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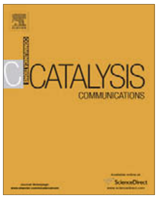

Carbonylative cross-coupling of aryl halides with sodium tetraphenylborate catalyzed by MCM-41-supported bidentate phosphine palladium(II) complex

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ABSTRACT

The first heterogeneous carbonylative cross-coupling reaction of aryl halides with sodium tetraphenylborate under an atmospheric pressure of carbon monoxide was achieved in DMF at 80 °C or 130 °C in the presence of a catalytic amount of MCM-41-supported bidentate phosphine palladium(II) complex [MCM-41-2P-Pd(II)] to yield unsymmetrical biaryl ketones in good to high yields. This polymeric palladium catalyst can be reused many times without any decrease in activity.

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1. Introduction

Biaryl ketones are important moieties in many biologically active molecules, natural products and pharmaceuticals and many methods for the preparation of them have been reported [1]. One general approach is the Friedel–Crafts acylation of substituted aromatic rings [2–4]. The crucial disadvantage of traditional Friedel–Crafts acylation is the use of more than a stoichiometric amount of aluminum trichloride, which is incompatible with many functional groups and generates a large amount of waste. Furthermore, the formation of *ortho* and *para* isomers with the untunable regioselectivity results in separation problems and makes the aryl ketones with *meta* substituent difficult to access. The transition metal-catalyzed three-component cross-coupling reaction between arylmetal reagents, carbon monoxide, and aryl electrophiles has provided a straightforward and convenient route for the synthesis of unsymmetrical biaryl ketones [5]. Sodium tetraphenylborate ($NaBPh_4$) is stable, non-toxic and commercially available phenylating agent and have been used for forming σ-phenyl complexes of various transition metals by the transfer of a phenyl group from boron to metals [6–9]. From the viewpoint of organic synthesis, several recent reports on its use in palladium catalyzed reactions are interesting; That is the phenyl substitution of allylic acetates [10] and chlorides [11] giving the corresponding allylbenzenes, synthesis of diaryl substituted norbornanes and norbornenes [12]. Very recently, Xia et al. described a highly efficient *N*-heterocyclic carbene–palladium complex-catalyzed multicomponent carbonylative Suzuki reaction of aryl iodides, carbon monoxide and sodium tetraphenylborate, providing a novel practical route for the synthesis of unsymmetrical aryl ketones [13]. However, the carbonylative Suzuki reaction proceeds in the presence of a homogeneous *N*-heterocyclic carbene–palladium complex, which makes the recovery of the metal tedious if not impossible and might result in unacceptable palladium contamination of the product. From the standpoint of green chemistry, the development of more environmentally benign conditions for the reaction, for example, the use of a heterogeneous palladium catalyst would be desirable [14]. So far, polymer-supported palladium catalysts have successfully been used for a variety of organic reactions [15]. However, to the best of our knowledge, there has been no general study of carbonylative cross-coupling reaction of aryl halides with sodium tetraphenylborate catalyzed by a polymer-supported palladium complex described to date.

Recent developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support to immobilize homogeneous catalysts [16]. MCM-41 has a regular pore diameter of *ca.* 5 nm and a specific surface area >700 $m^2\ g^{-1}$ [17]. 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 [18–20]. To date, a few palladium complexes on functionalized MCM-41 support have been prepared and used in organic reactions [21–24]. Recently, we have reported the synthesis of the MCM-41-supported bidentate phosphine palla-

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dium(0) complex [abbreviation: MCM-41-2P-Pd(0)] and found that this complex is a highly active and recyclable catalyst for Sonogashira reactions of aryl halides [25]. In this paper we wish to report the catalytic properties of MCM-41-supported bidentate phosphine palladium(II) complex [abbreviation: MCM-41-2P-Pd(II)] in the carbonylative cross-coupling reaction of aryl halides with sodium tetraphenylborate.

2. Experimental

All carbonylative cross-coupling products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were obtained on a Perkin–Elmer 683 instrument. ^{1}H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard in $CDCl_3$ as the solvent. Elemental analyses were measured using a Yanaco MT-3 CHN microelemental analyzer. All chemicals were reagent grade and used as purchased. X-ray photoelectron spectra were recorded on XSAM 800 (Kratos). The BET surface area was measured on ASAP2010 (Micromeritics) by N_2 physical adsorption–desorption at 77.4 K. Thermogravimetric analysis (TGA) was carried out on a Perkin–Elmer TGA-7 thermal analyzer at a heating rate of 10 °C/min in nitrogen. Palladium content was determined with inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation). The MCM-41-supported bidentate phosphine palladium(II) complex (abbreviation: MCM-41-2P-Pd(II)) was prepared according to our previous procedure [25]. Anal. Found: C, 19.74; H, 2.27; N, 0.77; P, 3.53; Cl, 3.91; Pd, 5.62; Si, 29.6%.

2.1. General procedure for carbonylative cross-coupling of aryl halides with $NaBPh_4$

A 50 ml round-bottomed flask equipped with a gas inlet tube, a reflux condenser, and a magnetic stirring bar was charged with MCM-41-2P-Pd(II) (38 mg, 0.02 mmol Pd), aryl iodide (1.0 mmol), and $NaBPh_4$ (1.2 mmol). The flask was flushed with carbon monoxide, and DMF (6 ml) was then added. After being stirred at 80 °C for 5–10 h under CO (1 atm), the reaction mixture was cooled to room temperature, filtered and the filtrate was poured into a saturated aqueous NaCl solution (100 ml) and extracted with methylene chloride (2×50 ml). The palladium catalyst was washed with DMF (2×5 ml), distilled water (3×10 ml), ethanol (2×5 ml) and ether (2×5 ml) and reused in the next run. The extract was washed with water (3×20 ml) and dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane–ethyl acetate = 10:1).

3. Results and discussion

The MCM-41-supported bidentate phosphine palladium(II) complex [MCM-41-2P-Pd(II)] was conveniently prepared according to our previous procedure [25]. The specific surface areas (S_{BET}) of the support MCM-41 and the MCM-41-2P-Pd(II) were determined to be 902.4 and 467.8 $m^2 g^{-1}$, respectively. A significant decrease in surface area indicated that the palladium complex was successfully introduced into the inner channels of the support MCM-41. The thermogravimetric analysis (TGA) curves of the support MCM-41 and the MCM-41-2P-Pd(II) are presented in Fig. 1. As shown in Fig. 1, the support MCM-41 exhibited excellent thermal stability, no weight loss was observed even at 500 °C. However, the removal of organopalladium complex in the MCM-41-2P-Pd(II) commenced at 250 °C and continued up to 480 °C. These results further demonstrated that the palladium complex was successfully grafted onto the inner channels of the support MCM-41 by chemical bonding. The MCM-41-supported bidentate phosphine palladium(II) complex [MCM-41-2P-Pd(II)] was employed as catalyst in the carbonylative cross-coupling reaction of aryl halides with $NaBPh_4$ under an atmospheric pressure of carbon monoxide. Initially, to determine the optimum conditions, the carbonylative cross-coupling reaction of $NaBPh_4$ (1.2 equiv) with 4-iodonitrobenzene was examined under different reaction conditions. The results are summarized in Table 1. For the temperatures evaluated (50, 80, and 100 °C), 80 °C gave the best result and no reaction occurred at 50 °C. The solvents affected the selectivity of the reaction. DMF and anisole were recognized to be highly effective solvents for preventing the formation of undesirable 4-nitrobiphenyl by-product. The use of DMF, dioxane, anisole, and toluene at 80 °C gave 4-nitrobenzophenone in good yields (85–94%) and DMF was the best choice. *N*-heterocyclic carbene–palladium complex-catalyzed carbonylative Suzuki reaction of aryl iodides with sodium tetraphenylborate requires use of 3 equiv K_2CO_3 to prevent the formation of undesirable biaryl by-products [13], however, the bases have no influences on the carbonylative coupling reaction catalyzed by MCM-41-2P-Pd(II) (entries 3, 6, 7). Increasing the amount of palladium catalyst could shorten the reaction time, but did not increase the yield of 4-nitrobenzophenone (entry 12). The low palladium concentration usually led to a long period of reaction, which was consistent with our experimental result (entry 11).

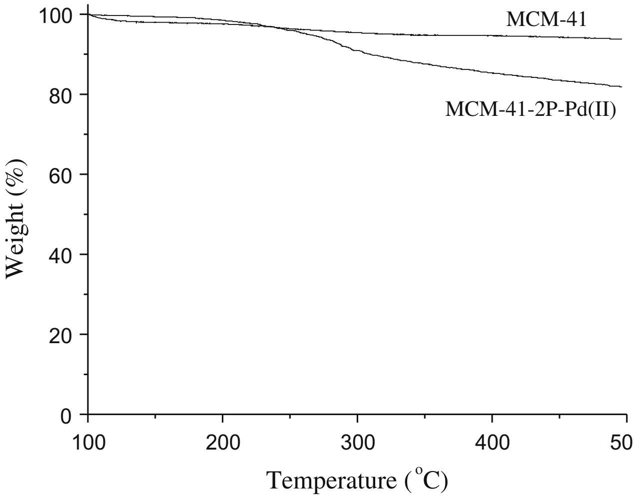

Fig. 1. TGA curves of MCM-41 and MCM-41-2P-Pd(II).

To examine the scope for this carbonylative cross-coupling reaction, a variety of aryl halides were coupled with $NaBPh_4$ in DMF at 80–130 °C in the presence of a catalytic amount of MCM-41-2P-Pd(II) under an atmospheric pressure of carbon monoxide (Scheme 1). The experimental results are summarized in Table 2. As shown in Table 2, the nature of substituents in aryl halides affected the reactivity of aryl halides. The carbonylative cross-coupling reaction of $NaBPh_4$ with a variety of electron-deficient aryl iodides proceeded smoothly under mild conditions giving the corresponding carbonylative coupling products in high yields. The reaction of 4-iodoanisole with strongly electron-donating substituent required higher temperature (100 °C) and longer time, giving 4-methoxybenzophenone in only 78% yield (entry 4). In general, electron-deficient aryl iodides typically gave higher amounts of Suzuki coupling product, non-carbonylative biaryl derivatives. It is known that insertion of carbon monoxide into active species is fast for the electron-rich aryl halides and the electron-withdrawing groups slow the insertion by reversely accelerating the rate of direct coupling [26,27]. For example, the carbonylative cross-coupling reaction of triphenylalane with 4-iodonitrobenzene was

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