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# One-pot palladium-catalyzed phosphination of aryl iodides with $Ph_2PSnR_3$

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**Abstract**

We found a very efficient one-pot phosphination reaction starting with $Ph_3P$, which by reaction with Na metal in liquid ammonia gives $Ph_2P^-$ ions that reacted with $R_3SnCl$ to afford (trialkylstannyl)diphenylphosphine. The palladium-catalyzed coupling reaction of these stannanes with aryl iodides yield functionalized phosphines in high yield (69–97%). The use of $Ph_3P$ as starting reagent, the endurance of the reaction to a wide variety of functional groups and the easiness of a one-pot reaction make this method a useful and versatile approach to tertiary phosphine oxides.


*Keywords:* Tertiary phosphines; Palladium catalysis; P–C cross-coupling

## 1. Introduction

Triarylphosphines are an important type of compound, both as intermediates in organic synthesis and as ligands in transition metal catalyzed reactions. Three general methods involving the formation of a C–P bond are available for the synthesis of phosphines: (i) highly reactive organolithium or organomagnesium compounds, which limit the presence of functionalities in both organometallic reagent and in phosphorus species; (ii) reaction of a $Ph_2P^-$ ions with aryl halides by the $S_{RN}1$ mechanism; or (iii) reaction of phosphines with electrophiles. In this case, the most attractive approach would be transition metal-catalyzed reactions.

Transition metal-catalyzed reactions of aryl halides with organoheteroatom compounds are widely used for the synthesis of different heteroatom-contained compounds [1]. Tertiary phosphines were obtained by nickel-catalyzed cross-coupling of aryl triflates with $Ph_2PCl$ [2] (this method is not tolerant to easy reducible functional groups) or $Ph_2PH$ as phosphinating agents [3].

The palladium-catalyzed coupling reactions are an extremely useful synthetic tool in organic chemistry, which has been used for C–C or C–heteroatom bond formation. However, only few reports of C–P bond formation are known on the synthesis of triarylphosphines by this reaction. The palladium-catalyzed coupling of aryl halides with $Me_3Si–PPh_2$ and $Me_3Sn–PPh_2$ was reported by Stille and coworker [4], but the method has remained largely unexplored. Also, aryl iodides were used in palladium-catalyzed cross-coupling reactions with $Ph_2PH$ to obtain water-soluble phosphines [5]. Other reported methods were the palladium-catalyzed coupling of aryl triflates with $Ph_2P(O)H$ followed by reduction [6]. Recently, the palladium-catalyzed C–P coupling reaction of aryl halides with (hydroxymethyl)phosphines was described [7]. Also, examples of cross-coupling reactions using phosphine–boranes are known [8].

Most of the above methods require the use of air- and moisture-sensitive phosphinating reagents. However, the synthesis of aryl phosphines by palladium-catalyzed phosphination with $Ph_3P$ has been recently reported [9–11]. Phosphination of aryl bromides [9] or aryl triflates [10] using $Ph_3P$ catalyzed by $Pd(OAc)_2$ has

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been developed, and the phosphination of aryl bromides and aryl triflates was catalyzed by a stable catalyst palladium on charcoal [11]. All these methods yield no more than 50% of the triarylphosphines.

Herein, we report the palladium catalyzed cross-coupling phosphination with $R_3SnPPh_2$, using $Ph_3P$ as the initial phosphination agent in a one-pot reaction. Although the $R_3SnPPh_2$ have been known for a long time, and a number of methods for their preparation have been reported [12], their chemistry has not been explored due to inherent difficulties in their preparation and manipulation. Only few examples of its application have been described [4,13]. All the existing methods of preparation include the use of a secondary phosphine as starting material. In this work, we report the $R_3SnPPh_2$ synthesis starting with $Ph_3P$ and their application in organometallic synthesis in a one-pot reaction. This method was found to be compatible with many functional groups.

## 2. Results and discussion

Using $Ph_3P$ as starting material to form $R_3SnPPh_2$, a variety of tertiary phosphines could be obtained by palladium-catalyzed coupling reactions with aryl halides. We found an efficient strategy for the generation and subsequent use of the $R_3SnPPh_2$ in a one-pot reaction. $R_3SnPPh_2$ was formed in almost quantitative yields from $PPh_3$, by the generation of the anion $Ph_2P^-$ with Na metal in dry liquid ammonia and the reaction with trialkyltin chloride. Previously, $R_3SnPPh_2$ was obtained from $Ph_2PH$ with trialkyltin chloride or bromide [11].

In a typical procedure, after formation of the anion $Ph_2P^-$ from $PPh_3$ (1 mmol) and Na metal (2 mmol) in 300 ml dry liquid ammonia under nitrogen atmosphere and after adding *t*-BuOH to neutralize the amide ions formed (Eq. (1)), trialkyltin chloride (1 mmol) was added. After that the ammonia was allowed to evaporate and toluene was added (Eq. (2)). The palladium-catalyzed cross-coupling reaction was carried out with the solution of $R_3SnPPh_2$ in toluene and the aryl halide (0.8 mmol) in the presence of $(PPh_3)_2PdCl_2$ (1.5 mol%) at 80 °C in a Schlenk tube (Eq. (3)). After the indicated reaction time, the phosphine $Ph_2PAr$ was oxidized with $H_2O_2$ (40%) (Eq. (4)). The oxidation was carried out in order to simplify the gas chromatography determinations. All the processes were done in a one-pot reaction.

$$Ph_3P \xrightarrow[\text{b) } t\text{-BuOH}]{\text{a) 2 Na}}{}^{NH_3} Ph_2P^- + PhH + t\text{-}BuO^- \quad (1)$$

$$Ph_2P^- \xrightarrow{R_3SnCl} \overset{NH_3}{\underset{PhMe}{\rightleftharpoons}} Ph_2P\text{-}SnR_3 \quad (2)$$

$$Ph_2P-SnR_3 + ArX \xrightarrow[PhMe]{Pd(0)} Ph_2P-Ar \quad (3)$$

$$Ph_2P-Ar \xrightarrow{H_2O_2} Ph_2P(O)Ar \quad (4)$$

We selected 1-iodonaphthalene (**1**) as model substrate, and the results are presented in Table 1. An excellent result for the reaction was obtained using **1** with *n*-$Bu_3SnPPh_2$, which afforded after oxidation the diphenyl-1-naphthylphosphine oxide (**2**) with total selectivity in 93% yield within 24 h (entry 1, Table 1). No improved rates could be observed at higher temperatures. The activity of the $(PPh_3)_4Pd$ catalyst is similar to the $(PPh_3)_2PdCl_2$ in the phosphination reaction. When the reaction time decreases from 24 to 12 h, the yields were lower (entry 2, Table 1).

The reaction of $Me_3SnPPh_2$ with **1** in the presence of palladium catalyst in the same conditions also afford **2**, but in lower yields (entry 3, Table 1). However, the reaction can be successfully carried out with $Me_3SnPPh_2$ if prior to the addition of $Me_3SnCl$, THF (5 ml) was added to the anion $Ph_2P^-$ (entry 4, Table 1). The difference in reactivity could be explained in terms of the formation of the solid trimethyltin chloride ammoniate [12a] when the liquid ammonia was evaporated and

Table 1
Phosphination of 1-halonaphthalenes with $R_3SnPPh_2$ in the presence of $(PPh_3)_2PdCl_2$ [a]

| Entry | 1-XNaph, X | $R_3SnCl$, R | Product **2** (%) [b] |
|---|---|---|---|
| 1 | I | *n*-Bu | 93 |
| 2 [c] | I | *n*-Bu | 84 |
| 3 | I | Me | 51 |
| 4 [d] | I | Me | 87 |
| 5 [e] | I | Me | 4 |
| 6 | I | – | 5 |
| 7 | Cl | Me | 2 |
| 8 [f] | Br | *n*-Bu | 13 |
| 9 [g] | I | *n*-Bu | 78 |
| 10 [g] | I | Me | 72 |

[a] Reaction conditions: $Ph_2P^-$ anion was prepared in 300 ml liquid ammonia from $Ph_3P$ (1 mmol) and Na metal (2 mmol) and then $R_3SnCl$ (1 mmol) was added. The coupling reaction was carried out with the aryl halide (0.8 mmol) and $(PPh_3)_2PdCl_2$ (1.5 mol%) in toluene at 80 °C for 24 h. The phosphines were oxidized to yield **2**.

[b] CG yields.

[c] Reaction time 12 h.

[d] To the solution of $Ph_2P^-$ ions in liquid ammonia 5 ml of THF was added.

[e] The reaction was carried out without the palladium catalyst.

[f] Reaction temperature 115 °C.

[g] The reaction was carried out with commercially available $Ph_2PK$–THF.

solvent was not present. The solid ammoniate turns the formation of $Me_3SnPPh_2$ less efficient. $Me_3SnPPh_2$ also acts as a promising reagent for introducing the phosphine group to aromatic ring.

When the phosphination reaction was carried out without the palladium catalyst, there was almost no reaction (entry 5, Table 1). The reaction with only $Ph_2P^-$ without the $Me_3SnCl$ under the same conditions above described for the palladium-catalyzed coupling resulted also in no reaction (entry 6, Table 1).

1-Chloronaphthalene is not phosphinated under the standard reaction conditions (entry 7, Table 1). With the bromo derivative almost no reaction of phosphination was observed, even at higher temperature (entry 8, Table 1).

On the other hand, the phosphination reaction could also be carried out with the commercially available $Ph_2PK$ in THF (entries 9 and 10, Table 1). The anion was used as received and the yields were lower than those obtained with the anion prepared in liquid ammonia from $Ph_3P$.

Table 2 shows the results of the reaction of *n*-$Bu_3SnPPh_2$ with various aryl iodides in the presence of a catalytic amount of $(PPh_3)_2PdCl_2$ in a toluene solution. When 4-chloroiodobenzene and 4-bromoiodobenzene were allowed to react, the chloro and bromo containing phosphine oxides **3** and **4** were obtained in very good yields (entries 2 and 3, Table 2). These were expected results because we already knew that chloro and bromo derivatives did not react under these conditions. This remarkable selectivity for the phosphination allowed further transformation in the products on the remaining halide.

In the case of 4-(trifluoromethyl)iodobenzene, [4-(trifluoromethyl)phenyl]diphenylphosphine oxide (**5**) was formed in 90% yield (entry 4, Table 2). Surprisingly, the transformation of the 4-iodoaniline to the corresponding phosphine oxide **6** was successfully carried out even though the substrate has strong coordination ability to the palladium center (entry 5, Table 2). The palladium-catalyzed cross-coupling reaction of stannanes with haloarenes substituted with the amino group gave low yields or no reaction. It is known that the amino group slows down the oxidative addition of palladium(0) [14]. Besides, 2-iodo benzoic acid underwent the phosphination reaction to give the tertiary phosphine oxide **7** in 69% isolated yield (entry 6, Table 2), which showed the phosphination tolerated redox sensitive functional group. Moreover, this method proves to be a good one for the synthesis of water-soluble phosphines.

Table 2
Phosphination of iodoarenes with *n*-$Bu_3SnPPh_2$ in the presence of $(PPh_3)_2PdCl_2$ [a]

| Entry | Substrate | Product | Yields (%) [b] |
|---|---|---|---|
| 1 | **1** | **2** | 93 |
| 2 | *p*-$ClC_6H_4I$ | *p*-$ClC_6H_4P(O)Ph_2$ (**3**) | 97 |
| 3 | *p*-$BrC_6H_4I$ | *p*-$BrC_6H_4P(O)Ph_2$ (**4**) | 93 |
| 4 | *p*-$F_3CC_6H_4I$ | *p*-$F_3CC_6H_4P(O)Ph_2$ (**5**) | 90 |
| 5 | *p*-$H_2NC_6H_4I$ | *p*-$H_2NC_6H_4P(O)Ph_2$ (**6**) | 88 |
| 6 | *o*-$HO_2CC_6H_4I$ | *o*-$HO_2CC_6H_4P(O)Ph_2$ (**7**) | 69 [c] |

[a] Reaction conditions: $Ph_2P^-$ anion was prepared in 300 ml of liquid ammonia from $Ph_3P$ (1 mmol) and Na metal (2 mmol) and then *n*-$Bu_3SnCl$ (1 mmol) was added. The coupling reaction was carried out with the aryl iodide (0.8 mmol) and $(PPh_3)_2PdCl_2$ (1.5 mol%) in toluene at 80 °C for 24 h. The phosphines were oxidized to yield the phosphines oxides **2**–**7**.

[b] GC yields.

[c] Isolated yield.

Although this palladium-catalyzed phosphination tolerated many functional groups, it was found to be incompatible with 4-nitroiodobenzene. The nitro group was reduced to an amino group during the reaction, and this amino did not further react, probably due to the consumption of the reactive. It is known from Fitton work that the oxidative addition of palladium(0) to halonitrobenzenes occur without reduction of the nitro group [15]. In order to determinate if the $R_3SnPPh_2$ compound was able to reduce the nitro group we carried out a reaction with *n*-$Bu_3SnPPh_2$ and 4-nitroiodobenzene in the same conditions as above described without the palladium catalyst. The nitro group was reduced to give the *p*-iodoaniline (52%). The phosphination of 4-iodophenol did not take place and the substrate remained unchanged.

On the other hand, the palladium-catalyzed cross-coupling reaction of organostannanes with aryl triflates is a versatile method for selective C–C bond formation [16]. However, aryl arenesulfonates are more stable and cost less than triflates, there are fewer examples for the palladium-catalyzed cross-coupling reaction with organostannanes [17]. We prepared the 1-naphthyl *p*-methylbenzenesulfonate [17] and performed the cross-coupling palladium-catalyzed phosphination reaction with this substrate. The reaction was carried out in the same conditions as above described for the 1-iodonaphthalene adding to the reaction mixture three equivalents of LiCl [16a]. The conversion of the arylsulfonate into the phosphinated product was only about 30% and substantial amount of the cleavage product 1-naphthol was formed (64%). No improved yields could be observed at higher temperatures or longer reaction times.

Although we did not examine the reaction mechanism in detail, the most probable mechanism of this reaction is likely to be similar to that described by Stille and coworker [4] for the phosphination with $Me_3SiPPh_2$ catalyzed by palladium. The first step involves the reductive elimination of the bisphosphide complex to give the palladium(0) catalyst. Then, the oxidative addition of the aryl iodide to the palladium catalyst generates an aryl palladium(II) iodide species. The

following step is the transmetalation, the ligand exchange between the transition metal and the $R_3SnPPh_2$. The subsequent reductive elimination affords the coupling product and regenerates the palladium(0) catalyst. More recently, Hartwig and coworker [18] proposed concerning to transfer of heteroatom nucleophiles of a stoichiometric reaction that the ligand exchanges between the palladium(II) complex and tin constitute an unusual type of dissociative ligand substitution and that these transmetalation was endothermic and reversible under some reactions conditions.

In conclusion, during the course of our ongoing study on the palladium-catalyzed phosphination, we found a very efficient one-pot reaction starting with $Ph_3P$ and via $R_3SnPPh_2$. In addition, a variety of functionalized phosphines could be prepared by a simple phosphination of aryl iodides by palladium-catalyzed cross-coupling reaction. The use of $Ph_3P$ as starting reagent, the endurance of the reaction to a wide variety of functional groups and the easiness of a one-pot reaction method have shown to be a useful and versatile approach to tertiary phosphines.

## 3. Experimental

### 3.1. General methods

Unless otherwise stated, the NMR spectra were obtained in $CDCl_3$. The multiplicity reported in the $^{13}C$-NMR spectra refer to the $^{31}P$–$^{13}C$ coupling. Column chromatography was performed on silica gel (70–270 mesh ASTM). The substrates, $(PPh_3)_2PdCl_2$, $(PPh_3)_4Pd$, $Me_3SnCl$, $n$-$Bu_3SnCl$, $Ph_3P$ and $Ph_2PK$–THF were commercially available and used as received. $p$-Iodonitrobenzene was obtained from the corresponding $p$-nitroaniline [4]. Naphthyl tosylate was prepared as previously reported from the corresponding phenol [17]. Toluene and THF were distilled under nitrogen from Na–benzophenone. All reactions were carried out under atmosphere of nitrogen.

### 3.2. General procedure for preparation of aryldiphenylphosphine oxides from aryl iodides

The following procedure is representative of these reactions. Ammonia (300 ml), previously dried over Na metal, was distilled into a 500 ml three-neck round-bottom flask with a cold finger condenser and a magnetic stirrer. To the $NH_3$ were added $Ph_3P$ (1 mmol) and then Na metal (2 mmol) in small pieces. The addition of Na metal continued until the blue solution from solvated electrons in excess remained for 20 min before it became orange–brown and no more solid was present. To this solution was added $t$-BuOH to decolorize and then 1 mmol extra to neutralize the amide ion formed. After that $Ph_2P^-$ anion was ready for use (clear orange solution) $n$-$Bu_3SnCl$ (1 mmol) was added slowly, the mixture was stirred for 5 min and then $NH_3$ was allowed to evaporate. Evaporation left a solid white residue, which was dissolved in dry $C_6H_5CH_3$ (30 ml). This solution was added via a cannula and syringe into a Schlenck tube. In the tube was previously placed $(PPh_3)_2PdCl_2$ (0.015 mmol), it was evacuated and filled with nitrogen three times, then 1-iodonaphthalene (0.8 mmol) and $C_6H_5CH_3$ (5 ml) were added. When the $n$-$Bu_3SnPPh_2$ solution was added, the reaction mixture turned deep brown. The reaction mixture was heated for 24 h in an oil bath at 80 °C. To the cool reaction mixture water was added and then extracted three times with $CH_2Cl_2$ (30 ml each). The organic phase was oxidized with aq. $H_2O_2$ (75 ml 40%) by following a previously described procedure [19]. After drying with anhydrous $MgSO_4$, the products were quantified by GC using the internal standard method. Diphenyl-1-naphtylphosphine oxide was purified by chromatography ($C_6H_{14}$–EtOAc) to give a white solid, m.p. 178–179 °C (lit. [20] m.p. 178–179 °C). $^1H$-NMR (200 MHz): $\delta$ 8.52 (d, $J$ = 7.67 Hz, 1H), 8.00 (d, $J$ = 7.31 Hz, 1H), 7.88 (d, $J$ = 8.04 Hz, 1H), 7.74–7.24 (m, 14H). $^{13}C$-NMR (60 MHz): $\delta$ 133.98, 133.90, 133.72 (d, $J$ = 12.21 Hz), 133.24 (d, $J$ = 4.07 Hz), 132.06 (d, $J$ = 10.85 Hz), 131.85 (d, $J$ = 2.72 Hz), 128.95 (d, $J$ = 101.73 Hz), 128.55 (d, $J$ = 12.20 Hz), 127.62 (d, $J$ = 5.43 Hz), 127.32, 126.46 (bs), 124.11 (d, $J$ = 13.56 Hz). MS (%): $m/e$ 328 (32), 327 (100), 249 (23), 202 (15), 127 (7), 77 (13), 51 (7).

#### 3.2.1. (4-Chlorophenyl)diphenylphosphine oxide (**3**, entry 2, Table 2)

White solid, m.p. 140–141 °C (lit. [21] 143–144 °C). $^1H$-NMR (200 MHz): $\delta$ 7.71–7.41 (m, 14H). $^{13}C$-NMR (60 MHz): $\delta$ 138.56 (d, $J$ = 2.71 Hz), 133.45 (d, $J$ = 9.50 Hz), 133.17, 132.09, 132.02 (d, $J$ = 12.21 Hz), 131.09, 128.96, 128.72, 128.45. MS (%): $m/e$ 314 (33), 312 (100), 277 (9), 237 (5), 235 (14), 201 (9), 183 (17), 152 (15), 77 (42), 51 (19).

#### 3.2.2. (4-Bromophenyl)diphenylphosphine oxide (**4**, entry 3, Table 2)

White solid, m.p. 151–153 °C (lit. [21] 154–156 °C). $^1H$-NMR (200 MHz): $\delta$ 7.70–7.41 (m, 14H). $^{13}C$-NMR (60 MHz): $\delta$ 133.57 (d, $J$ = 10.85 Hz), 133.93 (d, $J$ = 16.27 Hz), 132.14, 132.09, 131.90, 131.66, 130.86 (d, $J$ = 14.92 Hz), 128.60 (d, $J$ = 12.21 Hz), 127.15 (d, $J$ = 4.06 Hz). MS (%): $m/e$ 359/357 (100), 277 (42), 201 (19), 183 (37), 152 (31), 77 (72), 51 (32).

#### 3.2.3. [4-(Trifluoromethyl)phenyl]diphenylphosphine oxide (**5**, entry 4, Table 2)

Obtained as a solid, m.p. 89–91 °C (lit. [22] 90.5–91.2 °C). $^1H$-NMR (200 MHz): $\delta$ 7.78–7.20 (m, 14H). $^{13}C$-NMR (60 MHz): $\delta$ 137.08 (d, $J$ = 100.37 Hz),

133.52 (dd, $J = 10.85$, $J_{CF} = 32.55$ Hz), 132.50, 132.31, 132.23, 132.17, 131.85 (d, $J = 10.85$ Hz), 131.44, 128.58 (d, $J = 12.21$ Hz), 125.41–125.00 (m), 117.54 (d, $J_{CF} = 320.09$ Hz). MS (%): *m/e* 346 (36), 345 (100), 327 (2), 277 (2), 269 (8), 201 (17), 183 (12), 152 (11), 77 (40), 69 (2), 51 (17).

### 3.2.4. 4-(Diphenyl–phosphinoyl)phenylamine (*6*, entry 5, Table 2)

Solid, m.p. 237–238 °C (lit. [23] 238–239 °C). $^1$H-NMR (200 MHz): $\delta$ 7.73–7.34 (m, 12H), 6.67 (dd, $J =$ 2.38, 8.59 Hz, 2H), 4.06 (bs, 2H). $^{13}$C-NMR (60 MHz): $\delta$ 149.90 (d, $J = 2.71$ Hz), 133.79 (d, $J = 10.85$ Hz), 133.71, 132.14, 131.96, 131.63, 131.58, 128.45, 128.21, 114.41, 114.17. MS (%): *m/e* 293 (88), 292 (100), 277 (4), 216 (35), 200 (26), 183 (13), 169 (13), 152 (7), 77 (19), 51 (12).

### 3.2.5. 2-(Diphenyl–phosphinoyl)benzoic acid (*7*, entry 6, Table 2)

For isolation of the product the reaction solvent was removed under vacuum and the residue obtained was dissolved in 15 ml of water. After addition of KOH (2.02 mmol) the solution was extracted three times with $CH_2Cl_2$. The aqueous solution was acidified with HCl 2 N and again extracted with $CH_2Cl_2$. The collected organic phases were washed with water, dried over $MgSO_4$ and evaporated. The residue was recrystallized from MeOH–water. Solid, m.p. 266–270 °C (lit. [24] 268–272 °C). $^1$H-NMR ($Me_2SO$-$d_6$, 200 MHz): $\delta$ 13.23 (bs, 1H), 8.70–8.75 (m, 1H), 7.30–8.24 (m, 13H). $^{13}$C-NMR ($Me_2SO$-$d_6$, 60 MHz): $\delta$ 171.90, 133.95, 133.76, 133.51, 133.33, 132.55, 132.17, 131.31, 131.09, 130.20, 130.08.

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