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Silicadiphenyl phosphinite (SDPP)/Pd(0) nanocatalyst for efficient aminocarbonylation of aryl halides with $POCl_3$ and DMF

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ABSTRACT

Silicadiphenyl phosphinite (SDPP) as a new phosphorylated silica and catalytic amounts of Pd(II) generates nano SDPP/Pd(0) catalyst for the efficient aminocarbonylation of aryl halides in the presence of $POCl_3$ and *N*,*N*-dimethylformamide (DMF). Amides are obtained in high yields from aryl iodides and also activated aryl bromides, chlorides.

1. Introduction

During the last few years significant advances have been achieved in the development of cross-coupling methodologies for synthesis of different classes of aromatic carbonyl compounds. Transition metal-catalyzed carbonylation of aryl halides in the presence of nucleophiles is an efficient methodology for the preparation of such compounds [1]. Amides as an important subgroup of carbonyl compounds are widely used in medicinal chemistry [2]. So, development of new synthetic methods for their synthesis is greatly attracted chemists. After the first report of Heck for the Pd catalyzed formation of amides from aryl and alkenyl halides with amines and carbon monoxide [3], some other methods for aminocarbonylation of aryl halides have been developed [4]. For this aim, the use of CO with various palladium based catalytic systems such as silica-supported bidentate arsine–palladium complex [5], silica-supported bidentate sulfur and phosphine mixed palladium complex [6], $Pd(OAc)_2/PPh_3$ in ionic liquid [7], palladium-1,3-*bis* (dicyclohexylphosphino)propane H_2BF_4 [8], $Pd(OAc)_2$/xantphos [9], and palladium *bis* (2,2,6,6-tetramethyl-3,5-heptanedionate) [1] have been reported to achieve the above transformation. Indolese et al. have reported the use of carbon monoxide in conjunction with formamide as the amine source in the palladium-catalyzed aminocarbonylation to give primary amides [10]. Tsuji et al. reported the use of both carbon monoxide and formamides as carbonyl sources in carbonylation reactions in the presence of $Ru_3(CO)_{12}$ as catalyst to afford the amidation products [11].

However, these methods suffer from the difficulty in handling of the toxic carbon monoxide and do not work with unreactive aryl chlorides and fluorides. Many efforts have also been proposed to develop methods without the direct use of carbon monoxide. Varieties of metal carbonyls including $Ni(CO)_4$ [12], $Mo(CO)_6$ [13], $Cr(CO)_6$ [13], $W(CO)_6$ [13], carbamoylstannanes [14] and carbamoylsilanes [15], have been used for the *in situ* generation of carbon monoxide. Recently, transition metal-catalyzed aminocarbonylation using DMF in strongly basic condition as a source of carbon monoxide and dimethylamine have been reported both under thermal [16] and microwave irradiation [17]. Reports on the use of a combination of $POCl_3$ and DMF are very rare in the literature. Nozaki et al. reported the first example of aminocarbonylation of only aryl and alkenyl iodides in the presence of $Pd_2(dba)_3$, $POCl_3$ and DMF to produce the corresponding aromatic amides [18]. Later, Bhanage et al. reported on the synthesis of amides from only aryl iodides using this reagent system in the presence of a Pd/C catalyst [19]. The main disadvantage of this interesting protocol is that it could not be applied to aryl halides other than iodides.

2. Experimental

X-ray diffraction data obtained with XRD, D8, Advance, Bruker, axs. Transmission electron microscopy (TEM) analyses were performed on a Philips model CM 10 instrument. Scanning electron

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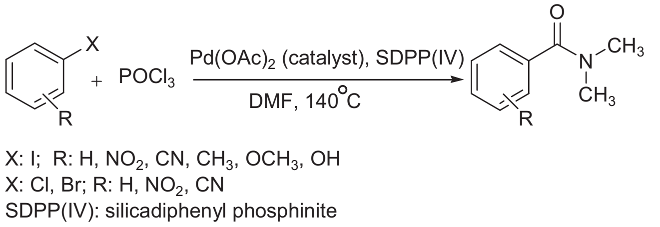


Scheme 1. Aminocarbonylation of aryl halides in the presence of *N*,*N*-dimethylformamide and $POCl_3$.

micrograph was obtained by SEM, XL-30 FEG SEM, Philips, at 20 kV. IR spectra were run on a Shimadzu FTIR-8300 spectrometer. The ^1H and ^{13}C-NMR spectra were recorded on a Brucker Avance DPX-250 MHz spectrometer using tetramethylsilane as internal standard. Mass spectra were obtained on a Shimadzu GCMS-QP 1000 EX instrument at 70 eV. The plate silica gel used for the preparation of phosphorylated silica was type 60 (15–40 μm) which was activated and dried in a vacuum oven at 200 °C for 24 h before use.

2.1. Typical procedure for the preparation of silicadiethyl phosphite (SDEP) and silicadiisopropyl phosphite (SDIPP)

To a flask containing silphos (I) prepared according to the literature [20] (0.10 g, 0.642 mmol) was added sodium ethoxide (0.19 g, 2.8 mmol) in ethanol (5.0 mL) to prepare SDEP and sodium isopropoxide (0.23 g, 2.8 mmol) in isopropanol (5.0 mL) to prepare SDIPP and stirred with a mechanical stirrer under reflux for 24 h. The mixture was filtered, washed with distilled water and then dried under vacuum. Silicaphosphites (II, III) were obtained as a white solid (0.11 g, 0.115 g) respectively. **IR**, KBr disk, ν (cm^{-1}) SDEP: 3427, 2922, 2832, 1429, 1062, 879, 790; SDIPP: 3427, 2921, 2832, 1380, 1370, 1062, 790.

2.2. Typical procedure for the preparation of silicadiphenyl phosphinite (SDPP)

Plate silica gel (type 60, 15–40 μm) was activated by refluxing in concentrated HCl for 4 h. It was then filtered and washed several times with distilled water to remove the produced HCl and dried at 200 °C under vacuum. Then, under an argon atmosphere, to a flask containing activated dried plate silica gel (0.30 g, 5.0 mmol) was added $ClPPh_2$ (2.0 mL, 10.0 mmol) at room temperature and stirred with a mechanical stirrer for 30 min. The mixture was then heated to 60 °C under pressure of argon for 3 h to remove all HCl. The reaction mixture was washed with 10.0 mL of diethyl ether and dried under vacuum. SDPP was obtained as a white solid (0.60 g). **IR**, KBr disk, ν (cm^{-1}) SDPP: 3425, 1435, 1160, 1126, 964, 725, 694. The reagent can be kept in a capped bottle without any change for months. In order to determine the amount of active phosphorus content of the reagent, silicaphosphinite was reacted with excess of iodine in acetonitrile and stirred for 5 h at room temperature. On the basis of titration of unreacted iodine with an aqueous solution of sodium thiosulfate (0.01 M) and the results obtained from several runs showed that the amount of active phosphorus content was 2.25 mmol per 1 g of SDPP.

2.3. General procedure for the aminocarbonylation of aryl halides and N,N-dimethylformamide with $Pd(OAc)_2$/SDPP

$Pd(OAc)_2$ (0.0035 g, 0.0156 mmol, 3.1 mol%), SDPP (0.003 g), aryl halide (0.5 mmol) in dry DMF (5 mL) were stirred for 10 min in a 25 mL two-necked flask equipped with a magnetic stirring bar at room temperature under nitrogen. Then $POCl_3$ (0.09 mL, 1.0 mmol) was added to the reaction mixture. After 15 min, the reaction mixture was heated at 140 °C. After completion, the reaction mixture was cooled to room temperature and the silicaphosphinite was filtrated and the filtrate was poured into saturated solution of $NaHCO_3$ (20.0 mL). The aqueous layer was then extracted with ethyl acetate and dried over anhydrous Na_2SO_4. The crude organic mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4:1) to obtain the desired product in moderate to excellent yield.

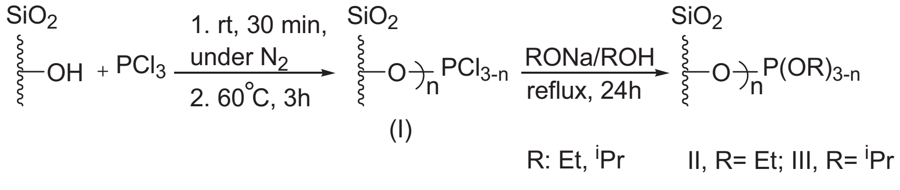
3. Results and discussion

Among the reported methods for aminocarbonyaltion of aryl halides, the use of DMF together with $POCl_3$ compared with the use of CO or *in situ* generation of CO using metal carbonyls seems to be a safer and more practical method. As it was mentioned earlier, the reported methods using this reagent system are rare [18,19] and they require long reaction time and greatly suffer from the limitation of applying to only aryl iodides. In this work we report a simple method for the synthesis of silicadiphenyl phosphinite, SDPP(IV) as a new class of phosphorylated silica, which reduces Pd(II) into nano-Pd(0) supported SDPP. This new nano-Pd catalyst acts efficiently for aminocarbonylation of aryl iodides, and activated aryl bromides as well as chlorides in the presence of *N*,*N*-dimethylformamide and $POCl_3$ (Scheme 1).

We have recently reported on the preparation and use of $P(Cl)_{3-n}(SiO_2)_n$ (silphos (I)) as a filterable phosphorus (III) reagent in various reactions [20]. In order to have easily prepared phosphorylated silica compounds, we reacted silphos (I) with ethanol and isopropanol to replace its chlorine atoms and obtained silicadiethyl phosphite, SDEP(II) and silicadiisopropyl phosphite, SDIPP(III) respectively as new silicaphosphites (Scheme 2).

In order to have diphenyl phosphoryl group on the silica, a plate silica gel was activated by refluxing in concentrated HCl for 4 h. It was then filtered and washed several times with distilled water to remove the produced HCl and dried at 200 °C under vacuum and then reacted with chlorodiphenyl phosphine to afford silicadiphenyl phosphinite, SDPP (IV) as another new phosphorylated silica (Scheme 3).

The amount of P(III) in these phosphorylated silica compounds (II–IV) were found by their reaction with molecular iodine and back titration with aqueous solution of sodium thiosulfate. This was found to be in the range of 1.66 mmol/g for II and III and 2.25 mmol/g for (IV). In continuation of our recent work on Pd-catalyzed coupling reactions [21], we applied these new silica bound phosphorous (III) compounds (II–IV) as cheap, easily prepared and air stable heterogeneous P(III) ligands in the pres-



Scheme 2. The preparation of silicadiethyl phosphite, SDEP(II) and silicadiisopropyl phosphite, SDIPP(III).