Organoheteroatom Stannanes in Palladium-Catalyzed Cross-Coupling Reactions with 1-Naphthyl Triflate

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Summary: We have studied the Pd-catalyzed cross-coupling reaction of organoheteroatom stannanes containing elements of groups 15 (P, As, Sb) and 16 (Se) with 1-naphthyl triflate (3). The stannanes n-Bu₃SnZPhₙ (Z = P, As, Sb, Se; n = 1, 2) were synthesized by the reaction of the PhₙZ⁻ anion with n-Bu₃SnCl. The cross-coupling reactions of these stannanes with 3 in a one-pot procedure afforded the C−heteroatom products PhₙZ-1-Naph in good yields for Z = As, Se (90 and 70% yields, respectively) and moderate yields for Z = P (51% yield). Only 18% of 1-naphthyldiphenylstibine was obtained. Optimization studies revealed that the combination of LiCl and free PPh₃ ligand proved to be particularly effective in enhancing the coupling reaction.

The palladium-catalyzed cross-coupling reaction of organic electrophiles with organostannanes is a widely used methodology for C−C[1] and C−heteroatom[2] bond formation under conditions compatible with a broad range of functional groups, the aryl halides being one of the most thoroughly studied groups.[1] However, as organic triflates are readily available, they have become important coupling partners in synthesis. Stille and co-workers have studied the scope and limitation of the cross-coupling reactions of triflates with organostannanes.[3] A number of effective palladium-catalyzed coupling reactions have been developed for vinyl and aryl triflates as electrophiles.[4] An extensive study of the mechanism of the coupling of triflates with vinyltributyltin was carried out.[5] Also, the rate and mechanism of the oxidative addition of vinyl triflates was studied.[6]

It should be noted that, although organotin compounds with group 14 (Si, Sn, Ge), 15 (N, P, As, Sb), and 16 elements (O,

S, Se, Te) have been used as nucleophiles in synthesis, only a few examples of their application in cross-coupling reactions with organic triflates have been reported. The Pd-catalyzed coupling of enol triflates with (Me₃Sn)₂ afforded the vinylstannanes regiochemically.[7] Furthermore, Pd-mediated C−S[8] and C−Se[9] bond forming reactions have been achieved. Other reported methods include the Pd-catalyzed coupling of aryl triflates with Ph₂P(O)H[10] and Ph₂PH.[11] Shibasaki and co-workers have described the nickel-catalyzed arsination of BINOL ditriflate using Ph₂AsH for the synthesis of the BINAs ligand.[12] Aryl sulfides have also been obtained by the Pd-catalyzed reaction of PhSH with ArOTf.[13]

We have developed a versatile methodology that allows for C−heteroatom bond formation through a cross-coupling Pd-catalyzed reaction of different electrophiles with the organoheteroatom stannanes R₃SnZPhₙ (Z = P, As, Sb, Se) in a one-pot, two-step reaction.[2e,g,i] The in situ generation of the stannanes R₃SnZPhₙ eliminates the isolation and purification of tin reagents. To extend the applications of this methodology, we studied the Pd-catalyzed cross-coupling of organoheteroatom stannanes containing group 15 (P, As, Sb) and 16 elements (Se) with 1-naphthyl triflate (Scheme 1). Herein, we report on the scope and limitations of the organoheteroatom stannanes R₃SnZPhₙ (Z = P, As, Sb, Se) in coupling reactions.

In previous work, we found that the one-pot cross-coupling reaction of 1-naphthyl triflate (**3**) with *n*-Bu₃SnAsPh₂ (**1a**) affords naphthalen-1-yldiphenylarsine (**4**) in 68% yield.[2g] Currently, we decided to study extensively the coupling reaction

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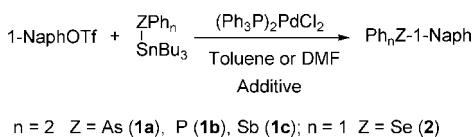
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Scheme 1

1-NaphOTf + ZPh$_n$–SnBu$_3$ $\xrightarrow[\text{Additive}]{\text{(Ph}_3\text{P)}_2\text{PdCl}_2}$ Ph$_n$Z-1-Naph
Toluene or DMF

n = 2 Z = As (**1a**), P (**1b**), Sb (**1c**); n = 1 Z = Se (**2**)

Table 1. Pd-Catalyzed Cross-Coupling Reactions with
n-Bu$_3$SnAsPh$_2$ (1a) and 1-Naphthyl Triflate (3)[a]

entry	solvent	ligand Pd:L (1:4)	amt of additive LiCl (equiv)	cocat. CuI (Pd:Cu)	4 (%)[b]
1	toluene				2
2	toluene		3		3
3	toluene	PPh$_3$			5
4	toluene	PPh$_3$	3		3
5	toluene	AsPh$_3$	3		3
6	toluene	PPh$_3$	3	1:2	3
7	DMF				35
8	DMF		3		25
9	DMF	PPh$_3$			28
10	DMF	PPh$_3$	3		68
11	DMF	PPh$_3$ (1:40)	3		59
12	DMF	PPh$_3$	3	1:2	90 (82)
13	DMF	AsPh$_3$			10
14	DMF	AsPh$_3$	3		15

[a] Reaction conditions: the Ph$_2$As$^-$ anion was prepared in liquid ammonia (300 mL) from AsPh$_3$ (1 mmol) and Na metal (2 mmol); then n-Bu$_3$SnCl (1 mmol) was added. The cross-coupling reaction was carried out with **3** (0.7 mmol) and (PPh$_3$)$_2$PdCl$_2$ (1.5 mol %) for 24 h at 80 °C when toluene was used or at 120 °C with DMF. [b] CG yields and isolated yields in parentheses.

with organoheteroatom stannanes. The experiments have been performed with the objective of gaining insight into the general effect of different additives, ligands, and solvent and of establishing the optimal reaction conditions. We selected 1-naphthyl triflate (**3**) as a model triflate (eq 1); the results of Pd-catalyzed cross-coupling with **1a** are shown in Table 1.

1-NaphOTf + AsPh$_2$–SnBu$_3$ $\xrightarrow[\text{Additive}]{\text{Pd(0)}}$ 1-NaphAsPh$_2$ (1)
3   **1a**   **4**
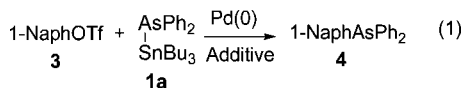
Both Pd(PPh$_3$)$_4$ and (PPh$_3$)$_2$PdCl$_2$ have been established to be effective catalysts for aryl triflate coupling reactions, although with the latter, faster rates were obtained.[3] The complexes generated by reduction of (PPh$_3$)$_2$PdCl$_2$, with which the oxidative addition of triflates took place, were also demonstrated to be more reactive than the complexes of Pd(PPh$_3$)$_4$.[14]

The cross-coupling reaction of **3** with **1a** catalyzed by (PPh$_3$)$_2$PdCl$_2$ in toluene at 80 °C only afforded 2% of **4**; a substantial amount of the cleavage product 1-naphthol was also formed (entry 1).[15] As a comparison, when 1-iodonaphthalene was used as a substrate in the same coupling conditions, **4** was obtained in 85% yield.[2g] Since the rate of the coupling reaction largely depends on the solvent, a more polar and coordinating solvent such as DMF was evaluated. When the reaction was carried out under the same conditions in DMF at 120 °C, **4** was obtained in 35% yield (entry 7). It has been reported that polar aprotic coordinating solvents (i.e., DMF, DMPU, HMPA, and DMSO) can act as ligands for Pd and are able to enhance significantly the coupling rate with triflates.[3b,c] In agreement with this, we observed a more efficient reaction in DMF.

Couplings of triflates show several experimental features that should be considered. One of them is the effect of the addition of LiCl to the catalytic mixture, whose role may be positive, negative, or neutral, depending on ligands and solvents. Stille et al. found that this addition was necessary to achieve couplings of organic triflates with organostannanes.[3] However, this finding cannot be generalized, since in many cases this salt can even retard the coupling.[16] Farina et al. studied this LiCl effect in depth and found it to lead either to acceleration or retardation, depending on the solvent and substrate used.[17] Indeed, Cl$^-$ modifies the kinetics of the oxidative addition of aryl triflates;[5,18] it also modifies the second step of the catalytic cycle of the Stille reaction[5] by the formation of neutral complexes [Pd(Ar)(Cl)-(PPh$_3$)$_2$], which then react with the organostannane.

In our system, the addition of LiCl did not produce any noticeable effect in toluene (entry 2), probably because of its low solubility.[5] When we carried out the reaction in DMF, 25% of **4** was obtained (entry 8). In this case, the reaction was slightly retarded. However, the accelerating effect of LiCl during the oxidative addition of Pd(PPh$_3$)$_4$ to **3** in DMF was observed.[18,19]

When additional PPh$_3$[17,20] was added to the reaction mixture in toluene, again no reaction was practically evidenced (entry 3). Likewise, when the reaction was carried out in DMF, the yield of **4** was similar to that obtained without the ligand (entry 9 vs 7).

The coupling reaction was delayed when AsPh$_3$ was employed, and the yields of **4** were lower than those obtained with PPh$_3$ (entry 9 vs 13). The low rates found with AsPh$_3$ as a ligand may be due to the slowness of the oxidative addition of **3** to Pd(0) species.[5]

A remarkable improvement in the yield of **4** (68%) was found when the cross-coupling reaction was carried out with both LiCl and PPh$_3$ in DMF (entry 10). An increased amount of product **4** was also observed with AsPh$_3$ as a ligand and LiCl (entry 14). Once again, practically no coupling reaction was observed in toluene under these conditions (entries 4 and 5). The role of LiCl appears to be strongly dependent not only on the solvent but also on the addition of the free ligand. The combination of PPh$_3$ and LiCl seems to be a key step in this system.

$trans$-[Pd(Ar)Cl(PPh$_3$)$_2$] complexes were proposed to be formed when the oxidative addition of the aryl triflate was carried out in the presence of Cl$^-$.[5,18] Furthermore, in the electrochemical[21] and chemical[22] reduction of (PPh$_3$)$_2$PdCl$_2$, anionic species of Pd(0) containing Cl were observed, and neutral $trans$-[Pd(Ar)Cl(PPh$_3$)$_2$] complexes were obtained when the oxidative addition of the triflate was performed with these species.[14]

Taking all this into account, in our reactions with (PPh$_3$)$_2$PdCl$_2$ and DMF after the oxidative addition of **3** to Pd(0), the complex $trans$-[Pd(Naph)Cl(PPh$_3$)$_2$] was obtained with or without the addition of LiCl. If this complex was formed in any case, the addition of LiCl should not produce an appreciable effect. Accordingly, we observed that the coupling reaction of **3** was barely affected by LiCl.

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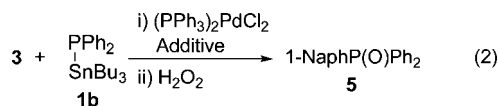
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The coupling reaction was also hardly affected by extra PPh₃; however, the addition of both LiCl and free Ph₃P ligand enhanced the rate of the reaction. One explanation for this particular effect may be the fact that this combination promotes the formation of different species of Pd(0) during the in situ reduction of Pd(II) by the stannane and thus facilitates the rate of the oxidative addition of the triflate to the Pd(0). The formation of different complexes of Pd(II) in the oxidative addition is also likely. It was shown that different organopalladium(II) intermediates could be formed and that these intermediate ratios depend on factors such as the concentration of free L, the nature of L, the solvent polarity, the solvent coordinating ability, the nature of Ar, and the temperature.[5] As the transmetalation step can occur at different rates on one or more different organopalladium(II) intermediates, the reaction can change dramatically depending on the factors mentioned.

It is important to notice that the final products of the cross-coupling reaction could be ligands for the catalyst. Although the 1-naphthyldiphenylarsine **4** obtained as a product is a more bulky and less σ-donor ligand than PPh₃, it is present in a large excess. This could be a problem for the scope of the coupling reaction. To evaluate the effect of an excess of ligand, we carried out the arsination reaction under the same conditions as described above (entry 10), with the addition of a large amount of PPh₃ (Pd:L = 1:40). Under these conditions, 59% of product **4** was obtained (entry 11). On comparison of this result with that of the previous reaction (entry 10), it is clear that the excess of a good σ-donor ligand affected the coupling reaction; nevertheless, it was not to a large extent.

Another important development in Pd-catalyzed cross-coupling reactions involves the use of Cu(I) as cocatalyst which improved rates and yields.[23] In the presence of CuI, the cross-coupling reaction with stannane **1a** became more efficient and the conversion of **3** proceeded almost to completion to give **4** in 90% yields (entry 12). As a possible mechanistic explanation for the copper effect, a preliminary transmetalation from the organostannane has been suggested.[23a] However, the copper effect could also be described by the ligand association mechanism.[23b,e] In our reaction both mechanistic explanations could be valid.[23b]

Having established the optimal reaction conditions for the Pd-catalyzed arsination of **3**, we studied the reactivity of other organoheteroatom stannanes containing phosphorus (**1b**) and antimony (**1c**) as a transferable group. The results of the cross-coupling reaction of **3** with **1b** (eq 2) are shown in Table 2.

$$3 + \underset{\substack{| \\ \text{SnBu}_3 \\ \textbf{1b}}}{\overset{\text{PPh}_2}{}} \xrightarrow[\text{ii) H}_2\text{O}_2]{\overset{\text{i) (PPh}_3)_2\text{PdCl}_2}{\text{Additive}}} \underset{\textbf{5}}{\text{1-NaphP(O)Ph}_2} \quad (2)$$

When the reaction was carried out under the optimal conditions found for arsination (DMF/PPh₃/LiCl/CuI), and after oxidation of the obtained phosphine, only a 29% yield of diphenyl-1-naphthylphosphine oxide (**5**) was observed (entry 1). Yields did not increase with the addition of 10 mol % of the catalyst (entry 2). With toluene as solvent in the phosphination, the coupled product **5** was obtained in 38% yield (entry 3). Nevertheless, the use of 10 mol % of the catalyst led to a

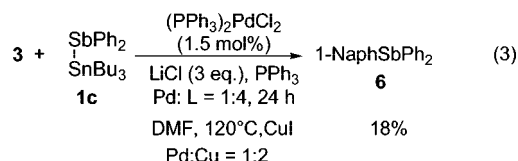**Table 2. Pd-Catalyzed Cross-Coupling with 1b and 3 with PPh₃, LiCl, and CuI[a]**

entry	solvent	amt of (PPh₃)₂ PdCl₂ (mol %)	time (h)	product **5** (%)[b]
1	DMF	1.5	24	29
2	DMF	10	24	25
3	toluene	1.5	24	38
4	toluene	10	24	51 (42)
5	toluene	1.5	36	46

[a] Reaction conditions: the Ph₂P⁻ anion was prepared in liquid ammonia (300 mL) from PPh₃ (1 mmol) and Na metal (2 mmol); then *n*-Bu₃SnCl (1 mmol) was added. The cross-coupling reaction was carried out with **3** (0.7 mmol), (PPh₃)₂PdCl₂, PPh₃ (Pd:L 1:4), LiCl (3 equiv), and CuI (Pd:Cu = 1:2) for 24 h at 80 °C when toluene was used or at 120 °C with DMF. [b] CG yields and isolated yields in parentheses.
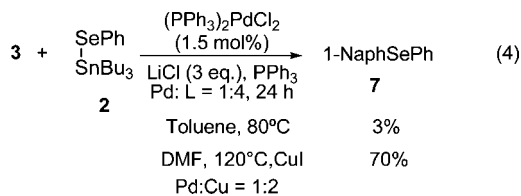
more active catalytic system (entry 4). Nearly the same effect was observed with longer reaction times (entry 5). In all cases the conversion of the substrate was almost complete and different amounts of cleavage product 1-naphthol were formed.

Although the oxidative addition pathway should be the same in arsination and phosphination reactions, a significant change occurs in the transmetalation when the organoheteroatom stannanes vary. The stannane *n*-Bu₃SnPPh₂ seems to be less reactive than *n*-Bu₃SnAsPh₂ in the coupling reaction with **3**. However, it should be noted that in this reaction the cross-coupling product was a strong Pd ligand, and the excess of ligand in solution produced autoretardation.

In addition, the cross-coupling reaction of **3** with **1c** was also examined. When **3** was allowed to react with **1c** in DMF and with PPh₃/LiCl/CuI, the yield of 1-naphthyldiphenylstibine **6** was only 18% (eq 3). When we attempted the reaction in toluene, the reaction did not proceed. The yield could not be improved when the reaction was performed under other conditions.

$$3 + \underset{\substack{| \\ \text{SnBu}_3 \\ \textbf{1c}}}{\overset{\text{SbPh}_2}{}} \xrightarrow[\substack{\text{LiCl (3 eq.), PPh}_3 \\ \text{Pd: L = 1:4, 24 h} \\ \text{DMF, 120°C, CuI} \\ \text{Pd:Cu = 1:2}}]{\substack{(\text{PPh}_3)_2\text{PdCl}_2 \\ (1.5 \text{ mol\%})}} \underset{\substack{\textbf{6} \\ 18\%}}{\text{1-NaphSbPh}_2} \quad (3)$$

To further study this methodology, we examined the Pd-catalyzed selenylation reaction with the stannane *n*-Bu₃SnSePh (**2**) and **3**. The coupling reaction catalyzed by (PPh₃)₂PdCl₂ in toluene at 80 °C with 3 equiv of LiCl and PPh₃ as free ligand afforded naphthalen-1-ylphenylselenide (**7**) in only 3% yield. However, the reaction could be successfully carried out using DMF as solvent and CuI as cocatalyst, which are the optimal conditions observed for the arsination reaction. Selenide **7** was obtained in 70% yield (eq 4).[24]

$$3 + \underset{\substack{| \\ \text{SnBu}_3 \\ \textbf{2}}}{\overset{\text{SePh}}{}} \xrightarrow[\substack{\text{LiCl (3 eq.), PPh}_3 \\ \text{Pd: L = 1:4, 24 h} \\ \text{Toluene, 80°C} \\ \text{DMF, 120°C, CuI} \\ \text{Pd:Cu = 1:2}}]{\substack{(\text{PPh}_3)_2\text{PdCl}_2 \\ (1.5 \text{ mol\%})}} \underset{\substack{\textbf{7} \\ 3\% \\ 70\%}}{\text{1-NaphSePh}} \quad (4)$$

In conclusion, there are two different general conditions for the cross-coupling reaction with **3** and organoheteroatom stannanes. Optimization studies revealed that the most effective conditions for *n*-Bu₃SnAsPh₂ and *n*-Bu₃SnSePh stannanes were (PPh₃)₂PdCl₂/PPh₃/LiCl/CuI in DMF. The most effective conditions for the stannane *n*-Bu₃SnPPh₂ were the same, except in toluene. In addition, the results of the reactions of triflate with

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n-Bu₃SnSbPh₂ indicated the limit of the application of stannanes of group 15 elements.

It is particularly noteworthy that the products of the arsination reaction are Pd ligands; nevertheless, the reaction proceeded almost to completion. In contrast, the phosphination reaction was more affected, which may be attributed to the fact that phosphines are stronger Pd ligands than arsines.

The combination of LiCl and free PPh₃ ligand was particularly effective in enhancing the cross-coupling reaction of **3** and organoheteroatom stannanes with (PPh₃)₂PdCl₂ as catalyst. These coupling reactions extended the use of organoheteroatom stannanes in the Stille reaction.

Experimental Section

Representative Procedure for Palladium-Catalyzed Cross-Coupling Reactions with Organoheteroatom Stannanes and 1-NaphOTf (3). The following procedure for the reaction of **3** with **1a** is representative of all these reactions. Into a three-necked, 500 mL, round-bottomed flask was condensed approximately 400 mL of ammonia previously dried with Na metal under nitrogen. AsPh₃ (1.0 mmol) and then 2 equiv of Na metal (2 mmol) in small pieces were added, with a pause for bleaching between each addition. At 20−30 min after the last addition, Ph₂As⁻ anion was formed, and *n*-Bu₃SnCl (2 mmol) was added slowly. The mixture was then stirred for 5 min and the liquid ammonia was allowed to evaporate. Evaporation left a white solid residue which was dissolved in dry DMF (30 mL). This solution was added via cannula and syringe into a Schlenk tube. In the tube, LiCl (3 equiv) was previously dried under vacuum at 150 °C for 4 h; after cooling at room temperature, (PPh₃)₂PdCl₂ (1.5 mol %), PPh₃ (6 mol %), CuI (3 mol %), **3** (1.4 mmol), and DMF (2 mL) were added. When the solution of **1a** was added, the reaction mixture turned deep brown. The reaction mixture was heated for 24 h in an oil bath at 120 °C. Water was added to the cold reaction mixture and then extracted three times with CH₂Cl₂ (30 mL each). The crude reaction mixture was treated with aqueous KF (ca. 2 equiv) to eliminate *n*-Bu₃SnI.[25] After drying with anhydrous MgSO₄, the product **4**[26] was quantified by CG using the internal standard method, yielding 90% of the product. The product was isolated from the reaction mixture by column chromatography on silica gel (hexanes−ethyl acetate), yielding 82% of **4**.

Supporting Information Available: Text and figures giving general experimental details and procedures and ¹H and ¹³C NMR spectral data for **4**, **5**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

(24) Naphthalen-1-ylphenylselenide was isolated in yields ca. 10−15% lower than those found in CG yield. This yield was not optimized.

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