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One-Pot Palladium-Catalyzed Cross-Coupling Reaction of Aryl Iodides with Stannylarsanes and Stannylstibanes

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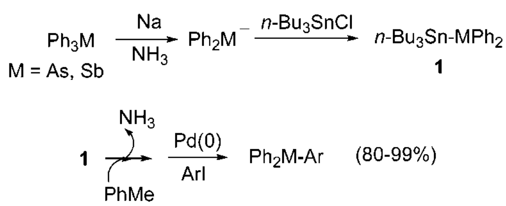
ABSTRACT



The reaction of Ph_3As and Ph_3Sb with Na metal in liquid ammonia gives Ph_2M^- ions (M = As, Sb) that react with *n*-Bu_3SnCl to afford *n*-Bu_3Sn-MPh_2 (1). The ammonia was allowed to evaporate, and toluene was added. The Pd-catalyzed cross-coupling reactions of these stannanes with aryl iodides afford functionalized triaryl-arsanes and triaryl-stibanes in high yields in a one-pot procedure (80–99%). The use of the commercially available, air-stable, and inexpensive Ph_3M as the initial reagent and the one-pot process make this method a useful approach. This is the first report on the synthesis of 1 and the exploration of its chemistry.

Transition metal-catalyzed reactions of aryl halides with organoheteroatom compounds are widely used for the synthesis of different heteroatom-containing compounds.[1] Organotin compounds are extensively utilized as nucleophiles in cross-coupling reactions with the formation of C−C, C−N, C−P, C−S, and C−Sn bonds.[2] The Pd-catalyzed coupling of alkyl and aryl halides or triflates with organostannanes (the Stille reaction) is a powerful tool in organic synthesis.[2a] Although the scope of the Pd(0)-catalyzed cross-coupling reactions of group-XV-derived organostannanes such as aminostannanes[3] and (trialkylstannyl)diphenylphosphanes[4,5] have been studied, the use of organotin-arsanes and organotin-stibanes to form C−As and C−Sb bonds has not been reported. To extend the applications of this already powerful methodology, we studied the Pd-catalyzed cross-coupling reaction of stannanes derived from arsenic and antimony [*n*-Bu_3Sn-MPh_2 (**1**), M = As (**1a**), Sb (**1b**)] with aryl iodides.

The chemistry of organoarsanes and organostibanes, analogues of organophosphanes, has been extensively developed, and the uses of these compounds in organic synthesis are of current interest.[6] They are an important class of compounds, both as intermediates in organic synthesis and as ligands in transition metal-catalyzed reactions. Arsanes have been reported to be more appropriate ligands than

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phosphanes in a number of transition metal-catalyzed organic reactions.[7] Synthetic applications of organostibane compounds are of increasing importance.[8] Such compounds have been used as efficient reagents in palladium-catalyzed C−C bond formation.[9]

Methods for preparation of tertiary arsanes and stibanes involve the reaction of organolithium or organomagnesium reagents with haloarsanes or halostibanes, reactions incompatible with many functional groups.[10,11] Another method is the reaction of aryl halides with R_2MLi/Na (M = As, Sb), prepared in situ, generally in liquid ammonia.[7a,12,13] Also, triaryl-arsanes and triaryl-stibanes were obtained by the photostimulated reactions of Ph_2As^- and Ph_2Sb^- ions with aryl halides by an $S_{RN}1$ mechanism in liquid ammonia, but scrambling of products was observed.[14] Shibasaki and coworkers described the catalyzed arsination using Ni(0) and Ph_2AsH.[7b] A synthesis of arsane sulfonic acids from 4-fluorobenzenesulfonate with $KAsPh_2$ was also described.[15]

The only straightforward method for functionalized arsanes has been recently reported, a catalytic, solvent-free, Pd-catalyzed aryl-aryl exchange reaction from phosphorus to arsenic. This method yields only 51% of the triaryl-arsanes.[16]

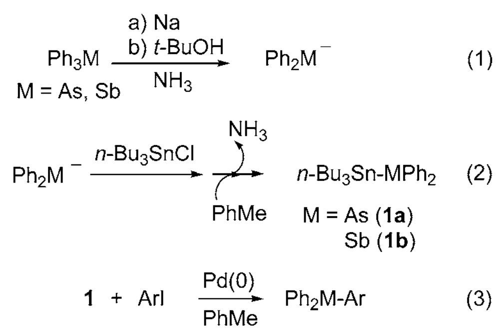
A new approach has recently been established for the preparation of Sb-chiral stibanes based on nucleophilic displacement of phenylethyl moieties in bis-ethynylstibane with Grignard and/or organolithium reagents.[17] Allylic arsanes and stibanes were obtained by allylation of arsenic and antimony trihalides by allylic stannanes.[18] Tertiary stibane containing heterocyclic aromatic groups were obtained from $SbCl_3$ and the organolithium reagents from the heterocycles.[19]

We herein report the Pd-catalyzed cross-coupling reaction of **1** using Ph_3M as the initial reagent in a one-pot process to obtain triaryl-functionalized arsanes and stibanes. This is the first report on the synthesis of **1** and the exploration of its chemistry.

We found an efficient strategy for the generation and subsequent use of **1** according to the procedure previously reported by us for the synthesis of tertiary phosphanes by Pd-catalyzed reaction of aryl iodides with $R_3Sn{-}PPh_2$ in a one-pot process.[5] Reagent **1** was formed in almost quantitative yield by the reaction of Ph_2M^- anion (generated from Ph_3M and Na metal in liquid ammonia) with *n*-Bu_3SnCl. To the best of our knowledge, this is the first report on the formation of organostannanes with arsines and stibines.

A typical procedure[20] involves the formation of Ph_2M^- ions from Ph_3M and Na metal in liquid ammonia (eq 1), followed by addition of *n*-Bu_3SnCl to obtain the *n*-Bu_3Sn-MPh_2 (eq 2). The Pd-catalyzed cross-coupling reaction was carried out with **1** and the aryl iodide in the presence of $(PPh_3)_2PdCl_2$ (eq 3). All the processes were done in a one-pot reaction under nitrogen (Scheme 1).

Scheme 1



We used *n*-Bu_3SnCl to obtain the stannane because, as discussed earlier in the phosphination reaction,[5] under the same conditions, the reaction of $Me_3Sn{-}PPh_2$ with 1-iodonaphthalene (**2**) in the presence of Pd catalyst affords the product in lower yields. Otherwise, tributylstannane derivatives are usually preferred because of their lower cost and

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(20) Typical procedure involves the formation of Ph_2M^- ions from Ph_3M (1 mmol) and Na metal (2 mmol) in 300 mL of dry liquid ammonia, and after addition of *t*-BuOH to neutralize the amide ions formed, *n*-Bu_3SnCl (1 mmol) was added. The ammonia was allowed to evaporate, and toluene was added. The Pd-catalyzed cross-coupling reaction was carried out with the solution of **1** in 25 mL of toluene and the aryl iodide (0.7 mmol) in the presence of $(PPh_3)_2PdCl_2$ (1.5 mol %) at 80 °C in a Schlenk tube. All processes were done in a one-pot reaction under nitrogen.

lower toxicity when compared with trimethylstannane derivatives.[2a]

We selected **2** as the model substrate, and the results are presented in Table 1. The reaction of **1a** with **2** catalyzed by $(PPh_3)_2PdCl_2$ afforded naphthalen-1-yl-diphenyl-arsane[21] with total selectivity in 85% yield in 24 h (entry 1, Table 1). The system was shown to be reasonably effective, since only 1.5 mol % of the Pd catalyst was used. No improved yields could be observed at higher temperatures.

Table 1. Reaction of **1** with **2** and $(PPh_3)_2PdCl_2$ as the Catalyst[a]

entry	reagent	catalyst	1-naphthylMPh$_2$ (% yield)[b]
1	**1a**	$(PPh_3)_2PdCl_2$	85
2	Ph_2As^-	$(PPh_3)_2PdCl_2$	10
3	**1a**		9
4[c]	**1a**	$(PPh_3)_2PdCl_2$	68
5	**1b**	$(PPh_3)_2PdCl_2$	62
6	**1b**	$(PPh_3)_2PdCl_2/Ph_3P$ [d]	80
7	Ph_2Sb^-	$(PPh_3)_2PdCl_2$	7
8	**1b**		10

[a] Reaction conditions: Ph_2M^- anion was prepared in 300 mL of liquid ammonia from Ph_3M (1 mmol) and Na metal (2 mmol), and then n-Bu_3SnCl (1 mmol) was added. The coupling reaction was carried out with **2** (0.7 mmol) and $(PPh_3)_2PdCl_2$ (1.5 mol %) in toluene at 80 °C for 24 h. [b] GC yields. [c] Electrophile was 1-naphthyl-trifluoromethanesulfonate. [d] Reaction was carried out with $(PPh_3)_2PdCl_2$ and PPh_3 as the ligand in a ratio 1:4; total Pd:L = 1:6.

We also examined the activity of the $(PPh_3)_4Pd$ catalyst. The results were found to be similar to those with $(PPh_3)_2PdCl_2$ as a catalyst.

It should be noticed that the reaction with only Ph_2As^- ions, but without n-Bu_3SnCl and under the same experimental conditions described above for the Pd-catalyzed cross-coupling reaction, affords only 10% yield of product. When the reaction was carried out without the Pd catalyst, there was almost no reaction (entries 2 and 3, Table 1).

The Pd-catalyzed cross-coupling reaction of organostannanes with aryl triflates is a versatile method for selective C−C bond formation.[22] The reaction of 1-naphthyl trifluoromethanesulfonate under the same reaction conditions as previously indicated, but adding to the reaction mixture 3 equiv of LiCl[23] and PPh_3 as ligand, affords naphthalen-1-yl-diphenyl-arsane in 68% yield. Without addition of LiCl, the reaction did not take place. No improved yields were observed at higher temperatures or longer reaction times.

On the other hand, the Pd-catalyzed coupling reaction can also be successfully performed with **1b** to obtain the corresponding triaryl-stibanes. The reaction of **1b** and **2** catalyzed by $(PPh_3)_2PdCl_2$ affords naphthalen-1-yl-diphenyl-stibane[24] in moderate yields (entry 5, Table 1). The observation of an important ligand effect in the Stille reaction and, in particular, the remarkable catalytic activity displayed by a Pd catalyst employing phosphines as ancillary ligands[25] promoted us to undertake the reaction with PPh_3 as a ligand for the catalyst. When this ligand was added to the reaction (1:4 with respect to the catalyst, total Pd:L = 1:6), the system became more efficient and the yield of the product increased (entry 6, Table 1). We have not done kinetic studies, so we could not address the benefit of the excess PPh_3 with respect to either a faster rate of reaction or the catalyst stability.

When the reaction was carried out without n-Bu_3SnCl, the conversion of the substrate was only about 7%. When the reaction was carried out without the Pd catalyst, only 10% yield of the product was afforded (entries 7 and 8, Table 1).

Substituted aryl iodides afford triaryl-arsane and triaryl-stibane compounds in very good yields, regardless of the electronic nature of the substituent. Table 2 shows the results of the reaction of **1** with aryl iodides in the presence of a catalytic amounts of $(PPh_3)_2PdCl_2$. Aryl bromides and chlorides do not react by these coupling reactions, as in the phosphination reaction.[5]

Table 2. Syntheses of Functionalized Triaryl-arsanes and Triaryl-stibanes from Iodoarenes and **1** with $(PPh_3)_2PdCl_2$ as the Catalyst[a]

entry	1	substrate	product	% yield[b]
1	**1a**	$4\text{-}MeOC_6H_4I$	$4\text{-}MeOC_6H_4AsPh_2$	98
2	**1a**	$4\text{-}ClC_6H_4I$	$4\text{-}ClC_6H_4AsPh_2$	50
3[c]	**1a**	$4\text{-}ClC_6H_4I$	$4\text{-}ClC_6H_4AsPh_2$	90
4	**1b**	$4\text{-}MeOC_6H_4I$	$4\text{-}MeOC_6H_4SbPh_2$	63
5[d]	**1b**	$4\text{-}MeOC_6H_4I$	$4\text{-}MeOC_6H_4SbPh_2$	99
6	**1b**	$4\text{-}ClC_6H_4I$	$4\text{-}ClC_6H_4SbPh_2$	72
7[c]	**1b**	$4\text{-}ClC_6H_4I$	$4\text{-}ClC_6H_4SbPh_2$	57
8[d]	**1b**	$4\text{-}ClC_6H_4I$	$4\text{-}ClC_6H_4SbPh_2$	98

[a] Reaction conditions: Ph_2M^- anion was prepared in 300 mL of liquid ammonia from Ph_3M (1 mmol) and Na metal (2 mmol), and then n-Bu_3SnCl (1 mmol) was added. The coupling reaction was carried out with the iodoarene (0.7 mmol) and $(PPh_3)_2PdCl_2$ (1.5 mol %) in toluene at 80 °C for 24 h. [b] GC yields. [c] DMF at 100 °C for 24 h. [d] Reaction was carried out with $(PPh_3)_2PdCl_2$ and PPh_3 as the ligand in a ratio 1:4; total Pd:L = 1:6.

The reaction can successfully be carried out with 4-methoxyiodobenzene. The (4-methoxyphenyl)diphenyl-arsane[16] was formed in 98% yield (entry 1, Table 2). When 4-chloroiodobenzene was allowed to react under the same experimental conditions, the (4-chlorophenyl)diphenyl-arsane[26] was obtained in moderate yields. To improve the product yield, we carried out the reaction with DMF as the solvent and a

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higher temperature (100 °C). Under these conditions, 90% of the product was obtained (entries 2 and 3, Table 2).

4-Methoxyiodobenzene reacts with **1b** to give (4-methoxyphenyl)diphenyl-stibane[20] in 63% yield. However, when we carried out the reaction with PPh_3 as the ligand, the product was obtained in 99% yield (entries 4 and 5, Table 2). As previously discussed for the arsination reaction, when 4-chloroiodobenzene was allowed to react with **1b** under the same experimental conditions, (4-chlorophenyl)diphenyl-stibane[27] was obtained in moderate yield; the yield was not improved when the reaction was conducted in DMF at a higher temperature. The transformation of 4-chloroiodobenzene to the corresponding triaryl-stibane was successfully carried out using PPh_3 as the ligand (entries 6−8, Table 2). The general reaction conditions for the Pd-catalyzed cross-coupling reaction of different aryl iodides with **1b** to obtain triaryl-stibanes in good yields required PPh_3 as an ancillary ligand.

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[4] for the phosphination with $Me_3Si{-}PPh_2$ catalyzed by Pd(0). The first step involves the catalyst activation of the phosphine complex to give the Pd(0) catalyst. Then, the oxidative addition of the aryl iodide to the Pd catalyst generates an arylpalladium iodide species. Next, transmetalation of this complex with **1** generates the aryl−Pd intermediate, which subsequently suffers reductive elimination to afford the coupling product and regenerates the Pd(0) catalyst.

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In summary, the first Pd-catalyzed cross-coupling reaction of aryl iodides with **1** was successfully carried out to yield functionalized triaryl-arsanes and triaryl-stibanes. We found a very efficient one-pot reaction starting with the commercially available, air-stable and inexpensive triphenyl-arsane and triphenyl-stibane to synthesize **1a** and **1b**, respectively. Once more, the specificity of the organotin compounds on transition metal catalysis can be realized, and of note is the fact that the reaction can be carried out in the presence of different functional groups.

Further studies are in progress to extend the application of this methodology to the synthesis of functionalized triaryl-arsanes and triaryl-stibanes ligands.

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Supporting Information Available: Experimental procedures and spectroscopic data (^{1}H NMR and ^{13}C NMR) for compounds mentioned herein. This material is available free of charge via the Internet at http://pubs.acs.org.

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