



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

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.<sup>10,11</sup> Another method is the reaction of aryl halides with R<sub>2</sub>MLi/Na (M = As, Sb), prepared in situ, generally in liquid ammonia.<sup>7a,12,13</sup> Also, triaryl-arsanes and triaryl-stibanes were obtained by the photostimulated reactions of Ph<sub>2</sub>As<sup>–</sup> and Ph<sub>2</sub>Sb<sup>–</sup> ions with aryl halides by an S<sub>RN</sub>1 mechanism in liquid ammonia, but scrambling of products was observed.<sup>14</sup> Shibasaki and co-workers described the catalyzed arsination using Ni(0) and Ph<sub>2</sub>AsH.<sup>7b</sup> A synthesis of arsane sulfonic acids from 4-fluorobenzenesulfonate with KAsPh<sub>2</sub> was also described.<sup>15</sup>

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.<sup>16</sup>

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.<sup>17</sup> Allylic arsanes and stibanes were obtained by allylation of arsenic and

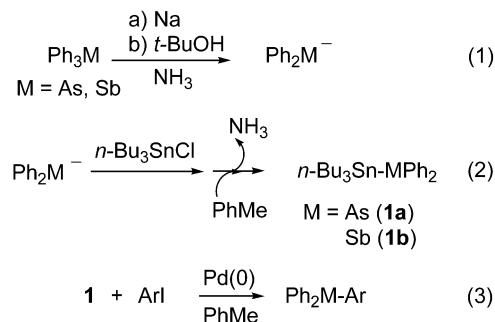
antimony trihalides by allylic stannanes.<sup>18</sup> Tertiary stibane containing heterocyclic aromatic groups were obtained from SbCl<sub>3</sub> and the organolithium reagents from the heterocycles.<sup>19</sup>

We herein report the Pd-catalyzed cross-coupling reaction of **1** using Ph<sub>3</sub>M 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<sub>3</sub>Sn–PPh<sub>2</sub> in a one-pot process.<sup>5</sup> Reagent **1** was formed in almost quantitative yield by the reaction of Ph<sub>2</sub>M<sup>–</sup> anion (generated from Ph<sub>3</sub>M and Na metal in liquid ammonia) with *n*-Bu<sub>3</sub>SnCl. To the best of our knowledge, this is the first report on the formation of organostannanes with arsines and stibines.

A typical procedure<sup>20</sup> involves the formation of Ph<sub>2</sub>M<sup>–</sup> ions from Ph<sub>3</sub>M and Na metal in liquid ammonia (eq 1), followed by addition of *n*-Bu<sub>3</sub>SnCl to obtain the *n*-Bu<sub>3</sub>Sn–MPh<sub>2</sub> (eq 2). The Pd-catalyzed cross-coupling reaction was carried out with **1** and the aryl iodide in the presence of (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> (eq 3). All the processes were done in a one-pot reaction under nitrogen (Scheme 1).

Scheme 1



We used *n*-Bu<sub>3</sub>SnCl to obtain the stannane because, as discussed earlier in the phosphination reaction,<sup>5</sup> under the same conditions, the reaction of Me<sub>3</sub>Sn–PPh<sub>2</sub> 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<sub>2</sub>M<sup>–</sup> ions from Ph<sub>3</sub>M (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<sub>3</sub>SnCl (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<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> (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.<sup>2a</sup>

We selected **2** as the model substrate, and the results are presented in Table 1. The reaction of **1a** with **2** catalyzed

**Table 1.** Reaction of **1** with **2** and (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> as the Catalyst<sup>a</sup>

entry	reagent	catalyst	1-naphthylMPh <sub>2</sub> (% yield) <sup>b</sup>
1	<b>1a</b>	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	85
2	Ph <sub>2</sub> As <sup>−</sup>	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	10
3	<b>1a</b>		9
4 <sup>c</sup>	<b>1a</b>	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	68
5	<b>1b</b>	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	62
6	<b>1b</b>	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub> /Ph <sub>3</sub> P <sup>d</sup>	80
7	Ph <sub>2</sub> Sb <sup>−</sup>	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	7
8	<b>1b</b>		10

<sup>a</sup> Reaction conditions: Ph<sub>2</sub>M<sup>−</sup> anion was prepared in 300 mL of liquid ammonia from Ph<sub>3</sub>M (1 mmol) and Na metal (2 mmol), and then *n*-Bu<sub>3</sub>SnCl (1 mmol) was added. The coupling reaction was carried out with **2** (0.7 mmol) and (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> (1.5 mol %) in toluene at 80 °C for 24 h. <sup>b</sup> GC yields. <sup>c</sup> Electrophile was 1-naphthyl-trifluoromethanesulfonate. <sup>d</sup> Reaction was carried out with (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> and PPh<sub>3</sub> as the ligand in a ratio 1:4; total Pd:L = 1:6.

by (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> afforded naphthalen-1-yl-diphenyl-arsane<sup>21</sup> 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.

We also examined the activity of the (PPh<sub>3</sub>)<sub>4</sub>Pd catalyst. The results were found to be similar to those with (PPh<sub>3</sub>)<sub>2</sub>-PdCl<sub>2</sub> as a catalyst.

It should be noticed that the reaction with only Ph<sub>2</sub>As<sup>−</sup> ions, but without *n*-Bu<sub>3</sub>SnCl 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.<sup>22</sup> The reaction of 1-naphthyl trifluoromethanesulfonate under the same reaction conditions as previously indicated, but adding to the reaction mixture 3 equiv of LiCl<sup>23</sup> and PPh<sub>3</sub> 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<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> affords naphthalen-1-yl-diphenyl-stibane<sup>24</sup> 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<sup>25</sup> promoted us to undertake the reaction with PPh<sub>3</sub> 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<sub>3</sub> with respect to either a faster rate of reaction or the catalyst stability.

When the reaction was carried out without *n*-Bu<sub>3</sub>SnCl, 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

**Table 2.** Syntheses of Functionalized Triaryl-arsanes and Triaryl-stibanes from Iodoarenes and **1** with (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> as the Catalyst<sup>a</sup>

entry	<b>1</b>	substrate	product	% yield <sup>b</sup>
1	<b>1a</b>	4-MeOC <sub>6</sub> H <sub>4</sub> I	4-MeOC <sub>6</sub> H <sub>4</sub> AsPh <sub>2</sub>	98
2	<b>1a</b>	4-ClC <sub>6</sub> H <sub>4</sub> I	4-ClC <sub>6</sub> H <sub>4</sub> AsPh <sub>2</sub>	50
3 <sup>c</sup>	<b>1a</b>	4-ClC <sub>6</sub> H <sub>4</sub> I	4-ClC <sub>6</sub> H <sub>4</sub> AsPh <sub>2</sub>	90
4	<b>1b</b>	4-MeOC <sub>6</sub> H <sub>4</sub> I	4-MeOC <sub>6</sub> H <sub>4</sub> SbPh <sub>2</sub>	63
5 <sup>d</sup>	<b>1b</b>	4-MeOC <sub>6</sub> H <sub>4</sub> I	4-MeOC <sub>6</sub> H <sub>4</sub> SbPh <sub>2</sub>	99
6	<b>1b</b>	4-ClC <sub>6</sub> H <sub>4</sub> I	4-ClC <sub>6</sub> H <sub>4</sub> SbPh <sub>2</sub>	72
7 <sup>c</sup>	<b>1b</b>	4-ClC <sub>6</sub> H <sub>4</sub> I	4-ClC <sub>6</sub> H <sub>4</sub> SbPh <sub>2</sub>	57
8 <sup>d</sup>	<b>1b</b>	4-ClC <sub>6</sub> H <sub>4</sub> I	4-ClC <sub>6</sub> H <sub>4</sub> SbPh <sub>2</sub>	98

<sup>a</sup> Reaction conditions: Ph<sub>2</sub>M<sup>−</sup> anion was prepared in 300 mL of liquid ammonia from Ph<sub>3</sub>M (1 mmol) and Na metal (2 mmol), and then *n*-Bu<sub>3</sub>SnCl (1 mmol) was added. The coupling reaction was carried out with the iodoarene (0.7 mmol) and (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> (1.5 mol %) in toluene at 80 °C for 24 h. <sup>b</sup> GC yields. <sup>c</sup> DMF at 100 °C for 24 h. <sup>d</sup> Reaction was carried out with (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> and PPh<sub>3</sub> as the ligand in a ratio 1:4; total Pd:L = 1:6.

of the reaction of **1** with aryl iodides in the presence of a catalytic amounts of (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>. Aryl bromides and chlorides do not react by these coupling reactions, as in the phosphination reaction.<sup>5</sup>

The reaction can successfully be carried out with 4-methoxyiodobenzene. The (4-methoxyphenyl)diphenyl-arsane<sup>16</sup> 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<sup>26</sup> 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<sup>20</sup> in 63% yield. However, when we carried out the reaction with PPh<sub>3</sub> 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-chloriodobenzene was allowed to react with **1b** under the same experimental conditions, (4-chlorophenyl)diphenyl-stibane<sup>27</sup> 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-chloriodobenzene to the corresponding triaryl-stibane was successfully carried out using PPh<sub>3</sub> 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<sub>3</sub> 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<sup>4</sup> for the phosphination with Me<sub>3</sub>Si–PPh<sub>2</sub> 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.

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 (<sup>1</sup>H NMR and <sup>13</sup>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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