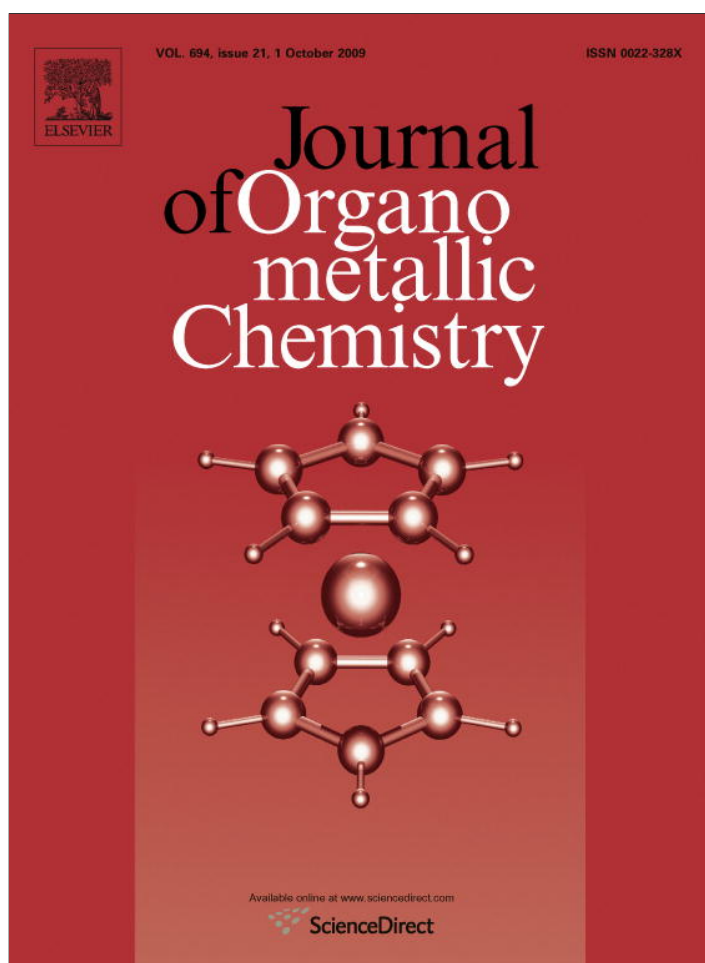


Provided for non-commercial research and education use.  
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

## Journal of Organometallic Chemistry

journal homepage: [www.elsevier.com/locate/jorganchem](http://www.elsevier.com/locate/jorganchem)

## Perfluoroalkylphosphines and arsines obtained by Pd-catalyzed cross-coupling reaction with organoheteroatom stannanes

Mario N. Lanteri, Roberto A. Rossi, Sandra E. Martín \*

INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Medina Allende y Haya de la Torre, 5000 Córdoba, Argentina

## ARTICLE INFO

## Article history:

Received 15 April 2009

Received in revised form 22 June 2009

Accepted 23 June 2009

Available online 28 June 2009

## Keywords:

Perfluoroalkylphosphines

Perfluoroalkylarsines

Pd-catalyzed reactions

Organoheteroatom stannanes

## ABSTRACT

Pd-catalyzed cross-coupling reaction of organoheteroatom stannanes containing elements of the groups 15 (P, As) and 16 (Se) with perfluoroalkyl iodides ( $R_fI$ ) was studied. Herein, a one-pot two-step reaction to form P– $R_f$ , As– $R_f$  and Se– $R_f$  bonds is reported. The stannanes  $n\text{-Bu}_3\text{SnZPh}_n$  ( $Z = \text{P, As, Se}$ ;  $n = 1\text{--}2$ ) were generated *in situ* by the reaction of the  $\text{Ph}_n\text{Z}^-$  anion with  $n\text{-Bu}_3\text{SnCl}$ . The cross-coupling reactions of these stannanes with  $R_fI$  afforded C-heteroatom products, new perfluoroalkylarsines and perfluoroalkylselenides in good yields (47–90%) and perfluoroalkylphosphines in moderate yields (15–48%).

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Organofluorine compounds have attracted particular interest in recent years for displaying unique reactivities and selectivities and for their promising applications in biological and material science [1]. Among organofluorine compounds, those containing perfluoroalkyl groups ( $R_f$ ) have become increasingly important; thus, it is required to develop new approaches to introducing these particular groups.

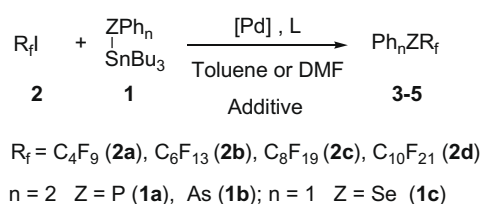
Among the perfluoroalkyl compounds we found those containing P– $R_f$  and As– $R_f$  bonds especially interesting. Perfluoroalkyl-substituted phosphines have lately drawn much attention due to their potential applications as ligands in organometallic chemistry [2]. Recently, a review describing the properties and synthesis of fluorarylphosphine ligands was reported [3].

A wide range of tertiary phosphine ligands with substituents such as alkyl or aryl groups was achieved because of their versatile tuning abilities via steric and electronic properties [4]. However, electron-poor or electroneutral phosphine ligands were less developed, probably due to the lack of methodologies for introducing electron-withdrawing substituents. The lack of electroneutral phosphine ligands was clearly shown in the evaluation of stereo-electronic profile of known phosphine ligands [5]. Steric and electronic effects of some tertiary arsine ligands were also evaluated [6]. Thus, the synthesis and application of new types of phosphines, and also of arsines ligands with unusual stereoelectronic properties, are pursued as the main goals of the present study.

Synthetic routes to perfluoroalkyl-substituted phosphines  $R_{3-n}P(R_f)_n$  are not numerous. Some methods for the synthesis of tris-perfluoroalkylphosphines have been reported [7]. Phosphines bearing fluoroalkyl and fluorovinyl groups have been obtained from  $\text{LiR}_f$  and appropriate phosphorus precursors [8]. Only few examples of aryl(bis)perfluoroalkylphosphines and diarylperfluoroalkylphosphines have been reported [8a,9]. For instance, the synthesis and coordination chemistry studies of  $\text{Ph}_2\text{P}(\text{C}_2\text{F}_5)_2$  were carried out, and the perfluoroalkylphosphine was characterized as a sterically bulky, electronically neutral ligand [2g–h,9d]. Alternatively,  $\text{Ph}_2\text{PR}_f$  ( $R_f = \text{C}_4\text{F}_9, \text{C}_6\text{F}_{13}$ ) were synthesized from  $\text{PPh}_3$  by the  $\text{S}_{\text{RN}}1$  mechanism in HMPA [10]. It should be noted that, in general, the synthetic methods reported have not worked effectively for perfluoroalkyl chains longer than  $\text{CF}_3$  or  $\text{C}_2\text{F}_5$ . Therefore, a suitable synthesis for a wide range of perfluoroalkylphosphines remains a challenging task. Furthermore, perfluoroalkylarsines have scarcely been mentioned in the literature [7e–f,11]. Our primary objective centers on the synthesis of arsines ligands in view of their growing applications as ligands in catalysis and on the fact that in many catalyzed reactions they are more active as ligands than their analogous phosphines [12].

On the other hand, we have developed a versatile methodology that allows for the C-heteroatom bond formation through a cross-coupling Pd-catalyzed reaction of different electrophiles with organoheteroatom stannanes  $R_3\text{SnZPh}_n$  ( $Z = \text{P, As, Sb, Se}$ ) in one-pot two-step reactions [13,14]. We have described the Pd-catalyzed cross-coupling reaction of stannane  $n\text{-Bu}_3\text{SnSePh}$  with  $\text{C}_8\text{F}_{17}\text{I}$  and  $\text{C}_{10}\text{F}_{21}\text{I}$  [14]. This approach provides a convenient route to obtain perfluoroalkylselenides; it being the first report of the Pd-catalyzed reaction for heteroatom– $R_f$  bond formation.

\* Corresponding author. Tel.: +54 351 4334170; fax: +54 351 4333030.  
E-mail address: [martins@fcq.unc.edu.ar](mailto:martins@fcq.unc.edu.ar) (S.E. Martín).



Scheme 1.

Only the introduction of R<sub>f</sub> groups to olefinic and acetylenic carbons by the Pd-catalyzed reaction between organotin and perfluoroalkyl iodides (R<sub>f</sub>I) was reported [15]. In addition, β-perfluoroalkyl-substituted alkyl iodide reacted with organostannanes in a Pd-catalyzed cross-coupling reaction [16]. The influence of fluorine atoms in alkyl iodides in Pd-catalyzed coupling was also investigated [17].

Our work focused on the development of a strategy to synthesize phosphines and arsines with R<sub>f</sub> of type Ph<sub>2</sub>ZR<sub>f</sub> (Z = P, As) and extend the previous studies with perfluoroalkylselenides. Herein, we report our results on the Pd-catalyzed cross-coupling reaction with R<sub>f</sub>I as electrophiles to obtain compounds containing P–R<sub>f</sub>, As–R<sub>f</sub> and Se–R<sub>f</sub> bonds (Scheme 1).

## 2. Results and discussion

In a previous work, we found for the first time that perfluoroalkyl iodides were viable electrophiles in the Pd-catalyzed cross-coupling selenylation with *n*-Bu<sub>3</sub>SnSePh, and thereby we described two examples of the synthesis of PhSeR<sub>f</sub> (R<sub>f</sub> = C<sub>8</sub>F<sub>17</sub>, C<sub>10</sub>F<sub>21</sub>) [14]. Considering that compounds containing P–R<sub>f</sub> and As–R<sub>f</sub> bonds have potential applications as ligands, we studied the Pd-catalyzed cross-coupling of organoheteroatom stannanes *n*-Bu<sub>3</sub>SnPPh<sub>2</sub> (**1a**) and *n*-Bu<sub>3</sub>SnAsPh<sub>2</sub> (**1b**) with R<sub>f</sub>I to achieve diphenylperfluoroalkylphosphines and novel arsines.

### 2.1. Optimization of the cross-coupling phosphination reaction

The experiments have been performed with the objective of gaining insight into the effect produced by different additives, li-

**Table 1**  
Pd-catalyzed cross-coupling reaction with *n*-Bu<sub>3</sub>SnPPh<sub>2</sub> (**1a**) and C<sub>8</sub>F<sub>17</sub>I (**2c**).<sup>a</sup>

Entry	Catalyst	Solvent	Ligand Pd:L (1:4)	Additive	Product <b>3c</b> (%) <sup>b</sup>
1	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	DMF	PPh <sub>3</sub>	CsF	<5
2	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	THF	PPh <sub>3</sub>	CsF	10
3	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	Toluene	PPh <sub>3</sub>	CsF	51
4	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	Toluene	PPh <sub>3</sub>	–	40
5	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	Toluene	–	CsF	11
6	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	Toluene	PPh <sub>3</sub>	CuI	14
7	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	Toluene	PPh <sub>3</sub>	CsF, CuI	14
8	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	Toluene (80 °C)	PPh <sub>3</sub>	CsF	39
9	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	Toluene (35 °C)	PPh <sub>3</sub>	CsF	32
10	Pd <sub>2</sub> (dba) <sub>3</sub>	Toluene	PPh <sub>3</sub>	CsF	6
11	Pd(PPh <sub>3</sub> ) <sub>4</sub>	Toluene	PPh <sub>3</sub>	CsF	<5
12	[(π-allyl)PdCl] <sub>2</sub>	Toluene	PPh <sub>3</sub>	CsF	<2
13	Pd(OAc) <sub>2</sub>	Toluene	PPh <sub>3</sub>	CsF	<5
14	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	Toluene	AsPh <sub>3</sub>	CsF	14
15	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	Toluene	P(2-furyl) <sub>3</sub>	CsF	26
16	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	Toluene	P( <i>o</i> -tol) <sub>3</sub>	CsF	23
17	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	Toluene	PCy <sub>3</sub>	CsF	<2
18	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	Toluene	P( <i>t</i> -Bu) <sub>2</sub> Me	CsF	<2
19	[(π-allyl)PdCl] <sub>2</sub>	Toluene	P( <i>t</i> -Bu) <sub>2</sub> Me	CsF	<2
20	Pd(OAc) <sub>2</sub>	Toluene	P( <i>t</i> -Bu) <sub>2</sub> Me	CsF	16
21	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	Toluene	P( <i>t</i> -Bu) <sub>2</sub> Biph	CsF	<5

<sup>a</sup> Reaction conditions: Ph<sub>2</sub>P<sup>–</sup> anion was prepared in liquid ammonia (300 mL) from PPh<sub>3</sub> (1 mmol) and Na metal (2 mmol); *n*-Bu<sub>3</sub>SnCl (1 mmol) was then added. The cross-coupling reaction was carried out with C<sub>8</sub>F<sub>17</sub>I (0.7 mmol), Pd catalyst (10 mol%, 0.07 mmol), L (Pd:L 1:4, 0.28 mmol), CsF (3 equiv., 2.1 mmol) and/or CuI (Pd:Cu 1:2) for 24 h at reflux when toluene or THF was used, or at 120 °C with DMF.

<sup>b</sup> GC yields (internal standard method). The informed yields represent at least the average of two reactions.

gands, solvents and catalysts, and of establishing the optimal reaction conditions. We selected C<sub>8</sub>F<sub>17</sub>I (**2c**) as a model substrate (Eq. (1)); the results of Pd-catalyzed cross-coupling with *n*-Bu<sub>3</sub>SnPPh<sub>2</sub> (**1a**) are shown in Table 1.



The generation and subsequent use of stannanes **1** were in agreement with the procedure previously reported by us for the synthesis of tertiary phosphines [13a], arsines [13b,c] and selenides [14]. Stannane **1a** was generated *in situ* by the reaction of Ph<sub>2</sub>P<sup>–</sup> anion with *n*-Bu<sub>3</sub>SnCl. Afterwards, the Pd-catalyzed cross-coupling reaction of **1a** with perfluoroalkyl iodide **2c** was carried out, all in a one-pot two-step procedure. The *in situ* generation of the stannanes eliminates the isolation and purification of tin reagents. After oxidation, the reaction afforded diphenylperfluoroalkyl phosphine oxide Ph<sub>2</sub>P(O)R<sub>f</sub> (Eq. (1)).

The initial conditions employed were the most effective ones obtained in the Pd-catalyzed selenylation, (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>/PPh<sub>3</sub>/CsF in DMF at 120 °C [14]. In these conditions, the cross-coupling reaction of **1a** with **2c** only afforded <5% of **3c** (entry 1, Table 1). However, the conversion of the substrate was complete, and the other product formed was C<sub>8</sub>F<sub>17</sub>H. It should be noted that in all reactions herein reported, no vestige of remaining substrate was found, and the other product achieved, in addition to the cross-coupling one, was the reduced perfluoroalkane.

### 2.2. Solvent

The yield could not be improved when the reaction was performed in THF (entry 2, Table 1). However, when the reaction was carried out under the same conditions in toluene at 80 °C, **3c** was achieved in 51% yield (entry 3, Table 1). Evidently, the non-polar solvent was the most effective. This is the first report for the synthesis of a perfluoroalkylphosphine with a perfluoroalkyl moiety of eight C atoms. Previously, only Ph<sub>2</sub>P(C<sub>2</sub>F<sub>5</sub>) [2g–h,9d], Ph<sub>2</sub>PC<sub>4</sub>F<sub>6</sub> and Ph<sub>2</sub>PC<sub>6</sub>F<sub>13</sub> [10] were obtained.

### 2.3. Fluoride and cooper(I) additives

The effect of the additives on coupling reaction was studied employing toluene as solvent. In this sense, Lewis-basic additives have been shown to facilitate certain Stille reactions, presumably by generating hypervalent stannane complexes [18]. Considering the role of Lewis-basic additives this aspect and the fact that the addition of F<sup>-</sup> ions could provide a more efficient cross-coupling reaction [19], we used CsF as an activator of the organotin reagent.

When only extra PPh<sub>3</sub> [20] was added to the reaction mixture, the yields of **3c** were lower than those found with PPh<sub>3</sub>/CsF (entry 4 versus 3, Table 1). When we carried out the reaction with CsF and without additional ligand, 11% of **3c** was achieved (entry 5, Table 1). In this case the reaction was retarded, indicating that the presence of ligand facilitated the reaction.

Another important development in Pd-catalyzed cross-coupling reactions involves the use of Cu(I) as cocatalyst which improved rates and yields [21]. In the presence of CuI, the cross-coupling reaction with stannane **1a** became less efficient (entry 6, Table 1). The copper negative effect could be attributed to the fact that a ligand association mechanism may have taken place [21b,e].

On the other hand, it was reported that in many cases the combination of CuI–CsF [22] significantly enhanced the Stille reaction. In our system, the addition of CuI–CsF did not produce such effect; instead, the reaction was retarded (entry 7, Table 1). Moreover, it seems that the Cu effect was the predominant one.

### 2.4. Substrate reduction

With the aim of decreasing the amount of reduced product, we carried out the reaction at 80 and 35 °C (entries 8 and 9, Table 1). However, the reduction of the substrate was barely affected and the yields of the coupling product were not high.

In previous research, we established the reductive power of the stannylphosphine reagent in the Pd-catalyzed phosphination when a nitro group was present as substituent [13a]. Thus, we performed the reaction of **2c** in the cross-coupling conditions without stannane in toluene at 35 °C. In this reaction, 80% of substrate **2c** was recovered, indicating the participation of stannane in the reduction of R<sub>f</sub>. Moreover, when the relation substrate:stannane was modified to 1:2 in the phosphination, no reaction occurred, and the reduction of substrate **2c** was complete.

### 2.5. Palladium source

Despite that, for all Pd-catalyzed cross-coupling reactions with organoheterostannanes studied, the best catalyst was (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> [13,14]; other sources of Pd were considered. Both Pd(0) catalysts, Pd<sub>2</sub>(dba)<sub>3</sub> and Pd(PPh<sub>3</sub>)<sub>4</sub>, with PPh<sub>3</sub> as ligand were less effective than (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> (entries 10 and 11, Table 1). A disadvantage of Pd(0) complexes is that the ligands needed to stabilize Pd(0) invariably have coordinating properties which hinder the formation of Pd(II) catalytic active species. The preligands associated with the Pd catalyst will have differing degrees of coordination ability, and they could also lead to the formation of different active Pd(0) species [23]. Studies showed that the species formed from Pd<sub>2</sub>(dba)<sub>3</sub> and PPh<sub>3</sub> is quite different from Pd(PPh<sub>3</sub>)<sub>4</sub> [24].

A Pd(II) catalyst is a feasible alternative to a Pd(0) catalyst, even though this requires an additional preactivation step to generate the active Pd(0) species. We evaluated [(π-allyl)PdCl]<sub>2</sub> and Pd(OAc)<sub>2</sub> as Pd(II) catalysts. However, it should be noted that these catalysts still have coordinating ligands that might interfere with the formation of the active species. The effectiveness of these two Pd sources was similar, and both were less effective than (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> (entries 12 and 13, Table 1). Therefore, on the basis of the experimental data, (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> was selected as Pd source.

### 2.6. Ligand

The low reactivity of R<sub>f</sub>I could be ascribed to its reluctance to participate in oxidative addition, the first step of the catalytic cycle, where the structure of the ligand has a remarkable influence. In view of this, we began by examining a variety of ligands.

When the coupling of **1a** and **2c** was carried out using (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> and AsPh<sub>3</sub> as the ligand, only a small amount of product **3c** was obtained (entry 14, Table 1). When extra AsPh<sub>3</sub> was added to the catalyst (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> (Pd:L 1:4), regardless of the presence of PPh<sub>3</sub> and their enhanced donicity, the influence of the extra ligand could be noticed and the yields of the reaction were lower than those with PPh<sub>3</sub>.

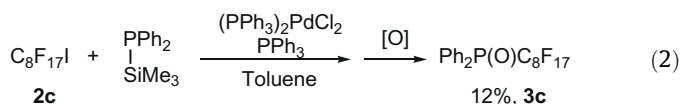
Additionally, P(2-furyl)<sub>3</sub> and P(o-tol)<sub>3</sub> proved to be less effective than PPh<sub>3</sub> in the coupling reaction (entries 15 and 16, Table 1). These ligands, as well as AsPh<sub>3</sub>, are believed to enhance Stille couplings by increasing the rate of transmetalation, which could imply that the rate-limiting step in these cases might be oxidative addition rather than transmetalation.

Significant progress has been made based on sterically demanding electron-rich phosphines as the supporting ligand for the Stille cross-coupling. With this possibility in mind, electron-rich PCy<sub>3</sub> and P(*t*-Bu)<sub>2</sub>Me [25] were investigated as ligands that might promote oxidative addition by increasing the nucleophilicity of the Pd(0) species. When the reaction of **1a** and **2c** was carried out with these ligands using (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>, essentially we obtained none of the desired coupling product (entries 17 and 18, Table 1). Using [(π-allyl)PdCl]<sub>2</sub> as catalyst and P(*t*-Bu)<sub>2</sub>Me there was almost no reaction (entry 19, Table 1). Under the same experimental conditions with Pd(OAc)<sub>2</sub> and P(*t*-Bu)<sub>2</sub>Me as ligand **3c** was obtained in only 16% yields (entry 20, Table 1). P(*t*-Bu)<sub>2</sub>Biph afforded also ineffective catalyst for the coupling reaction of **2c** (entry 21, Table 1).

Although we examined a wide variety of conditions, the yields of perfluoroalkylphosphine **3c** were moderate. We could mention two adverse effects on this particularly coupling reaction. One concerns the reduction of the substrate by the stannane, which competed with the phosphination reaction. It is also important to notice that the final products of the cross-coupling reaction could be ligands for the catalyst. These ligands could represent a problem for the scope of the coupling reaction, since they could affect the stability of the catalytic system.

### 2.7. Pd-catalyzed coupling with Me<sub>3</sub>SiPPh<sub>2</sub>

In addition, we have studied the cross-coupling reaction catalyzed by Pd(0) with Me<sub>3</sub>SiPPh<sub>2</sub>. Stille and coworkers have reported an example of Pd-catalyzed coupling of Me<sub>3</sub>SiPPh<sub>2</sub> with aryl halides to obtain arylidiphenylphosphine [26]. When we carried out the one-pot two-step phosphination reaction with Me<sub>3</sub>SiPPh<sub>2</sub> and **2c** catalyzed by (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> in toluene and PPh<sub>3</sub>, the cross-coupling product **3c** was achieved in only 12% yield (Eq. (2)). No improved yields were obtained in other conditions.



Having determined the best possible reaction conditions for the Pd-catalyzed phosphination of **2c**, we studied the reactivity of other R<sub>f</sub>I (**2a**, **2b** and **2d**); the results of Pd-catalyzed cross-coupling are shown in Table 2.

A significant influence of the perfluoroalkyl chain length was observed in the phosphination reaction. When the reaction was carried out under the optimal conditions found (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>/PPh<sub>3</sub>/CsF in toluene), and after oxidation of the phosphine obtained, only 22% and 15% yields of Ph<sub>2</sub>P(O)C<sub>4</sub>F<sub>9</sub> (**3a**) and Ph<sub>2</sub>P(O)C<sub>6</sub>F<sub>13</sub> (**3b**),

**Table 2**Pd-catalyzed cross-coupling with organoheteroatom stannanes **1** and R<sub>1</sub>I (**2a–d**) as electrophile.<sup>a</sup>

Entry	Substrate	Stannane	Solvent	Product	Yield (%) <sup>b</sup>
1	C <sub>4</sub> F <sub>9</sub> I	<i>n</i> -Bu <sub>3</sub> SnPPh <sub>2</sub>	Toluene	Ph <sub>2</sub> P(O)C <sub>4</sub> F <sub>9</sub> ( <b>3a</b> )	22
2	C <sub>6</sub> F <sub>13</sub> I	<i>n</i> -Bu <sub>3</sub> SnPPh <sub>2</sub>	Toluene	Ph <sub>2</sub> P(O)C <sub>6</sub> F <sub>13</sub> ( <b>3b</b> )	15
3	C <sub>8</sub> F <sub>19</sub> I	<i>n</i> -Bu <sub>3</sub> SnPPh <sub>2</sub>	Toluene	Ph <sub>2</sub> P(O)C <sub>8</sub> F <sub>19</sub> ( <b>3c</b> )	51
4	C <sub>10</sub> F <sub>21</sub> I	<i>n</i> -Bu <sub>3</sub> SnPPh <sub>2</sub>	Toluene	Ph <sub>2</sub> P(O)C <sub>10</sub> F <sub>21</sub> ( <b>3d</b> )	<5
5	C <sub>4</sub> F <sub>9</sub> I	<i>n</i> -Bu <sub>3</sub> SnAsPh <sub>2</sub>	Toluene	Ph <sub>2</sub> AsC <sub>4</sub> F <sub>9</sub> ( <b>4a</b> )	47
6	C <sub>6</sub> F <sub>13</sub> I	<i>n</i> -Bu <sub>3</sub> SnAsPh <sub>2</sub>	Toluene	Ph <sub>2</sub> AsC <sub>6</sub> F <sub>13</sub> ( <b>4b</b> )	43
7	C <sub>8</sub> F <sub>19</sub> I	<i>n</i> -Bu <sub>3</sub> SnAsPh <sub>2</sub>	Toluene	Ph <sub>2</sub> AsC <sub>8</sub> F <sub>19</sub> ( <b>4c</b> )	65
8	C <sub>10</sub> F <sub>21</sub> I	<i>n</i> -Bu <sub>3</sub> SnAsPh <sub>2</sub>	Toluene	Ph <sub>2</sub> AsC <sub>10</sub> F <sub>21</sub> ( <b>4d</b> )	48
9	C <sub>4</sub> F <sub>9</sub> I	<i>n</i> -Bu <sub>3</sub> SnSePh <sub>2</sub>	DMF	PhSeC <sub>4</sub> F <sub>9</sub> ( <b>5a</b> )	28
10	C <sub>6</sub> F <sub>13</sub> I	<i>n</i> -Bu <sub>3</sub> SnSePh <sub>2</sub>	DMF	PhSeC <sub>6</sub> F <sub>13</sub> ( <b>5b</b> )	37
11	C <sub>8</sub> F <sub>19</sub> I	<i>n</i> -Bu <sub>3</sub> SnSePh <sub>2</sub>	DMF	PhSeC <sub>8</sub> F <sub>19</sub> ( <b>5c</b> )	70 <sup>c</sup>
12	C <sub>10</sub> F <sub>21</sub> I	<i>n</i> -Bu <sub>3</sub> SnSePh <sub>2</sub>	DMF	PhSeC <sub>10</sub> F <sub>21</sub> ( <b>5d</b> )	90 <sup>c</sup>

<sup>a</sup> Reaction conditions: the Ph<sub>n</sub>Z<sup>-</sup> anion (Z = P, As, Se; n = 2, 1) was prepared in liquid ammonia (300 mL) from ZPh<sub>3</sub> (1 mmol) or Ph<sub>2</sub>Se<sub>2</sub> (0.5 mmol) and Na metal (2 mmol); *n*-Bu<sub>3</sub>SnCl (1 mmol) was then added. The cross-coupling reaction was carried out with R<sub>1</sub>I (0.7 mmol), (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> (10 mol%, 0.07 mmol), PPh<sub>3</sub> (Pd:L 1:4, 0.28 mmol) and CsF (3 equiv., 2.1 mmol) for 24 h at reflux when toluene was used, or at 120 °C with DMF.

<sup>b</sup> GC yields (internal standard method). The informed yields represent at least the average of three reactions.

<sup>c</sup> Ref. [14].

respectively, were found (entries 1 and 2, Table 2). Moreover, with perfluorodecyl iodide (**2d**) practically no product was achieved (entry 4, Table 2), and the substrate was completely consumed. The only product detected was the reduced perfluoroalkane. It seems that the limit of the phosphination reaction is defined with perfluorodecyl iodide and related to the substrate reduction.

### 2.8. Pd-catalyzed cross-coupling arsination and selenylation with perfluoroalkyl iodides

To study this methodology further, we examined the Pd-catalyzed arsination reaction with stannane *n*-Bu<sub>3</sub>SnAsPh<sub>2</sub> (**1b**). The results of the cross-coupling reaction of perfluoroalkyl iodides **2** with **1b** are shown in Table 2. The arsination reaction proceeded much better than the phosphination reaction. Novel perfluoroalkyldiphenylarsines with perfluoroalkyl chains between four and ten C atoms were obtained in moderate to good yields (entries 5–8, Table 2). With organoarsine stannane it was observed that the chain length had nearly no influence on the reactivity in the coupling reaction. In these reactions the conversion was complete and perfluoroalkane was the other product found.

We also examined the Pd-catalyzed selenylation of C<sub>4</sub>F<sub>9</sub>I and C<sub>6</sub>F<sub>13</sub>I. It is important to notice that there are not many synthetic routes to perfluoroalkylselenides [27]. Recently, aryl and alkyl perfluoroalkyl selenides were obtained from diselenides in the presence of sodium hydroxymethanesulfinate from fair to good yield [28].

The reaction of stannane **1c** with R<sub>1</sub>I **2a** and **2b** was performed in the best condition previously observed for C<sub>8</sub>F<sub>19</sub>I and C<sub>10</sub>F<sub>21</sub>I [14]. In these cases, it was found that although the reaction did not proceed in toluene at 80 °C, using DMF as solvent and a higher temperature, the selenylation reaction was allowed to proceed (entries 11 and 12, Table 2). In this condition, we carried out the selenylation with perfluoroalkyl iodides **2a** and **2b**, and obtained 28% and 37% yields of PhSeC<sub>4</sub>F<sub>9</sub> (**5a**) and PhSeC<sub>6</sub>F<sub>13</sub> (**5b**) (entries 9 and 10, Table 2).

### 3. Conclusion

We reported a one-pot two-step Pd-catalyzed cross-coupling reaction of organoheteroatom stannanes with perfluoroalkyl io-

ides to obtain perfluoroalkylphosphines and arsines. There are two different general conditions for the cross-coupling reaction with perfluoroalkyl iodides. Optimization studies revealed that the most favorable conditions for *n*-Bu<sub>3</sub>SnPPh<sub>2</sub> and *n*-Bu<sub>3</sub>SnAsPh<sub>2</sub> stannanes were (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>/PPh<sub>3</sub>/CsF in toluene. They were also the most effective conditions for stannane *n*-Bu<sub>3</sub>SnSePh, but in DMF.

Despite that a competitive reduction of the substrates took place, phosphines, arsines and selenides were obtained in good to moderate yields. By this methodology new types of potential perfluoroalkylarsine ligands were achieved. Particularly noteworthy is the fact the reaction worked for perfluoroalkyl chains longer than four. These coupling reactions extended the use of organoheteroatom stannanes in the Stille reaction.

## 4. Experimental

### 4.1. General methods

Gas chromatographic analyses were performed on a gas chromatograph with a flame ionization detector, and equipped with the following columns: HP1 25 m × 0.20 mm × 0.25 μm column. <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR and <sup>31</sup>P NMR were conducted on a High Resolution Spectrometer Bruker Advance 400, in CDCl<sub>3</sub> as solvent. Gas Chromatographic/Mass Spectrometer analyses were carried out on a GC-MS QP 5050 spectrometer equipped with a VF-5ms, 30 m × 0.25 mm × 0.25 μm column. Melting points were performed with an electrical instrument. The HRMS were recorded at UCR Mass Spectrometry Facility, University of California, USA.

The AsPh<sub>3</sub>, PPh<sub>3</sub>, P(*t*-Bu)<sub>2</sub>Biph, P(*o*-tolyl)<sub>3</sub>, P(2-furyl)<sub>3</sub>, PCy<sub>3</sub>, [HP(*t*-Bu)<sub>2</sub>Me]BF<sub>4</sub>, *n*-Bu<sub>3</sub>SnCl, (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>, Pd<sub>2</sub>(dba)<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, [(π-allyl)PdCl]<sub>2</sub>, Pd(OAc)<sub>2</sub>, CuI, and R<sub>1</sub>I were commercially available and used as received. CsF was dried under vacuum at 120 °C. All solvents were analytical grade and distilled before use. Hexane was HPLC grade. Toluene was distilled under nitrogen from *N*-benzophenone. DMF was stored under molecular sieves and then distilled under reduced pressure with bubbling of nitrogen. All reactions were carried out under atmosphere of nitrogen. Silica gel (0.063–0.200 mm) was used in column chromatography.

### 4.2. Representative procedure for Pd-catalyzed cross-coupling reaction with organoheteroatom stannanes and perfluoroalkyl iodides

The following procedure for the reaction of *n*-Bu<sub>3</sub>SnAsPh<sub>2</sub> (**1b**) with perfluorooctyl iodide (**2c**) is representative of all cross-coupling reactions. Into a three-necked, 500-mL, round-bottomed flask equipped with a cold finger condenser charged with dry ice-ethanol, a nitrogen inlet, and a magnetic stirrer, approximately 400 mL of ammonia previously dried with Na metal under nitrogen was condensed. AsPh<sub>3</sub> (1.0 mmol) and then 2 equiv. of Na metal (2 mmol) in small pieces were added, waiting for bleaching between each addition. Following 20–30 min of the last addition, Ph<sub>2</sub>As<sup>-</sup> anion was formed (clear orange-red solution), and *n*-Bu<sub>3</sub>SnCl (1 mmol) was added slowly. The mixture was then stirred for 5 min and the liquid ammonia allowed to evaporate. The evaporation left a solid white residue which was dissolved in dry toluene (12 mL). This solution was added via cannula and syringe into a Schlenk tube. In the tube, CsF (3 equiv., 2.1 mmol) was previously dried under vacuum at 120 °C for 3 h; after cooling at room temperature, (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> (10 mol%, 0.07 mmol), PPh<sub>3</sub> (Pd:L 1:4, 0.28 mmol), **2** (0.7 mmol) and toluene (3 mL) were added. When the solution of **1** was added, the reaction mixture turned deep brown. The reaction mixture was heated for 24 h in an oil bath. Water was added to the cool reaction mixture and then extracted three times with CH<sub>2</sub>Cl<sub>2</sub> (30 mL each). After drying with anhydrous

MgSO<sub>4</sub>, product **3c** was quantified by CG using the internal standard method, yielding 65% of the product.

The products were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, GC–MS and HRMS. All these spectroscopic data agreed with those reported in the literature for compounds **3a** [10], **3b** [10], **5a** [28,27a], **5b** [28], **5c** [28,14], and **5d** [14].

#### 4.3. (Perfluorooctyl)diphenylphosphine oxide (**3c**)

Compound **3c** was obtained according to the general procedure. After the cross-coupling reaction and extraction, the organic phase was oxidized with aqueous H<sub>2</sub>O<sub>2</sub> (75 mL 40%) by following procedure previously described [29]. The product was isolated from the reaction mixture by silica-gel column chromatography (diethyl ether/dichloromethane, 90:10 → 30:70) to give **3c** as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.56–7.61 (4H, m), 7.66–7.71 (2H, m), 8.00 (4H, dd, <sup>3</sup>J = 12.26 Hz, <sup>4</sup>J = 7.28 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 104.00–120.00 (C–F, partially overlapping multiplets), 125.85 (d, J<sub>C–P</sub> = 104.63 Hz), 129.00 (d, J<sub>C–P</sub> = 12.81 Hz), 132.32 (d, J<sub>C–P</sub> = 9.82), 133.77 (d, J<sub>C–P</sub> = 3.00). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 24.66 (t, J<sub>P–C</sub> = 69.31 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ –126.18–(–126.09) (m, CF<sub>2</sub>), –122.74 (s, CF<sub>2</sub>), –121.93 (s, CF<sub>2</sub>), –121.79 (s, CF<sub>2</sub>), –121.54 (s, CF<sub>2</sub>), –118.21 (t, J<sub>F–F</sub> = 14.60, CF<sub>2</sub>), –118.03 (t, J<sub>F–F</sub> = 15.04, CF<sub>2</sub>), –80.80 (t, J<sub>F–F</sub> = 9.62, CF<sub>3</sub>). MS: m/z (%): 601 (1), 202 (13), 201 (100), 183 (3), 154 (2), 153 (2), 152 (2), 131 (2). HRMS (EI): Calc. for C<sub>20</sub>H<sub>11</sub>F<sub>17</sub>OP 621.0271, found [M–H]<sup>+</sup> 621.0276. M.p.: 97.5–98.7 °C.

#### 4.4. (Perfluorobutyl)diphenylarsine (**4a**)

Compound **4a** was obtained according to the general procedure. The reaction mixture was purified by silica-gel column chromatography (hexane) to give **4a** as colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.42–7.45 (6H, m), 7.59–7.62 (4H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 104.00–120.00 (C–F, partially overlapping multiplets), 128.96 (s), 130.12 (s), 130.91 (s), 134.53 (s). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ –(125.88–125.80) (m, CF<sub>2</sub>), –118.34–(–118.26) (m, CF<sub>2</sub>), –108.92 (t, J<sub>F–F</sub> = 13.62, CF<sub>2</sub>), –81.080 (t, J<sub>F–F</sub> = 9.66, CF<sub>3</sub>). MS: m/z (%): 448 (4), 429 (2), 230 (12), 229 (100), 227 (57), 154 (12), 153 (10), 152 (19), 151 (12). HRMS (EI): Calc. for C<sub>16</sub>H<sub>11</sub>OF<sub>9</sub>As 464.8882, found [M+OH]<sup>+</sup> 464.9863.

#### 4.5. (Perfluorohexyl)diphenylarsine (**4b**)

Compound **4b** was obtained according to the general procedure. The product was isolated from the reaction mixture by silica-gel column chromatography (hexane) to give **4b** as colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.39–7.45 (6H, m), 7.59–7.62 (4H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 104.00–120.00 (C–F, partially overlapping multiplets), 128.92 (s), 130.04 (s), 130.84 (s), 134.41 (s). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ –126.25–(–126.13) (m, CF<sub>2</sub>), –122.88–(–122.76) (m, CF<sub>2</sub>), –121.79–(–121.68) (m, CF<sub>2</sub>), –117.40–(–117.30) (m, CF<sub>2</sub>), –108.72–(–108.62) (m, CF<sub>2</sub>), –81.08–(–80.72) (m, CF<sub>3</sub>). MS: m/z (%): 548 (1), 529 (2), 230 (13), 229 (100), 227 (62), 154 (15), 153 (14), 152 (26), 151 (18), 119 (6). HRMS (EI): Calc. for C<sub>18</sub>H<sub>11</sub>OF<sub>13</sub>As 564.9813, found [M+OH]<sup>+</sup> 564.9829.

#### 4.6. (Perfluorooctyl)diphenylarsine (**4c**)

Compound **4c** was obtained according to the general procedure. The product was isolated from the reaction mixture by silica-gel column chromatography (hexane) to give **4c** as colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.39–7.47 (6H, m), 7.69–7.76 (4H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 104.00–120.00 (C–F, partially overlapping multiplets), 128.92 (s), 130.03 (s), 130.81 (s), 134.43 (s). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ –126.62–(–125.88) (m, CF<sub>2</sub>), –123.23–(–122.55) (m, CF<sub>2</sub>),

–122.42–(–121.22) (m, CF<sub>2</sub>), –118.68–(–118.16) (m, CF<sub>2</sub>), –117.51–(–117.11) (m, CF<sub>2</sub>), –108.86–(–108.40) (m, CF<sub>2</sub>), –81.09–(–80.68) (m, CF<sub>3</sub>). MS: m/z (%): (M–F)<sup>+</sup> 629 (1), 230 (12), 229 (100), 227 (41), 154 (10), 153 (7), 152 (14), 151 (9). HR MS (EI): Calc. for C<sub>20</sub>H<sub>11</sub>OF<sub>17</sub>As 664.9749, found [M+OH]<sup>+</sup> 664.9762.

#### 4.7. (Perfluorodecyl)diphenylarsine (**4d**)

Compound **4d** was obtained according to the general procedure. The product was isolated from the reaction mixture by silica-gel column chromatography (hexane) to give **4d** as colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.38–7.45 (6H, m), 7.57–7.63 (4H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 104.00–120.00 (C–F, partially overlapping multiplets), 128.94 (s), 130.05 (s), 130.85 (s), 134.42 (s). <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ –126.32–(–125.88) (m, CF<sub>2</sub>), –123.15–(–122.84) (m, 2CF<sub>2</sub>), –122.13–(–121.24) (m, 3CF<sub>2</sub>), –118.62–(–118.26) (m, CF<sub>2</sub>), –117.44–(–116.93) (m, CF<sub>2</sub>), –108.80–(–108.43) (m, CF<sub>2</sub>). MS: m/z (%): 729 (1), 230 (12), 229 (100), 227 (33), 154 (8), 153 (6), 152 (10), 151 (7). HRMS (EI): Calc. for C<sub>22</sub>H<sub>11</sub>OF<sub>21</sub>As 764.9685, found [M+OH]<sup>+</sup> 764.9702.

#### Acknowledgements

We thank ACC, CONICET, FONCYT, and SECYT, Universidad Nacional de Córdoba for their continuous support to our work. M.N.L. thanks CONICET for the fellowship granted.

#### Appendix A. Supplementary material

Supplementary data (general experimental details and procedures, and characterization of **3c** and **4a–d**) associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.06.035.

#### References

- [1] (a) K. Uneyama, *Organofluorine Chemistry*, Blackwell Publishing Ltd., Oxford, England, 2006; (b) M. Shimizu, T. Hiyama, *Angew. Chem., Int. Ed.* 44 (2005) 214–231; (c) P. Kirsch, *Modern Fluoroorganic Chemistry*, Wiley-VCH, Weinheim, Germany, 2004; (d) J.-A. Ma, D. Cahard, *Chem. Rev.* 104 (2004) 6119–6146; (e) K. Mikami, Y. Itoh, M. Yamanaka, *Chem. Rev.* 104 (2004) 1–16; (f) W. Zhang, *Tetrahedron* 59 (2003) 4475–4489; (g) P.G. Jessop, T. Ikariya, R. Nyori, *Chem. Rev.* 99 (1999) 475–494; (h) R.H. Fish, *Chem. Eur. J.* 5 (1999) 1677–1680; (i) E.G. Hope, A.M. Stuart, *J. Fluorine Chem.* 100 (1999) 75–83; (j) I.T. Horváth, *Acc. Chem. Res.* 31 (1998) 641–650; (k) B.E. Smart, *Ed. Chem. Rev.* 96 (1996) 5.
- [2] (a) I.G. Phillips, R.G. Ball, R.G. Cavell, *Inorg. Chem.* 27 (1988) 4038–4045; (b) M.F. Ernst, D.M. Roddick, *Organometallics* 9 (1990) 1586–1594; (c) R.C. Schnabel, P.S. Carroll, D.M. Roddick, *Organometallics* 15 (1996) 655–662; (d) R.C. Schnabel, D.M. Roddick, *Organometallics* 15 (1996) 3550–3555; (e) J.F. Houllis, D.M. Roddick, *J. Am. Chem. Soc.* 120 (1998) 11020–11021; (f) S. White, B.L. Bennett, D.M. Roddick, *Organometallics* 18 (1999) 2536–2542; (g) J.L. Butikofer, J.M. Hoerter, R.G. Peters, D.M. Roddick, *Organometallics* 23 (2004) 400–408; (h) J.D. Palcic, R.G. Baughman, M.V. Golynskiy, S.B. Frawley, R.G. Peters, *J. Organomet. Chem.* 690 (2005) 534–538; (i) J.D. Palcic, R.G. Baughman, R.G. Peters, *J. Coord. Chem.* 58 (2005) 521–527.
- [3] C.L. Pollock, G.C. Saunders, E.C.M.S. Smyth, V.I. Sorokin, *J. Fluorine Chem.* 129 (2008) 142–166.
- [4] (a) J.H. Downing, M.B. Smith, *Phosphorus ligands*, in: A.B.P. Lever (Ed.), *Comprehensive Coordination Chemistry II*, Vol. 1, Elsevier, Oxford, 2004, pp. 253–296; (b) C.A. McAuliffe, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), *Comprehensive Coordination Chemistry*, Vol. II, Pergamon, Oxford, 1987, pp. 990–1066; (c) O. Kühl, *Coord. Chem. Rev.* 249 (2005) 693–704; (d) C.A. Tolman, *Chem. Rev.* 77 (1977) 313–348.
- [5] K.D. Cooney, T.R. Cundari, N.W. Hoffman, K.A. Pittard, M.D. Temple, Y. Zhao, *J. Am. Chem. Soc.* 125 (2003) 4318–4324.
- [6] S. Otto, A. Rood, *Inorg. Chim. Acta* 357 (2004) 1–10.

- [7] (a) F.W. Bennett, H.J. Emel us, R.N. Haszeldine, *J. Chem. Soc.* (1953) 1565–1571;  
(b) H.J. Emel us, J.D.J. Smith, *Chem. Soc.* (1959) 375–381;  
(c) L.J. Krause, J.A. Morrison, *J. Am. Chem. Soc.* 103 (1981) 2995–3001;  
(d) T. Mahmood, J.M. Shreeve, *Inorg. Chem.* 25 (1986) 3128–3131;  
(e) E.A. Ganja, C.D. Ontiveros, J.A. Morrison, *Inorg. Chem.* 27 (1988) 4535–4538;  
(f) E.A. Ganja, J.A. Morrison, *Inorg. Chem.* 29 (1990) 33–38;  
(g) J.J. Kampa, J.W. Nail, R.J. Lagow, *Angew. Chem., Int. Ed.* 34 (1995) 1241–1244;  
(h) M. G org, G.-V. R osenthaler, A.A. Kolomeitsev, *J. Fluorine Chem.* 79 (1996) 103–104.
- [8] (a) M.F. Ernst, D.M. Roddick, *Inorg. Chem.* 28 (1989) 1624–1627;  
(b) K.K. Banger, A.K. Brisdon, A. Gupta, *Chem. Commun.* (1997) 139–140;  
(c) R.G. Peters, B.L. Bennett, R.C. Schnabel, D.M. Roddick, *Inorg. Chem.* 36 (1997) 5962–5965;  
(d) K.K. Banger, R.P. Banham, A.K. Brisdon, W.I. Cross, G. Damant, S. Parsons, R.G. Pritchard, A.J. Sousa-Pedrares, *Chem. Soc., Dalton Trans.* (1999) 427–434.
- [9] (a) M.A.A. Beg, H.C. Clark, *Can. J. Chem.* 40 (1962) 283–288;  
(b) E. Lindner, H. Kranz, *Chem. Ber.* 101 (1968) 3438;  
(c) K. Gosling, D.J. Holman, J.D. Smith, B.N.J. Ghose, *Chem. Soc. A* (1968) 1909–1914;  
(d) J.D. Palcic, P.N. Kapoor, D.M. Roddick, R.G. Peters, *Dalton Trans.* (2004) 1644–1647;  
(e) M.B. Murphy-Jolly, L.C. Lewis, A.J.M. Caffyn, *Chem. Commun.* (2005) 4479–4480.
- [10] S.E. Vaillard, A. Postigo, R.A. Rossi, *Organometallics* 23 (2003) 3003–3007.
- [11] (a) W.R. Cullen, *Can. J. Chem.* 39 (1961) 2486;  
(b) W.R. Cullen, *Can. J. Chem.* 38 (1960) 439;  
(c) D. Naumann, G. Nowicki, K.-J. Sassen, *Z. Anorg. Allg. Chem.* 623 (1997) 1183–1189;  
(d) N. Buford, C.L.B. Macdonald, D.J. LeBlanc, T.S. Cameron, *Organometallics* 19 (2000) 152–155;  
(e) S.K. Shukla, A. Ranjan, A.K. Saxena, *J. Fluorine Chem.* 122 (2003) 165–170.
- [12] (a) Arsines as ligand, some examples: R. Rossi, F. Bellina, A. Carpita, F. Mazzarella, *Tetrahedron* 52 (1996) 4095–4110;  
(b) S.Y. Cho, M. Shibasaki, *Tetrahedron Lett.* 39 (1998) 1773–1776;  
(c) D.D. Hennings, T. Iwama, V.H. Rawai, *Org. Lett.* 1 (1999) 1205–1208;  
(d) S. Ceccarelli, U. Piarulli, C. Gennari, *J. Org. Chem.* 65 (2000) 6254–6256;  
(e) M. Cai, Y. Huang, H. Zhao, C. Song, *J. Organomet. Chem.* 682 (2003) 20–25;  
(f) R.B. Bedford, C.S.J. Cazin, S.J. Coles, T. Gelbrich, M.B. Hursthouse, V.J.M. Scordia, *Dalton Trans.* (2003) 3350–3356;  
(g) K.C.Y. Lau, H.S. He, P. Chiu, P.H. Toy, *J. Comb. Chem.* 6 (2004) 955–960;  
(h) M. Cai, Y. Huang, R. Hu, C. Song, *J. Mol. Catal. A* 212 (2004) 151–154;  
(i) R.A. Baber, S. Collard, M. Hooper, A.G. Orpen, P.G. Pringle, M.J. Wilkinson, R.L. Wingad, *Dalton Trans.* (2005) 1491–1498.
- [13] (a) S.E. Mart n, M. Bonaterra, R.A. Rossi, *J. Organomet. Chem.* 664 (2002) 223–227;  
(b) M. Bonaterra, S.E. Mart n, R.A. Rossi, *Org. Lett.* 15 (2003) 2731–2734;  
(c) M. Bonaterra, R.A. Rossi, S.E. Mart n, *Organometallics* 28 (2009) 933–936.
- [14] M. Bonaterra, S.E. Mart n, R.A. Rossi, *Tetrahedron Lett.* 47 (2006) 3511–3515.
- [15] S. Matsubara, M. Mitani, K. Utimoto, *Tetrahedron Lett.* 28 (1987) 5857–5860.
- [16] R. Shimizu, T. Fuchikami, *Tetrahedron Lett.* 37 (1996) 8405–8408.
- [17] R. Shimizu, T. Fuchikami, *Tetrahedron Lett.* 42 (2001) 6891–6894.
- [18] (a) E. Vedejs, A.R. Haight, W.O. Moss, *J. Am. Chem. Soc.* 114 (1992) 6556–6558;  
(b) V. Farina, *Pure Appl. Chem.* 68 (1996) 73–78;  
(c) E. Fouquet, M. Pereyre, A.L. Rodriguez, *J. Org. Chem.* 62 (1997) 5242–5243.
- [19] (a) W.J. Scott, J.K. Stille, *J. Am. Chem. Soc.* 108 (1986) 3033–3040;  
(b) A. Garc a Mart nez, J. Os o Barcina, A. de Fresno Cerezo, L.R. Subramanian, *Synlett* (1994) 1047–1048;  
(c) A.F. Littke, G.C. Fu, *Angew. Chem., Int. Ed.* 38 (1999) 2411–2413. and references cited therein;  
(d) A.F. Littke, L. Schwarz, G.C. Fu, *J. Am. Chem. Soc.* 124 (2002) 6343–6348.
- [20] (a) V. Farina, B. Krishnan, *J. Am. Chem. Soc.* 113 (1991) 9585–9595;  
(b) V. Farina, S.R. Baker, D.A. Benigni, S.I. Hauck, C.J. Sapino, *Org. Chem.* 55 (1990) 5833–5847;  
(c) J. Louie, J.F. Hartwig, *J. Am. Chem. Soc.* 117 (1995) 11598–11599;  
(d) A.L. Casado, P. Espinet, *Organometallics* 17 (7) (1998) 954–959;  
(e) A.L. Casado, P. Espinet, *J. Am. Chem. Soc.* 120 (1998) 8978–8985.
- [21] (a) L.S. Liebeskind, R.W. Fengl, *J. Org. Chem.* 55 (1990) 5359–5364;  
(b) V. Farina, S. Kapadia, B. Krishnan, C. Wang, L.S. Liebeskind, *J. Org. Chem.* 59 (1994) 5905–5911;  
(c) J. Ye, R.K. Bhatt, J.R. Falck, *J. Am. Chem. Soc.* 116 (1994) 1–5;  
(d) X. Han, B.M. Stolz, E.J. Corey, *J. Am. Chem. Soc.* 121 (1999) 7600–7605;  
(e) A.L. Casado, P. Espinet, *Organometallics* 22 (2003) 1305–1309.
- [22] S.P.H. Mee, V. Lee, J.E. Baldwin, *Chem. Eur. J.* 11 (2005) 3294–3308.
- [23] A. K llhofer, T. Pullmann, H. Plenio, *Angew. Chem., Int. Ed.* 42 (2003) 1056–1058.
- [24] C. Amatore, A. Jutand, *Coord. Chem. Rev.* 178–180 (1998) 511–528. and references therein.
- [25] The air- and moisture-stable salt [HP(*t*-Bu)<sub>2</sub>Me]BF<sub>4</sub> was used as ligand instead of P(*t*-Bu)<sub>2</sub>Me. It is commercially available and furnishes yields similar to phosphine itself. See: K. Menzel, G.C. Fu, *J. Am. Chem. Soc.* 125 (2003) 3718–3719.
- [26] S.E. Tunney, J.K. Stille, *J. Org. Chem.* 52 (1987) 748–753.
- [27] (a) C. Pooput, W.R. Dolbier Jr., M. M debielle, *J. Org. Chem.* 71 (2006) 3564–3568;  
(b) G. Blond, T. Billard, B.R. Langlois, *Tetrahedron Lett.* 42 (2001) 2473–2475;  
(c) T. Billard, S. Large, B.R. Langlois, *Tetrahedron Lett.* 38 (1997) 65–68;  
(d) T. Billard, B.R. Langlois, *Tetrahedron Lett.* 37 (1996) 6865–6868;  
(e) I.J. Ruppert, *Fluorine Chem.* 29 (1985) 98;  
(f) N.V. Kondratenko, A.A. Kolomeitsev, V.I. Popov, L.M. Yagupolskii, *Synthesis* (1985) 667–669.
- [28] E. Magnier, E. Vit, C. Wakselman, *Synlett* (2001) 1260–1262.
- [29] (a) M.I. Denniston, D.R. Martin, *Inorg. Synth.* 17 (1977) 183–185;  
(b) J.J. Brophy, K.L. Freedman, M.J. Gallegher, *J. Chem. Soc.* (1968) 2760–2762.