



# Diphenylphosphinite ionic liquid (IL-OPPh<sub>2</sub>): A solvent and ligand for palladium-catalyzed silylation and dehalogenation reaction of aryl halides with triethylsilane

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## ABSTRACT

The use of an imidazolium-based phosphinite ionic liquid (IL-OPPh<sub>2</sub>) as both solvent and ligand for Pd offers an efficient catalytic system for silylation of aryl iodides, bromides and also chlorides by triethylsilane in the presence of Cs<sub>2</sub>CO<sub>3</sub>. In the absence of base, this system is also performed for catalytic dehalogenation of aryl halides. The ionic liquid containing its corresponding Pd(0) complex can be easily recovered and reused in several runs without losing its efficiency.

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## 1. Introduction

Arylsilanes are considered as one of the important intermediates in modern organic chemistry, and therefore, numerous synthetic methods have been proposed for their preparation [1]. Traditional synthetic routes to arylsilanes consist of the reaction of silicon electrophiles with aryl Grignard or aryllithium compounds [2–4]. Drawback of this methodology is the limited number of substrates available. Another method is the catalytic conversion of C–H bonds to C–Si bonds in the presence of transition-metal complexes [5,6]. Different research groups separately reported on the transition-metal-catalyzed coupling reaction of aryl halides with trialkoxysilanes [7–11]. Although, trialkylsilanes (e.g., Et<sub>3</sub>SiH) have not been found suitable silylating agent in some catalytic systems [12], recently, their use to attain the silylation of aryl halides under Pd and Pt catalysis have been reported [13,14]. Similar transformation has been achieved using Pd<sub>2</sub>(dba)<sub>3</sub>/P(*o*-tol)<sub>3</sub> and Me<sub>6</sub>Si<sub>2</sub> as a silylating agent [15,16]. Conversion of aryl halides to aryltrialkylsilane by trialkylsilane has also been reported under rhodium catalyzes [17–19]. As part of the recent developments, ionic liquids as green solvents [20,21] have also been considered as potential media for this purpose [22].

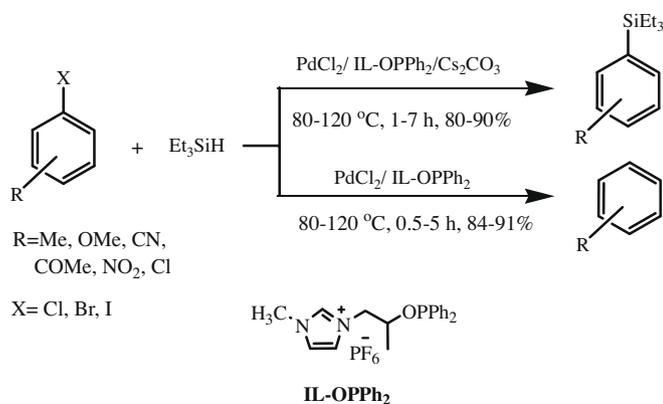
In the continuation of our studies on the use of diphenylphosphinite ionic liquid (IL-OPPh<sub>2</sub>) [23] both as potential complexing agent and also media for Pd(0)-catalyzed reactions [24,25], we now report on its use for the efficient silylation of ArX (X = I, Br, Cl) with triethylsilane in the presence of Cs<sub>2</sub>CO<sub>3</sub> and also dehalogenation of aryl halides in the absence of base at 80–120 °C (Scheme 1).

Among the studied bases for silylation of bromobenzene with PdCl<sub>2</sub> in this ionic liquid, Cs<sub>2</sub>CO<sub>3</sub> was found to be more suitable (Table 1, entry 2). The silylation of aryl halides in the presence of trialkylsilane is competitive with dehalogenation to form the reduced arene. In this reaction, it was observed that in the absence of base, the reduced arene is formed as the major product (Table 1, entry 1). As shown in Table 1, entry 2, the reaction of bromobenzene with Et<sub>3</sub>SiH in the presence of Cs<sub>2</sub>CO<sub>3</sub> gave only 5% benzene as the side product. Therefore, we selected Cs<sub>2</sub>CO<sub>3</sub> as the most suitable base under our optimized reaction conditions for the silylation reaction.

Under our optimized reaction conditions, 0.5 mmole of IL-OPPh<sub>2</sub>, 0.05 mmole of PdCl<sub>2</sub>, 1.5 mmole of Cs<sub>2</sub>CO<sub>3</sub>, and 1.5 mmole of Et<sub>3</sub>SiH, the silylated products were obtained in good yields for a wide array of aryl iodides and bromides at 80 °C and for chlorobenzene at 120 °C. Triethylsilylbenzene and 4-triethylsilyltoluene were obtained in high yields from the reaction of iodobenzene, bromobenzene and 4-bromotoluene, respectively (Table 2, entries 1, 3, 4). The presence of an electron-donating substituent like

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Scheme 1.

**Table 1**  
Effect of different bases on silylation of bromobenzene.<sup>a</sup>

Entry	Base	Time (h)	Silylation (dehalogenation) Conversion <sup>b</sup> (%)
1	None	3	0 (100)
2	Cs <sub>2</sub> CO <sub>3</sub>	2	95 (5)
3	Na <sub>2</sub> CO <sub>3</sub>	3	80 (20)
4	NaOAc	1	85 (15)
5	Et <sub>3</sub> N	1.5	90 (10)

<sup>a</sup> Reaction conditions: 0.5 mmol of IL-OPPh<sub>2</sub>, 0.05 mmole of PdCl<sub>2</sub>, 1.0 mmole of bromobenzene, 1.5 mmole of Et<sub>3</sub>SiH and 1.5 mmole of base.

<sup>b</sup> GC yield of benzene as dehalogenated product is shown in the parentheses.

**Table 2**  
PdCl<sub>2</sub>/IL-OPPh<sub>2</sub>-catalyzed silylation and dehalogenation of aryl halides with Et<sub>3</sub>SiH.

Entry	ArX	Silylation reaction <sup>a</sup>		Dehalogenation reaction <sup>b</sup>	
		Time (h)	Isolated yield <sup>c</sup> (%)	Time (h)	Conversion <sup>d</sup> (isolated) (%)
1		1	85 (7)	0.5	100
2		2	80 (5)	1.5	100 (91)
3		2	85 (5)	1	100
4		2	83 (5)	1.5	100
5		4	80 (8)	4.5	95 (84)
6		5	82 (7)	4	97 (90)
7		6	80 (8)	4	89 (80)
8		5	85 (5)	4	93 (87)
9		5	90 (7)	4.5	90 (85)
10		7	89 (4) <sup>e</sup>	5	88 <sup>e</sup>

<sup>a</sup> The reaction was performed in the presence of Cs<sub>2</sub>CO<sub>3</sub> as the base.

<sup>b</sup> The reaction was performed without adding Cs<sub>2</sub>CO<sub>3</sub>.

<sup>c</sup> GC yield of the dehalogenated product is shown in the parentheses.

<sup>d</sup> GC yield using *n*-octane as an internal standard and the isolated yield is shown in the parentheses.

<sup>e</sup> The reaction was performed at 120 °C.

methoxy on the iodobenzene increased the reaction time from 1 to 2 h (Table 2, entries 1, 2). The longer reaction time of electron-deficient bromides could be due to the lower solubility of these compounds in this ionic liquid (Table 2, entries 5–7). By using 3-bromopyridine and triethylsilane as substrates satisfactory result was obtained and its silylated product was isolated in 90% yield (Table 2, entry 9). Chlorobenzene was also successfully converted into triethylsilylbenzene in the presence of this catalytic system at 120 °C (Table 2, entry 10). Also, the results of dehalogenation of aryl halides in the absence of base are tabulated in Table 2.

The desired products were simply isolated by diethyl ether extraction. Then the remaining mixture which contains the ionic liquid and its corresponding Pd(0) complex was washed with water followed by diethyl ether and dried under vacuum. The presence of Pd(0) in the complex before and after use was studied by X-ray Powder Diffraction. The powder X-ray diffraction (XRD) patterns for the catalyst showed the expected pattern of Pd(0) (Fig. 1). The same results were also obtained for the XRD patterns of the catalysts after its use for at least six cycles in the coupling reaction of bromobenzene with triethylsilane in the presence of Cs<sub>2</sub>CO<sub>3</sub> to give triethyl(phenyl)silane (Table 3). The obtained diffraction rings can be ascribed to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystallographic planes of the Pd(0) particles which reveals the excellent stability and recovery of the catalysts. In addition, the absence of the peak at 420 nm due to Pd(II) supports the complete conversion of Pd(II) to Pd(0).

Although, the exact mechanism of these reactions is not clear, we proposed that the silylation reactions could occur through the generally accepted PdCl<sub>2</sub>/IL-OPPh<sub>2</sub>/base association with generation of the active species Pd(0) followed by the oxidative addition of triethylsilane and aryl halide to give Pd(IV) species (I). In the presence of base, the rapid base-promoted elimination of HX fol-

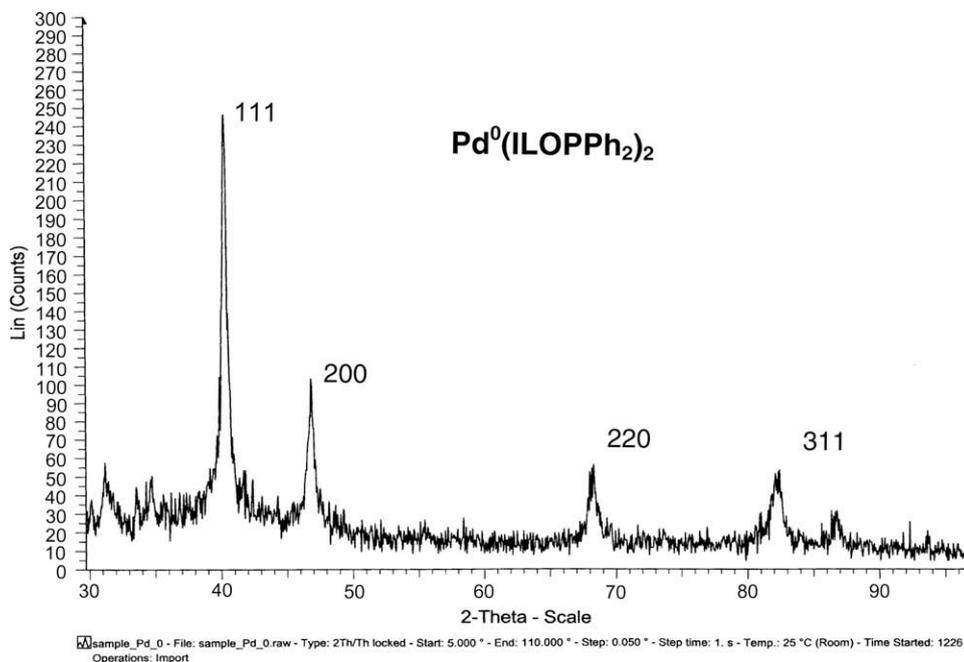
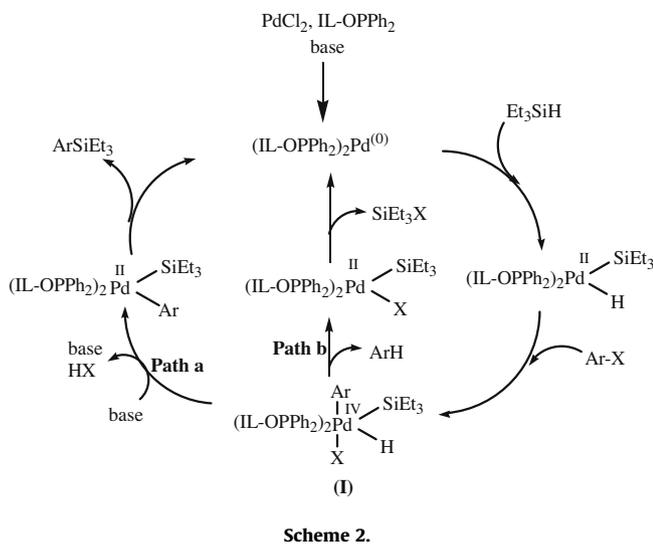


Fig. 1. Powder XRD patterns resulted from the mixture of PdCl<sub>2</sub> and IL-OPPh<sub>2</sub>.



Scheme 2.

lowed by the reductive elimination can offer the silylated product (Ar-SiEt<sub>3</sub>) together with the Pd(0) complex to continue the cycle (Path a). In the absence of base, the reductive elimination of (I) offers ArH and Et<sub>3</sub>SiX (Path b) (Scheme 2). In order to see the effect of produced HX on the silylation process, we performed a reaction between triethyl(phenyl)silane and equimolar of HBr in diphenylphosphinite ionic liquid at 80 °C for 5 h. Monitoring of the reaction did not show the formation of any product and the unreacted triethyl(phenyl)silane was isolated in 81% yield. This result shows that in the silylation process, the produced HX has no effect on the silylated product.

## 2. Conclusion

In summary, the present paper shows that this phosphinite ionic liquid (IL-OPPh<sub>2</sub>) as both the reaction media and ligand for Pd(0) proved to be a recyclable and efficient catalytic system for direct trialkylsilyl transfer to varieties of electron-deficient, electron-

Table 3

Silylation of bromobenzene using recycled ionic liquid and its Pd complex.

Cycle	Conversion (%)	Yield <sup>a</sup> (%)
1	100	85
2	100	83
3	100	80
4	100	80
5	100	82
6	100	82
7	93	74

<sup>a</sup> Isolated yields.

rich and also neutral aryl halides using triethylsilane as silylating reagents in the presence of Cs<sub>2</sub>CO<sub>3</sub>. This catalytic system can also be applied for dehalogenation reaction of aryl halides in the absence of base. The reusability of this phosphinite ionic liquid together with its IL/Pd(0) complex, simplicity of the isolation of the product by extraction in diethyl ether, and the possibility of applying the system to aryl iodides, bromides and chlorides can also be considered as strong practical advantages of this method.

## 3. Experimental

The chemicals were obtained from Fluka or Merck chemical companies and used without further purification. The progress of the reactions was followed with TLC using silica gel SILG/UV 254 plates or GLC on a Shimadzu model GC-10A instrument. IR spectra were run on a Shimadzu FTIR-8300 spectrophotometer. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance DPX-250, FT-NMR spectrometer. X-ray diffractions were obtained using XRD, D8, Avance, Bruker, axs.

### 3.1. Typical procedure for the silylation of bromobenzene with triethylsilane in the presence of PdCl<sub>2</sub>/IL-OPPh<sub>2</sub>

PdCl<sub>2</sub> (0.05 mmole, 8.83 mg) and CsCO<sub>3</sub> (1.5 mmole, 0.29 g) were added to a flask equipped with a condenser containing IL-OPPh<sub>2</sub> (0.5 mmole, 0.23 g). The flask was placed in an 80 °C oil bath and stirred for 15 min. Then Et<sub>3</sub>SiH (1.5 mmole, 0.19 mL) and bro-

mobenzene (1.0 mmole, 0.105 mL) were added to the mixture, respectively. GC and TLC of the reaction mixture showed the completion of the reaction after 2 h. After completion of the reaction, the mixture was cooled to room temperature and triethyl(phenyl)silane was extracted with diethyl ether (3 × 5 mL). Evaporation of the solvent followed by chromatography on a short column of silica gel using *n*-hexane/ethyl acetate (5/1) as eluent gave triethyl(phenyl)silane in 85% yield. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) 7.55–7.50 (m, 3H), 6.88–6.85 (m, 2H), 0.98 (t, 9H, *J* = 7.5 Hz), 0.80 (q, 6H, *J* = 7.5 Hz) ppm; <sup>13</sup>C NMR (60 MHz, CDCl<sub>3</sub>) 142.3, 133.2, 128.1, 126.5, 7.5, 3.4 ppm.

### 3.2. Typical procedure for the dehalogenation of 4-bromoacetophenone with triethylsilane in the presence of PdCl<sub>2</sub>/IL-OPPh<sub>2</sub>

To a flask equipped with a condenser containing IL-OPPh<sub>2</sub> (0.5 mmole, 0.23 g), PdCl<sub>2</sub> (0.05 mmole, 8.83 mg) was added. The flask was placed in an 80 °C oil bath for aryl iodides and bromides and at 120 °C for aryl chlorides and stirred for 15 min. Then, Et<sub>3</sub>SiH (1.5 mmole, 0.19 mL) and 4-bromoacetophenone (1.0 mmole, 0.19 g) were added to the mixture, respectively. GC and TLC analysis of the reaction mixture showed the completion of the reaction after 4 h. After completion of reaction, the mixture was cooled to room temperature and acetophenone was extracted with diethyl ether (3 × 5 mL). Evaporation of the solvent gave the crude product which was purified by chromatography on a short column of silica gel using *n*-hexane/ethyl acetate (5/1) as eluent gave acetophenone in 90% yield. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) 7.86 (d, 2H), 7.37–7.45 (m, 3H), 2.76 (s, 3H) ppm; <sup>13</sup>C NMR (60 MHz, CDCl<sub>3</sub>) 197.5, 136.8, 133.2, 128.7, 128.8, 27.8 ppm.

### 3.3. Typical procedure for the silylation of bromobenzene with triethylsilane in the presence of recycled ionic liquid and its Pd complex

To a flask equipped with a condenser containing recycled ionic liquid and its Pd complex; CsCO<sub>3</sub> (1.5 mmole, 0.29 g), Et<sub>3</sub>SiH (1.5 mmole, 0.19 mL) and bromobenzene (1.0 mmole, 0.105 mL) were added, respectively. The flask was placed in an 80 °C oil bath. GC and TLC of the reaction mixture showed the completion of the reaction after 2 h. After completion of the reaction, the mixture was cooled to room temperature and triethyl(phenyl)silane was extracted with diethyl ether (3 × 5 mL). Evaporation of the solvent

followed by chromatography on a short column of silica gel using *n*-hexane/ethyl acetate (5/1) as eluent gave triethyl(phenyl)silane in 83% yield. The remaining mixture which contains the ionic liquid and its corresponding Pd complex was washed with water (2 mL) followed by diethyl ether (2 mL) and dried in vacuum. The obtained mixture was reused as mentioned above for the next run.

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