



Silicadiphenyl phosphinite (SDPP)/Pd(0) nanocatalyst for efficient aminocarbonylation of aryl halides with POCl₃ 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 POCl₃ and *N,N*-dimethylformamide (DMF). Amides are obtained in high yields from aryl iodides and also activated aryl bromides, chlorides.

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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/PPh₃ in ionic liquid [7], palladium-1,3-bis(dicyclohexylphosphino)propane H₂BF₄ [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 Ru₃(CO)₁₂ as catalyst to afford the amidation products [11].

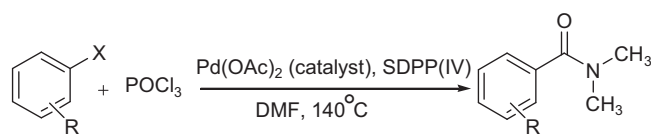
However, these methods suffer from the difficulty in handling of the toxic carbon monoxide and do not work with unreactive aryl chlorides and fluorides. Many efforts have also been proposed to develop methods without the direct use of carbon monoxide. Varieties of metal carbonyls including Ni(CO)₄ [12], 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 POCl₃ 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 Pd₂(dba)₃, POCl₃ 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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X: I; R: H, NO₂, CN, CH₃, OCH₃, OH
 X: Cl, Br; R: H, NO₂, CN
 SDPP(IV): silicadiphenyl phosphinite

Scheme 1. Aminocarbonylation of aryl halides in the presence of *N,N*-dimethylformamide and POCl₃.

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 ¹³C-NMR spectra were recorded on a Bruker 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 ClPPh₂ (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 POCl₃ (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 filtered and the filtrate was poured into saturated solution of NaHCO₃ (20.0 mL). The aqueous layer was then extracted with ethyl acetate and dried over anhydrous Na₂SO₄. 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.

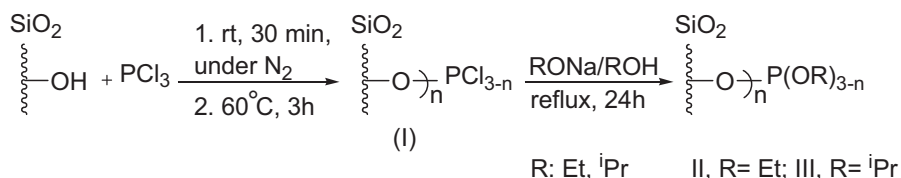
3. Results and discussion

Among the reported methods for aminocarbonylation of aryl halides, the use of DMF together with POCl₃ 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 POCl₃ (Scheme 1).

We have recently reported on the preparation and use of P(Cl)_{3-n}(SiO₂)_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).

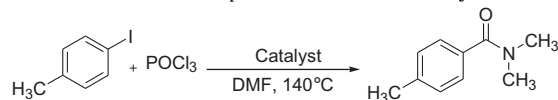
In order to have diphenyl phosphoryl group on the silica, a plate silica gel was activated by refluxing in concentrated HCl for 4 h. It was then filtered and washed several times with distilled water to remove the produced HCl and dried at 200 °C under vacuum and then reacted with chlorodiphenyl phosphine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

Table 1
Effect of different reaction parameters on aminocarbonylation of 4-iodotoluene.^a



Entry	Catalyst	Pd(II) (mol%)	Time (h)	Yield (%) ^b	TON ^f	TOF (h ⁻¹) ^g
1	Pd(OAc) ₂ /SDPP	6.2	2:15	85	14	6.2
2	Pd(OAc) ₂ /SDPP	6.2	10 ^c	82	13.1	1.3
3	Pd(OAc) ₂ /SDPP	6.2	19 ^c	9	1.4	0.076
4	Pd(OAc) ₂ /SDPP	6.2	24 ^c	Trace	–	–
5 ^e	Pd(OAc) ₂ /SDPP	6.2	12	16	2.6	0.2
6	PdCl ₂ /SDPP ^d	6.2	2:30	83	18	7.2
7	Pd(OAc) ₂ /SDIPP	6.2	2:30	81	13	5.2
8	Pd(OAc) ₂ /SDEP	6.2	3:10	81	13	4
9	Pd(OAc) ₂ /SDPP	3.1	3:15	85	27	8.3
10	Pd(OAc) ₂ /Ph ₃ P	3.1	13	79	25.3	1.9
11	Pd(OAc) ₂ /Ph ₃ P/SiO ₂	3.1	18	80	25.6	1.4

^a Reaction conditions: 4-iodotoluene (0.5 mmol), POCl₃ (1.0 mmol), DMF (5.0 mL), the amounts of SDPP, SDIPP and SDEP are 6.0 mg for entries 1–8 and 3.0 mg of SDPP, Ph₃P, Ph₃P/SiO₂ for entries 9, 10, 11.

^b Isolated yield.

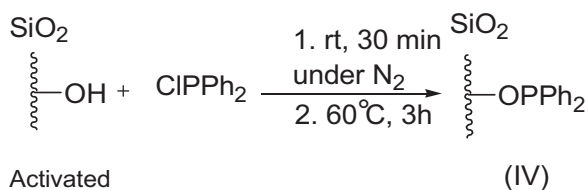
^c The amounts of DMF is reduced to 2.5, 1.5 and 0.5 mL for entries 2, 3, and 4, respectively.

^d PdCl₂ is used instead of Pd(OAc)₂.

^e Temperature of the reaction is 120 °C.

^f TON = mmol of products/mmol of catalyst.

^g TOF = TON/time.



Scheme 3. The preparation of silicadiphenyl phosphinite, SDPP.

ence of Pd(OAc)₂ for aminocarbonylation of aryl halides. We initially studied the aminocarbonylation of 4-iodotoluene with *N,N*-dimethylformamide/POCl₃ as a model reaction in the presence of these three new silica compounds (II–IV). The influence of various parameters is illustrated in Table 1.

As the results of Table 1 show, all three compounds (II–IV) are suitable ligands for this transformation, but the amidation reaction occurs slightly faster in the presence of SDPP(IV). The use of PdCl₂ as catalyst is also suitable, however, the reaction time for Pd(OAc)₂ is slightly shorter. In a comparative study, we used PPh₃ (P(III) content is equal to its amount in SDPP) instead of SDPP, but the reaction time was found to be much longer (Table 1, entry 10). To assess the effect of silica gel we repeated the reaction using a combination of PPh₃ and SiO₂ (Table 1, entry 11). It was observed the use of this combination is not as suitable as using SDPP. This comparative study clearly shows that when –PPh₂ moiety is attached to SiO₂, a synergic effect is observed which greatly accelerates the

reaction. We therefore chose SDPP as the ligand of choice which its P(III) capacity is the highest among the three P(III) bound silica compounds (II–IV) and optimized its amount by carrying out amidation of 4-iodotoluene. The results obtained from this study are shown in Table 2.

The results of Table 2 show that increasing the amounts of SDPP(IV) extends the reaction time from 3.15 to 10 h. This could probably be due to the overligation in the silica matrix.

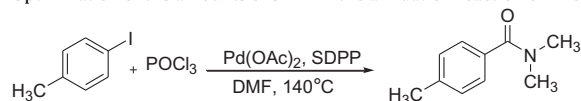
In the absence of POCl₃, the starting material remained unchanged. Decreasing the amount of POCl₃ from two equimolar to one, increases the reaction time from 3.15 to 5 h. In order to have some insight on the nature of the *in situ* produced catalyst in this reaction system, we reacted Pd(OAc)₂ with SDPP(IV) in DMF under the same reaction conditions as we used for aminocarbonylation and isolated the obtained complex. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) of the obtained catalyst are shown in Figs. 1 and 2, respectively.

According to the obtained TEM, the size of nanoparticles is found to be ~7 nm.

The formation of Pd(0) is also shown by the XRD of the catalyst (Fig. 3).

We then applied our optimized reaction conditions (0.5 mmol aryl halide, 3.5 mg (3.1 mol%) Pd(OAc)₂, 3.0 mg SDPP, 1 mmol POCl₃ in 5.0 mL of dry DMF), for amidation of different aryl halides and the desired products were obtained in good to excellent yields at 140 °C (Table 3).

Table 2
Optimization of the amounts of SDPP in the amidation reaction of 4-iodotoluene.^a



Entry	Pd(OAc) ₂ (mg)	SDPP (mg)	Time (h)	Yield (%) ^b	TON ^c	TOF (h ⁻¹) ^d
1	3.5	None	10	16	5.1	0.5
2	3.5	3	3:15	85	27	8.3
3	3.5	6	4	86	27.5	6.9
4	3.5	9	5	83	27	5.3
5	3.5	18	10	80	25.6	2.5

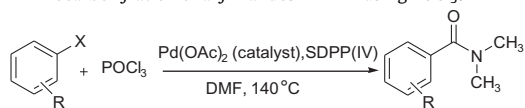
^a Reaction conditions: 4-iodotoluene (0.5 mmol), Pd(OAc)₂ (3.5 mg, 3.1 mol%), POCl₃ (1.0 mmol), DMF (5.0 mL) at 140 °C.

^b Isolated yields.

^c TON = mmol of products/mmol of catalyst.

^d TOF = TON/time.

Table 3
Aminocarbonylation of aryl halides in DMF using POCl_3 .^a



X: I; R: H, NO_2 , CN, CH_3 , OCH_3 , OH

X: Cl, Br; R: H, NO_2 , CN

SDPP(IV): silicadiphenyl phosphinite


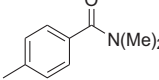

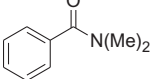
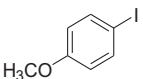
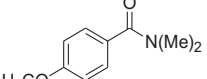
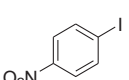
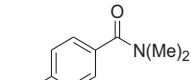
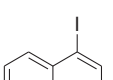
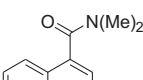

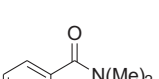

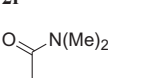
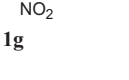
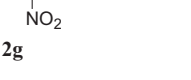
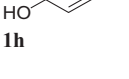
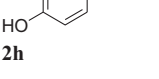
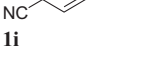
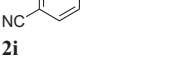

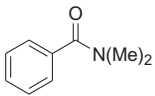
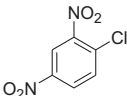
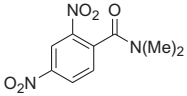
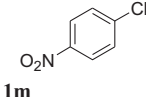
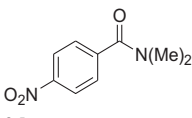
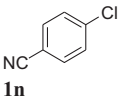
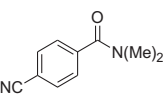

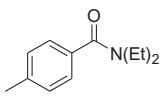
Entry	Reactant	Time (h)	Product	Yield (%) ^b	TON ^c	TOF (h^{-1}) ^f
1	 1a	3:15	 2a	85	27	8.3
2	 1b	2:30	 2b	88	28	11.2
3	 1c	5:45	 2c	80	25.6	4.4
4	 1d	5:15	 2d	73	23.4	4.4
5	 1e	3:10	 2e	78	25	7.8
6	 1f	3:20	 2f	60	19	5.7
7	 1g	24	 2g	51	16	0.68
8	 1h	24	 2h	62	20	0.83
9 ^c	 1i	15	 2i	81	8.6	0.57
10 ^c	 1j	15	 2d	45	5	0.3

Table 3 (Continued)

Entry	Reactant	Time (h)	Product	Yield (%) ^b	TON ^e	TOF (h ⁻¹) ^f
11 ^c	 1k	60	 2b	21	2.2	0.037
12	 1l	4	 2l	70	22	5.6
13 ^c	 1m	60	 2d	41	4.3	0.07
14 ^c	 1n	60	 2i	75	8	0.13
15 ^d	 1a	5	 2o	26	4	0.8

^a Reaction conditions: aryl halide (0.5 mmol), Pd(OAc)₂ (3.5 mg, 3.1 mol%), SDPP (3.0 mg), POCl₃ (1.0 mmol), DMF (5.0 mL) at 140 °C.

^b Isolated yields.

^c Reaction conditions: aryl halide (0.5 mmol), Pd(OAc)₂ (10.0 mg, 9 mol%), SDPP (9.0 mg), POCl₃ (1.0 mmol), DMF (5.0 mL) at 140 °C in sealed tube under vacuum.

^d Reaction conditions: aryl halide (0.5 mmol), Pd(OAc)₂ (7.0 mg, 6.2 mol%), SDPP (6.0 mg), POCl₃ (1.0 mmol), *N,N*-diethylformamide (5.0 mL) at 140 °C.

^e TON = mmol of products/mmol of catalyst.

^f TOF = TON/time.

The cross-coupling reaction proceeded smoothly for iodobenzene and iodobenzenes bearing either an electron withdrawing or an electron donating group at the *para* position (Table 3, entries 1–4, 8). A substituent such as methyl at the *ortho* position has some steric effect and slightly decreases the yield of *N,N*-dimethyl(2-methyl)benzamide (Table 3, entry 6). Since the substrates bearing –NO₂ groups can also produce the dehalogenated product, their amidation product usually is obtained in slightly lower yield (Table 3, entries 4, 7). Aminocarbonylation of sterically hindered 1-iodonaphthalene afforded a good yield of *N,N*-dimethylnaphthamide (Table 3, entry 5). The applicability of this catalytic system was extended to aryl bromides, and chlorides. For these aryl halides, the presence of electron withdrawing groups is necessary to achieve the amide. The coupling

of DMF with 4-cyano and 4-nitro substituted bromo and chloro benzene and also 2,4-dinitrochlorobenzene proceeded successfully (Table 3, entries 9–10, 12–14). For comparison, the reaction of 2,4-dinitrochlorobenzene as a reactive substrate was performed in the absence of SDPP. In this case the reaction was completed, but the reaction time was increased to 6 h. We tried this method for the coupling of *N,N*-diethylformamide with 4-iodotoluene but the obtained yield for the corresponding product was relatively low (Table 3, entry 15).

Table 3 shows the results of aminocarbonylation using Pd(OAc)₂ and SDPP.

In order to show the efficiency of this catalytic system, we compared some of our results with those of the reported methods in the literature using POCl₃ and DMF system (Table 4).

Table 4

Comparison of this method with the literature for aminocarbonylation of 4-iodotoluene and iodobenzene.^a

Entry	Ar-x	Temp. (°C)	Catalyst (mol %)	Time (h)	Isolated yield (%)	Reference
1	4-Iodotoluene	140	Pd(OAc) ₂ /SDPP (3.1)	3:15	85	– ^a
2	4-Iodotoluene	120	Pd ₂ (dba) ₃ (2.5)	20	92	18
3	4-Iodotoluene	140	Pd/C (10)	24	73	19
4	Iodobenzene	140	Pd(OAc) ₂ (10)	24	59 (GC)	19
5	Iodobenzene	140	Pd(OAc) ₂ /SDPP (3.1)	2:30	88	– ^a
6	Iodobenzene	140	Pd/C (10)	24	76	19
7	4-Bromobenzonitrile	140	Pd(OAc) ₂ /SDPP (10)	15	81	– ^a
8	4-Bromobenzonitrile	140	Pd/C (10)	40	78	Our observation
9	4-Bromobenzonitrile	120	Pd ₂ (dba) ₃ (2.5)	–	No reaction	18

^a Present method.

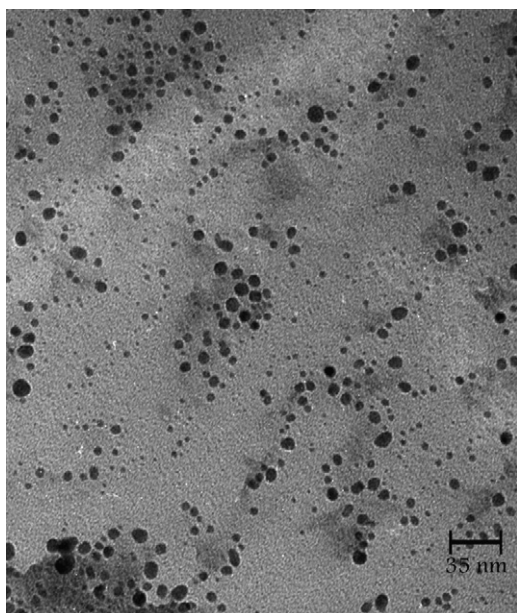


Fig. 1. Transmission electron microscopy (TEM) of Pd-supported SDPP.

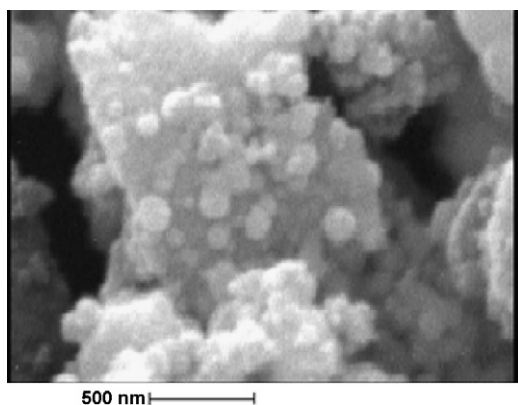


Fig. 2. Scanning electron micrograph (SEM) image of Pd-supported SDPP.

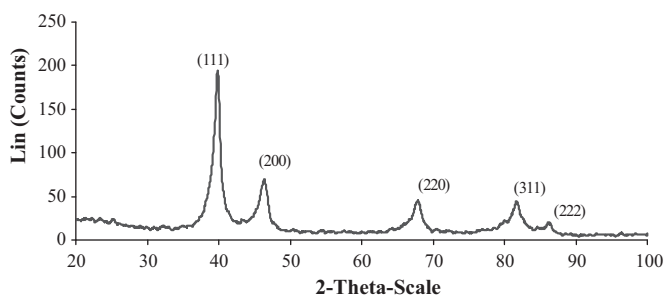


Fig. 3. XRD pattern of Pd-supported SDPP.

Comparison of the present method with the other two reported methods in the literature using the combination of POCl_3 and DMF shows that *in situ* generated SDPP/Pd(0) catalyst is more efficient than Pd/C in terms of reaction time and yield. The presented catalyst; SDPP/Pd(0) can also be applied for amidation of activated aryl bromides, but according to the literature, $\text{Pd}_2(\text{dba})_3$ is inert.

4. Conclusion

In summary, we have introduced that the bonding of $-\text{PPh}_2$ moiety to SiO_2 gives SDPP as a new, stable and easily prepared silicaphosphinite which acts as a suitable heterogeneous ligand for the efficient aminocarbonylation of aryl iodides. The possibility of converting ArX ($\text{X} = \text{Cl}, \text{Br}$) having electron withdrawing groups to their amides can be considered as other advantageous of using this new heterogeneous system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.10.021.

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