Palladium-Catalyzed Arsination Reactions and their applications on the Synthesis of Arsine Ligands

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Abstract: In the synthesis of new ligands for metal-catalyzed reactions, arsine are attracting particular attention, because arsine ligands have been shown to be better ligands than structurally related phosphines in several catalyzed reactions. However, the synthesis and applications of arsine ligands is not widely extended in the literature. One of the main barriers to develop new arsine ligands is found in the synthetic methodologies to obtain arsine compounds. Therefore, to expand the applications of arsine ligands it is necessary to develop new synthetic strategies. To improve the classic arsination reactions metal-catalyzed C-As bond formation reactions appears to be a promising approach. This article highlights the palladium-catalyzed arsination reactions, providing the synthetic approaches used to obtain arsines. In addition, the few described examples of other metal-catalyzed arsination reactions are included. The synthesis of structurally diverse arsine ligands by catalyzed arsination reactions is summarized, as well as the most relevant issues of their applications in homogeneous catalysis.

Keywords: palladium**;** Pd-catalyzed arsination; catalyzed arsination; arsine ligands; aryl arsines; coupling reactions; Heck;

1. INTRODUCTION

The catalytic activity of homogeneous Pd-catalysts principally depends on the nature of ligands; hence, the structural and electronic properties of the ligands delineate the reactivity and selectivity of catalysts. Thus, development of novel ligands plays a central role in the evolution toward highly efficient Pd catalysts. The group of ligands most widely used in transition metal catalysis is the tertiary phosphines, primarily due to the versatile fine-tuning of their properties. However, disappointing outcomes may be observed even with the outlined phosphine ligands, thus novel sorts of ligands are required, in order to achieve improvements in catalysis area. The search of ligands with diverse coordination abilities and structures are required. The distinctive electronic properties of arsine make them excellent candidate to complement phosphines behavior as ligands.

In this context, arsines are increasing their consideration as alternative ligands in metal-catalyzed reactions. Even though phosphines and arsines homologues had slight differences in steric parameters, their electronic properties are in essence distinct. Arsine ligands have poorer σ-donor properties compared to the structurally related phosphines, and the π-acceptor character is reduced in arsine ligands. Thus, arsines are thought to be modifying ligands.

In many transition metal-catalyzed reactions arsine ligands proved to be more active or selective ligands than phosphines. Some of these reactions employed Ph_3As as ligand, including Stille [1] and Suzuki-Miyaura coupling processes [2], Negishi reaction [3], Heck and related reactions [4], Sonogashira [5], cross-coupling with arylsilanol [6], hydroformylation of terminal alkenes [7], carbonylations [8], polymerizations [9], and Buchwald coupling reactions [10]. Moreover, biologically active molecules were synthesized by Pd-catalyzed reactions using Ph_3As as ligand [11].

Besides Ph_3As, limited examples of structurally diverse arsine ligands compared to the broadly extended phosphines, were synthetized and successfully used in coupling reactions [12] (Figure 1). Likewise, in similar catalytic systems as the above-mentioned [13] (Figure 1), arsine ligands demonstrated better catalytic activity than the structurally related phosphine. One of the major barriers to develop new arsine ligands is found in the synthetic methodologies to obtain arsine compounds. Thus, the improvement of new strategies to acquire arsines is progressively appeared as central in the synthesis of new ligands.

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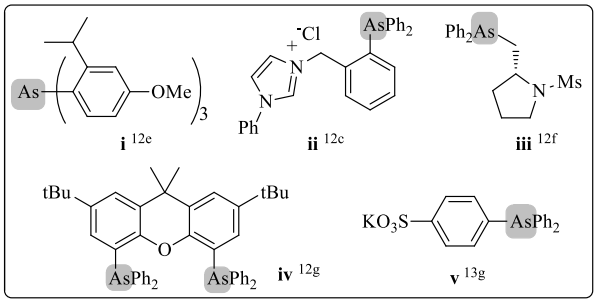


Figure 1. Illustrative examples of arsine ligands.

In the same way, few examples of chiral arsine ligands have been described, rather than the numerous chiral phosphine-based ligands that have been prepared. The scarce examples of chiral arsine ligands synthesized [14] and applied in asymmetric catalysis [15] includes chiral arsine ligands in intramolecular Heck reaction [16], Heck-type hydroarylation [12f], hydrosilylation of 1,3-dienes [17], and allylic alkylation reactions [18]. Therefore, the application of chiral arsine ligands in asymmetric Pd-catalyzed reactions remains at the beginning of their development.

As previous mentioned, arsine ligands improvement has been delayed, and this postponed development could be mostly because of the absence of promptly accessible As-containing compounds. Most of the available synthetic methods to obtain aryl arsines are complicated or limited in scope. For example, the classic arsination consist in the reaction of either electrophilic or nucleophilic As reagents (Figure 2).

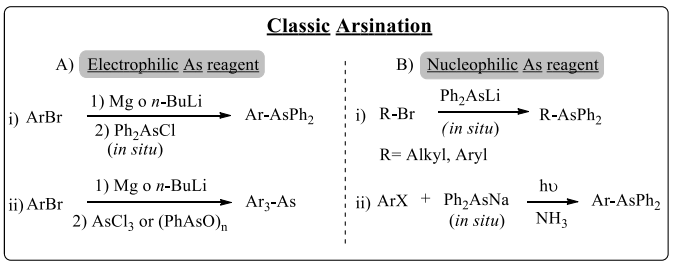


Figure 2. Classical methods for preparation of arsine derivatives.

The reactions that involves electrophilic arsine reagent usually consist in the employment of organolithium or organomagnesium reagents with haloarsines [12c, 19] or arsine oxide derivatives [20] (A, Figure 2). This type of methodology was used to prepare ligands **i**, **ii** and **iv** (Figure 1). Recently, with this last alternative highly electrophilic α-cationic arsine ligands were synthesized by the reaction of iododiphenylarsine and carbenes moieties, obtaining moderate to good yields [21].

On the other hand, an additional method involves the reaction of aryl halides with nucleophilic arsine reagents like Ph_2AsM (M = Li, Na, K) prepared *in situ* [12d, 13g, 22] (B, Figure 2). By the photostimulated reactions of Ph_2As^- ions with aryl halides in liquid ammonia triarylarsines were obtained; however, a scrambling of products was observed [22c-e]. The nucleophilic arsenic precursor could also be prepared using cyclooligoarsines, allowing the synthesis of aliphatic and aromatic arsines. By this methodology, besides the preparation of ligand **iii** and **v** (Figure 1), $AsPh_2$ moiety was incorporated into silica support to obtain a recyclable supported Pd-catalyst [12d]. In addition, simple bidentate ligands were prepared in good yields [12g, 23].

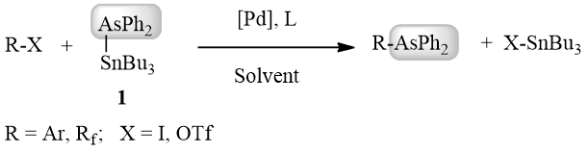
Despite transition-metal catalyzed C-heteroatom bond formation reactions are employed to obtain different heteroatom-contained compounds, only few examples of this type of methodology were accounted for the synthesis of arsine compounds.

This article reviews the palladium-catalyzed arsination reactions, providing the limited synthetic approaches used to obtain arsines. In addition, the few described examples of other metal-catalyzed arsination reactions are included. Furthermore, the synthesis of structurally diverse arsine ligands synthesized by catalyzed arsination reactions is summarized, as well as the most relevant applications of the ligands.

2. Pd-Catalyzed Arsination Reactions

2.1. Pd-Catalyzed Arsination with *n*-$Bu_3SnAsPh_2$

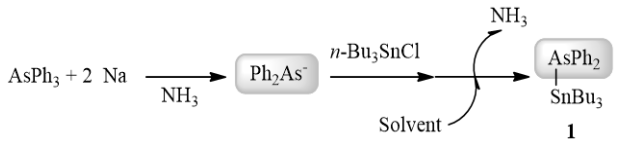
The C-As bond formation by the Pd-catalyzed Stille reaction of different electrophiles with arsine stannane *n*-$Bu_3SnAsPh_2$ (**1**) in a one-pot two-step reaction was recently described (Scheme 1) [24]. In this work, the synthesis of stannane *n*-$Bu_3SnAsPh_2$ and the examination of its chemistry was carried out for the first time.



Scheme 1. Pd-catalyzed arsination with *n*-$Bu_3SnAsPh_2$ in a one-pot, two-step reaction.

The Stille reaction, *i.e.* the transition-metal-catalyzed cross-coupling of organostannanes with organic electrophiles, is a widely used strategy for C-C [25], as well as for C-heteroatom bond formation [26]. While the extend of the Pd-catalyzed coupling reactions of group-15-derived organostannanes, for example, aminostannanes [26a-c] and (trialkylstannyl)phosphines [26d-e] has been studied, the formation of C-As bonds by this type of reactions was unexplored. Moreover, the Pd-catalyzed cross-coupling of organoheteroatom stannanes holding Sn-P and Sn-Se bonds was also achieved by the same methodology [26e, k; 27].

The useful methodology to undertake C-As bond formation by the cross-coupling Pd-catalyzed reaction with the stannane *n*-$Bu_3SnAsPh_2$ (**1**) involved the *in-situ* preparation of the stannane **1**, through the reaction of Ph_2As^- anion (anion produced from $AsPh_3$ and Na metal in liquid ammonia) with *n*-Bu_3SnCl (Scheme 2) [24].

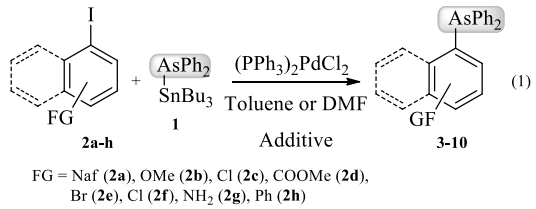


Scheme 2. I*n situ* preparation of *n*-$Bu_3SnAsPh_2$ (**1**).

Afterwards, the Stille cross-coupling reaction of **1** with several electrophiles in the presence of Pd-catalyst was carried out in a one-pot procedure. In the next sections, the scope of this Pd-catalyzed arsination will be discussed.

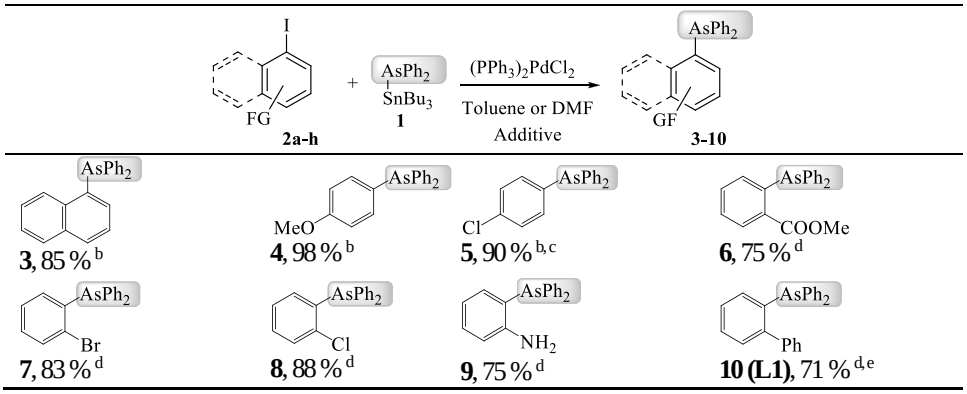
2.1.1. Pd-Catalyzed Arsination of Aryl Iodides with n-$Bu_3SnAsPh_2$

On the first report, only few triaryl-functionalized arsines were synthetized by the Pd-catalyzed arsination of aryl iodides [24]. Afterward, the application of this methodology was extended to more sterically hindered aryl iodides and to other electrophiles [28]. The Pd-catalyzed arsination of **1** with aryl iodides (**2a-h**) was carried out in a one-pot two-step procedure with $(PPh_3)_2PdCl_2$ as Pd source (eq. 1). Other Pd catalyst were evaluated for arsination and cross-couplings reactions, and always the best catalyst was the stable and easy to handle $(PPh_3)_2PdCl_2$.



The most significant results of the Pd-catalyzed arsination are shown on Table 1. High yields of triarylarsines were achieved using only 1.5 mol % of the Pd catalyst. A variety of aryl iodides with different functional groups were employed, in order to establish the scope of the reaction. Remarkable, sterically hindered *ortho*-substituted aryl iodides reacted efficiently. Chemioselectivity for bromide and chloride halides was observed, since only aryl iodides reacted under these conditions, allowing further transformation in the products containing halides. Both electron-donating and electron-withdrawing groups showed similar rates and yields, and no substantial electronic effects were observed. The reaction proceeded almost to completion, although the products of the arsination reaction could be active Pd ligands.

Table 1. Pd-catalyzed arsination of ArI (**2a-h**) with *n*-$Bu_3SnAsPh_2$ (**1**) in the presence of $(PPh_3)_2PdCl_2$.[a]



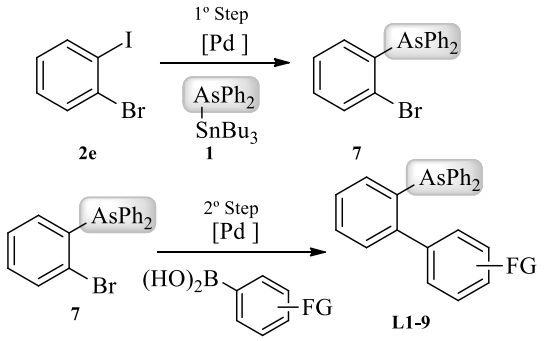
[a] Reaction conditions: Ph_2As^- anion was obtained in liquid ammonia (300 mL) from $AsPh_3$ (1 mmol) and Na metal (2 mmol); *n*-Bu_3SnCl (1 mmol) was then added. The cross-coupling reaction was achieved with ArI (0.7 mmol) and $(PPh_3)_2PdCl_2$ (1.5 mol%) for 24 hours at 80 ºC toluene. [b] GC yields. [c] DMF was used at 120 ºC. [d] Isolated yields. [e] Additives: PPh_3 (Pd:L 1:4) and CuI (Pd:Cu 1:2).

Finally, with this simple synthetic methodology, a new biphenyl arsine ligand was synthetized. The arsine ligand biphenyl-2-yldiphenylarsine (**10**, **L1**, BAs) was achieved through the arsination reaction of 2-iodobiphenyl (**2h**) catalyzed by $(PPh_3)_2PdCl_2$ (71% of isolated yield, Table 1). This coupling reaction turn out to be more effective using Cu(I) as co-catalyst. Additionally, 2-(diphenylarsino)aniline (**9**) could likewise be viewed as a bidentate [As,N] ligand itself [29]. As a general trend, the triarylarsines (**3-10**) were obtained as air-stable solid compounds, in very good to excellent isolated yields.

Biphenyl Arsine Ligands: Synthesis and Applications. The biaryl unit was recognized as a main structure in diverse significant monodentate [30] and bidentate phosphine ligands [31]. The well-designed electron-rich biaryl monophosphines, first presented by Buchwald [32], have shown to be outstanding ligands for Pd-catalyzed reactions [33]. The coupling reactions performance with Buchwald-type biphenyl phosphines ligands has been further improved by increasing the substituents steric bulk and by introducing substituents on the *ortho*-positions of non-phosphine-containing aromatic ring [34].

The biaryl framework has been used as a main building-block to develop alternative ligands [35]. This basic design concept was used in the synthesis of novel biphenyl-based arsine ligands by an approach including the Pd-catalyzed arsination of aryl halide **2e**, follow by a Suzuki-Miyaura

coupling as the main synthetic tool for biaryl building (Scheme 3) [36, 37].



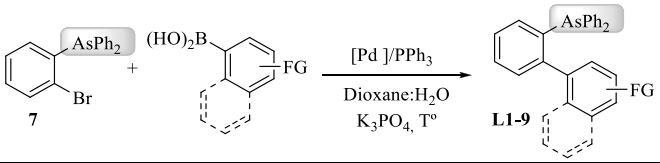
Scheme 3. Synthetic pathway to biarylarsine ligand **L1-9** synthesis.

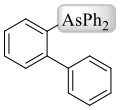
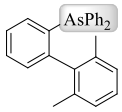
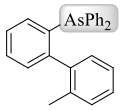
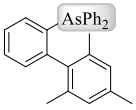
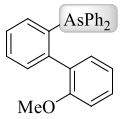
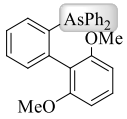
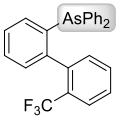
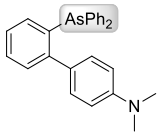
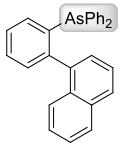
The Suzuki-Miyaura coupling step was performed by conventional [36] and MW-assisted heating [37]. The most relevant results are summarized on Table 2.

Novel biphenyl arsine ligands **L1-9** were obtained in excellent yields (70-99%), with overall isolated yields for the two steps up to 82%. When MW-irradiation was used, short reaction times were achieved in the Suzuki-Miyaura coupling on the described protocol. Based on this synthetic strategy, the properties of the arsine ligands can be fine-tuning according to the electronic and steric effects changing the substituents in the biaryl backbone.

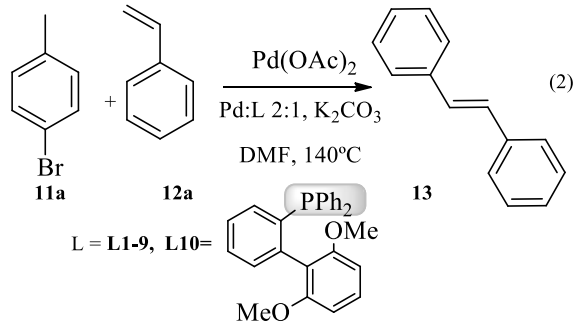
The catalytic activity of these biphenylarsine ligands was explored in Pd-catalyzed Stille cross-coupling reaction with R_f-I, which will be described on Section *2.1.3.*, and in Heck coupling reactions of aryl halides with alkenes [37]. Particularly, the activity of these ligands was investigated in Pd-catalyzed Heck reaction taking into account the high performances demonstrated by bulky triarylarsine ligands in these coupling (eq. 2) [12c,e].

Table 2. Pd-catalyzed Suzuki reaction of **7** with boronic acids under conventional and MW-assisted heating.[a]



 **L1** Conv.: 98 % (1440 min) [b] MW: 93 % (10 min) [c]	 **L2** Conv.: 61% (2880 min) [b,d,e] MW: 70 % (80 min) [c,d,e]	 **L3** Conv.: 98 % (1440 min) [b] MW: 96 % (20 min) [c]
 **L4** Conv.: 89% (2880 min) [b,d,e] MW: 71 % (100 min) [c,d,e]	 **L5** Conv.: 96% (1440 min) [b] MW: 90 % (20 min) [c]	 **L6** Conv.: 83% (1440 min) [b] MW: 91 % (40 min) [c]
 **L7** Conv.:– [f] MW: 86 % (50 min) [c]	 **L8** Conv.: – [f] MW: 99 % (50 min) [c]	 **L9** Conv.: 80 % (1440 min) [b] MW: 80 % (10 min) [c]

[a] Reaction conditions: bromoarsine **7** (1 equiv.), boronic acid (1.5 equiv.), 1 mol % $Pd(AcO)_2$, PPh_3 (Pd/L, 1:4), a K_3PO_4 (2 equiv.), and dioxane:H_2O (4:1, 5 mL), under nitrogen. GC yields are informed and time in parentheses. [b] Conventional heating: 100 ºC. [c] MW dynamic method in sealed vessels at a fixed 150 °C. [d] 3 mol % $Pd(dba)_2$. [e] An extra 1.5 equiv. of boronic acid was added after half reaction time. [f] Not performed.



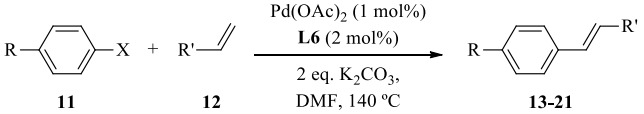
A wide range of reaction conditions were systematically evaluated in the coupling of *p*-bromotoluene (**11a**) and styrene (**12a**) as typical reaction [37]. DMF was the solvent of choice, since the reaction rates enhanced with polar nonprotic solvents, indicating that the coordination abilities of this solvent play an important role in the catalyst activity [38]. Under the optimized conditions, the catalytic activity of biphenyl-based arsine ligands **L1-L9** was evaluated (Table 3), in addition to the diphenylphosphine ligand **L10**, a phosphorus ligand homologue of **L6** [39] (eq. 2). Product **13** was achieved with high selectivity for the *trans*-product.

The study revealed that the biphenyl ligand structure had a significant impact over the conversion of substrate **11a**. With arsine ligand **L1** a remarkable inhibition of the reaction was observed, probably due to the formation of stable palladacycles [40]. However, the more efficient ligands to performed the coupling reaction (**L3**, **L4**, **L6**, **L7**, **L8** and **L9**) were those with ''blocked'' *ortho*-positions on the non-arsine containing ring of the biphenyl backbone. A combination of factors could be responsible for this effect; the steric bulk that favored the development of active monophosphine complex [LPd(0)] and the absence of *ortho*-hydrogens that prevents the formation of palladacycles [34, 41]. Although ligands **L6** and **L7** exhibit very different electronic characteristics, both provided the highest yields of the alkene product. The higher catalytic efficiency of the Pd-**L6** complex may be due to the Pd-O interactions within **L6** that contribute to the stability of the catalyst. Alternatively, with the more electron-withdrawing **L7** the formation of a less electron-rich Pd complex could account for the high activity, by easily promote the alkene coordination or insertion [42]. The presence of the arsine group was shown to produce an important effect over the catalytic activity. It was demonstrated that the biphenylphosphine ligand **L10** (eq. 2), homologue of **L6**, gave lower conversion of **11a** than **L6** in the same reaction conditions.

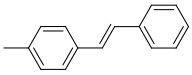
In consequence, in agreement with the results obtained by Pringle and co-workers [12e], the catalysts resulting from Pd/biphenylarsine complexes were efficient in the Heck reaction. This is not a new finding, faster overall Heck reactions can be accomplished allowing a suitable balance between steric and basicity properties of ligands, as previous studies suggested [42]. The extent of the Pd- catalyzed Heck coupling employing **L6** was examined with several aryl halides and alkenes under the optimized reaction conditions [37]. The coupling products were achieved in excellent yields (70-96 %) and high selectivity with activated electrophiles, in relative short reaction time, and with low catalyst loadings (Table 3).

With more challenging electrophiles, good to moderate yield of alkene products were obtained (32-65 %). Thus, the Pd-**L6** system proved to be an efficient catalyst system to achieve the coupling reaction with different substrates and olefins, and also with demanding substrates like non-activated aryl halides and heterocycles, *orto*-substituted.

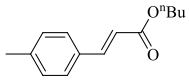
Table 3. Heck coupling reaction of aryl halides with alkenes catalyzed by Pd-**L6**.[a]



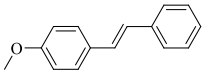
11 **12** **13-21**



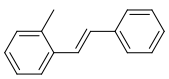
13 (X= I)
78 % (2.5 h) [c]



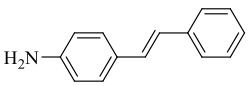
14 (X= I)
96 % (2.5 h)



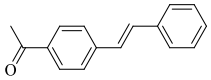
15 (X= I)
84 % (24 h)



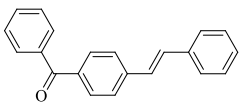
16 (X= I)
88 % (24 h)



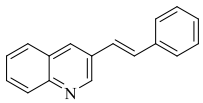
17 (X= I)
79 % (5 h)



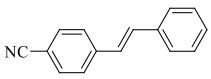
18 (X= Br)
95 % (2.5 h)



19 (X= Br)
83 % (2.5 h)



20 (X= Br)
76 % (2.5 h)



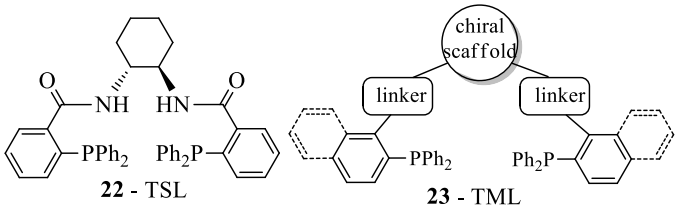
21 (X= Br)
90 % (2 h)

[a] Reaction conditions: 1 mmol of ArX 5, 1.5 mmol of an alkene, 1 mol% $Pd(OAc)_2$, 2 mol% **L6**, 2 mmol K_2CO_3, 4 mL of DMF, 140 °C, under nitrogen. GC yields are informed.

Chiral Bisarsine-Ligand: Synthesis and applications. As previously mentioned, the use of enantiomerically pure arsine ligands in asymmetric catalysis is far from being exploited.

One of the most powerful tools for the asymmetric C−C and C−heteroatom bond formation is the Pd-catalyzed allylic alkylation. This reaction found a wide range of applications in the synthesis of valuable molecules and complex natural products [43]. Chiral biphosphine ligands have been one of the largest classes of ligands used in these transformations, affording excellent enantioselectivities [43a-e]. However, the applications of chiral arsine ligands remain practically unexplored in the Pd-catalyzed allylic alkylation.

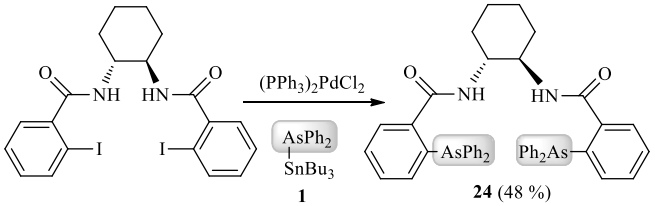
Trost and co-workers reported the synthesis and many applications of ligand **22**, typically namely "Trost standard ligand" (TSL) (Scheme 4) [44].



Scheme 4. Phosphine Trost Standard Ligands (**22**-TSL) and Trost Modular Ligands (**23**-TML).

The TSL was effectively used in a large number of asymmetric allylic alkylation reactions. Due to this, the general scaffold of Trost modular ligand (TML) (**23**, Scheme 4) has been expanded, producing a large number of related ligands largely applied in asymmetric metal-catalyzed reactions [45].

The first example of a chiral bisarsine ligand based on the framework of TML, the 1,2-bis-*N*-[2'-diphenylarsinobenzoyl]-1(*R*),2(*R*)- diamine cyclohexane (BiAsBA, **24**) was recently synthesized (Scheme 5) [18]. The key step in this strategy was introducing the -$AsPh_2$ group on the ligand skeleton, in which the Pd-catalyzed arsination reaction with stannane *n*-$Bu_3SnAsPh_2$ (**1**) was employed.



Scheme 5. Synthesis of bisarsine ligand **24** by Pd-catalyzed arsination with $Bu_3SnAsPh_2$ (**1**), 1.5 mol % [Pd], PPh_3 (Pd:L 1:4), CuI (Pd:Cu 1:2), DMF 120ºC, 72 h.

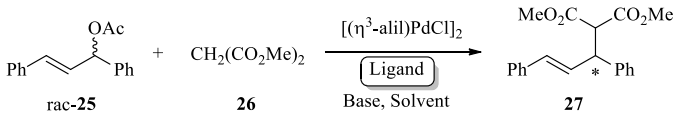
This simple strategy allowed obtaining the new chiral bisarsine ligand **24** in 48% isolated yield, as an air-stable solid. The structure of the bisarsine ligand was confirmed by X-ray crystallography [18]. Regardless of the moderate yield obtained in the disubstitution arsination reaction, it should be notice that two simultaneous coupling reactions were taking place. Besides, similar yields were obtained in the synthesis of other chiral arsine ligands [15, 16].

The chiral ligand **24** was evaluated in Pd-catalyzed asymmetric allylic alkylation of 1,3-diphenylpropenyl acetate (**25**) with dimethyl malonate (**26**) (Table 4). The catalyst was formed *in situ* from $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and ligand **24** and allowed to react at room temperature under the standard conditions reported by Trost *et. al* (NaH as base in THF) [46]. This catalyst was found to be effective for the allylic alkylation, and the alkylated malonate **27** was obtained in 98 % yields, however with only 23 % *ee* (Table 5). Regardless of the low enantioselectivity observed, this outcome demonstrated the substantial potential of the bisarsine ligand **24**, since the **22**-TSL gave allylic malonate **27** in 29 % yields and 12 % *ee* under the same reaction condition [46].

After several optimizations, the combination *N,O*-bis(trimethylsilyl)acetamide (*BSA*) with LiAcO as base and changing the solvent to CH_2Cl_2 led to improve the reaction enantioselectivity, since 49 % *ee* were accomplished (Table 4). The use of LiAcO/*BSA* reagents facilitates the deprotonation of dimethyl malonate **26** and the production of nucleophile in catalytic amounts [47]. The structural dynamics associated with the steric strain induced by the Ph-As moiety with the allyl termini was attributed to be responsible for the modest asymmetric induction observed with ligand **24**.

The exceptional enhance in the catalytic activity using ligand **24** offers new chances to manage allylic alkylation reactions. It was established in the literature that the catalytic cycle involves an oxidative addition to afford the $[Pd\text{-}allyl]^+$ intermediate, followed by a nucleophilic attack. Taking into account that under catalytic conditions the $[Pd\text{-}allyl]^+$ intermediate is the "resting-state" of the catalytic cycle [48], a less σ-donor arsine ligand could increase the electrophilicity of $[Pd\text{-}allyl]^+$ complex leading to a easily nucleophilic attack by malonate **26**.

Table 4. Allylic alkylation of 1,3-diphenyl-2-propenyl acetate (**25**) with dimethyl malonate (**26**) catalyzed by $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/L.[a]

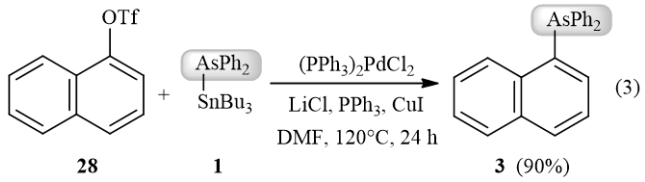


Ligand	Base	Solvent	Yield (%)[b]	ee % (config.)[c]
24	NaH	THF	98	23 (*R*)
22-TSL [46]	NaH	THF	29	12 (*R*)
24	LiAcO/*BSA*[d]	CH_2Cl_2	95	49 (*S*)

[a] Reaction conditions: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.5 mol%) and chiral ligand (7.5 mol%), 1 mL of solvent, room temperature, 24 hours under nitrogen atmosphere. [b] Determined by GC with internal standard method. [c] Enantiomeric excess determined by ^{1}H NMR using $Eu(hfc)_3$ as the chiral shift reagent. [d] 1 mol% of LiAcO and 3 equivalents of BSA.

2.1.2. Pd-Catalyzed Cross-Coupling Reaction of Aryl Triflates with n-Bu$_3$SnAsPh$_2$

Organic triflates, readily available substrates, have become important coupling partners in coupling reaction. An extensive report on the scope and limitations of the reaction of organoheteroatom stannanes R_3SnZPh_n (Z = P, As, and Sb with n = 2; Se with n = 1) with aryl triflates was informed [27]. Thus, the arsination reaction above described was further extended, by studying the Pd-catalyzed arsination with stannane **1** and 1-naphthyl triflate (**28**). The 1-naphthalenarsine **3** was obtained in excellent yields (eq.3).

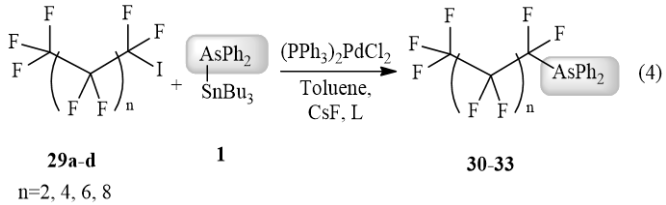


Generally, the coupling reactions with triflates revealed some experimental issues that should be considered. The effect of the addition of LiCl is one of them. When both LiCl and PPh_3 as ligand were added to the coupling reaction with stannane **1**, an improvement in the yield of **3** was observed. This combination seems to be a key step in this system. Additionally, the cross-coupling reaction became more effective in the presence of CuI. Two mechanistic explanations could account for the observed copper effect of Cu(I) as co-catalyst: *i)* a preliminary transmetallation from the organostannane to the Cu [49], or *ii)* a ligand association mechanism [50].

2.1.3. Pd-Catalyzed Arsination with n-Bu$_3$SnAsPh$_2$ and Perfluoroalkyl Iodides

In recent years, organofluorine compounds have attracted interest for exhibiting unique reactivities and selectivities, as well as for their favorable applications in biological and material science [51]. Particularly, compounds containing perfluoroalkyl groups (R_f) have become increasingly important [52]. Although, these types of compound present an unusual combination of electronic and steric properties, few examples for their synthesis have been reported [52a]. Due to their potential applications as ligands in metal catalyzed reaction perfluoroalkyl-substituted phosphines have attracted much attention. Recently, the properties and synthesis of phosphine ligands holding perfluoroalkyl substituent have been reviewed [53]. On the other hand, perfluoroalkylarsines have barely been pointed out in the literature [54].

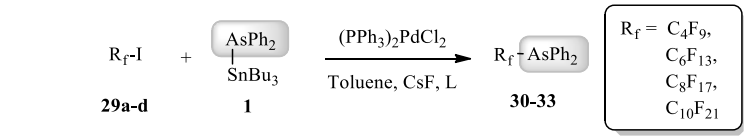
In the first place, the Pd-catalyzed reaction of stannane *n*-$Bu_3SnSePh$ with $C_8F_{17}I$ and $C_{10}F_{21}I$ to obtain perfluoroalkylselenides was informed [26k]. Following the same methodology, the Pd-catalyzed coupling reaction of *n*-$Bu_3SnAsPh_2$ (**1**) and R_fI **29a-d** to accomplish new diphenylperfluoroalkylarsines was developed (eq. 4) [55]. When the optimization studies of the arsination reaction were performed with these particular electrophiles, the most favorable conditions accomplished were those of $(PPh_3)_2PdCl_2/PPh_3$/CsF in toluene.

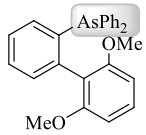


Novel perfluoroakyl diphenylarsines with perfluoroalkyl chains between four and ten C atoms were achieved (Table 5). In all reactions, the substrate (R_fI) was completely consumed, founding the corresponding coupling produce as well as the reduced perfluoroalkane (R_fH). It was demonstrated that the stannane was involved in the reduction of the R_fI.

Considering that the structure of the ligand has a crucial influence in oxidative addition step, the authors reported that a variety of phosphine and arsine ligands were screened in order to improve the low reactivity of R_fI in Pd-catalyzed arsination (entry 1, Table 5) [28]. This study revealed a deeply influence of the ligand on the yields of perfluoroalkyl arsines, establishing that **L1** was the most effective one (entry 2, Table 5). The possible formation of monoligated Pd species with this sterically demanding ligand [56], might be responsible for a rapid oxidative addition of the R_fI to the Pd(0) center. Moreover, catalysts derived from biarylarsine ligand **L6**, with a methoxy group on the non-arsine-containing aromatic ring, led to a highly effective catalytic complex (entry 3, Table 5) [57].

Table 5. Pd-catalyzed arsination of R_fI (**29a-d**) with *n*-$Bu_3SnAsPh_2$ (**1**) in the presence of $(PPh_3)_2PdCl_2$.[a,b]



Ligand	**30**	**31**	**32**	**33**
PPh_3 [Ref. 55]	47 %	43 %	65 %	48 %
L1 [Ref. 28]	45 %	55 %	87 %	78 %
 **L6** [Ref. 36]	57% (43%)	63% (50%)	100% (92%)	92% (81%)

[a] Reaction conditions: Ph_2As^- anion was obtained in liquid ammonia (300 mL) from $AsPh_3$ (1 mmol) and Na metal (2 mmol); then *n*-Bu_3SnCl (1 mmol) was added. The coupling reaction was carried out with R_fI (0.7 mmol), $(PPh_3)_2PdCl_2$ (10 mol%), ligand (Pd:L 1:4) and CsF (3 equiv) for 24 h in toluene at reflux. [b] CG yields, isolated yields in brackets. The yields reported represent at least the average of two reactions.

When the chain length of R_fI expand, progressively improved yields of the couplings reactions were detected, observing the quantitative conversion of R_fI **29c-d** to perfluoroalkyl arsines **32-33** (entry 3, Table 5). The efficiency of this catalyst could be attributed to the Pd-O interactions with the methoxy groups of ligand **L6**, which contribute to the stability of the catalyst.

In summary, even so, arsines are poorer σ-donors and less bulky ligand than the comparable phosphines, Pd-arsine ligand catalysts proved to be more efficient in this particular coupling reaction. Additionally, the potential usefulness of the coupling products Ph_2AsR_f as a new class of electron-deficient arsine ligands further enhanced the interest in this arsination reaction.

2.1.4. Mechanistic Consideration

The mechanism of the Stille reaction for C–C bond formation has been continuously investigated since its discovery and after the simplified mechanism originally proposed by Stille [58]. Although the classical widely accepted mechanisms proceed via three fundamental, namely oxidative addition, transmetalation, and reductive elimination, the process itself is known to be far more complex.

Despite the broad amount of mechanistic studies focused on the Stille C–C bond-forming reaction, the first work on C-heteroatom bonds formation through the Stille cross-coupling reaction has been recently reported [59]. On this work, the formation of C-P and C-As bonds through the Pd-catalyzed Stille reaction was computationally explored within the Density Functional Theory (DFT) framework. The reaction profiles of the processes involving different aryl halides (PhCl, PhI) and heterostannanes (Me_3SnZR_2, Z = As, P; R = Ph, Me) in the presence of Pd catalyst was investigated to gain more insight into the differential reactivity observed experimentally. It was found that the reaction with the heterostannanes proceeds according to the typical Stille-three steps mechanism, i.e. oxidative addition, transmetalation and final reductive elimination. A detailed figure of the catalytic cycle, including all the steps studied for the reaction between PhX (I, Cl) and organostannanes, is provided in Figure 1.

The transmetalation and the reductive elimination reactions, where the influence of the stannane-transferring group -PPh_2 and -$AsPh_2$ should be greater, were analyzed in detail. Thus, the transmetalation reaction occurs via the so-called cyclic mechanism, involving the four-membered cyclic transition state **TS-5** (Figure 3). The alternative open mechanism required high endergonicity for the initial phosphine/halide ligand interchange. The overall relative reaction profile for the transmetalation step involving heterostannanes with Z = P is energetically favored than that involving species having Z = As, which agrees with the

experimental observations. This observation can be mainly attributed to the relative strength of Sn–Z bond, which is broken during the transmetalation step (Sn–P < Sn–As) [59].

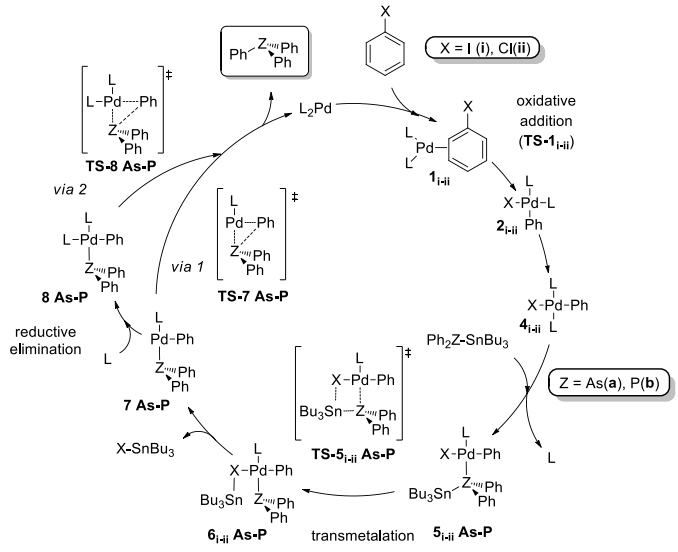
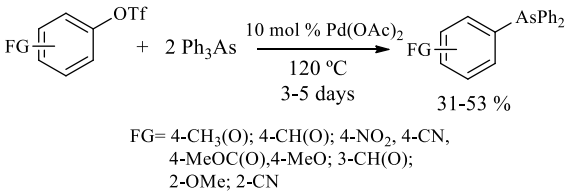


Figure 3. Catalytic cycle for the Stille coupling reaction between PhX (X= I, Cl) and heteroestannanes (a, b), through a cyclic transmetalation transition state (**TS-5**), with L= PMe_3.

The process ends up with the irreversible reductive elimination step from the T-shaped tricoordinated intermediate $\mathbf{7}_{\mathbf{As\text{-}P}}$ via transition state **TS-7** (Figure 3) that leads to final reaction products. It was concluded that although the reductive elimination step with organoheterostannanes is less exergonic than the respective process for leading to C–C bond formation, it compensates the previous endergonic transmetalation step and drives the complete catalytic cycle forward.

2.2. Pd-catalyzed arsination by a Pd-Ar/As-Ph exchange

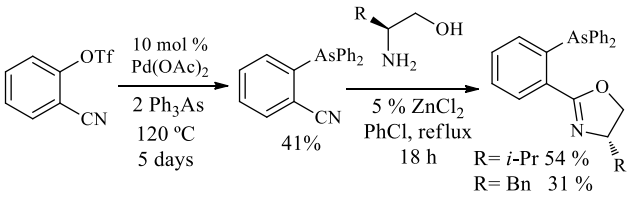
By extending the application of the transition metal-catalyzed aryl-aryl exchange reactions, functionalized arsines were achieved by a solvent free Pd-catalyzed arsination of aryl triflates [60] (Scheme 6). The arsination reaction did not proceed with aryl bromides and no significant electronic effect was observed in the reaction.



Scheme 6. Pd-catalyzed arsination by Pd-Ar/As-Ph exchange between aryl triflates and Ph_3As.

The major improvement of this methodology was the use as arsinating agent of commercially available and air stable Ph_3As. However, the reaction gave moderated yields of the functionalized aryl arsines, yielding only 50% of the triarylarsines after long reaction times (4-5 days).

By this Pd-catalyzed arsination a chiral [As,N] oxazoline ligands were achieved in two steps with low overall yields of 22 % and 13 % (Scheme 7) [**¡Error! Marcador no definido.**60b].

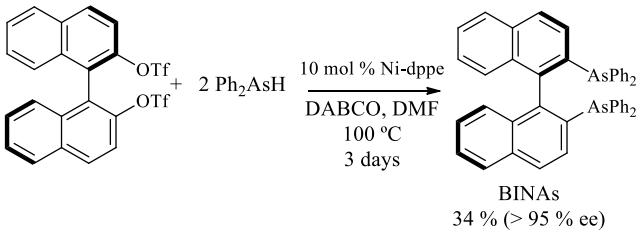


Scheme 7. Synthesis of chiral [As,N] oxazoline ligand by Pd-catalyzed arsination between aryl triflates and Ph_3As.

These new bidentate [As,N] ligands proved to be more stables than the corresponding [P,N] ligands. In addition, they smoothly reacted with $PdCl_2$ or K_2PtCl_4 in acetonitrile to afford the corresponding Pd- or Pt-complexes. Further X-ray analysis for Pt-complex revealed that $–AsPh_2$ group presented a larger *trans*-directing influence into the complex than the imino group.

2.3. Other catalyzed arsination reactions

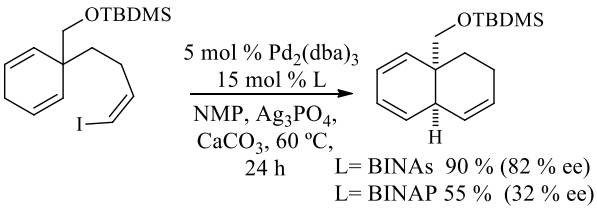
The first transition-metal catalyzed arsination was described by Shibasaki and co-workers using Ni as active metal, for the synthesis of binaphtyl arsine ligands BINAs ligand [16a] (Scheme 8).



Scheme 8. Synthesis of binaphtyl arsine ligand BINAs by Ni-catalyzed arsination with Ph_2AsH.

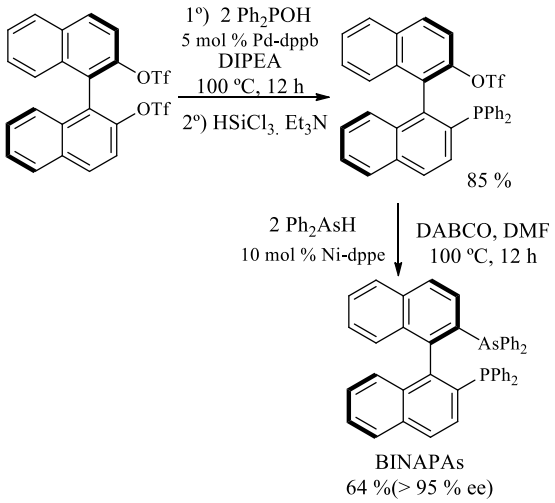
Using a slight modified method reported for the synthesis of BINAP [61], the arsine ligand was achieved by the reaction of BINOL ditriflate with Ph_2AsH catalyzed with Ni-dppe. This methodology allowed obtaining the enantiomerically pure ligand BINAs in modest yield of 34 % after 3 days, (Scheme 8).

Catalytic activity of BINAs ligand was investigated in asymmetric intramolecular Heck coupling reaction (Scheme 9). As in other examples previously discuss, the arsine ligand showed a superior catalytic activity over the phosphine analog BINAP when alkenyl iodide was employed (Scheme 9). However, when triflates were employed as leaving group, the reactivity was reversed, being BINAP more effective than BINAs.



Scheme 9. Evaluation of asymmetric induction by BINAs ligand in asymmetric intramolecular Heck coupling reaction.

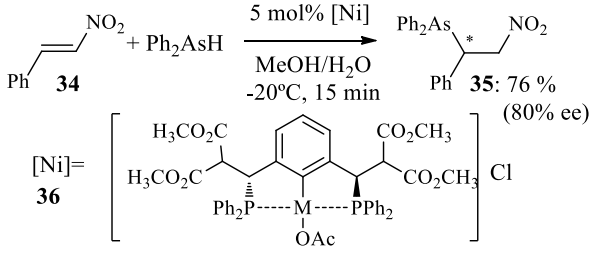
Furthermore, Shibasaki group extended this methodology to obtain the combined [As,P] ligand, BINAPAs [16b] (Scheme10).



Scheme 10. Synthesis of [As,P] ligand BINAPAs by Ni-catalyzed arsination.

In order to obtain the [As,P] ligand, a three step synthesis was proposed, combining a Pd-catalyzed phosphination reaction with $Ph_2P(O)H$, a reduction step to obtain phosphine derivative, and finally a Ni-catalyzed arsination reaction using Ph_2AsH. Thus, the ligand BINAPAs was obtained in a 54 % of overall yield with 95 % of ee [16b]. This [As,P] ligand was evaluated in intramolecular and intermolecular asymmetric Heck coupling reaction of aryl triflates. In this case, the [As,P] ligand BINAPAs was a chiral ligand more effective than phosphine homologue, given higher yields of coupling product, at lower temperature, shorter reaction times and with very good ee % (>80 % ee).

Recently, a Ni-catalyzed asymmetric hydroarsination reaction to obtain a chiral tertiary arsine was reported [62]. The reaction was carried out using the air-sensitive Ph_2AsH and nitro-styrene alkene (**34**) under mild conditions (Scheme 11).



Scheme 11. Ni-catalyzed asymmetric hydroarsination of nitro-styrene.

When the hydroarsination reaction was catalyzed by the chiral nickel pincer complex **36** arsine **35** was obtained in 76% yields with 80% ee within a short reaction time. The absolute stereochemistry of arsine **35** was confirmed by the single crystal X-ray diffraction of a Au(I)-arsine complex [62].

The efficient palladacycles catalyst for the analogous asymmetric hydrophosphination reaction failed to afford the arsine product. On the other hand, pincer Pd complex even though they were active catalyst, gave low enantiomeric excess.

CONCLUSION

Although there are few examples of metal-catalyzed arsination reactions, the reported reactions are mostly versatile and efficient approachs for obtaining arsine compounds. The Pd-catalyzed arsinations have some improvement over the classical methods which involve organolithium or organomagnesium reagents or the reaction of air-sensitive nucleophilic arsine reagents. Some advantages that could be mentioned for Pd-catalyzed arsinations, *i.e.* coupling arsination of stannanesaryl and aryl exchange reactions, would be: (i) starting with the commercially available, air-stable and inexpensive triphenylarsine; (ii) good to high-yield of the functionalized arsines; and (iii) a high functional group compatibility.

In addition, most of the described methods for catalyzed C-As bonds formation have been successfully applied in the synthesis of new arsine ligands. Therefore, broadening the synthetic methodologies to obtain arsines compounds would contribute to a great extent to the development of new ligands.

We expect that this article encourages further improvement of metal-catalyzed arsination reactions that might contribute to the development of novel arsine ligands.

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