follows: a mixture of aryl chloride (3.0 mmol), phenylboronic acid (3.3 mmol), potassium phosphate (3.0 mmol), the catalyst (0.1–0.3 mol% with respect to palladium), and 4-*tert*-butyltoluene (430 mg) as an internal standard for gas chromatograph analysis were stirred in 1,4-dioxane (3 mL) at 100 °C. The reaction mixture was periodically sampled to follow the progress of the reaction by gas chromatography. After the reaction, the catalyst was separated by centrifugation, and the supernatant was analyzed on a Shimadzu GC-14B gas chromatograph (GC) equipped with a thermal conductivity detector and a column (2 mm × 3 m) packed with 3% OV-101 on Chromosorb WHP (100/120 mesh) to determine the product yields.

When the nitrogen adsorption/desorption isotherm of the catalyst after the reaction was measured, the catalyst was recovered by filtration and washed successively with 1,4-dioxane, water, and ethanol.

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