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Note

A practical synthesis of unsymmetrical triarylphosphines by heterogeneous palladium(0)-catalyzed cross-coupling of aryl iodides with diphenylphosphine

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ABSTRACT

The heterogeneous cross-coupling reaction of aryl iodides with diphenylphosphine was achieved in DMAc at 130 °C in the presence of 1.0 mol% of MCM-41-supported tridentate nitrogen palladium(0) complex [MCM-41-3N-Pd(0)] with KOAc as base, yielding a variety of unsymmetrical triarylphosphines in good to excellent yields. The turnover frequency (TOF) of the catalyst can reach 30.67 h^{-1}. This new heterogeneous palladium(0) catalyst could easily be prepared by a simple procedure from commercially readily available reagents, and exhibited the same catalytic activity as homogeneous $Pd(OAc)_2$ or $Pd(PPh_3)_4$, and could be recovered by filtration of the reaction solution and recycled at least seven times without significant loss of catalytic activity.

1. Introduction

Tertiary arylphosphines have widely been applied in many organic transformations catalyzed by transition metals as one of the most useful ligands and are ubiquitous in organometallic chemistry [1–7]. Besides, triarylphosphines can also be used as catalysts [8–10] and fundamental building blocks [11,12] in organic synthesis. The traditional routes to arylphosphines involve reactions of phosphine halides with arylmagnesium or aryllithium reagents, and are therefore intolerant to a wide range of functional groups [1–3]. Among various methods for the preparation of arylphosphine ligands, direct carbon-phosphorous (C–P) bond formation via transition metal-catalyzed cross-coupling between unprotected secondary phosphines and aryl halides/triflates is one of the most valuable and highly efficient routes due to the tolerance of a wide variety of functional groups. Since Stelzer and coworkers first reported the palladium-catalyzed cross-couplings between aryl iodides/bromides and diarylphosphines [13,14], considerable effort has been devoted to the development of palladium- [15–24], copper- [25–28], and nickel [29–34]-catalyzed phosphinations of aryl iodides/bromides or aryl triflates for the synthesis of tertiary phosphines. Recently, catalytic reduction of tertiary phosphine oxides has also proven to be an alternative method for the synthesis of tertiary phosphines [35–38].

Despite significant progress made in homogeneous Pd-, Cu- and Ni-catalyzed synthesis of triarylphosphines, the use of expensive palladium catalysts as well as difficult recovery and non-recyclability of the metal catalysts make these methods of limited synthetic utility from environmental and economic points of view [39]. What's more, homogeneous catalysis might result in heavy metal contamination of the desired isolated product due to the easy formation of complexes of palladium, nickel and copper with triarylphosphines. Recycling of homogeneous metal catalysts is a task of great economic and environmental importance in the chemical and pharmaceutical industries, especially when expensive and/or toxic heavy metal complexes are utilized [40]. The heterogenization of the existing homogeneous metal catalysts appears to be a logical solution to these problems [41,42]. In recent years, heterogeneous palladium catalysts have been successfully applied in carbon-carbon and carbon-heteroatom bond formation reactions [43,44]. However, to the best of our knowledge, no examples of heterogeneous palladium-catalyzed C–P bond construction via direct

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coupling of secondary phosphines with aryl halides/triflates have been described until now.

Mesoporous MCM-41 materials have recently been shown to be powerful supports for immobilization of homogeneous catalysts [45–47]. So far, some functionalized MCM-41-immobilized palladium [48–52], rhodium [53], molybdenum [54], gold [55,56], and copper [57,58] complexes have been successfully used as highly efficient and recyclable catalysts in organic reactions. In continuing our efforts to develop greener synthetic pathways for organic transformations [50–52,57,58], herein we report the first synthesis of an MCM-41-supported tridentate nitrogen palladium(0) complex [MCM-41-3N-Pd(0)] and its successful application to cross-coupling of aryl iodides with diphenylphosphine leading to a variety of unsymmetrical triaylphosphines in good to excellent yields (Scheme 1).

2. Experimental

2.1. General remarks

All chemicals were reagent grade and used as purchased. The mesoporous material MCM-41 was prepared according to a literature procedure [45]. The products were purified by flash chromatography on silica gel. Mixture of CH_2Cl_2 and hexane was generally used as eluent. All coupling products were characterized by comparison of their spectra and physical data with authentic samples. ^{1}H NMR spectra were recoded on a Bruker Avance 400 MHz spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra (100 MHz) were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ as solvent. ^{31}P NMR spectra (121 MHz) were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ as solvent. Palladium content was determined with inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation). X-ray powder diffraction patterns were obtained on Damx-rA (Rigaku). Nitrogen adsorption/desorption isotherms were obtained using a Bel Japan Inc. Belsorp-HP at 77 K. Prior to gas adsorption measurements materials were degassed for 6 h at 423 K. TEM images were recorded in a transmission electron microscope operated at an accelerated voltage of 200 kV. X-ray photoelectron spectra were recorded on XSAM 800 (Kratos).

2.2. Preparation of MCM-41-3N-Pd(0) complex

A solution of 1.54 g of 3-(2-aminoethylamino)propyltrimethoxysilane in 18 mL of dry $CHCl_3$ was added to a suspension of 2.2 g of the MCM-41 in 180 mL of dry toluene under Ar. The mixture was stirred at 100 °C for 24 h. 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 (1.725 g) was then reacted with pyridine-2-carboxaldehyde (0.251 g, 2.34 mmol) in 10 mL of dry ethanol at 80 °C for 24 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 1.813 g of hybrid material MCM-41-3 N. The nitrogen content was found to be 2.62 mmol/g by elemental analysis.

In a small Schlenk tube, 1.70 g of the above-functionalized MCM-41 (MCM-41-3 N) was mixed with 0.177 g (1.0 mmol) of $PdCl_2$ in 40 mL of dry acetone. The mixture was refluxed for 72 h under an argon atmosphere. The solid product was filtered, washed with distilled water (2 × 10 mL) and ethanol (2 × 10 mL), and dried under vacuum. The yellow solid was then mixed with hydrazine hydrate (1.5 mL) in ethanol (20 mL) at 30 °C for 5 h. The resulting product was filtered, washed with distilled water (3 × 10 mL) and acetone (2 × 10 mL) and dried under vacuum at 60 °C for 5 h to afford 1.82 g of a gray palladium(0) complex [MCM-41-3N-Pd(0)]. The nitrogen and palladium contents were found to be 2.36 mmol/g and 0.49 mmol/g, respectively.

2.3. General procedure for C–P coupling reaction of various aryl iodides with diphenylphosphine

MCM-41-3N-Pd(0) (21 mg, 0.01 mmol), KOAc (1.5 mmol) and aryl iodide **1** (1.0 mmol) (if solid) were placed in an oven-dried 20 mL Schlenk tube, the reaction vessel was evacuated and filled with argon for three times. Then aryl iodide **1** (1.0 mmol) (if liquid), diphenylphosphine (1.2 mmol) and DMAc (1 mL) were added with a syringe under a counter flow of argon. The reaction mixture was stirred at 130 °C for 3 h. After completion of the reaction, the mixture was cooled to room temperature and diluted with CH_2Cl_2 (20 mL) and filtered. The MCM-41-3N-Pd(0) catalyst was washed with distilled water (2 × 5 mL) and ethanol (2 × 5 mL), and reused in the next run. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel to provide the product **2**.

2.3.1. Triphenylphosphine, *2a* [26]

White solid, m.p.: 79–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.44–7.23$ (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 137.3$, 137.2, 133.9, 133.7, 128.8, 128.6, 128.5; ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = -5.45$ (s).

2.3.2. Diphenyl(4-methylphenyl)phosphine, *2b* [26]

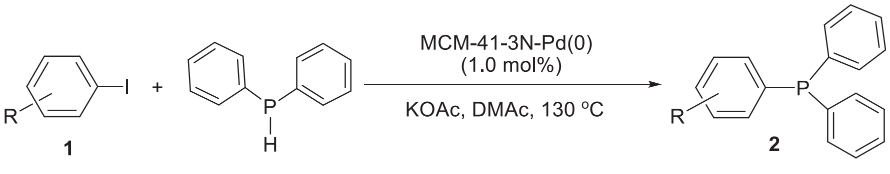
White solid, m.p.: 68–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.37–7.14$ (m, 14H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.9$, 137.5, 137.4, 134.1, 133.9, 133.7, 133.6, 129.5, 129.4, 128.7, 128.5, 128.4, 21.4; ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = -6.30$ (s).

2.3.3. Diphenyl(4-methoxyphenyl)phosphine, *2c* [59]

White solid, m.p.: 67–68 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.25–7.16$ (m, 12H), 6.82 (d, $J = 8.0$ Hz, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 160.4$, 137.8, 137.7, 137.6, 135.8, 135.6, 133.6, 133.4, 128.6, 128.5, 128.4, 114.3, 114.2, 55.2; ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = -7.10$ (s).

2.3.4. Diphenyl(3-methylphenyl)phosphine, *2d* [60]

White solid, m.p.: 50–51 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.42–7.06$ (m, 14H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.1$, 137.1, 134.6, 134.4, 133.9, 133.7, 132.1, 130.9, 130.7, 129.6, 128.7, 128.5, 128.4, 21.5; ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = -5.23$ (s).



Scheme 1. Heterogeneous Pd(0)-catalyzed C–P coupling of aryl iodides with Ph_2PH.